

# Thermal Degradation of LC Epoxy Thermosets

M. G. LU,<sup>1</sup> M. J. SHIM,<sup>2</sup> S. W. KIM<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, The University of Seoul, Seoul 130-743, South Korea

<sup>2</sup> Department of Life Science, The University of Seoul, Seoul 130-743, South Korea

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**ABSTRACT:** A novel liquid crystalline (LC) epoxy monomer was cured with different types of hardeners. The thermal-degradation properties of cured thermosets were evaluated by thermogravimetric (TG) analysis. Several widely used kinetic models were reviewed and used to fit the TG data. The experimental results showed that the methods from one constant heating rate are insensitive to the magnitude of reaction order  $n$ . The Kissinger and Osawa methods from multiple processes would give more confident kinetic parameters in these observed systems. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1514–1521, 2000

**Key words:** LC thermosets; thermal degradation; TGA; kinetics

## INTRODUCTION

It is impossible to understand the properties of polymers if the transitions that occur in such materials and, especially, the temperatures at which these occur are not known. The main transitions are the glass–rubber transition, the crystalline melting point, and the heat-degradation temperatures. These “structure-sensitive” transition temperatures are often used to characterize the thermal properties of polymers, determining the use temperature ranges and the thermal resistance of polymeric materials.

In general, thermal degradation does not occur until the temperature is so high that primary chemical bonds are separated. For many polymers, thermal degradation is characterized by the breaking of the weakest bond and is, consequently, determined by a bond-dissociation energy. Since the change in entropy is of the same order of magnitude in almost all dissociation re-

actions, it may be assumed that, also, the activation energy will be approximately the same, meaning that, in principle, the bond-dissociation energy determines the phenomenon.<sup>1,2</sup>

It is well known that liquid crystalline (LC) polymers containing large aromatic repeating units have, in general, good thermal resistance. A number of analytical methods have been developed for the determination of the thermal stability and thermal-decomposition kinetics of polymers.<sup>3–5</sup>

The attractive feature of isothermal experiments is that the rate constants at each temperature are better defined and the constants obtained at different temperatures would permit the determination of the activation energy associated with the thermal degradation. However, the nature of the reactions and the final products may differ at different temperatures, and the kinetic parameters thus obtained are not without ambiguity.<sup>6</sup>

Dynamic experiments, conducted at a specified heating rate, will yield conversion–time–temperature data that are comprehensive enough to permit direct evaluations of the kinetic parameters. A single dynamic run gives as much information

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Correspondence to: S. W. Kim (swkim@uoscc.uos.ac.kr).  
Contract grant sponsor: Han Yang Petrochemical Co. Ltd., South Korea.

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as do several isothermal runs. Furthermore, dynamic measurements can provide kinetic information over a larger temperature range and there are no preheating problems as is the case with isothermal experiments in which the sample must be first heated to the isothermal hold temperature during which decomposition of the samples may take place. It is valuable as a precursor to isothermal studies and is often the only means to analyze the cure kinetics of systems with multiple degradation.<sup>7</sup> One shortcoming of this method based on the mechanistic model is the requirement of an assumed reaction order.

Compared with the isothermal method, the case of dynamic degradation is theoretically more difficult for the phenomenological kinetic model due to the complex temperature dependence of the rate constant and the peculiar feature of decomposition, although it is a case which more closely simulates the factual process.<sup>8</sup>

We have reported the thermal stability and degradation kinetics of epoxy and other polymeric materials.<sup>9,10</sup> In this present article, TGA data obtained at different heating rates are used to provide an alternative model of kinetics of LC epoxy thermoset degradation. The kinetic parameters from various published models are compared and used to elucidate the thermal behavior.

## THEORY ANALYSIS OF TG

For many kinetic processes, a rate of reaction may be expressed as a product of a temperature-dependent function,  $k(T)$ , and a composition or conversion-dependent term,  $f(\alpha)$ :

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where  $T$  is absolute temperature,  $\alpha$ , the conversion (= weight of polymer volatilized/initial weight); and  $d\alpha/dt$ , the rate of change of the conversion or composition per unit time ( $t$ ). The temperature-dependent term in (1) is the reaction rate constant, which is assumed to obey the usual Arrhenius relationship:

$$k(T) = Z \exp\left(-\frac{E_d}{RT}\right) \quad (2)$$

where  $R$  is the universal gas constant.

The conversion-dependent function,  $f(\alpha)$ , is normally very complicated because many reactive processes may occur simultaneously. A particular term is usually valid only for a limited range of experimental conditions. However, if it is assumed that a simple  $n$ th-order kinetic relationship holds for the conversion-dependent term such that

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

and that the quantity  $(1 - \alpha)$  can be replaced by  $W$ , the weight fraction remaining in a TGA run, then

$$\frac{dW}{dt} = ZW^n \exp\left(-\frac{E_d}{RT}\right) \quad (4)$$

As mentioned above, it is increasingly popular to collect dynamic data, which are obtained under the condition of a fixed rate of temperature change—a condition which may be closely realized in modern scanning instruments. However, a debate is surfacing in regard to whether such data can be analyzed to identify, unambiguously, the explicit form of the kinetic function.

Many ingenious methods have been proposed by which  $f(\alpha)$  as well as  $Z$  and  $E_d$  may be derived. These methods are based on either the differential eq. (4) or its integral form.

Integration of eq. (4) proceeds as follows:

$$\begin{aligned} g(\alpha) &= \int_0^\alpha \frac{d\alpha}{f(\alpha)} \\ &= Z \int_0^t e^{-E_d/RT} dt \\ &= \frac{Z}{\beta} \int_{T_0}^T e^{-E_d/RT} dT \\ &\approx \frac{Z}{\beta} \int_0^T e^{-E_d/RT} dT \\ &\approx \frac{AE_d}{\beta R} p(E_d/RT) \end{aligned} \quad (5)$$

where  $\beta = dT/dt$  is the heating rate;  $T_0$ , the initial temperature in the TGA analysis;  $T$ , the final temperature and

$$p(x) = \int_{\infty}^x \frac{e^{-x}}{x^2} dx$$

where  $x$  is a polynomial versus  $(E_d/RT)$ . The different integral methods involve an approximation to the right-hand integral term in eq. (5).

### One Constant Heating Rate

Representative integral methods involving a single TG thermogram were presented in the works by Van Krevelen et al.,<sup>11</sup> Coats and Redfern,<sup>12</sup> Horowitz and Metzger,<sup>13</sup> and Broido.<sup>14</sup>

Van Krevelen approximated the exponential integral by making the substitution

$$e^{-E_d/RT} = e^{(-T_{\max}/T)E_d/RT_{\max}} \approx 0.368 \left( \frac{T}{T_{\max}} \right)^{E_d/RT_{\max}} \quad (6)$$

Thus,

$$\ln g(\alpha) = \ln B + \left[ \frac{E_d}{RT_{\max}} + 1 \right] \ln T \quad (7)$$

where

$$B = \frac{Z}{\beta} \left[ \frac{E_d}{RT_{\max}} + 1 \right]^{-1} \left[ \frac{0.368}{T_{\max}} \right]^{E_d/RT_{\max}}$$

and  $T_{\max}$  is the temperature at the maximum of the heating derivative weight loss curve. A plot of  $\ln g(\alpha)$  versus  $\ln T$  gives a straight line for a correctly selected  $n$ , and the activation energy is involved in the slope obtained.

In the method of Coats and Redfern, the temperature integral was approximated as

$$\int_0^t e^{-E_d/RT} dt \approx \frac{RT^2}{\beta E_d} \left( 1 - \frac{2RT}{E_d} \right) \exp\left( -\frac{E_d}{RT} \right) \quad (8)$$

which gives

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left( \frac{ZR}{\beta E_d} \right) \left( 1 - \frac{2RT}{E_d} \right) - \frac{E_d}{RT} \quad (9)$$

For  $n = 1$ ,

$$\ln \left[ -\ln \frac{(1-\alpha)}{T^2} \right] = \ln \left( \frac{ZR}{\beta E_d} \right) \left( 1 - \frac{2RT}{E_d} \right) - \frac{E_d}{RT} \quad (10)$$

For  $n \neq 1$ ,

$$\ln \left[ \frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left( \frac{ZR}{\beta E_d} \right) \left( 1 - \frac{2RT}{E_d} \right) - \frac{E_d}{RT} \quad (11)$$

The Horowitz and Metzger method simplified  $p(x)$  and introduced a characteristic temperature  $T_s$  and a parameter  $\theta$  such that

$$\theta = T - T_s \quad (12)$$

If the reaction order is 1,  $T_s$  is defined as the temperature at which  $(1-\alpha)_s = 1/e$  and the kinetic expression is

$$\ln(-\ln W) = \frac{E_d \theta}{RT_s^2} \quad (13)$$

A plot of  $\ln g(\alpha)$  versus  $\theta$  can yield the activation energy.

### Multiple Constant Heating Rates

Two of the more popular integral methods involve multiple heating rates and are used here. A summary of these methods is as follows:

1. Ozawa used a linear empirical approximation given by Doyle to approximate the above integral.<sup>15,16</sup> This is applicable to a limited range of  $p(x)$  values:  $20 < p(x) < 60$ . The resulting equation is

$$\log \beta = -0.4567 \frac{E_d}{RT} + \left( \log \frac{ZE_d}{R} - \log g(\alpha) - 2.315 \right) \quad (14)$$

Thus, at the same conversion, a plot of  $\log \beta$  versus  $-1/T$  should be a straight line with a slope of  $0.4567E_d/R$ . If  $E_d$  does not change with  $\alpha$ , a series of parallel straight lines are obtained.  $\log Z$  can be calculated from the intersection of the  $Y$  axis as

$$\log Z = \log \beta + \frac{0.457}{RT} + 2.315 - \log E_d + \log R + \log g(\alpha) \quad (15)$$

2. Kissinger, however, used an approximation based on successive integration by parts and then retained only the first term in a rapidly converging series.<sup>17</sup> The final expression is

$$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E_d}{RT} + \left[ \ln\left(\frac{ZR}{E_d} - \ln g(\alpha)\right) \right] \quad (16)$$

Thus, a plot of  $\ln(\beta/T^2)$  versus  $-1/T$  at a constant conversion should be a straight line of the slope  $-E_d/R$ . This expression is also given by the American Society for Testing and Materials (ASTM).

## EXPERIMENTAL

### Materials

The LC epoxy monomer was a diglycidyl ether of biphenol (DGEBP). The preparation was described previously.<sup>18</sup> The diepoxide was cured with methylene dianiline (MDA) and 4,4'-aminophenoxy hexane (APOH) at 140°C for 5 h and 180°C for another 30 min. The resulting polymers were used for TG analysis.

### Instruments

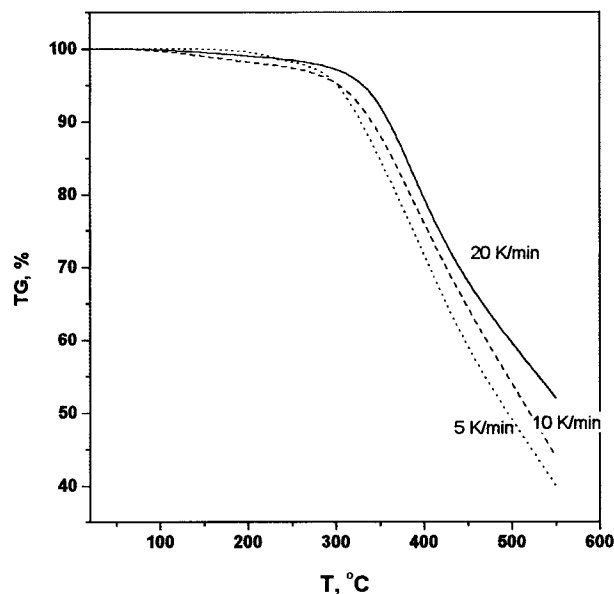
A Setaram TG/DTA 92 simultaneous thermogravimetric/differential thermal analyzer is used to obtain weight loss data for the degradation of cured LC thermosets. For the thermal degradative runs, the samples are purged with argon gas at a flow rate of 50 mL/min. Constant heating rates of 5, 10, 15, and 20°C/min are used. The sample weights are 5–15 mg in all cases.

## RESULTS AND DISCUSSION

### Thermal Degradation

A number of experimental indices are often used to characterize the process of thermal decomposition, including

- (a) The temperature of initial decomposition ( $T_{d,0}$ ). This is the temperature at which the loss of weight during heating is just measur-

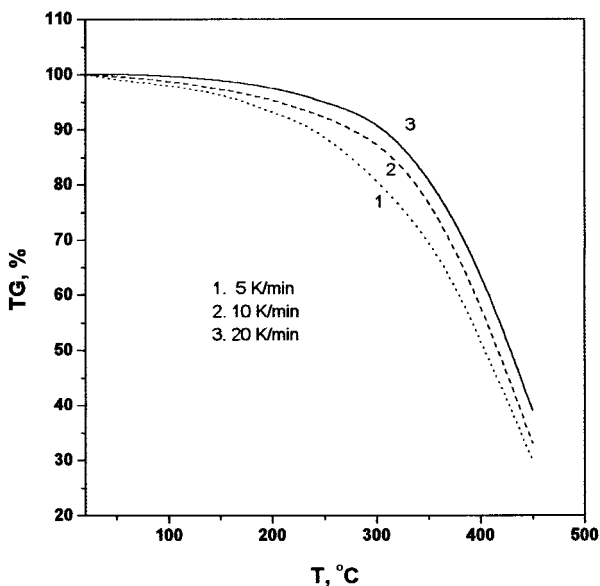


**Figure 1** TG thermograms of DGEBP/MDA at various heating rates.

able (inclination point of the loss of weight/temperature curve).

- (b) The temperature of half-decomposition ( $T_{d,1/2}$ ). This is the temperature at which the loss of weight during heating (at a constant rate of temperature increase) reaches 50% of its final value.
- (c) The temperature of the maximum rate of decomposition ( $T_{d,max}$ ), measured as the rate of loss of weight (at a standardized rate of temperature increase).
- (d) The average energy of activation ( $E_d$ ), determined from the temperature dependence of the rate of loss of weight.

These indices, especially the characteristic temperatures, are dependent on the rate of the heating rate applied during the pyrolysis. The thermogravimetric (TG) curves for the thermal degradation of three LC thermoset powders are shown in Figures 1 and 2. The TG thermograms obtained from argon-purged samples shifted to higher temperatures as the heating rate  $\beta$  increases from 5 to 20°C/min. The shift of onset to higher temperature with increasing  $\beta$  is due to the shorter time required for a sample to reach a given temperature at the faster heating rates. The initial decomposition temperature  $T_{d,0}$  and the temperature of half-decomposition  $T_{d,1/2}$  for both thermosets conducted at various heating rates are listed in Table I.



**Figure 2** TG thermograms of DGEBP/APOH at various heating rates.

It has been reported that the measured values of the main indices appear to be interrelated:

$$T_{d,0} \approx 0.9T_{d,1/2} \quad (17)$$

Obviously, the empirical relationship in eq. (17) is invalid here for LC polymer systems. Especially, the values of  $T_{d,0}$  are much less  $0.9 T_{d,1/2}$ . On the other hand, the LC thermosets degrade more slowly. It is attributed to the local orientation in LC polymers. Some researchers have pointed out that, as LC epoxy was curing, the transverse properties increased. The mesophases formed persist by the crosslinked network until decomposition.<sup>18</sup> Therefore, differing from the linear LC polymers, the thermal degradation in LC thermosetting polymers not only includes the cleavage of network bonds, but also have to destroy the ordered LC domains. It is reasonable for LC thermosets to exhibit excellent high-temperature resistance.

Table I indicates clearly that sample DGEBP/MDA shows a higher initial decomposition temperature because of its higher content of aromatic rings. However, the values of  $T_{d,0}$  of DGEBP/APOH don't seem to be as low as expected when the flexible linkage was introduced. It may be associated with its higher degree of orientation. As reported previously, the introduction of a flexible spacer into the main chain plays an important role in determining the transition tempera-

tures, the mesomorphic range, and the nature of the LC phase. The increase in the molecular segment length drives the formation of the LC phase. In fact, the addition and chemical bonding of several rigid units via short flexible spacers effectively increase the "Kuhn length." As a consequence, the LC phase is stabilized by geometric constraints during curing. In some cases, with extensive chain alignment and good chain regularity, crystallization even proceeds so quickly that it results in the transition from the smectic phase to crystal.<sup>19</sup> However, DGEBP/APOH still exhibits a lower  $T_{d,1/2}$  because the methylene linkage exists as weak bonds and the active species of thermal decomposition.

### Kinetic Analysis of Thermal Degradation

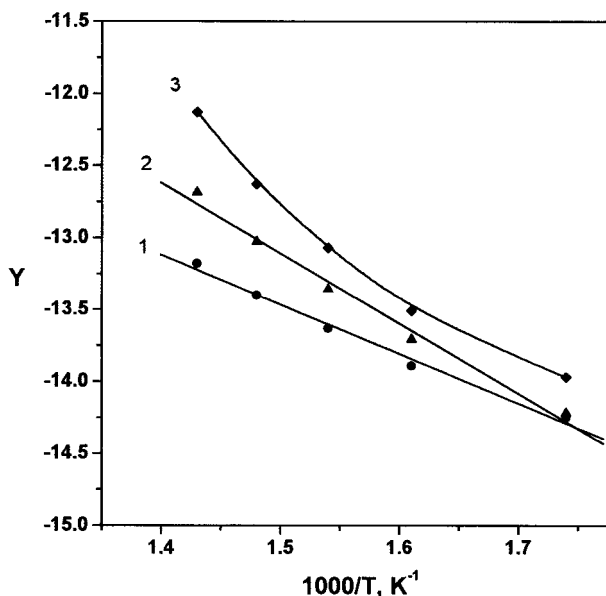
Random thermal degradation can usually be described as a first-order reaction (loss of weight as a parameter) if the decomposition products are volatile. Although there are several methods for calculating kinetic parameters as reviewed before, it is commonly believed that nonisothermal methods can describe the degradation process better. Here, the integral methodologies are used to deduce the activation energies, including the methods of Kissinger and Ozawa, Coats-Redfern, and Horowitz and Metzger.

The kinetic parameters for both systems were analyzed in the 40–90% degradation range. The initial 10% degradation zone is not considered to avoid errors from an overlap from the previous degradation zone. The Coats-Redfern equation is used for evaluation of the  $n$  values. The kinetic plots of DGEBP/APOH at 5 K/min are shown in Figure 3 for  $n = 1, 2,$  and  $3,$  respectively. It is unexpected that the linearity of the plots seems to be insensitive to the magnitude of  $n, 1,$  or  $2.$  However, for the DGEBP/MDA system, only  $n = 1$  can fit the linearity of the plots. The relation-

**Table I**  $T_{d,0}, T_{d,1/2},$  and  $T_{d,max}$  for Both Systems

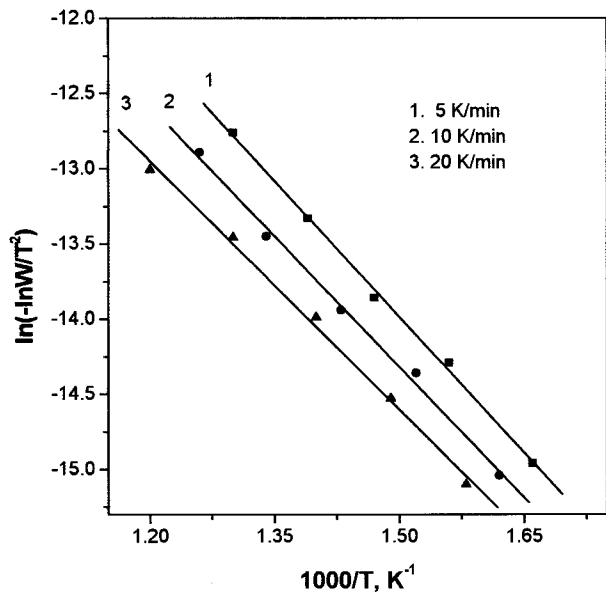
Sample		$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)	$T_{d,max}$ (°C)
DGEBP/MDA	5°C/min	297	498	436
	10°C/min	313	521	455
	20°C/min	342	563	475
DGEBP/APOH	5°C/min	284	403	370
	10°C/min	297	417	386
	20°C/min	321	429	402



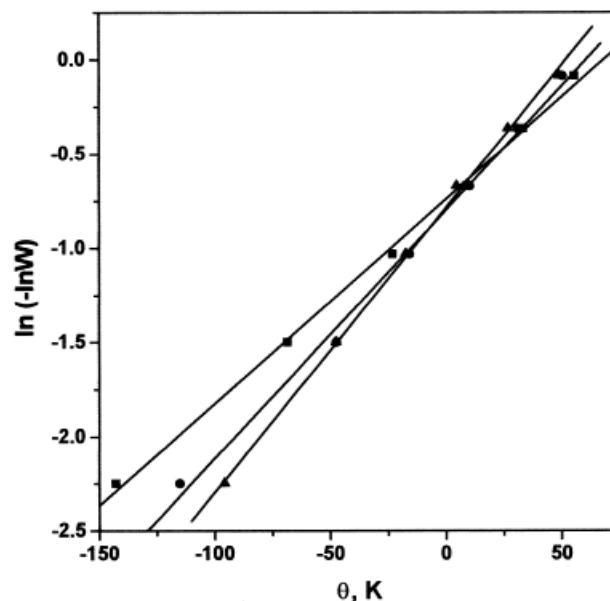


**Figure 3** Coats-Redfern plots for DGEBP/APOH system at  $n = 1, 2,$  and  $3.$

ship between  $\ln(-\ln W/T^2)$  versus  $1/T$  for DGEBP/MDA at  $n = 1$  and different heating rates is shown in Figure 4. Although the mechanism is not clear, as is obvious from Figure 3, the values of the activation energy and, to some extent,  $Z$  so calculated will change with the  $n$  chosen. The calculated decomposition activation energies for DGEBP/MDA and DGEBP/APOH at 5



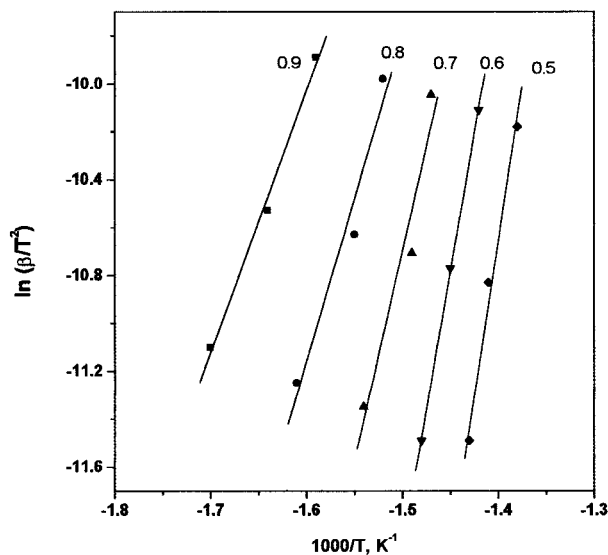
**Figure 4** Coats-Redfern plots for DGEBP/MDA at  $n = 1$  and different heating rates.



**Figure 5** Application of Horowitz and Metzger method for DGEBP/APOH at different heating rates.

K/min are 125 and 56 kJ/mol, respectively. We can find that the activation energy of the thermal degradation for DGEBP/MDA is much higher than that for the DGEBP/APOH system. However, we cannot assert that the linear sensitivity of the plot to  $n$  was only determined by  $E_d$ . The low decomposition activation energies for DGEBP/APOH may be affected by the flexible structure of the curing agent. As mentioned previously, the weak methylene linkage makes the decomposition easier as the degradation starts. Besides, it is observed that in these rapid decomposition zones the thermal degradation process is not affected significantly by the heating rates. On the other hand, the kinetic parameter can be given by a single constant heating rate.

Application of the Horowitz and Metzger method in the same conditions is shown in Figure 5. Due to the good linearity obtained in the curves  $\ln(-\ln W)$  versus  $\theta$ , it shows that the thermal degradation can be described by the reaction order  $n = 1$  for the DGEBP/APOH system. However, at  $n = 2$ , a linear plot of  $\ln g(\alpha)$  versus  $\theta$  is still obtained although it is not as good as that at  $n = 1$ , which implies that the methods from one constant heating rate are insensitive to the magnitude of the reaction order  $n$  in our systems. The value of the activation energy calculated for DGEBP/APOH at 5 K/min is 62 kJ/mol. It is in good agreement with that from the Coats-Redfern method.

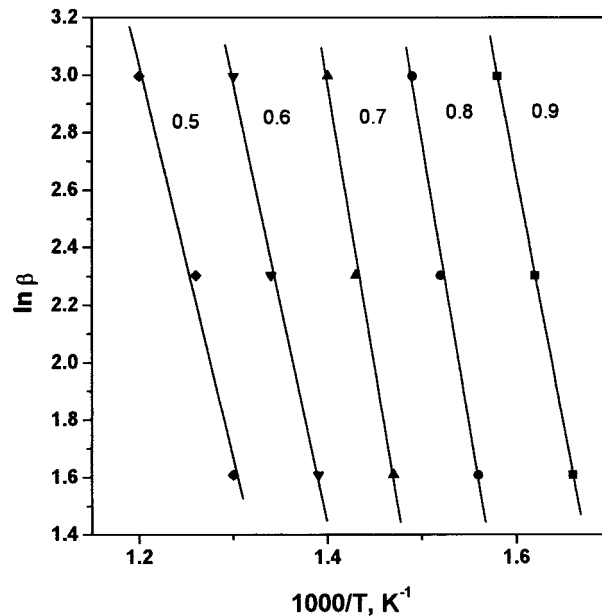


**Figure 6** Kissinger plots for DGEBP/MDA at different conversions.

Figure 6 shows Kissinger's plots. The decomposition activation energies at different conversions are obtained and listed in Table II. The values are in good agreement with those given by the methods described above. Similar results can also be obtained by the method of Osawa (Fig. 7). However, compared with the results from one constant heating rate, the Kissinger and Osawa methods exhibit the higher values of activation energy. The difference between both systems observed by the Osawa method is that there is no marked decreased tendency in the activation energy with increasing conversion for both systems (the values of the activation energy at different conversions are included in Table III). It is not surprising since the two methods are based on the approximation of the same nonclosed exponential

**Table II** Activation Energy from Kissinger's Method

Conversion	Activation Energy (kJ/mol)			
	DGEBP/MDA		DGEBP/APOH	
	Kissinger	Osawa	Kissinger	Osawa
0.9	207	144	68	74
0.8	153	164	72	74
0.7	151	164	65	86
0.6	115	127	54	89
0.5	101	114	47	72



**Figure 7** Osawa plots for DGEBP/MDA at different conversions.

integral. Graydon et al. showed that the method of Osawa is identical with that of Kissinger when it is adjusted by Flynn's correction factor.<sup>20</sup> Since the Kissinger and Osawa methods do not take the reaction order into account in the calculation of the activation energy, we think that both methods are superior to other methods.

## CONCLUSIONS

The thermal degradation experiment shows that the LC epoxy resins have good high-temperature resistance. However, it can be decreased as the resin is cured with the aliphatic linkage containing the curing agent in which the lower decomposition activation energy is observed. The kinetic analytical methods from one constant heating rate are insensitive to the magnitude of the reaction order  $n$  in our observation, although the activation energies obtained are in agreement with those from the multiple processes described by Kissinger and Osawa.

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