

Kinetic Rate Equation Combining Ultraviolet-Induced Curing and Thermal Curing. I. Bismaleimide System

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ABSTRACT: A novel and general kinetic rate equation combining ultraviolet-induced (UV-induced) curing and thermal curing was successfully derived from the conventional thermal-kinetic rate equation. This proposed novel kinetic rate equation can be applicable to the curing system either simultaneously or individually by UV-induced and thermal cure methods. This general kinetic rate equation is composed of the reaction order n , activation energy E_a , curing temperature T , energy barrier of photoinitiation E_Q , intensity of UV radiation Q , concentration of photoinitiator $[I]$, and a few other parameters. The proposed equation was supported by experimental data based on the curing systems of 4,4'-bismaleimidodiphenylmethane (BMI) and 2,2-bis(4-(4 maleimido phenoxy) phenyl) propane (BMIP). The BMI and BMIP systems were isothermally cured at various temperatures, or simultaneously cured with varying intensity of UV radiation (wavelength 365 nm). Conversion levels for the various cured samples

were subsequently measured with a FTIR spectrometer. The reaction order $n = 1.2$, activation energy $E_a = 40,800$ J/mol, and $E_Q = 7.5$ mW/cm² were obtained for curing BMI system. The reaction order $n = 1.3$, activation energy $E_a = 53,000$ J/mol, and $E_Q = 9.1$ mW/cm² were obtained for curing BMIP system. The values of n and E_a in the same curing system (BMI or BMIP) are irrespective of the curing method (either simultaneously or individually by UV-induced and thermal cure methods). The salient results of this study show that UV radiation only enhances the initiation rate and UV radiation do not influence the activation energy E_a . The experimental results are reasonably well represented by these semi-empirical expressions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 935–947, 2010

Key words: kinetics; curing of polymers; bismaleimide; UV cure

INTRODUCTION

Bismaleimide resins are some of the most important thermosetting polymers because of their outstanding dielectric and mechanical properties at elevated temperatures.¹ Some examples of their application include the multilayer-printed circuit boards for large-scale computers, encapsulation resins and passivation layers for IC dies, advanced carbon fiber composites for the aerospace industry, and structural adhesives.²

The cure kinetics of ultraviolet-induced (UV-induced) curing or thermal curing have been individually and substantially investigated for various thermosetting polymers and recent inorganic/organic hybrids such as epoxy hybrid³ and acrylate

hybrid.^{4,5} UV-induced curing of polymer coatings has until recently been dominated by photoinitiated radical polymerization processes, partly because of their curing efficiency. UV-induced curing of thermosetting systems involving maleimides have been investigated with regard to the resulting structures,^{6,7} kinetics and mechanism,^{7–10} bulk and surface properties¹¹ reactivity,^{8,9} effect of the UV dosage,¹⁰ effect of the photoinitiators, and curing temperature.¹² None of these studies, however, have proposed a generally valid kinetic rate equation, with the sole exception of the Decker's study,⁹ in which a kinetic rate equation was introduced for a special system. Decker investigated the influence of the light intensity on the cure kinetic of a DVE-3/Q-bond system, where DVE-3 refers to divinyl ether of triethyleneglycol, and Q-bond is a liquid bismaleimide with a 36-carbon-atom cycloaliphatic branched structure from Quantum Materials; Decker proposed the following kinetic rate equation:

$$R_p = kQ^{0.6}[M]$$

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where R_p refers to the rate of polymerization of the maleimide monomer, Q is the light intensity, and $[M]$ is the concentration of the maleimide monomer.

A kinetic rate equation in an UV-induced curing system based on 2-hydroxyethyl methacrylate (HEMA)-terminated polyurethane (PU) was further proposed by Hsieh et al.¹³:

$$-\frac{d[C=C]}{dt} = k[C=C]^1[I]^{0.5}[Q]^{0.5}[T]^{-1}$$

This equation contains the film thickness $[T]$, the initiator concentration $[I]$, the unreacted carbon-carbon double bond concentration $[C=C]$, and the light intensity $[Q]$.

The above two equations indicate that when UV light is not applied ($Q = 0$), polymerization apparently does not take place (i.e., the rate equation is equal to zero), even at an elevated temperatures. These forms of the rate equation are therefore not applicable to the curing systems which can be cured either by a UV-induced or thermal method, or by both. It is known that the curing system Hsieh et al.¹³ investigated can be cured either simultaneously or individually by UV-induced and thermal cure methods. However, the proposed equation is not applicable to the case of a sole thermal cure reaction. Consequently, a kinetic rate equation of general validity for all curing methods still needs to be determined.

In the cases of thermal cure, a general phenomenological model equation (autocatalytic kinetic equation) is currently in widespread use for the curing of the various thermosetting polymers, and is expressed as follows^{14,15}:

$$\frac{dx}{dt} = (k_1 + k_2x^m)(1-x)^n \quad (1)$$

where x is the percentage of conversion, $k_1(T)$ and $k_2(T)$ are reaction rate constants with two different activation energies and pre-exponential factors, and n and m are the reaction orders. The item k_2x^m in eq. (1) results from the autocatalytic part of reaction; it is the weighting factor of the autocatalytic part of the reaction as compared with the regular reaction (k_1). An autocatalyzed reaction assumes that at least one of the reaction products is also involved in the propagating reaction. It is thus characterized by an accelerating isothermal conversion rate, with its maximum occurring well after the conversion initiation. This result is because the reactants can be converted via alternative paths. In some cases, the autocatalytic part of the reaction does not occur. Under these circumstances, eq. (1) can then be reduced to a simple form:

$$\frac{dx}{dt} = k_1(1-x)^n \quad (2)$$

Presently, only limited information is available for accurate modeling of the bismaleimide curing mechanism. Several reaction paths, occurring simultaneously or in sequence, have been proposed for the curing process of bismaleimide-related resins.¹⁶ Bismaleimide can be cured via a sole thermal process^{17,18} or with a peroxide initiator.¹⁹ Because of the complicate reaction mechanisms involved, it is not easy to derive an accurate kinetic rate equation from them. Most researchers therefore treated the all reaction paths as a whole course (i.e., these reaction paths occur simultaneously), and utilized eq. (1) or (2) to analyze the kinetics of the thermal cure.^{19–21} Acevedo¹⁹ investigated the curing kinetics of a system containing *N*-phenylmaleimide with dicumylperoxide as a curing initiator in the temperature range of 393–433 K. Although there exists autocatalytic characterization in this curing system, he still used the first-order model without the autocatalytic part [eq. (2)] to fit his experimental data, and found that this model could better fit his experimental data up to 70% conversion. Goodwin²⁰ explored the cure kinetics of 4,4'-bismaleimido-diphenylmethane (MDA-BMI) and a bisphenol A derivative in the temperature range of 453–473 K. He also tried to use the simple n -th order model [eq. (2)] to fit his experimental data; however, only a first-order model can fit the data obtained at 478 K to some extent. Boey²¹ investigated the curing kinetics of a system containing four main components (MDA-BMI, amine, epoxy, and diallylbisphenol A) at a temperature of 443, 463, and 483 K. He found that autocatalytic reactions did indeed take place in the studied system, and thus employed the autocatalytic model [eq. (1)] to fit the experimental data at first. However, eq. (1) does not fit the data over the entire range of the cure reaction process, and is particularly weak for higher curing temperatures. He therefore utilized eq. (2) with different values of n to fit the experimental data obtained at different curing temperatures, and found that this equation better fit his data after 10% conversion. It should be pointed out that the curing systems described in Refs. 19–21 consist of at least two components, and thus undergo multiple cure reactions. Each reaction path proceeds at a different temperature range, which results in the poor fitness of eq. (1) or (2) for these systems.

In the literature, cure kinetics for various thermosetting polymers has been investigated individually either by ultraviolet-induced (UV-induced) curing or by thermal curing. There is not a kinetic rate equation, which can be applicable to the curing system simultaneously associating ultraviolet-induced (UV-induced) curing with thermal curing.

Accordingly, in this work we try to propose a novel and general kinetic rate equation which can be applicable to the curing system either simultaneously or individually by UV-induced and thermal cure methods. This kinetic rate equation should contain the UV light intensity (Q , mW/cm^2), the energy barrier for photoinitiation (E_Q , mW/cm^2), the temperature (T), and the apparent activation energy (E_a , J/mol). Meanwhile, this proposed kinetic rate equation is going to be further supported by the experimental data of the bismaleimide curing systems. In this work, neat bismaleimide monomers were used for simplicity. Cure reactions of neat bismaleimide proceed merely via a double-bond opening, rather than reacting with functional groups on another monomer. Neat bismaleimide monomers can be cured by either the UV-induced method or the thermal method, or by both. For reasons of efficiency, most neat bismaleimide monomers would be cured with UV radiation at an elevated temperature. To verify the applicability of the proposed kinetic rate equation, two different bismaleimide monomers, 4,4'-bismaleimidodiphenylmethane (BMI) and 2,2-bis(4-(4-maleimido phenoxy) phenyl) propane (BMIP), were chosen. In BMI system, thermal curing occurs (466 K) immediately after being melted (413 K). But in BMIP system, there exists a long temperature range between melting temperature (363 K) and the thermal curing temperature (523 K). As the curing system of the BMIP monomer requires a higher curing temperature than the curing system of the BMI monomer, the photoinitiator presumably plays a more influential role in the UV-induced curing system of the BMIP monomer than in the BMI monomer system.

DERIVATION OF A KINETIC RATE EQUATION COMBINING ULTRAVIOLET-INDUCED CURING AND THERMAL CURING

The curing rate of neat bismaleimide at constant temperature is mainly determined by the amount of active sites (possibly free-radicals); this amount, in turn, is dependent on the initiation rate. The produced intermediate species are not capable of autocatalyzing the curing reaction. Accordingly, it may be reasonably assumed that the simple form of the kinetic rate equation [eq. (2)] can be applied to the neat bismaleimide curing system. Nevertheless, this fact needs to be evidenced by definite experimental results. In this work, we intend to expand eq. (2) into a new form of kinetic rate equation that contains both UV term and thermal term.

$$\frac{dx}{dt} = k_1(1-x)^n \quad (2)$$

where k_1 is the rate constant.

(a) The case of sole thermal cure without UV radiation.

k_1 is a function of temperature only, and the Arrhenius relationship is expressed by:

$$k_1 = f(T) = A \exp(-E_a/RT) \quad (3)$$

where E_a is the activation energy, R is the gas constant, T is the absolute temperature, and A is the pre-exponential or frequency factor.

Taking the natural logarithm (to the base e) of both sides, we get

$$\ln(k_1) = \ln A - E_a/RT \quad (4)$$

A plot of $\ln(k_1)$ versus $1/T$ should produce a straight line; A can be obtained from the y -intercept, and E_a is determined from the slope. Alternatively, eq. (2) can be written as:

$$\frac{dx}{dt} = A \exp(-E_a/RT)(1-x)^n \quad (5)$$

(b) The case of thermal cure with UV radiation.

When UV radiation is used in a thermal cure, UV radiation will induce the photoinitiator to generate much more free radicals (i.e., the initiation rate is higher), thereby increasing the curing rate. Thereafter, the curing rate will further increase with increasing curing temperature. The initiation rate of the thermal cure system will increase with the participation of UV radiation. The initiation rate resulted from UV light depends on the energy barrier of the photoinitiation (E_Q , mW/cm^2). The rate constant k_1 is composed of thermal term and UV-induced term. The presence of UV radiation only increases the initiation rate, but does not influence the activation energy (E_a) itself. Accordingly, the Arrhenius relationship can be rewritten as follows:

$$k_1 = f(T, Q) = A(1 + \omega \exp(-E_Q/Q)) \exp(-E_a/RT) \quad (6)$$

where Q refers to the light intensity (mW/cm^2), and ω is the weighting factor of the UV-induced term of the reaction as compared to the thermal part of reaction. A general kinetic rate equation containing both UV term and thermal term can be expressed as:

$$\frac{dx}{dt} = A(1 + \omega \exp(-E_Q/Q)) \exp(-E_a/RT)(1-x)^n \quad (7)$$

This equation can be reduced to eq. (5) if UV light is not applied to the curing system or E_Q is very high (i.e., $\omega \exp(-E_Q/Q) \ll 1$). On the other hand, if the influence of the UV-induced term is greater

than that of the thermal term (i.e., $\omega \exp(-E_Q/Q) \gg 1$), eq. (7) can be simplified into the following form:

$$\frac{dx}{dt} = A_1 \exp(-E_Q/Q) \exp(-E_a/RT)(1-x)^n \quad (8)$$

The weighting factor ω in eq. (7) is related to the UV-induced term of the reaction and supposedly a function of the photoinitiator concentration $[I]$, in the form of $\omega = \phi[I]^y$.

Introducing this relationship into eq. (7), we get

$$\frac{dx}{dt} = A(1 + \phi[I]^y \exp(-E_Q/Q)) \exp(-E_a/RT)(1-x)^n \quad (9)$$

This is a general kinetic rate equation for a system with both UV radiation and thermal cure.

ANALYSIS PROCEDURES

- (i) The rate constant k_1 , reaction order n , activation energy E_a , and pre-exponential factor A were first evaluated in a system without UV radiation.

In a first step, curing experiments were conducted at different temperatures without UV radiation. For a designed curing temperature, the data of conversion (x) versus the curing time (t) were measured, and subsequently a plot of $\ln(dx/dt)$ versus $\ln(1-x)$ was drawn. Using eq. (10), we obtained the rate constant k_1 from the y -intercept, and the reaction order n from the slope of the straight line.

$$\ln\left(\frac{dx}{dt}\right) = \ln k_1 + n \ln(1-x) \quad (10)$$

Equation (10) was obtained by taking natural logarithm (to the base e) of both sides of eq. (2). Various k_1 values for the different curing temperatures (T) were thus collected. Then, using the eq. (4), we obtained the activation energy E_a and the pre-exponential factor.

- (ii) The energy barrier of photoinitiation (E_Q , mW/cm²) and the weighting factor of UV-induced part of reaction (ω) were subsequently evaluated in a system with both UV radiation and thermal cure.

In this step, curing experiments were performed with various intensity of UV radiation at different specified temperatures. Using eq. (4), we obtained the various rate constants k_1

and reaction order n values. Theoretically, the n value obtained in this step (with UV radiation) should be identical to that in step (i) (without UV radiation). If we define $F(T)$ as $F(T) = A \exp(-E_a/RT)$, then $F(T)$ should be a constant value for a specified curing temperature. Various $F(T)$ values for each specified curing temperature were thus calculated by using the A and E_a values obtained in step (i). eq. (6) can thus be rewritten as follows:

$$k_1 = F(T)(1 + \omega \exp(-E_Q/Q)) \quad (11)$$

Taking the natural logarithm (to the base e) of both sides of above equation and reorganizing the resulting relationship, we get

$$\ln(k_1/F(T) - 1) = \ln(\omega) + (-E_Q/Q) \quad (12)$$

A plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ was made, and we obtained the ω value from the y -intercept, and E_Q , from the slope of the straight line.

- (iii) The value of y and ϕ in the form of $\omega = \phi[I]^y$ was finally determined. Taking the natural logarithm of both sides of equation $\omega = \phi[I]^y$, we get

$$\ln \omega = \ln \phi + y \ln[I] \quad (13)$$

Various values of ω were collected by varying the photoinitiator concentration $[I]$ in the curing systems. Then, a plot of $\ln \omega$ versus $\ln[I]$ was drawn. We obtained the ϕ value from the y -intercept, and the y value from the slope of the straight line.

Finally, all the parameters (n , E_Q , E_a , y , a , and A) obtained by the previously stated procedures were substituted into eq. (9), and a generally valid kinetic rate equation containing both UV-induced term and thermal term was thus obtained.

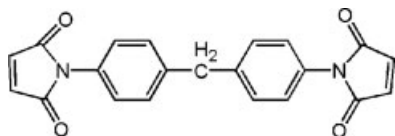
EXPERIMENTAL

Materials

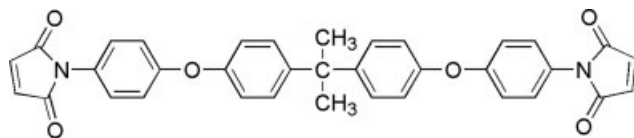
4,4'-bismaleimidodiphenylmethane (BMI) (Aldrich, USA) and diphenyl(2,4,6-trimethyl benzoyl)phosphine oxide (TPO) (TCI, Japan) were used as purchased. TPO served as a photoinitiator. Another bismaleimide of 2,2-bis(4-(4-maleimido phenoxy)phenyl)propane (BMIP) was synthesized and characterized in our laboratory.¹⁸

The chemical structures of BMI and BMIP are shown below:

BMI:



BMIP:



Instrumentation

Differential scanning calorimetry

Samples approximately 3–6 mg in weight were sealed in hermetic pans and scanned in a differential scanning calorimeter (Perkin-Elmer DSC-7) calibrated with an indium standard. A stream of nitrogen at a flow rate of 20 mL/min was used to purge the DSC cell.

Fourier-transform infrared

FTIR spectra were recorded on a Digi-Lab FTS-40 FTIR spectrometer. The samples were mixed with dried KBr powder and pressed into pellets. Spectra were obtained in an optical range of 400 cm⁻¹ to 4000 cm⁻¹ by averaging 32 scans at a resolution of 8 cm⁻¹.

UV light source

A UV light source emitting radiation of 365 nm in wavelength and a power output of 6 W was installed in a light-shielded box. A temperature-controllable heating plate was placed just under the UV light source, and the distance between the heating plate and the UV light source is adjustable. The intensity of this UV light source was adjusted between 2.3 and 5.4 mW/cm².

UV light detector (UVX Radiometer, UVP)

The detection range for the 365 nm detector is between 20 mW/cm² and 0.2 mW/cm². The detector was placed ~1.5–1 cm under the UV light for measurements. Intensities were measured for each 3 min interval and an average value was taken.

Sample preparation

All hybrid samples of bismaleimide (BMI or BMIP) with photoinitiator (TPO) were homogeneously mixed

with acetone according to the designed formulation, and then vacuum-distilled at 65°C to remove the residual solvent. All procedures were performed under light-shielding conditions to avoid interaction from UV light present in daylight. The dried hybrid samples were mixed with dried KBr powder and pressed into thin pellets (0.2 mm thickness); these pellets contained 20 wt % of the active sample. The cure reaction of the bismaleimide in the pellet proceeded in a light-shielded box equipped with a UV light source (365 nm) according to the designed UV intensity, curing temperature and curing time. A stream of nitrogen was used to purge the cure box. Conversion levels for the various cured samples were subsequently measured via a FTIR spectrometer.

RESULTS AND DISCUSSION

BMI curing system

Determination of conversion level via FTIR measurement

Before the cure systems were performed simultaneously by UV radiation and thermal cure, curing experiments were preliminarily conducted at different temperatures without UV radiation, and the results were examined via FTIR spectra. Photoinitiator TPO probably does not play any significant role in the thermal cure system. However, for the comparison with the UV-induced curing systems, photoinitiator TPO was added to the sole thermal curing systems. Figure 1(b) shows the DSC thermogram for the curing system of the BMI monomer containing 3 phr TPO at a heating rate of 20 K/

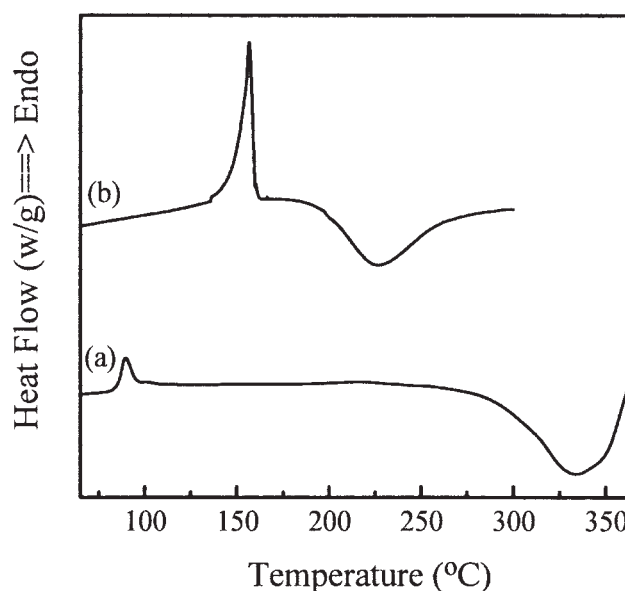


Figure 1 DSC thermogram for curing bismaleimide monomer containing 3 phr TPO at a heating rate of 20°C/min. (a) BMIP monomer; (b) BMI monomer.

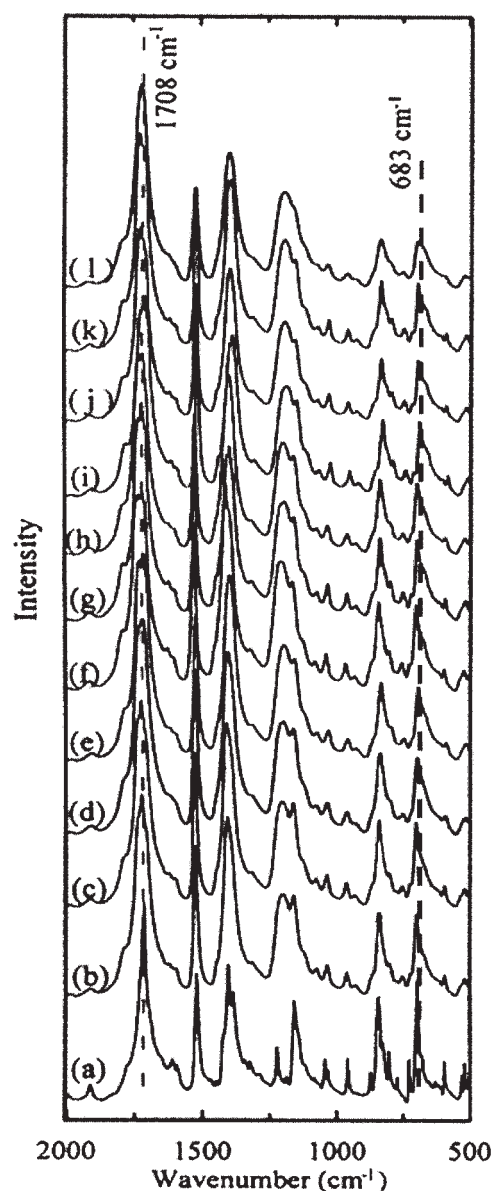


Figure 2 FTIR spectra for curing BMI monomer containing 3 phr TPO at 513 K without UV radiation for different curing times: (a) 0 min, (b) 3 min, (c) 6 min, (d) 9 min, (e) 12 min, (f) 15 min, (g) 18 min, (h) 21 min, (i) 24 min, (j) 27 min, (k) 30 min, and (l) completely cured.

min. Only one reaction exotherm was observed over the temperature range of 470–540 K, suggesting that the cure reaction did not occur at temperatures lower than 470 K. Therefore, the curing experiments for the curing system of the BMI monomer containing 3 phr TPO were conducted isothermally at 493, 513, and 533 K, respectively, for different curing times without UV radiation. The curing extents (conversions) for the precured samples were then measured via FTIR spectra. Figure 2 can be taken as an example to illustrate the measurement of the curing extent of the precured samples for the different curing times. It shows the

FTIR spectra for the curing system of the BMI monomer containing 3 phr TPO at 513 K without UV radiation for different curing times. The characteristic absorption band of the =C–H bending vibrations of the maleimide moiety, which appeared at 683 cm^{-1} in the monomer, gradually disappeared during the curing process, suggesting curing of the maleimide group. The absorption peak at 830 cm^{-1} , attributable to the out-of-plane bending of the =CH group of the maleimide moiety, and the absorption at 683 cm^{-1} disappeared simultaneously. However, these peaks did not disappear completely in the spectra of the completely cured polymer, most likely because of concomitant absorption due to the bending vibration of other C–H groups (aromatic) at the same frequency.¹⁷ Figure 2(l) shows the spectrum of a completely cured sample obtained by conducting a dynamic DSC run to 680 K. The absorption peak at 1708 cm^{-1} , attributable to the carbonyl group (C=O) of the maleimide moiety, was taken as an internal standard. Consequently, the conversion of the maleimide group (x) can be determined by the following relationship:

$$x = \frac{\frac{A_{683}}{A_{1708}} - \frac{A'_{683}}{A'_{1708}}}{\frac{A_{683}}{A_{1708}} - \frac{A''_{683}}{A''_{1708}}} \quad (14)$$

where A_{683} and A_{1708} are the areas of the corresponding peaks before sample was cured, A'_{683} and A'_{1708} are the areas of the corresponding peaks after sample was partially cured, and A''_{683} and A''_{1708} refer to the areas of the corresponding peaks after sample was completely cured.

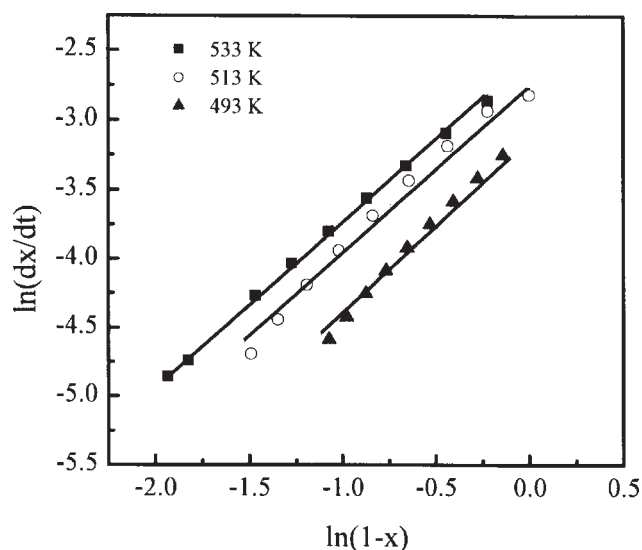


Figure 3 Plot of $\ln(dx/dt)$ versus $\ln(1-x)$ for isothermal curing of the BMI monomer containing 3 phr TPO at 493, 513, and 533 K, respectively, without UV radiation.

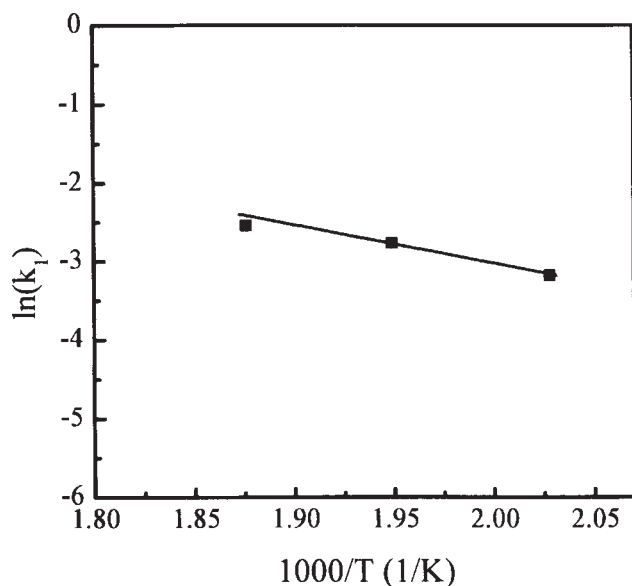


Figure 4 Plot of $\ln(k_1)$ versus $1/T$ for isothermal curing of the BMI monomer containing 3 phr TPO, without UV radiation.

Evaluation of kinetic parameters k_1 , n , E_a , and A for thermal cure systems without UV radiation

The relationship of the conversion (x) with respect to the curing time (t) for the isothermal cure was obtained by calculations based on eq. (14), and hence dx/dt can be calculated at the specified conversions (x). Figure 3 shows the plot of $\ln(dx/dt)$ versus $\ln(1-x)$ for the isothermal curing of the BMI monomer system containing 3 phr TPO at 493, 513, and 533 K, respectively, without UV radiation. In Figure 3, straight lines were obtained by the regression analysis; all of these straight lines for the different curing temperatures are parallel. Based on eq. (10), we obtained the rate constants k_1 from the y -intercept of the straight lines and reaction order n from the slope of straight lines. Values of k_1 are 0.079, 0.063, and 0.042 min^{-1} for the curing temperatures of 533, 513, and 493 K, respectively. The reaction order n is 1.2 for all the curing temperatures. As expected, values of k_1 increase with increasing the curing temperature (T). Using these k_1 values, a plot of $\ln(k_1)$ versus $1/T$ was drawn, as shown in Figure 4, suggesting a straight line. Based on the calculation of eq. (4), we obtained the activation energy $E_a = 40,800$ J/mol and the pre-exponential factor $A = 900$ min^{-1} .

Substituting all of the above kinetic parameters into eq. (5), (7), or (9), we obtained the following semi-empirical equation for the thermal cure system without UV radiation.

$$\frac{dx}{dt} = 900 \exp(-40800/8.314T)(1-x)^{1.2} \quad (15)$$

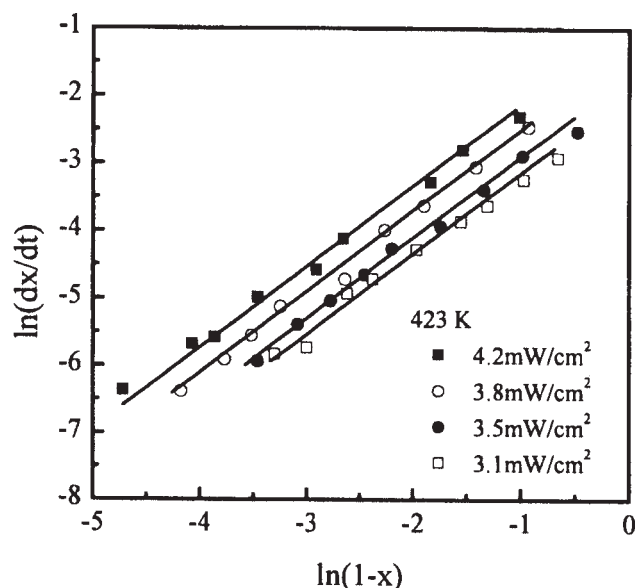


Figure 5 Plot of $\ln(dx/dt)$ versus $\ln(1-x)$ for isothermal curing of the BMI monomer containing 3 phr TPO at 423 K, with different intensity of UV radiation.

Evaluation of kinetic parameters E_Q and ω for the system with both UV radiation and thermal cure

Figures 5 and 6 show the plots of $\ln(dx/dt)$ versus $\ln(1-x)$ for isothermal curing of the BMI monomer containing 3 phr TPO at 423 and 433 K, respectively, with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm^2) for each cure temperature. In these figures, straight lines were obtained for each UV intensity (Q) by the regression analysis. All of the straight lines are parallel, indicating they have

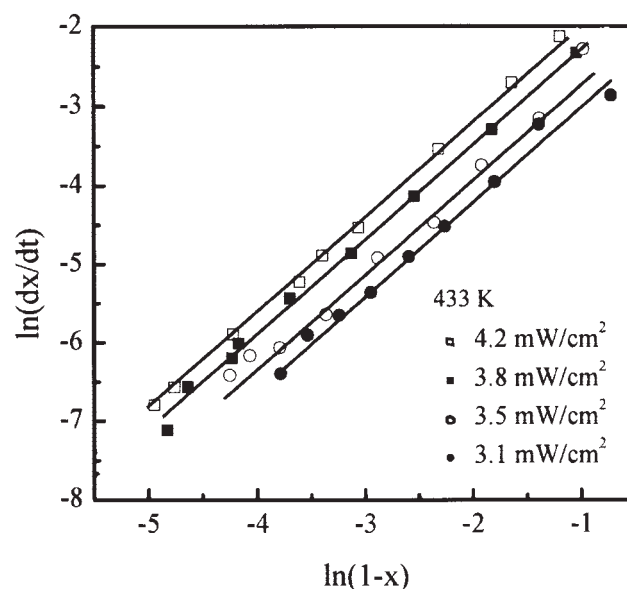


Figure 6 Plot of $\ln(dx/dt)$ versus $\ln(1-x)$ for isothermal curing of the BMI monomer containing 3 phr TPO at 433 K, with different intensity of UV radiation.

TABLE I
 k_1 and n Values for Isothermally Curing BMI Monomer Containing 3 phr TPO at 423 and 433 K, respectively, with Different Intensity of UV Radiation

Curing temperature (K)	Intensity of UV (mW/cm ²)	k_1 (min ⁻¹)	n
423	4.2	0.38	1.2
	3.8	0.27	1.2
	3.5	0.18	1.2
	3.1	0.15	1.2
433	4.2	0.43	1.2
	3.8	0.33	1.2
	3.5	0.22	1.2
	3.1	0.17	1.2

the same slope, and hence the identical reaction order n . As previously analyzed, the various values of the rate constant k_1 and the reaction order n were obtained for each curing temperature, and are summarized in Table I. As expected, values of $k_1(T, Q)$ increase with increasing intensities of the UV radiation (Q) at a specified curing temperature. Based on the above definition of $F(T) = A(-E_a/RT)$, $F(T)$ should be a constant value for a specified curing temperature, irrespective of the intensity of the UV radiation (Q). As previously mentioned, the various $F(T)$ values for each specified curing temperature can be calculated using the A and E_a values (900 min⁻¹ and 40,800 J/mol) previously obtained ("Evaluation of Kinetic Parameters k_1 , n , E_a , and A for Thermal Cure Systems Without UV Radiation" section). Considering eq. (12), a plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ was made for a specified cure temperature, as shown in Figure 7. The ω value was obtained from the y -intercept of the straight line and E_Q from the slope of this line. We found a common straight line for the different curing temperatures of 433 and 423 K, implying that ω and E_Q are independent of the cure temperature (T) and the intensity of UV radiation (Q). It was as expected. With eq. (12), we obtained $\omega = 190$ and $E_Q = 7.5$ mW/cm².

Substituting these kinetic parameters into eq. (7), we obtained the following semi-empirical equation for the system containing 3 phr TPO with both UV radiation and thermal cure.

$$\frac{dx}{dt} = 900(1 + 190 \exp(-7.5/Q)) \exp(-40800/8.314T)(1-x)^{1.2} \quad (16)$$

Evaluation of kinetic parameters ϕ and γ in eq. (9)

To evaluate the parameters ϕ and γ in eq. (9), we varied the concentration of the photoinitiator ([I]) in the cure system under isothermal conditions at 423 K. In addition to the previous curing system

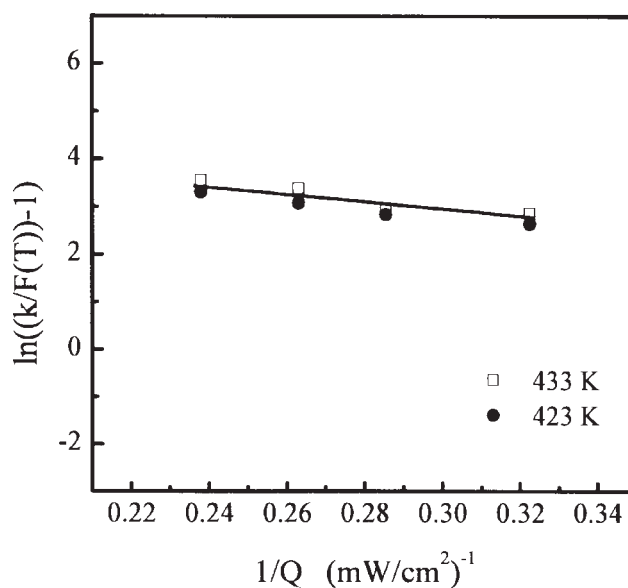


Figure 7 Plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ at specified curing temperatures of 433 and 423 K.

with 3 phr TPO, two other systems with 1 and 5 phr TPO were investigated. The plots of $\ln(dx/dt)$ versus $\ln(1-x)$ for the curing system of BMI monomer containing 1 and 5 phr TPO at 423 K, respectively, with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm²) are similar to those in Figure 5. They are not shown for brevity. In the same way as above, the various values of the rate constant k_1 and the reaction order n were obtained for each TPO concentration, and were summarized in Table II. The data in Tables I and II indicate that all curing systems for BMI have the same reaction order ($n = 1.2$) and that the k_1 values increase with increasing TPO concentration ([I]) for the same intensity of UV radiation and cure temperature. A plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ was drawn for the different TPO concentrations (1, 3, and 5 phr) at a curing temperature of 423 K, as shown in Figure 8. The ω values were obtained from the y -intercept of the straight lines and E_Q from the slope of these lines. As above, we

TABLE II
 k_1 and n Values for Curing BMI Monomer Containing Different Level of TPO and Different Intensity of UV Radiation at 423 K

Content of TPO (phr)	Intensity of UV (mW/cm ²)	k_1 (min ⁻¹)	n
1	4.2	0.17	1.2
	3.8	0.14	1.2
	3.5	0.12	1.2
	3.1	0.09	1.2
5	4.2	0.36	1.2
	3.8	0.27	1.2
	3.5	0.23	1.2
	3.1	0.18	1.2

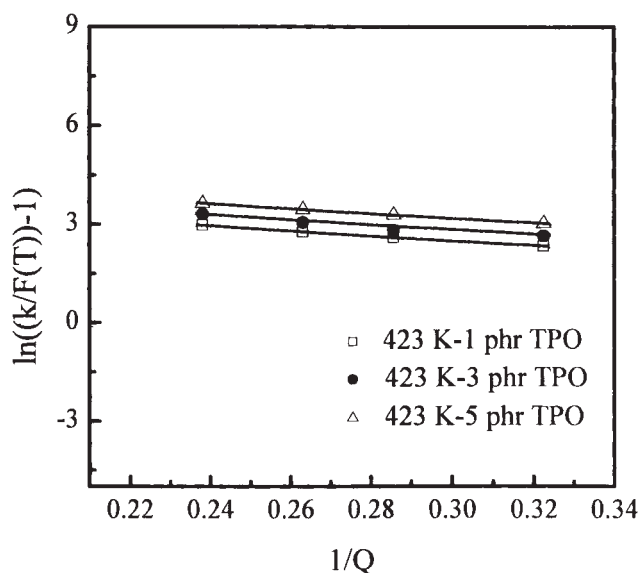


Figure 8 Plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ for different TPO concentrations (1, 3, and 5 phr) at curing temperature of 423 K.

found parallel straight lines for the different TPO concentrations, implying that the curing systems with different TPO concentrations bear the same energy barrier of photoinitiation ($E_Q = 7.5$ mW/cm²). Supposedly, the energy barrier of the photoinitiation (E_Q , mW/cm²) is related to the type of photoinitiator and irrespective of the TPO concentration. Meanwhile, ω values increase with increasing TPO concentration. A plot of $\ln(\omega)$ versus $[I]$ was made for the curing temperature of 423 K, as shown in Figure 9. The values of $\phi = 117$ and $y = 0.4$ were obtained based on the calculation of eq. (13).

Substituting all the kinetic parameters into eq. (9), we obtained the following semi-empirical equation for the curing system with both UV radiation and thermal cure.

$$\frac{dx}{dt} = 900(1 + 117[I]^{0.4} \exp(-7.5/Q)) \exp(-40800/8.314T) (1-x)^{1.2} \quad (17)$$

Fitting results

A general kinetic rate equation for a system with both UV radiation and thermal cure was derived as eq. (9); its semi-empirical equation for a curing system of BMI monomer containing TPO as a photoinitiator with both UV radiation and thermal cure was given by eq. (17). This semi-empirical equation was used to fit the experimental data obtained from three cases of different curing condition.

Case 1. System with sole thermal cure, without UV radiation. The semi-empirical eq. (17) can be simpli-

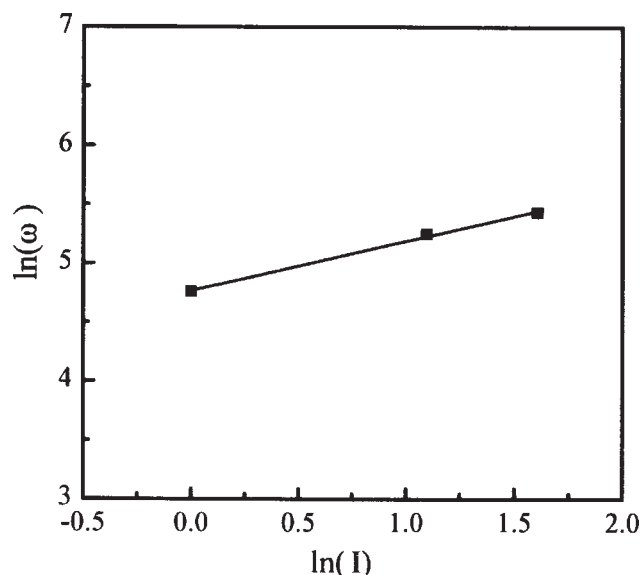


Figure 9 Plot of $\ln(\omega)$ versus $[I]$ for curing temperature of 423 K.

fied to eq. (15) for a system at elevated temperatures without UV radiation. Figure 10 shows a plot of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (15)] for isothermal curing of BMI monomer at 493, 513, and 533 K, respectively, without UV radiation. As observed, the experimental results are reasonably well represented by these semi-empirical expressions.

Case 2. System with both thermal and UV radiation curing at constant concentration of photoinitiator TPO. The

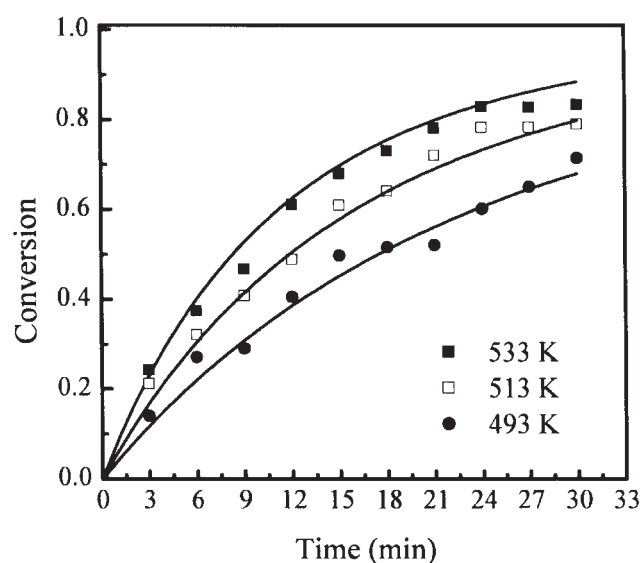


Figure 10 Plot of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (17) or (15)] for isothermal curing of the BMI monomer at 493, 513, and 533 K, respectively, without UV radiation.

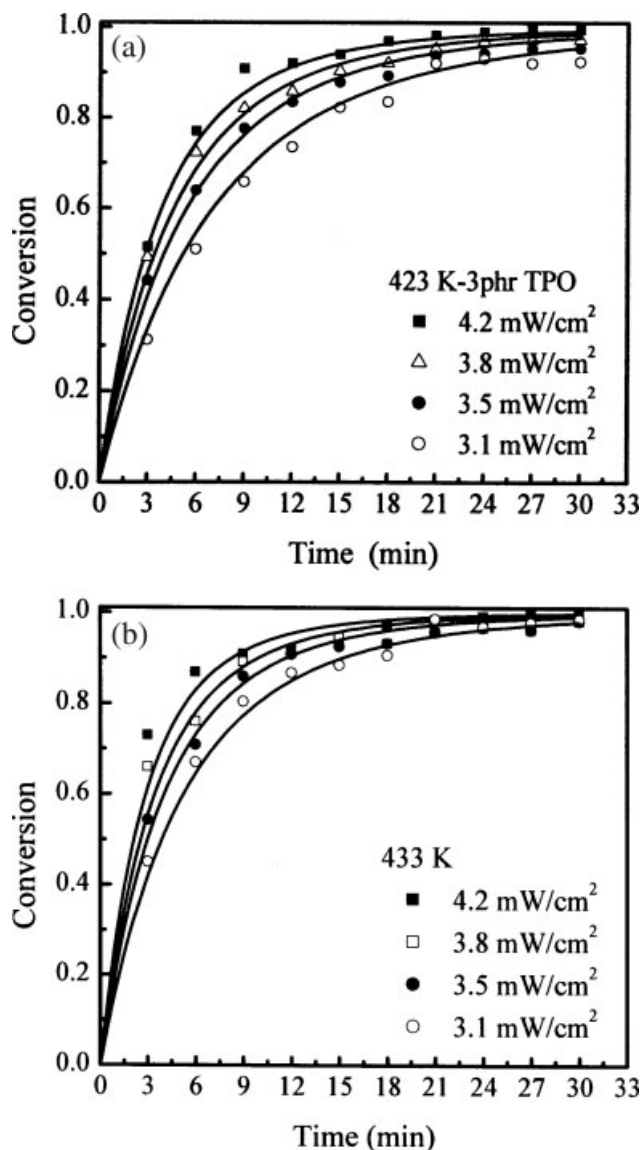


Figure 11 Plots of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (17) or (16)] for isothermal curing of the BMI monomer containing 3 phr TPO at 423 (Plot a) and 433 K (Plot b), respectively, with different intensities of UV radiation.

semi-empirical eq. (17) can be simplified to eq. (16) for a system with both thermal and UV radiation curing at a constant concentration of the photo-initiator TPO. Shown in Figure 11 are plots of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (16)] for isothermal curing of BMI monomer containing 3 phr TPO at 423 (Plot a) and 433 k (Plot b), respectively, with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm^2) for each cure temperature. As above, the experimental results were reasonably well represented by these semi-empirical expressions.

Case 3. System with both thermal and UV radiation curing, at different concentrations of photoinitiator TPO. Figure 12 shows the plots of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (17)] for the curing system of BMI monomer containing 1 (Plot a) and 5 phr (Plot b) TPO at 423 K, respectively, with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm^2). Again, the experimental results could be satisfactorily represented by the semi-empirical expressions.

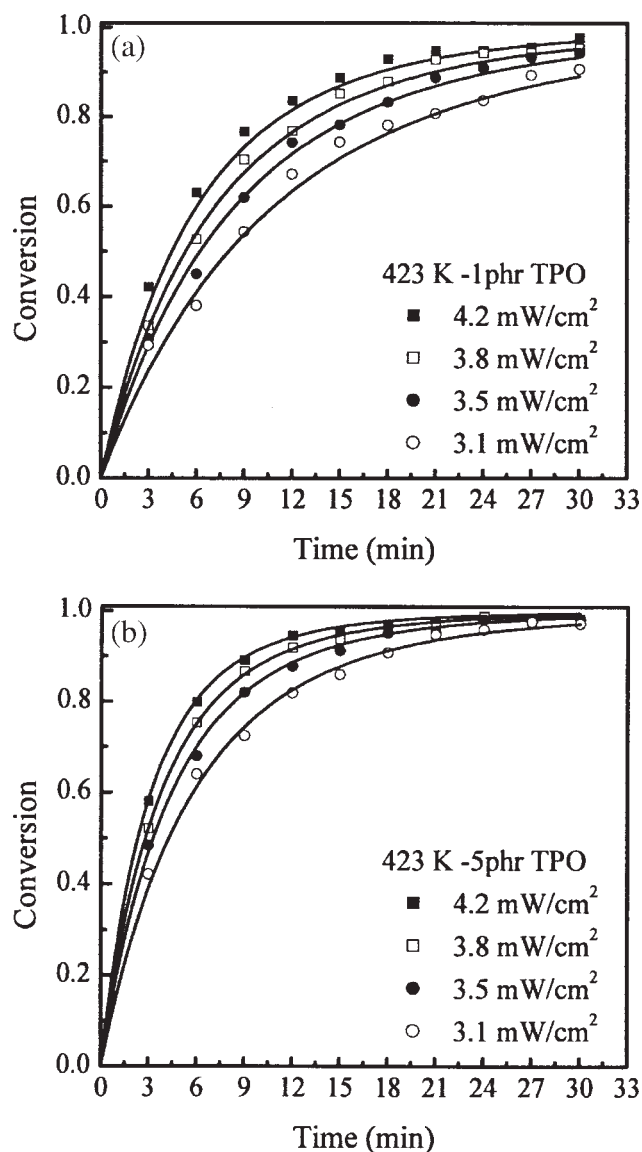


Figure 12 Plots of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (17)] for the curing system of BMI monomer containing 1 (Plot a) and 5 phr (Plot b) TPO at 423 K, respectively, with different intensities of UV radiation.

TABLE III
 k_1 and n Values for Isothermally Curing BMIP Monomer Containing 3 phr TPO at 373, 413, and 473 K, respectively, with Different Intensity of UV Radiation

Curing temperature (K)	Intensity of UV (mW/cm ²)	k_1 (min ⁻¹)	n
373	4.2	0.0098	1.3
	3.8	0.0079	1.3
	3.5	0.0064	1.3
	3.1	0.0046	1.3
413	4.2	0.052	1.3
	3.8	0.041	1.3
	3.5	0.034	1.3
	3.1	0.024	1.3
473	4.2	0.364	1.3
	3.8	0.287	1.3
	3.5	0.238	1.3
	3.1	0.171	1.3

It follows that the general kinetic rate equation [eq. (9)] is applicable to any cases of BMI curing system.

BMIP curing system

Figure 1(a) shows the DSC thermogram for the curing system of the BMIP monomer containing 3 phr TPO at a heating rate of 20°C/min. Similar to the BMI thermogram, only one reaction exotherm is observed over the temperature range of 523–623 K, suggesting that the cure reaction does not occur at temperatures lower than 523 K. Therefore, curing experiments for the BMIP monomer containing 3 phr TPO were conducted isothermally at 573, 593 and 613 K without UV radiation with different curing times. Since the curing system of the BMIP monomer requires a higher curing temperature than the curing system of the BMI monomer, the photoinitiator presumably plays a more influential role in the UV-induced curing system of the BMIP monomer than in the BMI monomer system.

Determination of the kinetic parameters

The conversion of the maleimide group (x) in the BMIP monomer system can be determined by the following relationship:

$$x = \frac{\frac{A_{688}}{A_{1723}} - \frac{A'_{688}}{A'_{1728}}}{\frac{A_{688}}{A_{1723}} - \frac{A''_{688}}{A''_{1723}}} \quad (18)$$

There is a small shift in the absorption peak of the maleimide moiety (688 cm⁻¹) and the internal standard (1723 cm⁻¹) in the BMIP curing system as compared to the peaks in the BMI curing system. The definitions of A_{688} , A_{1723} , A'_{688} , A'_{1723} , A''_{688} , and A''_{1723} are analogous to the ones given earlier.

All the experimental steps and analytic procedures are virtually the same as previously stated. Values of k_1 are 0.085, 0.058, and 0.039 min⁻¹ for the curing temperatures of 613, 593, and 573 K, respectively. The reaction order n is 1.3 for all curing temperatures. Using these k_1 values, a plot of $\ln(k_1)$ versus $1/T$ yielded a straight line, and an activation energy $E_a = 53,000$ J/mol and pre-exponential factor $A = 2700$ min⁻¹ were obtained. Substituting these kinetic parameters into eqs. (5), (7), or (9), we got the following semi-empirical equation for the thermal curing system without UV radiation:

$$\frac{dx}{dt} = 2700 \exp(-53000/8.314T)(1-x)^{1.3} \quad (19)$$

Subsequently, curing experiments of the systems were conducted with both UV radiation and thermal cure. Plots of $\ln(dx/dt)$ versus $\ln(1-x)$ were printed out for the isothermal curing of the BMIP monomer containing 3 phr TPO at 373, 413, and 473 K, respectively, with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm²) for each curing temperature. The kinetic parameters were thus obtained and summarized in Table III. As expected, values of $k_1(T, Q)$ increase with increasing intensity of the UV radiation (Q) at a specified cure temperature. The plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ for a specified cure temperature yielded $\omega = 830$ from the y -intercept of the straight line and $E_Q = 9.1$ mW/cm² from its slope. Substitution of the kinetic parameters into eq. (5), (7), or (9) results in the following semi-empirical equation for the system containing 3 phr TPO with both UV radiation and thermal cure:

$$\frac{dx}{dt} = 2700(1 + 830 \exp(-9.1/Q)) \exp(-53000/8.314T) \times (1-x)^{1.3} \quad (20)$$

Finally, curing experiments of the systems were conducted with both UV radiation and thermal cure, with different concentrations of the photoinitiator TPO. Again, $\ln(dx/dt)$ versus $\ln(1-x)$ was plotted for the curing system of the BMIP monomer containing 3, 4, and 5 phr TPO at 413 K, respectively, with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm²). As analyzed before, the various values of the rate constant k_1 , the reaction order n , and the other kinetic parameters were obtained for each TPO concentration, and are summarized in Tables IV and V. Substituting the kinetic parameters into eq. (9), we had the following semi-empirical equation for the system with both UV radiation and thermal cure:

TABLE IV
 k_1 and n Values for Curing BMIP Monomer Containing Different Level of TPO and Different Intensity of UV Radiation at 413 K

Content of TPO (phr)	Intensity of UV (mW/cm ²)	k_1 (min ⁻¹)	n
3	5.1	0.075	1.3
	4.8	0.067	1.3
	4.5	0.059	1.3
	4.2	0.052	1.3
	3.8	0.041	1.3
	3.5	0.034	1.3
4	3.1	0.024	1.3
	4.2	0.062	1.3
	3.8	0.050	1.3
	3.5	0.040	1.3
5	3.1	0.029	1.3
	4.2	0.070	1.3
	3.8	0.056	1.3
	3.5	0.046	1.3
	3.1	0.033	1.3

$$\frac{dx}{dt} = 2700(1 + 435[I]^{0.6} \exp(-9.1/Q)) \exp(-53000/8.314T)(1-x)^{1.3} \quad (21)$$

Fitting results

A semi-empirical equation for the curing system of the BMIP monomer containing TPO as a photoinitiator with both UV radiation and thermal cure is given by eq. (21). This semi-empirical equation was taken to fit the experimental data obtained from the different curing cases. All experimental results were reasonably well represented by the semi-empirical equation. For brevity, only two cases are shown for comparison. Figure 13 shows plots of comparison between the experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (21)] for isothermal curing of the BMIP monomer system containing 4 phr TPO at 413 K (Plot a), 3 phr TPO at

473 K (Plot b), with different intensities of UV radiation ($Q = 3.1, 3.5, 3.8,$ and 4.2 mW/cm^2). The results indicate that the factors of curing temperature (413, 473 K) and concentration of TPO (3, 4 phr) may be involved in the kinetic rate equation, and that a discrepancy exists on the conversion-time ($x-t$) curves. If BMIP systems are cured under sole thermal conditions without UV radiation, the curing temperature has to be higher than 523 K. However, if the curing experiments of these systems were performed with both UV radiation and thermal cure, the addition of a photoinitiator (say, 4 phr) may facilitate the cure

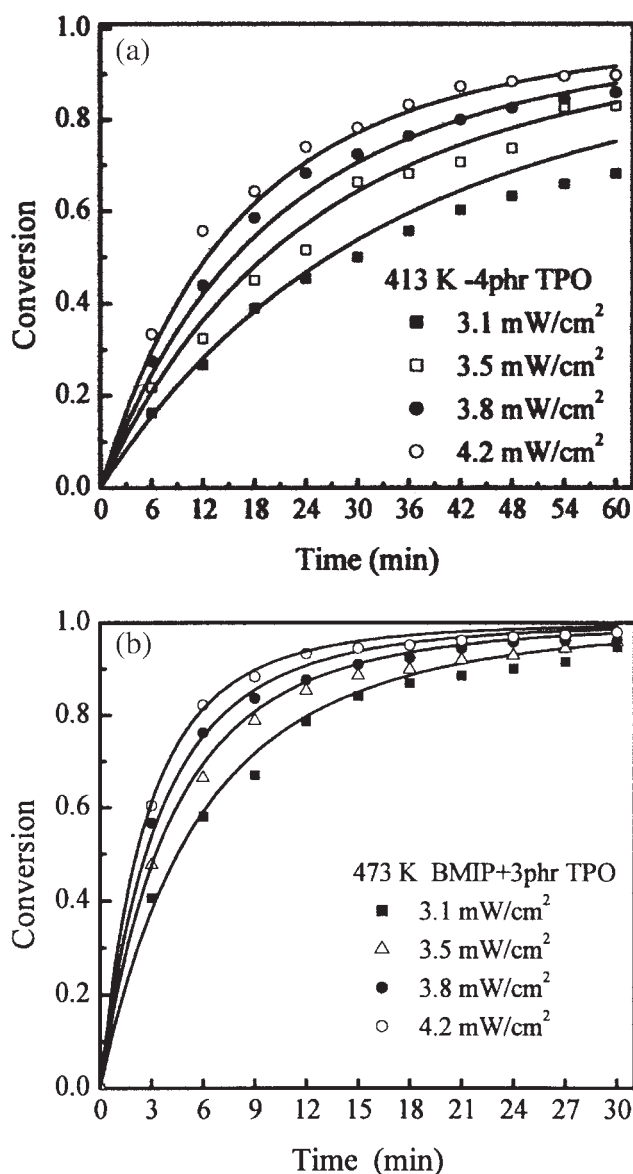


Figure 13 Plots of comparison between experimentally determined conversion curves (symbols) and those (solid line) calculated from the semi-empirical rate equation [eq. (21)] for BMIP monomer curing system containing: (a) 4 phr TPO at 413 K, (b) 3 phr TPO at 473 K, with different intensities of UV radiation.

TABLE V
 Kinetic Parameters for Curing BMIP Monomer with Both UV Radiation and Thermal Cure, Containing Different Level of TPO

Parameters	Values
n	1.3
A (min ⁻¹)	2700
E_a (J/mol)	53000
E_Q (mW/cm ²)	9.1
ϕ	435
y	0.6

reaction even at the lower temperature of 413 K [Fig. 13(a)]. But, as compared with Figure 13(a), Figure 13(b) suggests that a higher curing temperature (473 K) obviously improves the curing efficiency (i.e., curing rate) at the comparable level of TPO concentration.

CONCLUSIONS

In the literature, cure kinetics of various thermosetting polymers was usually investigated by UV-induced curing or thermal curing individually. In this study, a novel and generally valid kinetic rate equation [eq. (9)] combining UV-induced curing and thermal curing was successfully derived and was supported by the experimental data. This general kinetic rate equation was derived based on a premise that the general kinetic rate constant k_1 is composed of thermal term and UV-induced term. The presence of UV radiation only increases the initiation rate, but does not influence the activation energy (E_a) itself. This general kinetic rate equation is composed of term for the reaction order n , activation energy E_a , curing temperature T , energy barrier of photoinitiation E_Q , intensity of UV radiation Q , concentration of photoinitiator $[I]$, and some other parameters.

Incidentally, the activation energy E_a , reaction order n , and pre-exponential factor A are identical for a system with sole thermal curing (without UV radiation), and a system with both UV radiation and thermal curing. This salient result implies that the previously mentioned premise is right, i.e., UV radiation only enhances the initiation rate and has no influence on the activation energy (E_a). The initiation rate resulted from UV light depends on the energy barrier of the photoinitiation (E_Q).

Ultraviolet-induced and thermal curing of bismaleimide systems could be adequately modeled by the derived general kinetic rate equation [eq. (9)];

however, autocatalytic characteristics are not yet included. The derived general kinetic rate equation will be further investigated in the other curing systems, and autocatalytic characteristics may probably be included in the future.

References

1. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Plenum Press: New York, 1990.
2. Takao, I.; Hidehiko, S.; Wakichi, F.; Masao, T. *J Appl Polym Sci* 1997, 65, 1349.
3. Ceccia, S.; Turcato, E. A.; Maffettone, P. L.; Bongiovanni, R. *Prog Org Coat* 2008, 63, 110.
4. Nebioglu, A.; Soucek, M. D. *Eur Polym J* 2007, 43, 3325.
5. Sangermano, M.; Lak, N.; Malucelli, G.; Samakande, A.; Sanderson, R. D. *Prog Org Coat* 2008, 61, 89.
6. Kohli, P.; Scranto, A. B.; Blanchard, G. J. *Macromolecules* 1998, 31, 5681.
7. Martuscelli, E.; Musto, P.; Ragosta, G.; Scarinzi, G. *Polymer* 1996, 37, 4052.
8. Morel, F.; Decker, C.; Jonsson, S.; Clark, S. C.; Hoyle, C. E. *Polymer* 1999, 40, 2447.
9. Decker, C.; Morel, F.; Jonsson, S.; Clark, S.; Hoyle, C. *Macromol Chem Phys* 1999, 200, 1005.
10. Decker, C.; Bianchi, C. *Polym Int* 2003, 52, 722.
11. Bongiovanni, R.; Sangermano, M.; Malucelli, G.; Priola, A. *Prog Org Coat* 2005, 53, 46.
12. Abadie, M. J. M.; Xiong, Y.; Boey, F. Y. C. *Eur Polym J* 2003, 39, 1243.
13. Hsieh, K. H.; Kuo, C. H.; Dai, C. A.; Chen, W. C.; Peng, T. C.; Ho, G. H. *J Appl Polym Sci* 2004, 91, 3162.
14. Boey, F. Y. C.; Qiang, W. *Polymer* 2000, 41, 2081.
15. Lin, R. H.; Hong, J. L.; Su, A. C. *Polymer* 1995, 36, 3349.
16. Jovan, M.; Sasa, A. *Macromolecules* 1996, 29, 239.
17. Lin, R. H.; Lu, W. H.; Lin, C. W. *Polymer* 2004, 45, 4423.
18. Lin, R. H.; Liu, Y. H.; Chen, Y. H.; Lee, A. C.; Ho, T. H. *Eur Polym J* 2007, 43, 4197.
19. Acevedo, M.; De Abajo, J.; De La Campa, J. G. *Polymer* 1990, 31, 1955.
20. Goodwin, A. A. *Polym Int* 1993, 32, 87.
21. Boey, F. Y. C.; Song, X. L.; Yue, C. Y.; Zhao, Q. *J Polym Sci Part A: Polym Chem* 2000, 38, 907.