Kinetic Study of the Curing Behavior of Bismaleimide Modified with Diallylbisphenol A

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ABSTRACT: The curing kinetics of bismaleimide modified with diallylbisphenol A were investigated for different ratios of 1,1′-(methylene di-4,1-phenylene) bismaleimide and diallylbisphenol A with differential scanning calorimetry. Multiheating-rate and isothermal methods were used to study the kinetics of the curing process. The results indicated that the activation energy changed with the extent of conversion. The activation energy obtained by the multiheating-rate method was higher than that obtained by the isothermal method. Two kinetic models (autocatalytic and *n*th-order) were successfully used to model the curing process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2229–2240, 2003

Key words: copolymerization; modeling; kinetic study; modified BMI; curing

INTRODUCTION

Increasing demands for high-performance resin systems exceeding what most epoxy systems can offer has led to the application of polyimide systems in the aerospace and electronics industries, polyimide systems having the advantage of excellent mechanical property retention at elevated temperatures and in wet environments. Condensation-type polyimides usually suffer from processing problems because of their insolubility and infusibility and the volatiles evolving during ring formation.[1] These invariably result in unacceptable problems when they are used in the autoclave production of composite parts or even for microelectronic encapsulation, for which often difficult-to-access parts require low viscous flow before curing. In contrast, some important addition-type bisimides, such bismaleimides (BMIs), are able to produce suitably low viscosity and low volatility to give almost epoxy-like processing ease. Although less thermally resistant than the former condensation types, BMIs nevertheless have been shown to be able to withstand acceptably high temperatures above 200°C and up to 300°C.[2–4]

BMIs, since first reported in 1968,[5] are not usually used alone because of their brittle nature. Extensive research has been undertaken for enhancing the toughness of BMIs by reducing the crosslink density in neat resin systems. Methods include the addition of reactive elastomers,[6] Michael addition chain reactions,[1,7] copolymerization with allyl-terminated copolymers,[8,9] eutectic mixtures,[10] and modification with thermoplastics.[11,12] In some cases, commercial formulations have been made by a combination of these methods.[3,13] So far, the copolymerization of BMI with allylphenyl/allylphenol compounds has been shown to be the most effective method for toughening BMI. The most promising modifier has been diallylbisphenol A (DABA). These modified BMI formulations offer easy processability and cured networks with excellent toughness. Allylphenol compounds coreact with BMI to give linear chain extension by an ene-type reaction, and this is followed by a Diels–Alder reaction at a high temperature. This chain extension results in tougher networks with only minimum reductions in the thermal properties.

Although some attempts have been previously made to elucidate the curing pathways and structure–property relationships of BMI/DABA systems, these have been impeded by the complexities of the reaction paths and multiple reactions taking place because a clear picture of the chemical transformations occurring during curing has not yet been established. The following reaction types have been proposed to be involved in the curing process: ene, Diels–Alder, homopolymerization, and alternating compolymerization.[8,9] These processes are outlined in Figure 1. In all these reactions, the maleimide moieties are converted into succinimide groups.

Most of the attempts made so far to delineate the reaction paths involved have used *in situ* real-time Fourier transform infrared to follow the reacting functional groups.[14–16] Other techniques, which have been used by different researchers, include fluorescence studies[17] and NMR.[18,19] However, to our knowledge, no studies have been reported so far about the effect of

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formulations on the curing kinetics of BMI-based resins. As mentioned previously, copolymerization and homopolymerization reactions occur during the curing process.[8,9] If this is true, the molar ratio between BMI and DABA in a formulation should have a large impact on the curing kinetics.

The kinetic study of a curing process by differential scanning calorimetry (DSC) is based on the assumption that the measured heat flow (dH/dt) is proportional to the rate of conversion at a constant temperature ($d\alpha/dt$). $d\alpha/dt$ can be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{\text{Rxn}}} \tag{1}$$

where ΔH_{Rxn} is the total heat flow of the reaction. The conversion at any time t (α_t) can be defined as follows:

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{\text{Rxn}}} \tag{2}$$

All kinetic studies start with a basic rate equation, which relates $d\alpha/dt$ to a function of the concentrations of the reactants [$f(\alpha)$] through a rate constant (k):

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{3}$$

where α is the chemical conversion or extent of reaction and $f(\alpha)$ is assumed to be independent of temperature.

k is assumed to follow an Arrhenius equation:

$$k = A\exp(-E/RT) \tag{4}$$

where E is the activation energy, R is the gas constant (8.3 J/mol/K), T is the absolute temperature, and A is the pre-exponential or frequency factor. Therefore, E can be obtained with the following equation:

$$\ln k = \ln A - E/RT \tag{5}$$

The function $f(\alpha)$ is generally expressed in the form of two equations, an nth-order equation and an autocatalytic equation :

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{6}$$

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \tag{7}$$

Therefore, the objective of the kinetic study of the curing process is to determine the reaction equation, the reaction orders (m and n), E, and A. To this end, two methods have generally been proposed.

Nonisothermal method

The nonisothermal method includes a single-heating-rate method and a multiheating-rate method. The single-heating rate method measures the curing process at only one constant heating rate, by which $d\alpha/dt$ and α are determined. The data are then analyzed with eq. (6), with nth-order kinetics assumed. The kinetic parameters n, ln A, and E, are, therefore, determined from the plot of $\ln[(d\alpha/dt)/(1-\alpha)^n]$ versus T^{-1}. A linear result will validate the assumption of nth-order kinetics. Ln A and E are then determined from the intercept and slope of the linear line, respectively. To the extent that the nth-order reaction kinetics are not always correct, this method lacks some degree of reliability.

The multiheating-rate method is an isoconversional method that assumes that E is temperature-independent but may change with conversion. This method is, therefore, suitable for systems with multiple reactions (including the overlapping of degradation with cure) and for which the thermal analysis baselines are often not resolvable. The two kinetic analysis methods for multiheating-rate data that have been proposed and widely used are those of Ozawa[20,21] and Kissinger.[22] The Ozawa method relates E to the heating rate (ϕ) and isoconversional temperature (T_i) by a simple equation:

$$E = \frac{-R}{1.052}\frac{\Delta \ln \phi}{\Delta(1/T_i)} \tag{8}$$

The advantage of the Ozawa method is that E can be measured over the entire course of the reaction.

The Kissinger method is based on the assumption that the conversion at the peak curing exotherm is constant and independent of the heating rate. E can be calculated with the peak exotherm temperature (T_p) and ϕ as follows:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = \frac{E}{R} \tag{9}$$

The Kissinger method assumes that the DSC peak exotherm is isoconversional, and so its value is not dependent on the heating rate. It also distinguishes the changes in the reaction mechanism via changes in E with conversion. For both nth-order and autocatalytic reactions, the obtained values of E, ln A, and $d\alpha/dt$ are comparable to those of isothermal methods.

Isothermal method

Theoretically, the isothermal method can best distinguish between different reaction mechanisms and so give the most accurate and reliable description of the cure. This is because many reactions are invari-

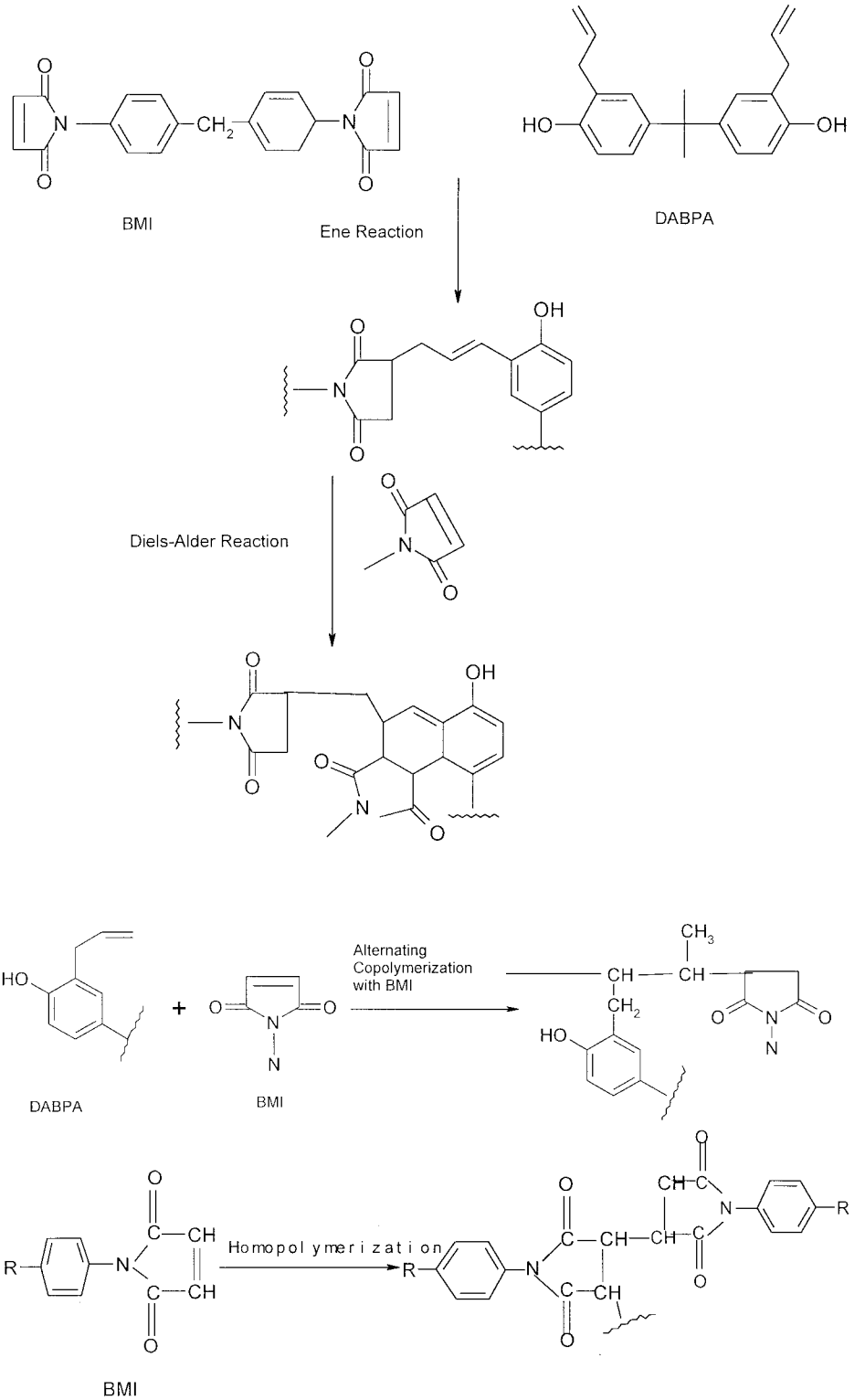

Figure 1 Proposed curing mechanisms for BMI/DABA resins.

ably activated at different temperature levels or ranges. The isothermal procedure follows the following steps. First, a kinetic equation is selected according to the characteristics of the isothermal curing process. In an *n*th-order reaction, the maximum rate occurs at zero conversion. If not, an autocatalytic equation should be chosen. Once the rate equation is selected, k and m or n can be determined. For an *n*th-order reaction, eq. (6) can be rewritten as follows:

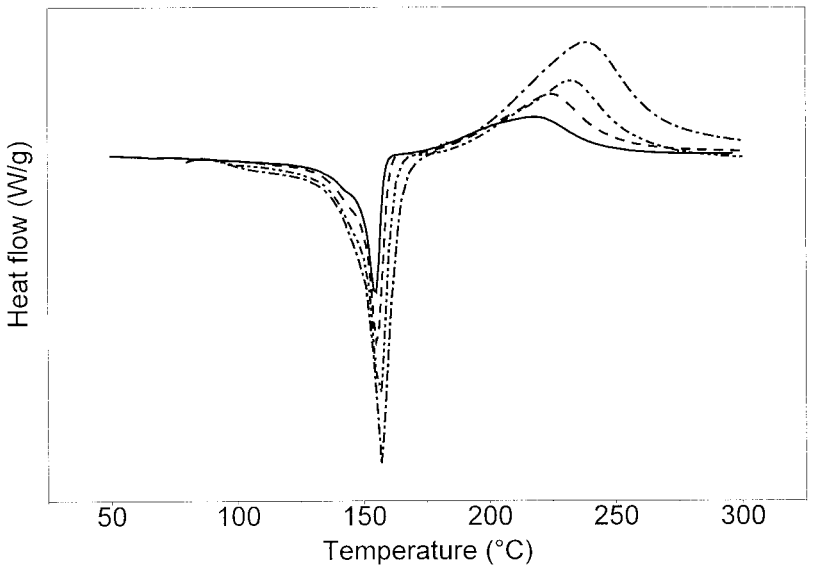

Figure 2 DSC curing exotherms at different heating rates for pure BMI: (—) 7, (–) 10, (- · · -) 15, and (- · -) 20°C/min.

$$\log\frac{d\alpha}{dt} = \log k + n\log(1-\alpha) \tag{10}$$

Kinetic parameters k and n can be obtained from a graph of $\log(d\alpha/dt)$ versus $\log(1 - \alpha)$. For an autocatalytic reaction, eq. (7) can be rewritten as follows:

$$\log\frac{d\alpha}{dt} = \log k + n\log(1 - \alpha)\alpha^{m/n} \tag{11}$$

If m and n are selected properly, the relationship between $\log(d\alpha/dt)$ and $\log(1 - \alpha)\alpha^{m/n}$ is linear. Then, k and n can be determined from the intercept on the y axis and the slope of the line, respectively. E, therefore, can be determined from a plot of $\log k$ versus T^{-1} because k follows an Arrhenius equation . E is the slope of the plot, and the intercept of the plot is $\log A$.

Because the single-heating-rate method is not quite accurate for complex curing systems, it was not used in this study. Both the multiheating-rate method and isothermal method were used to study the effect of the formulation on the curing process.

EXPERIMENTAL

1,1′-(Methylene di-4,1-phenylene) bismaleimide was purchased from Hu Bei Feng Guang Chemicals (Beijing, China), and *o,o*′-diallyl bisphenol A (DABA) was purchased from Ciba Geigy (Singapore). Formulations with different stoichiometric ratios of BMI and DABA were prepared by the mixing of both components at the desired molar ratios at room temperature. The formulations with molar ratios of BMI and DABA of 1:*r* are represented as *xy-r*, *r* being the moles of DABA used.

DSC studies were performed with a modulated DSC 2920 instrument (TA Instruments, New Castle, DE) attached to a refrigerated cooling system. The kinetic data were obtained by two methods:

1. Multiheating-rate method: The sample was initially placed in the DSC cell and equilibrated at 40°C. After that, the sample was heated at a certain heating rate (7, 10, 15, or 20°C/min) up to 380°C.
2. Isothermal method: The DSC cell was first heated to one of the predetermined temperatures (200, 210, or 220°C). Then, the sample was placed in the DSC cell as quickly as possible. When the cell temperature recovered to within 4°C of the set temperature, the procedure was begun.

RESULTS AND DISCUSSION

Figure 2 shows DSC exotherms of pure BMI samples scanned at different heating rates. At all heating rates, the exotherms show an endothermic peak at about 155°C followed by a broad curing peak from about 180 to 300°C. BMI monomers occur as solid crystals at room temperature. The large endothermic peak at 155°C is, therefore, the melting peak of the crystals. This occurs just before the onset of curing (Fig. 2). There is a slight overlap between the melting peak and the onset of the curing exotherm for the slowest heating rate. In this case, the accurate measurement of the conversion at very low-conversion values becomes difficult. For this reason, the analysis of the activation energy was performed only for conversions greater than 10%.

The DSC results shown in Figure 2 were analyzed with the Ozawa equation to obtain the activation

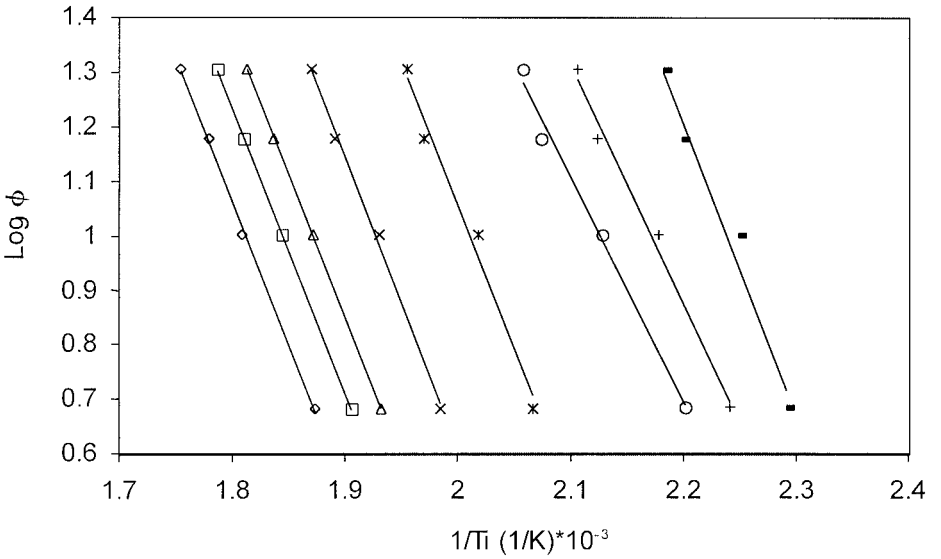

Figure 3 Plots of ln ϕ versus $1/T_i$ at different conversions for the calculation of E: (◇) 90, (□) 80, (△) 70, (×) 50, (ж) 30, (○) 15, (+) 10, and (■) 5%.

energies at different conversions. Figure 3 shows a plot of log ϕ against $1/T_i$ for a 1:1 stoichiometric ratio of BMI to DABA. Log ϕ is linear with $1/T_i$. The activation energy was obtained with eq. (8). The activation energies for all three formulations (pure BMI, 1:1, and 1:0.5) were similarly analyzed with this method, with the derived activation energy plotted against the corresponding conversion values in Figure 4.

One of the disadvantages of using Ozawa's method, which is based on a nonisothermal multiheating rate, is that it is not possible to experimentally obtain α values greater than 25% for the curing of pure BMI. This is because the high crosslink density of BMI makes the reaction rate too low to proceed beyond $\alpha > 25\%$. For this reason, the activation energy values of pure BMI are shown only for a conversion range lower than 25% in Figure 4. For the 1:1 and 1:0.5 formulations, the conversion goes much further, as the introduction of DABA helps to extend the maximum conversion into the 70–80% range.

Figure 4 also shows that the activation energies of both modified BMI formulations increase with conversion from 65 kJ/mol to a maximum at 90 kJ/mol at higher conversions, remaining fairly constant thereafter. The activation energy for pure BMI, within the range of $10\% < \alpha < 25\%$, is constant, with a value of 92–96 J/g.

This observation is in contrast to our findings for an epoxy system,[23] in which the activation energy re-

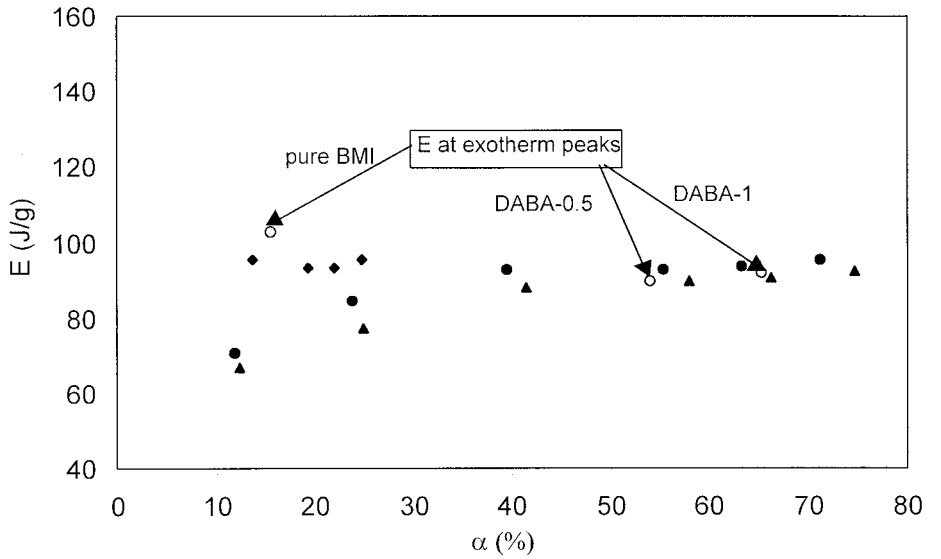

Figure 4 Comparison of E values of different formulations: (♦) pure BMI, (●) DABA-0.5, and (▲) DABA-1.

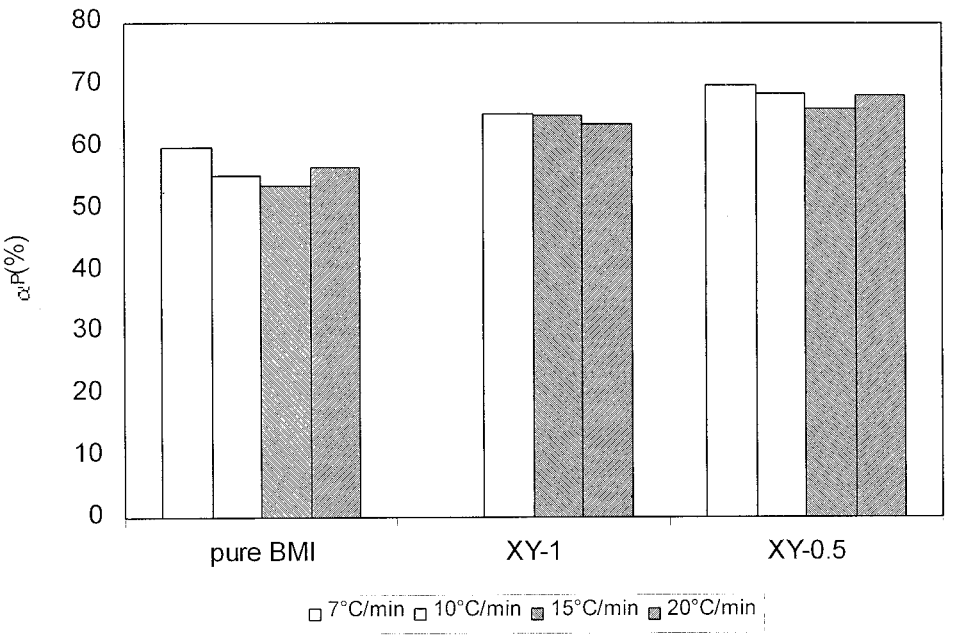

Figure 5 Conversions at the peak exotherm (α_p) for different formulations at different heating rates.

mains almost constant throughout the entire conversion range. This is because the curing of the epoxy system involves a step condensation process, in which each epoxy function represents a reactive center. The diffusion rate does not have much impact on the whole curing rate. The activation energy of epoxy, therefore, does not change considerably with the conversion. However, the curing reaction of BMI is driven by radical chain propagation. The concentration of reactive centers is very low. The reaction rate significantly depends on the diffusion rate of the reactive center. The change in the activation energy for the BMI/DABA system with increasing conversion is due to the reaction path changing from chemical control to diffusion control.

Another method frequently used for kinetic analysis is Kissinger's, which is used with a multiheating-rate measure. The premise of the Kissinger equation is that the degree of conversion at the peak exotherm is the same for different heating rates (the conversion is independent of the heating rate). Therefore, before we consider the application of Kissinger's method to the

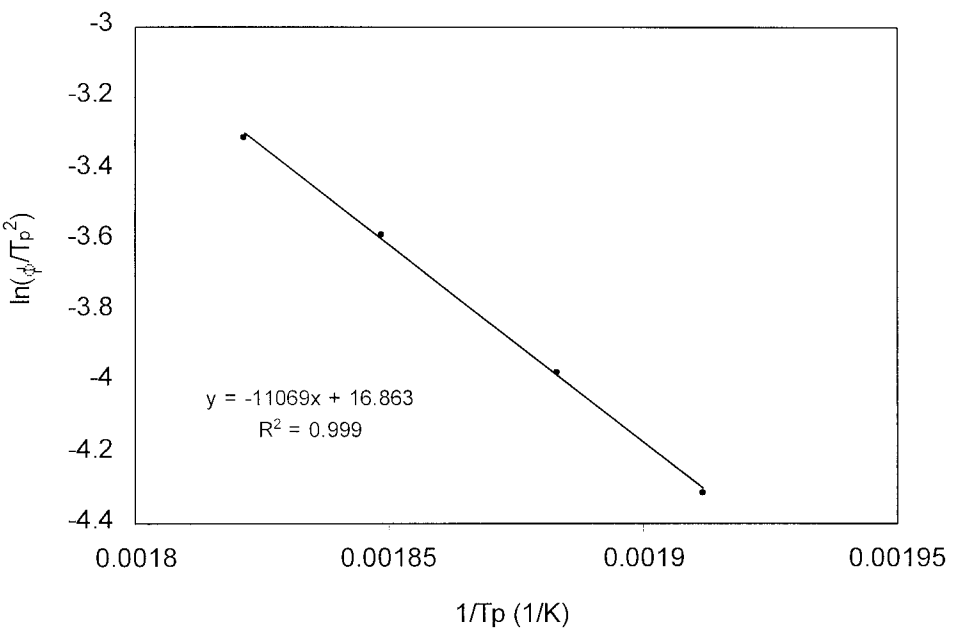

Figure 6 Plot for the determination of E by the Kissinger method for *xy*-1.

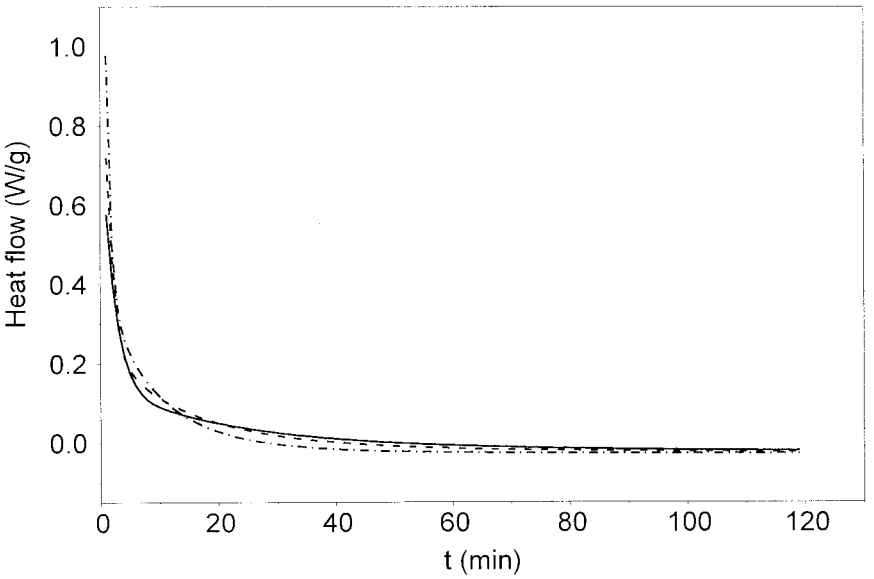

Figure 7 Isothermal DSC curves of the 1:1 formulation: (—) 200, (–) 210, and (- · -) 220°C.

curing system under study, it would be useful to look at a plot of α at the peak of the exotherm at different heating rates. Figure 5 presents such a plot. The peak exotherms are located within similar conversion values, within the experimental error, at different heating rates. This verifies that the conversion is independent of the heating rate and that Kissinger's method is quite suitable to the curing system under consideration.

Figure 6 presents a plot of $\ln(\phi/T_p^2)$ versus $1/T_p$, for the 1:1 formulation, based on eq. (9). The resulting linear plot has a fitting degree, $R^2 = 0.999$, again confirming the validity of the Kissinger method for the curing system under study. The activation energy was obtained by the determination of the value of the slope. With the same method, the activation energies for all three formulations (pure BMI, DABA-1, and DABA-0.5) were obtained, and they are marked as hollow circles in Figure 4. From a comparison of these values with those obtained with Ozawa's method (Fig. 4), it is evident that both methods produce very similar results for DABA-1 and DABA-0.5, but they differ significantly for pure BMI. The discrepancies observed in the latter case could be due to the incomplete curing of pure BMI during the DSC scan.

A thermal analysis method using a DSC approach relies on the ability of the method to accurately measure the total enthalpy of curing for 100% conversion. Unfortunately, for very highly crosslinked systems such as BMI, this is not as simple as it appears. As discussed previously, dynamic temperature scans do not achieve complete conversions of BMI/DABA systems. At the same time, simple isothermal curing steps do not achieve complete curing either. Figure 7 shows the results of DSC runs performed under three different isothermal conditions—200, 210, and 220°C—for DABA-1. The rate of reaction is greatest at the commencement of the cure, but it falls exponentially with the cure time in all three cases, with the maximum rate of reaction being highest at the highest cure temperature. This is not helpful experimentally because it is precisely at the initial cure stage when the isothermal DSC measurements lose some data on account of the time taken for the instrument to return to a set equilibrium temperature (an instrumental drawback). Curing at lower temperatures would reduce this problem, but invariably, when the cure reaction becomes too slow, vitrification sets in to impede any further reaction. Additionally, during the last stage of curing, the reaction rate becomes too slow to be accurately detected.

For these reasons, we preferred to adopt a two-step isothermal curing schedule. The sample was first isothermally cured at 220°C for 2 h, and this was followed by isothermal curing at 300°C for 20 min. The total enthalpy of the curing reaction was obtained as the sum of both exotherms. This method more or less avoids enthalpy loss during measurement and almost guarantees the curing reaction going to completion. After two-step curing, a dynamic temperature scan showed a flat DSC curve, which indicated that the reaction was complete. The second isothermal curing temperature was selected on the basis of our thermo-

TABLE I
Total Heat Flow Values (J/g) of the Different Formulations

Pure BMI	505
DABA-1 formulation	340
DABA-0.5 formulation	398

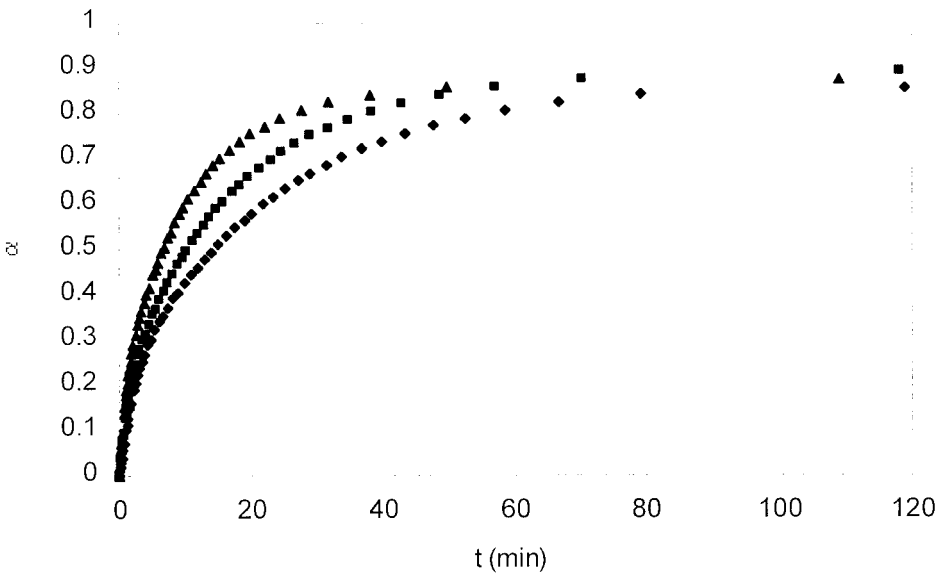

Figure 8 Curing time (t)/conversion (α) relationship at different isothermal curing temperatures for the 1:1 formulation: (♦) 200, (■) 210, and (▲) 220°C.

gravimetric analysis results, which indicated that a curing temperature higher than 340°C would induce significant degradation[24] for DABA-1.

With the aforementioned method, the total enthalpies of the curing reaction for all three formulations were obtained, and they are tabulated in Table I. These values were then used to determine the conversion percentages for DABA-1, DABA-0.5, and pure BMI. The percentage conversion for DABA-1 is plotted against the cure time in Figure 8.

The conversion increases rapidly with the curing time but reaches a maximum asymptotically. This typical profile basically reflects the change of the reaction mechanism from a chemically controlled process to a diffusion-controlled process. Once the maximum conversion is reached, vitrification occurs, stopping the reaction completely. Figure 9 plots the rate of change of conversion against the conversion. The maximum peak occurs at about $\alpha = 0.05$. Because of the relative inaccuracy in measuring α near the zero time, the peak can be taken to occur at zero conversion. The characteristics of autocatalytic reactions is that the reaction rate reaches its maximum between 20 and 40% conversion.[25] The reaction for DABA-1, therefore, would

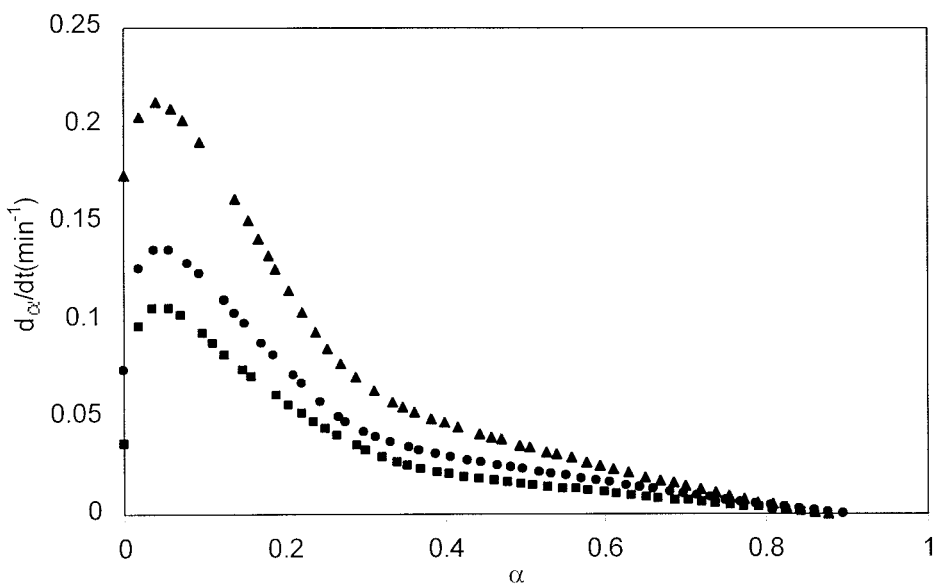

Figure 9 $d\alpha/dt$ versus α for the 1:1 formulation: (♦) 200, (■) 210, and (▲) 220°C.

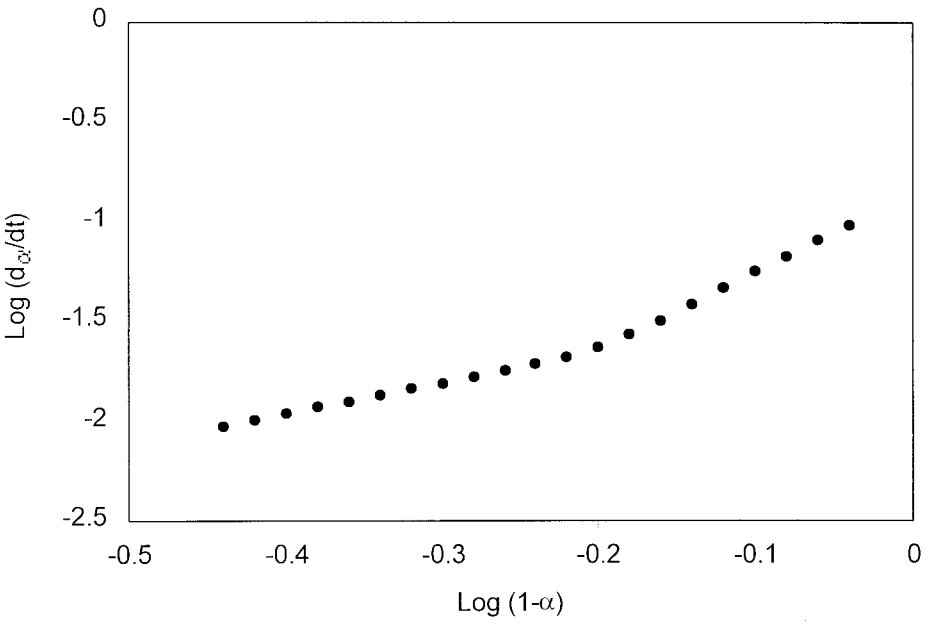

Figure 10 Kinetic analysis for the 1:1 formulation from the isothermal exotherm at 200°C.

be better modeled by the *n*th-order reaction model, rather than the autocatalytic model.

To verify the validity of the *n*th-order equation for this system, we plotted $\log(d\alpha/dt)$ against $\log(1 - \alpha)$ (Fig. 10). The resulting plot should be linear, with the slope representing the value of n and the intercept representing the value of $\log k$ [eq. (6)].

In Figure 10, the plot appears to be a sequential combination of two linear curves. This could mean that the reaction order changes with conversion (at the intersection, at which the slope changes). A similar observation was reported by Goodwin.[26] However, he did not provide any explanation for the observed behavior. A plausible explanation, given here, involves the radical characteristics of the curing mechanism. As reported in the literature,[27,28] the homopolymerization of pure BMI and the copolymerization of BMI/DABA are radical reactions. The reaction shows characteristics typical of radical reactions, in which a large molecule is formed by several monomers instantly. The reaction order, however, is greater than 3, something rarely encountered. In the diffusion-control stage, the probability of several monomers colliding with one another at the same time is very small. Therefore, the reaction order is small.

Therefore, under the assumption that the same cure reaction actually went through two stages in which the reaction order was different, the kinetic parameters (k and n) were obtained from Figure 10 for the two stages, that is, for $0 < \alpha < 30\%$ and for $\alpha > 30\%$. The activation energies for both stages were then calculated from the respective k values, obtained at different temperatures, on the basis of eq. (5). The regressed kinetic parameter results for both stages, together with the respective activation energies, are tabulated in Table II.

Figure 11 compares the experimental and modeling results from Table II (only for $0 < \alpha < 0.3$) for DABA-1. The modeling curve fits the experimental data very well for $\alpha < 0.3$ but significantly deviates from the experimental data thereafter. The curve also verifies that the reaction rate drops in two sequential stages, the decrease being faster in the first step. Therefore, the curing course should be modeled by a different set of kinetic parameters in the high-conversion range.

TABLE II
Kinetic Parameters Obtained from Isothermal Analysis

	Kinetic parameter					
	Log A (1/min)		E (kJ/mol)		n	
Conversion (%)	0–30	30–80	0–30	30–80	0–30	30–80
Pure BMI	6.22		65		6.7	
DABA-0.5 formulation	6.13	7.10	64	76	3.9	2.2
DABA-1 formulation	7.35	7.11	75	76	3.8	1.6

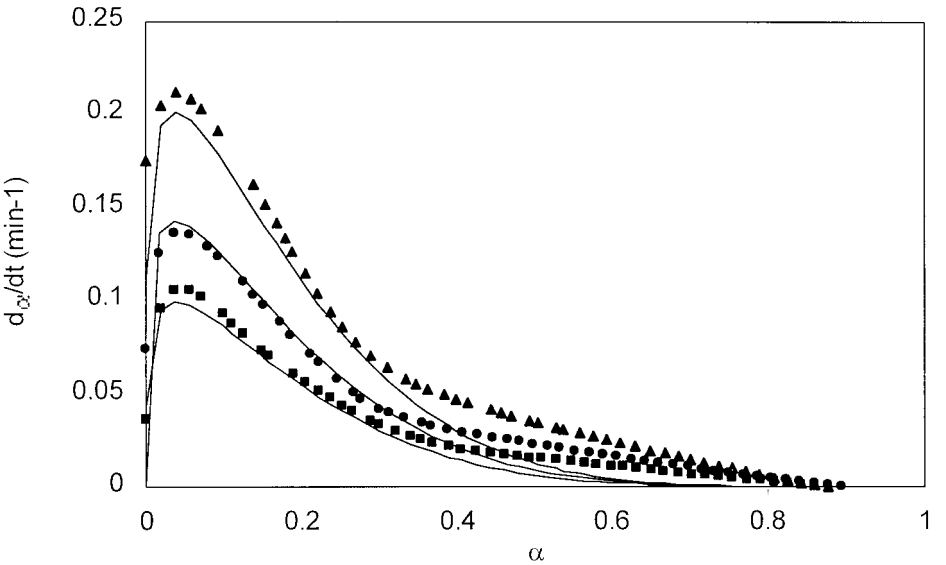

Figure 11 Comparison of experimental data with an *n*th-order model with one set of kinetic parameters for the 1:1 formulation: (■) 200 (experiment), (●) 210 (experiment), and (▲) 220°C (experiment) and (—) 220°C (model).

Figure 12 presents the experimental results for DABA-1 (as in Figure 11), along with a combined model, which uses the first-stage regressed kinetic parameters in Table II, for $0 < \alpha < 0.3$, and the regressed kinetic parameters of the second stage, for $\alpha > 0.3$. The combined modeling curve fits the experimental data very well at all conversion levels.

Correspondingly, the reactions of DABA-0.5 have also been modeled with the aforementioned method, with the kinetic parameters for both stages listed in Table II. The model curve fits the experimental data very well, as shown in Figure 13.

For pure BMI, the cure reaction at the respective temperatures yields only a 30–40% conversion. At higher conversions, the diffusion-controlled reaction rate is too low to be detected because of the high crosslink density of the network. The reaction is, therefore, modeled only in the chemical-control region, which only needs one set of model equation and kinetic parameters. This is shown in Figure 14. The rate profiles predicted by the *n*th-order model and kinetic parameters listed in Table II are in good agreement with the experimental data for pure BMI.

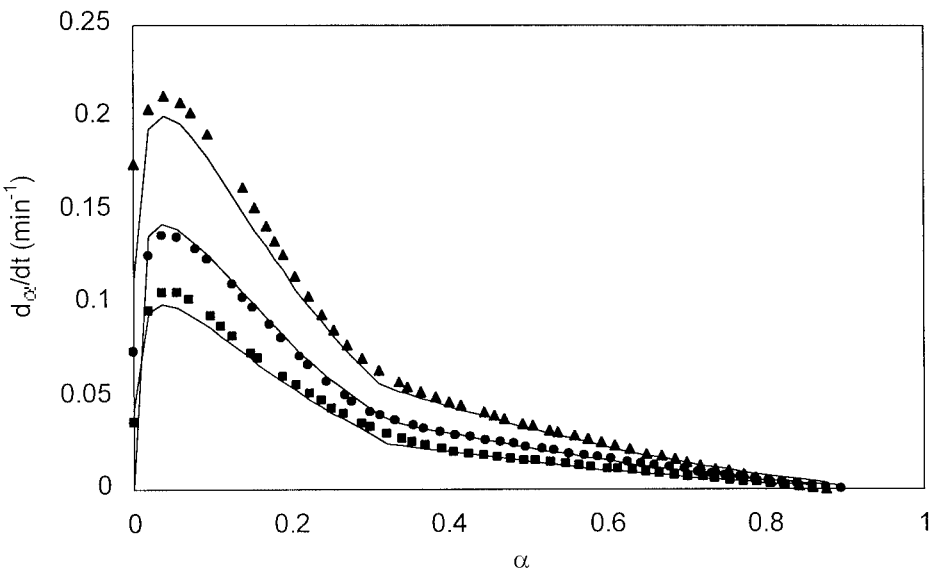

Figure 12 Comparison of the experimental data with an *n*th-order model with two sets of kinetic parameters for the 1:1 formulation: (■) 200 (experiment), (●) 210 (experiment), and (▲) 220°C (experiment) and (—) model.

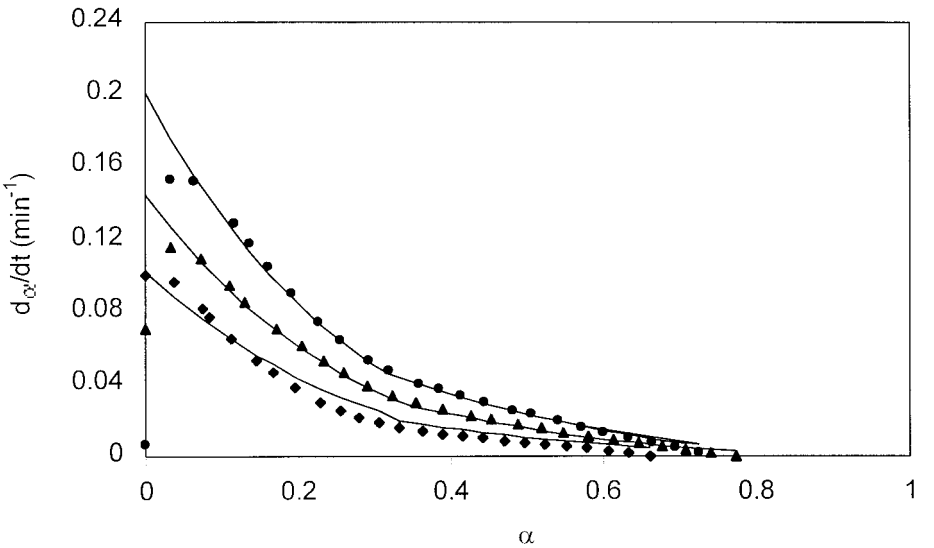

Figure 13 Comparison of the experimental data with an *n*th-order model with two sets of kinetic parameters for the 1:0.5 formulation: (♦) 200 (experiment), (▲) 210 (experiment), and (●) 220°C (experiment) and (—) model.

Comparing the kinetic parameters listed in Table II, one finds that, for all three formulations, the kinetic parameters change at the same conversion, about 30%. This means that the cure reaction goes into a diffusion-control regime at the same conversion for all three formulations. In the low-conversion region, all the kinetic parameters are the same for DABA-1 and DABA-0.5. This is easily understood because, in the low-conversion regime, the predominant reaction is the copolymerization of BMI and DABA.[24] In the high-conversion region, only copolymerization occurs for DABA-1, whereas both the copolymerization and homopolymerization of BMI monomer occur for DABA-0.5. This means that, in the high-conversion region, the reaction mechanisms of DABA-1 and DABA-0.5 are different. However, both formulations go into a diffusion-control regime in the high-conversion region. The diffusion-controlled activation energies of both formulations are the same. This may be the reason that the activation energies of both formulations are the same in the high-conversion region. The higher reaction order of DABA-0.5 can be attributed to the high reaction order of the BMI homopolymerization.

A comparison of the activation energies obtained by the dynamic method and the isothermal method shows that the results are different. This is because the results are obtained at different temperatures. The dynamic method can detect a change in the activation

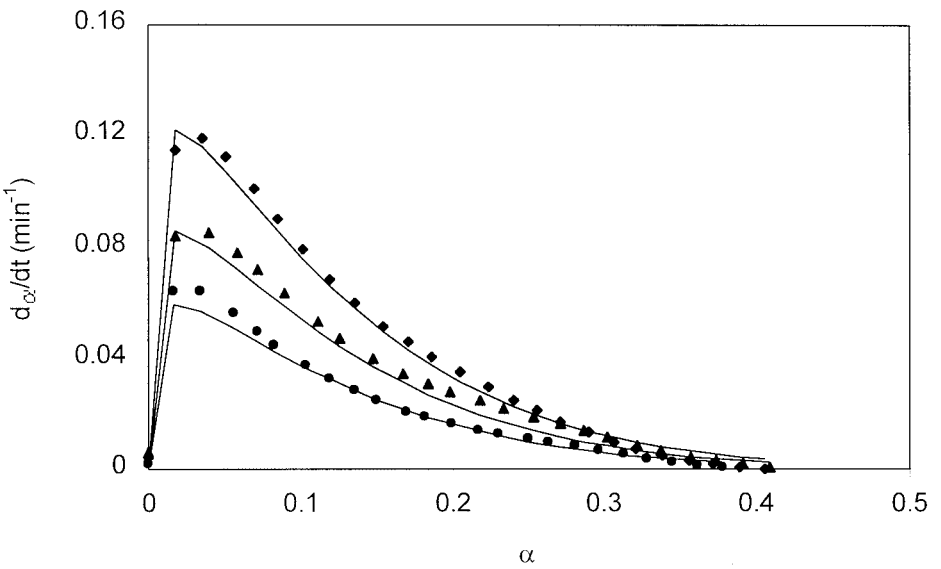

Figure 14 Comparison of the experimental data with an *n*th-order model for pure BMI: (●) 190 (experiment), (▲) 200 (experiment), and (♦) 210°C (experiment) and (—) model.

energy with the temperature, whereas the isothermal method can detect the change with conversion. In our case, the activation energy changes with the temperature and remains constant with the conversion.

CONCLUSIONS

The activation energy of BMI modified with DABA has been obtained with both a multiheating-rate method and an isothermal method. The activation energy changes with the temperature and remains constant with conversion. When the reaction switches over to the diffusion-control regime, the activation energy becomes high with a reduction in the reaction order. It is not possible to model the curing reaction of the BMI/DABA system with any one equation.

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