Cure Kinetics of an Epoxy-Novolac Molding Compound

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Synopsis

The cure reaction of an epoxy-novolac molding compound was studied by means of differential scanning calorimetry using the dynamic (i.e., temperature scanning) approach. Based on a modified version of Friedman's method, a procedure aiming at the phenomenological description of cure kinetics was developed. This method was found capable of following satisfactorily the thermokinetics of the molding compound. Our results indicate that the cure reaction is autocatalytic in nature and does not follow simple nth-order kinetics.

INTRODUCTION

As a current practice in the electronic industry, integrated circuits are often encapsulated with epoxy-novolac molding compounds by means of a transfer molding process.[1-3] Despite of the extensive usage of the epoxy-novolac molding compounds over the last decade, only very limited information may be found in the literature concerning the cure kinetics or the change in properties of these molding compounds during the cure process.[4-6] Reported here are results of our kinetic study of a commercial epoxy-novolac molding compound by means of differential scanning calorimetry (DSC).

As comprehensively reviewed by Prime,[7] the differential scanning calorimeter may be operated under isothermal (i.e., time-sweep) or dynamic (i.e., temperature-scan) modes for the kinetic study of thermosetting systems. In a manner similar to conventional methods for the study of chemical kinetics, kinetic parameters for cure reactions may be obtained by a series of isothermal DSC runs at different temperatures. This approach becomes inadequate for the present system which gels within 20 s at the mold temperature: isothermal DSC measurements in the processing temperature range would be highly inaccurate since it typically takes 1 min or so for the calorimeter to equilibrate at the set temperature, during which the cure reaction would have already proceeded in an uncontrolled manner. In the present study, this difficulty was avoided by the use of programmed temperature rise from a low initial temperature where the rate of cure is negligible.

EXPERIMENTAL

The molding compound studied was HC-10-2-8 from Nitto Electric Industrial Co., Ltd., Japan. This molding compound is highly filled (ca. 70 wt %) with silica and, according to the supplier, gels in 20 s at 175°C. A DuPont DSC 910

cell connected to a DuPont 9900 data station was used in this study. Samples approximately 10 mg in weight were scanned in the calorimeter with a heating rate (ϕ) of 40, 20, 10, or 5°C/min in the range of 50 to 300°C. To test the extrapolation ability of the present kinetic model, additional runs were also made using ϕ = 2, 1, and 0.5°C/min. The carrier gas was nitrogen at a flow rate of ca. 10 mL/min. Calibration of the calorimeter was conducted for each heating rate using indium standard.

METHOD OF ANALYSIS

Rate Expression

Various rate expressions have been proposed in the literature for the cure reaction of thermosets. Based on a simplified mechanism for the reaction of epoxide and secondary amine hardener, Horie et al.[8] have obtained a rate expression of

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)(B - \alpha) \tag{1}$$

where k_1 and k_2 are rate constants and B is the initial ratio between epoxide and amine hydrogen equivalents. For some thermosetting systems,[9,10] the nth order rate expression,

$$d\alpha/dt = k(1 - \alpha)^n \tag{2}$$

where k is the rate constant, has been adopted for the description of cure kinetics. To take the autocatalytic characteristics typical to many thermosetting systems into account, Kamal and Sourour[11] suggested a generalized expression of

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{3}$$

and m and n represent reaction orders. Alternative expressions in the form of

$$d\alpha/dt = k(1 + C\alpha^m)(B - \alpha)^n \tag{4}$$

where C represents relative weighting for the autocatalytic part of the cure reaction, has also been proposed.[12] In view of the complex nature of cure reactions, all these rate expressions should be considered empirical. In this study, we have chosen to start with a simplified general rate expression of

$$d\alpha/dt = kf(\alpha) = Af(\alpha)\exp(-E_a/RT) \tag{5}$$

where $k = A \exp(-E_a/RT)$ is the apparent rate constant, A is the pre-exponential factor, E_a is the apparent activation energy, and $f(\alpha)$ is an empirical function representing the conversion-dependent part of the rate expression.

Interpretation of DSC-Determined Rate of Reaction

For kinetic studies using DSC, the rate of reaction is usually operationally defined as

$$(d\alpha/dt)_{DSC} = (dq/dt)_{DSC}/\Delta H_{rxn} \tag{6}$$

where $(dq/dt)_{DSC}$ is the rate of heat generation (or, differential heat flow) determined by DSC at any instant and ΔH_{rxn} is the heat of reaction. In isothermal DSC experiments, the rate of reaction may be directly equated to the selected rate expression $d\alpha/dt = f(\alpha, T)$ such as eq. (5), i.e.,

$$(d\alpha/dt)_{DSC} = f(\alpha, T) \tag{7}$$

In the case of dynamic DSC experiments, however, ambiguity exists regarding the interpretation of experimentally determined (i.e., eq. (6)) $(d\alpha/dt)_{DSC}$. Many researchers consider eq. (7) to be also valid in the dynamic case. Others have suggested that, considering

$$\alpha = \alpha(t, T) \tag{8}$$

$(d\alpha/dt)_{DSC}$ should be expressed as

$$(d\alpha/dt)_{DSC} = (\partial\alpha/\partial t)_T + (dT/dt)(\partial\alpha/\partial T)_t$$
$$= (\partial\alpha/\partial t)_T + \phi(\partial\alpha/\partial T)_t \tag{9a}$$

where $(\partial\alpha/\partial t)_T$ corresponds to the selected rate expression, i.e.,

$$(\partial\alpha/\partial t)_T = f(\alpha, T) \tag{9b}$$

Controversies in the literature concerning the use of either exact or partial differentials (similar in form to eqs. (7) and (9)) in the nonisothermal characterization of reactive systems may be dated back some twenty years[13-15] as previously reviewed by Prime[16] and Dutta and Ryan[17] but it appears that no general agreement has been reached yet. For example, some researchers still prefer the use of eq. 9 in their recent works[18,19] while others[20-26] use eq. (7). It is interesting to note that Prime, as one of the first to suggest the use of eq. (9), seems to have turned to the use of eq. (7) in his more recent review article.[7]

In our opinion, however, eq. (9) is *inappropriate* simply because α is *not* a *single-valued* function of time and temperature as eq. (8) implies. (For example, imagine that a simple reaction system has been allowed to react at temperature T for a period of time t, and its conversion reaches, say, α. Now, if the same system has been kept at a very low temperature so that no reaction occurs and then subject to a temperature jump to T at time t, the conversion is essentially zero at this very moment. In both cases the system is at time t and temperature T but the conversion may be different.) In other words, the relationship of eq. (9) does *not* exist at all if the physical meaning of α is carefully considered. In this work, we have used eq. (7) for the interpretation of $(d\alpha/dt)_{DSC}$.
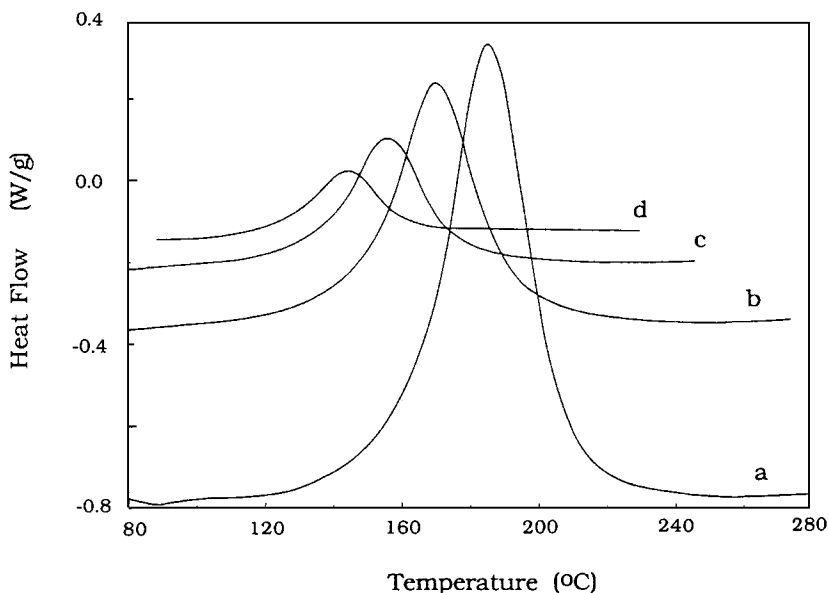
Fig. 1. DSC thermograms obtained using heating rates: (a) 40°C/min; (b) 20°C/min; (c) 10°C/min; (d) 5°C/min.

RESULTS AND DISCUSSION

Heat of Reaction

Given in Figure 1 are thermograms obtained at different heating rates. The rate of cure may be obtained according to eq. (5) in which $(dq/dt)_{DSC}$ corresponds to the height (with respect to the baseline) of the thermogram at a given temperature. The specific heat of the cure reaction (ΔH_{rxn}) corresponds to the total area under the cure peak divided by the heating rate whereas the fractional conversion (α) is the ratio between the heat evolved per gram of the molding compound up to a given moment and ΔH_{rxn}. The thermogram corresponding to a heating rate of 5°C/min does not exhibit a linear baseline. In this case the sigmoidal baseline routine in the DuPont data analysis software was used. Values of ΔH_{rxn} from runs of different heating rates are given in Table I and an average of 13.8 cal/g may be assigned.

TABLE I
Specific Heat of Reaction (ΔH_{rxn}), Fractional Conversion at Thermogram Peak (α_p), and the Temperature at Thermogram Peak (T_p) Determined Using Different Heating Rates (ϕ)

ϕ (°C/min)	ΔH_{rxn} (cal/g)	α_p	T_p (°C)
40	13.2	0.532	186.0
20	13.9	0.512	170.4
10	14.1	0.524	156.5
5	13.9	0.513	145.0

Apparent Activation Energy

It may be observed from Table I that α_p, the fractional conversion at the peak temperature (T_p), is nearly independent of heating rate, as have been observed for some other thermosetting systems.[16,27,28] For systems obeying eq. (5), Prime[7] has suggested that the apparent activation energy may be estimated through the dependence of T_p on heating rate according to

$$E_a = -0.951 Rd \ln \phi / d(1/T_p) \tag{10}$$

where R is the gas constant. As shown in Figure 2, good linear relationship between $\ln \phi$ and the reciprocal peak temperature is observed. Using eq. (10), the apparent activation energy of the present system is estimated to be ca. 18.5 kcal/mol.

A more complete accessment of E_a throughout the entire conversion range may be obtained using Friedman's method[29] in which the rate of reaction $(d\alpha/dt)$ at a selected conversion is plotted against the corresponding temperature for different heating rates. If the data points fall into a straight line, the slope should then correspond to E_a/R at this particular conversion. Given in Figure 3 are Friedman plots for $\alpha = 0.1$ to 0.9. Values of E_a obtained in this manner at different conversions are shown in Figure 4. It may be observed that values of E_a scatter in the range of 17 to 20 kcal/mol up to $\alpha = 0.9$. Taking the experimental errors into account, the apparent activation energy of the present reaction system may be considered as constant throughout the entire conversion range. The average value of 18.4 kcal/mol, which is in good agreement with that estimated using Prime's method, was then assigned to E_a in the following analysis.

The Empirical Function $f(\alpha)$

When the apparent activation energy is taken as constant, eq. (5) may be rewritten as
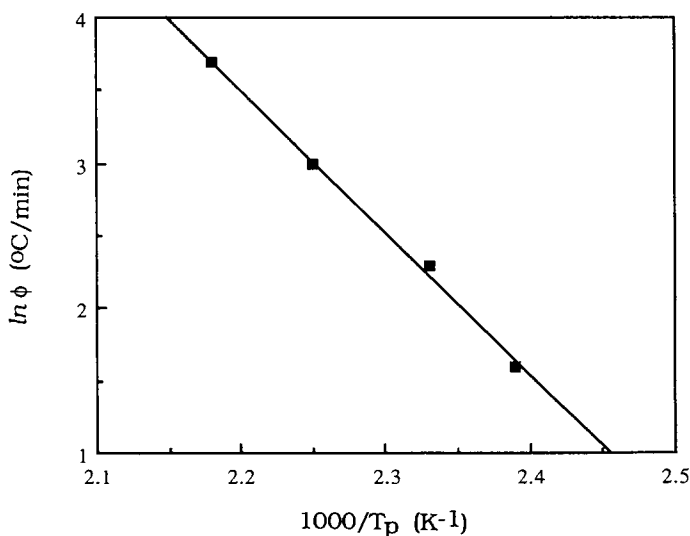

Fig. 2.   Linear relationship between $\ln \phi$ and reciprocal peak temperature.
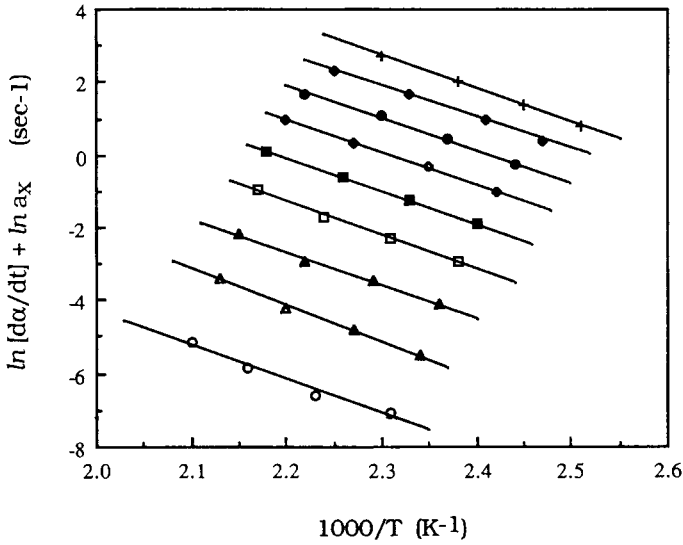
Fig. 3. Friedman plots at various conversions. Data points have been vertically shifted for the sake of clarity. Lines are corresponding least-square fits. (+) α = 0.1, shift factor $\ln a_x$ = 8; ($\blacklozenge$) α = 0.2, $\ln a_x$ = 7; ($\bullet$) α = 0.3, $\ln a_x$ = 6; ($\diamondsuit$) α = 0.4, $\ln a_x$ = 5; ($\blacksquare$) α = 0.5, $\ln a_x$ = 4; ($\square$) α = 0.6, $\ln a_x$ = 3; ($\blacktriangle$) α = 0.7, $\ln a_x$ = 2; ($\triangle$) α = 0.8, $\ln a_x$ = 1; ($\bigcirc$) α = 0.9, $\ln a_x$ = 0 (unshifted).

$$\ln[d\alpha/dt] = \ln[Af(\alpha)] - E_a/RT \qquad (11)$$

For nth-order reactions, i.e., $f(\alpha) = (1 - \alpha)^n$ in eq. (5), Friedman[29] suggested that the relationship
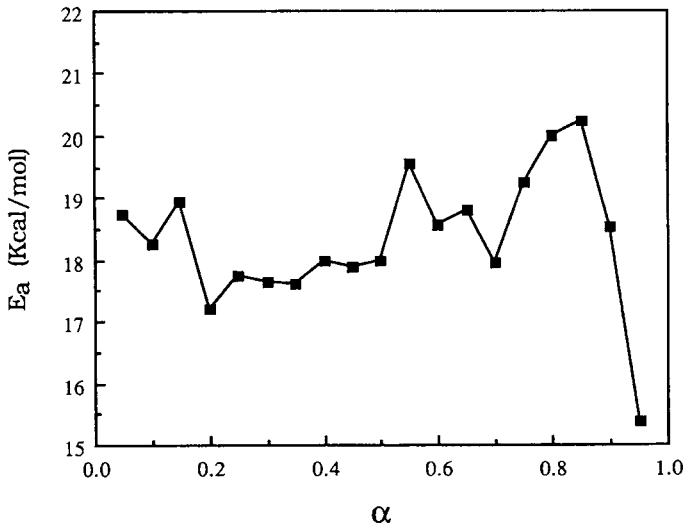

Fig. 4. Values of the apparent activation energy obtained from Friedman plots (Fig. 3) at different conversions.

$$\ln[Af(\alpha)] = \ln A + n\ln(1-\alpha) \tag{12}$$

should hold and thus plotting $\ln[Af(\alpha)]$ against $\ln(1-\alpha)$ should yield a straight line where the slope corresponds to n. According to Friedman's original proposal, $\ln[Af(\alpha)]$ may be obtained by extrapolation of experimentally determined values of $d\alpha/dt$ at a given conversion from different heating rates (and thus different temperatures at which the particular conversion is reached) to $1/T = 0$. However, E_a values for the present system has been observed to fluctuate with conversion in the range of ca. 17 to 20 kcal/mol. Direct adoption of Friedman's original method would then result in unacceptable $\ln[Af(\alpha)]$ values in such a long extrapolation procedure. For the sake of self-consistency, we have chosen to rewrite eq. (11) as

$$\ln[Af(\alpha)] = \ln[d\alpha/dt] + E_a/RT \tag{13}$$

and calculate $\ln[Af(\alpha)]$ values from experimentally determined $d\alpha/dt$ and E_a/RT where the average value of E_a (i.e., 18.4 kcal/mol) is used. As may be observed from the resulting plot (Fig. 5), the data from different heating rates form a single curve representing the conversion-dependent part of the rate expression. Since $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ are not linearly related, we have concluded that the present system does not follow simple nth-order kinetics. The existence of a maximum (at $\alpha = $ ca. 0.38) in the master curve indicates that the cure reaction is autocatalytic in nature.

Alternatively, without presuming any particular kinetic expression, we may simply plot $Af(\alpha)$ against α as shown in Figure 6. The data points appear slightly more scattered due to the change from logarithmic to linear scales but the basic feature of a single "master curve" remains a valid approximation.
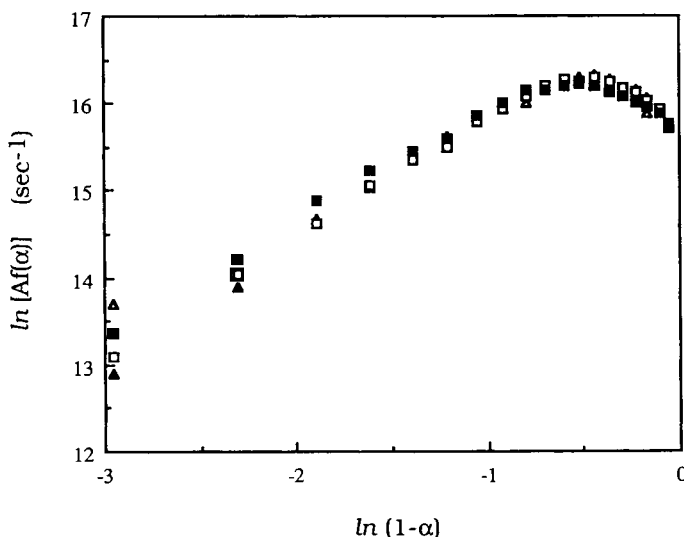

Fig. 5.   Variation of $\ln[Af(\alpha)]$, where $Af(\alpha)$ represents the conversion-dependent part of the rate expression, with $\ln(1-\alpha)$. Nonlinearity indicates that nth-order kinetics is not followed.
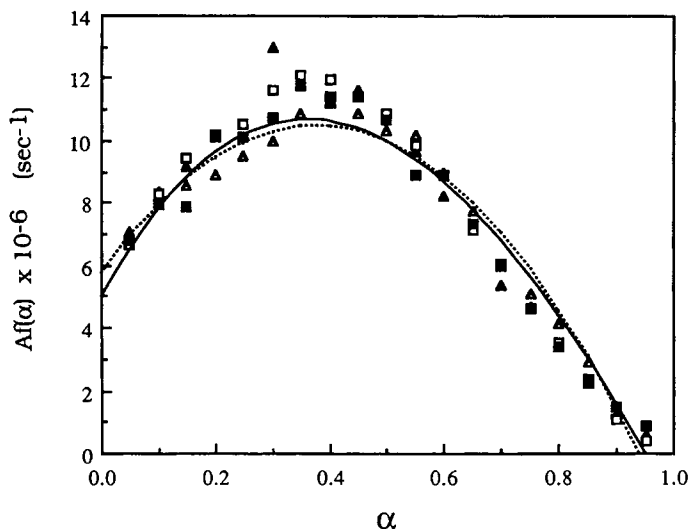
Fig. 6. Variation of $Af(\alpha)$ with α at different heating rates: ($\triangle$) 40°C/min; ($\blacktriangle$) 20°C/min; ($\square$) 10°C/min; ($\blacksquare$) 5°C/min. The dotted curve and the solid curve are, respectively, the second- [eq. (14)] and third-order [eq. (15)] polynomial fits.

The master curve may be fitted with any desired form of $f(\alpha)$. In the spirit of our strictly empirical methodology, however, we have chosen to use second- and third-order polynomials and the resulting equations are, respectively,

$$Af(\alpha) = 5.8 \times 10^{6}(1 + 4.7\alpha - 6.5\alpha^{2})\,\text{sec}^{-1} \qquad (14)$$

and

$$Af(\alpha) = 4.1 \times 10^{6}(1 + 11.4\alpha - 21.1\alpha^{2} + 8.4\alpha^{3})\,\text{sec}^{-1}. \qquad (15)$$

Calculated conversion curves [using eqs. (5) and (14) or eqs. (5) and (15)] are compared to our experimental results in Figure 7. Both expressions [eq. (14) and eq. (15)] appear to follow satisfactorily the experimental curves except at the high conversion end. The third-order expression [eq. (15)] gives slightly better descriptions for the experimental results in the high conversion region. To test the extrapolation ability of the present kinetic model, additional runs were also made using heating rates lower than those used in the fitting procedure above. As shown in Figure 8, results of these additional runs are reasonably well predicted, although discrepancies become more apparent at the lowest heating rate. For the purpose of further comparison, we are currently studying the isothermal cure of the present molding compound in a lower temperature range by means of DSC and Fourier-transform infrared spectroscopy. Results are to be reported in the near future.

In conclusion, we have modified Friedman's method and developed a procedure for the kinetic study of thermosetting systems which cure rapidly in the elevated processing temperature range. When applied to Nitto HC-10-2-8, the method was found effective. Our results indicate that the cure reaction is
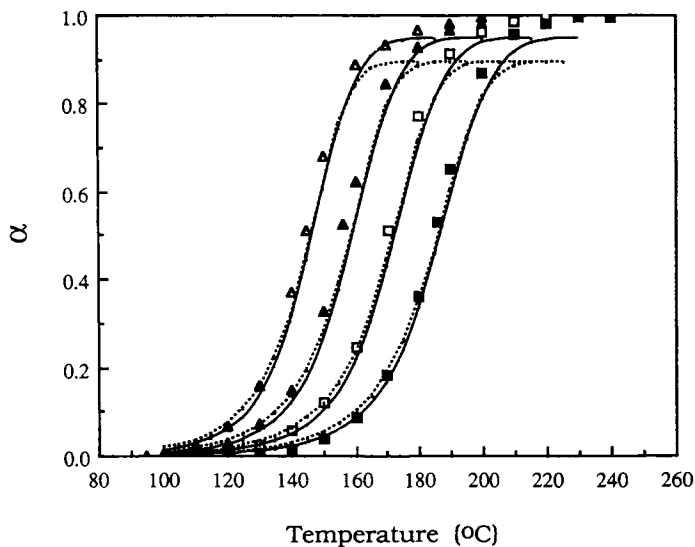
Fig. 7. Comparison between experimental and calculated conversion curves at different heating rates: (■) 40°C/min; (□) 20°C/min; (▲) 10°C/min; (△) 5°C/min. Corresponding dotted curves and solid curves are predictions from eqs. (14) and (15), respectively.

strongly autocatalytic. The present approach bears no assumption on the actual reactions involved in the cure process and is only phenomenological. However, due exactly to its phenomenological nature, the method is general and should be capable of presenting the thermokinetics of thermosetting systems in a self-consistent manner.
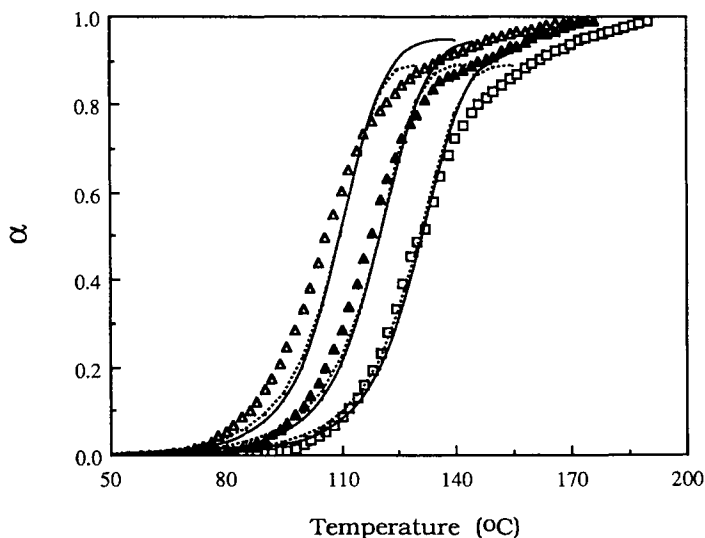

Fig. 8. Comparison between experimental and calculated conversion curves at different heating rates: (□) 2°C/min; (▲) 1°C/min; (△) 0.5°C/min. Corresponding dotted curve and solid curve are predictions from eqs. (14) and (15), respectively. Results from these three heating rates were not used in the fitting process from which eqs. (14) and (15) were obtained.

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