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Models of reaction commonly employed in the curing of thermosetting resins

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Abstract

In order to study the kinetics of the complex curing processes of thermoset resins, the rate of reaction $d\alpha/dt$ at constant temperature is related to some function of the reaction $f(\alpha)$. Two empirical kinetic functions $f(\alpha)$ are usually used: nth-order kinetics ($f(\alpha)=(1-\alpha)^n$) where α is the degree of conversion and n is a reaction order, and autocatalyzed reaction kinetics (such as $f(\alpha)=\alpha^m(1-\alpha)^n$) where m is also a reaction order.

Applying both models to data obtained with isothermal experiments, we can obtain the kinetic parameters n and m, the rate constant k and, assuming that its temperature dependence is an Arrhenius-type equation ($k = A\exp(-E/RT)$), the activation energy of the process (E) and the frequency factor (A). Despite some criticism with regard to the mechanistic interpretation, both models are also applied to non-isothermal experiments.

In this paper we present studies that we have made in order to simulate the curing process of unsaturated polyesters with both nth-order and autocatalyzed kinetics and for isothermal and non-isothermal processes. In the isothermal process, we solved the kinetic equations in order to determine α and $d\alpha/dt$ as a function of time and also to obtain the heat generation curve (dH/dt) as a function of time. In the non-isothermal process we solved the kinetic equations in order to obtain α, $d\alpha/dt$ and dH/dt as a function of temperature.

INTRODUCTION

Kinetic analysis of thermoset cure involves a search for the kinetic parameters of the process according to a mechanistic model that fits the experimentally observed values of the degree of conversion α and the setting time t in isothermal measurements, or α and scanning temperature T, in dynamic measurements. The required properties $d\alpha/dt$ and α can be evaluated by DSC, assuming that the reaction rate $d\alpha/dt$ is directly

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proportional to the rate of heat generation $\mathrm{d}H/\mathrm{d}t$ during the exothermic cure reaction (ordinate of DSC curve) [1]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\mathrm{d}H/\mathrm{d}t}{\Delta H_{\mathrm{R}}} \tag{1}$$

where ΔH_{R} is the exothermic heat of reaction. A value of 500 J g^{-1} has been found experimentally for the exothermal heat of reaction released during curing of an unsaturated polyester resin [2].

In general, a kinetic model relates the rate of conversion to some function of α and T. In kinetic practice it is a common assumption that the functional dependence upon α is separated from the dependence upon T, so that the basic rate equation is [3]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)\,f(\alpha) \tag{2}$$

In both isothermal and dynamic experiments the temperature dependence is an Arrhenius-type equation

$$k(T)=A\,\exp(-E/RT) \tag{3}$$

with E the activation energy, A the frequency factor, R the gas constant and T the temperature. When the process is isothermal, the temperature is constant, but in the non-isothermal process the temperature is usually increased according to a constant heating rate $\beta=\mathrm{d}T/\mathrm{d}t$ $(T=T_0+\beta t)$.

With regard to $f(\alpha)$, two empirical mechanistic models are usually used in the kinetics of the curing of thermosetting materials [4]; (a) an nth-order reaction model, where $f(\alpha)=(1-\alpha)^n$ and n is the reaction order, and (b) an autocatalyzed reaction model, such as $f(\alpha)=\alpha^m(1-\alpha)^n$, where exponent m is also a reaction order.

Dynamic case

In spite of some criticism [5,6], for dynamic experiments the following relationship between $\mathrm{d}\alpha/\mathrm{d}t$ and $\mathrm{d}\alpha/\mathrm{d}T$ is accepted [7]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{4}$$

so the basic rate equation is now written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp(-E/RT)\,f(\alpha) \tag{5}$$

Separation, rearrangement of variables and integration in eqn. (5) yields the relationship

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\int_{T_0}^{T}\frac{A}{\beta}\exp(-E/RT)\,\mathrm{d}T \tag{6}$$

where the limits for integration are $\alpha=0$ at $T=T_0$ and $\alpha=\alpha$ at $T=T$.

The second term of the equation is called the temperature integral, and can be evaluated by introducing the variable $x = E/RT$. Thus eqn. (6) becomes

$$g(\alpha) = \frac{A}{\beta}\,\frac{E}{R}\,p(x) \tag{7}$$

The function $p(x)$ is usually separated into two parts [8]

$$p(x) = \frac{\exp -x}{x}\,\pi(x) \tag{8}$$

The term $\pi(x)$ is a dimensionless correction that depends on the calculation method. In this paper we used the third degree rational approximation, developed by Senum and Yang [9]

$$\pi(x) = \frac{x^2 + 10x + 8}{x^3 + 12x^2 + 36x + 24} \tag{9}$$

Isothermal case

Here, the former procedure leads to the expression

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_0^t k\ \mathrm{d}t = kt \tag{10}$$

where it has been assumed that the rate constant k does not depend on time, since in an isothermal process the temperature is held constant.

SIMULATED SHAPES OF THEORETICAL DSC CURVES

Theoretical considerations

The theoretical shape of isothermal or non-isothermal DSC curves can be calculated from the kinetic parameters A, E and ΔH_R [7–10]. It is obvious that the shape of the simulated curve can be influenced by varying one of these parameters, while the other parameters are held constant. In the following sections we give the results of a study of this effect.

Non-isothermal case

In this case the integration of the basic rate equation leads to

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{AE}{RT}\,\frac{\exp -x}{x}\,\frac{x^2 + 10x + 18}{x^3\ 12x^2 + 36x + 24} \tag{11}$$

The first term of the equation is the kinetics integral $g(\alpha)$. It can easily be integrated for an nth-order reaction model to give

$$g(\alpha)=\begin{cases}\ln(1-\alpha) & \text{if } n=1\\ \dfrac{\left[-1+(1-\alpha)^{(1-n)}\right]}{n-1} & \text{if } n\neq 1\end{cases} \tag{12}$$

For the autocatalyzed model, $f(\alpha)=\alpha^m(1-\alpha)^m$, the kinetics integral $g(\alpha)$ cannot be evaluated so easily. There is a solely analytical expression when the sum $n+m$, also called the order of reaction, is an integer. Then the integration leads to one of the Chevyshev integrals [11]

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{\alpha^m(1-\alpha)^n} \tag{13}$$

In this case the integral can be solved by introducing the change of variable $z^s=(1/\alpha)-1$, where s is a multiple of one of the denominators of fraction n or m. The zero value of the lower limit of the integral imposes a condition: only solutions with $m<1$ have physical meaning. Otherwise the solution will be divergent at $\alpha=0$.

Table 1 shows a summary of the solutions of the kinetic integral $g(\alpha)$ for two mechanistic models. As can be seen, in the case of the autocatalyzed model and $n+m=1$, there is a different solution of the kinetic integral for each value of n with $m<1$. For $n+m>1$ and $m<1$ it is possible to obtain a general expression for different values of n.

By means of a numerical method of solving equations, it is possible to obtain values of α for different values of T in eqn. (11). In the calculation we used Newton's method [12]. Thus, for a given heating rate β, we can simulate a set of kinetic parameters (A, E, n and m) and heat of reaction ΔH_R: (i) the degree of conversion α as a function of temperature, (ii) the rate of reaction $\mathrm{d}\alpha/\mathrm{d}t$, vs. temperature T (taking into account that the heat of reaction released is calorimetrically $\mathrm{d}H/\mathrm{d}t=\Delta H_R\ \mathrm{d}\alpha/\mathrm{d}t$, the flux of heat as a function of temperature is also obtained, which is the DSC curve), (iii) by eliminating the temperature in the former expressions of α vs. T and $\mathrm{d}\alpha/\mathrm{d}t$ vs. T, we can obtain the rate of reaction as a function of the degree of conversion ($\mathrm{d}\alpha/\mathrm{d}t$ vs. α).

Isothermal case

In this case, the integration of the basic rate equation leads to the expression

$$g(\alpha)=kt \tag{14}$$

Here, the reaction constant k is not dependent on time, since in an isothermal experiment the temperature is held constant. The kinetics integral, $g(\alpha)$, is the same as in the non-isothermal case. For the nth-order

TABLE 1

Summary of solutions for the kinetic integral $g(\alpha)$ using the two mechanistic models: nth-order and autocatalyzed

nth-order model	$g(\alpha)$	
$n=1$	$\ln(1-\alpha)$	
$n \neq 1$	$\dfrac{\left[-1+(1-\alpha)^{-(n-1)}\right]}{(n-1)}$	
Autocatalyzed model ($m < 1$)	$g(\alpha)$	
$m+n=1$		
$m=1/2 \quad n=1/2$	$\pi - 2\operatorname{arctg}\left[\dfrac{\sqrt{(1-\alpha)}}{\alpha}\right]$	
$m=1/3 \quad n=2/3$	$\left(\dfrac{\sqrt{3}}{2}\right)\pi + \ln\dfrac{z+1}{\sqrt{z^2-z+1}} - \left(\dfrac{1}{\sqrt{3}}\right)\operatorname{arctg}\dfrac{2z-1}{\sqrt{3}}$	$z=\sqrt[3]{\dfrac{1-\alpha}{\alpha}}$
$m=2/3 \quad n=1/3$	$\left(\dfrac{\sqrt{3}}{2}\right)\pi - \ln\dfrac{z+1}{\sqrt{z^2-z+1}} - \left(\dfrac{1}{\sqrt{3}}\right)\operatorname{arctg}\dfrac{2z-1}{\sqrt{3}}$	$z=\sqrt[3]{\dfrac{1-\alpha}{\alpha}}$
$m=1/4 \quad n=3/4$	$\sqrt{2}\pi + \left(\dfrac{\sqrt{2}}{2}\right)\ln\dfrac{z^2-\sqrt{2}z+1}{z^2+\sqrt{2}z+1}$ $-\sqrt{2}\operatorname{arctg}[\sqrt{2}z+1] - \sqrt{2}\operatorname{arctg}[\sqrt{2}z-1]$	$z=\sqrt[4]{\dfrac{1-\alpha}{\alpha}}$
$m=3/4 \quad n=1/4$	$\sqrt{2}\pi - \left(\dfrac{\sqrt{2}}{2}\right)\ln\dfrac{z^2-\sqrt{2}z+1}{z^2+\sqrt{2}z+1}$ $-\sqrt{2}\operatorname{arctg}[\sqrt{2}z+1] - \sqrt{2}\operatorname{arctg}[\sqrt{2}z-1]$	$z=\sqrt[4]{\dfrac{1-\alpha}{\alpha}}$
$m+n=2$	$\dfrac{z^{(1-n)}}{(n-1)}$	$z=\dfrac{1-\alpha}{\alpha}$
$m+n=3$	$\dfrac{z^{(1-n)}}{(n-1)} + \dfrac{z^{(2-n)}}{(n-2)}$	$z=\dfrac{1-\alpha}{\alpha}$

reaction model, separation and rearrangement of variables yields these expressions of α as a function of t

$$\alpha = \begin{cases} 1-\exp(-kt) & \text{if } n=1 \\ 1-\left[kt(n-1)+1\right]^{1/(1-n)} & \text{if } n \neq 1 \end{cases} \qquad (15)$$

For the autocatalyzed model, only in the case $n+m=2$ and $m<1$ is it possible to find α as a function of t, according to

$$\alpha=\frac{At^{B}}{1+At^{B}} \tag{16}$$

where A and B are two constants that depend on the reaction constant k and the order of reaction n or m

$$A=\left[k(n-1)\right]^{1/(n-1)} \qquad B=1/(n-1) \tag{17}$$

Therefore, for a given temperature T, a set of kinetic parameters (A, E, n, m) and the reaction heat ΔH_{R}, it is also possible to obtain the following relationships: (i) the degree of conversion as a function of setting time, (ii) the flux of heat released as a function of setting time, and (iii) the rate of reaction vs. degree of conversion, by eliminating the time in the expressions of α vs. t and $\mathrm{d}\alpha/\mathrm{d}t$ vs. t.

Therefore, in both isothermal and non-isothermal cases, we can study the effect of the variation of each of these parameters on the curves: α vs. t (or T), $\mathrm{d}H/\mathrm{d}t$ vs. t (or T) and $\mathrm{d}\alpha/\mathrm{d}t$ vs. α, while the rest of parameters are held constant.

Simulated curves

The kinetic parameters frequency factor $A=6\times10^{5}$ s^{-1}, activation energy $E=50$ kJ mol^{-1}, reaction order $n=1, 2, 3$ for nth-order reaction model and $n+m=1$, 2 and 3 with $m=0.25$, 0.5, 0.75 and 0.9 were used in this study. The temperature range for isothermal simulated curves was 10–40°C and we assumed an isothermal reaction heat value of 500 J g^{-1}. This value was found experimentally by the authors for the curing reaction of an unsaturated polyester resin [2]. In the dynamic simulation of data, a heating rate value of 10 deg min^{-1} and a dynamic reaction heat of 500 J g^{-1} were used.

Non-isothermal case

The results for dynamics curves corresponding to the nth-order model are shown in Figs. 1–3. The shape of the exothermal peak does not change when the activation energy and frequency factor are varied, but the position and size of the peak do change. When E is increased, the peak shifts to higher temperatures, the size decreases and the shape is slightly affected. The effect of increasing A is the opposite of increasing E, so the effects can be counteracted reciprocally to some extent. The plots α vs. t (see Fig. 3) indicate that the activation energy can be considered as a time–temperature factor. The effect on the rate of reaction is to increase or decrease the maximum, but the position does not change if the mecha-

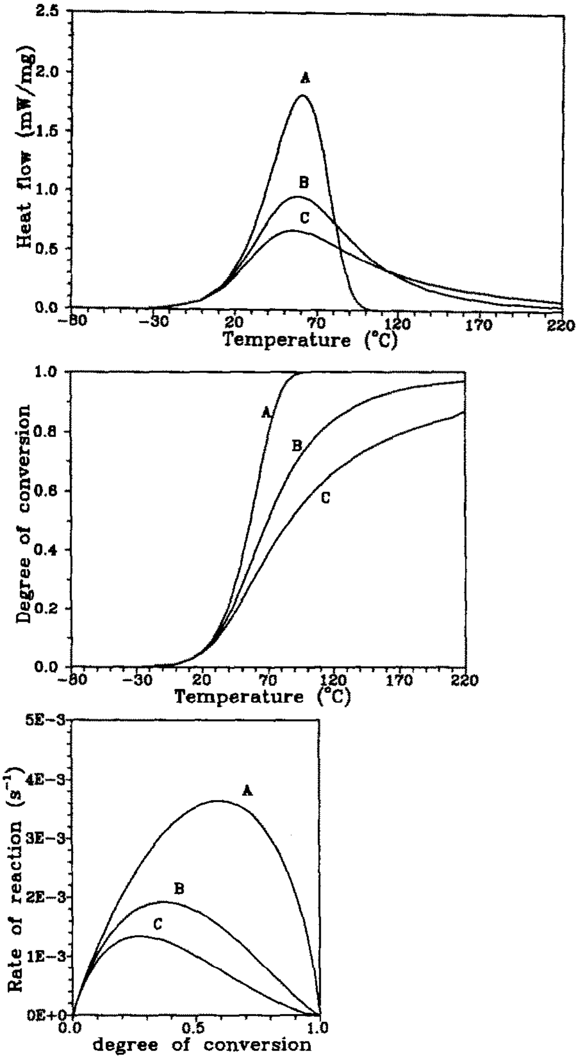

Fig. 1. Effect of reaction order n on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t$–T, α–T and $\mathrm{d}\alpha/\mathrm{d}t$–$\alpha$. Kinetic parameters: $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, heating rate 10 deg min^{-1} and dynamic heat of reaction 500 J g^{-1}. Curve A, $n = 1$; curve B, $n = 2$; curve C, $n = 3$.

nistic model, $f(\alpha)$, is not changed. Dynamic plots of $\mathrm{d}\alpha/\mathrm{d}t$ vs. α show the existence of a maximum for $\alpha \neq 0$.

The influence of variations in the order of reaction is represented in Fig. 1. Note that an increase in n causes a drastic change in the shape of the DSC curve, which becomes flatter. In addition, the rate of reaction is slower, as can be seen in plots of α vs. T and $\mathrm{d}\alpha/\mathrm{d}t$ vs. α in Fig. 1. The α–temperature curves are displaced to high temperatures and their shape changes. The size of curves $\mathrm{d}\alpha/\mathrm{d}t$ vs. α decreases when n increases, and

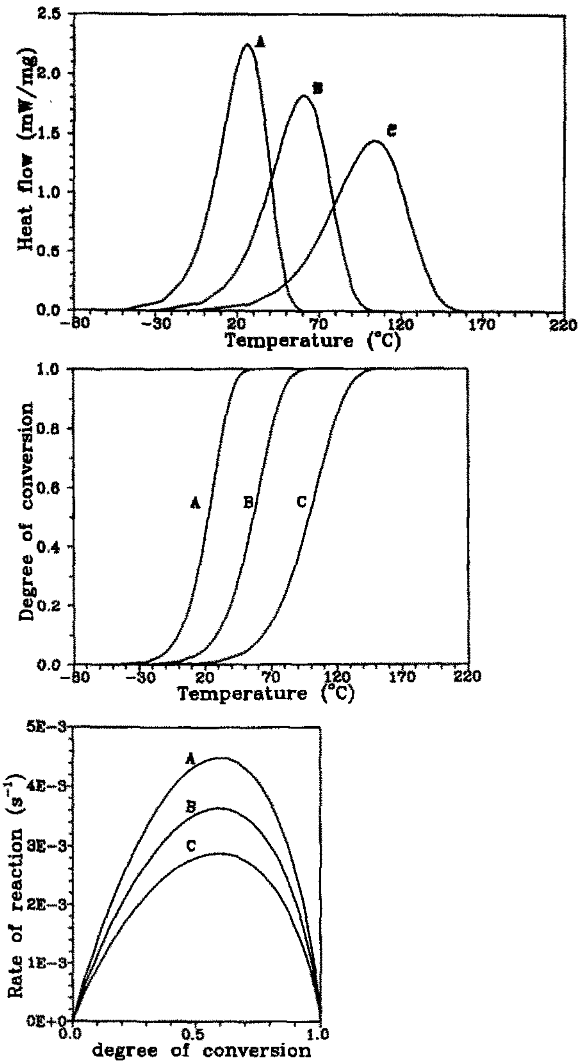

Fig. 2. Effect of frequency factor A on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t-T$, $\alpha-T$ and $\mathrm{d}\alpha/\mathrm{d}t-\alpha$. Kinetic parameters: $E = 50$ kJ mol^{-1}, $n = 1$, heating rate 10 deg min^{-1} and dynamic heat of reaction 500 J g^{-1}. Curve A, $A = 6\times10^6$ s^{-1}; curve B, $A = 6\times10^5$ s^{-1}; curve C, $A = 6\times10^4$ s^{-1}.

the maxima occur at higher degrees of conversion. Some of these changes were also observed by other authors [10].

In Figs. 4–6 we represent the dynamic curves for the autocatalyzed model. As seen, an increase in the order of reaction, $n + m$, causes a decrease in the size of the peak. In its turn, for a constant value of $n + m$ the peak increases its size, which is sharper and shifted to higher temperatures, as the value of exponent m increases. The reaction rate is slower, i.e.

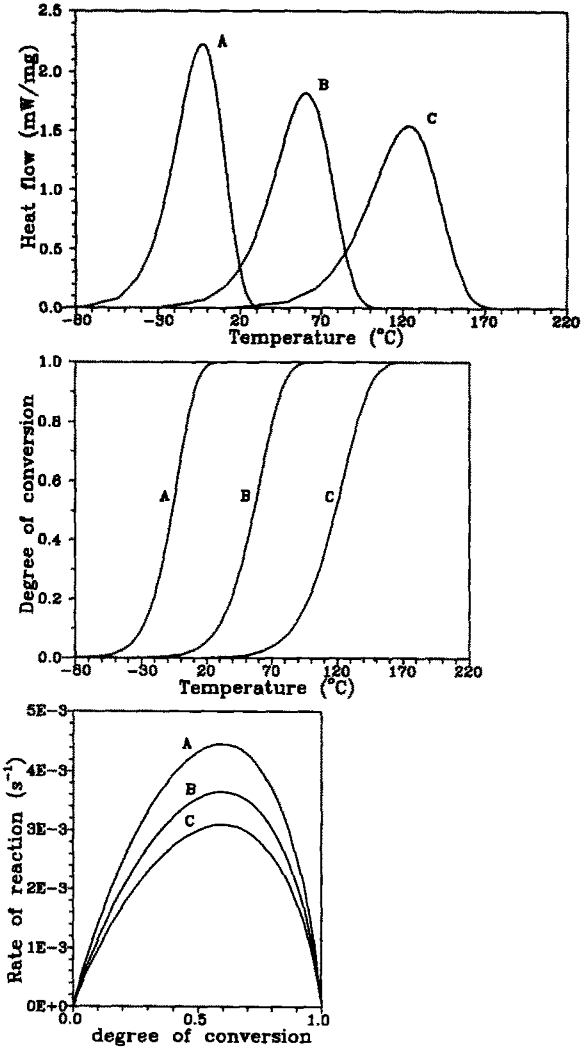

Fig. 3. Effect of activation energy E on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t - T$, $\alpha - T$ and $\mathrm{d}\alpha/\mathrm{d}t - \alpha$. Kinetic parameters: $A = 6 \times 10^5\ \mathrm{s}^{-1}$, $n = 1$, heating rate 10 deg min^{-1} and dynamic heat of reaction 500 J g^{-1}. Curve A, $E = 40$ kJ mol^{-1}; curve B, $E = 50$ kJ mol^{-1}; curve C, $E = 60$ kJ mol^{-1}.

a higher temperature is needed to start up the reaction, but as m is increased, then less time is needed to complete the reaction (see plots α vs. T in Figs. 4–6). Finally, the maximum reaction rate is displaced to higher degrees of conversion when exponent n increases, or for $n + m =$ constant, when exponent m decreases. The influence of parameters A and E on the simulated theoretical curves is completely the same as the corresponding effects in dynamic curves for nth-order reaction kinetics and

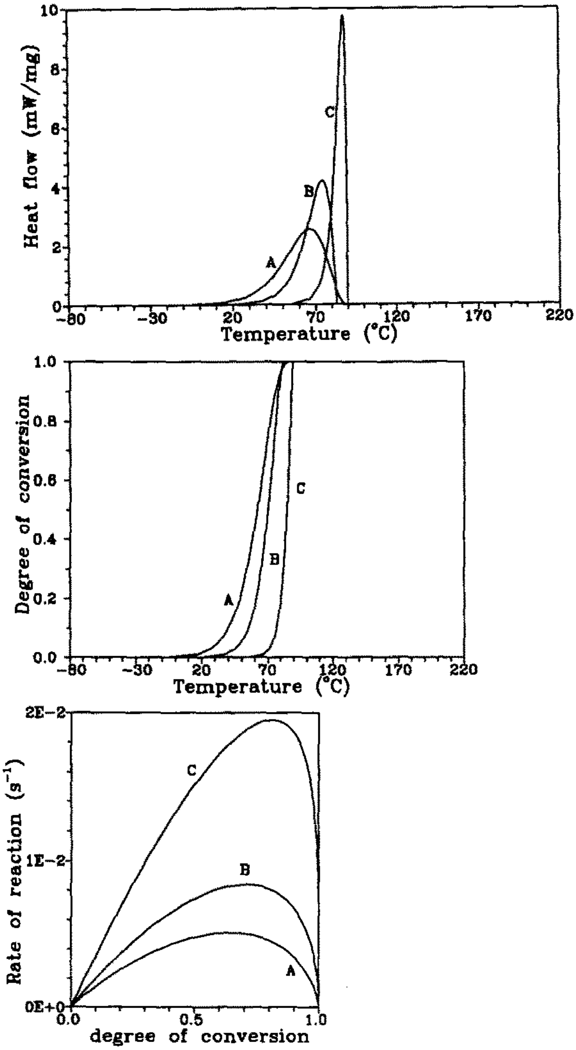

Fig. 4. Effect of exponent m on the shape of theoretical curves: $dH/dt-T$, $\alpha-T$ and $d\alpha/dt-\alpha$. Kinetic parameters: $A=6\times10^5$ s^{-1}, $E=50$ kJ mol^{-1}, order of reaction $n+m=1$, heating rate 10 deg min^{-1} and dynamic heat of reaction 500 J g^{-1}. Curve A, $m=0.25$; curve B, $m=0.50$; curve C, $m=0.75$.

will not be considered here. Tables 2 and 3 summarize these results for both models of reaction.

Dependency between the peak exotherm and the heating rate

The influence of variation in heating rate is shown in Figs. 7 and 8 for the two mechanistic models considered here ($n=2$ for the nth-order and $n+m=2$ with $m=0.4$ for the autocatalyzed model were used in the calculation). As can be seen, the peak exotherm temperature (T_p) varies in

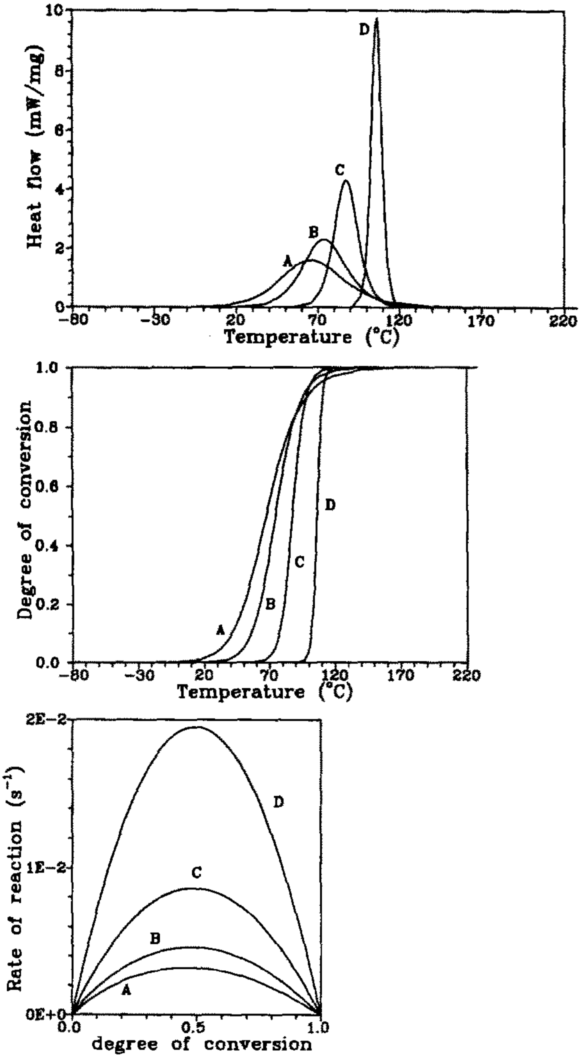

Fig. 5. Effect of exponent m on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t - T$, $\alpha - T$ and $\mathrm{d}\alpha/\mathrm{d}t - \alpha$. Kinetic parameters: $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, order of reaction $n + m = 2$, heating rate 10 deg min^{-1} and dynamic heat of reaction 500 J g^{-1}. Curve A, $m = 0.25$; curve B, $m = 0.50$; curve C, $m = 0.75$; curve D, $m = 0.9$.

a predictable manner with the heating rate β in both cases. When the heating rate is increased the temperature T_p increases too.

However, the variation in heating rate seems to have a considerable effect on the size, but little effect on the location, of a maximum rate of reaction, which always occurs when the same degree of conversion is achieved independently of the heating rate. Only the value of the maximum is affected by the heating rate. In Tables 4 and 5 we give the results of variation in T_p with the heating rate for different values of β.

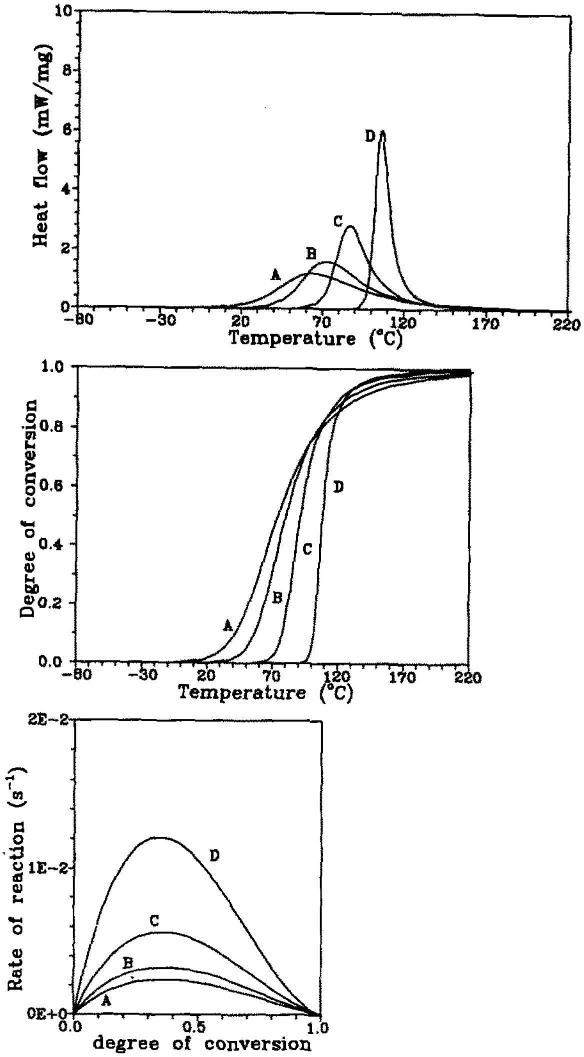

Fig. 6. Effect of exponent m on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t-T$, $\alpha-T$ and $\mathrm{d}\alpha/\mathrm{d}t-\alpha$. Kinetic parameters: $A=6\times10^{5}\ \mathrm{s}^{-1}$, $E=50\ \mathrm{kJ\ mol}^{-1}$, order of reaction $n+m=3$, heating rate, 10 deg min^{-1} and dynamic heat of reaction 500 J g^{-1}. Curve A, $m=0.25$; curve B, $m=0.50$; curve C, $m=0.75$; curve D, $m=0.9$.

There are basically two methods based on roughly approximate formulae for obtaining the activation energy by using the relationship between the reciprocal absolute peak temperature ($1/T_p$) and the heating rate β, namely the Kissinger and Ozawa methods. It would be interesting to make a critical examination of these approximate procedures in order to obtain the activation energy, starting from the simulated theoretical curve. In the

TABLE 2

Effect of kinetic parameters on appearance of dynamic theoretical curves simulated using an *n*th-order model

Increase in	Effect on DSC curve			Effect on $\alpha-T$		Effect on $d\alpha/dt-\alpha$		
	Size	Position of peak	Shape	Position	Shape	Size	Position of maximum	Shape
A	Increases	Shifts to lower T	Little change	Shifts to lower T	No change	Increases	No change	No change
E	Decreases	Shifts to higher T	Little change	Shifts to higher T	No change	Decreases	No change	No change
n	Decreases	No change	Drastic change	No change	Lower slope	Decreases	Shifts to lower α	Drastic change

TABLE 3

Effect of kinetic parameters on appearance of dynamic theoretical curves simulated using an autocatalyzed model

Increase in	Effect on DSC curve			Effect on $\alpha-T$		Effect on $d\alpha/dt-\alpha$		
	Size	Position of peak	Shape	Position	Shape	Size	Position of maximum	Shape
T	Increases	Shifts to lower times	Sharper	Shifts to lower times	No change	Increases	No change	No change.
m	Decreases	Shifts to higher times	Flatter	Shifts to higher times	Higher slope	Decreases	Shifts to higher α	Drastic change
n	Decreases	No change	Flatter	Intersection at lower times	Lower slope	Decreases	Shifts to lower α	Drastic change

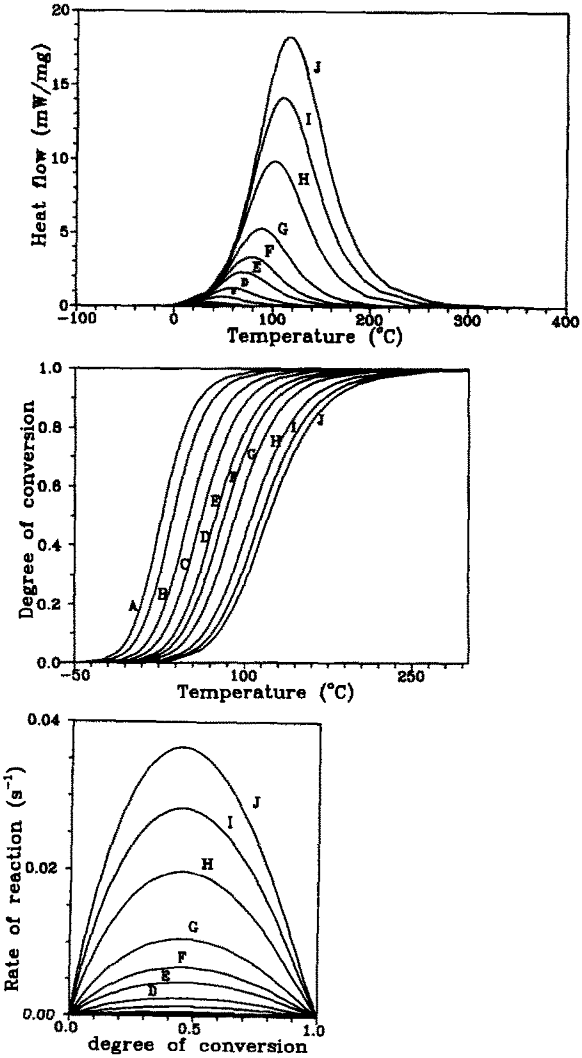

Fig. 7. Effect of heating rate β on the shape of theoretical curves: $dH/dt-T$, $\alpha-T$ and $d\alpha/dt-\alpha$. Kinetic parameters: $A = 6\times10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, order of reaction $n = 2$ and dynamic heat of reaction 500 J g^{-1}. Curve A, $\beta = 0.5$; curve B, $\beta = 1$; curve C, $\beta = 2$; curve D, $\beta = 5$; curve E, $\beta = 10$; curve F, $\beta = 20$; curve G, $\beta = 30$; curve H, $\beta = 50$; curve I, $\beta = 100$; curve J, $\beta = 150$; curve K, $\beta = 200$°C min^{-1}.

Ozawa calculation procedure, the following equation is derived [13]

$$\ln\beta = -5.33 + \ln\frac{AE}{RT} - \ln g(\alpha_p) - 1.052\frac{E}{RT_p} \tag{18}$$

This expression shows a linear dependence of the reciprocal absolute peak temperature on the logarithm of the heating rate. The term $g(\alpha_p)$ is the kinetics integral particularized at $\alpha = \alpha_p$, the degree of conversion achieved

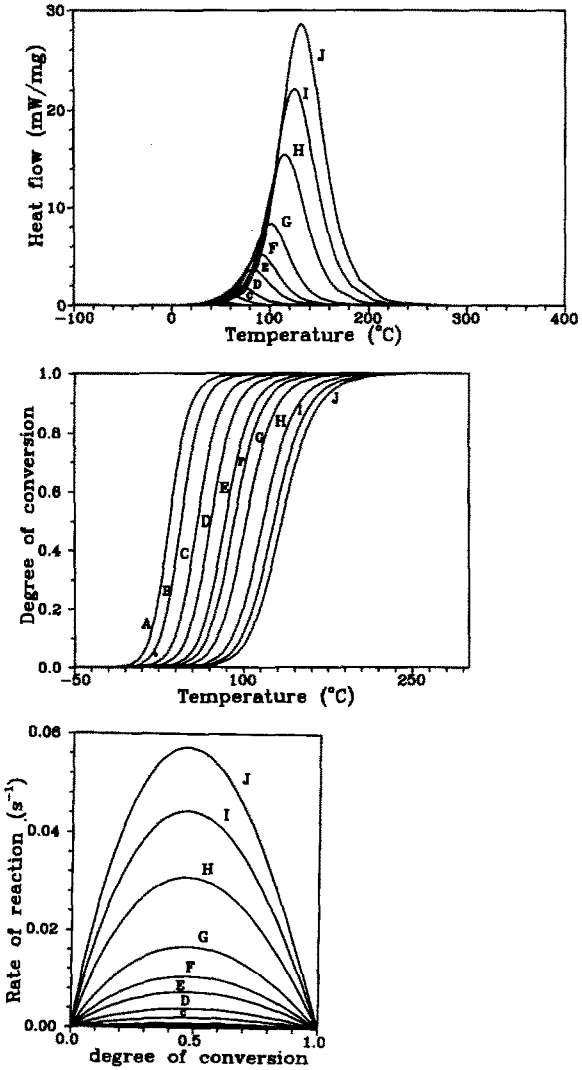

Fig. 8. Effect of heating rate β on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t-T$, $\alpha-T$ and $\mathrm{d}\alpha/\mathrm{d}t-\alpha$. Kinetic parameters: $A=6\times10^{5}\ \mathrm{s}^{-1}$, $E=50\ \mathrm{kJ\ mol}^{-1}$, exponent $m=0.4$, exponent $n=1.6$ and dynamic heat of reaction 500 J g^{-1}. Curve A, $\beta=0.5$; curve B, $\beta=1$; curve C, $\beta=2$; curve D, $\beta=5$; curve E, $\beta=10$; curve F, $\beta=20$; curve G, $\beta=30$; curve H, $\beta=50$; curve I, $\beta=100$; curve J, $\beta=150$; curve K, $\beta=200$°C min^{-1}.

when temperature is equal to the peak exotherm temperature. In the cases considered.

$$g(\alpha_\mathrm{p})=\begin{cases}\dfrac{\alpha_\mathrm{p}}{1-\alpha_\mathrm{p}} & \text{for } n=2\\[2ex] \dfrac{1}{n-1}\left(\dfrac{1-\alpha_\mathrm{p}}{\alpha_\mathrm{p}}\right)^{1-n} & \text{for } n+m=2\end{cases}\tag{19}$$

TABLE 4

Values of peak exotherm temperature T_p obtained from theoretical simulation of dynamic curves by varying the heating rate β

β (°C min^{-1})	T_p (°C)	α_p	H_p (mW mg^{-1})
0.5	15.7	0.45	0.082
1	24.7	0.45	0.153
2	35.5	0.47	0.288
5	48.0	0.45	0.664
10	59.1	0.45	1.245
20	71.0	0.45	2.322
30	78.4	0.45	3.343
50	88.1	0.45	5.303
100	102.6	0.45	9.864
150	109.0	0.43	14.159
200	117.1	0.45	18.296
300	126.4	0.45	26.241
500	138.8	0.45	41.279
1000	156.9	0.45	76.198

Kinetics model, nth-order; kinetics parameters, $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, $n = 2$, heat of reaction $\Delta H_R = 500$ J g^{-1}.

The activation energy E (kJ mol^{-1}), is calculated from the slope of the straight line obtained (Ozawa plot), either graphically or by linear regression. Figure 9 shows the Ozawa plot for both the nth-order and autocatalyzed models.

TABLE 5

Values of peak exotherm temperature T_p obtained from theoretical simulation of dynamic curves by varying the heating rate β

β (°C min^{-1})	T_p (°C)	α_p	H_p (mW mg^{-1})
0.5	24.0	0.47	0.129
1	33.6	0.47	0.243
2	43.8	0.47	0.456
5	58.3	0.47	1.050
10	70.1	0.47	1.960
20	82.8	0.47	3.657
30	90.6	0.47	5.265
50	100.9	0.47	8.317
100	115.9	0.47	15.447
150	125.2	0.47	22.148
200	132.0	0.47	28.605
300	142.1	0.47	40.950
500	155.4	0.47	64.300
1000	174.9	0.47	118.262

Kinetics model, autocatalyzed; kinetics parameters, $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, exponent $m = 0.4$, exponent $n = 1.6$ ($n + m = 2$), heat of reaction $\Delta H_R = 500$ J g^{-1}.

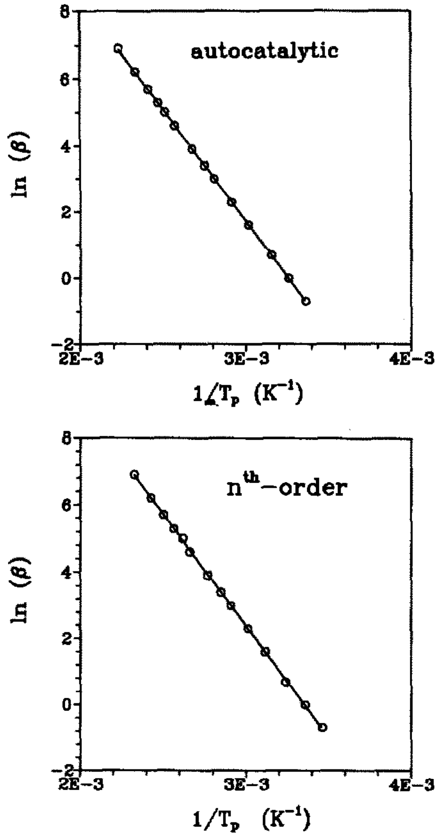

Fig. 9. Ozawa plot: linear representation of $\ln(\beta)$ vs. $(1/T_\mathrm{p})$. Heating rate $\beta = 0.5$, 1, 2, 5, 10, 20, 30, 50, 100, 150, 200, 300, 500 and 1000°C min^{-1}.

In the Kissinger calculation procedure a similar relationship between the logarithm of the heating rate divided by the square of the absolute peak temperature and the reciprocal absolute peak temperature is also obtained [14]

$$\ln\frac{\beta}{T_\mathrm{p}^2} = \ln\frac{AR}{E} + \ln\left[-f'(\alpha_\mathrm{p})\right] - \frac{E}{RT_\mathrm{p}} \tag{20}$$

This expression was deduced by Elder [15], who generalized Kissinger's method for any mechanistic model of reaction. The slope of the Kissinger plot, $\ln(\beta/T_\mathrm{p}^2)$ vs. $1/T_\mathrm{p}$, yields the activation energy. In Fig. 10 we represent the Kissinger plot for the two mechanistic models of reaction.

The values of $f'(\alpha_\mathrm{p})$ are

$$f'(\alpha_\mathrm{p}) = \begin{cases} -n\left(1-\alpha_\mathrm{p}\right)^{(n-1)} & \text{for } n \\ \alpha_\mathrm{p}^{(m-1)}\left(1-\alpha_\mathrm{p}\right)^{(n-1)}\left[m-\alpha_\mathrm{p}(m+n)\right] & \text{for } n+m \end{cases} \tag{21}$$

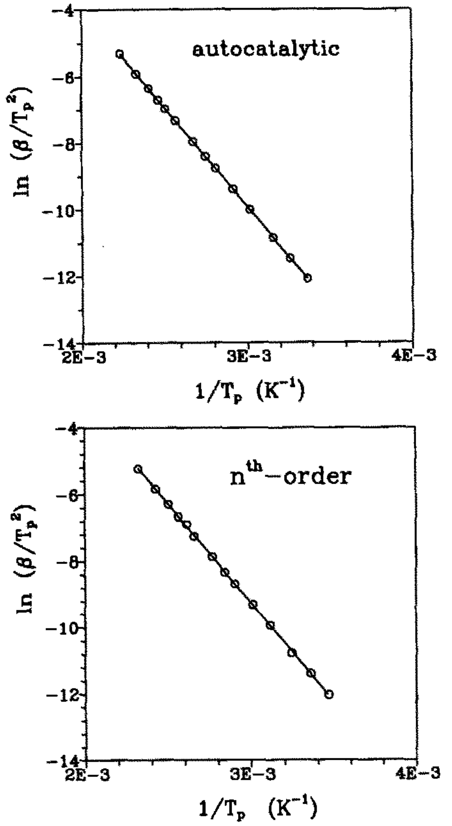

Fig. 10. Kissinger plot: linear representation of $\ln(\beta/T_p^2)$ vs. $(1/T_p)$. Heating rate $\beta = 0.5$, 1, 2, 5, 10, 20, 30, 50, 100, 150, 200, 300, 500 and 1000°C min^{-1}.

The frequency factor A (s^{-1}) can be estimated from the ordinate intersections of the straight lines obtained for two methods of calculation. Table 6 summarizes the results of calculated parameters A and E. As seen, the accuracy of these methods for the estimation of the activation energy is high, though the approximation utilized in the methods is a rough one. Duswalt [16] has found that, from the peak reaction temperatures as a

TABLE 6

Values for activation energy E (kJ mol^{-1}) and frequency factor A ($\times 10^5$ s^{-1}) obtained from the calculation procedures of Ozawa and Kissinger. (Theoretical values, $E = 50$ kJ mol^{-1} and $A = 6 \times 10^5$ s^{-1})

*n*th-order model				Autocatalyzed model			
E^a	E^b	A^a	A^b	E^a	E^b	A^a	A^b
52.9	49.8	18.6	3.0	52.9	50.0	21.3	11.4

[a] Ozawa procedure. [b] Kissinger procedure.

function of heating rate, the activation energy can be obtained with a precision of ±3% and an estimated accuracy of ±10%. As the data in Table 4 suggest, the observed accuracy is better in the Kissinger procedure than in the Ozawa procedure. Nevertheless, the frequency factor is estimated with a high error and these methods should not be used to estimate it.

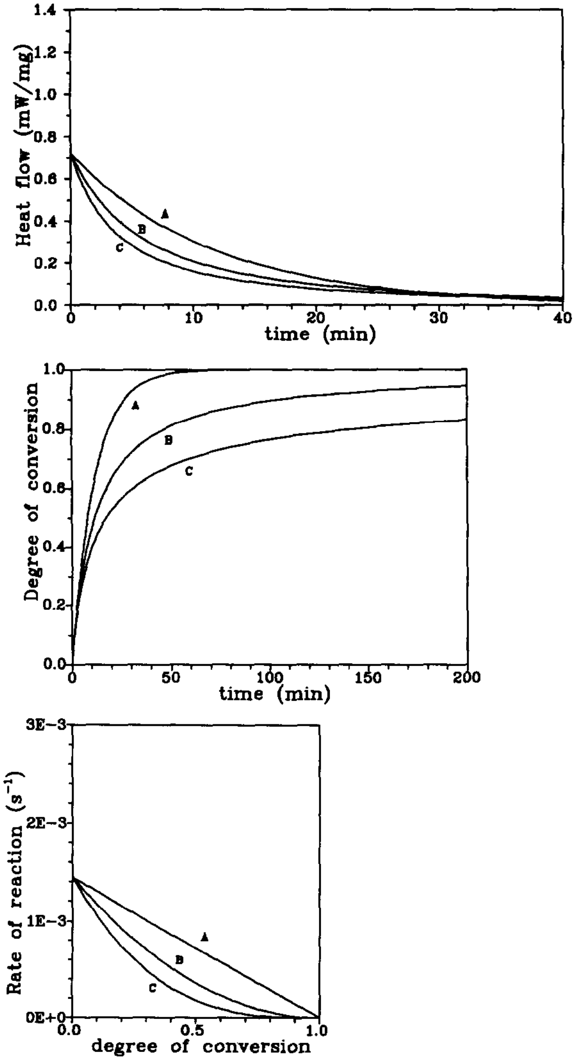

Fig. 11. Effect of reaction order n on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t - t$, $\alpha - t$ and $\mathrm{d}\alpha/\mathrm{d}t - \alpha$. Kinetic parameters: $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, temperature $T = 30$°C and isothermal heat of reaction 500 J g^{-1}. Curve A, $n = 1$; curve B, $n = 2$; curve C, $n = 3$.

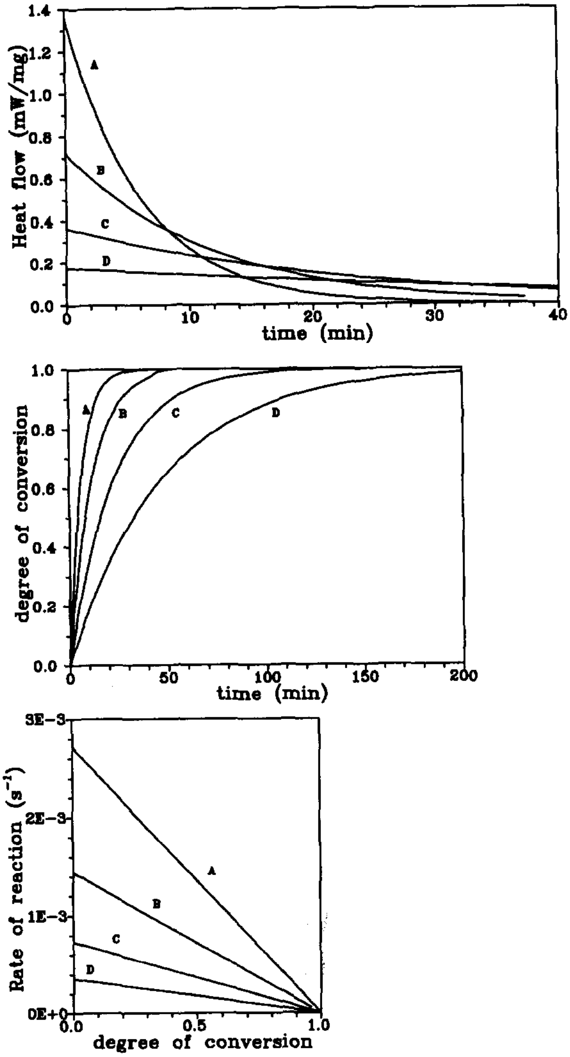

Fig. 12. Effect of temperature T on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t - t$, $\alpha - t$ and $\mathrm{d}\alpha/\mathrm{d}t - \alpha$. Kinetic parameters: $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, $n = 1$ and isothermal heat of reaction 500 J g^{-1}. Curve A, $T = 40$°C; curve B, $T = 30$°C; curve C, $T = 20$°C; curve D, $T = 10$°C.

Isothermal case

Figures 11 and 12 represent a set of plots $\mathrm{d}H/\mathrm{d}t$ vs. t, α vs. t and $\mathrm{d}\alpha/\mathrm{d}t$ vs. α, which show the influence of reaction order and temperature on an nth-order kinetic model for an isothermal curing reaction. As can be seen, the rate of reaction decreases as the reaction order is increased or the temperature is decreased. The maximum reaction rate is reached when the setting time or degree of conversion is zero. Thus, the generation of exothermal heat is maximum at the beginning of reaction and decreases as the reaction proceeds toward the formation of one infinite network. Experimentally, this occurs at a high isothermal cure temperature, when a significant portion of the reaction takes place during the establishment of instrument equilibrium and it cannot be recorded by the calorimeter.

With regard to the influence of frequency factor and activation energy, the effects that they cause in theoretical curves are completely the same as

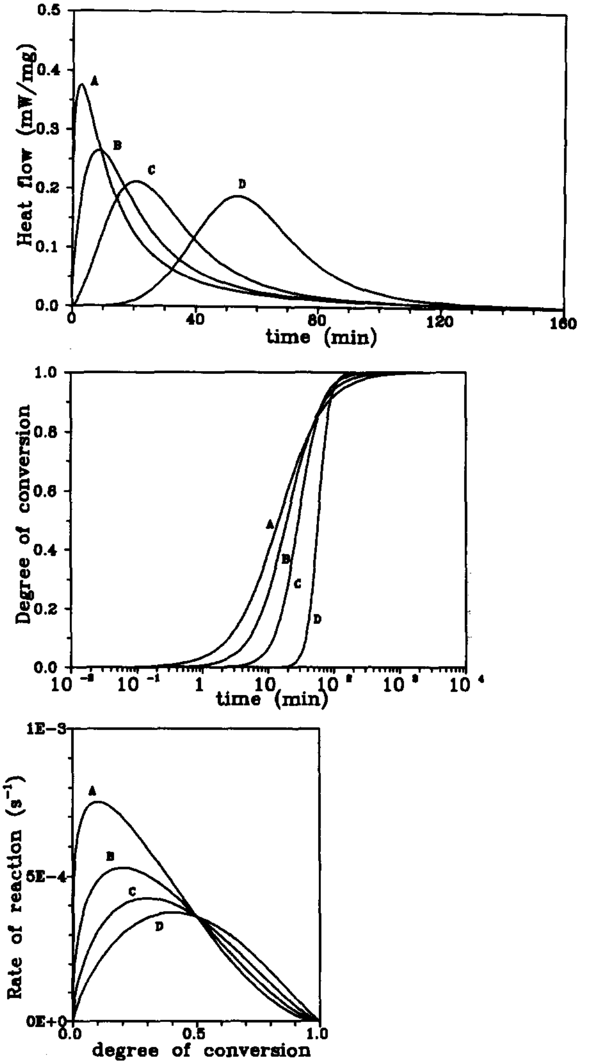

Fig. 13. Effect of exponent m on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t-t$, $\alpha-t$ and $\mathrm{d}\alpha/\mathrm{d}t-\alpha$. Kinetic parameters: $A=6\times10^5$ s^{-1}, $E=50$ kJ mol^{-1}, order of reaction $n+m=2$, temperature $T=30°\mathrm{C}$ and isothermal heat of reaction 500 J g^{-1}. Curve A, $m=0.2$; curve B, $m=0.4$; curve C, $m=0.6$; curve D, $m=0.8$.

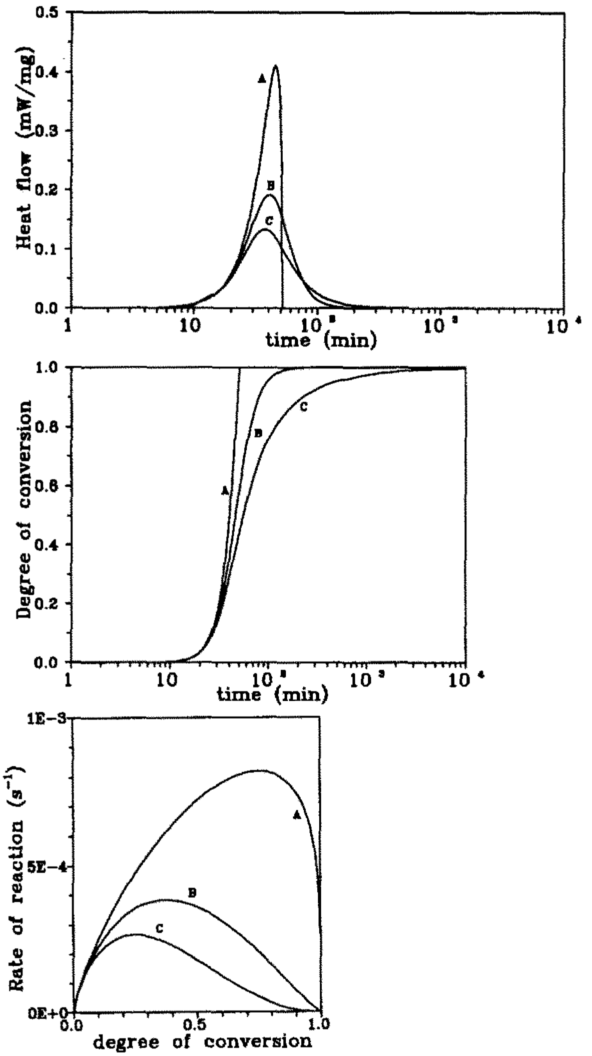

Fig. 14. Effect of reaction order $n+m$ on the shape of theoretical curves: $dH/dt-t$, $\alpha-t$ and $d\alpha/dt-\alpha$. Kinetic parameters: $A = 6 \times 10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, exponent $m = 0.75$, temperature $T = 30$°C and isothermal heat of reaction 500 J g^{-1}. Curve A, $n+m=1$; curve B, $n+m=2$; curve C, $n+m=3$.

the effects produced in dynamic curves for an nth-order reaction model, and will not be discussed here.

As distinguished from nth-order reaction kinetics, the autocatalyzed kinetics is characterized by the existence of an induction time. This is the time needed for the reaction to start up. The existence of an induction time in simulated curves can be observed in Figs. 13–16. As can be seen, the induction time increases at lower temperatures or at higher values of exponent m for $n+m=$ constant. The reaction is more rapid when the

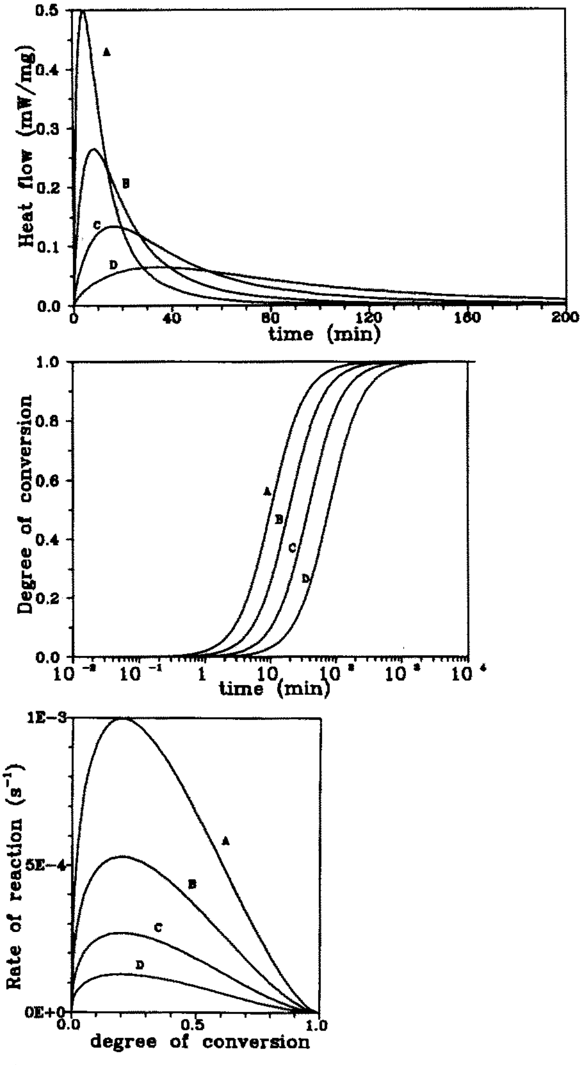

Fig. 15. Effect of temperature T on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t-t$, $\alpha-t$ and $\mathrm{d}\alpha/\mathrm{d}t-\alpha$. Kinetic parameters: $A = 6\times10^5$ s^{-1}, $E = 50$ kJ mol^{-1}, order of reaction $n + m = 2$, exponent $m = 0.4$ and isothermal heat of reaction 500 J g^{-1}. Curve A, $T = 40$°C; curve B, $T = 30$°C; curve C, $T = 20$°C; curve D, $T = 10$°C.

temperature is increased or the exponent m is decreased. For high temperatures the shape of the theoretical DSC curves is sharper (see Figs. 15 or 16). The exponent n has a drastic effect on the shape of the theoretical thermogram, which is flatter, as seen in $\mathrm{d}\alpha/\mathrm{d}t$ vs. α curves. Moreover, the reaction is slower (see α vs. t plot in Fig. 14). In Tables 7 and 8 we summarize the results of these effects.

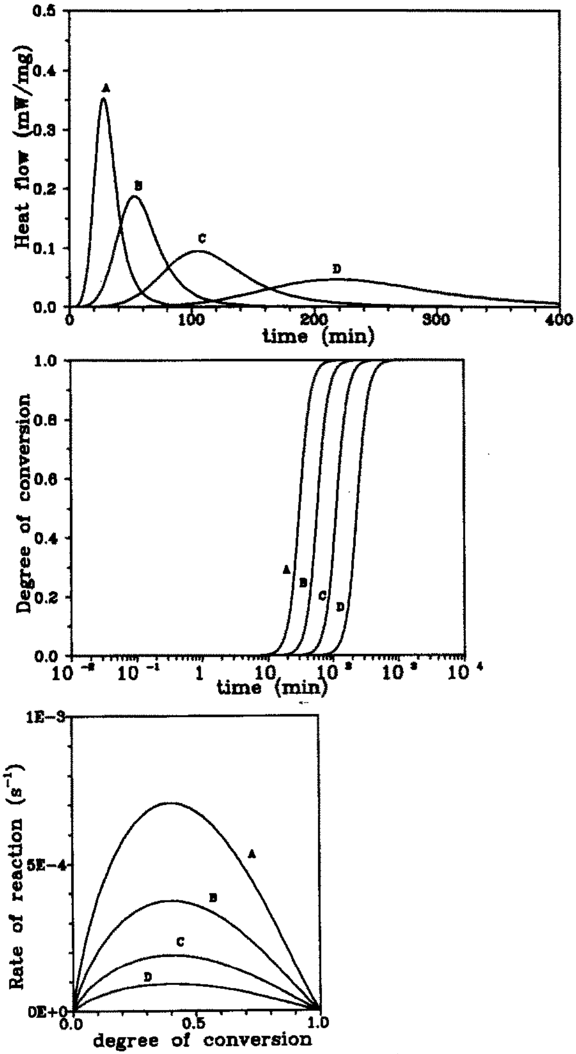

Fig. 16. Effect of temperature T on the shape of theoretical curves: $\mathrm{d}H/\mathrm{d}t-t$, $\alpha-t$ and $\mathrm{d}\alpha/\mathrm{d}t-\alpha$. Kinetic parameters: $A=6\times10^{5}$ s^{-1}, $E=50$ kJ mol^{-1}, order of reaction $n+m=2$, exponent $m=0.8$ and isothermal heat of reaction 500 J g^{-1}. Curve A, $T=40$°C; curve B, $T=30$°C; curve C, $T=20$°C; curve D, $T=10$°C.

CONCLUSIONS

Studies have been made in order to simulate the curing process of unsaturated polyesters with both nth-order and autocatalyzed kinetics and for isothermal and non-isothermal processes. In isothermal processes, we solved the kinetic equations in order to determine α and $\mathrm{d}\alpha/\mathrm{d}t$ as a function of time and also to obtain the heat generation curve $(\mathrm{d}H/\mathrm{d}t)$ as a function of time. In non-isothermal processes, we solved the kinetics

TABLE 7

Effect of kinetic parameter on appearance of isothermal theoretical curves simulated using an *n*th-order model

Increase in	Effect on DSC curve			Effect on $\alpha - T$		Effect on $d\alpha/dt - \alpha$		
	Size	Position of peak	Shape	Position	Shape	Size	Position of maximum	Shape
T	Increases	No change	Little change	Shifts to lower times	No change	Increases	No change	No change
n	Decreases	No change	Little change	Intersection at lower times	Lower slope	Decreases	No change	Drastic change

TABLE 8

Effect of kinetic parameters on appearance of isothermal theoretical curves simulated using an autocatalyzed model

Increase in	Effect on DSC curve			Effect on $\alpha - T$		Effect on $d\alpha/dt - \alpha$		
	Size	Position of peak	Shape	Position	Shape	Size	Position of maximum	Shape
n	Increases	Shifts to higher T	Sharper	Shifts to higher T	Higher slope	Increases	Shifts to higher α	Drastic change
m	Decreases	No change	Flatter	Shifts to lower T	Lower slope	Decreases	Shifts to lower α	Drastic change

equations in order to obtain α, $d\alpha/dt$ and dH/dt as a function of temperature.

Starting with kinetic parameters obtained from experimental results by a multiple linear regression analysis, we studied the influence on simulated processes produced by their variation. From the study of simulated data and comparison with the experimental results, it can be concluded that the autocatalyzed model reproduces the curing process of unsaturated polyesters better than the nth-order kinetic model in the case of isothermal processes. In the case of non-isothermal experiments, the differences are not so obvious. These results will be extensively reported in a future publication.

Variations in n, A and E which produce variations in position, size and shape of the simulated calorimetric curve allow us to construct a set of reference curves that can be used to simulate the real kinetic process.

A similar effect is also produced by variation in the heating rate, β. From the dependence between the peak exotherm and the heating rate, it is possible to obtain the activation energy of the overall reaction by using the Kissinger and Ozawa methods. Even though these methods are based on roughly approximate formulae, for the cases considered here we have verified that the activation energy can be obtained with good precision and accuracy by means of them. However, results for the frequency factor, which is estimated with a high error, are poor.

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