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EFFECT OF THE VALUE OF HEATING RATE IN DSC ON THE KINETIC PARAMETERS, WHEN THERE IS HIGH ENTHALPY OF REACTION

J Y ARMAND and J M VERGNAUD

Laboratory of Materials and Chemical Engineering, Faculty of Sciences, University of Saint-Etienne, 23, Dr P Michelon, Saint-Etienne, 42100 (France)

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ABSTRACT

A basic study is made of determination of the effect of the heating rate selected in calorimetry working in the scanning mode on the values obtained for the kinetic parameters The general problem is complicated by the fact that the rate of heat transfer through the sample is generally very low, and this can become a limiting factor if the heating rate is too high As a result, gradients of temperature are developed within the sample, especially when the reaction takes place The temperature in the sample can be very different from that of the calorimeter Moreover, this increase in temperature in the sample provokes an abnormal increase in the reaction rate Thus, the kinetic parameters determined from the usual methods (such as that of Freeman–Carroll), which do not take into account the heat transfer may be incorrect, if the value selected for the heating rate is too high The right value for the heating rate must be chosen by considering the enthalpy of reaction, the size of the sample, and the thermal properties of the material

INTRODUCTION

In calorimetry techniques, the enthalpy changes accompanying chemical or even physical events in the sample are monitored. The result is the profile of the rate of enthalpy changes either as a function of time, when the calorimeter is held at constant temperature (DC), or as a function of temperature as the sample is heated at a known linear rate (DSC) These enthalpy profiles allow certain critical parameters relevant to the actual manufacturing process to be rapidly determined and the profiles can sometimes be treated as a fingerprint of the system for purposes of quality control Moreover, a detailed kinetic analysis of the enthalpy profiles is possible especially in the case of simple reactions, although the determination of meaningful kinetic parameters is quite not as feasible for complex reactions For the latter however, it is possible to obtain kinetic equations able to describe the whole process, as has been shown in the case of sulphur vulcanization processes [1,2] or in the case of epoxy resin [3–8]

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The principle of the DC experiment appears very simple at first The calorimeter is stabilized at the desired constant temperature, the sample introduced and time base recording is started, allowing the enthalpy of all reactions occurring at this constant applied temperature to be determined up to a defined time. In fact, various drawbacks make this technique very difficult to use

(i) The applied temperature is not the true sample temperature because of local heating arising from the exothermic reactions, in the case of reactions with low enthalpy [9] and especially with high enthalpy [10].

(ii) As the sample at room temperature is introduced into the heated calorimeter, some time is required for the calorimeter–sample system to establish thermal equilibrium after introduction. As a result of the high endothermic heat flux following this high heating period, the first part of the reaction exotherm cannot be obtained.

(iii) Two experimental limitations on the temperature range over which meaningful data can be obtained result. The lowest temperature is determined by the sensitivity of the calorimeter and stability of the system, the rate of enthalpy change being too small to be recorded if the reaction rate is very low On the other hand, the highest temperature at which measurements can be obtained is determined by the induction period required for reactions to initiate As a result, a temperature window of 20–40 ° C width is found over which meaningful data can be obtained.

In the DSC experiment, starting with unreacted stock, the sample is scanned at a selected heating rate up to a temperature at which the reaction exotherm is complete The following drawbacks for this technique occur

(i) After cure in the calorimeter, the sample can be cooled and rescanned to give the temperature dependence of the specific heat of the reacted product as formed after the initial DSC experiment. The rescan curve is superimposed on the initial curve to give a baseline which would be observed in the absence of reaction A shift in baseline appears when the specific heat of the initial and final materials differ significantly

(ii) Because of the heating rate imposed by the calorimeter and low heat conductivity of the material, gradients of temperature are developed throughout the sample These gradients are proportional to the heating rate and the square of the dimension when there is no reaction, and are also proportional to the enthalpy of reaction and the heating rate when the reaction takes place [11–14]

There is another drawback for both these calorimetry techniques The small sample size used in calorimetry requires that all the gradients in the sample be well dispersed Dispersion problems do arise on occasion and are generally indicated by lack of reproducibility It is questionable how representative a 10 mg sample is when taken from a large batch. It is often better to use larger samples of (100–200 mg) especially when mixtures are studied. On the other hand, these large samples (e.g., a cylinder of 0.5 cm height and 0.5 cm diameter) become heated more slowly than smaller samples, the heating rate being proportional to the square of the mean dimension [14].

Two parameters are also to be considered:

(i) The quality of contact, either between the sample and holder or between the holder and calorimeter. This parameter has been observed to play an important role especially in isothermal calorimetry, being responsible for a significant retardation in the heat flux–time history [9,10].

(ii) The low heat conductivity exhibited by various materials, and especially by polymeric materials. As a result, high gradients of temperature are developed through the sample in DC, when the sample is introduced into the calorimeter, producing very high endothermal heat flux which masks the beginning of the reaction [15,16]. It is also possible that these gradients of temperature through the sample are able to disturb the determination of the kinetic parameters not only in DC, but also in DSC.

The purpose of this work is to show that the heating rate in DSC not only plays an important role, but also must be controlled by using a sufficiently low value. The combination of the heat of reaction and low heat conductivity is responsible for an increase in temperature within the sample, and this higher temperature produces in turn a higher rate of reaction. The result is a thinner and higher peak for the heat flux–temperature (or time) history, this peak being described by kinetic parameters which are different from the values obtained under slower conditions of heating. In order to achieve this, without disturbing the quality of contact which is difficult to control, we determine successively: (i) the heat flux–temperature (or time) history by taking into account the heat transfer through the sample and the reaction heat, with the help of a mathematical model with finite differences, (ii) better kinetic parameters which are able to describe this heat flux–temperature curves, by using the usual methods [17] where the heat flux is not considered.

THEORETICAL

Mathematical treatment

The following assumptions are made in order to clarify the problem in the case where heat transfer is taken into account:

(i) The sample is cylindrical in shape, and radial heat by conduction through the circular cross-section only is considered.

(ii) The thermal parameters, as thermal conductivity and heat capacity, are constant during heating and reaction
(iii) The kinetic parameters are kept constant during the process The rate of heat evolved from the reaction is described by an Arrhenius law In the case when heat transfer is not considered, other assumptions are made for determining the kinetic parameters of the reaction
(iv) The heat transfer rate is very fast within the sample, so that the temperature in the sample is constantly the same as that of the calorimeter.
(v) The kinetic parameters are constant during the reaction The rate of reaction heat is described by an Arrhenius law

The equation of the rate of heat conduction through the cross-section is

$$\rho c \frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda\frac{\partial T}{\partial r}\right) + \rho\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

where the contribution of heat conduction and of internal heat generated by the reaction may be observed

The rate of heat evolved from the overall reaction is given by the classical equation

$$\frac{1}{Q_\infty}\frac{\mathrm{d}Q_{(r,t)}}{\mathrm{d}t} = k_0\left(1 - \frac{Q_t}{Q_\infty}\right)^n \exp\left(-\frac{E}{RT}\right) \tag{2}$$

The initial and boundary conditions are

$t = 0 \quad 0 \leqslant r \leqslant R \quad T$ sample (3)
$t > 0 \quad r = r \quad T$ calorimeter (4)
$\quad 0 \leqslant r < R \quad T$ sample

with a constant increase in temperature of the calorimeter

$$r = R \qquad T = T_0 + bt \tag{5}$$

Numerical analysis

As previously shown [12,13] no analytical solution can be found for the problem the solution is obtained by a numerical method with finite differences

By considering the various following circles of radius r, $r + \Delta r$, $r + 2\,\Delta r$, taken on a circular cross-section, the heat balance is determined for every ring of thickness Δr For instance, for the ring between $r + \Delta r/2$ and $r - \Delta r/2$, it is found that

$$TN_r = \frac{1}{M}\left[T_{r+\Delta r} + (M-2)T_r + T_{r-\Delta r}\right] + \frac{\Delta r}{2M_r}\left[T_{r+\Delta r} - T_{r-\Delta r}\right] + \frac{1}{C}\frac{\mathrm{d}Q}{\mathrm{d}t}\,\Delta t \tag{6}$$

where TN_r is the new temperature at radius r after the elapse of the finite increment of time Δt, and T is the temperature at time $i\,\Delta t$.

At the middle of the cylinder, for $r = 0$, the following equation is used

$$TN_0 = \frac{4}{M}[T_{\Delta r} - T_0] + \left(\frac{1}{C}\right)\frac{\mathrm{d}Q}{\mathrm{d}t}\,\Delta t + T_0 \tag{7}$$

where the dimensionless number M is given by

$$M = \frac{(\Delta r)^2}{\Delta t}\,\frac{\rho c}{\lambda} \tag{8}$$

For the calorimeter–sample interface, another equation has been tested to take into account the quality of the contact [12,13]

$$TN_r = \left(\frac{H}{1+H}\right)T_{\mathrm{cal}} + \left(\frac{1}{1+H}\right)T_r \tag{9}$$

the coefficient H being evaluated by

$$H = \left(\frac{\alpha_{\mathrm{cal}}}{\alpha_{\mathrm{s}}}\right)^{0.5}\left(\frac{\lambda_{\mathrm{s}}}{\lambda_{\mathrm{cal}}}\right) \tag{10}$$

The heat flux HF transferred to (or from) the calorimeter detector is obtained by the simple equation

$$HF = \lambda_{\mathrm{s}}\frac{T_r - T_{r-\Delta r}}{\Delta r} \tag{11}$$

The heat evolved from the cure reaction is obtained by the recurrent relation

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t = Q_{i+1} - Q_i = k_0(Q_\infty - Q_i)^n Q_\infty^{1-n} \exp - \frac{E}{RT_i} \tag{12}$$

with

$$Q_i = \sum_{i=0}^{i-1}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_i \Delta t \text{ and } Q_0 = 0 \tag{13}$$

The calculated curves obtained at various heating rates are evaluated with the help of the Freeman–Carroll technique with finite increments of temperature [18] in order to find the kinetic parameters. The validity of these kinetic parameters is then tested by calculating the thermogram and superposing experimental and simulated thermograms [17].

EXPERIMENTAL

The sample of about 150 mg was placed in a stainless steel holder, cylindrical in shape with an external diameter of about 5.5 mm. A DSC III (Setaram) was used. Operating conditions were: programming of tempera-

TABLE 1

Thermal and kinetic parameters of the resin

$k_0 = 4 \times 10^{11}\ \mathrm{s}^{-1}$ $E = 27\,140\ \mathrm{cal\ mol}^{-1}$ $H = 152\ \mathrm{cal\ g}^{-1}$
$\lambda = 10^{-3}\ \mathrm{cal\ cm}^{-1}\ \mathrm{s}^{-1}\ \mathrm{K}^{-1}$ $C = 0\ 2 + 3 \times 10^{-3} \times T(^\circ\mathrm{C})\ \mathrm{cal\ g}^{-1}\ \mathrm{K}^{-1}$ $n = 1\ 5$

ture for the calorimeter from room temperature to the final temperature, this final temperature being chosen as sufficiently high for the heat flux–time history to be completely obtained The rate of heating is constant for each operation, and is chosen within the 2–20 °C min^{-1} range

An unsaturated polyester of high enthalpy was chosen for this study The thermal properties of this material had been previously determined, especially heat diffusivity α and thermal conductivity λ, as well as heat capacity C The values obtained are shown in Table 1, for thermal properties, and kinetic parameters These kinetic parameters were determined from DSC curves obtained at a low heating rate (1 and 2 °C min^{-1})

RESULTS

The heat flux-temperature histories obtained for various heating rates, and the determination of the kinetic parameters corresponding is the reaction under these conditions are important In order to find an explanation for these differences, it was necessary to show how the temperature at the middle of the sample varies with the scanning process In addition some profiles of temperature developed through the sample have been calculated

Heat flux–temperature histories for various heating rates

Two types of heat flux–temperature histories are compared

(i) The experimental curve which is in good agreement with the curve calculated with the model taking into consideration the reaction with its enthalpy and kinetics and also the heat transfer through the sample
(ii) The curve described above is analysed step by step by using the Freeman–Carroll technique and a computer coupled with the DSC Another curve is then obtained by using the Arrhenius equation (eqn (2)) and the kinetic parameters obtained from the Freeman–Carroll treatment
(iii) A third curve is drawn to exhibit the difference between the above two DSC curves

The results are shown in Figs 1–4 for the heating rates 2, 5, 10, 20 °C min^{-1} The following conclusions can be drawn from these curves (Figs 1–4) and the kinetic parameters shown in Table 2

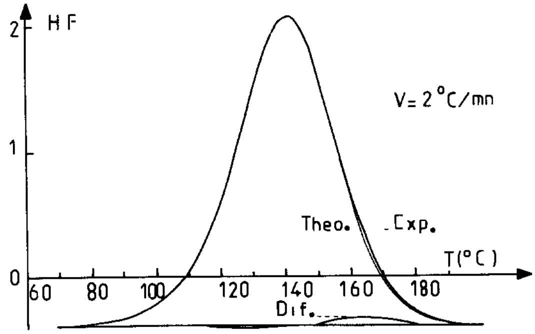

Fig 1 Heat flux as a function of temperature, ——theoretical, —— experimental, heating rate = 2 °C min^{-1}

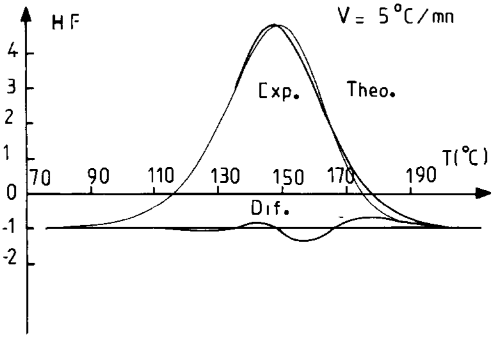

Fig 2 Heat flux as a function of temperature ——theoretical, —— experimental, heating rate = 5 °C min^{-1}

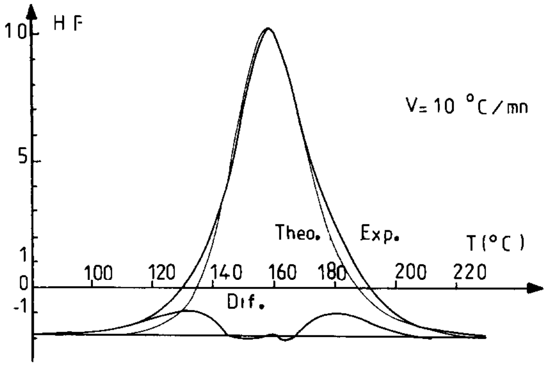

Fig 3 Heat flux as a function of temperature —— theoretical, —— experimental, heating rate = 10 °C min^{-1}

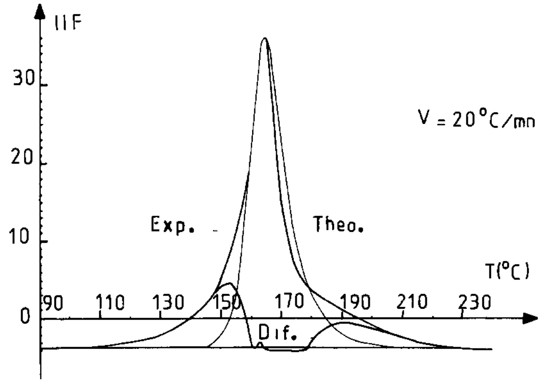

Fig 4 Heat flux as a function of temperature ——— theoretical, ——— experimental, heating rate = 20 °C min^{-1}

(i) Perfect agreement is obtained between these curves for the heating rate 2 °C min^{-1} Also the kinetic parameters determined by the Freeman–Carroll technique are close to those used for the calculation made by taking the heat transfer into account.

(ii) When the heating rate was 5 °C min^{-1}, the agreement between the two curves is still acceptable, but is not perfect The position of the maximum of the heat flux is well placed, as is the position of the points D′ and D corresponding to half this maximum value However, some slight differences appear, for instance for the points C, E and F Other couples such as E, k_0 cannot give a better result

(iii) The difference between the two curves appears to be significant in the case where heating rates are higher For instance, with a heating rate of 10 °C min^{-1}, the maximum of the heat flux is well placed in B, in fact as well as the other points D and C However, there are considerable differences at the beginning of the curve in A, and especially at the tail from D to F In addition it was necessary to have high values of the activation energy and kinetic constant k_0 as shown in Table 2, in order to describe the peak expressing heat flux (which is very thin)

TABLE 2

Kinetic parameters

	E	k_0	n
Curves with heat transfer	27 140	4×10^{11}	1 5
Freeman–Carroll (2 °C min^{-1})	27 600	1×10^{12}	1 5
Freeman–Carroll (5 °C min^{-1})	28 300	$1\ 8 \times 10^{12}$	1 54
Freeman–Carroll (10 °C min^{-1})	47 000	2×10^{22}	2 5
Freeman–Carroll (20 °C min^{-1})	100 000	5×10^{58}	3 3

(iv) For the higher value for the heating rate (20 ° C min^{-1}) it is clear that it is impossible to obtain kinetic parameters able to describe the heat flux–temperature history The value noted in Table 2 is certainly not real

We conclude that the value chosen for the heating rate must be sufficiently low, or the kinetic parameters obtained from the curve will be incorrect

Temperature profiles at the middle of the sample

In order to obtain an explanation for these results, we have calculated the temperature at the middle of the sample throughout its variation during the scanning process, by using the mathematical model taking into account the kinetics of reaction and heat transfer

As shown in Fig 5 for heating rates 2 and 5 ° C min^{-1} and in Fig. 6 for the higher heating rates (10 and 20 ° C min^{-1}), these curves have about the same shape and position as the heat flux–temperature histories This has been reported in the case of lower enthalpy of reaction [15,16]. The following conclusions can be drawn from Figs. 5 and 6, and from Table 3

(i) The shape of the heat flux and temperature at the middle of the histories is about the same, for various heating rates, with the same position of the maximum

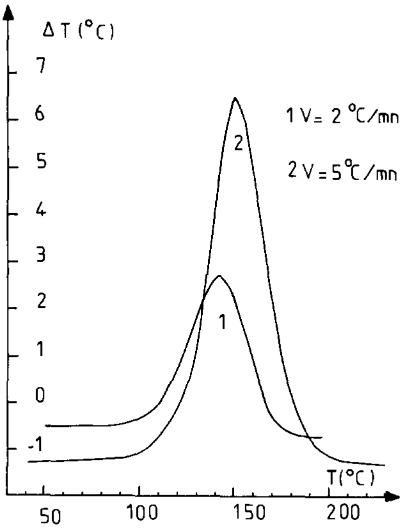

Fig 5 Difference of temperature between the middle and the face of the sample (ΔT) as a function of the temperature of calorimeter 1, heating rate = 2 ° C min^{-1}, 2, heating rate = 5 ° C min^{-1}

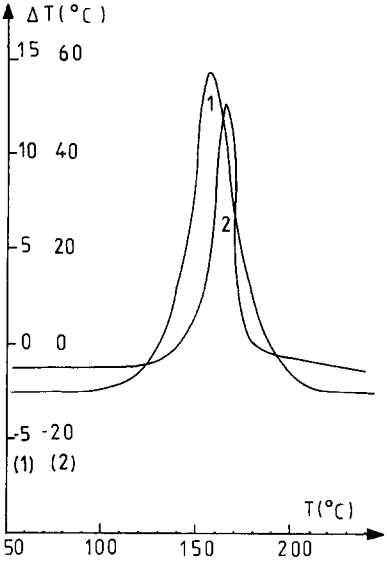

Fig 6 Difference of temperature between the middle and the face of the sample (ΔT) as a function of the temperature of calorimeter 1, Heating rate = 10 °C min^{-1}, 2, heating rate = 20 °C min^{-1}

(ii) The increase in the temperature at the middle is almost proportional to the value of the heat flux during the reaction, and especially at the maximum (Table 2)

(iii) The maximum value for the heat flux and also for the increase in temperature at the middle of the sample varies proportionally with the value of the heating rate

Profiles of temperature through the sample

The mathematical model is able to produce the profiles of temperature and state of cure as they are developed through the sample either during the

TABLE 3

Characteristics of heat flux histories

	Heating rate (°C min^{-1})			
	2	5	10	20
Temperature for max HF (°C)	142 54	151 69	158 05	164 85
Temperature for max ΔT (°C)	42 54	151 69	157 34	163 51
Maximum HF (°C)	2 066	4 826	10 159	36 049
Maximum ΔT (°C)	2 7	6 48	14 58	53 7

ΔT = difference of the temperature at the middle of the sample obtained at the maximum of reaction and without reaction

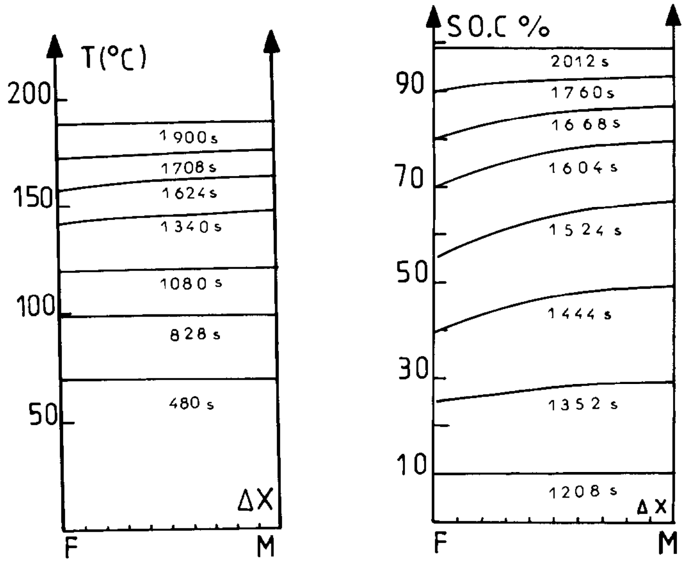

Fig 7 Profiles of temperature (left) and state of cure (right) developed through the sample at various times Heating rate = 2 °C min^{-1}

heating period or during the period of reaction These profiles have been drawn for heating rates 2 °C min^{-1} and 20 °C min^{-1} (Figs 7 and 8) From these curves it may be seen that

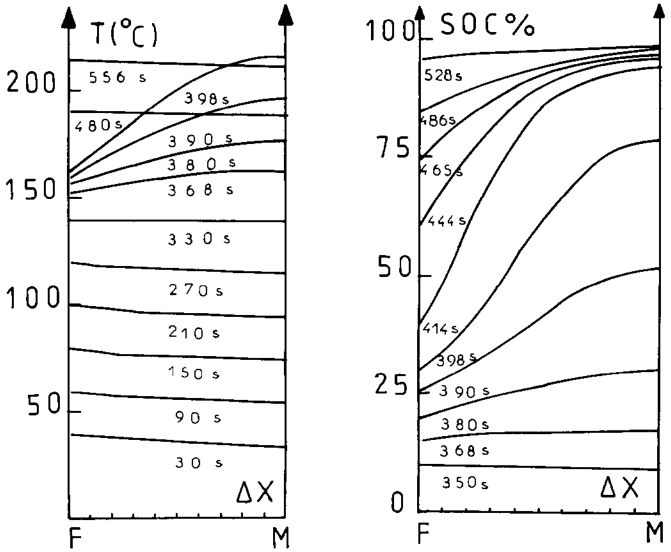

Fig 8 Profiles of temperature (left) and state of cure (right) developed through the sample at various times Heating rate = 20 °C min^{-1}

(i) For the low heating rate, rather low gradients of temperature are developed within the sample. The highest value of these gradients is obtained when the heat flux is maximum, as shown in Figs. 1 and 7

(ii) For the lower heating rate, the value of the state of cure (indicating the actual extent of the reaction) is about the same within the sample throughout.

(iii) For the high heating rate, high gradients of temperature are developed throughout the sample When no reaction occurs, the temperature is higher on the face than at the middle, as shown previously this retardation is proportional to the heating rate of the square of the dimension of the sample [14] Other gradients of temperature are expanded during the reaction, the temperature becoming higher at the middle of the sample

(iv) For the higher heating rate, the values of the state of cure are quite different from one place to another in the sample, and high gradients for the state of cure occur during the reaction period, the higher value being attained at the middle of the sample

CONCLUSIONS

Calorimetry working in scanning mode is certainly the best technique for determining the kinetics of the heat evolved from the overall reaction taking place in the sample However, the heating rate is a most important parameter Too low a value for the heating rate causes very low heat flux emitted through the calorimeter detector On the other hand, with high values of the heating rate, high gradients of temperature are developed within the sample allowing higher rates of reaction which in turn produce higher gradients of temperature At high heating rates, very high heat fluxes are obtained, the maximum value being proportional to the value chosen for the heating rate Error can occur however when the kinetic parameters are determined from the heat flux–temperature history by using the usual methods (for instance that of Freeman–Carroll) which consider the kinetics of reaction and not the heat transferred through the sample In fact, the rate of the heat transferred through the sample, is a limiting factor, both for the heating period of the sample and for the reaction period The heat transfer can be neglected when determining the kinetic parameters only when the heating rate of the calorimeter is sufficiently low This convenient value of the heating rate must depend on various factors the enthalpy of reaction, the size of the sample, and the thermal properties of the sample

REFERENCES

1 A Accetta, P Le Parlouer and J M Vergnaud, Thermochim Acta, 59 (1982) 149

2 D W Brazier, in N Grassie (Ed), Developments in Polymer Degradation, vol 3, Applied Science Publishers, 1981, Ch 2, p 27

3 A Dutta and M E Ryan, J Appl Polym Sci , 24 (1979) 635

4 S Sourour and M R Kamal, Thermochim Acta, 14 (1976) 41

5 S Sourour and M R Kamal, Polym Eng Sci , 16 (1976) 480

6 R P Kreahling and D E Kline, J Appl Polym Sci , 13 (1969) 2411

7 J Mijovic, K Jinhwan and J Slaby, J Appl Polym Sci , 9 (1983) 1449

8 M Chater, D Labart, F Michel-Dansac and J M Vergnaud, Eur Polym J , 22 (1986) 805

9 A Khouider, J B Rochette and J M Vergnaud, Thermochim Acta, 89 (1985) 81

10 G Chataing, M Chater and J M Vergnaud, Thermochim Acta, 89 (1985) 107

11 J Y Armand, J Bourgois and J M Vergnaud, Thermochim Acta, 116 (1987) 301

12 M Chater, G Chataing and J M Vergnaud, Thermochim Acta, 90 (1985) 135

13 A Khouider, J Bouzon and J M Vergnaud, Thermochim Acta, 98 (1986) 285

14 J Y Armand, R Gonnet, R Jones, J Bouzon, M Touchard and J M Vergnaud, Thermochim Acta, 103 (1986) 341

15 J Y Armand and J M Vergnaud, Thermochim Acta, 121 (1987) 381

16 J M Vergnaud, Thermochim Acta, 114 (1987) 15

17 K Kretzschmar and K W Hoffmann, Thermochim Acta, 83 (1985) 139

18 E S Freeman and B Carroll, J Phys Chem , 62 (1958) 394