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# EFFECTS OF EXPERIMENTAL SAMPLE MASS ON THE CALORIMETRIC STUDY OF THERMOSET RESINS

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It is known that experimental parameters may affect peak characteristics in DSC studies. Kinetic parameters calculated from isothermal and dynamic runs, can also be affected by the choice of experimental conditions.

The sample mass can affect the determination of reaction parameters because of the heat transport and the self-insulating properties of large masses.

In the curing process of thermoset resins like unsaturated polyester crosslinked by styrene, the exothermal heat results from the reaction advance but it also produces an autocatalytic process that induces an increase in the reaction rate. The sample mass, in this kind of experiments, can influence the determination of reaction parameters not only through the effect of heat transport or thermal lag on the calorimetric results but also through the action that the sample mass exerts on the exothermal heat, and consequently, on the autocatalytic process.

In this paper we intend to present the results obtained in the study of the curing kinetics of thermoset resins by DSC technique using different sample masses. We will point out that the reaction heat determined by dynamic measurement was found to be independent of the sample mass. We have obtained differences in the kinetic parameters like the reaction order, activation energy and preexponential factor when the sample mass was changed.

**Keywords**: effect of sample mass, kinetic parameters, thermoset resins

## Introduction

Isothermal and dynamic DSC scans are often used for monitoring the changes accompanying a chemical reaction. Results obtained from the study of chemical reactions are the heat change in the reaction, the onset and temperature range over which the reactions proceed, the extent of reaction of partially reacted samples, and reaction kinetic data [1].

Experimental variables may affect peak characteristics in differential scanning calorimetry. It has been stated that kinetic parameters calculated from DSC peaks are also affected by the choice of experimental conditions [2].

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In isothermal experiments, flat temperature profiles through the sample at the beginning or end of the curing process can mask the DSC signal and the parameters calculated from it. In dynamic experiments, the study of reactions taking place in the calorimeter are very often complicated by various phenomena (heat transfer, reaction and heat flux) [3, 4]. In both cases, the effect of sample weight and sample size can be important and it has to be taken into account.

In case of thermosets, the sample mass, in this kind of experiments, can influence the determination of reaction parameters not only through the effect of heat transport or thermal lag on the calorimetric results but also through the action that the sample mass exerts on the amount of exothermal heat, and consequently, on the autocatalytic process.

The main purpose of this paper is to present the results obtained in the study of the curing kinetics of thermoset resins by DSC technique using different sample masses and to show its effects.

## Theoretical assumptions

In calorimetric analysis it is assumed that every conversion d$\alpha$ corresponds to a proportional enthalpy change d$H$. Therefore, the quantities d$\alpha$/d$t$ and $\alpha$ needed for the regression analysis in the kinetic analysis of experimental results, can be calculated from the DSC curves as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\frac{\mathrm{d}H}{\mathrm{d}t}}{\Delta H_{\mathrm{R}}} \quad \text{and} \quad \alpha=\frac{\Delta H_{\mathrm{part}}}{\Delta H_{\mathrm{R}}} \tag{1}$$

where $\alpha$ is the degree of conversion, $\Delta H_{\mathrm{R}}$ the heat of reaction, and $\Delta H_{\mathrm{part}}$, the partial area up to time $t$, or temperature $T$, in dynamic experiments.

Some authors also obtain conversions by subtracting from unity the ratio of the partial heat of reaction at time $t$, $\Delta H_{\mathrm{res}}$, to the overall dynamical heat, $\Delta H_{\mathrm{din}}$, [5]

$$\alpha=1-\left(\frac{\Delta H_{\mathrm{res}}}{\Delta H_{\mathrm{din}}}\right) \tag{2}$$

The mathematical model used to describe the kinetics is

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

where $k$ is the reaction rate constant in $s^{-1}$. Two models for $f(\alpha)$ are usually used in thermoset kinetic studies: the $n^{th}$-order reaction model, $f(\alpha)=(1-\alpha)^n$, and the autocatalytic reaction model: $f(\alpha)=\alpha^m(1-\alpha)^n$ where $n$ and $m$ are reaction orders. Its dependence on temperature is given by the Arrhenius equation:

$$k = k_o \cdot e^{-E/RT} \tag{4}$$

where $k_o$ is the preexponential factor, $E_A$ the activation energy, and $R$ the gas constant.

On substituting the Arrhenius equation into Eq.(3) and taking the logarithm we get

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k_o - \frac{E_A}{RT} + \ln f(\alpha) \tag{5}$$

Multiple linear regression analysis provides the required kinetic parameters, using triples of measured values $[d\alpha/dt, \alpha, T]_i$ from dynamic DSC curves [6]. A similar procedure is also used in isothermal experiments, using $[\alpha, d\alpha/dt]$ values. In this case, a plot of $\ln k$ *vs.* $1/T$ allows to find the activation energy $E_A$.

If we are only interested in obtaining the activation energy, $E_A$, the well known methods of Kissinger [7] and Ozawa [8] are used.

## Experimental

A general purpose polyester resin (commercial name A228) supplied by Rio Rodano (Spain) was used. The base polyester resin was prepared using phthalic anhydride, maleic anhydride and propyleneglycol, with a mole ratio of 2:1:3 obtained by NMR. As a crosslinking agent, styrene monomer had been added to the resin by the supplier. The styrene content was determined as 35%. A 50% solution of methyl ethyl ketone peroxide (MEKP) in dibutyl phthalate was used as initiator, and a 6% cobalt octoate solution in xylene was added as accelerator.

The calorimetric measurements were carried out using a Mettler DSC apparatus, equipped with a control and programming unit (microprocessor TC 10A) and a calorimetric cell (DSC20) arranged to permit temperature scans from –10° to 600°C.

A standard resin sample was catalysed by mixing it with MEKP peroxide (1% by weight) and cobalt octoate solution (0.1% by weight) for about 1 min. Weighing was done on a Mettler electronic microbalance.

The DSC runs for isothermal experiments were performed at 20°, 25°, 30°, 35°, 40° and 50°C and setting time of 240 min. The heating rate for dynamic experiments (in deg·min$^{-1}$ were: 2, 5, 10, 15, 20, 30 and 50; and the sample mass (in mg): 5, 10, 20, 30 and 40.

## Results and discussion

The DSC curves and normalized curves for isothermal experiments performed at 25°C for different sample masses are shown in Fig. 1. They exhibit different induction times which increase when the sample mass decreases. It provides evidence of the existence of an overall autocatalytic reaction mechanism.

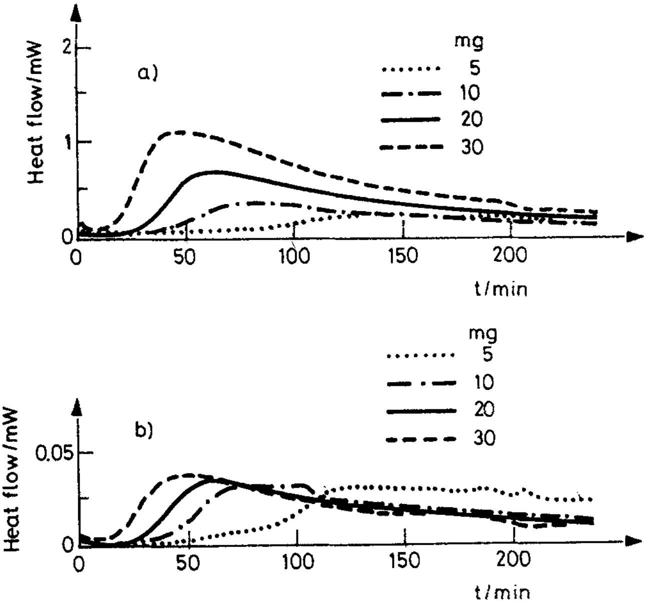

**Fig. 1** a) Experimental DSC isothermal curves for different sample weights. b) Normalized DSC isothermal curves (per unit of mass) for different sample weights. Temperature of curing: 25°C

Figure 2 shows the DSC curves and normalized curves for dynamic experiments performed at a heating rate of 10 deg·min$^{-1}$ for different sample masses. As can be observed, there is no evidence of the effect of sample mass on the exothermic peak.

The experimental values of the reaction heat determined by dynamic measurement were found to be independent of the sample mass, as it can be seen in Fig. 3, in which also reaction enthalpies corrected according to [9] were plotted.

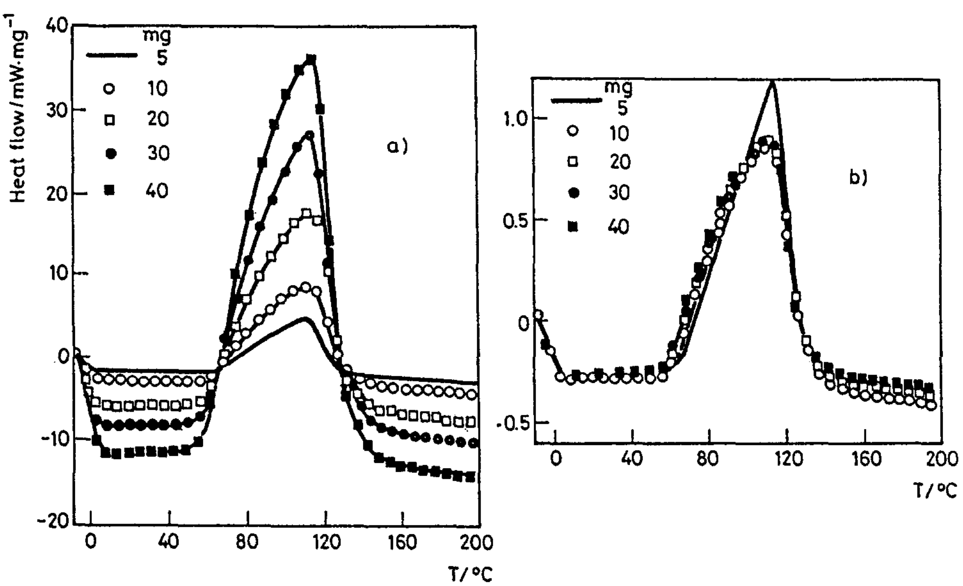

**Fig. 2** a) Experimental DSC dynamic curves for different sample weights. b) Normalized DSC dynamic curves (per unit of mass) for different sample weights. Heating rate: 10 deg·min$^{-1}$

An experimental value of 340 J·g$^{-1}$, or corrected value of 500 J·g$^{-1}$ of the overall curing heat has been obtained.

Figures 4a and 4b show the isothermal reaction heat, $\Delta H_{\mathrm{iso}}$, and the corrected isothermal reaction heat, $\Delta H^{c}_{\mathrm{iso}}$, obtained as the difference between the dynamic reaction heat, $\Delta H_{\mathrm{din}}$ and the residual heat, $\Delta H_{\mathrm{res}}$, as function of the curing temperature for different sample masses. The most evident discrepancies are at low temperature isothermal experiments where, probably, part of the reaction heat is unrecorded by the calorimeter.

**Table 1** Activation energies obtained from Kissinger and Ozawa plots in experiments with different sample weights

| Weight / mg | Kissinger<br>$E_A$ /kJ· mol$^{-1}$ | Ozawa<br>$E_A$ /kJ· mol$^{-1}$ |
|---|---|---|
| 5 | 43.7 | 50.1 |
| 10 | 40.4 | 46.2 |
| 20 | 40.0 | 45.8 |
| 30 | 37.3 | 43.6 |
| 40 | 33.8 | 40.0 |

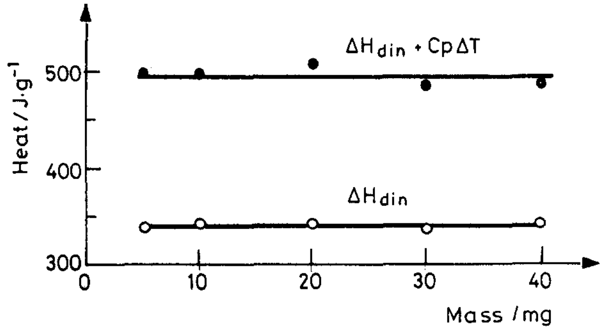

**Fig. 3** Experimental and corrected dynamic heat values for different sample weights. Heting rate: 10 deg·min$^{-1}$

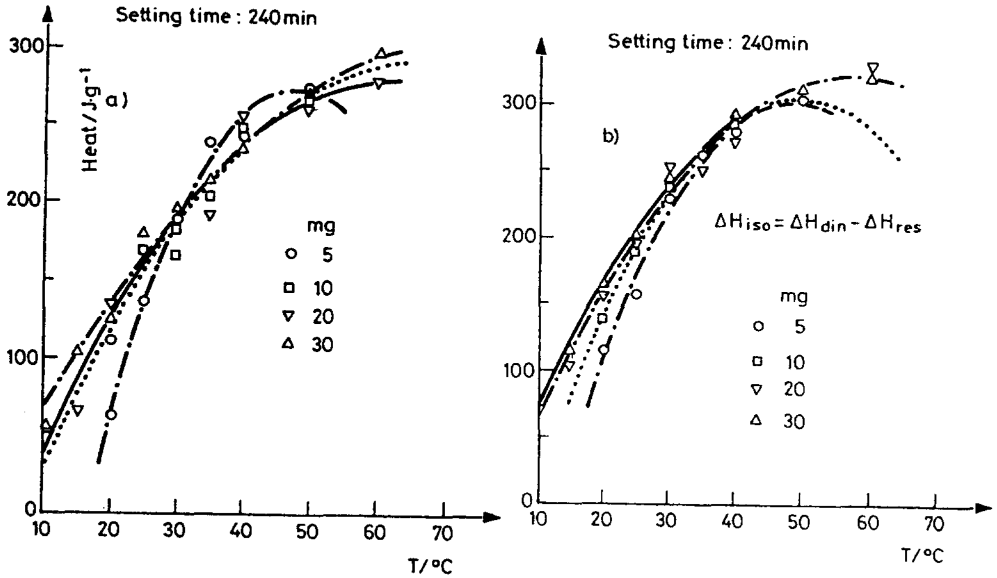

**Fig. 4a)** Experimental isothermal heat values for different sample weights. b) Isothermal heat values for different sample weights obtained from dynamic curves of the residual heat of reaction after the isothermal runs

Figure 5 shows a typical DSC run performed in order to obtain Kissinger and Ozawa plots. Figure 6 shows such plots for different sample masses. The activation energies obtained from the slope of the plots are given in Table 1. It can be seen that $E_A$ increases when the sample weight decreases. This demonstrates that the kinetics of curing is sensitive to the sample weight if the reaction involves an autocatalytic effect. The values of $E_A$ calculated from Ozawa plots are higher than those calculated by the Kissinger method.

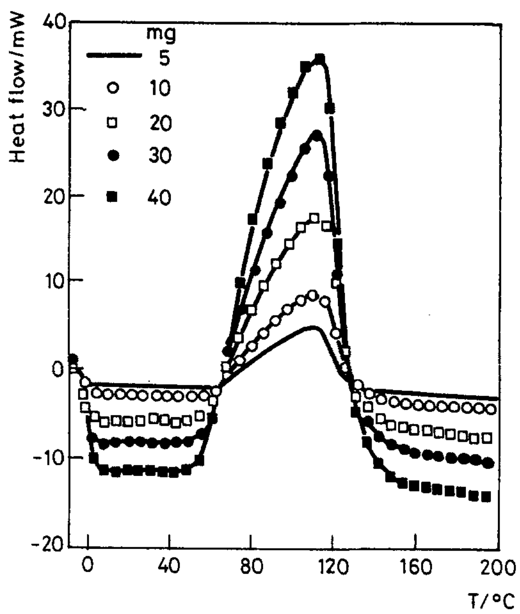

**Fig. 5** Typical dynamic DSC runs at different heating rates in order to obtain Kissinger and Ozawa plots. Heating rate: 10 deg·min$^{-1}$

A kinetic analysis has been performed also by comparing the experimental isothermal and dynamic curves with kinetic data obtained applying the $n^{th}$-order and autocatalytic models and using a multiple linear regression analysis [10, 11]. Figures 7 and 8 show some typical results. For isothermal experiments performed at different temperatures and sample masses, the agreement between experimental values and the predicted values for the autocatalytic model is very good, and it is poor when $n^{th}$-order reaction model is used. In dynamic experiments, both models fit the experimental curves, the autocatalytic model showing the better fit.

**Table 2.** Activation energies obtained from kinetics applying an autocatalytic model of isothermal curing measurements with different sample weights

| Weight /mg | $E_A$ / kJ·mol$^{-1}$ | Reaction order: $n+m$ |
|---|---|---|
| 5 | 39.5 | 2 |
| 10 | 38.87 | 2 |
| 20 | 36.86 | 2 |
| 30 | 34.1 | 2 |

Table 2 shows the activation energies obtained from kinetic data using the autocatalytic model of isothermal curing measurements with different sample weights. As it can be expected, $E_A$ increases when the sample mass decreases and the values obtained are in accordance with those obtained applying the

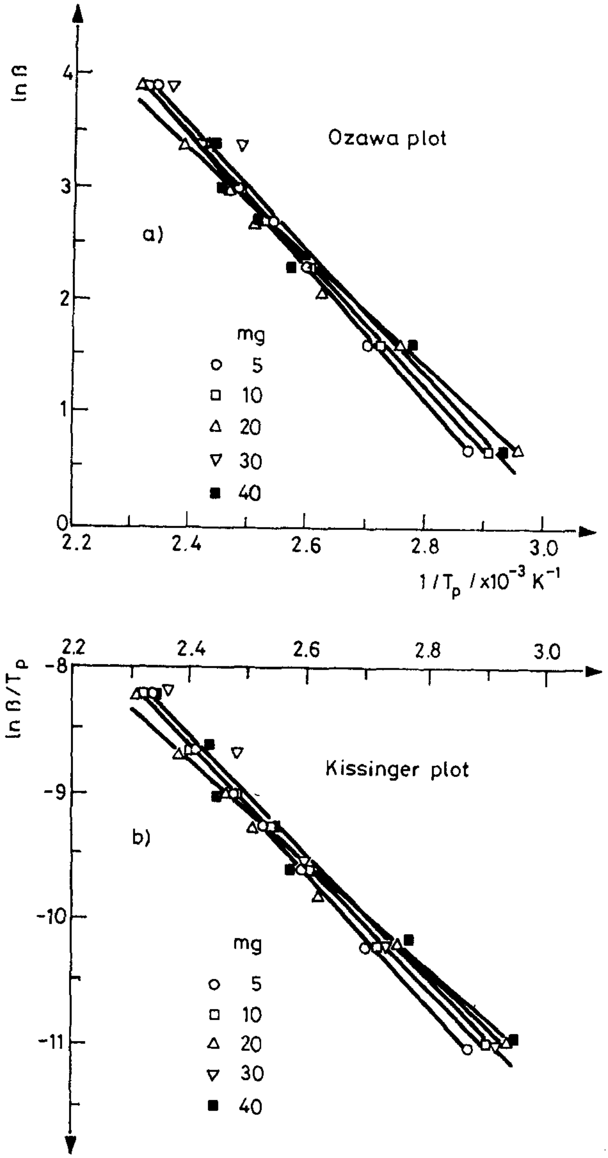

**Fig. 6** a) Kissinger plots and b) Ozawa plots of dynamic experiments with different sample weights

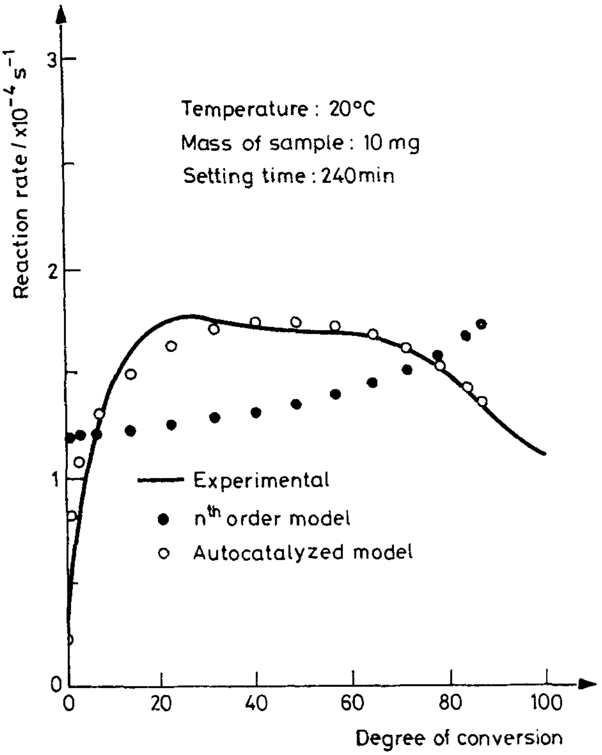

**Fig. 7** Comparison of experimental DSC isothermal values and simulated values obtained from $n^{\text{th}}$-order and autocatalytic models

Kissinger and Ozawa methods. A very different response is obtained when the activation energies are analyzed using adjusted kinetic data of dynamic experiments. As it can be seen in Table 3, the values of activation energies deduced do not reflect clearly the effect of sample weight and some of them have values impossible to relate to a real activation energy as usual.

## Conclusions

In the study of the curing process of thermoset resins, the sample mass exerts significant effect on the experimental results obtained.

In isothermal experiments, from the induction times obtained and an analysis of the activation energies it was concluded that an autocatalytic effect existed. The results obtained were found to be affected by the different DSC traces recorded with different sample masses.

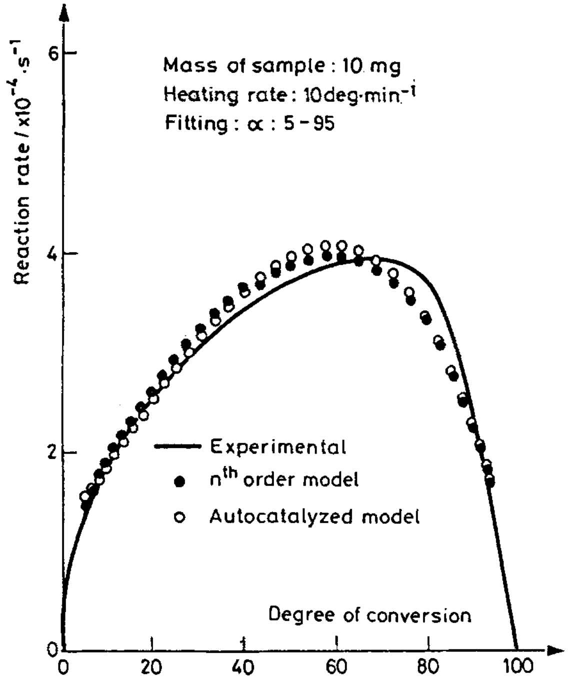

**Fig. 8** Comparison of experimental DSC dynamic values and simulated values obtained from $n^{th}$-order and autocatalytic models

**Table 3** Activation energies obtained from kinetics applying a $n^{th}$-order and an autocatalytic model of dynamic curing measurements with different sample weights

| Weight / | Heating rate / deg·min$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| mg | 2 | 5 | 10 | 15 | 20 | 30 |
| 5 | 106.1 | 66.9 | 54.2 | 45.2 | 48.3 | 48.1 |
| 10 | 94.6 | 67.0 | 46.9 | 46.3 | 44.5 | 49.1 |
| 20 | 73.0 | 56.1 | 42.4 | 44.5 | 43.4 | 51.5 |
| 30 | 82.9 | 48.2 | 46.7 | 41.2 | 45.0 | 52.5 |
| 40 | 73.8 | 51.4 | 47.4 | 43.3 | 41.3 | 46.9 |

| Weight / | Heating rate / deg·min$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| mg | 2 | 5 | 10 | 15 | 20 | 30 |
| 5 | -39.3 | 141.7 | 109.5 | 103.3 | 124.1 | 140.6 |
| 10 | -111.6 | 131.3 | 90.4 | 92.2 | 101.4 | 126.6 |
| 20 | 56.9 | 95.1 | 70.9 | 102.7 | 97.8 | 141.4 |
| 30 | -40.0 | 67.1 | 93.5 | 75.7 | 102.3 | 127.5 |
| 40 | 18.5 | 68.9 | 68.5 | 84.6 | 72.2 | 82.6 |

From dynamic experiments it may be concluded that the overall reaction heat and the reaction extent are not affected by the sample mass.

Simulated kinetic data have been used to reproduce the experimental curves. In isothermal kinetic determinations, the kinetic parameters obtained from the autocatalytic model reflect the expected effect of sample weight. In dynamic determinations, the activation energy obtained from simulated kinetic data shows a difference from typical values which cannot be accounted for.

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**Zusammenfassung** — Es ist bekannt, daß experimentelle Parameter die Peak-Charakteristik in DSC-Studien beeinflussen können. Aus isothermen und dynamischen Aufnahmen berechnete kinetische Parameter können außerdem durch die Wahl der Versuchsbedingungen beeinflußt werden.

Wegen des Wärmetransportes und den selbstisolierenden Eigenschaften von großen Probenmassen kann die Probenmasse die Bestimmung der Reaktionsparameter beeinflussen.

Beim Vernetzungsvorgang von Duroplasten wie z.B. bei der Vernetzung von ungesättigten Polyestern mit Styrol resultiert die exotherme Wärme aus dem Voranschreiten der Reaktion, es entsteht aber auch ein autokatalytischer Prozeß, der den Anstieg der Reaktionsgeschwindigkeit nach sich zieht. In derartigen Experimenten kann sich die Größe der Probenmasse nicht nur über die Beeinflussung des Wärmetransportes oder über thermische Verzögerung auf die kalorimetrischen Ergebnisse auswirken, sondern auch über jenen Einfluß der Probenmasse, den sie auf die exotherme Wärme und auf den autokatalytischen Vorgang nimmt.

Es werden hier die Ergebnisse der Untersuchung der Vernetzungskinetik von Duroplasten mittels DSC-Techniken mit unterschiedlichen Probenmassen dargestellt. Dir mittels der dynamischen Messungen ermittelte Reaktionswärme war unabhängig von der Probenmasse. Unterschiede wurden dagegen für die kinetischen Parameter gefunden, wie z.B. für Reaktionsordnung, Aktivierungsenergie, präexponentieller und Faktor.