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ARE KINETIC PARAMETERS OF NON-ISOTHERMAL THERMOGRAVIMETRIC DEGRADATION OF POLYMERS UNEQUIVOCAL?*

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Due to the complex character of the thermal degradation of polymers as a solid-gas chain reaction, an unequivocal kinetic characterization is possible only for stationary states of both radical concentration and reaction mechanism. These conditions are hardly realizable in non-isothermal thermogravimetry. Additional the weight losses are dependent on the volatility of the reaction products. That is not always certain in polymer degradation. As a consequence the deduced 'kinetic parameters' are not unequivocal. They are conversion and heating rate dependent and may be influenced by sample shape and size. Thus the 'kinetic parameters' are in fact from the point of view of mathematics the fitting parameters of a 'rate equation' like relation, specific for the used reaction conditions only. From the point of view of chemical kinetics they are neither attributable to a determined reaction mechanism nor can they be used for predictions.

Keywords: degradation of polymers, kinetic parameters, thermogravimetry

Introduction

Thermal degradation of polymers is rather a complex solid-gas reaction, occuring usual via a radicalic chain reaction. As a consequence thermal degradation of polymers shows the typical characteristics both of a solid-gas process and of a chain reaction. As a solid-gas reaction, thermal degradation of polymers will be affected by the diffusibility of the volatile reaction products out from the reaction zone and by the heat transfer through the bad conducting polymer layer into the

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reaction zone. Thus shape and size of sample and sample holder may influence decisive the thermal degradation process.

As a chain reaction, polymer degradation will show the typical elementary reaction steps of initiation, propagation, transfer and termination. Mainly the initiation reaction, as the reaction with the highest activation energy, will be affected by temperature changes because it relates to the probability of scission bonds. As a consequence at low temperatures scission will occure preferentially on weak chemical bonds. As higher the temperature as less important will be the role of weak bonds, the thermal energy being high enough to break any chemical bond, i.e. random scission will prevail.

Besides the accelerating role of oxigen on polymer degradation has to be considered. Depending on the substituents, the activation of scission of a C–C- bond will be in the absence of oxigen in the range of 250–370 kJ/mol [1].

$$P_n \xrightarrow{k_i} R_i + R_{n-i}$$

whereas in the presence of oxigen the activation energy of initiation will be of only 160–240 kJ/mol [2].

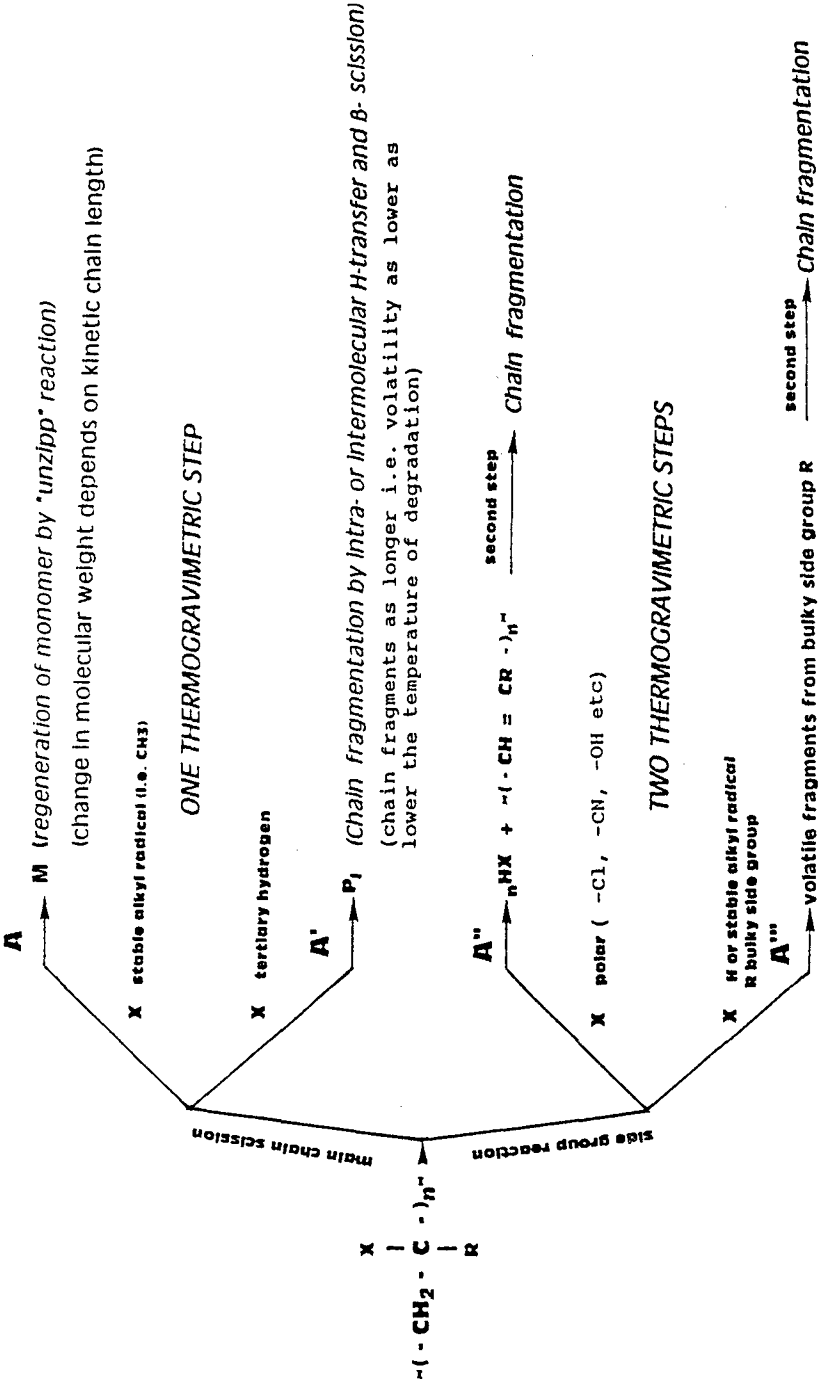
$$P_n\cdot\cdot(H) + O_2 \xrightarrow{k_i} HO_2 + R_n$$

Taking into account that the volatile reaction products will dislocate the oxygen out from the sample holder, the initiation by oxygen will be of major importance only at the beginning of the degradation reaction.

Unequivocal kinetic discussion of polymer degradation is possible only for well defined stationary states, which appear in isothermic conditions only. Supplementary in thermogravimetry of polymers the volatility of the reaction products has to be considered and it is not allowed to overlook in any kinetic analysis that rates of weight losses (i.e. of the evolution and volatilization of reaction products) are the basis of calculation.

Results and discussion

The cours of the thermal degradation of polymers depends on the chemical structure. Polymerization polymers show at least two different thermal degradation paths: main chain scission and side group reactions [3]. Correspondingly in non-isothermal thermogravimetry are observed either one weight loss step, if degradation occures by main chain scission, or two weight loss steps if degradation starts by side group reaction. The main chain will then decompose in a second step at higher temperatures. Although it is possible to formulate four limiting degradation mechanisms (see reaction scheme 1), in reality they will more or less superposed. Generally main chain fragmentation and formation of



Reaction scheme I

smaller chain fragments will be favoured by higher temperatures. Supplementary are possible curing reactions accompanied by reticulation as well as cyclizations by interaction of side groups.

Taking into account the above formulated path-ways of main chain scission, in chain fragmentation processes (*A'*) the volatility of the reaction products as well as the accompanying weight losses are as more accentuated as higher the temperature. Polyethylene, for instance, exhibits in thermogravimetry weight losses in the range of 293°–444°C, the yield in monomer being of only 0.13% [3]. Nevertheless, changes in viscosity (and thus of molecular weight) are observed starting with 123°C [4] and during thermal degradation various chain fragments are formed including such with more as 30 C-atoms [5]. These latter fragments will volatilize only above 300°C. It can thus be supposed that the longer chain fragments will first accumulate at the lower temperatures and volatilization will be observed at higher temperatures only. Thus at least besides weight loss, accompanying molecular weight measurements are recommended to appreciate thermal stability of polymers, for instance.

In depolymerization processes, on the contrary, both molecular weight changes and weight losses are dependent mainly on the chain length of the 'unzip' reaction. As longer the kinetic chain length as more intense is the weight loss and as less important are the molecular weight changes (Fig. 1).

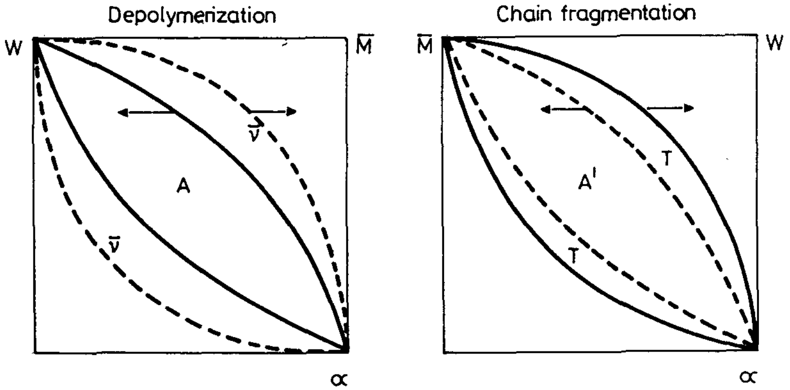


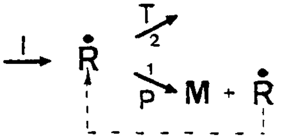
Fig. 1 Dependence of the weight, *W*, and molecular weight, *M*, on the kinetic chain length (in depolymerization, *A*) and on the temperature (in degradation by chain fragmentation, *A'*)

The thermal behaviour of polymers which degradate by side group reaction, like PVC, shows in the first thermogravimetric step rather the characteristics of a depolymerization reaction. Only in the second thermogravimetric step fragmentation of the main chain occures.

For polycondensation polymers monomer regeneration is less probable (at best for polycondensation polymers obtained by polyaddition). Thermal degradation occures thus either by main chain fragmentation or by degradation of bulky side groups, followed by the main chain fragmentation at higher temperatures.

Kinetic discussions concerning the thermal degradation of polymers deal generally with the simplest reaction mechanism only, i.e. with the isothermal depolymerization reaction [6]. But even in this case analyses are resticted to stationary states of radical concentration and depending on the nature of the initiation (chain end or random), termination (recombination or disproportionation) and the kinetic chain length, different solutions are formulated for the overall activation energy of the depolymerization process and for the molecular weight changes during conversion [7].

In non-isothermal thermogravimetry stationary states for the radical concentration are improbable. Restricting the discussion to the most simplified depolymerization process, the following reaction scheme can be formulated. It includes the elementary reaction steps of initiation (*I*), propagation (*P*) and termination (*T*).



$E_i > E_p$
$E_t \cong 0$

For this oversimplified reaction mechanism, according to Semenov [8] the following expressions can be formulated for the time dependence of the radical concentration $[R]$ and the overall reaction rate (W), the latter being expressed by the rate of monomer, M, formation.

$$d[R]/dt = W_i - (V_p + V_t)[R];\ W = d[M]/dt = V_p[R]$$

$$[R] = \{W_i/(V_p + V_t)\}[1 - \exp(-(V_p + V_t)t)]$$

$$W = W_i\{V_p/(V_p + V_t)\}[1 - \exp(-(V_p + V_t)t)]$$

W_i is the rate of initiation and V_p and V_t are the frequencies of propagation and termination. $1/(V_p + V_t)$ is the 'life time', τ, of the radicals and $V_p/(V_p + V_t)$ the 'probability of propagation'. The 'kinetic chain length', ν, is defined as the ratio of the probabilities of propagation and termination, i.e. V_p/V_t. Stationary state of radical concentration implies $t \gg \tau$, i.e. $\exp(-t/\tau) \to 0$ and it is assured by the egality of the rates of initiation and termination. For stationary state the kinetic chain length is given by the ratio of the rate of propagation and rate of initiation:

$$\nu = W_p/W_i = k_p[R]/k_i[P]$$

The time dependence of the radical concentration and of the overall reaction rate is illustrated in Fig. 2.

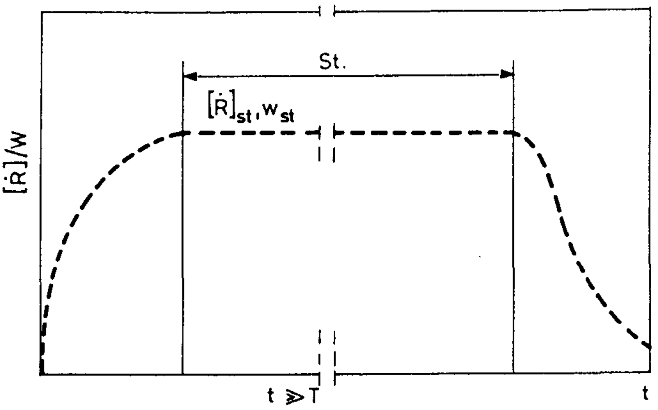


Fig. 2 Time dependence of the radical concentration, $[R]$, and of the overall reaction rate, W, in a simple chain reaction (St. St. -stationary state; τ-life time of the radicals)

Because of the different temperature dependences of the elementary steps in non-isothermal conditions, the range of stationary radical concentration (marked St.St. in Fig. 2) is limited to a point on the time scale. That means during conversion the radical concentration passes through a well defined maximum. Correspondingly the overall kinetic parameters will show a conversion dependence, even if the reaction mechanism is not changing because of the temperature increase during conversion. Thus for the evaluation of the kinetic parameters of polymer degradation in non-isothermal conditions only such methods has to be used which allow to evidence conversion dependence and it has been shown [9] that one of the most predicative methods for this respect is the method proposed by Flynn-Wall [10] and Ozawa [11], respectively. It has also been demonstrated that a conversion dependence of the kinetic parameters results always in a heating rate dependence too [12]. First references concerning the conversion dependence of the activation energy of polymer degradation in non-isothermal thermogravimetry were published 1970 [13], whereas an influence of the heating rate was observed even earlier [14]. A critique review of the problems encountered with thermogravimetry of polymers has been published in 1983 [15].

If for simple depolymerization reactions conversion and heating rate dependent kinetic parameters ar accesible, this is not more the case if during conversion changes in reaction mechanism occure. This is also valid if the volatilization of the degradation products are retarded like in polyethylene degradation [15]. In the latter cases by non of the recomended methods unequivocal evaluation is possible.

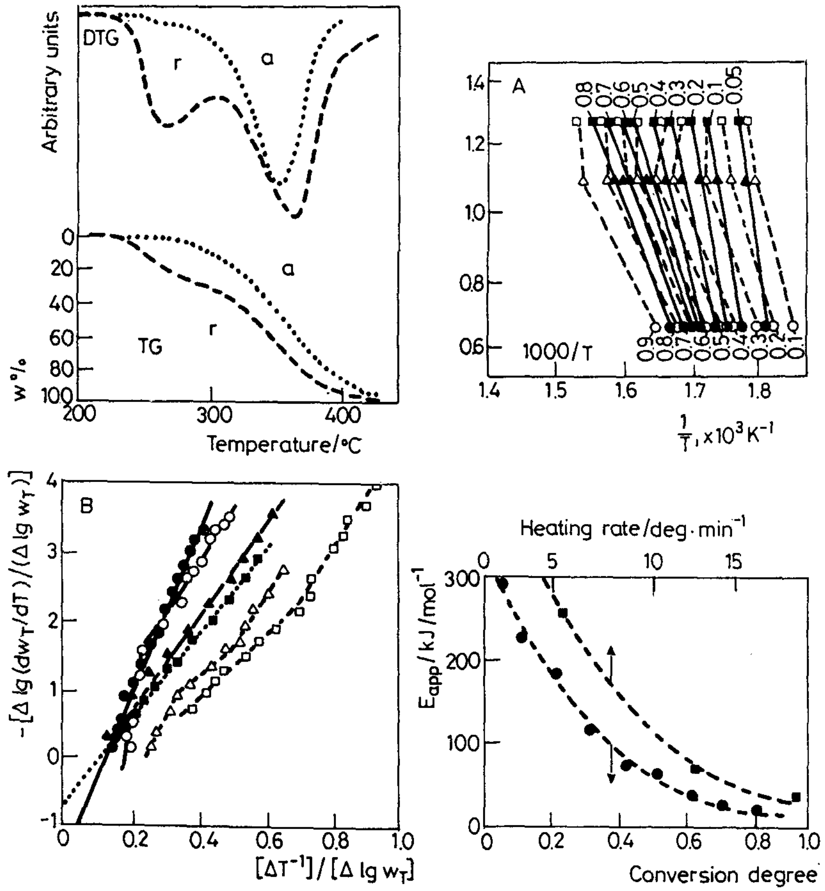


Fig. 3 TG and DTG-curves of the degradation of anionic- and radicalic-PMMA in nitrogen (sample size 2.5 mg, degradation in nitrogen, hr = 10 deg·min^{-1}) Attempts of evaluation of the activation energy of the degradation in air of a -PMMA (M_w = 93.800) – full signs – and of r-PMMA (M_w = 84.500) – open signs A. Flynn-Wall-Ozawa plot for conversion dependence (the numbers on the lines indicate the conversion degree) B. Freeman-Carroll plot for heating rate dependence (the numbers indicate the heating rate in deg·min^{-1}) C. Conversion and heating rate dependence of the apparent activation energy of the thermal degradation in air of a-PMMA in non-isothermal thermogravimetry

For illustration are shown in Fig. 3-A the respective attempts to evaluate conversion dependent kinetic parameters for the thermogravimetric degradation in air of anionic- (full signs) and radicalic-PMMA (open signs) [16]. The corresponding heating rate influence is shown by the Freeman-Carroll [17] plot in

Fig. 3-B. It is out of the question that only the data for the anionic-PMMA are unequivocal evaluable. The reason is that due to the content of end-unsaturated radicalic-PMMA molecules resulted by disproportionation beside the normal saturated molecules, a change from chain-end to random initiation will occure during the temperature increase. But even if conversion and heating rate dependent 'activation energies' are accessible, (Fig. 3-C), their attribution to a definite reaction mechanism remains always an open question.

An other fact which is always overlooked in kinetic analysis of thermogravimetric results is the non-constancy of the heating rate during conversion because of the reaction heat. Any simultaneous scaned DTA-curve confirms this affirmation and to my knowledge non of the commercial thermobalances uses the power-flux heating principle to annihilate the influence of the reaction heat. Never- theless all of the recommended methods in literature for evaluation of kinetic parameters, both differential and integral, assume constant heating rate. Using computers, however, this problem can be overcomed by solving directly the thermogravimetric rate equation in the supposition of conversion, i.e. temperature dependent kinetic parameters.

$$\mathrm{d}a/\mathrm{d}t(T) = A(T)\exp[-E(T)/RT]\ \{f[a](T)\}$$

a is the conversion degree, in thermogravimetry defined by the ratio of the weight loss at a given instant and at the end of the degradation step, i.e. $a = W_T/W_f$ and $f[a]$ the unknown conversion function. Although for solid-gas reactions various forms of conversion functions are recommended [18], mostly the very simple relation used in gas kinetics is accepted.

$$\mathrm{d}a/\mathrm{d}t(T) = A(T)\exp[-E(T)/RT]\{(1-a)^{n(T)}\}$$

This expression contains in non-isothermal conditions three temperature (i.e. conversion) dependent parameters. The 'activation energy', E, the 'preexponential factor', A, and the 'reaction order', n. The equation can thus be used mathematical to fit experimental thermogravimetric curves. In Fig. 4 are shown the results for the fit of the thermogravimetric degradation results obtained with a 20 mg sample of poly(vinyl chloride) with chlorine partially substituted by benzene (chlorine content 41.6%) [19]. The degradation in air, using a heating rate of 12.4 $\mathrm{deg \cdot min^{-1}}$ was recorded on a Derivatograph, MOM Budapest. It is interesting to observe that the DTG-curve can not be fitted by using constant 'kinetic parameters' which were computed by the last squares method (Fig. 4a). The temperature (conversion) dependence of the parameters obtained for optimal fit of the experimental TG and DTG curves is illustrated in Fig. 4b. (Experimental points were read along the curves at 1.2 K intervals). Fig. 4b suggests that the computed parameters obey the so called kinetic 'compensation effect' (Fig. 4c for the log A *vs.* E dependence). It may thus be concluded that the presented solution

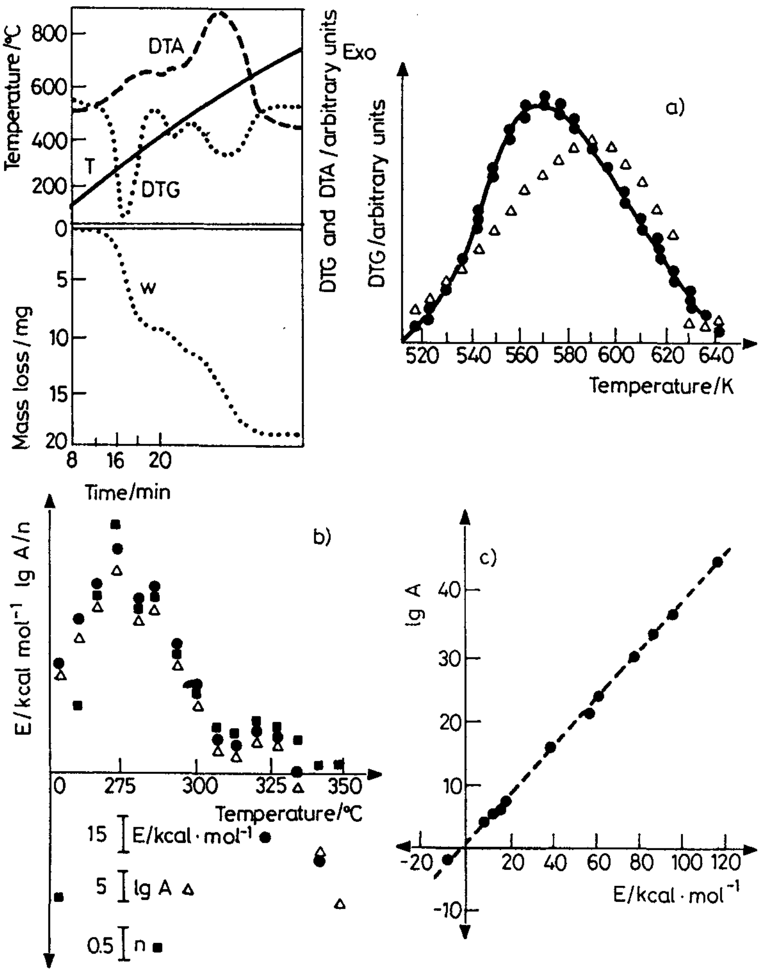


Fig. 4 Thermogravimetric degradation of PVC with chlorine partially substituted by benzene (20 mg sample, degradation in air at 12.4 deg·min^{-1}) a. Fit of the experimental DTG-curve (full line) by using constant – open signs – and temperature dependent kinetic parameters – full signs b. Temperature (conversion) dependence of the kinetic parameters c. log *A* *vs.* *E* plot ('kinetic compensation effect')

is mathematical not unique and other sets of parameters can also be used. Similar conversion dependences were observed in other thermogravimetric studies on polymer degradation, and one of the recent published papers deals with the thermogravimetric degradation of linear polyethylene in air [20].

It is evident that the set of the obtained 'kinetic parameters' verify the weight loss data for the given conditions of the thermogravimetric study but they have no 'kinetic' background. They can thus be used neither for elucidation of the reaction mechanism, nor for predicting the thermal behaviour of the polymer in both isothermic and other non-isothermic conditions. As a consequence these 'kinetic parameters' are fictive from the point of view of chemical kinetics.

Conclusions

Due to the complex character of the polymer degradation processes in non-isothermal thermogravimetry the computed 'kinetic parameters' are valid for the weight loss in the used conditions only and they are neither related to the reaction mechanism, nor can they be used for predicting the course of the reaction in other conditions. Thus the so called 'kinetic parameters' are in fact only parameters of a given mathematic equation which has the form of a kinetic 'rate equation' and which is used to fit the weight loss curves accompanying the thermal degradation of polymers in non-isothermal conditions.

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Zusammenfassung — Wegen des komplexen Charakters des thermischen Abbaues von Polymeren als eine Feststoff-Gas-Kettenreaktion ist eine eindeutige kinetische Beschreibung nur für den stationären Zustand von Radikalkonzentration und auch Reaktionsmechanismus möglich. Diese Bedingungen können bei der nichtisothermen Thermogravimetrie nur schwerlich erfüllt werden. Hinzu kommt, daß die Massenverluste von der Flüchtigkeit der Reaktionsprodukte abhängig sind. Dies ist beim Polymerabbau nicht immer der Fall. Als Folge davon sind die hergeleiteten "kinetischen Parameter" nicht eindeutig. Sie sind abhängig von Konversion und Aufheizgeschwindigkeit und können durch Probenform und -größe beeinflußt werden. Somit sind die "kinetischen Parameter" aus mathematischer Sicht her eigentlich die Fitting-Parameter einer nur für die verwendeten Reaktionsbedingungen spezifischen Gleichung, die der Geschwindigkeitsgleichung ähnelt. Aus Sicht der chemischen Kinetik her können sie weder einem bestimmten Reaktionsmechanismus zugeschrieben, noch für Prognosen verwendet werden.