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THE BASIC PROCESSES OF DEPOLYMERIZATION AND ITS REAL KINETIC ANALYSIS

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Abstract

The method of computer-experiments can be applied successfully on the radical depolymerization under inclusion of initiation, depropagation and termination. The comfortable PC-program 'TA-kin' for the non-linear estimation of parameters for TG- or DSC-experiments was applied to the determination of activation parameters of depropagation and termination. Therefore the overall- evaluation of three or more data sets is a prerequisite. The determination of kinetic parameters runs satisfactory if the measured curves are strongly different, e.g. by varying the heating rate, including acceptable experimental errors. Several recommendations for laboratory experts are given. A great support for a very sufficient estimation is the inclusion of simultaneous analysis of the radical concentration.

Keywords: depolymerization, kinetics

Introduction

In last time considerable effort has been spent to improve the kinetic analysis of thermoanalytical data [1–4]. Both the development of careful selected kinetic models by using corresponding formulated complex systems of differential rate equations and the increased accuracy of the acquirement of experimental data have contributed to an improvement of the precision of kinetic analysis of complex thermoanalytical processes. Although actual procedures of the estimation of overall kinetic parameters still assume the validity of the Arrhenius equation, the use of the related linear evaluation programs is not further justifiable taking into account the experimental TG results of complex reaction. Thus applying the well-known linear evaluation programs for the estimation of the overall kinetic parameters of complex depolymerization processes, both heating rate and conversion dependencies were observed [5]. The authors of the paper have gained meanwhile promising experiences in the development and application of non-linear fitting programs for evaluation of kinetic parameters, realising that the use of non-linear programs on principle can increase the reliability of ki-

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netic estimation. During a recently closed international comparison of 12 laboratories the utility of non-linear fitting programs for kinetic evaluation has been proved for more than 600 experimental data sets and it resulted that an improvement of the mathematical procedures necessarily requires at the same time an increased accuracy of the acquisition of experimental TA data too [6].

Taking into account the multitude of experiences and the promising results obtained during computer studies of complex chemical reactions comprising two, three or even four elementary processes [7], in the present paper an extension of these non-linear programs for polymer degradation processes is attempted, first for the most simple depolymerization by radical chain reaction accompanied by the regeneration of monomer. Typical examples are the thermal degradation of poly(methylmethacrylate) - PMMA [8]-, poly(α-methyl-styrene) [9] - PαMS - and poly(formaldehyde) i.e. poly(oxymethylene) - POM - [10].

The kinetic description of the radicalic depolymerization

Neglecting possible radical transfer reactions and assuming both a regular structure of the polymer molecules and equal reactivity for radicals irrespective of their size the depolymerization involves the following three elementary reactions:

- Thermal initiation by random scission of a C–C bond of the polymer backbone, P_n, accompanied by formation of free radicals, R^*
- Depolymerization with regeneration of monomer molecules by a zip-like chain mechanism

$$P_n \rightarrow R^*_{n-i} + R^*_i \tag{1}$$

$$R^*_i \rightarrow M + R^*_{i-1} \tag{2}$$

As long as the radical R^*_i contains more than 1 repeating unit, the overall radical concentration will be not affected by the depolymerization zip. It is assumed that radicals containing a single repeating unit, R^*_1, disappear like the monomer molecule by volatilization.

- Termination

– either of second order, by recombination (disproportionation) of radicals, accompanied by the regeneration of polymer molecules

$$R^*_i + R^*_k \rightarrow P_{i+k} \tag{3}$$

– or of first order

$$R^*_i + Ih \rightarrow P_i \tag{3a}$$

Ih being any homogenous or heterogeneous (reactor wall, for instance) acting radical trapping agent.

The kinetic description of the above complex depolymerization model applies for each individual reaction step a simplified approach for the differential rate equations, with α the dimensionless conversion degree of the reaction ($0 \leq \alpha \leq 1$).

$$\dot{\alpha} = k(T)f(\alpha) \tag{4}$$

It is supposed that the temperature dependence of the rate constants of each elementary reactions of the complex process, $k_j(T)$, obey the Arrhenius law

$$K_j(T) = K_{o,j} \exp\left(-\frac{E_{A,j}}{RT}\right) \tag{5}$$

For expressing the differential rate equations of the complex reaction system instead of the conversion degree, α, dimensionless concentrations of the participants are used, e.g. for a simple reaction $c^{red} = 1 - \alpha$.

In a first approximation the conversion functions $f(\alpha)$ of all elementary reactions of the complex depolymerization process are assumed to be of first order, i.e.

$$f(\alpha) = (1 - \alpha) = c^{red} \tag{6}$$

Accordingly to the above formulated reaction sequences (1–3) the complex depolymerization process can be described by the following system of differential rate equations (DRE):

$$\frac{d[P]^{red}}{dt} = -k_1(T)f_1([P]^{red}) + k_T(T)f_T([R^*]^{red})$$

$$\frac{d[R^*]^{red}}{dt} = k_1(T)f_1([P]^{red}) - k_T(T)f_T([R^*]^{red}) - \frac{k_p(T)}{N} f_P([R^*]^{red}) \tag{7}$$

$$\frac{d[M]^{red}}{dt} = \frac{k_P(T)}{N} f_P([R^*]^{red})$$

The last term in the rate equation for radicals, $d[R^*]^{red}/dt$, i.e. $-1/Nk_p(T)f_p([R^*]^{red})$, accounts for the volatilization of the low molecular radicals, R_1^*. As stated above, for simplification first order is assumed for termination too.

For the evaluation of the kinetic parameters of complex chemical reactions investigated by calorimetry and mainly by thermal analytical methods (thermogravimetry, TG and differential scanning calorimetry, DSC) the TA-kin-program in Turbo-Pascal was developed. The numerical integration of the above complex DRE-system was realized by an adaptive fifth order Runge-Kutta type procedure [11]. For the estimation of the kinetic parameters of the above formulated DRE-system the iterative last square minimization algorithm of Marquardt and Levenberg was used [12].

The developed TA-kin program offers for the user the possibility of simultaneous evaluation of experimental data sets obtained by different methods of investigation, as well as for different experimental conditions. The direct estimation of the kinetic parameters for the presumed model DRE-systems by non-linear methods has two essential advantages in comparison to the linear programs.

– Both non or partially linearizable complex DRE-systems can be used for estimation of kinetic parameters.

– The use of linear evaluation programs for non-linear processes is always accompanied by distortions of some particular ranges of the conversion curves. This is not observed with the non-linear programs.

The simulation of experimental probably depolymerization processes

More than 350 computer experiments on depolymerization were performed to be able for appreciating the usefulness of the TA-kin program and in the following several representative results will be presented.

Our efforts of estimating kinetic parameters of the complex depolymerization process presuming the relatively reliable knowledge of the reaction mechanism. The commonly accepted elementary reaction steps (1–3) of the de-

Table 1 Activation parameters of initiation, recombination and degradation for simulations of depolymerization according to Eq. (7)

Row	$\ln(k_{0,I}/s^{-1})$	$E_{A,I}$/ kJ mol^{-1}	$\ln(k_{0,T}/s^{-1})$	$E_{A,T}$/ kJ mol^{-1}	$\ln(k_{0,P}/s^{-1})$	$E_{A,P}$/ kJ mol^{-1}
1						110
2	35	200	20	120	20	120
3						130
4						110
5	35	180	20	120	20	120
6						130
7						110
8	35	220	20	120	20	120
9						130

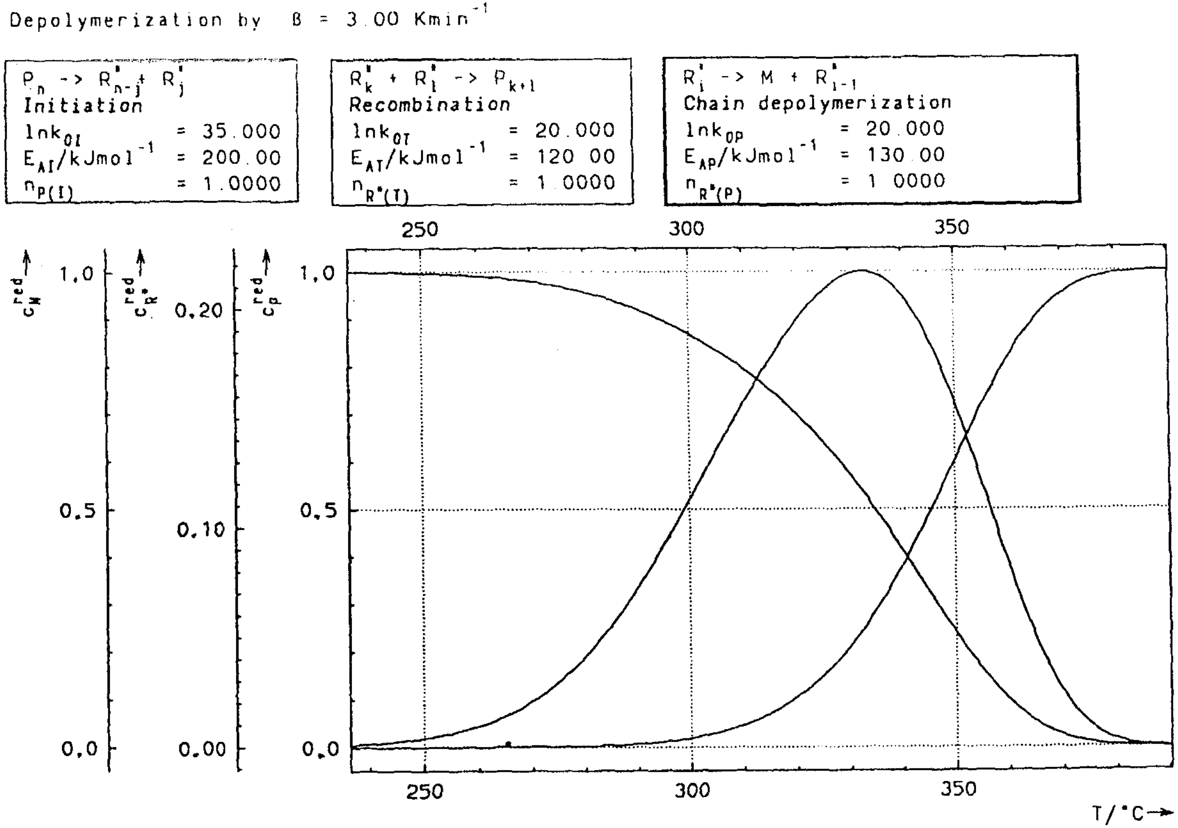

Fig. 1 Simulation of DRE-System (7), using kinetic parameters of the third row in Table 1 with reduced concentrations of monomer, radical and polymer; β=3 K min^{-1}

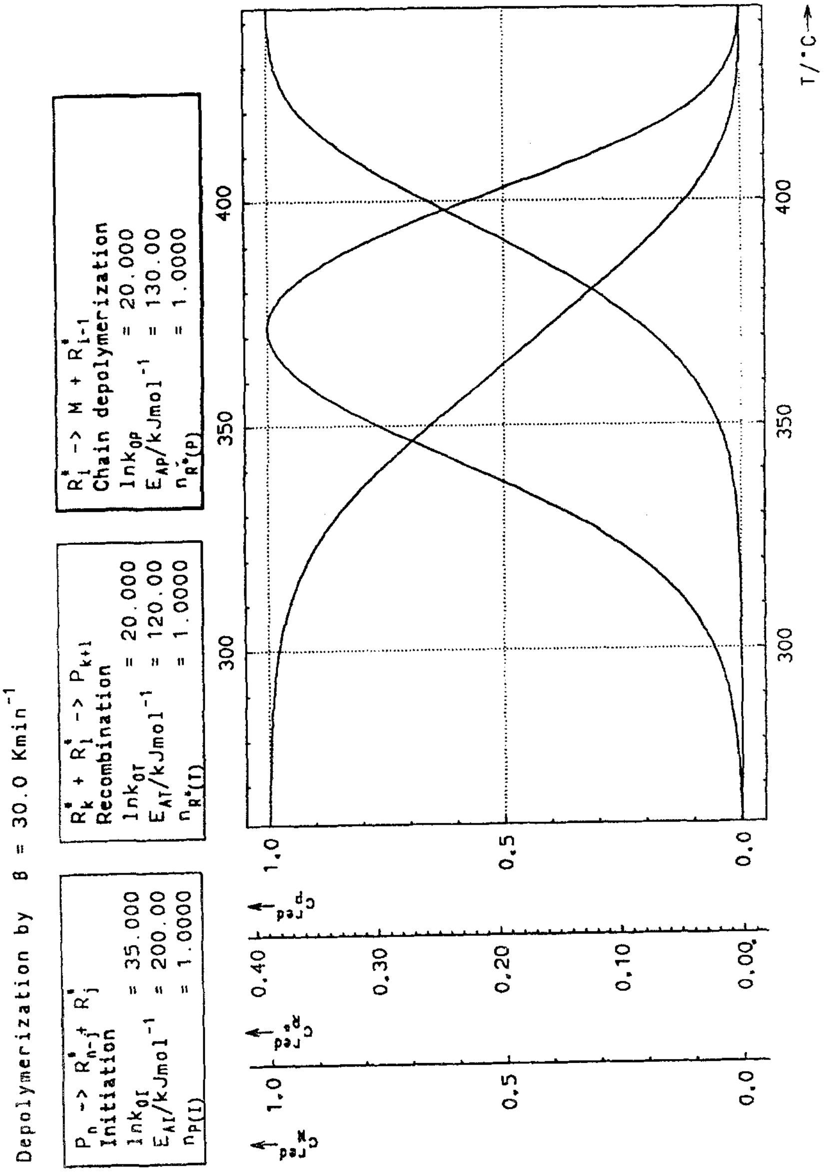

Fig. 2 Simulation of DRE-System (7), using kinetic parameters of the third row in Table 1, β=30 K min^{-1}

polymerization mechanism are used as starting point for a first simulation of the experimentally to be expected TG curves. Based on literature data [13] the kinetic parameters shown in Table 1 (rows 1–9) were used for simulation of the TG conversion curves, The assumed possibly variations of the activation energies of initiation, $E_{A,I}$ and propagation, $E_{A,P}$ reflect at the same time the uncertainties concerning the reported literature data.

Using the kinetic parameters shown in row 3 of Table 1, the kinetic curves presented in Figs 1 and 2 were obtained by using the version 2.05 of the TA-kin program. The conversion curves for the reduced concentrations of the polymer, $[P]^{red}$, monomer $[M]^{red}$ and the radicals, $[R^*]^{red}$ for two different heating rates, 3 K min^{-1} (Fig.1) and 30 K min^{-1} (Fig.2), respectively, are shown in the figures. Beside a shift of the simulated curves to higher temperatures by increasing the heating rate, a twofold increase of the maximal radical concentration is observed. The time of simulation by using an up-to-date PC is of about 3/4 sec for the TA-kin program.

At this point one of the possibilities to improve the fit of experimental data could be a stepwise modification of the kinetic parameters until the simulated TG curves superposes with sufficient exactness the experimental ones. This procedure has by our opinion, however, at least two basic disadvantages. On the one hand the procedure is extremely time spending and on the other hand there is no possibility to confirm the unambiguity of the finally obtained kinetic parameters, because the same acceptable fit of any experimental TG curve, in principle, can be realized by using a multitude of kinetic parameter sets.

Thus, only the exact knowledge that the studied process in fact is a simple chemical reaction would justify a certainly fit of single experimental conversion curves and the estimation of reliable kinetic parameters.

Kinetic evaluation of depolymerization processes

The evaluation of the kinetic parameters of the individual elementary reactions of a complex depolymerization process has been performed almost exclusively for non ideal conditions, i.e. every assembly of simulated conversion curves was provided with a certain experimental error, which probably is encountered during measurements.

The values presented in row l, Table 2 were used as the starting point for the evaluation of simulated curves, which are not provided with possible experimental errors. The apparent success of the data obtained by TA-kin is, however, for the user of no significance.

All other computer tests presented in Table 2 were executed assuming for the simulated curves an usual scatter of the data, characterized by a standard deviation of 0.005. In Table 2 there are results illustrated of two different modalities of evaluation. The groups 14–16 use for estimation of the kinetic parameters the

Table 2 Determination of parameters of recombination and degradation from computed data sets of concentratiion of monomer c_M and radicals c_{R*}, respectively. The data were loaded with a normal scatter of error ($\sigma=0.005$). The groups 1–13 are overall estimations for heating rates of 3, 10, 20 and 30 K min^{-1} (groups 5–7 without 30 K min^{-1})

Simulation				Parameter estimation			
Group	Data/comments	$E_{A,I}$/kJ mol^{-1}	$E_{A,P}$/kJ mol^{-1}	ln$k_{0,T}$/s^{-1}	$E_{A,T}$/kJ mol^{-1}	ln$k_{0,P}$/s^{-1}	$E_{A,P}$/kJ mol^{-1}
1	$c_M/\sigma=0$	200	120	20.0±4E-13	120±2E-12	20.0±2E-13	120.0±1E-12
2	c_M	200	110	18.4±2.2	112±11	18.9±1.2	104.8±6.1
3	c_M		120	20.3±1.2	121.6±6.1	20.27±0.72	121.3±3.6
4	c_M		130	20.11±0.66	120.3±3.5	19.92±0.38	129.4±2.1
5	c_M+c_{P*}		110	19.3±1.3	116.7±6.4	20.04±0.69	110.2±3.4
6	c_M+c_{P*}		120	19.67±0.32	118.4±1.6	19.85±0.19	119.23±0.96
7	c_M+c_{P*}		130	20.00±0.13	120.00±0.66	19.940±0.085	129.69±0.45
8	c_M	180	110	19.3±3.8	117±17	20.02±0.34	110.1±1.5
9	c_M		120	21.7±3.3	128±15	20.18±0.23	120.9±1.1
10	c_M		130	22.2±3.4	128±14	19.74±0.29	128.5±1.7
11	c_M	220	110	17±11	104±58	18±10	96±55
12	c_M		120	19.3±3.9	116±21	19.2±3.6	116±20
13	c_M		130	19.9±2.2	120±13	20.0±2.0	130±12
Evaluations of single data sets applying simple process models							
14	Fn[1]	200	130	–	–	34.73±0.51	211.7±2.6
15	D3			–	–	57.2±1.0	345.5±5.4
16	D4			–	–	51.3±1.3	315.5±7.1

[1] $n=1.226\pm0.027$

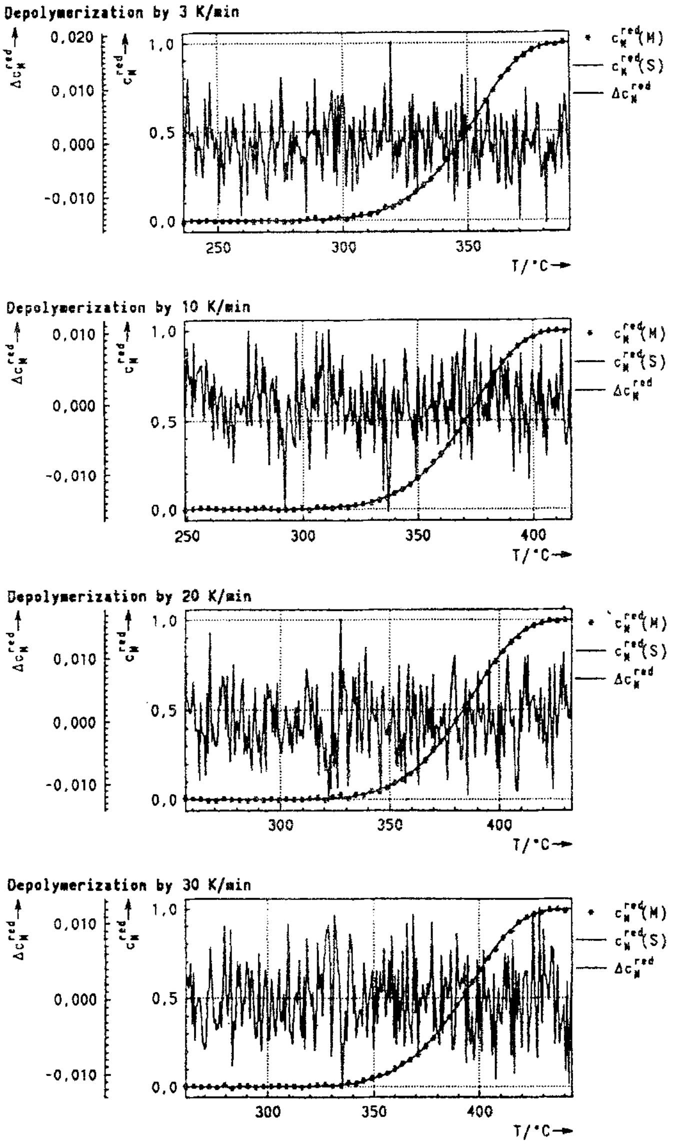

Fig. 3 Global evaluation of 1000 data points distributed over four data sets of reduced monomer concentration; see also fourth group in Table 2; (M) ... 'measured' data, (S) ... simulated data, Δ... difference between (M) and (S)

Least squares minimization by Marquardt and Levenberg

Estimated Parameters	3	Starting values	
$\ln k_{0T}$	= 20.11 ± 0.66	$\ln k_{0T}$	= 20.00000
E_{AT}/kJmol^{-1}	= 120.3 ± 3.5	E_{AT}/kJmol^{-1}	= 120.0000
$\ln k_{0P}$	= 19.92 ± 0.38	$\ln k_{0P}$	= 20.00000
E_{AP}/kJmol^{-1}	= 129.4 ± 2.1	E_{AP}/kJmol^{-1}	= 130.0000
Normalized SDS	= 2.6468E-05	Normalized SDS	= 2.6567E-05

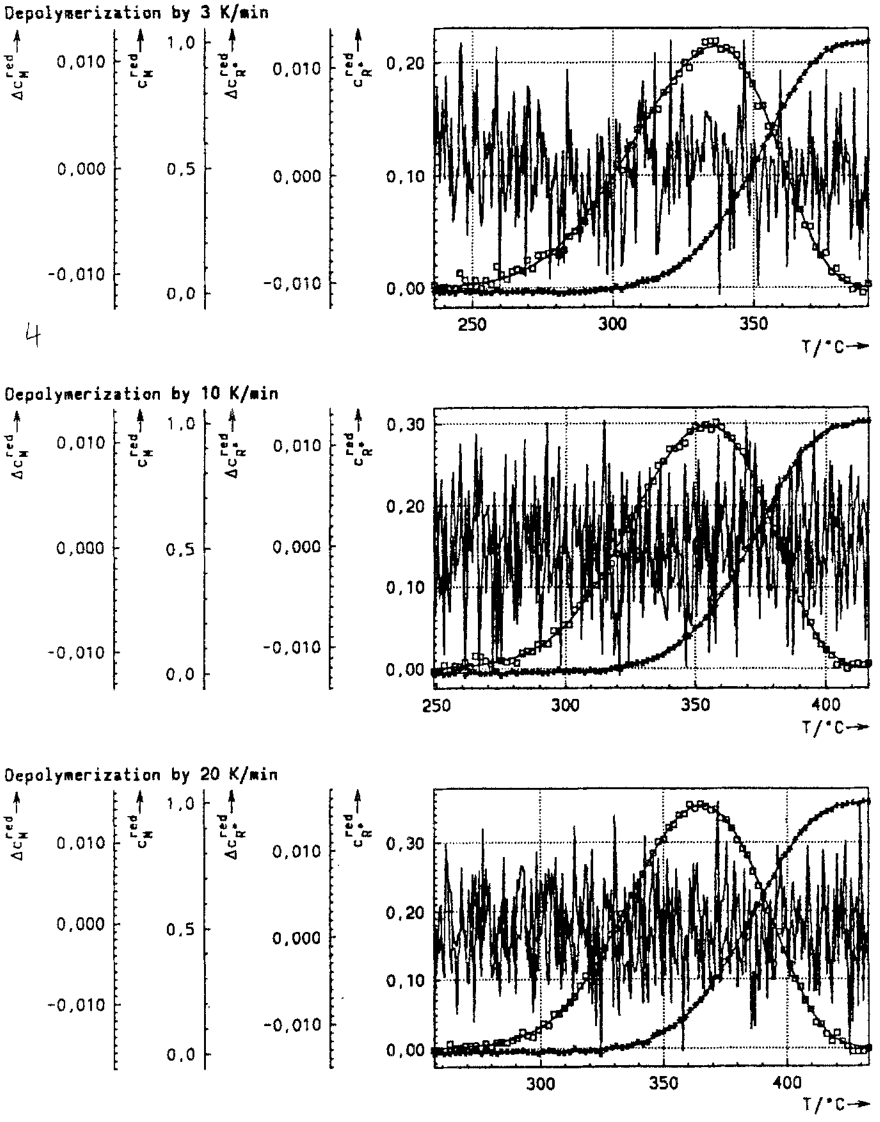

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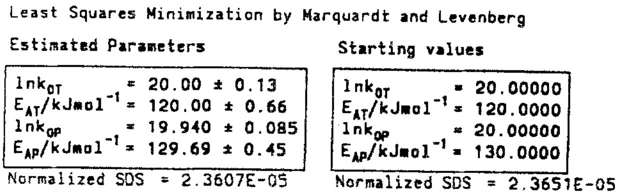
Fig. 4 Global evaluation of 1000 data points distributed over four data sets of reduced monomer concentration; see also seventh group in Table 2



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Least Squares Minimization by Marquardt and Levenberg
Estimated Parameters                  Starting values
lnk_OT          =  20.00 ± 0.13        lnk_OT          =  20.00000
E_AT/kJmol^-1   = 120.00 ± 0.66        E_AT/kJmol^-1   = 120.0000
lnk_OP          =  19.940 ± 0.085      lnk_OP          =  20.00000
E_AP/kJmol^-1   = 129.69 ± 0.45        E_AP/kJmol^-1   = 130.0000
Normalized SDS  = 2.3607E-05           Normalized SDS  = 2.3651E-05
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data of a single conversion curve, the other use data sets of several conversion curves obtained at different heating rates.

The data presented in groups 2–4, Table 2 refer to the estimation of the kinetic parameters of computed curves, using the same parameters as shown in row 1–3, Table 1 without systematic errors, but multiple heating rate conversion data sets (i.e. for heating rate β =3, 10, 20 and 30 K min^{-1}, respectively). The results of the simulated fit by using the TA-kin program were realized assuming given values of $E_{A,I}$ and $\ln k_{0,I}$. For the kinetic parameters of recombination there were obtained satisfactory and for propagation acceptable results. Generally, the results are substantially improved by using multiple independent data sets and mainly the parameters presented in group 4 can be considered as very satisfactory (see also Fig.3), taking into account the difficulties of the kinetic problem to be solved. An additional improvement of the estimated kinetic parameters can be achieved if beside TG weight loss data used for the estimation of the monomer conversion, are employed simultaneously scanned ESR data for the evaluation of the radical concentration, $[R^{*}]$. This is confirmed by the data shown in groups 5–7, Table 2 and Fig. 4, respectively.

The next step of simulation attempted to appreciate the effect of uncertain starting parameters. First the influence of the rapidity of initiation was studied. Accordingly for the beginning the rate of initiation was increased by reducing the activation energy, $E_{A,I}$ from 200 to 180 kJ mol^{-1} (results see groups 8–10, Table 2). Considerable difficulties are encountered in the estimation of the respective activation parameters of recombination (the confidence interval being much too large). The increase of the radical concentration is so large, that no additional influence by increasing the heating rate from 3 to 30 K min^{-1} is observed.

The influence of a decreased rate of initiation (by increasing $E_{A,I}=$ 220 kJ mol^{-1}) is shown in groups 11–13, Table 2. Even if (except of group 11) acceptable kinetic parameters are the result, the confidence interval of the obtained values for all elementary steps is again excessively large.

The only recommendation for obtaining improved kinetic parameters by estimating multiple heating rate TG curves is thus to improve the accuracy of experimental data. Finally the parameters presented in groups 14–16, Table 2 were obtained, as usual in TA-kinetics, by applying simple kinetic models, e.g. a single diffusion controlled DRE for the complex depolymerization process for single heating rate conversion curve (β=3 K min^{-1}), because the evaluation of multiple heating rate curves was at all disappointing. The position 14 shows the results of assessment obtained by assuming that the process can be described by a simple chemical reaction of order *n* (*Fn*). The obtained kinetic parameters, although of acceptable confidence, are valid for the given heating rate conversion curve only. The results presented in the last two groups in Table 2, were obtained by using the diffusion models of Jander D3 [14] and Ginstling and

Table 3 Estimation of parameters of recombination and degradation from computed data sets of concentration of monomer c_M and radicals c_{R^*} respectively, $\sigma = 0.005$, and additionally systematic errors. The overall estimation used heating rates of 3, 10 and 20 K min^{-1}, 30 K min^{-1} was included if only the concentration of monomer is known

Group	Simultaion			Parameter estimation			
	Systematic error	Data	$E_{A,P}$/kJ mol^{-1}	$\ln k_{0,T}/s^{-1}$	$E_{A,T}$/kJ mol^{-1}	$\ln k_{0,P}/s^{-1}$	$E_{A,P}$/kJ mol^{-1}
1	$\frac{dm}{dT} = +1$ μg/K^{-1}	c_M	110	23.4±1.8	137.9±8.7	22.97±0.97	125.7±4.8
2			120	24.0±1.2	141.2±5.8	22.88±0.65	135.2±3.2
3			130	19.26±0.80	119.3±4.1	21.77±0.32	140.8±1.8
4		$c_M+c_{P^*}$	110	20.7±1.2	123.6±6.1	21.54±0.66	117.4±3.3
5			120	20.05±0.34	120.2±1.7	20.50±0.20	122.6±1.0
6			130	20.12±0.15	120.59±0.78	20.36±0.10	131.92±0.53
7	$\Delta T = +2$ K	c_M	110	18.3±1.8	109.0±8.9	20.3±1.3	112.6±6.3
8			120	19.3±1.2	116.4±6.1	20.33±0.69	122.7±3.5
9			130	19.86±0.67	120.2±3.5	20.83±0.35	135.5±1.9
10		$c_M+c_{P^*}$	110	18.42±0.93	108.5±4.6	19.90±0.68	109.9±3.4
11			120	19.00±0.30	114.0±1.5	19.93±0.19	120.08±0.99
12			130	19.22±0.14	115.58±0.72	20.074±0.095	130.80±0.50
13	$\Delta T = +4$ K	c_M	110	19.9±1.7	115.6±8.2	21.7±1.3	120.7±6.3
14			120	20.7±1.2	123.8±6.0	21.76±0.67	131.1±3.4
15			130	19.33±0.62	118.2±3.2	21.43±0.31	139.6±1.8
16		$c_M+c_{P^*}$	110	17.04±0.90	99.5±4.5	19.69±0.74	109.1±3.7
17			120	17.98±0.33	108.1±1.7	19.76±0.22	119.6±1.1
18			130	18.74±0.16	112.70±0.80	19.95±0.11	130.54±0.57

Table 3 Continued

Group	Simulation			Parameter estimation			
	Systematic error	Data	$E_{A,P}$/kJ mol^{-1}	ln$k_{0,T}$/s^{-1}	$E_{A,T}$/kJ mol^{-1}	ln$k_{0,P}$/s^{-1}	$E_{A,P}$/kJ mol^{-1}
19			110	19.1±1.7	110.4±8.7	21.9±1.4	123.7±6.9
20		c_M	120	20.1±1.2	121.7±6.0	22.87±0.61	139.0±3.1
21	ΔT = +8 K		130	19.48±0.79	121.3±4.0	23.55±0.30	153.0±1.7
22			110	17.30±0.88	98.2±4.4	19.92±0.78	111.1±3.9
23		c_M+c_{P*}	120	16.34±0.39	98.3±2.0	19.39±0.28	118.5±1.5
24			130	17.50±0.20	105.5±1.0	19.90±0.15	131.14±0.78

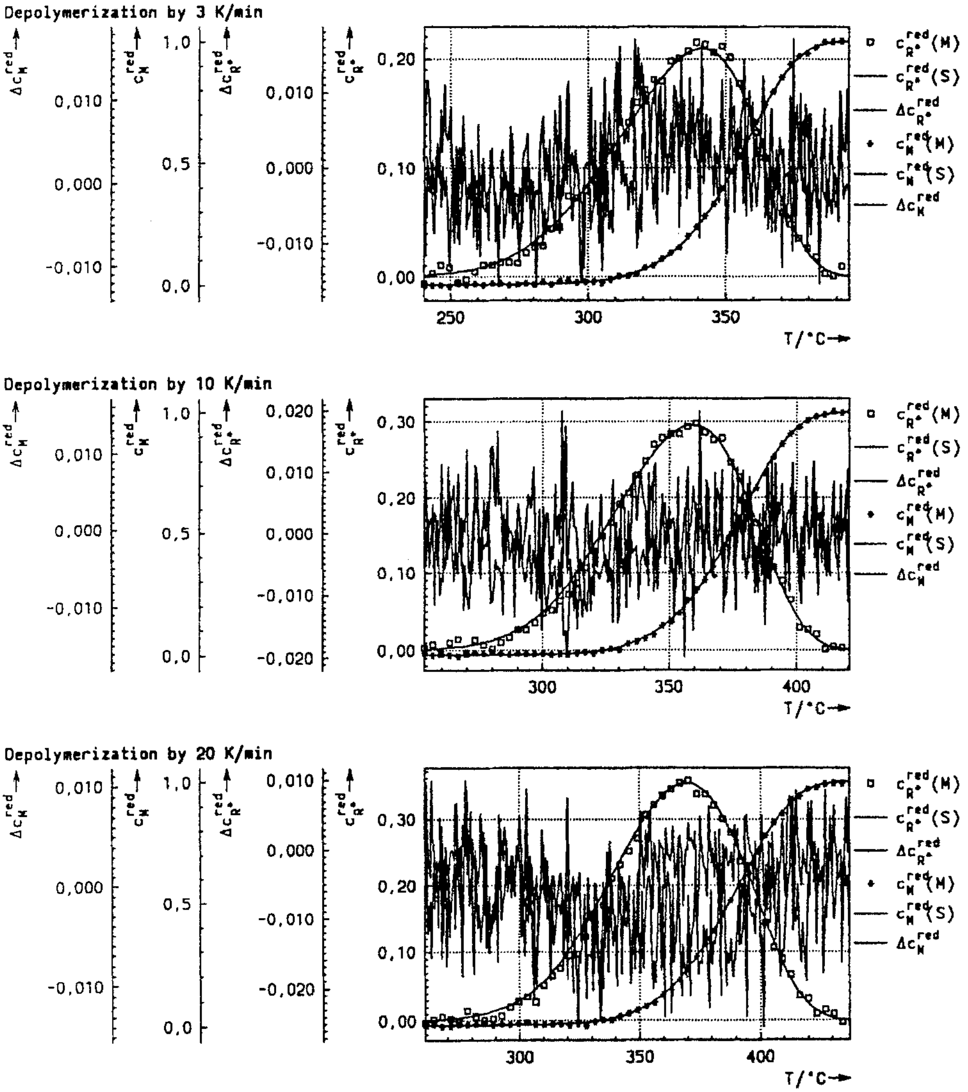

Fig. 5 Global evaluation of 1000 data points distxibuted over three data sets of reduced monomer concentration and of reduced radical concentration; see also 18th group in Table 3 (M) … 'measured' data, (S) … simulated data, Δ … difference between (M) and (S)

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Least squares minimization by Marquardt and Levenberg

Estimated Parameters                  Starting values

lnkOT           = 18.74 ± 0.16        lnkOT           = 20.00000
EAT/kJmol-1     = 112.70 ± 0.80       EAT/kJmol-1     = 120.0000
lnkOP           = 19.95 ± 0.11        lnkOP           = 20.00000
EAP/kJmol-1     = 130.54 ± 0.57       EAP/kJmol-1     = 130.0000
Normalized SDS  = 3.9299E-05          Normalized SDS  = 0.00088618
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Table 4 The influence of the number of included data sets with different heating rates on the estimation of parameters. The total amount of measured pairs is fixed on 1000, σ=0.005

Group	Simulation		Parameter estimation			
	$E_{A,P}$/kJ mol^{-1}	β/K min^{-1}	ln$k_{0,T}$/s^{-1}	$E_{A,T}$/kJ mol^{-1}	ln$k_{0,P}$/s^{-1}	$E_{A,P}$/kJ mol^{-1}
1	110	3	20.2±3.9	123±16	17.3±7.8	98±35
2		3/10	20.1±2.5	120±12	20.5±1.6	112.4±7.9
3		3/10/20	19.6±2.2	118±11	19.6±1.3	108.4±6.6
4		3/10/20/30	20.6±2.1	123±10	20.4±1.3	111.8±6.2
5		3/10/20/30/50	20.0±2.0	119.6±9.7	19.7±1.1	108.5±5.5
6	120	3	24.0±3.4	139±15	23.7±3.3	137.±15
7		3/10	21.6±1.4	127.8±6.9	20.99±0.91	124.9±4.5
8		3/10/20	20.3±1.4	121.7±6.7	20.15±0.82	120.7±4.1
9		3/10/20/30	19.4±1.2	116.9±6.0	19.59±0.70	117.9±3.5
10		3/10/20/30/50	20.12±0.98	120.6±5.0	20.11±0.54	120.5±2.8
11	130	3	19.9±2.3	120±12	20.0±1.5	130.1±7.7
12		3/10	20.1±1.1	120.8±5.6	20.17±0.65	131.0±3.5
13		3/10/20	19.83±0.78	119.2±4.0	19.95±0.45	129.8±2.5
14		3/10/20/30	20.63±0.68	123.5±3.5	20.42±0.37	123.3±2.0
15		3/10/20/30/50	20.22±0.56	121.3±2.9	20.13±0.30	130.7±1.7

Brounshtein D4 [15], respectively. The parameters obtained show, however, no connection to the real occurring depolymerization process.

A next aspect analyzed by computer simulation tests was the investigation of the influence of systematic errors during measurement on the kinetic evaluation of thermogravimetric curves. The influence of two main possible errors was analyzed and the results are summarized in Table 3. On the one hand possible errors in mass scale by temperature, $\mathrm{d}m/\mathrm{d}T$, are discussed. The obtained results are shown in groups 1–3 for TG data sets and in groups 4–6 for both TG and ESR data sets, respectively, by assuming a systematic error of the weight scale of $+1.0\ \mu\mathrm{g\ K}^{-1}$. On the other hand errors in the temperature determination were considered, which can be due either to non equivalent geometric positions of the temperature sensors or to an erroneous calibration. For all simulations by TA-kin conversion curves for four different heating rates (TG data only) or for three heating rates (both TG and ESR data) were employed.

Concerning the influence of possible mass errors, the results shown in groups 1–3 indicate for the estimated activation parameters deviations of the order of 15–20%. Evidently the non-linear TA-kin fails in these conditions. The advantage of TA-kin, however, is offered by the possibility of using concomitant a second set of experimental data. Obviously the simultaneous knowledge of the ESR-radical concentration data sets, as before demonstrated, improves substantially the kinetic evaluation (see groups 4–6); the uncertainty of the values decreases finally to 0.5% in group 6.

The influence of systematic errors in temperature determination was analyzed subsequently. The obtained results are shown in groups 7–12 for an error of $\Delta T = +2$ K, in groups 13–18 for +4 K and in groups 19–24 for +8 K. Generally, it is observed that the accompanying errors in determination of the kinetic parameters of the elementary reactions increase with increasing error in temperature determination. If beside monomer concentration (via weight loss) the radical concentration is known, the evaluation by TA-kin is substantially improved, the obtained values of the kinetic parameters approaching the ideal ones. Typical simulated conversion curves corresponding to the data in group 18, Table 3 are illustrated in Fig. 5.

The main problem concerning the temperature influence on TG data is, however, not a possible systematic error in temperature measurement, but due to experimental observation that because of the heat of reaction, the temperature is changed in a non-linear manner during conversion, which is confirmed by any simultaneous scanned DTA or DSC curves [16]. This particular aspect of the temperature influence on TG data will be analyzed in a subsequent paper.

The results shown in Table 3 illustrate that in principle an overall fit is possible, even for data provided with systematic errors. By using data sets obtained with different TA methods of investigation, possible systematic errors can be evidenced through the exactness of the resulted kinetic parameters. That means, however, that at least data of one of the TA instruments are erroneous and it has to be calibrated. As larger the real systematic errors, so greater the number of independently acquired experimental data sets which have to be used to eliminate the influence of systematic errors.

In Table 4, finally it is attempted to characterize the influence of the number of independent acquired experimental TG data on the estimation of the kinetic parameters of the depolymerization process. We used up to five independent data sets obtained by using different heating rates. They are all provided with a normal scatter of $\sigma=0.005$. It is obvious that the worser data are obtained by using a single data set and only for three and more data sets really acceptable values are obtained.

Conclusions

Based on the results obtained during our systematic computer study it may be stated that in principle it is possible to estimate the kinetic parameters of a complex depolymerization process including initiation, radicalic chain degradation and termination. One of the conditions is the use of at least three sets of independent experimental TG data, obtained by using different heating rates. The increase of the number of experimental data within a single heating rate data set has relative low influence on the reliability of the results, the obtained kinetic parameters being for the respective reaction conditions only.

An additional requirement for a serious kinetic analysis is the use of accurate experimental data sets over the whole range of conversion. But even in this case, certainly more than four independent kinetic parameters can not be fitted reliable. Thus for the complex depolymerization process comprising three elementary reaction steps at least the kinetic parameters of one of the belonging elementary reactions has to be known or to be independently evaluable. A less probable assumption could be that one of the elementary reactions is irrelevant for the overall depolymerization process. A possibility could be the measurement of the radical concentration, by ESR for instance. If the radical concent- ration is too small for an unambiguous determination, than the initiation or the depropagation, respectively, should be the rate determining step of the depolymerization.

Generally, the additional use of several (at least three) data sets for the evolution of the radical concentration beside the respective sets concerning the variation of the monomer concentration (evaluated *via* weight loss data) during conversion contributes to an substantial increase of the precisian of estimation of the kinetic parameters of the individual elementary reactian steps comprised in the complex depolymerization process.

Finally, taking into account the non avoidable influence of the reaction heat, it is recommended to use for TG analysis sample masses as small as possible to prevent as much as possible serious influences on the planned heating rates. For excessive deviations of the temperature of the programmed heating rates the presented TA-kin program has to be extended correspondingly.

In closing may be pointed out: The request of the authors is not only to show the advantage of mathematical methods for the evaluation of relevant chemical processes, but to emphasize, that only the common effort on the improvement of experiments in the lab and at the computer leads to success. To any interested expert in polymerization kinetics we can post the simulated curves and graphics af evaluation belonging to the tables as well as a detailed description of the evaluation procedure to obtain reliable results. The manuscript can be requested from the authors.

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