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THE BASIC PROCESSES OF POLYMERIZATION AND ITS REAL KINETIC ANALYSIS

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Abstract

The method of computer experiments can be successfully applied to radical polymerization with the inclusion of initiation, propagation and termination. The convenient PC-program 'TA-kin' for non-linear estimation of the parameters of calorimetric and thermoanalytical experiments was applied for determination of the activation parameters of chain propagation and termination. The overall evaluation of three or more data sets was preferred. The determination of the kinetic parameters proceeds satisfactorily of the measured curves are strongly different, e.g. with a changed start temperature of modified application of batch and semi-batch technique, including acceptable experimental errors. Eight recommendations for laboratory experts are given.

Keywords: kinetics, polymerization

Introduction

In the past decade, the kinetic analysis of thermoanalytical experiments has received an essential impulse [1–4] from the greater availability of mathematically supported structures of kinetic models, resulting from the combination of chemically based knowledge and kinetic expectations, and from new possibilities of performing TA experiments with increased accuracy. Accordingly, estimations of kinetic parameters according to the Arrhenius equation (1) have been attempted by renouncing linear evaluation procedures.

$$k(T) = k_o \exp\left(-\frac{E_A}{RT}\right) \tag{1}$$

The developed nonlinear methods [5–7] lead to a higher certainly of the evaluation. In particular, a recent interlaboratory test [8] demonstrated for the more difficult conditions of the investigation of heterogeneous samples that a successful kinetic analysis can be expected if the unity of the experimental reproducibility and the application of modern optimization procedures is ensured.

After the successful evaluation of processes characterized by a single reaction step, we set out to extend the findings to complex reaction models. Because of the importance for chemical practice, it was obvious to try first the applica-

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bility of mathematical optimization procedures to the basic model of polymerization. The literature reveals that radical polymerization may be characterized with the least mathematical effort, because only the three elementary reaction steps of initiation, chain growth and termination are sufficient for a complete description [9].

The authors have developed some nonlinear evaluation methods for the handling at such kinetic problems, and it will be shown that radical polymerization provides a representative example for the achieved state of parameter estimation.

Radical polymerization

It is generally accepted nowadays that radical polymerization can be characterized by three reaction steps according to Eqs (2–4). The decomposition of the initiator I (Eq. (2)) results in the formation of two radicals P_o^*, which yield polymer radicals P_n^* (n>0) by addition of monomers. Each step of chain growth (Eq. (3)) is presumed to be characterized by the same kinetic parameters:

$$I \rightarrow 2P_o^* \tag{2}$$

$$P_n^* + M \rightarrow P_{n+1}^* \tag{3}$$

$$P_n^* + P_m^* \rightarrow \left| \begin{matrix} P_{n+1} \\ P_n \quad + \quad P_m \end{matrix} \right| \tag{4}$$

Termination (Eq. (4)) occurs either by recombination or by disproportionation of two polymer radicals. Since the kinetics is not influenced by the nature of the termination process, in contrast with the average degree of polymerization, we will not distinguish effect of termination as, compared with that of chain growth, can be neglected, so that the simultaneous determination of the activation parameters of both recombination and disproportionation by means of temperature signals and the concentrations of monomer and of initiator becomes uncertain. The kinetic parameters used for the termination reaction are thus mixed ones, describing both processes (Eq. (4)). Occasionally, additional steps are taken into account for the polymerization of certain monomers (e.g. transfer to the monomer or solvent). The restriction to Eqs (2–4) is based on experience of the polymerization methyl methacrylate (MMA) and styrene [9].

In the present paper, an attempted is made to estimate kinetic parameters for the assumed equation step on the basis of thermal experiments such as DSC and calorimetry, where in principle isoperibolic and isothermal, but also adiabatic working is possible. As a particularity, the influence of marginal experimental conditions usually to be expected in laboratory techniques is considered. This includes the batch technique and the semi-batch technique and also the influence of Gaussian distributed errors.

Kinetics of polymerization

The mathematical description by the ordinary differential equations (ODE) (Eqs (5–7)) and Eqs (8) and (12) is based on the kinetic description of the reaction system presented earlier:

$$\frac{\mathrm{d}x_\mathrm{I}}{\mathrm{d}t} = k_\mathrm{I}[I] \tag{5}$$

$$\frac{\mathrm{d}x_\mathrm{P}}{\mathrm{d}t} = k_\mathrm{P}[P^*][M] \tag{6}$$

$$\frac{\mathrm{d}x_\mathrm{T}}{\mathrm{d}t} = k_\mathrm{T}[P^*]^2 \tag{7}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{1}{c_\mathrm{p}}\left(\nu\sum_{\mathrm{i}=1}^{\mathrm{R}} \dot{x}_\mathrm{i}\Delta H_\mathrm{i} + k\Delta T\right) \tag{8}$$

Accordingly, six activation parameters have to be determined by the optimization procedure. The formulation of the ODE system taking into account Eq. (8) with regard to the concentrations of reactants, considering continuous mass flow in the reactor, leads to Eqs. (9–12):

$$\frac{\mathrm{d}[I]}{\mathrm{d}t} = \frac{\mathrm{d}[I]_\mathrm{add}}{\mathrm{d}t} - k_\mathrm{I}[I] \tag{9}$$

$$\frac{\mathrm{d}[P^*]}{\mathrm{d}t} = \frac{\mathrm{d}[P^*]_\mathrm{add}}{\mathrm{d}t} + 2k_\mathrm{I}[I] - 2k_\mathrm{T}[P^*]^2 \tag{10}$$

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = \frac{\mathrm{d}t[M]_\mathrm{add}}{\mathrm{d}t} - k_\mathrm{P}[P^*][M] \tag{11}$$

$$\begin{gathered}\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{1}{c_\mathrm{p}}\left(\sum_{\mathrm{i}=1}^{\mathrm{R}} \frac{\mathrm{d}q_\mathrm{i}}{\mathrm{d}t} + K\Delta T\right) \\ \sum_{\mathrm{i}=1}^{\mathrm{R}} \frac{\mathrm{d}q_\mathrm{i}}{\mathrm{d}t} = \nu k_\mathrm{I}[I]\Delta H_\mathrm{I} + \nu k_\mathrm{T}[P^*]^2\Delta H_\mathrm{T} + \nu k_\mathrm{P}[P^*][M]\Delta H_\mathrm{P}\end{gathered} \tag{12}$$

In order to reduce the number of parameters to be estimated to lower than five, further decisions have been reached. The authors suggest that the reaction enthalpies for steps (2–4) be estimated average values of literature data and also that one of the reactions should be assumed to be known. For radical polymerization, one can assume that the decomposition of a given initiator, 2,2'-azo-bis-isobutyronitrile (AIBN), can be determined in an independent run and that therefore it can be assumed to be known. For a given polymerization, the problem to be solved still requires the adoption of the parameters of chain growth, $\ln k_{o,P}$ and $E_{A,P}$, and termination, $\ln k_{o,T}$ and $E_{A,T}$.

For the realization of a kinetic evaluation program of calorimetrically studied reactions in the batch and semi-batch modes and also by TG and DSC, we have elaborated the object-oriented application TA-kin* involving Turbo Pascal language. Numeric integration of the assume ode model is performed by an adaptive Runge-Kutta procedure of fifth order. For estimation of the parameters in the ODE system, an algorithm for iterative minimization of the SDS function according to Marquardt and Levenberg is used. TA-kin offers the user the possibility of simultaneous evaluation of data sets of different experimental techniques, e.g. batch and semi-batch, and also the evaluation of experiments carried out under different conditions, e.g. with variation of the start concentrations and temperatures. The direct estimation of kinetic parameters according to the supposed model of ODE by using nonlinear methods offers two main advantages in comparison with linearization methods:

1) Complex system of ODE which cannot be transformed into linear equations are applicable for reaction kinetics.

2) Distortion of curve ranges is often observed during the application of approximate linear equations to nonlinear processes.

Simulation of experimental probable polymerization reaction

The kinetic parameters (mean values in Table 1) of the well-known polymerization of MMA [10] initiated by were used to simulate the reaction first under given conditions.

Figure 1 demonstrates typical evolutions of temperature, and amounts of initiator, free radicals and monomer during the polymerization in a batch reaction (see also Table 2, row 13) and Fig. 2 shows the same simulation of the semi-batch technique with a continuous feed flow of the initiator. For the simulation, we assumed a cylindrical reactor with a diameter of 5.1 cm. The figures differ from each other in the more moderate course of the semi-batch experiment, which is reflected by the height and the width of the signals.

In all simulations, we supposed lower amounts of initiator than of monomer, so that the propagation predominates over the termination. This is the basis for

Table 1 Simulation parameters of polymerizations given by the ODE system (Eqs (9–11)) and (Eqs 8 and 12); specific constant of reactor and substances: K_{sp}=0.045 J K^{-1} s^{-1} cm^{-2}, c_{sp}=2.67 J K^{-1} g^{-1}, ρ=0.8 g cm^{-3}, d=5.1 cm (diameter of the cylindrical reactor

Reaction	$\ln k_o$	E_A/kJ mol^{-1}	ΔH/kJ mol^{-1}
initiation	32.859	123.44	40.0
termination	12.717	11.9	–70.0
chain growth	15.436	26.40	–55.5

the simplification assumed earlier, that the activation parameters of recombination and disproportionation may be combined.

A multitude of simulated curves demonstrate how the starting temperature T_o controls both the reaction time and the maximum temperature reached during the polymerization. Other parameters, e.g. those of activation, do not have an influence of a similar extent. The section 'simulation of TA-king thus proved to be a convenient tool to fix the expected reaction courses. These simulated curves of the temperature and the amounts of the components were used as starting points to prepare data sets involving both random errors and systematic errors occurring in calorimetric experiments. The plots of simulated and experimental data allow a first comparison with the effective activation parameters.

Examples of evaluation

Several groups of experimental conditions were assigned in order to investigate their influence on the parameter estimation. Accordingly, one or two reaction conditions were changed step by step. The aim was to examine two different ways of obtaining kinetic parameters by nonlinear evaluation. The first was to evaluate single curves. In the second, several experimental files were used to improve the validity of the estimated parameter sets. The following changes were included:

- the concentrations of the initiator, the radicals and the monomer at the start and during the polymerization itself;
- the concentrations, the volume rate and the period of the feed flow of one of these components;
- the starting temperature T_o.

The simulated data were provided with random errors defined by a standard deviation of σ=0.01 K. With the use first of the data sets without any experimental errors, the expected activation values were obtained exactly by the nonlinear parameter estimation.

The starting temperature T_o was gradually increased from 320 to 340 K in the group of simulated curves shown in Figs 2, 3 and 4. The other reaction con-

Table 2 Results concerning the parameter estimation for chain growth and termination using three simulated data sets of reactor temperature and of the sizes of monomer shown in rows 2 and 4, which were provided with random errors. The temperature was superimposed with regular distributed errors of the standard deviation $\sigma=0.01$ K. Initial volume: 45 ml (50 ml in row 11)

Varied conditions	T_o/K	$c_o(I)$/ $c_o(M)$/ mol l^{-1}	$c_{add}(I)$/ $c_{add}(M)$/ mol l^{-1}	$dv_{add}(I)dt$ $dv_{add}(M)/dt$ ml min–1	$t_{add}(I)$/ $t_{add}(M)$/ s	Chain growth: $\ln k_o$ E_A/kJ mol^{-1}	Termination: $\ln k_o$ E_A/kJ mol^{-1}
T_o	320/330/340	0.0	0.1	1.0	1800	15.34±0.25	12.51±0.52
		3.0	0.0	0.0	0	26.15±0.70	11.3±1.5
T_o (evaluation with T and n_M)	320/330/340	0.0	0.1	1.0	1800	15.54±0.17	12.89±0.35
		3.0	0.0	0.0	0	26.70±0.48	12.40±0.99
$c_{add}(I)$	340	0.0	0.1/0.05/0.025	1.0	1800	15.46±0.67	12.8±1.4
		3.0	0.0	0.0	0	26.5±1.9	12.1±3.91
$c_{add}(I)$ (evaluation with T and n_M)	340	0.0	0.1/0.05/0.025	1.0	1800	15.26±0.49	12.17±0.99
		3.0	0.0	0.0	0	25.9±1.4	10.3±2.8
$c_{add}(M)$	340	0.01	0.0	0.0	0	10±26	15±51
		0.0	1.0/2.0/3.0	1.0	3000	8±76	10±148
$c_{add}(M)$	340	0.01	0.0	0.0	0	15.59±0.50	13.07±0.27
		0.0	1.0/2.0/3.0	10.0	300	26.8±1.3	12.82±0.93
T_o	330/340/350	0.0	3.0	0.1	3000	15±2.4	12±4.8
		0.0	3.0	1.0	3000	25±6.6	9±13
T_o $\sigma=0.01$K	330/340/350	0.0	0.3	0.1	3000	15.3±0.57	12±1.2
		0.0	3.0	10.0	300	26±1.7	11±3.4
T_o $\sigma=0.1$K	330/340/350	0.0	0.3	0.1	3000	14±6.5	10±13
		0.0	3.0	10.0	300	20±19	9±38
T_o $\sigma=0.5$K	330/340/350	0.0	0.3	0.1	3000	20±22	20±46
		0.0	3.0	10.0	300	30±64	0±132

Table 2 Continued

Varied conditions	T_o/K	c_o(I)/ c_o(M)/ mol l^{-1}	c_{add}(I)/ c_{add}(M)/ mol l^{-1}	dv_{add}(I)dt dv_{add}(M)/dt ml min^{-1}	t_{add}(I)/ t_{add}(M)/ s	Chain growth: lnk_o E_A/kJ mol^{-1}	Termination: lnk_o E_A/kJ mol^{-1}
batch/ semi-batch	340	0.01	0.0	0.0	0	15.11±0.76	11.7±1.3
		0.0/1.0/2.0	2.0/1.0/0.0	1.0	3000	25.5±2.2	9.0±3.7
c_{add}(M)	340	0.01	0.0	0.0	0	14.0±2.8	9.3±5.3
		1.0	1.0/2.0/3.0	1.0	3000	22.4±8.1	2±15
T_o (batch)	320/330/340	0.003	0.0	0.0	0	15.56±0.32	13.01±0.65
		3.0	0.0	0.0	0	26.76±0.89	12.8±1.8

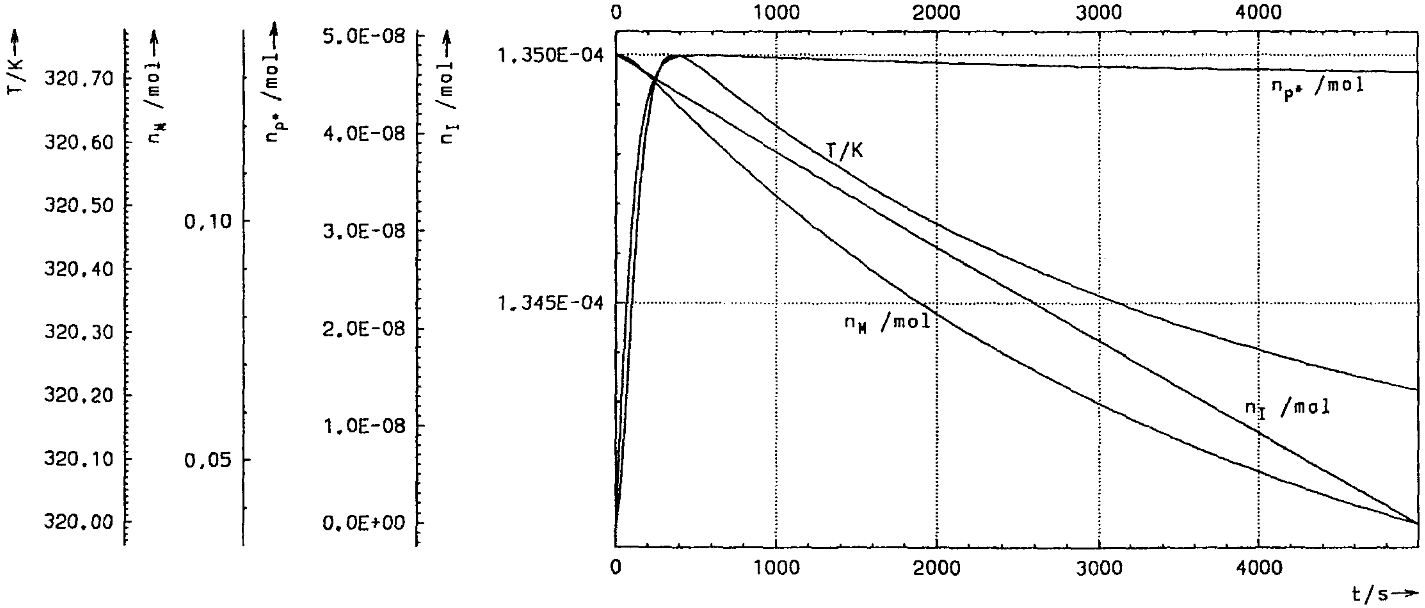


Fig. 1 Batch polymerization (T_o=320 K, $c_{o,I}$=0.003 mol l^{-1}, $c_{o,M}$=3.0 mol l^{-1})

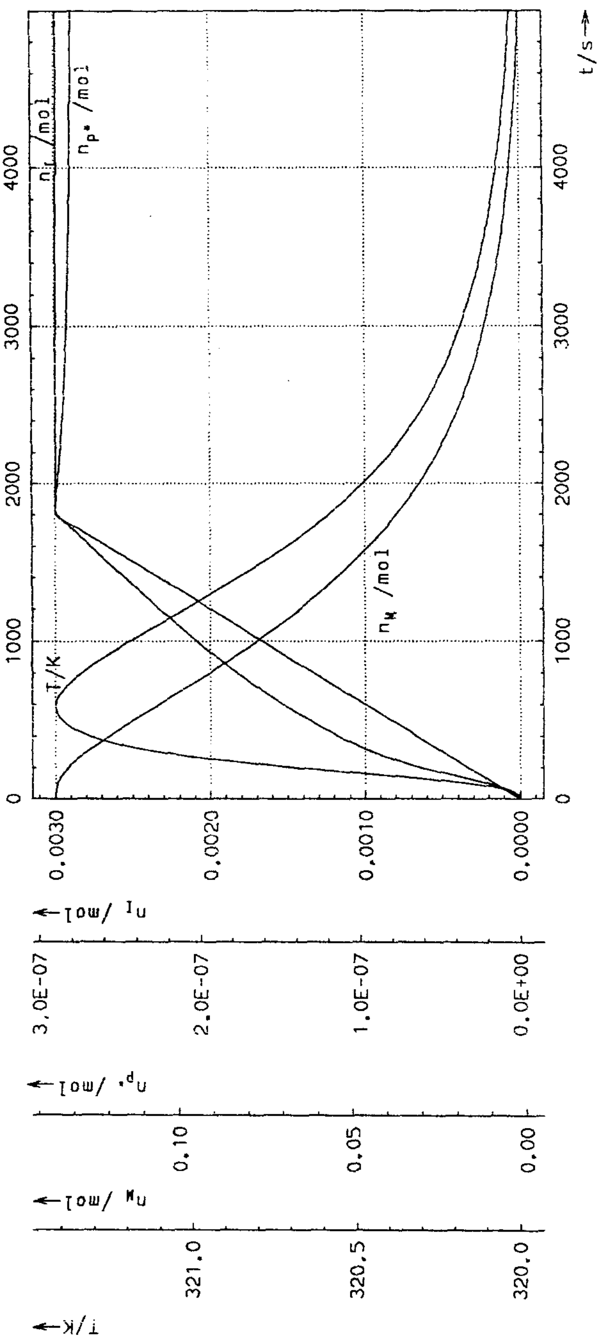


Fig. 2 Semi-batch polymerization (T_o=320 K, $c_{o,M}$=3.0 mol l^{-1}, $c_{add,I}$=0.1 mol l^{-1}, d$v_{add,I}$/dt=1.0 ml min^{-1}, $t_{add,I}$=1800 s)

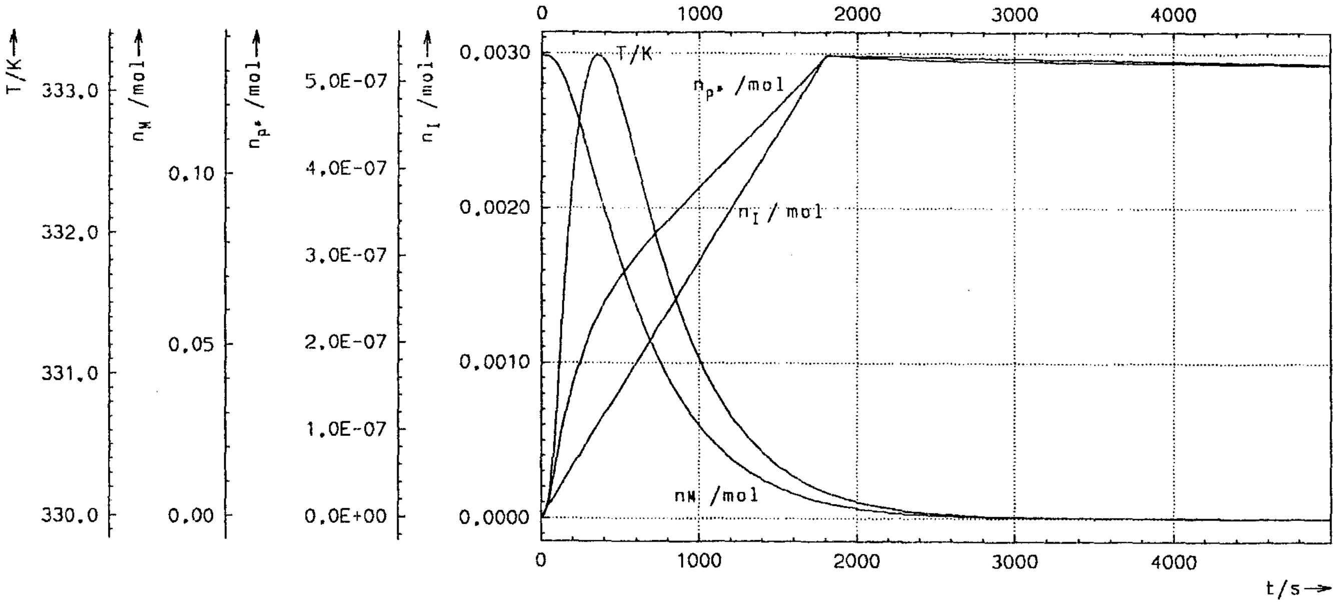


Fig. 3 Semi-batch polymerization (T_o=330 K, $c_{o,M}$=3.0 mol l^{-1}, $c_{add,I}$=0.1 mol l^{-1}, $dv_{add,I}/dt$=1 ml min^{-1}, $t_{add,I}$=1800 s)

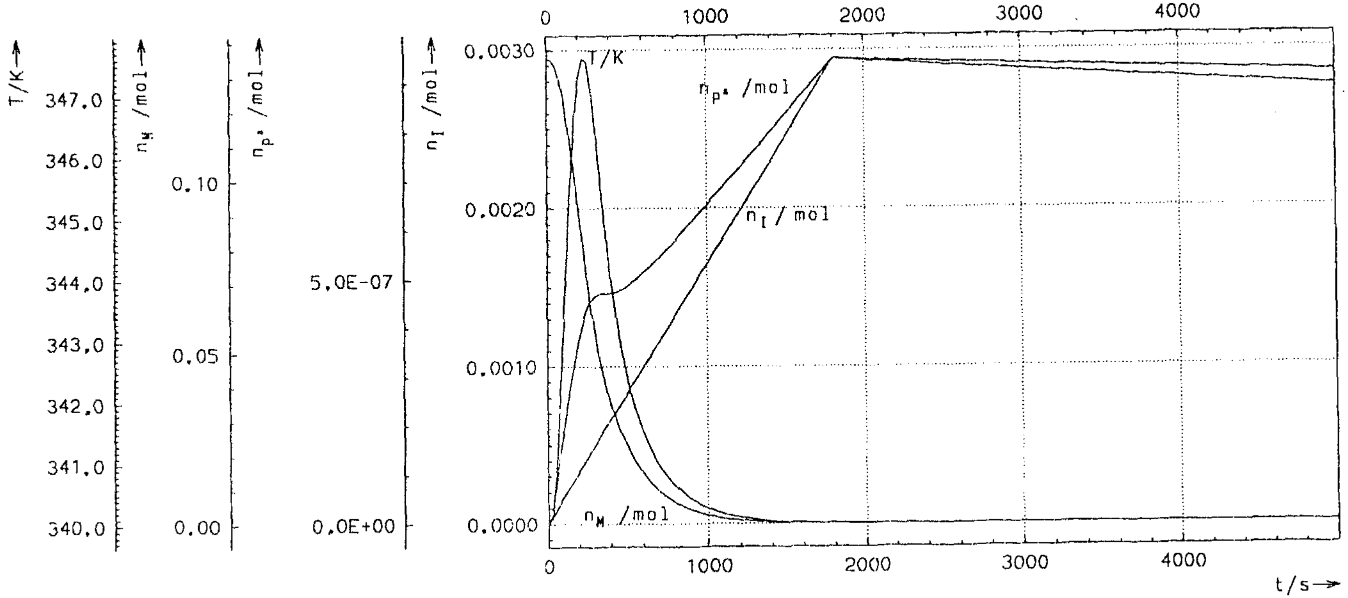


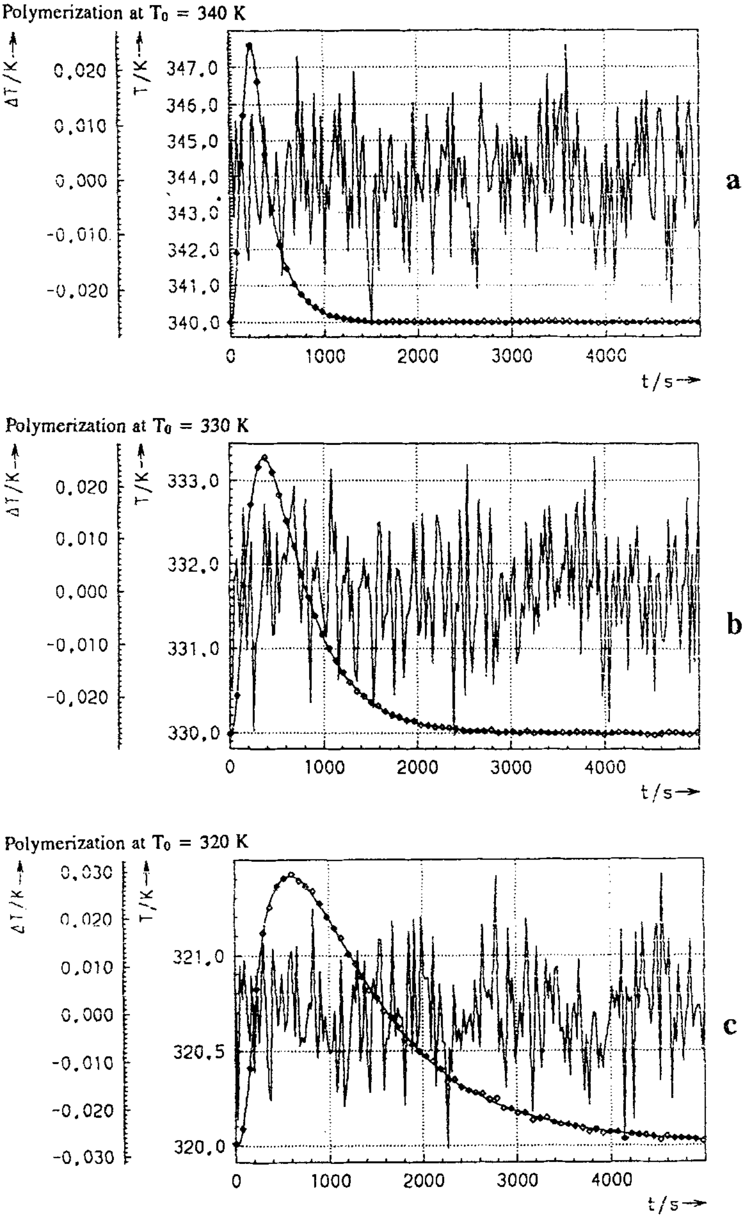
Fig. 4 Semi-batch polymerization (T_o=340 K, $c_{o,M}$=3.0 mol l^{-1}, $c_{add,I}$=0.1 mol l^{-1}, $dv_{add,I}/dt$=1.0 ml min^{-1}, $t_{add,I}$=1800 s)

ditions were kept constant. The initiator was added at constant rate for 1800 s. The ordinates show the reactor temperature T and the amounts of the initiator, n_I, the radicals, n_p^*, and the monomer, n_M. The initiator rate increases about tenfold from 320 to 340 K, which is why the reaction finishes after 1000 s at the higher temperature, compared with 5000 s at the lower. The data obtained from the simulations in Figs 2, 3 and 4 were used for the overall kinetic analysis shown in Fig. 5. Minimization of the SDS function, applying the algorithm of Marquardt and Levenberg, resulted in a joint set of activation parameters found to be near the simulation set of parameters shown in the top of the Figure and in Table 2/1. Obviously, for $T_o=320$ K the fit may be satisfactory, although the error distribution reaches about 1% of the maximum temperature ($\Delta T=1.4$ K). The evolution of the differences, also plotted in Fig. 5, between the experimental curve of the computer experiment and the simulated curve, using the set of estimated parameters, reflects a structure of regularly distributed errors.

The next group of data characterizes (for a common starting temperature of $T_o=340$ K) the influence of variation of the concentration of the initiator in the feed flow. The value n_I in Fig. 4 is reduced to half in Fig. 6 and to a quarter in Fig. 7. In this series the maximum temperature difference in the calorimeter decreases from 8 to 4 K. The end of the polymerization in Fig. 4 is reached after 1200 s, before the initiator flow is finished, while in Fig. 6 both events occur at nearly the same point, after 1800 s, whereas in Fig. 7 polymerization is finished after about 2200 s. Thus, if the initiator concentration is reduced to a quarter, the time of polymerization doubles. The results concerning the parameter estimation are shown in Table 2, row 3. It is evident that the confidence intervals of the parameters are larger than those in the first row. This is probably due to the strong decrease in the initiator concentration, which results in low radical concentrations.

If the total amount of initiator is introduced into the reactor from the beginning and a monomer flow rate of 1.0 ml min^{-1} is assumed at 340 K, the results shown in Table 2/5 are obtained. The maximum temperature difference ΔT_{max} rises from 0.25 to 0.70 K, as c_M is varied. When the monomer flow finishes, the value of ΔT breaks down. At this time, the degree of conversion of the polymerization reaction is about 85%. The overall estimation of this group is not satisfactory (Table 2/5), as the applied error distribution ($\sigma=0.01$ K) comprises up to 4% of ΔT_{max} in the worst case. The same series with a faster flow of monomer solution should lead to the desired temperature signals. As expected, this condition furnishes a higher accuracy of the estimated parameters (Table 2/6). This example demonstrates how an experimental series has to be prepared in order to get acceptable results by an overall estimation of a complex reaction system, which almost agree with the original simulation parameters.

In the next two groups (Table 2/7 and Table 2/8–10), the T_o values were varied, while the initiator and the monomer flowed into the reactor, which was filled from the beginning with 45 ml pure solvent. The added quantities of the


Polymerization at T_0 = 340 K

Polymerization at T_0 = 330 K

Polymerization at T_0 = 320 K

Fig. 5 Determination of activation parameters of termination and chain growth using data sets of reactor temperature in semi-batch techniques (Table 2/row 1 and Figs 2–4)

Estimated-Parameters

$\ln k_{0T} = 12.51 \pm 0.52$
$E_{AT}/\mathrm{kJmol}^{-1} = 11.3 \pm 1.5$
$\ln k_{0P} = 15.34 \pm 0.25$
$E_{AP}/\mathrm{kJmol}^{-1} = 26.15 \pm 0.70$

SDS = 0.00010366

Original-Parameters

$\ln k_{0T} = 12.71700$
$E_{AT}/\mathrm{kJmol}^{-1} = 11.90000$
$\ln k_{0P} = 15.43600$
$E_{AP}/\mathrm{kJmol}^{-1} = 26.40000$

SDS = 0.00010431

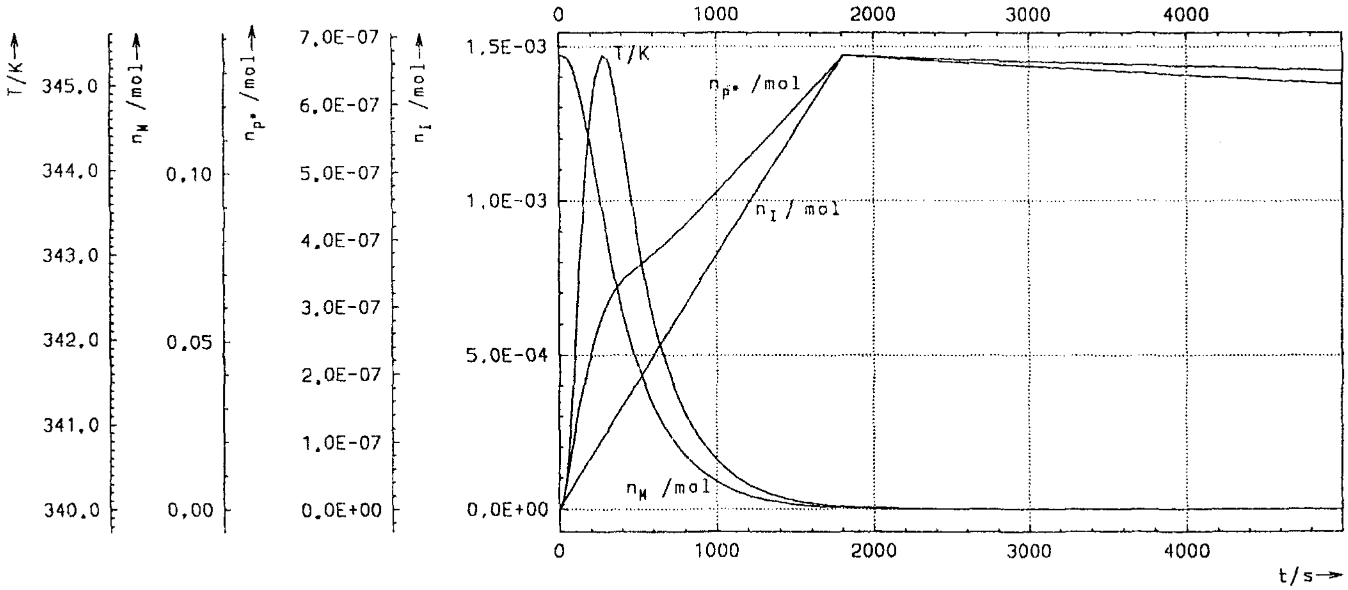


Fig. 6 Semi-batch polymerization (T_o=340 K, $c_{o,M}$=3.0 mol l^{-1}, $c_{add,I}$=0.05 mol l^{-1}, d$v_{add,I}$/dt=1.0 ml min^{-1}, $t_{add,I}$=1800 s)

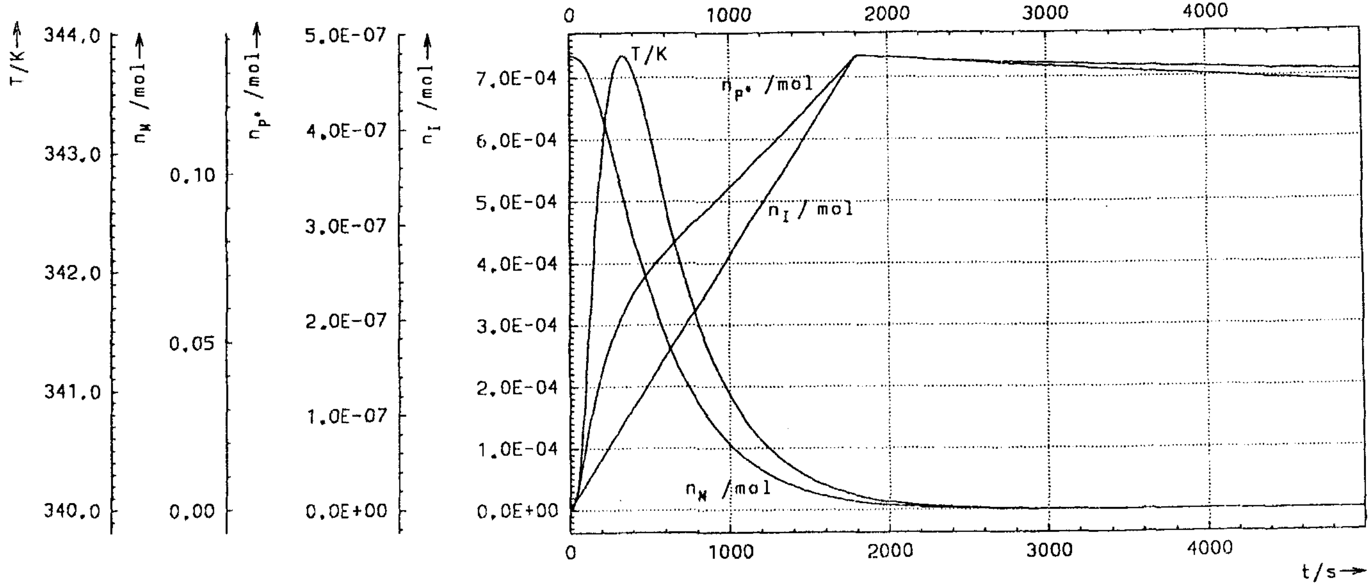


Fig. 7 Semi-batch polymerization (T_o=340 K, $c_{o,M}$=3.0 mol l^{-1}, $c_{add,I}$=0.025 mol l^{-1}, d$v_{add,I}$/dt=1.0 ml min^{-1}, $t_{add,I}$=1800 s)

two substances were the same. The two groups differed from each other in the concentrations in the feed flow, and also in the flow rate and its duration:

I. $c_{add,I}=c_{add,M}$, $dv_I/dt=10dv_M/dt$, $t_{add,I}=t_{add,M}$
II. $c_{add,I}=1/10c_{add,M}$, $dv_I/dt=1/100dv_M/dt$, $t_{add,I}=10t_{add,M}$

The result of the overall estimation of the first group corresponds essentially to the original parameter values; only the activation energy of termination differs somewhat. This is certainly caused by the experimental conditions, which produce a maximum temperature difference of only about 1.1 K. In contrast, in the second group the temperature signals increase step by step from 1.0 to 4.5 K. This leads to successful parameter estimation in the case of $\sigma=0.01$ K, but for a larger scatter of the experimental data, characterized by higher standard deviations, $\sigma=0.1$ to 0.5 K (Table 2/9, 10), the evaluated parameters deviate from rough to nonacceptance. Of course, working with such bad data files is not the normal practice, but the test should show that in such cases the application of modern mathematical methods fails.

The results of kinetic evaluations of a radical polymerization described by activation parameters typical for the polymerization of MMA initiated by AIBN demonstrate the interaction between the chosen experimental conditions connected with the characteristics of the reactor and the variation of the parameters during the experiment. As long as the chemist experienced in applying nonlinear evaluation procedures pays attention to this interaction between convenient conditions for kinetic evaluation (variation of starting temperature, concentration of initiator and flow rates), a relatively sure estimation of activation parameters can be expected, provided the knowledge of the reaction model (mechanism) is sufficiently safe.

Additional computer experiments were performed on the assumption of the knowledge of independent data sets of temperature and of the concentration of one substance taking part in the reaction. For radical polymerization, this could be either to monomer concentration, which could be obtained from absorption measurements, or the concentration of chain radicals, determinable by ESR spectroscopy. Starting with such double files loaded with an error distribution of $\sigma=0.01$ K and 1% of the maximum concentration value, respectively, it is possible to improve the estimated sets of parameters. This is clear from the breaking down of the confidence intervals (Table 2/4). This mode of operation is of course more lavish, but ensures improved kinetic investigations.

Finally, attention is drawn to the fact that alteration of other variables of reaction than temperature, for example to concentration of the flow of monomer or of the initiator, does not improve the results sufficiently (Table 2/12). Important knowledge is obtained if semi-batch experiments are combined with batch experiments at the same temperature (Figs 8–10). Although the maximum tem-

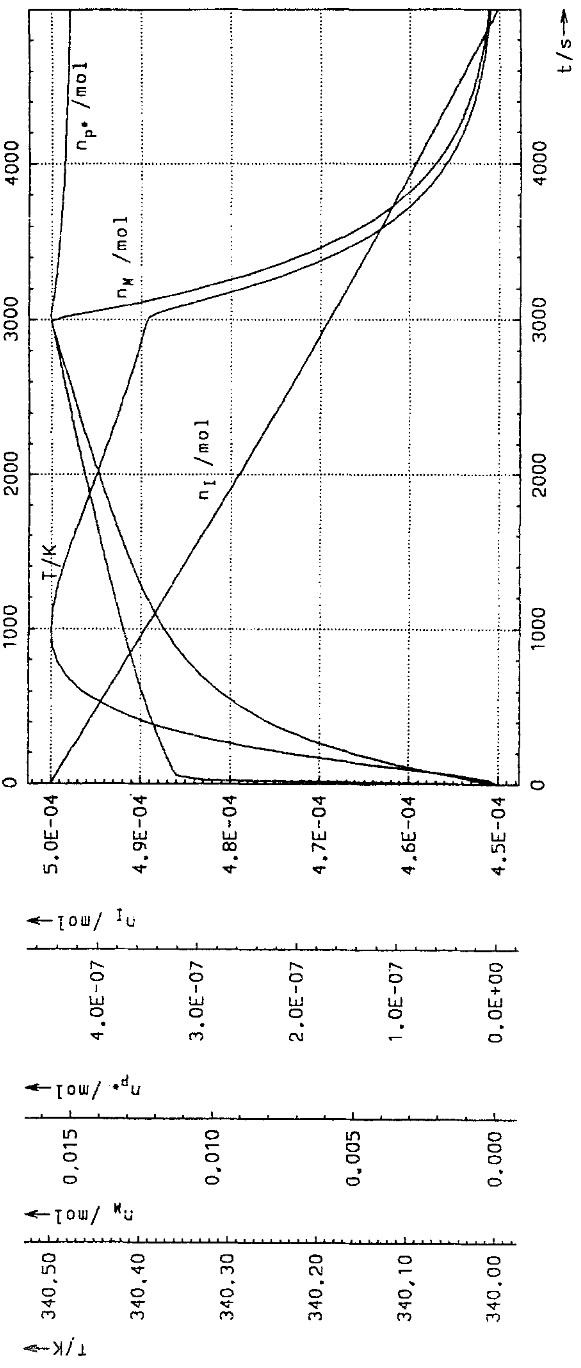


Fig. 8 Semi-batch polymerization (T_o=340 K, $c_{o,M}$=0, $c_{add,M}$=2.0 mol l^{-1}, d$v_{add,M}$/dt=1.0 ml min^{-1}, $t_{add,M}$=3000 s)

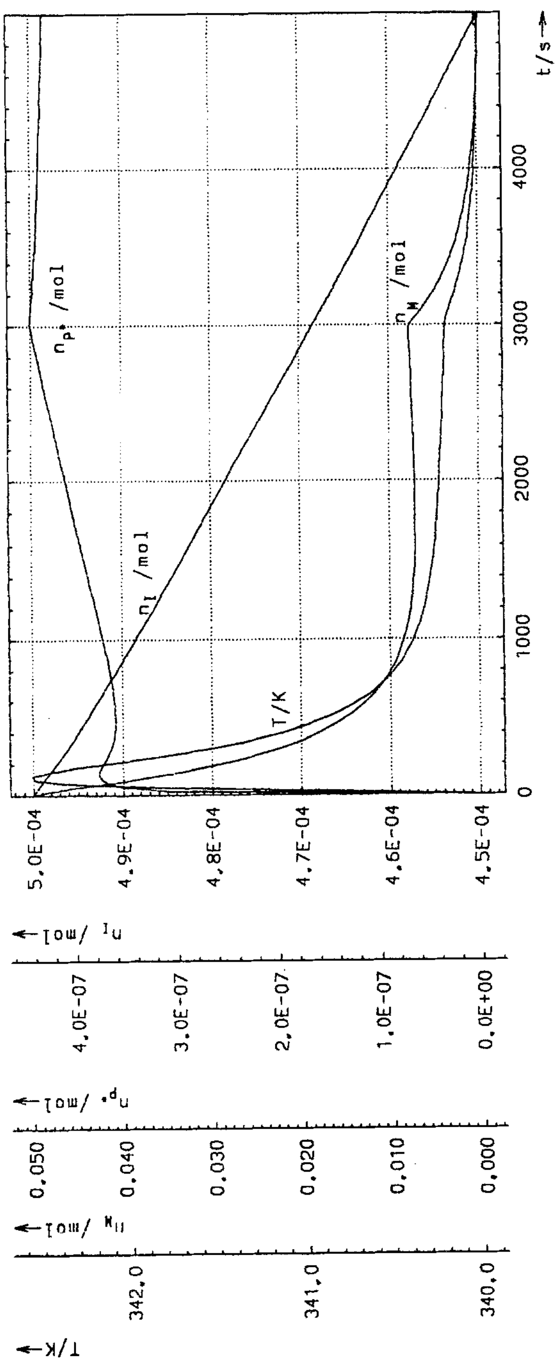


Fig. 9 Semi-batch polymerization (T_o=340 K, $c_{o,M}$=1.0 mol l^{-1}, $c_{add,M}$=1.0 mol l^{-1}, d$v_{add,M}$/dt=1.0 ml min^{-1}, $t_{add,M}$=3000 s)

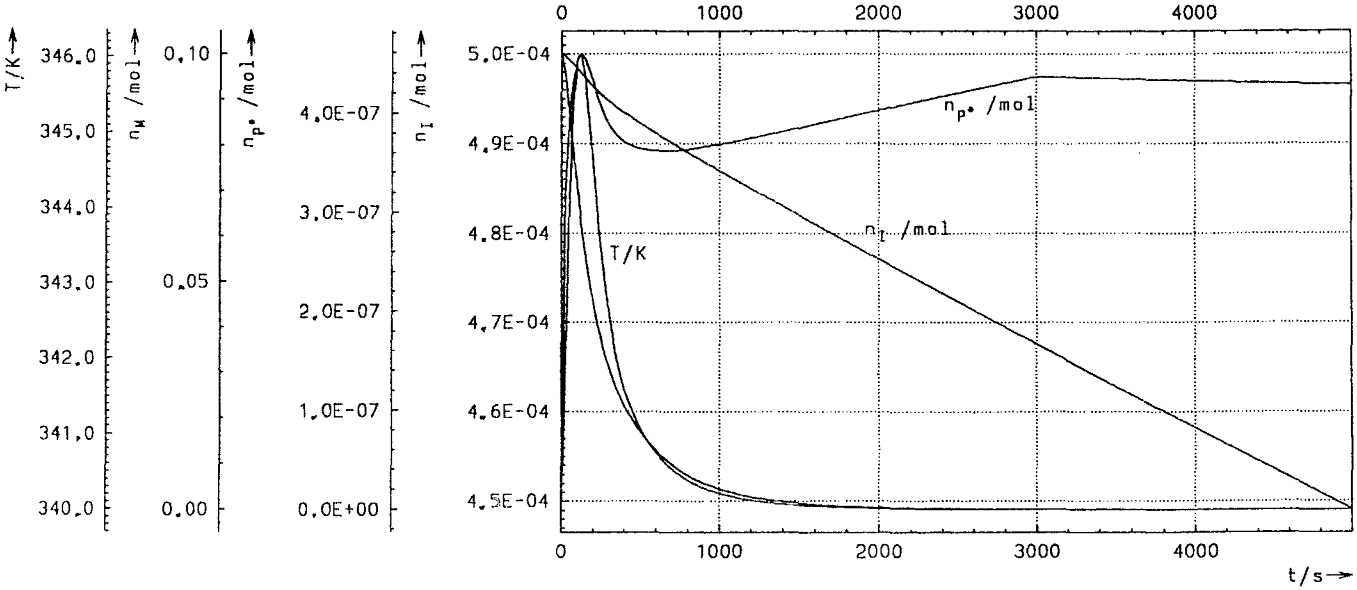


Fig. 10 Semi-batch polymerization (T_o=340 K, $c_{o,M}$=2.0 mol l^{-1}, $c_{add,M}$ =0, d$v_{add,M}$/dt=1.0 ml min^{-1}, $t_{add,M}$=3000 s)

perature differences are situated between 0.5 and 6.0 K and for this reason the common error in measuring has a different effect on the curves, satisfactory optimization was nevertheless possible (Table 2/11). This means that the user should choose experimental conditions for which very different evolutions are expected for the studied polymerization system. On the other hand, the computer expert supporting the practising user will take up such instructions to consider them in simulations and optimization experiments. Thus, important hints can be derived for the laboratory experimenter. This cyclic exchange results in a high efficiency in the evolution of sure kinetic activation parameters for the individual elementary reaction steps of the total reaction.

Conclusion

Taking into account the experience acquired during the kinetic evaluation of more than 400 computer experiments in the field of radical polymerization, some rules can be recommended which ensure a sure and easier evaluation.

0. There is no problem concerning the exact evaluation of faultless data sets.

1. The kinetic evaluation of nonlinear processes requires the inclusion of experimental data over the whole range, since the operation with only a section of a data file does not permit an unequivocal attribution to a certain kinetic model.

2. Since two or even more kinetic parameters have to be determined, the nonlinear fitting to the experimental data set is frequently not sufficient for an unequivocal attribution. The polymerization systems considered here require not only a knowledge of the initiation, but also investigation of the termination and chain growth. Recommendation: overall evaluation of several data sets obtained under very different conditions.

3. The best prerequisites are realized by variation of the starting temperature, but also by the combination of batch and semi-batch experiments.

4. If this is not feasible, only files of high experimental accuracy or curves with high maximum temperature differences should be used.

5. The variation of the starting concentration (batch) or of the flow concentration (semi-batch) alone mostly leads to unacceptable results in the evaluation.

6. If possible, the kinetic parameters of elementary reactions should be determined by independent methods, thereby diminishing the total number of unknown parameters. This is feasible mainly for the initiation.

7. For overall evaluation, it is more favourable to increase the number of experimental data files than the number of measured data within the single files.

8. The inclusion of conversion curves, obtained by independent methods during the polymerization, for example of the monomers or of the radicals (by ESR), leads to a distinctly higher sureness of parameter estimation.

To close, it may be pointed out that, the concern of the authors was not only to show the advantage of mathematical methods for the evaluation of relevant chemical processes, but also to emphasize that only common effort during the improvement of both laboratory experiments and computer experiments leads to success. Those interested in polymerization kinetic will receive the simulated curves and graphs of evaluation relating to Table 2 on request.

Appendix

I	initiator/initiation
M	monomer
P	polymer / chain growth
P^*	radical
AIBN	2,2′-azo-bis-isobutyro-nitrile
MMA	methyl methacrylate
PMMA	Poly(methyl methacrylate)
R	molar gas constant/number of chemical reactions
v	volume
$\mathrm{d}v/\mathrm{d}t$	volumetric flow rate
c(A), [A]	molar concentration of component A
x	conversion of reaction, $\mathrm{d}x=\mathrm{d}[A]/\nu_A]$
k	rate constant
k_o	frequency factor
E_A	molar activation energy
ΔH	molar heat of reaction
T	temperature of reaction mixture/termination
K	heat exchange constant
c_p	heat capacity
$\mathrm{d}q/\mathrm{d}t$	heat production
σ	standard deviation
SDS	sum of deviation squares

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