ELSEVIER

Thermochimica Acta 361 (2000) 21–29

thermochimica
acta

www.elsevier.com/locate/tca

Formal-kinetic evaluation of polyaddition reactions — results of a round-robin test, initialised by the working group 'Polymers' of the German Society for Thermal Analysis (GEFTA)

H.J. Flammersheim*

Chem. Geowiss. Fak., Inst. für Phys. Chem., Friedrich-Schiller-Universität Jena, Lessingstr. 10, 07743 Jena, Germany

Received 2 December 1999; accepted 16 December 1999

Abstract

A simple and well-known polyaddition reaction is used as test reaction. The formal-kinetic evaluation of the data sets from 11 participants of laboratories in industry, universities and manufacturing companies permits representative and well-founded conclusions. In spite of always possible statistical and systematic measurement errors and mathematical artefacts, all calculated individual parameter sets for the most probable formal-kinetic model allow reliable predictions of the reaction behaviour for any complex temperature–time conditions. The simultaneous evaluation of non-isothermal measurements at different heating rates and isothermal data sets at various temperatures is not only possible but even highly desirable. The DSC as well as other thermoanalytical methods are in combination with multivariate kinetic analysis, a powerful tool for process prediction and optimisation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polyaddition; Kinetics; Round-robin test

1. Introduction

A number of thermoanalytical methods, above all DSC, TG and DMA, are frequently used for the study and optimisation of technical processes. Two main problems have to be solved in the kinetic evaluation of the underlying chemical reactions. In the first step, a series of measurements with many data points is reduced to few parameters of a (formal) kinetic model. Using this model, it should be possible in the second step to make reliable predictions concerning the reaction behaviour for any temperature–time conditions. Most reactions occur in a sequence of elementary reactions. Therefore, in DSC, the measured heat flow rate is the overall signal of all simultaneous and/or consecutive steps.

From the physico-chemical point of view, the objective of a kinetic evaluation is the description of the overall process as the sum of all or at least of all important elementary steps. Each of these steps are characterised by its heat of reaction and its (Arrhenius) activation parameters. Such a procedure is extremely time-consuming, requires the knowledge of the initial, final and all intermediate states and is not possible without the coupling with numerous other analytical techniques [1].

The alternative and custom-made evaluation for the practician is the use of a formal-kinetic model [2]. Using vocabulary and basic ideas of the usual reaction kinetics, the overall reaction is now described by the combination of formal reaction steps. As a rule, these

---

* Fax: +49-3641-948302.
E-mail address: c7flha@uni-jena.de (H.J. Flammersheim).

PII: S0040-6031(00)00544-X

steps may not be interpreted as really existing chemical reaction steps. The main advantages of this procedure are the low consumption of time and the possibility to evaluate also systems of unknown chemical composition. Only a small disadvantage results from the fact that the obtained process parameters and derived conclusions are valid just for this tested composition.

Of course, the so-called model-free analysis [3–5] as a further variety of formal-kinetic evaluation often permits the description of the overall process by an apparent and conversion-dependent activation energy. But this procedure is not so versatile and fails if independent parallel reactions, reversible reactions, reactions with combinations of endo- and exothermic reactions and reactions with partial diffusion control exist in the reaction mechanism [6].

The round-robin test concerning the formal-kinetic evaluation of a relatively simple and well-known polyaddition reaction was initiated by the working group 'Polymers' of the German Society for Thermal Analysis (GEFTA). The two principal objectives were as follows:

1. Is it possible to describe the data sets obtained in different laboratories and with different types of DSC devices with the same formal-kinetic model and with comparable fit quality?
2. Which influence have the scattering formal-kinetic process parameters on the predictions of the reaction behaviour? In other words, is the scatter acceptable for the practician?

Evaluating the data sets from 11 participants of laboratories in industry, universities and manufacturing companies, it should be possible to obtain representative and well-founded results.

2. Experimental

The investigated test reaction was the linear step-growth and solvent-free polymerisation of the 1:1 mixture of bisphenol-A-diglycidyl ether (DGEBA) and *N*,*N*′-dibenzyl-4,4′-diamino-diphenylmethane (DBMDA). The glass transition temperature of the produced polymer with M_n>10,000 is T_g=(88±3)°C. The fundamental steps of the reaction mechanism are known [7]. Some individual steps are autocatalytically activated. The small differences in the heat capacities between reactants and product are advantageously for the construction of the peak baseline. A further advantage of the chosen system is the low T_g, which was always clearly lower than the programme temperature for all planned dynamic and isothermal experiments. This avoids complications by an eventual partial diffusion control of the reaction [8].

The micro-heterogeneous mixture of the both solid components was obtained by careful and intensive mixing of the solid components. It is absolutely stable below of the melting temperature of the epoxide (41°C). The mixture was given to all participants of the round-robin test.

Further, the following recommendations were made to obtain measurements which are appropriate for kinetic evaluations:

1. General conditions of the test programme:
   - 1.1. temperature programmed (dynamic) measurements using at least three strongly differing heating rates;

     The highest heating rate should not be higher than 5 K min^{-1}, because at higher heating rates the final temperature for a quantitative reaction is clearly higher than 525 K and disturbing side reactions cannot be avoided.
   - 1.2. isothermal measurements at 400, 430 and 460 K;

     These temperatures are a compromise between an acceptable reaction time (<6 h) and the reliable possibility of correcting the initial phase of the reaction. This correction is necessary because the steady state conditions are disturbed by the insertion of the sample in the DSC.
   - 1.3. a second run with the reaction product immediately after the reaction and using identical measuring conditions.
2. Conditions for sample preparation:
   - 2.1. melting of the sample and consequently homogenising of the reaction mixture by rapid heating to 115°C in the DSC, holding time about 30 s;
   - 2.2. quenching of the molten sample to 70–80°C; the sample remains in a subcooled liquid state;

Table 1
Code number of the participants, equipment and measurements carried out

Code no.	Equipment	Heating rates ($K\ min^{-1}$)	Isothermal reaction temperatures (K)
1	SETARAM 141	0.25, 1, 4	–
2	NETZSCH, DSC 204	1, 2, 5	400, 430, 460
3	Perkin-Elmer, DSC7	0.5, 1, 2, 5	400, 430, 460
4	TA Instruments, MDSC 2920	0.5, 1, 2, 4	–
	Perkin-Elmer, DSC2	0.25, 0.5, 1, 2, 5	400, 410, 430, 440, 460, 470
5	NETZSCH, DSC 204	1, 2, 5	–
6	Perkin-Elmer, DSC7	1, 2, 5	400, 430, 460
7	METTLER, DSC 821	1, 2, 5	–
8	TA Instruments, MDSC 2920	0.5, 2, 5	–
9	Perkin-Elmer, DSC7	1, 2, 5	–
10	Perkin-Elmer, DSC7	0.25, 1, 5	–
	METTLER, DSC 820	0.25, 1, 5	–
11	TA Instruments, MDSC 2920	0.25, 1, 5	–

   2.3. immediate start of the measurement after reaching the thermal steady state conditions.

   The small partial reaction during this pre-treatment can be neglected, as the rate of the non-catalysed reaction is much slower than that of the autocatalysed reaction steps [7].

3. Further conditions:
   3.1. sample weights about 10 mg; use of standard aluminium pans with pierced lids;
   3.2. an additional run with an indium calibration sample (heating rate $2\ K\ min^{-1}$) in order to realise the later desmearing of the reaction curves.

The correct temperature, caloric and heat flow rate calibration and the careful correction of the zero-line behaviour of the DSC is presupposed [9]. Table 1 summarises for all participants code number, available equipment and the experiments carried out.

3. Evaluation and pre-treatment of the DSC raw data

The kinetic modelling by means of multivariate non-linear regression was carried out using the software 'NETZSCH Thermokinetics' [2,10]. This program calculates the optimal parameters for the chosen model, which can include single or multi-step processes (to a maximum of four steps). It is possible to combine concurrent, reversible and consecutive partial reactions. Every step can be described by the usual rate laws of reactions in homogeneous or heterogeneous phases. The present software version allows eight measurements to be loaded in the same project. Therefore, the model calculations were carried out separately for each participant of the round-robin test. After loading in the data and before starting the kinetic evaluation, all measurements were desmeared, smoothed and temperature-corrected with regard to slight self heating of the samples. The required correction function for this operation is calculated in the kinetics software from the individual shape of the melting peak of high purity indium. For the chosen heating rates and isothermal temperatures the influence of this correction is very small.

If a participant had made both temperature-programmed and isothermal runs, the corresponding data sets were evaluated separately as well as combined in a common data set.

In a recent paper [11], it is claimed that dynamic and isothermal data sets cannot be described by the same process parameters, if a fitting procedure, based on a model, is used. The results of this round-robin test prove definitely that this statement is not correct. It is correct that under some conditions, dynamic and isothermal measurements cannot evaluated commonly via the same kinetic model. But this is almost always due to the fact that the path of reaction changes with the different measurement conditions. Therefore, the failing of a common analysis is not a deficiency of the procedure of kinetic analysis, but a clear indication that the used model has no general validity for the conditions of all measurements. If, for example, during annealing the diffusion control becomes significant, this must be considered by the kinetic model. Then a common evaluation of dynamic and isothermal measurements will be successful [8].

The main sources for systematic errors are uncertainties in constructing the baseline of the DSC measurement. This is true for both dynamic measurements (caused by temperature intervals of more than 200 K) and for isothermal experiments (caused by measuring times of several hours). Assuming a perfect stability of all device parameters and an ideal correction of possible device asymmetries by subtracting the zero-line from the measurement, one should expect a linear baseline with a small slope towards the endothermic direction. This was concluded from some additional measurements of the participants 3, 4 and 11 using the temperature-modulated DSC [12]. The temperature-modulated DSC allows the direct measurement of the baseline by splitting the total heat flow into two components. The so-called reversing heat flow rate is proportional to the temperature dependent heat capacity $\Delta_r C_p(T)$ of the reaction mixture and corresponds to the required baseline. Considering the repeatability of the heat capacity curves (Fig. 1) within the same laboratory (±2.5 to ±3%) and an only insignificantly worse reproducibility of the different laboratories (±4 to ±5%), one obtains a heat capacity, which increases nearly linear by $0.2\ \mathrm{J\ g^{-1}\ K^{-1}}$ between start and end of the reaction. If one assumes a heating rate of $1\ \mathrm{K\ min^{-1}}$, the calculated offset of the DSC signal between start and end of the reaction amounts to $3.3\times10^{-3}\ \mathrm{W\ g^{-1}}$. This corresponds to about 3% of the maximum heat flow rate caused by the chemical reaction. Because this value is within the errors of the measured heat flow rates, it is possible to assume a nearly constant heat capacity to a fairly good approximation.

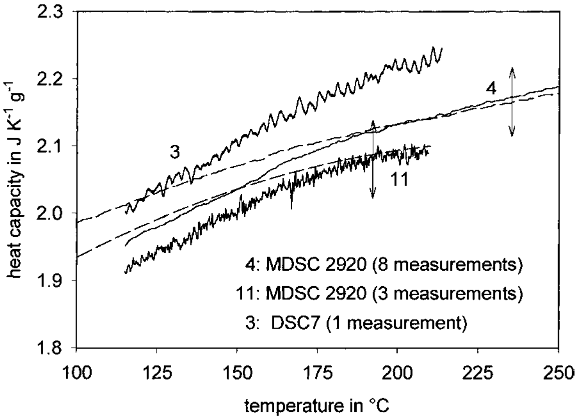

Fig. 1. Heat capacity functions, obtained from MDSC measurements by the participants 3, 4 and 11; solid lines: first run; broken lines: second run; the arrows indicate the error probabilities.

The quality of the DSC curves can be estimated by comparison with the second run of the reaction product, considering temperature ranges without reaction. Possible deviations from the ideal situation are clearly indicated by different curvatures, slopes >3% or even slopes in the false (exothermic) direction. Such deviations were the rule and not the exception. If first and second run showed the same curvature and/or only insignificant differences in the slope, it was assumed that it is justifiable to obtain the curve for the kinetic evaluation by subtraction of both runs. The most probable reasons for curvatures and pronounced slopes are different sample geometries and heat transport conditions for zero-line and measurements.

Three participants had made only the zero-line corrected first run. This is somewhat problematic, because a possible curvature of the baseline can be neither detected nor corrected. In these cases, the baseline was taken as simple straight line between the most probable starting and end points of the reaction.

In two cases, a further uncertainty factor resulted from the necessary pre-treatment period, because the molten reaction mixture could not be cooled down to the start temperature fast enough due to large furnace inertia and/or insufficient cooling capacity. In such cases, the start of the reaction is interfering with a broad melting peak.

The baseline of isothermal measurements is constructed by extrapolating the measured heat flow rate value after completion of reaction. This is correct if there is no noticeable drift of the signal at this moment, of course, in the hope that this is also valid for the total reaction time. Only such curves were included in the kinetic evaluation. For all isothermal

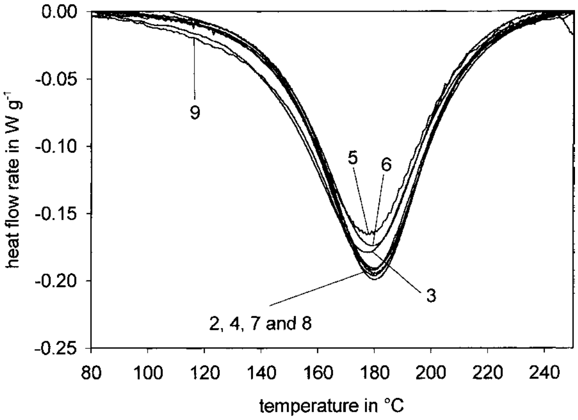

Fig. 2. Start situation for the formal-kinetic evaluation: comparison of the experimental DSC curves at 2 K min^{-1} after applying the most probable base line (curves are shifted and slope corrected); code numbers 2, 4, 7 and 8: rather good comparability; 3, 5, 6 and 9: more distinctive differences.

measurements, the initial phase (60–600 s, strongly dependent on the thermal inertia of the device) could not be evaluated precisely. The necessary correction was made in two steps. In the first one, the rerun of the fully reacted sample was subtracted from the first run. This eliminates the error to the greatest part. Thereafter, the remaining uncertainty during the first 60 s should be strongly reduced by extrapolation of the signal at later reaction times [1].

The Fig. 2 shows dynamic experiments for a heating rate (2 K min^{-1}) chosen by most of the participants. It is representative for the scatter of the DSC curves after applying all mentioned corrections. As already mentioned, the kinetic analysis is a peak shape analysis and therefore one would state a rather unfavourable initial situation. The average heat of reaction for 51 measurements is $-(273\pm15)$ J g^{-1} and is consistent with the published value of -272.2 J g^{-1} [7].

Table 2
The optimum formal-kinetic parameters for all participants of the round-robin test[a]

Code no.	Mode of measurements	log A_1 (s^{-1})	$E_{A,1}$ (kJ mol^{-1})	log A_2 (s^{-1})	$E_{A,2}$ (kJ mol^{-1})	n	m	Correlation coefficient
1	Dynamic	4.92±0.05	70.52±0.43	3.59±0.04	52.72±0.36	1.42±0.01	1.10±0.02	0.999838
2	Dynamic	5.14±0.04	72.97±0.31	3.32±0.03	50.96±0.28	1.49±0.01	1.10±001	0.999915
	Isothermal	5.19±0.04	73.14±0.39	3.75±0.04	54.72±0.38	1.59±0.02	1.10±0.02	0.999796
	Mixed	5.43±0.03	75.27±0.31	3.42±0.03	51.10±0.28	1.49±0.01	1.09±0.01	0.999757
3	Dynamic	5.15±0.04	70.89±0.30	3.33±0.05	50.39±0.43	1.48±0.01	1.29±0.02	0.999787
	Isothermal	5.27±0.03	72.98±0.24	3.29±0.03	49.74±0.28	1.46±0.01	1.14±0.01	0.999871
	Mixed	4.57±0.04	66.68±0.34	3.71±0.05	53.92±0.45	1.49±0.02	1.10±0.02	0.999415
4	Dynamic	5.00±0.06	71.60±0.49	4.01±0.03	56.45±0.31	1.48±0.01	1.01±001	0.999770
	Dynamic	4.80±0.02	69.73±0.17	3.65±0.01	52.84±0.09	1.51±0.01	1.13±0.01	0.999939
	Isothermal	5.12±0.03	72.53±0.25	3.64±0,03	53.03±0.23	1.42±0.01	1.10±001	0.999828
	Mixed	4.95±0.01	70.92±0.14	3.57±0.01	52.18±0.09	1.50±0.01	1.14±0.01	0.999909
5	Dynamic	4.82±0.05	69.10±0.42	3.14±0.06	48.53±0.50	1.47±0.01	1.21±0.02	0.999841
6	Dynamic	4.39±0.04	66.29±0.33	3.50±0.03	51.92±0.30	1.42±0.01	1.09±0.01	0.999890
	Isothermal	3.74±0.05	60.91±0.47	3.97±0.06	56.45±0.49	1.39±0.02	0.96±0.02	0.999774
	Mixed	4.11±0.03	64.14±0.24	3.73±0.03	54.11±0.25	1.41±0.01	1.02±0.01	0.999750
7	Dynamic	4.67±0.06	69.45±0.45	3.88±0.04	55.35±0.32	1.42±0.01	0.96±0.01	0.999838
8	Dynamic	4.39±0.05	66.58±0.36	3.85±0.03	54.74±0.31	1 55±001	1.06±0.01	0.999934
9	Dynamic	3.94±0.12	62.01±0.93	4.19±0.09	57.87±0.82	1.41±0.01	1.13±0.04	0.999049
10	Dynamic	5.27±0.07	74.81±0.69	3.52±0.02	52.49±0.18	1.40±0.01	0.88±0.01	0.999827
11	Dynamic	4.76±0.06	68.42±0.46	3.28±0.05	49.10±0.50	1.73±0.03	1.34±0.03	0.999633

[a] In the mixed mode of evaluation dynamic and isothermal measurements are analysed simultaneously; the standard deviations of parameters are calculated using known procedures [14].

4. Results and discussion

The most simple formal-kinetic model that produces a nearly perfect fit of the scans of all data sets corresponds to a process with the following two competitive reactions:

$$e \underset{2}{\overset{1}{\rightrightarrows}} p$$

$$-\frac{\mathrm{d}e}{\mathrm{d}t} = A_1 \exp\left(-\frac{E_{A,1}}{RT}\right)e^2 + A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)e^n p^m$$

where e and p are concentrations of reactant and product, A and E_A the Arrhenius parameter and n and m are the formal reaction orders.

If during the kinetic calculation the formal order of the reaction 1 is also optimised, then one always obtains values very close to 2. Therefore, it was set constant at 2 for all further calculations. The reaction 2 is autocatalytic, its formal reaction orders n and m are used as free optimisation parameters. The model corresponds approximately to a frequently used overall equation for the epoxy curing, known as Sourour–Kamal equation [13]. In this equation, the formal reaction order for the reaction 1 is identical to n of the reaction 2.

In Table 2, the formal-kinetic process parameters are summarised for the data sets of all participants. Each data set is self-consistent, indicated by high correlation coefficients and a very small sum of least squares. This is valid for both, power compensated and heat flux DSC's. But the differences of corresponding process parameters are relatively high for all participants. This seems to confirm the above-mentioned reservations with respect to the usefulness of the experimental data for a kinetic evaluation. The standard deviations of parameters, determined by using common statistic procedures [14] for one and the same data set, are always much smaller than differences between the parameters of various data sets (Table 2). This apparent contradiction results from the erroneous measurements (Fig. 2), from the correlation between the measurement errors within a single scan (see Appendix A), and above all from the mathematical structure of the Arrhenius equation [15,16]. The correlation matrix shows for both formal reaction steps an extremely high correlation between activation energy and pre-exponential factor. The consequence of this is the so-called apparent compensation effect between the two quantities (Fig. 3). Because the sum of least squares to be minimised during the kinetic modelling is situated in a narrow and very long-extended valley [17], the same fit quality is achieved with large variations of corresponding parameters (log A, E). Likewise, the correlation matrix indicates a pronounced correlation between activation parameters and formal reaction orders n and m. For instance, n and m can be held constant at 1.5 and 1 without any remarkable reduction of the fit quality and only with insignificant changes of the activation parameters (see Appendix B).

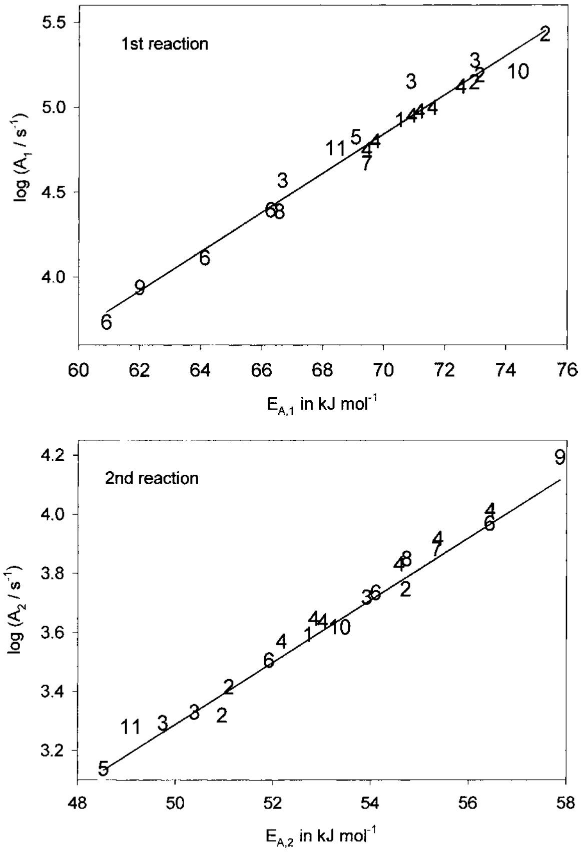

Fig. 3. The effect of the high correlation between the activation parameters (apparent compensation effect) for the two reactions of the formal-kinetic model; repeated code numbers: results for non-isothermal, isothermal and mixed data sets, compare Table 2.

Of course, the high correlation between all model parameters means a very unfavourable situation. On the other side and fortunately, there are no conse-

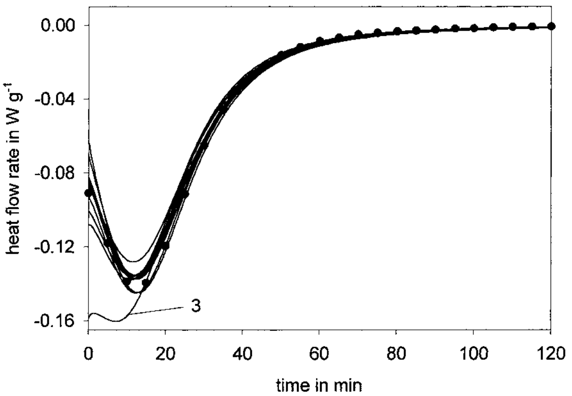

Fig. 4. Prediction of isothermal heat flow rate at 167°C, using all individual parameter sets for the non-isothermal data sets (solid lines) and comparison with the experiment (points, measured by no. 4); distinctive deviations only for participant 3.

quences for the practitioner with respect to predictions of the reaction behaviour. This fortunate situation is confirmed by the fact that if each data set is fitted with the parameter set of the other data set, the fit has practically the same perfect quality. But we think that using the individual parameter sets, the results obtained for predicted isothermal heat flow rate curves (Fig. 4) and the corresponding conversion–time curves (Fig. 5) are much more instructive. Similar results are obtained also for other isothermal temperatures, temperature programmed runs and combined temperature–time regimes. The differences among all curves are always very small and the agreement with

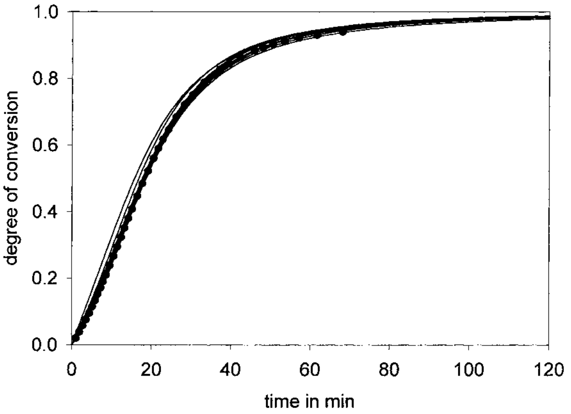

Fig. 5. Predicted and measured conversion–time curves, see Fig. 4.

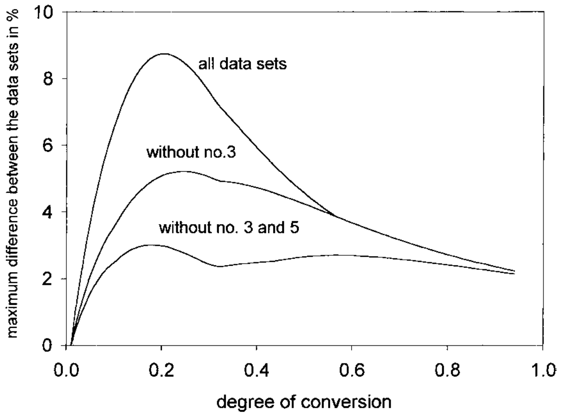

Fig. 6. Maximum differences between the predicted degrees of conversion for all participants of the round-robin test.

the measured curve is very good. This can also be derived from Fig. 6 which summarises the maximum percentual differences for a certain degree of reaction. If one neglects the two strongly scattering parameter sets 3 and 5, the differences are generally smaller than 3%! This result is very pleasant for the practician. In spite of all individual random and systematic errors of the raw material, the formal-kinetic evaluation allows reliable predictions of the reaction behaviour.

The experiments of the round-robin test were planned and carried out with different heating rates. A single curve evaluation is meaningless [10]. This statement also holds well if a number of curves with the same heating rate but from different laboratories is included in a data set. Dependent on the chosen combination (number and origin of the included data sets, used heating rate) very different and extremely scattering results are obtained. If on the other hand at least two differing heating rates are used in such calculations, the solutions become stable and comparable with the values in Table 2. The more reaction curves with strongly varying heating rates are measured, the more stable are the results of a formal-kinetic evaluation.

5. Conclusions

The existing measurement technique and the use of modern kinetic evaluation allow routinely and independent of the device type of the DSC.

- the measurement of polymer producing reactions within an acceptable period of 2–3 days, using at least three heating rates or three isothermal temperatures;
- the selection of the simplest and most appropriate formal-kinetic model and the reliable estimation of its activation parameters;
- reliable predictions of the reaction behaviour, using any complex temperature–time regimes.

The simultaneous evaluation of non-isothermal and isothermal data sets is not only possible but even highly recommended. Always present statistical and systematic measurement errors and mathematical artefacts do not hinder the great use of such investigations for the practitioner. The DSC as well as other thermoanalytical methods in combination with multivariate kinetic analysis are now a powerful tool for the process prediction and optimisation.

6. Participants of the round-robin test[1]

B. Benzler, Mettler-Toledo-GmbH, D-35353 Gießen; E. Born, FhG-IFAM, D-28359 Bremen; M. Dohn, C. Froschauer, BMW AG, Sparte Labor SL 23, D-84122 Dingolfing; H.J. Flammersheim, Friedrich-Schiller-Universität Jena, Chemische Fakultät, D-07743 Jena; M. Gedan-Smolka, lnstitut für Polymerforschung Dresden, D-01069 Dresden; L. Häußler, G. Pompe, Institut für Polymerforschung Dresden, D-01069 Dresden; E. Hempel, Martin-Luther-Universität Halle, FB Physik, D-06099 Halle; S. Knappe, Netzsch-Gerätebau GmbH, D-95100 Selb; K. Könnecke, Elenac GmbH, Werk Frankfurt, Industriepark Höchst, D-65926 Frankfurt; H. Utschick, M. Wiese, TA Instruments Deutschland, Applikationslabor, D-63755 Alzenau: C. Schick, Universität Rostock, FB Physik, D-18051 Rostock.

Acknowledgements

I would like to thank J. Opfermann, Selb for numerous intensive and fruitful discussions and for his permanent readiness to modify and improve the kinetics software according to newer points of view.

Appendix A

In all least squares procedures, there are two preconditions:

Condition 1: The weighting of the residues should be done in such a way that the weights are inversely proportional to the square of the expected deviations.

$$\chi^2 = \sum_m \sum_i \frac{(y_{m,i} - c_{m,i})^2}{s_y^2 - s_c^2}$$

where $y_{m,i}$: measured data; $c_{m,i}$: calculated values; s_y^2: standard deviation of measured data; s_c^2: standard deviation of calculated data; m: number of measurements; i: number of data points. Then the sum of least squares is transformed to χ^2.

Condition 2: The residues are uncorrelated.

In general, in thermoanalytical measurements information regarding to the expected deviations is not taken into account. But the experience during the last years has shown that it is recommended to apply a weighting inversely proportional to the square of the (absolute) maximum of the single scan. In the result, the scans with smaller heating rates exert the same influence than scans with higher heating rates.

If the condition 2 is not fulfilled then the values of standard errors of the optimised parameters, estimated by well-known routines [14], are too small [18]. A raw estimation of the underestimation is given by the formula

$$f = \frac{1}{\sqrt{1-\rho^2}}$$

The variable ρ is the value of auto-correlation, estimated by means of Durbin–Watson analysis [19,20]. In general, a strong auto-correlation of the residues is observed, so that the factor f exceeds the value of 10.

Appendix B

If for data sets of all participants the parameters n, m, $E_{A,1}$ and $E_{A,2}$ are fixed at constant values (1.0, 1.5, 71 and 56 kJ mol^{-1}) and only $\log A_1$ and $\log A_2$ are

---

[1] The sequence of the participants is not identical with the code number.

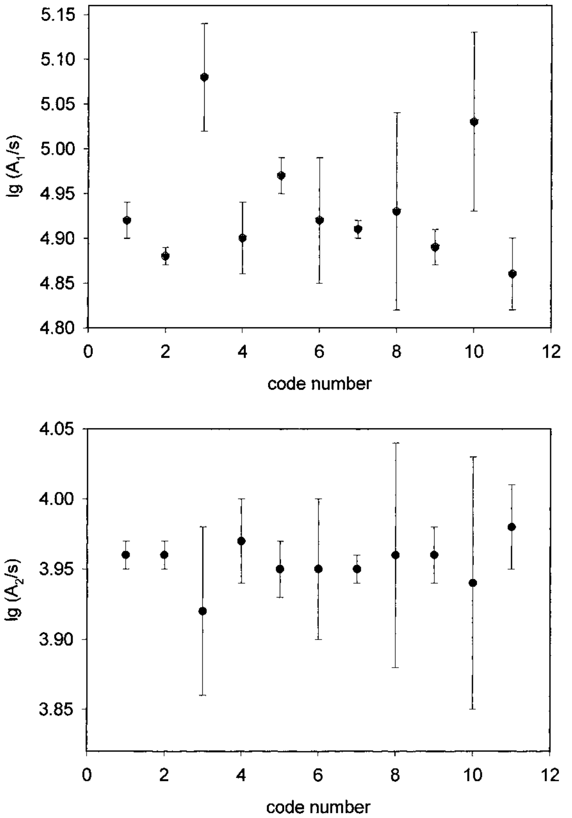

Fig. 7. Variation of $\log A_1$ and $\log A_2$ at fixed values for the activation energies ($E_{A,1}$=71 and $E_{A,2}$=56 kJ mol^{-1}) and fixed values for the formal reaction orders (n=1.0 and m=1.5) for all data sets. The standard deviations are multiplied with the factor f, defined in Appendix A.

handled as freely varying parameters then all individual data sets are fitted without remarkable loss of the fit quality. Fig. 7 shows the values and deviations of the pre-exponentials $\log A_1$ and $\log A_2$. All calculated values overlap within their error limits for the reaction 2. This is also valid for the reaction 1 with exception of the data sets belonging to the code nos. 3, 5 and 10. Obviously and not unexpectedly, the discussed uncertainties in constructing the peak baseline influence primarily reaction 1. This is also reflected by somewhat stronger deviations of model calculations for low degrees of conversion (above all for code no. 3, compare Figs. 4 and 6).

The high correlation between model parameters, especially between $\log A$ and E, is a result of the mathematical structure of the Arrhenius equation. There is only one possibility to improve the confidence of these parameters: the enlargement of the working temperature interval. For dynamic measurements this means that at least a variation of heating rates by a factor of 10 is recommended. It is worth to notify that the same problems are existing also in model-free kinetic analysis. But because the calculation of activation energy and pre-exponential is consecutively in this procedure, these problems are not visible.

References

[1] G. Höhne, W. Hemminger, H.J. Flammersheim, Differential Scanning Calorimetry — An Introduction for Practitioners, Springer, Berlin, 1996.

[2] J. Opfermann, J. Therm. Anal. Calorimetry, 60 (2000) 641.

[3] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.

[4] J. Flynn, L.A. Wall, Polym. Lett. 4 (1966) 232.

[5] S. Vyazovkin, Int. J. Chem. Kinet. 28 (1996) 95.

[6] J. Opfermann, E. Kaisersberger, H.J. Flammersheim, J. Thermochim. Acta, Calorimetry, submitted for publication.

[7] J.E. Klee, R.E. Grützner, H.H. Hörhold, H.J. Flammersheim, Macromol. Chem. Phys. 199 (1998) 1603.

[8] H.J. Flammersheim, J. Opfermann, Thermochim. Acta 337 (1999) 141.

[9] S.M. Sarge, W. Hemminger, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Eysel, Thermochim. Acta 247 (1994) 129.

[10] J. Opfermann, G. Wilke, J. Jung, W. Ludwig, S. Hagen, M. Gebhardt, E. Kaisersberger, in: Therm. Analysenverf. in Industrie und Forschung, FSU Jena, 1991, 51 pp.

[11] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Chem. Phys. 200 (1999) 2294.

[12] M. Reading, A. Luget, R. Wilson, Thermochim. Acta 238 (1994) 295.

[13] S. Sourour, M.R. Kamal, Thermochim. Acta 14 (1976) 41.

[14] P.R. Bevington, D.K. Robinson, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1994.

[15] N. Koga, J. Šestac, Thermochim. Acta 182 (1991) 201.

[16] N. Koga, J. Šestac, J. Therm. Anal. 37 (1991) 1103.

[17] N. Eisenreich, J. Therm. Anal. 19 (1989) 289.

[18] E. Förster, B. Rönz, Methoden der Korrelations — und Regressionsanalyse, Die Wirtschaft, Berlin, 1979.

[19] J. Durbin, G.S. Watson, Biometrika 37 (1950) 409.

[20] J. Durbin, G.S. Watson, Biometrika 38 (1951) 159.