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Thermochimica Acta 452 (2007) 59–64
thermochimica acta
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Thermokinetic analysis of two-step curing reactions in melt
Part I. Investigation of low molecular model systems

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Received 18 May 2006; received in revised form 29 September 2006; accepted 4 October 2006

Abstract

Kinetic investigations of thermo-controlled two-step reactions between an uretdione cross-linker and OH-groups are undertaken. Non-isothermal DSC measurements are chosen for the determination of the kinetic parameters (E, A, n) using of THERMOKINETICS software. The system can be described very accurately with a four-step kinetic model of consecutive reactions. On the basis of the kinetic model and parameters the realization of the first reaction step, which is the formation of the allophanate network is simulated. Finally, the result of the calculated progress of the reaction is evaluated by FT-IR and isothermal DSC measurements.

Keywords: DSC; Kinetics; Two-step curing; Uretdione cross-linker

1. Introduction

The kinetic analysis is a useful tool for the characterization of the curing behavior of reactive polymeric systems. Besides the evaluation of a certain curing mechanism kinetic analysis is of certain technical importance. On the basis of a kinetic model and kinetic parameters, the reaction behavior at different temperature/time regimes can be predicted [1–5]. The development of kinetic analysis on the basis of multivariate non-linear regression has established the determination of very reliable results [6]. DSC measurements are a favored instrument for the kinetic analysis due to their experimental simplicity. In a relatively short time, a number of DSC measurements can be carried out without time-consuming sample preparation. In view of the optimization of the curing process of powder coatings a large number of investigations were carried out in this direction [7–10].

Most of the investigated powder coatings are epoxy systems as well as PUR systems with externally blocked isocyanate cross-linkers. A completely new two-step curing mechanism based on internally blocked isocyanate cross-linkers has been reported a few years ago [11]. In the presence of a suitable catalyst the reaction between a polyol and an uretdione cross-linker occurs via an allophanate structure (Fig. 1). This reaction is thermo-controlled and can be realized at temperatures below 150 °C. Raising the curing temperature enables the transformation of the allophanate into the urethane network. In consideration of the volatile organic compounds (VOC) guidelines this reaction exhibits a great potential for powder coatings since no emissions are set free. In the present paper, we report on the kinetic analysis of the thermo-controlled two-step curing reaction between an uretdione cross-linker and OH-groups in melt.

2. Experimental

2.1. Materials

1,8-Octanediol was purchased from Fluka (≥98%) and used without further purification. The commercial uretdione cross-linker Vestagon® BF 1320 (NCO-equivalent: 315.6 g/mol, T_g: 73.0 °C) was donated by Degussa AG and the zinc(II)-acetylacetonate catalyst TEGOKAT® 623 was provided by Goldschmidt TIB GmbH.

2.2. Sample preparation

The components of the low molecular model systems were directly weighed into the vessel of a laboratory mini mill (Fritsch

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doi:10.1016/j.tca.2006.10.006

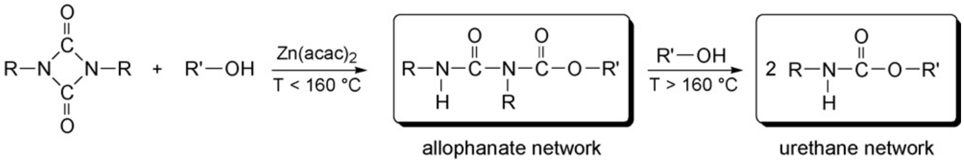

Fig. 1. Two-step curing mechanism of the catalyzed reaction between an uretdione cross-linker and OH-groups in melt according to [11].

Pulverisette 23) and mixed twice for 2 min at a frequency of 50 Hz. Then, the samples were dried in vacuo at 25 °C for 24 h in the presence of P_2O_5. All the samples were stored in a desiccator over P_2O_5 in a refrigerator.

2.3. DSC measurements

All non-isothermal and isothermal DSC measurements were run on a DSC Q1000 from TA Instruments. The device was calibrated with a pure indium sample according to the guidelines of the PTB Braunschweig, Germany (onset temperature of the melting peak: 156.6 °C, heat of fusion: −28.6 J/g). Heating rates of the non-isothermal runs were annotated directly in the corresponding diagrams or tables. The sample masses for the non-isothermal measurement were approximately 5 mg. The measurements were carried out using standard aluminum pans with a pierced lid.

The temperatures of the isothermal measurements were reached applying a temperature ramp of 100 K/min.

2.4. Kinetic analysis

The kinetic parameters of the molecular model system were determined using the NETZSCH THERMOKINETICS software. For calculations the raw DSC data were imported as ASCII files and corrected by the software using device-specific correction parameters.

2.5. FT-IR measurements

FT-IR measurements were recorded on a Bruker Tensor 27 FT-IR spectrometer equipped with an ATR unit.

3. Results and discussion

The simulation of the reaction behavior of curing processes enables the reduction of time-consuming curing experiments. However, it is difficult to analyze the curing reaction in a real powder coating composition due to its complexity. The pure curing reaction is superposed by many side processes. Therefore, the investigations are carried out on low molecular model systems in which the hydroxyl functionalized polyester is replaced by 1,8-octanediol. The model systems contain, furthermore, the commercial uretdione cross-linker Vestagon® BF 1320 and 1 wt.% of zinc(II)-acetylacetonate as catalyst.

The kinetic studies of the two-step curing reaction are performed using the NETZSCH THERMOKINETICS software. For the determination of the kinetic parameters (A, E, n) non-isothermal DSC measurements with different heating rates are considered. Here, A is a pre-exponential factor; E the activation energy; n is the reaction order. Fig. 2 shows the typical signals for all the transitions and reactions of the model system. Besides the melting peak of the 1,8-octanediol at approximately 59 °C a second endothermic signal is observed at 79 °C. This can be assigned as the enthalpy recovery of the glass transition of the uretdione cross-linker Vestagon® BF 1320 (T_g: 73 °C). The two exothermic signals at 125.0 and 182.9 °C represent the two steps of the curing reaction, where the first peak results from the allophanate step and the latter one from the transformation to the urethane network.

3.1. Non-isothermal DSC measurements

The use of DSC scans with different heating rates ensures the adaptability of the kinetic model over a broad temperature range. For our investigations, we consider five different heating rates from 1.25 up to 20 K/min where the used heating rate is doubled with each step. The resulting DSC curves are shown in Fig. 3. As expected the signal for the melting of the system is not influenced by the heating rates. In contrast, we detect a shift of the reaction maxima to higher temperatures with increasing heating rates. The reactive system is slow, hence it cannot respond immediately to the higher heating rates. Furthermore, the separation of both reaction peaks depends also on the heating rate. This phenomenon indicates that the activation energy for the allophanate reaction is lower than that for the following reaction to the urethane network.

As shown in Fig. 3 and Table 1 both reaction peaks are separated better at lower heating rates.

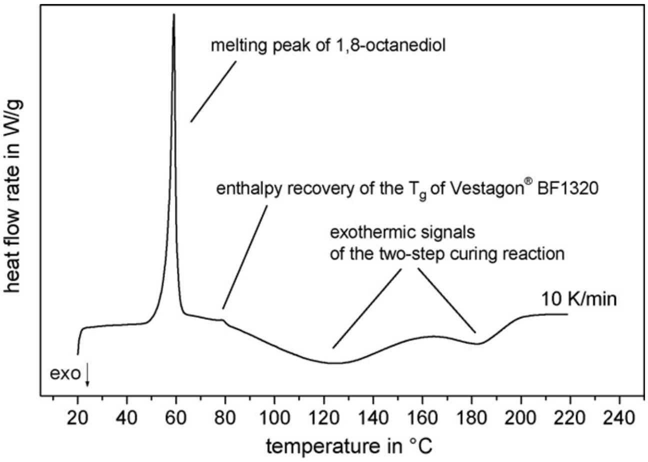

Fig. 2. Non-isothermal DSC measurement of the model system (heating rate: 10 K/min).

Table 1
Results of the non-isothermal DSC measurements with different heating rates

Measurement	Heating rate (K/min)	T_{max1} (°C)	T_{max2} (°C)	ΔH (J/g)	T_g (°C)[a]	Mass loss (%)
1	1.25	90.1	159.4	144.5	70.7	3.9
2	2.5	102.4	165.0	143.8	71.1	2.4
3	5	116.6	179.4	138.3	72.5	1.4
4	10	125.0	182.9	142.1	71.5	1.0
5	20	138.8	188.9	165.0	72.5	1.1

[a] Glass transition of the cured system, determined in a second heating run.

3.2. Determination of the kinetic parameters

The determination of the kinetic parameters using the THERMOKINETIC software implies the presetting of an appropriate kinetic model and furthermore the knowledge of different starting parameters such as activation energy, pre-exponential factor and proportion of the partial reaction to the complete chemical process. These parameters should be obtained without the knowledge of the real kinetic model; therefore, we use a model-free estimation of the activation energy by the aid of an isoconversion method. A very useful tool is the Friedman analysis [12] of non-isothermal measurements provided that no competitive reactions do occur. This fact can be taken for granted since the reaction enthalpies of the two-step reactions are almost equal for all heating rates. The results of the Friedman analysis and the herefrom deduced energy plot are shown in Figs. 4 and 5. Since the Friedman plot shows no less than two maxima the selected kinetic model should have at least two steps. Furthermore, the energy plot also shows two different levels of activation energies. The activation energy of the first reaction that can be assumed as the allophanate reaction is about 75 kJ/mol. The value of the partial area of this first reaction step is half of the overall peak area. The following reaction can be assigned an activation energy of about 140 kJ/mol. These results reflect the observed decrease of the peak separation at higher heating rates.

The consideration of the melting process into the kinetic model is advantageous. Especially, at low heating rates the beginning of the allophanate reaction is superimposed by the preliminary melting that makes it impossible to separate clearly the two processes.

The measured data are fitted by the software using a multivariate non-linear regression. This type of analysis carried out by the software is a curve shape analyis. The software applies a

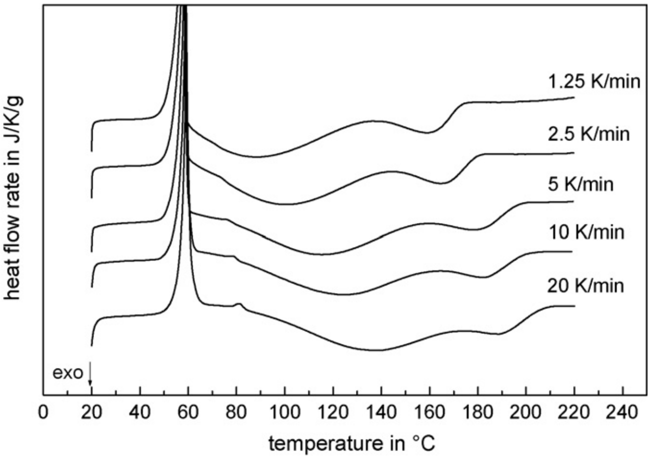

Fig. 3. Curves of non-isothermal DSC measurements with different heating rates.

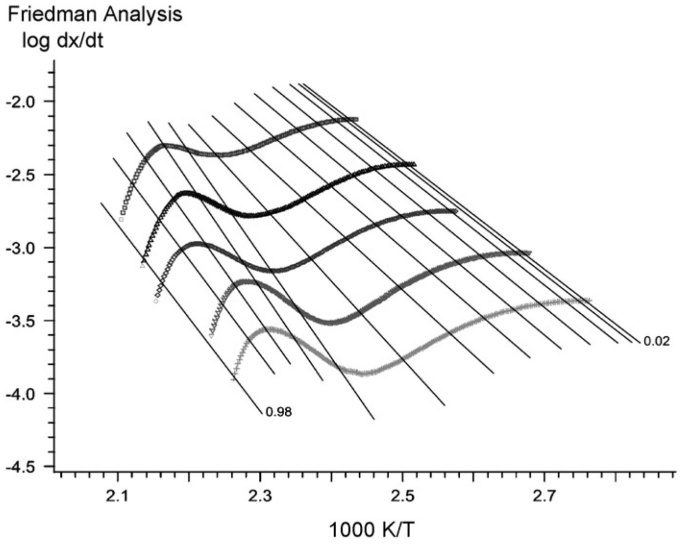

Fig. 4. Results of the Friedman analysis.

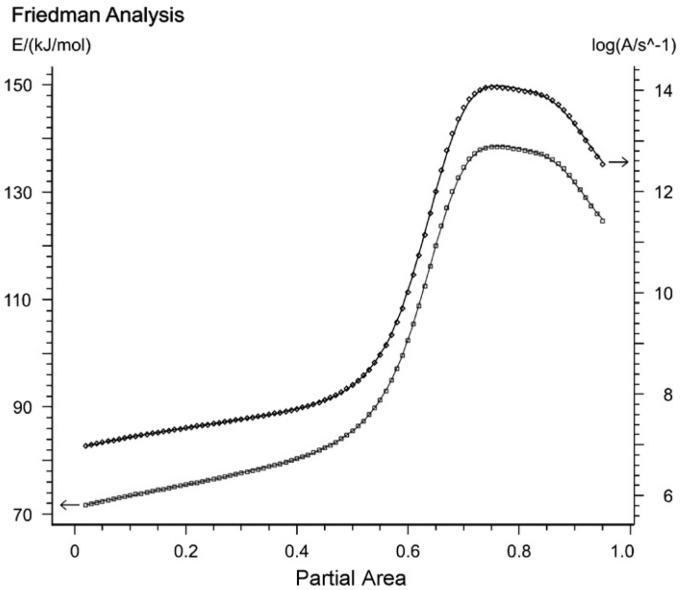

Fig. 5. Energy plot of the Friedman analysis.

Table 2
Kinetic parameters determined by applying a four-step kinetic model with consecutive reactions (A → B → C → D → E)

	Kinetic parameters	S.D.
$\log A_1$ (s^{-1})	111.1	0.48
E_{a_1} (kJ/mol)	709.5	3.27
n_1	1.27	0.22
$\log A_2$ (s^{-1})	3.8	1.51
E_{a_2} (kJ/mol)	36.4	9.81
n_2	1.14	0.17
$\log A_3$ (s^{-1})	7.9	0.35
E_{a_3} (kJ/mol)	76.3	2.54
n_3	1.47	6.55×10^{-2}
$\log A_4$ (s^{-1})	14.5	0.47
E_{a_4} (kJ/mol)	141.7	4.13
n_4	0.86	5.98×10^{-2}
Foll-react 1[a]	−0.35	1.49×10^{-2}
Foll-react 2[b]	−0.12	0.48
Foll-react 3[c]	1.13	3.27
Area 1 (J/g)[d]	−99.7	0.22
Area 2 (J/g)[d]	−92.0	1.51
Area 3 (J/g)[d]	−88.1	9.81
Area 4 (J/g)[d]	−86.9	0.17
Area 5 (J/g)[d]	−86.0	0.35

[a] Share of reaction step 1 (A → B) in the total reaction enthalpy (value of the overall reaction = 1; negative value describes an endothermal process).

[b] Share of reaction step 2 (B → C) in the total reaction enthalpy.

[c] Share of reaction step 3 (C → D) in the total reaction enthalpy; the share of reaction step 4 (D → E) is given by 1-Σ(foll-react).

[d] Area 1–area 5: calculated reaction enthalpies of the DSC curves with different heating rates from 20 K/min to 1.25 K/min.

Runge–Kutta process in a modified Marquardt procedure. A system of differential equations based on the differential equations of the relevant reaction types is solved [6].

The choice of a four-step kinetic model with consecutive reactions of *n*th order (*q*:*f*, *f*, *f*) results in a very good fit with a correlation coefficient *r* of 0.9671. In the reaction code (*q*:*f*, *f*, *f*) *q* stands for a four-step reaction and *f* assigns the reaction steps 2–4 as following reactions. The formal kinetic reaction model can be written as A → B → C → D → E. The determined kinetic parameters are listed in Table 2 and Fig. 6 shows the results of the non-linear regression. However, the slight deviation of the correlation coefficient from maximal fitting quality can be assigned to the difference between the calculated and measured data in the range of the melting peak and the aging peak of the hardener.

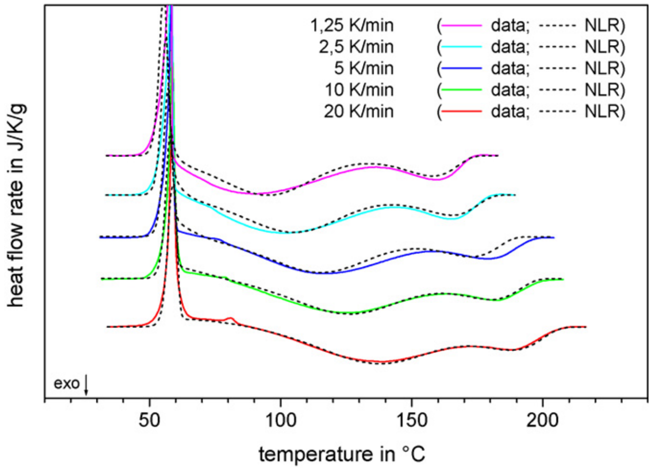

Fig. 6. Results of the multivariate non-linear regression of the model system with a four-step kinetic model *q*:*f*, *f*, *f* (A → B → C → D → E).

The high activation energy of 709 kJ/mol for the first reaction can be accepted since in reality it represents the melting process and is only considered in the formal kinetic model as a chemical reaction. Also the second endothermic reaction step is added to get a better fit of the aging peak of the hardener. These values are only of mathematical meaning and can be neglected for the interpretation of the results. The real chemical process is considered in the last two reaction steps of the kinetic model.

The share in the allophanate reaction (A → D) is about 65% of the overall reaction, which is in accordance with the determined partial area of the first process given by the Friedman analysis. Furthermore the activation energy of the first reaction step is 76 kJ/mol. As discussed before, the activation energy for the following reaction should be higher indicated by the better peak separation for lower heating rates and the result of the Friedman analysis. An activation energy of 142 kJ/mol is obtained for the further transformation to the urethane product.

The non-linear regression on the basis of the chosen kinetic model results in reaction enthalpies in the range of −86 to −100 J/g. These values differ from the determined reaction enthalpies gained from the DSC curves because the calculated peak areas include also the melting peaks.

The good fitting of the curves and the agreement of the model-free and calculated activation energies for the two-step reaction implies that the chosen formal kinetic model describes the system very accurately. In the following, predictions of the reaction behavior are made simulating different reaction conditions. Based on these results we prove the accuracy of the kinetic model for the description of the chemical process.

3.3. Prediction and verification of the reaction behavior on the basis of the determined kinetic model

The results of the non-linear regression and the choice of the four-step kinetic model are proved simulating different reaction conditions.

However, at first glance it is not possible to assign the components of the formal kinetic model to the appropriate chemical products. Only the final product E is definitely the urethane network. As we consider a formal kinetic analysis not all intermediate products are chemically traceable. Both reactions of the investigated system are thermally controlled so it is possible to separate them applying appropriate reaction conditions. The non-isothermal DSC curve with a heating rate of 10 K/min shows unambiguously that the allophanate step occurs at temperatures of about 120 °C. Isothermal simulation of the reaction at 120 °C shows that the main product is component D, so we can identify D as the allophanate. Further isothermal predictions are made from 70 to 150 °C, where the reaction time is fixed for 30 min. The results of these predictions are shown in Fig. 7 where the concentration of component D is plotted against the isothermal reaction temperature. The curve shows a maximum at 115 °C

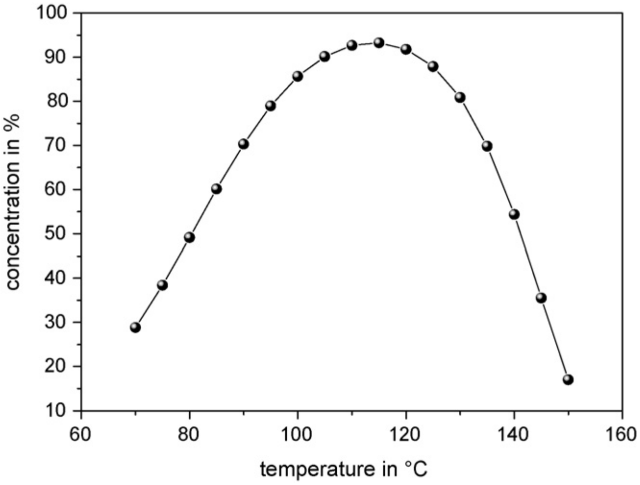

Fig. 7. Concentration of component D (allophanate) after isothermal treatment for 30 min.

where the concentration of the allophanate is 93.22%. Hence, the rise of the allophanate concentration results in the insertion of the 1,8-octanediol into the uretdione cross-linker. At about 115 °C, most of the uretdione has been transformed and the second reaction step occurs with a higher reaction rate whereas the rate of the first reaction step diminishes. Then the allophanate reacts with further 1,8-octanediol to the final urethane network, as a result its concentration decreases. At 150 °C, almost all the allophanate is converted to the urethane.

Finally, it has to be checked whether the predictions reflect the true reaction course. For this purpose, FT-IR spectroscopy is a very useful tool. Isothermal DSC measurements are carried out applying the pre-assigned conditions. Then the reaction products are investigated by FT-IR spectroscopy by observing the characteristic uretdione band at 1771 cm^{-1}. The results are illustrated in Fig. 8. The uretdione band decreases significantly upon raising the temperature for the isothermal treatment of the sample. Only a slight absorption of the uretdione can be found after heating at 125 °C.

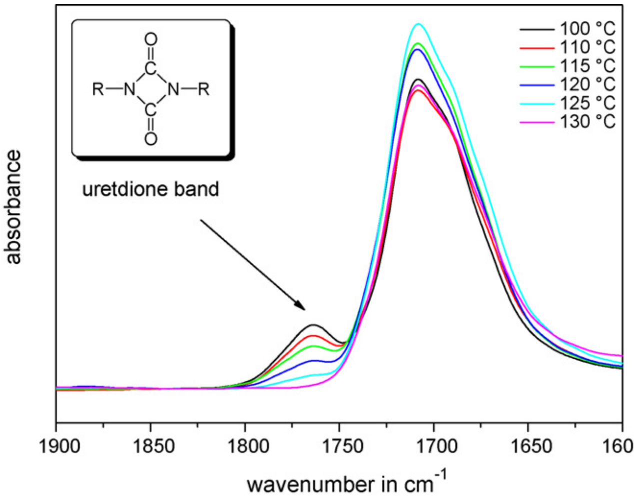

Fig. 8. FT-IR spectra of the model system after 30 min of isothermal treatment at various temperatures.

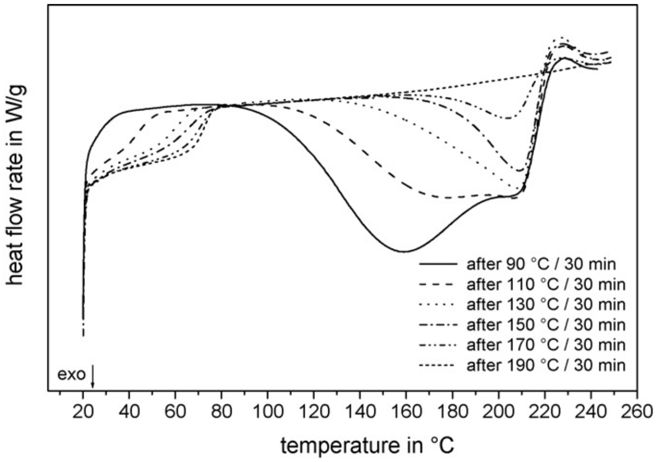

Fig. 9. Non-isothermal DSC measurements of the model systems after heating the sample at different temperatures.

A further method to verify the kinetic model is to cure the sample in an isothermal DSC experiment. The remaining reaction enthalpy can be determined in a subsequent non-isothermal DSC measurement. In Fig. 9, the results of the DSC curves of these non-isothermal DSC runs are shown. Both reactions of the investigated model are thermo-controlled, so we can separate the allophanate step and the urethane step. After heating the sample at 90 and 110 °C the allophanate step can be detected in the DSC curve as a first reaction maximum. At 130 °C only the second maximum for the urethane reaction is found. This enforces the conclusion, that the first reaction step is finished at temperatures below 130 °C. These results are in accordance with the predictions made on the basis of the four-step kinetic model. So, the chemical process can be described very accurately with the determined kinetic parameters and the kinetic model.

4. Conclusions

The thermo-controlled two-step reaction between uretdione and OH-groups can be described by a four-step kinetic model with four consecutive reactions of *n*th order. Although a formal kinetic model is regarded, it is possible to assign clearly the allophanate reaction, which can be separated applying appropriate reaction conditions. These conditions are determined using the calculated kinetic parameters and the kinetic model. Component D can be identified unambiguously as the allophanate, which is verified applying FT-IR spectroscopy and isothermal DSC experiments. The first reaction stage can be realized at temperatures of about 120 °C. The formal kinetic analysis of the investigated low molecular model system enables the prediction of its reaction behavior. Due to this result, it should be possible to extend the investigations to polymeric model systems, which consist of the reactive components of a polymeric system.

Acknowledgements

The authors thank the German Research Foundation (DFG, project HE 4466/1-1) for the financial support of this work. Furthermore, we thank the Degussa AG for donating the uretdione cross-linker Vestagon® BF 1320 and Goldschmidt TIB GmbH for supplying the zinc(II)-acetylacetonate catalyst TEGOKAT® 623. For the discussion and solution of problems working with the THERMOKINETICS software, we thank Dr. E. Moukhina and Dr. G. Kaiser from NETZSCH Gerätebau GmbH.

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