Thermochimica Acta 499 (2010) 160–165

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermokinetic analysis of two-step curing reactions in melt: Part II. Investigation of polymeric model systems

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ARTICLE INFO

Article history:
Received 25 May 2009
Received in revised form
10 December 2009
Accepted 14 December 2009
Available online 22 December 2009

Keywords:
DSC
Formal kinetic analysis
Isoconversional analysis
Two-step curing
Uretdione cross-linker

ABSTRACT

Thermo-controlled two-step curing reactions in melt are of particular interest for reactive polymeric systems. These reaction types are e.g. observed in thermal curing polyurethane (PUR) powder coatings. Illustrated by the uretdione/OH-reaction we describe the formal kinetic analysis of two-step curing processes in melts. The two reaction steps (allophanate- and uretdione reaction) can be separated applying special reaction conditions.

The curing reaction of polymeric model systems was monitored by non-isothermal DSC measurements with different heating rates. On the basis of these data the kinetic parameters (activation energies, pre-exponential factors and reaction orders) were determined and analyzed with the aid of formal kinetic analysis. Our investigations are of particular interest in view of the simulation of curing processes of low temperature powder coatings. In this way, time consuming curing experiments can be minimized.

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 also of technical importance. On the basis of a kinetic model and corresponding kinetic parameters the reaction behavior at different temperature/time regimes can be predicted [1–4]. Considerable work on the isoconversional cure kinetics of epoxy systems has been done by Vyazovkin and Sbirrazzouli and co-workers in the 1990s [5–9]. The development of the kinetic analysis on the basis of multivariate non-linear regression has established the determination of very reliable results [10]. Hereby, DSC measurements are a favored instrument for the kinetic analysis due to their experimental simplicity. In a relatively short period of 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 [11–17]. The cross-linking kinetics of a cold-setting polyurethane system for injection molding has been investigated by Vergnes et al. [18]. This process could be described using a three-step model.

Recently, a completely new two-step curing mechanism based on internally blocked isocyanate cross-linkers has been reported [19,20]. 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 performed at temperatures below 150 °C. Raising the curing temperature enables the transformation of the allophanate into the urethane network. In view of the volatile organic compounds (VOC) guidelines this reaction exhibits a great potential for powder coatings since no emissions are set free. In a previous paper we investigated the two-step curing reaction on the basis of low molecular model systems [21]. In the prevailing paper we expanded our investigations on the formal kinetic investigation of the curing reaction of an aliphatic hydroxyl functionalized polyester with a commercial uretdione cross-linker in melt.

2. Experimental

2.1. Materials

All substances were used without further purification. Tetrabutylammonium bromide (≥98%, Fluka). TEGOKAT® 623 was donated by Goldschmidt TIB. Uretdione cross-linker Vestagon® BF 1320 (T_g 73 °C; NCO-eqiuvalent 300 g/mol) was donated by Evonik Industries AG. Araldite PT 910® (epoxy equivalent 147 g/mol) was donated by Huntsman. Hydroxy functionalized polyester

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doi:10.1016/j.tca.2009.12.006

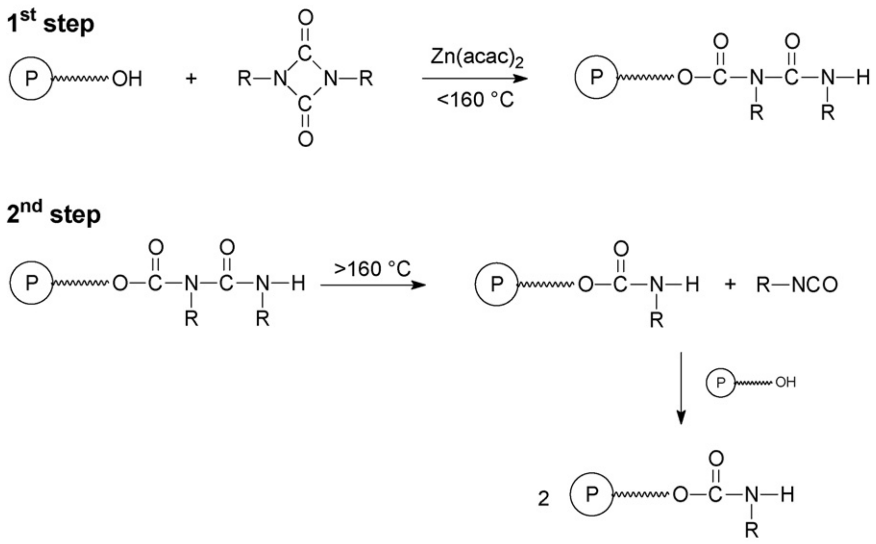

Fig. 1. Two-step curing mechanism of the catalyzed reaction between an uretdione cross-linker and OH groups in melt according to [19].

DLE 04-210 (T_g 43 °C; acid value 4.5; hydroxyl number 57.0) was donated by Synthopol Chemie.

2.2. Sample preparation

The substances were homogenized in a Haake Rheomix 600p melt mixer at 80 °C with a rotational frequency of 30 rpm. At first, the polyester, the uretdione cross-linker and the epoxide were added to the mixer and melted. Then the catalysts were added and the melt was mixed for 3 min. The resulting melt was poured into liquid nitrogen and then milled. Then the pulverized samples were dried at 25 °C in vacuo for 24 h and stored in a desiccator over P_2O_5.

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 approx. 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.

3. Results and discussion

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 is the activation energy and n the reaction order.

The examined polymeric model systems consist of the reactive components of a polyurethane powder coating. The used aliphatic polyester DLE 04-210 contains some residual carboxylic end groups which deactivate the curing catalyst zinc(II)–acetylacetonate. Therefore, it is necessary to transform these endgroups by an esterification using an epoxide (Araldite PT 910) and tetrabutylammonium bromide as catalyst. This reaction occurs *in situ* prior the two-step curing process. Due to the low amount of carboxylic groups in the polyester this exothermal reaction is not observed in the thermograms of the non-isothermal DSC experiments. Fig. 2 shows the typical signals for all the transitions and reactions of the polymeric model system. At 40 °C the glass transition of the unreacted polymeric model system is observed. The exothermic signals at 144.6 and 171.9 °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

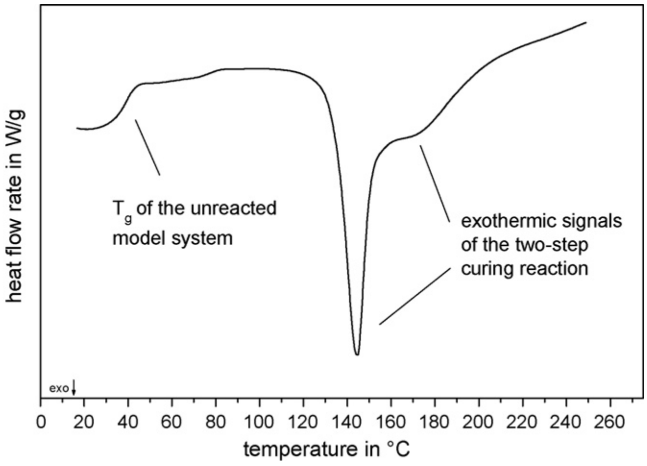

Fig. 2. Non-isothermal DSC measurement of the polymeric model system (heating rate: 10 K/min).

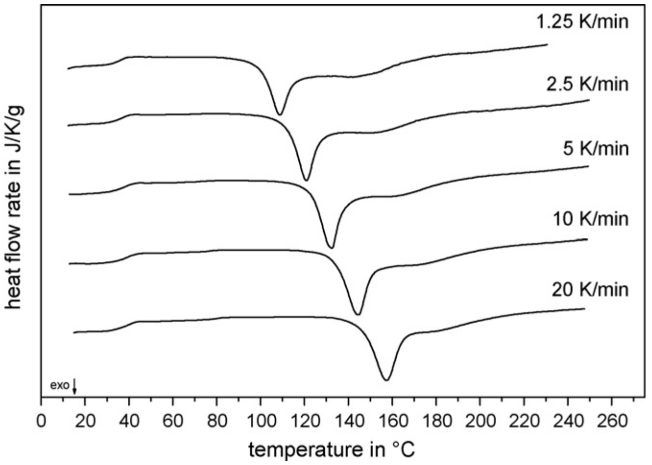

Fig. 3. Curves of non-isothermal DSC measurements with different heating rates.

each step. The resulting thermograms of the different DSC measurements are shown in Fig. 3 and the results are summarized in Table 1. The glass transition of the unreacted model system is not influenced strongly by the different heating rates. In contrast, we detect a significant shift of the two reaction maxima to higher temperatures with increasing heating rates. The beginning of the curing reaction depends not only on the temperature but also on the time. Hence, there is a dependence of the course of the reaction on the heating rate of the measurement. Low heating rates result in an earlier start of the reaction. Furthermore, the separation of both reaction peaks depends also on the heating rate. The two exothermal signals for the two-step curing reaction are separated better at lower heating rates. This situation indicates that the activation energy for the allophanate reaction is lower than that for the following reaction to the urethane network.

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 reactions 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 [22] of non-isothermal measurements, provided that no competitive reactions do occur. In the investigated model system the OH-functionalized polyester can only react with the uretdione cross-linker to the allophanate which is converted in a consecutive reaction with a further OH group of the polyester into the urethane. 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. The pre-exponential factor *A* in Fig. 5 was calculated by the THERMOKINETICS software out of the isoconversional lines, assuming a first order reaction.

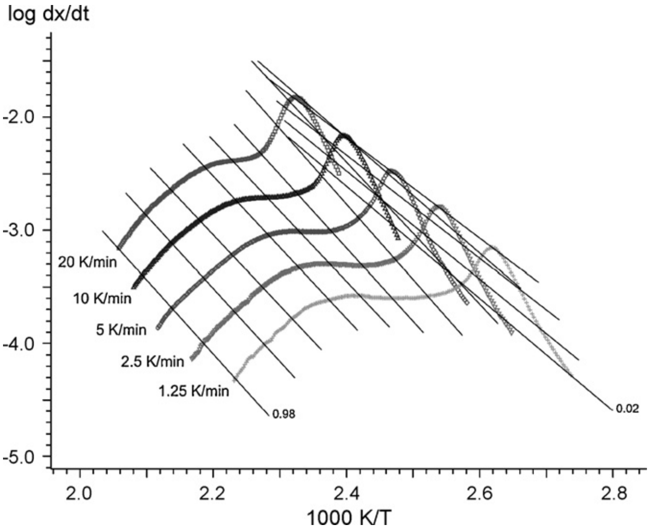

Fig. 4. Results of the Friedman analysis of the polymeric model system. *x* describes the degree of conversion.

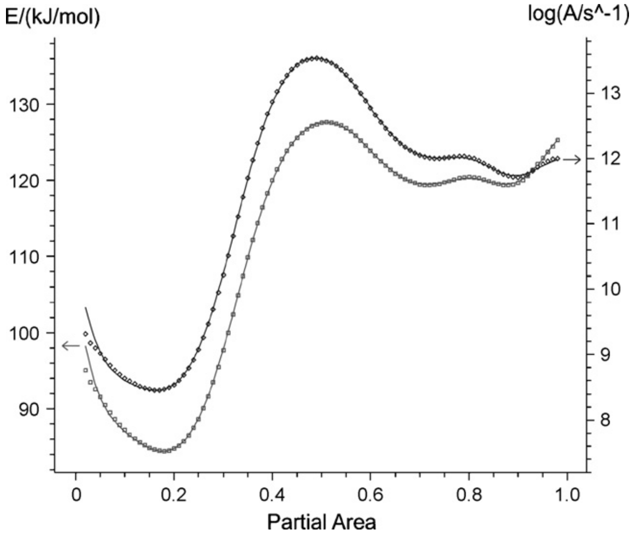

Fig. 5. Energy plot of the Friedman analysis of the polymeric model system.

After the determination of the starting parameters and the choice of an appropriate formal kinetic model 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 analysis. The software applies a 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].

Table 1
Results of the non-isothermal DSC measurements of the polymeric model system with different heating rates.

Measurement	Heating rate (K/min)	$T_{\max_1}$ (°C)	$T_{\max_2}$ (°C)	ΔH (J/g)	T_{g_1} (°C)	T_{g_2}[a] (°C)	Mass loss (%)
1	1.25	108.8	142.4	−54.8	36	64	4.8
2	2.5	121.0	154.5	−55.8	38	65	3.9
3	5	132.5	161.3	−55.1	39	66	2.3
4	10	144.6	171.9	−55.3	40	66	2.0
5	20	157.3	180.0	−51.9	40	65	1.8

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

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, which can be assumed as the allophanate reaction, is about 80 kJ/mol. The value of the partial area of this first reaction step is about half of the overall peak area. The following reaction can be assigned an activation energy of about 120 kJ/mol. These results reflect the observed decrease of the peak separation at higher heating rates.

Furthermore, the isoconversion lines in the Friedman analysis (Fig. 5) exhibit in the start range of the reaction, which means at high values of 1000 K/*T*, a lower slope than the experimental data. This fact indicates an autocatalyzed starting reaction A → B. The first fit of the experimental DSC data was performed applying a two-step reaction model A → B → C with consecutive reactions. As a result, the curves with higher heating rates were fitted very accurately while at lower heating rates the regression data deviated from the experimental data. Therefore, a further reaction step was inserted prior to the curing reaction. Then, the DSC curves showed an endothermal process prior the curing reaction due to the melting of the sample. The results of the non-linear regression could be improved by adding a further reaction step prior the two-step curing process. The three-step reaction model A → B→ C → D with consecutive reactions of *n*th order (t:f, f) leads to a higher fit quality of the experimental data. In the reaction code (t:f, f) t stands for a three-step reaction and f assigns the reaction steps two and three as following reactions. In this reaction model the second reaction step B → C was autocatalyzed. The results of the non-linear regression are given in Table 3. However, the first reaction step indicates an endothermal process which is not a chemical process. Rather, it describes the melting of the polymeric model system. The fitting quality could be improved, as demonstrated, by an increase of the correlation coefficients from 0.9973 to 0.9988. The determined kinetic parameters are listed in Table 2, and Fig. 6 shows the results of the non-linear regression.

The first reaction step was added to fit the endothermal signal at about 80 °C which results from the melting of the polymeric model system.

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

	Kinetic parameters	Standard deviation
Log A_1 (s^{-1})	11.7	0.31
E_{a_1} (kJ/mol)	107.2	2.20
n_1	2.04	0.19
Log A_2 (s^{-1})	4.6	0.16
E_{a_2} (kJ/mol)	58.6	1.53
n_2	0.76	5.97×10^{-2}
Log k_{cat_2}[a]	1.61	5.33×10^{-2}
Log A_3 (s^{-1})	14.6	0.77
E_{a_3} (kJ/mol)	140.1	6.46
n_3	1.85	0.16
Foll-react 1[b]	-2.98×10^{-2}	7.90×10^{-3}
Foll-react 2[c]	0.76	3.84×10^{-2}
Area 1 (J/g)[d]	−49.2	0.23
Area 2 (J/g)[d]	−52.1	0.32
Area 3 (J/g)[d]	−55.5	0.54
Area 4 (J/g)[d]	−56.6	1.02
Area 5 (J/g)[d]	−54.7	1.89

[a] Logarithm of the autocatalytic coefficient.

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

[c] Share of reaction step 2 (B → C) in the total reaction enthalpy; the share of reaction step 3 (C → D) is given by 1 − Σ (foll-react).

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

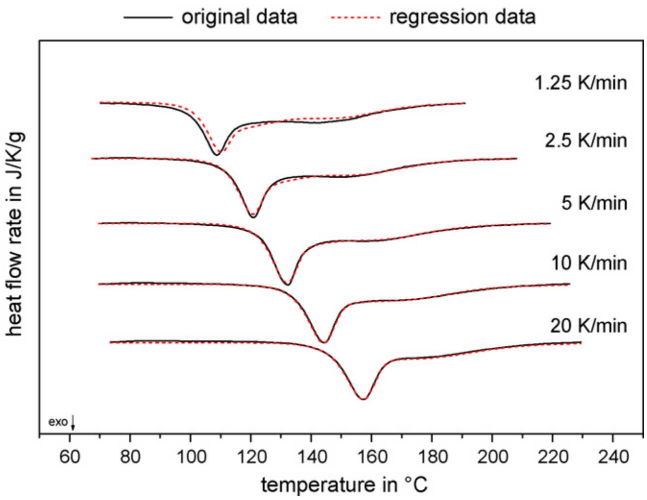

Fig. 6. Results of the multivariate non-linear regression of the model system with a three-step kinetic model t:f, f (A → B → C → D).

The share in the allophanate reaction (A → C) is about 76% of the heat 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 59 kJ/mol. The deviation from the result of the Friedman analysis can be explained by the autocatalysis. As discussed before, the activation energy for the following reaction should be higher, indicated by the better peak separation for lower heating rates. An activation energy of 140 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 −49 to −55 J/g. These values are in accordance to the determined reaction enthalpies gained from the DSC curves.

The good fitting of the curves and the agreement of the model-free and calculated activation energies for the three-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 three-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 D represents 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 following predictions are made assuming that component C represents the allophanate network. Following the curing of powder coatings the isothermal predictions of the reaction system are carried out for 30 min. The results of these predictions are shown in Fig. 7 where the concentrations of components C and D are plotted against the isothermal reaction temperature. The calculated concentration of the allophanate network (component C) runs through a maximum at 120 °C. At 170 °C the concentration of the allophanate is only about 10%. The formation of the urethane (component D) starts already at 115 °C.

Table 3
Results of the non-isothermal and following DSC measurements at different temperatures for 30 min.

T_{iso} (°C)	t_{min} (min)	T_{g_1} (°C)	T_{g_2}[a] (°C)	T_{max} (°C)	ΔH (J/g)	$\Delta H/\Delta H_0$[b]
110	9.43	51	68	170.2	−32.3	0.58
120	4.43	54	67	176.8	−29.0	0.52
130	2.83	58	68	196.1	−19.0	0.34
140	1.45	60	67	204.1	−11.9	0.22
150	0.89	61	67	207.9	−9.2	0.17
160	0.53	62	65	211.8	−4.6	0.08

[a] Glass transition of the cured system, determined in a second heating run.
[b] ΔH_0: enthalpy of the DSC measurement with 10 K/min without isothermal pretreatment.

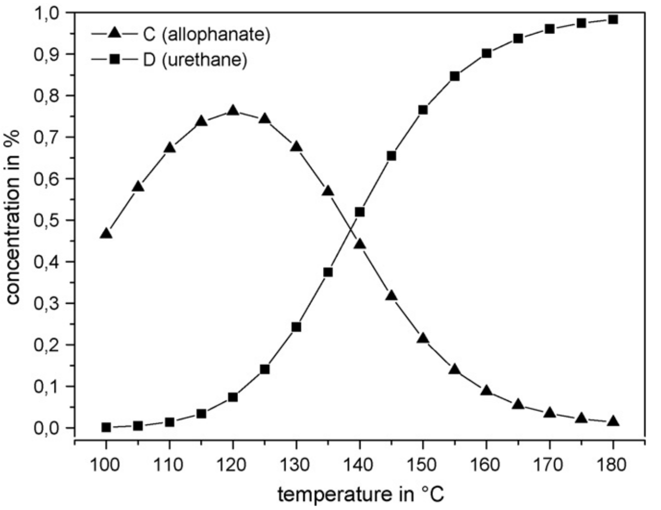

Fig. 7. Calculated concentrations of components C (allophanate) and D (urethane) after isothermal treatment for 30 min based on the three-step kinetic model A → B → C → D.

The results of the simulation of the reaction behavior were verified applying isothermal and non-isothermal DSC measurements. In a first isothermal DSC experiment the polymeric model system was cured using the parameters of the simulations. Then, two non-isothermal DSC runs were added to determine the residual enthalpies of the partially cured systems and the glass transition temperatures. The results of the DSC measurements are illustrated in Figs. 8 and 9 as well as in Table 3.

As expected, the curing reaction of the polymeric model system starts earlier at higher curing temperatures. The determined maxima of the isothermal reaction enthalpy decrease within the time interval from 9.43 to 0.53 min increasing the isothermal curing temperature from 110 to 160 °C. The degree of conversion was determined in subsequently carried out non-isothermal DSC experiments. The resulting thermograms are shown in Fig. 9. After heating the sample at 110 °C, the signal for the first reaction step is almost disappeared. The calculated concentration of the allophanate is 67.3% and reaches its maximum at 120 °C with 76.2%. At higher curing temperatures, the thermograms show only the exothermal signal for the urethane reaction. These results are in accordance with the predictions made on the basis of the three-step kinetic model (Fig. 7). The two reactions are thermo-controlled and can be separated applying suitable reaction conditions. The allophanate is formed nearly selectively at temperatures below 120 °C. So, the two-step curing process of the polymeric model system can be described very accurately with the determined kinetic parameters and the kinetic model. However, these investigations show that of the two reaction steps in the polymeric model system could not be separated as well as in case of the previously described low molecular model systems [13]. The urethane reaction sets already in, even at curing temperatures of 120 °C.

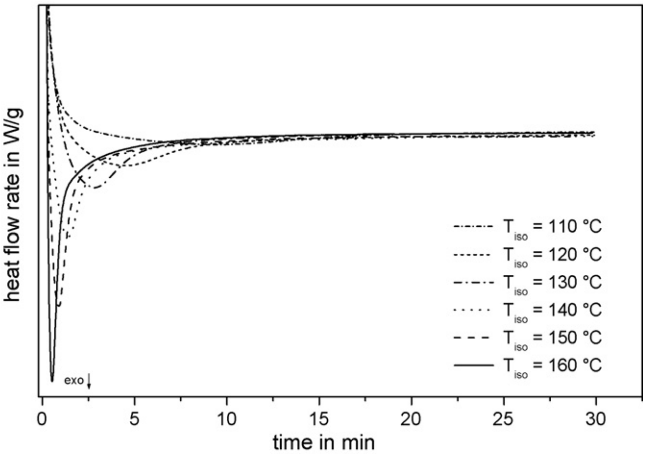

Fig. 8. Isothermal DSC measurements of the polymeric model systems at different temperatures.

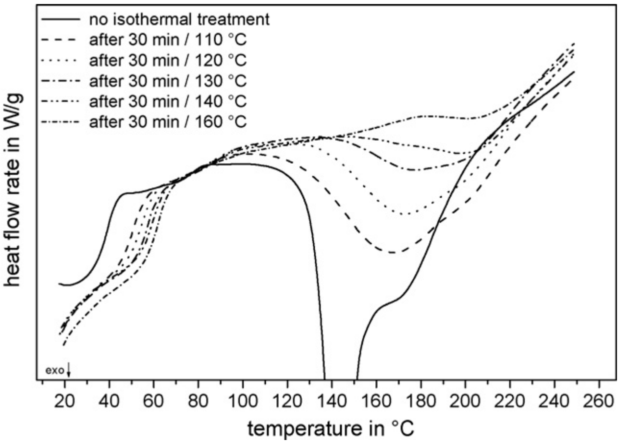

Fig. 9. Non-isothermal DSC measurements of the polymeric model systems after isothermal treatment of the samples at different temperatures (heating rates: 10 K/min).

4. Conclusions

The thermo-controlled two-step reaction between uretdione and OH groups of the aliphatic polyester in the investigated polymeric model system can be described by a three-step kinetic model with three 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 C can be identified unambiguously as the allophanate which is verified applying isothermal DSC experiments. The first reaction stage can be realized at temperatures of about 120 °C. The formal kinetic analysis of the investigated polymeric model system enables the prediction of the reaction behavior of the system.

Acknowledgements

The authors thank the German Research Foundation (DFG, project HE 4466/1-2) for the financial support of this work. Furthermore, we thank the Evonik Industries AG for donating the uretdione cross-linker Vestagon® BF 1320 and Goldschmidt TIB GmbH for supplying the zinc(II)-acetylacetonate catalyst TEGOKAT® 623. We also thank Synthopol Chemie for the donation of the hydroxy functionalized polyester DLE 04-210 and Huntsman for subscribing the Araldite® PT 910. 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, Selb (Germany).

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