

Determination of kinetic parameters of polymerizations by differential scanning calorimetry¹

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Abstract

Differential scanning calorimetry is well suited to record heat productions of chemical and physical processes as data for the following kinetic analysis. To obtain kinetic parameters of complex reactions, nonlinear optimization methods have to be used. Such complex reaction systems are polymerizations. We tried to evaluate measurements of the epoxy cure and the polymerization of β -propiolactame with simple and complex models. In both cases the simple models did not produce satisfactory results. But by using complex models a successful fitting of the measured data was possible. Our investigation shows that the combination of DSC and modern nonlinear evaluation methods presents a suitable tool for the kinetic investigation of polymerizations. © 1998 Elsevier Science B.V.

Keywords: Complex reactions; Curing; DSC; Kinetics; Polymerization

1. Introduction

Differential scanning calorimetry (DSC) is well suited to record heat productions of chemical and physical processes to get data for the following kinetic analysis. Modern software makes it possible to determine kinetic parameters even of complex chemical reactions [1]. This will be demonstrated in the present paper for two different polymerization reactions.

2. Experimental

The reactions characterized below were performed in a power-compensated DSC (DSC-7, Perkin–Elmer

Corp.). We used sample masses of 5 to 10 mg in sealed aluminum crucibles which were heated two times in the DSC at constant heating rates ranging from 2 to 20 K/min. To separate the reaction heat flow rate from that of the zero line and that of the heat capacity (baseline), the result of the second run was subtracted before evaluation.

In reality the heat capacity of the product is often somewhat different from that of the reactants, but the error in determining the true reaction heat flow rate by this method is small compared to other sources of errors. Subtracting the zero line separately would not help to reduce this error. However, it should be borne in the mind that any change of the heat capacity during the reaction will influence the reliability of the evaluation. In addition, the heat flow rate curves measured in a dynamic calorimeter are always been somewhat different from the truth (smeared) because of limited

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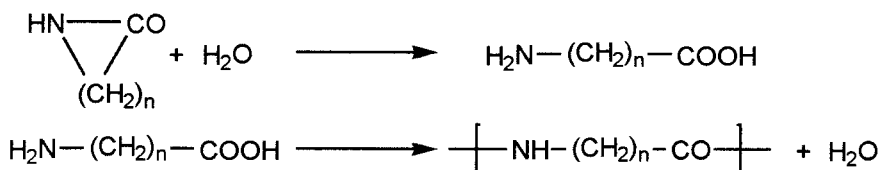
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heat conductivity. This error is greater for greater heating rates. A ‘desmearing’ procedure is, however, possible but has not been done for these measurements.

3. ‘Hydrolytic’ polymerization of lactams

The polymerization of an lactam is a complex reaction. For this reason it needs a complex kinetic model. Neglecting this the evaluation fails, because the simulated curves cannot be fitted to the measured data or kinetic parameters will be found which have no physico-chemical sense. The attempt at non-linear evaluation with a simple rate law of n th order is shown in Fig. 1. The comparison of the simulation curve and the measured data points indicates the insufficiency of this simple model. A more complex kinetic model is necessary to describe this reaction course. Two mechanisms of the polymerization of β -lactams are proposed in the literature.

3.1. Step-growth polymerization



In this type of polymerization the β -lactam rings will be broken down hydrolytically forming ω -amino acid. This amino acid forms the polyamide by polycondensation. Such a mechanism can be described as a consecutive reaction by a complex kinetic model with two differential equations:



A: lactam

B, B': polyamide or ω -amino acid in the first step

(B and B' will not be distinguished by the kinetic rate law)

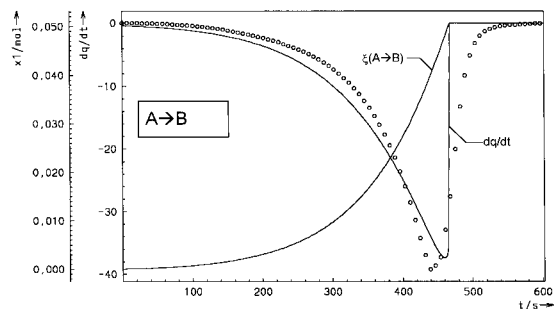


Fig. 1. Overall evaluation (2.5 K/min, 5 K/min and 10 K/min) of the polymerization of β -propiolactam as a reaction of n th order shown for 10 K/min. The model given in the box does not describe the measured data (circles).

The corresponding system of differential equations has the following structure:

$$\frac{d\xi_1}{dt} = k_1(T) \cdot [A]$$

$$\frac{d\xi_2}{dt} = k_2(T) \cdot [B]^2$$

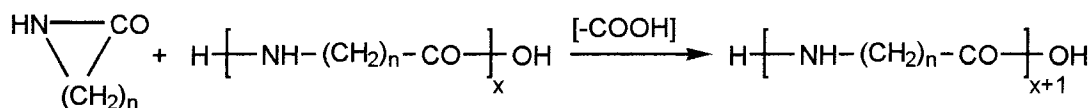
For the temperature dependence of the rate constants k_1 and k_2 the Arrhenius equation can be used:

$$k(T) = k_0 \cdot \exp\left(-\frac{E_A}{RT}\right)$$

The kinetic parameters activation energy E_A and frequency factor k_0 of both reactions can be determined by non-linear optimization. We applied our software package ‘TA-kin for Windows’, which enables a free definition of the expected reaction models.

As the effective rate of the total polymerization reaction is higher than that of a simple polycondensation, an additional reaction step has been assumed and proved [2].

3.2. Chain-growth polymerization



In the case of chain-growth the β -lactam ring will be directly added to the amino group of the polyamide. The carboxyl groups have a catalytic effect to this reaction.

The hydrolysis of the β -lactam rings may again be supposed as starting reaction. The kinetics of this reaction mechanism can be described by the model of a competitive consecutive reaction with the following autocatalytic step:



A: lactam

B, B': polyamide or ω -amino acid in the first step

(B and B' will not be distinguished by the kinetic rate law)

To describe the simultaneous effect of mechanism 1 and 2 a combination of both models with a total number of three differential equations would be necessary. Our non-linear evaluation test using such a model shows that the kinetic parameters of the polycondensation step (1b) cannot be found exactly in the cases of the polymerization of β -propiolactam. This is supposed by the fact that the difference between the simulated and the experimental data does not change significantly by varying of the kinetic parameters in a wide range. Therefore we tried to evaluate the DSC

Fig. 2 shows the kinetic evaluation of the polymer-

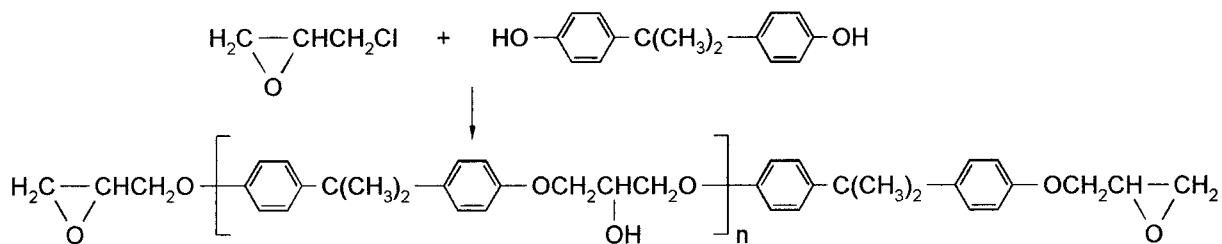
ization of β -propiolactam assuming an autocatalytic second reaction step (2b). The reaction of the polyamide may be of second order, because it works, not only as a reactant, but also as a catalyst.

An additional prerequisite is the independence of the kinetic parameters on the chain length of the polymer.

A comparison of measured data and simulated curves shows that they fit well. Thus we have a suitable kinetic model for the description of the experimental curve. To ensure this result we tried to evaluate the DSC curves as a simple consecutive reaction like a step-growth polymerization (type 1). This does not result in a satisfactory fit. The interpretation of our results may start from the idea that the polymerization of β -propiolactam is dominated by the direct reaction of the monomer with the polyamide. The polycondensation is pushed into the background. This assumption is supported by the fact that the high ring strain favors the ring-scission polymerization.

4. Curing of epoxides

The technical production of epoxides is performed in two steps [2]. First, prepolymers arise from simple epoxide compounds, for example, epichlorohydrine, and bisphenole:



measurements as pure chain-growth polymerization under-neglecting the polycondensation.

In the following P denotes a part of a prepolymer that contains an epoxide ring.

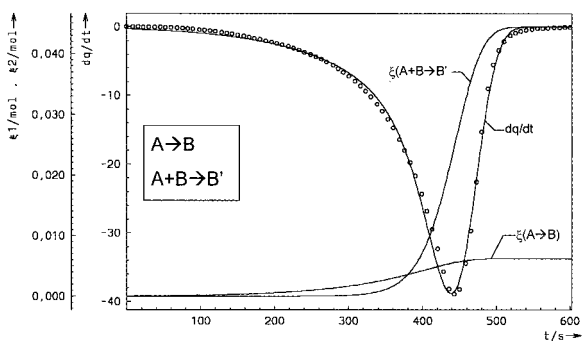
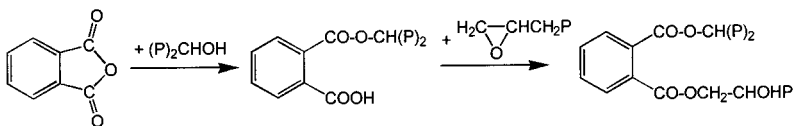


Fig. 2. Overall evaluation (2.5 K/min, 5 K/min and 10 K/min) of the polymerization of β -propiolactam as a complex autocatalytic reaction (as given in the box) shown for 10 K/min.

These oligomers will be cured by a suited cure agent, for example, phthalic acid anhydride, forming the real polyepoxide.



This paper deals with the evaluation of DSC measurement of the second process step, the epoxy cure. This reaction should be described by a complex model. To test this supposition we evaluate the DSC measurements using a kinetic model of n th order. As shown in Fig. 3, this evaluation does not lead to a satisfactory result. Thus a complex kinetic model has to be applied to describe the course of this reaction.

Actually the mechanism of the reaction corresponds to a consecutive reaction. If the concentration of the curing agent is nearly constant during the process, then the model can be formulated in the following manner:



A: hydroxyl groups of the prepolymers

B: carboxyl groups of the intermediate compounds

C: bond between prepolymers

As the prepolymers contain a different number of reactive groups, not the concentrations of the reactants

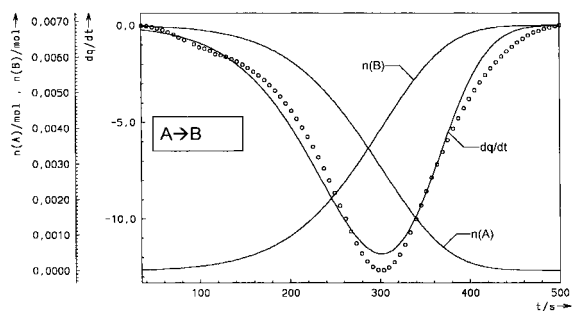


Fig. 3. Overall evaluation (5 K/min, 10 K/min and 20 K/min) of the epoxy cure as a simple reaction of n -th order shown for 20 K/min. The model given in the box does not describe the measured data (circles.)

but the concentration of functional groups will be taken into account in the kinetic rate law. These reactions are really reactions between different mole-

cules. The following reaction step is not monomolecular as formulated in reaction Eq. (3b) but rather a connection between two prepolymers. The reaction Eq. (3b) only describes that every carboxyl group B leads to a bond C. Since the real reaction is a reaction between two similar molecules, reaction (Eq. (3b)) is of second order, as in the case of a fast starting reaction most of the prepolymers already contain carboxyl

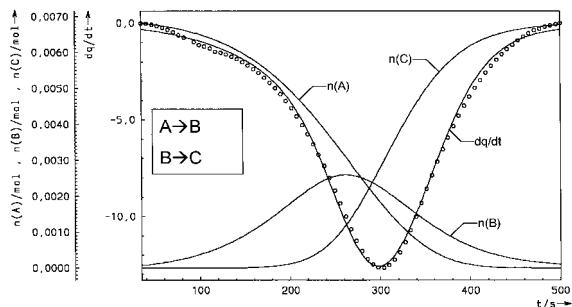


Fig. 4. Overall evaluation (5 K/min, 10 K/min and 20 K/min) of the epoxy cure as a consecutive reaction (as given in the box) shown for 20 K/min.

groups after a short time. Fig. 4 shows the result of the non-linear evaluation of DSC curves applying 'TA-kin for Windows' using this kinetic model. The small differences between the simulated curves and the measured data indicate the successful fitting.

Additionally the evaluation shows the course of the intermediate carboxyl groups. It accumulates in the first range of the reaction, but then its concentration forms a maximum. After this maximum the concentration of carboxyl groups decreases progressively. This behavior is an indication of a fast rate of the starting step (3a). Since this fast starting step was an assumption for the determination of the reaction order

two for the second reaction step, this conclusion is within the valid range of the reaction model.

This and the successful evaluation indicates sufficient applicability of the used kinetic model for the description of the epoxy cure with phthalic acid anhydrides as curing agent.

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