Cure Schedule of Epoxides and Their Sulfur-Containing Derivatives. Kinetic Study

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ABSTRACT: A series of model epoxides and their sulfur-containing derivatives have been cured by hexahydrophthalic anhydride. The curing process was kinetically analysed using differential scanning calorimetry data. It has been found by means of Friedman and Ozawa–Flynn–Wall methods that the apparent activation energy (E) values of the cure process are higher for (1,3-oxothiolane-2-thione)s than for model epoxides and lay in the range of $100.1–119.6 \, kJ \, mol^{-1}$. Some instability regions of E *vs.* degree of cure, which were observed for all samples under investigation, confirm the complex kinetic scheme and comes probably from intermediate steps between different rate-controlling mechanisms. This supposition was supported by further kinetic analysis by means of advanced non-linear regression based approach which made it possible to determine reaction models of the cure, changing from 'reaction 1st order' to 'one-dimensional diffusion' models. Other aspects, such as the possibility of existence of non-elastically contributing species–the products of inter-or intramolecular cyclization–which are not incorporated directly into the growing network, but may changes the mechanism on molecular, 'transition-state' level, are also discussed. Finally, kinetic predictions of the system behavior in extrapolated range of degree of cure, time and temperature are presented on the basis of obtained kinetic parameters.
    KEY WORDS   Epoxides / (1,3-Oxothiolane-2-thione)s / Cure / Kinetic Parameters / Differential Scanning Calorimetry (DSC) /

Epoxy resins find broad application as surface coatings, adhesives, fiber-reinforced composites, and printed circuit boards. Literature search reveals however that there is still a need for modified epoxides or their analogues compounds, which can be cured to give polymeric products with enhanced properties. For such products of reaction with carbon disulphide several advantageous properties, *e.g.*, higher reactivity in subambient temperature, have been observed.[1, 2] Since the first classical works of Culvenor *et al.* in 1946,[3, 4] showing the way of formation of 1,3-ditiolane-2-tione (Scheme 1) many other synthetic routes were presented,[5—7] as this proposed by Hayashi *et al.*[8] (Scheme 2).

The resulting products may be further utilized after a curing reaction which proceeds in the presence of common curatives used for epoxy resins, as it was proved for thioetherglycidyl resins by Charmas and Podkoscielny.[9—11] Fundamental questions concerning kinetics of the complex process of curing, in which reaction- and diffusion-controlled subprocesses are present, remain however still not answered, making it impossible

to (i) deduce the rate of reaction and its change *vs.* time or temperature, and (ii) quantitatively monitor the extent (and resulting therefrom quality) of cure.

In the present investigation, kinetics of the curing process of several (1,3-oxothiolane-2-thione)s with hexahydrophthalic anhydride has been studied by differential scanning calorimetry (DSC). The results obtained should complete our previous work on thermal characterization of these novel materials, published elsewhere.[12]
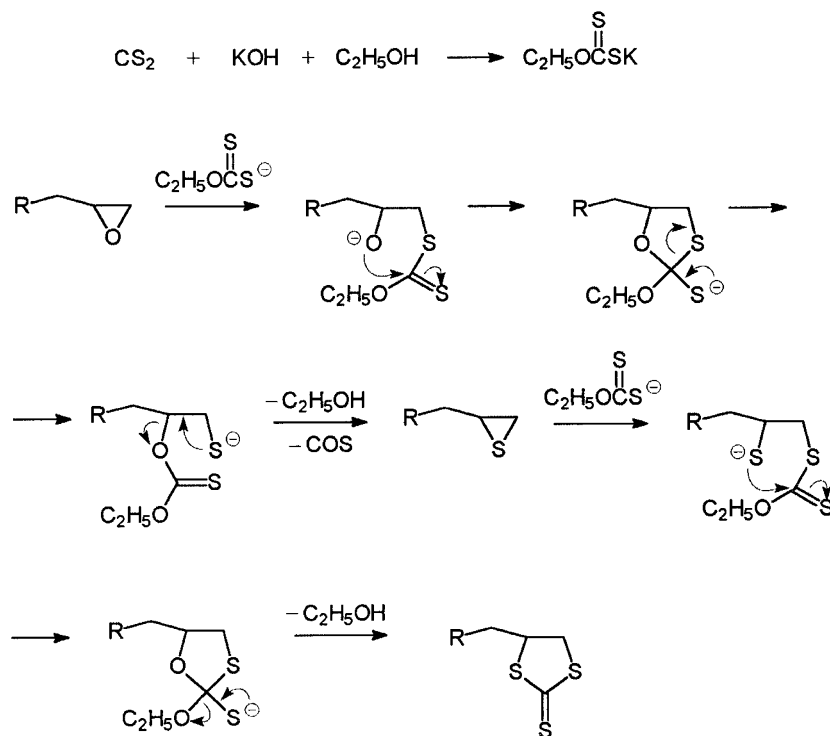
EXPERIMENTAL

Materials

Initial epoxy compounds, carbon disulphide, diethyl ether and Al_2O_3 were commercial products from Merck. Carbon disulphide was purified by distillation prior to use. Sulfur-containing derivatives have been obtained by the reaction of epoxides with carbon disulphide[13] (Scheme 3).

The reaction has been carried out at boiling temperature of diethyl ether used as solvent and in the pres-
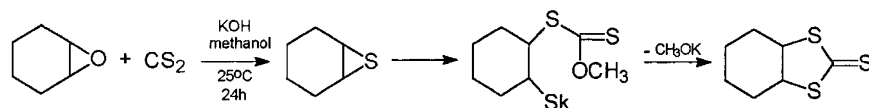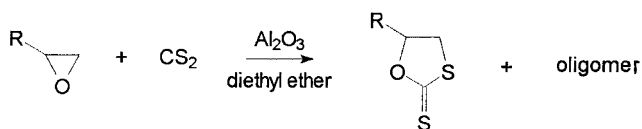

Scheme 1.

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Scheme 2.

Scheme 3.

		R
1	1 A	(phenyl)
2	2 A	CH_3, CH_3 >—O—CH_2
3	3 A	(phenyl)—O—CH_2
4	4 A	CH_3, CH_2 / O—CH_2

ence of Al_2O_3 as catalyst. 1,3-Oxothiolane-2-thione as a main product and oligomer can be then easy separated on short silicagel column. A series of differently substituted (1,3-oxothiolane-2-thione)s, as presented in Table I, have been obtained.

Curing process of (1,3-oxothiolane-2-thione)s was accomplished using hexahydrophthalic anhydride as-curing agent and 2,4,6-tri(dimethylaminomethyl) phenol as catalyst. 1,3-Oxothiolane-2-thione/hexahydr-ophthalic anhydride/and 2,4,6-tri(dimethyl-aminom-ethyl) phenol ratio was 10:8:1 by weight. Molecular weight was determined by gel permeation chromatog-raphy; results are given in ref 12.

Technique

The DSC data were recorded on a Netzsch DSC 200, operating in a dynamic mode, with the following con-ditions: sample weight ~ 4 mg, heating rate = 2.5; 5; 10 or 20 K min^{-1}, temperature range = 25–300°C, atmosphere–argon (30 cm^3 min^{-1}), sealed aluminium pan. The calorimeter was calibrated with an indium standard; an empty aluminium pan was used as a refer-ence. The raw data were converted to ASCII files and kinetic analysis was carried out using an in-house pro-gram and a Netzsch Thermokinetic Program (v. 97.12)
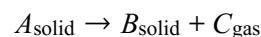
on a IBM-compatible computer with Pentium 2 proces-sor.

The Kinetic Equations and Models

In general, the thermal process of solids is a very complex phenomena even in the simple case of the re-action expressed by the stoichiometric equation

$$A_{solid} \rightarrow B_{solid} + C_{gas}$$

The rate of reaction can be described in terms of two functions: $k(T)$ and $f(\alpha)$, thus:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

Table II. The kinetic models

Model	Symbol	$f(\alpha)$
Phase boundary-controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$
Phase boundary-controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$
Random nucleation. Unimolecular decay law	F1	$(1-\alpha)$
Reaction n-th order	Fn	$(1-\alpha)^n$
Johnson–Mehl–Avrami	JMA	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Two-dimensional growth of nuclei (Avrami equation)	A2	$2[-\ln(1-\alpha)^{1/2}](1-\alpha)$
Three-dimensional growth of nuclei (Avrami equation)	A3	$3[-\ln(1-\alpha)^{2/3}](1-\alpha)$
One-dimensional diffusion	D1	$1/2\alpha$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$
Three-dimensional diffusion (Jander equation)	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$
Three-dimensional diffusion (Ginstling–Brounshtein)	D4	$3/2[(1-\alpha)^{-1/3}-1]$
n-Dimensional nucleation (Avrami–Erofeev equation)	An	$n[-\ln(1-\alpha)^n](1-\alpha)$
Reaction of 1 st order with autocatalysis	C1	$(1-\alpha)(1+K_{kat.}\alpha)$
Reaction of n-th order with autocatalysis	Cn	$(1-\alpha)^n(1+K_{kat.}\alpha)$
Prout–Tompkins equation	Bna	$(1-\alpha)^n\alpha^a$

where α is the degree of conversion.

By substitution of the Arrhenius equation ($k(T) = A\exp(-E/RT)$) the following equation results:

$$d\alpha/dt = A\exp(-E/RT)f(\alpha) \qquad (2)$$

After introduction of the constant heating rate $\beta = dT/dt$ and rearrangement, one obtains

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right)\exp\left(-\frac{E}{RT}\right)dT \qquad (3)$$

where T the temperature in kelvins, $f(\alpha)$ the type of reaction, $k(T)$ the rate constant, E the activation energy, A the pre-exponential factor, and R the gas constant.

A subsequent integration of eq 3 leads to the equation

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^T \exp\left(\frac{-E}{RT}\right)dT \qquad (4)$$

which cannot be expressed by a simple analytical form since its right-hand side corresponds to a series of infinite γ functions. In mathematical practice logarithms are taken:

$$\ln G(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln\beta + \ln p(x) \qquad (5)$$

and exponential integral $p(x)$ is introduced:

$$p(x) = \frac{e^{-x}}{x} - \int_\infty^x \frac{e^{-x}}{x}dx \qquad (6)$$

where $x = E/RT$.

Using an approximation of the exponential integral in a form proposed by Doyle[14]

$$\ln p(x) = -5.3305 + 1.052x \qquad (7)$$

it is possible to determine the activation energy of the thermal process by following the specific heat flow of a process at several different heating rates

$$\ln\beta = \ln\left(\frac{AE}{R}\right) - \ln G(\alpha) - 5.3305 + 1.052x \qquad (8)$$

Equation 8 generates a straight line when $\ln(\beta)$ is plotted against $1/T$ for isoconversional fractions, the slope of the line being equal to $-1.052 E/R$ during a series of measurements with a heating rate of $\beta_1\cdots\beta_j$ at a fixed degree of conversion of $\alpha = \alpha_k$. The temperatures T_{jk} are those at which the conversion α_k is reached at a heating rate of β_j. This method was developed independently by Ozawa[15] and Flynn and Wall.[16]

Another isoconversional procedure, introduced by Friedman,[17] use as its basis the following relationship

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha) + \ln A - \frac{E}{RT} \qquad (9)$$

which makes it possible to find the activation energy value from the slope of the line ($m = -E/R$) when $\ln(d\alpha/dt)$ is plotted against $1/T$ for isoconversional fractions.

In eq 1 term $f(\alpha)$ represents the mathematical expression of the kinetic model. The most frequently cited basic kinetic models are summarized in Table II.

Non-isothermal curves of a thermal reaction can satisfy the kinetic equations developed for the kinetic analysis of "n-th order reactions", even if they follow a quite different mechanism. Results of the comparative studies lead to the conclusion that the actual mechanism of a thermal process cannot be discriminated from the kinetic analysis of a single DSC trace.[18] Besides, both activation energy and pre-exponential factor, given in eq 2 may be mutually correlated. As a consequence of this correlation any DSC curve can be described by an apparent kinetic model instead of the appropriate one for a certain value of apparent activation energy. Therefore, the kinetic analysis of DSC data cannot be successful unless the true value of the activation energy is known.[19–21]
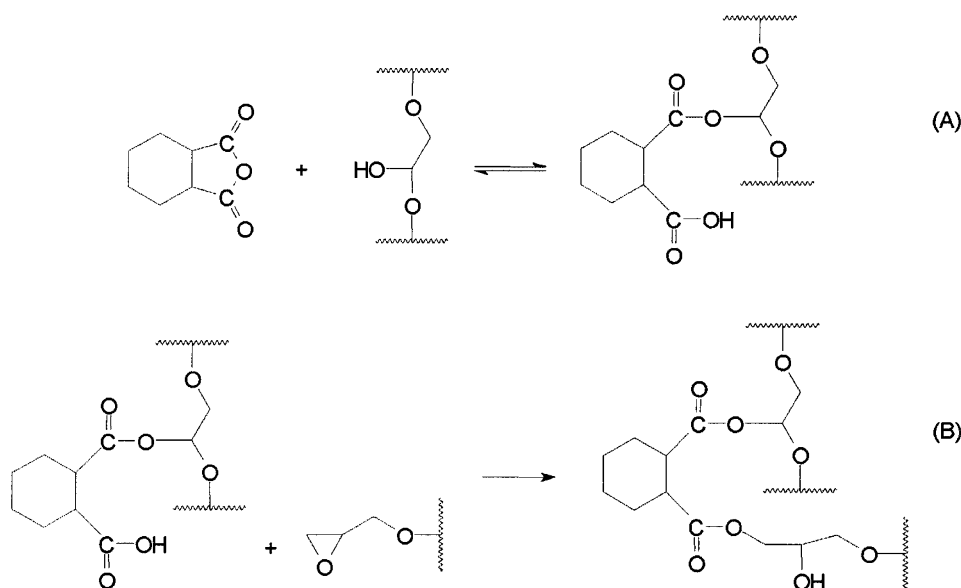
Scheme 4.

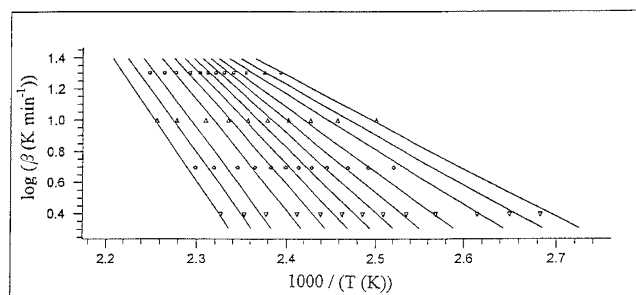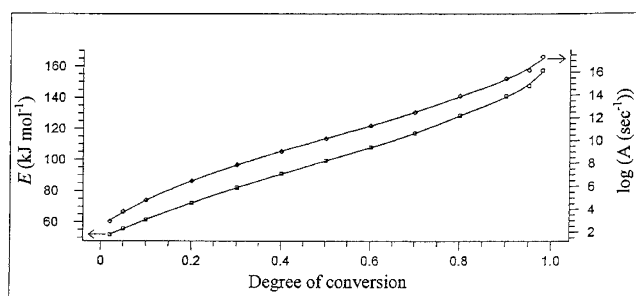**Table III.** Kinetic analysis results for the cure process of model epoxides

Sample	E/kJ mol^{-1}	Model
1	58.2	Cn
2	35.0	Fn
3	38.7	An
4	25.6	A2

Figure 1. Ozawa–Flynn–Wall analysis of the cure process of sample 1A; symbols , , , and show isoconversional levels at given β.

Figure 2. Activation energy (E) and pre-exponential factor (A) as a function of degree of conversion for the cure process of sample 1A calculated by Ozawa–Flynn–Wall method.

RESULTS AND DISCUSSION

First, kinetic process of cure of a series of epoxides has been investigated. Results are presented in Table III.

The obtained results are comparable with those reported for another carboxylic acid anhydride cure[22] and show that first-order kinetic approach yields no sufficient description for the process under investigation. For the reaction scheme in which the first step is the formation of a monoester, rate-controlling step is a chemical reaction. Further interaction of the monoester with epoxide can give the diester and a terminal hydroxyl group, and repetition of this sequence can produce the polyester (Scheme 4), assuming the stationary-state hypothesis for active species this model predicts a first-order kinetic dependence on anhydride concentration, but at higher level of conversion gelation can introduce a degree of diffusion-control of the kinetics.[23, 24] At that point viscosity increases the rate of cure that depends on diffusion of reactant to a reactive centre. Not only is it necessary for the mutual reorientation of potentially reactive groups to occur but a prior requirement is that they should diffuse together so that they are within a "reaction-zone".

Then, next study was done for 5-phenyl-1,3-oxothiolane-2-thione, sample 1A, Ozawa–Flynn–Wall analysis results are shown in Figures 1 and 2.

Figure 2 illustrates the variation of the activation energy E (and the pre-exponential factor A) against degree of conversion α. One can see that E is increasing with the extent of cure–this effect can be explained by lower mobility of the reactive groups while the degree of cure increases. As a consequence of the freezing of chemical reaction, the conversion degree tends to a practically constant limiting value, which is lower than unity–the
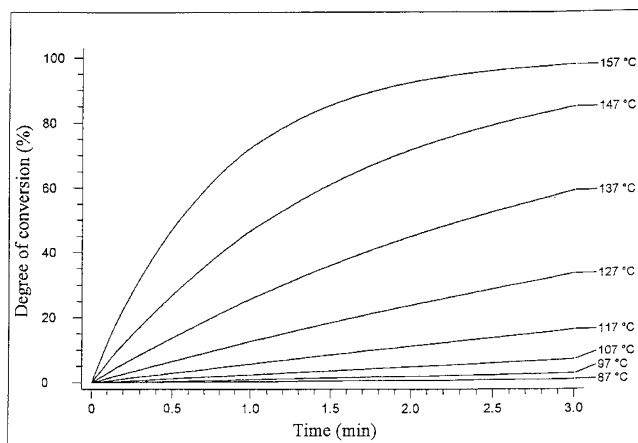
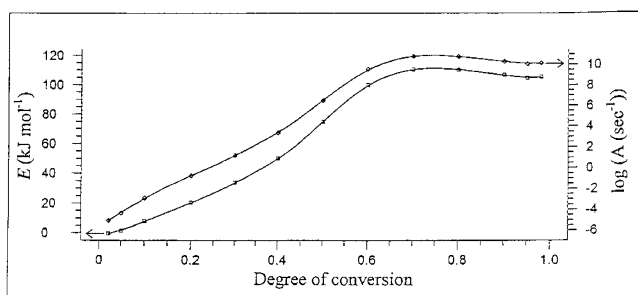**Figure 3.** Degree of conversion vs. time plot for the cure process of sample 1A.

Figure 5. Isoconversional curves of the curing process of sample 2 A.

Figure 4. Activation energy (E) and pre-exponential factor (A) as a function of degree of conversion for the cure process of sample 2A calculated by Ozawa–Flynn–Wall method.

Figure 6. Activation energy (E) and pre-exponential factor (A) as a function of degree of conversion for the cure process of sample 3A calculated by Friedman method.

Table IV. Results of F-test of the distinctiveness between the models for curing process of sample 3A

Model	F exp.
An	1.00
F2	1.08
F1	1.40
C1	1.44
Cn	2.14

system becomes partially cured after a long time of curing. The kinetic of the residual curing change from the uncured resin to the partially cured. This change of the kinetic parameters is probably due to secondary reactions which are favoured at higher temperatures.

Further calculations by non-linear regression method revealed that best fit was found for '1st order reaction' model which in turn made it possible to predict conversion *vs.* time dependencies, Figure 3.

For the sample 2 A another E *vs.* a plot was identified–for $\alpha > 0.6$ E reaches its plateau of *ca.* 100 kJ mol^{-1}, as displayed in Figure 4.

At lower temperatures system presents a better regularity of the reactive chemical groups that require a lower activation energy to react than in material cured at higher temperatures.

It is noteworthy that isoconversional kinetic analysis has been successfully applied to non-isothermal DSC data on the cure of an epoxynovolac resin[25] and the dependence of E *vs.* α has been straightforward utilized not only to disclose the complexity of an epoxy system cure kinetic scheme but also for further modelling of isothermal cure schedules.

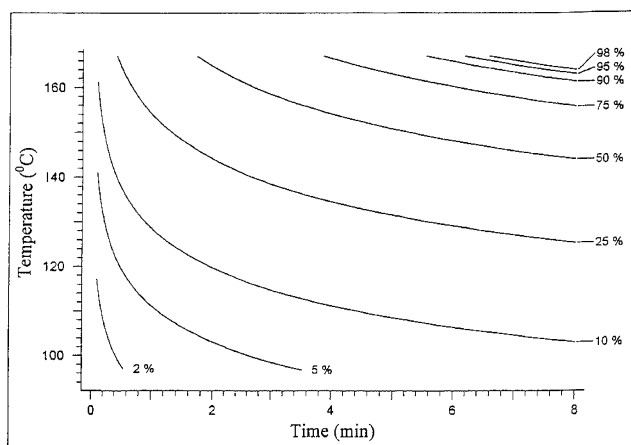Isoconversional curves for 'one-dimensional diffu-

sion' model suitably show area of the curing process, Figure 5.

A very unique, lobe-type route of E describes curing of sample 3A, indicating an existence of a complex kinetic scheme with 'n-dimensional nucleation' as best description of the rate-controlling step, Figure 6 and Table IV.

The character of E *vs.* α curve demonstrates a changeable kinetic behavior with a maximum at $\alpha = 0.5$; this observation may suggest that after relatively undisturbed course of reaction, the partially-crosslinked spatial structure formed interferes further reaction due to geometrical constraints that, however, for $\alpha > 0.5$ seem not to play any limiting role during a nucleation-controlled reaction.

The last sample under investigation, sample 4A, is

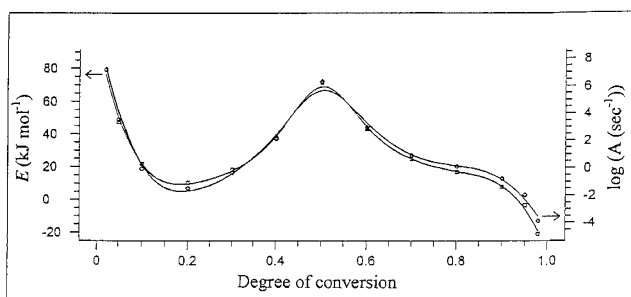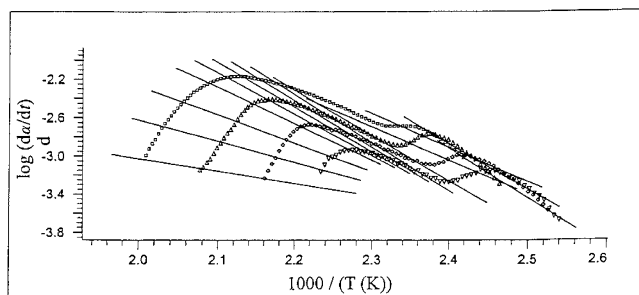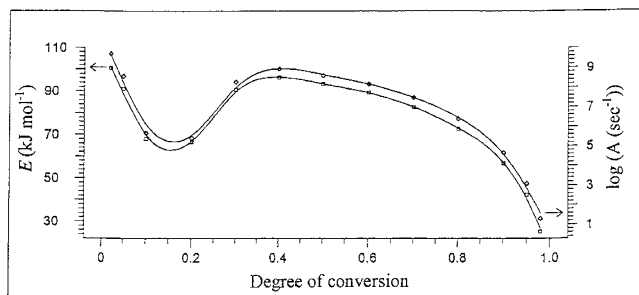**Figure 7.** Friedman analysis of the cure process of sample 4A.

Figure 8. Activation energy (E) and pre-exponential factor (A) as a function of degree of conversion for the cure process of sample 4A calculated by Friedman method.
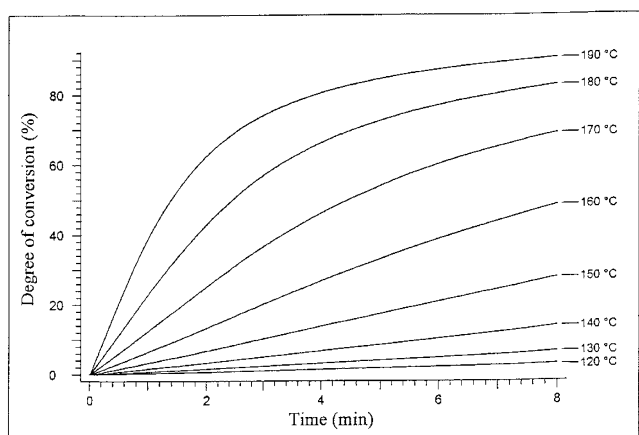

Figure 9. Degree of conversion *vs.* time for sample 4A.

characterized during cure by a similar to sample 3A route of E *vs.* α, as shown in Figures 7 and 8.

Autocatalytical n-th order kinetic scheme was applied as best approximation yielding partial reaction *vs.* time plot, Figure 9.

Similar trends were observed for epoxy-based vinyl ester resin by Lee and Lee.[26] They have developed a graphical estimation technique for the determination of kinetic parameters describing an autocatalytical reaction. In this work DSC was used to monitor the reaction kinetics of an epoxy-based vinyl ester resin. The method used information from a zero initial reaction rate, conversion at vitrification, ratio of reaction rate constants under different isothermal conditions and characteristics of the phenomenological kinetic model

with assumptions about the overall reaction order.

The cure process of 1,3-oxothiolane-2-thione derivatives is characterized by higher activation energy values than curing of model epoxides–the reasons for such a difference may lay in structural features of sulfur-derivatives which in turn may strongly influence the molecular and architectural paths of the cure. Moreover, there is the possibility of non-elastically contributing species–the products of inter-or intramolecular cyclization (particularly in case of sample 4)–which are not incorporated directly into the growing network, but may changes E values on molecular, 'transition-state' level. The main problem to be addressed to elucidation of the mechanism of the chemical reactions occurring during cure is connected with the apparent lack of establishment of a steady state during the polymerization. From the three possible reasons, the first one is associated with active propagating centres which do not stabilize quickly during the polymerization due to concentration's changes. Shifts in the equilibria are probably the result of the reduction of polarity of the medium as the polymerization consumes the polar anhydride and epoxide groups. The second factor affecting the steady state is that increases in viscosity occurring during the reaction and particularly near the gel point may affect the rates of some reactions more than others. Finally, the reaction kinetics of epoxy cure may be complicated by inhomogeneities in the system itself, also due to free volume when the volume occupied by the products of reaction diminishes the available volume increasing the 'local concentration' of the reactants and therefore the rate of reaction.[27-30]

The advantage of kinetic analysis based on heat flow measurement (DSC) relies on possibility of ignoring the actual complexicity in kinetic pattern of partial reactions and makes it possible to reduce these intricate mechanisms to an effective kinetic scheme which in turn may be further used for prediction and modelling of (thermal) properties.

For the (1,3-oxothiolane-2-thione)s under investigation, kinetic models found by advanced non-linear regression procedures are of different types, and diffusion-controlled mechanism, often meet in amine-cured systems with nodular structures that support the concept of a two-phase model of more-and less-crosslinked regions, was detected for sample 2A only.

CONCLUSIONS

A kinetic study on the curing process of some model epoxides and their novel sulfur-containing analogues was carried out. Application of isoconversional methods made it possible to find out values of apparent

activation energy over the whole conversion range. From its characteristic course one can conclude that the observed instability regions are due to different rate-controlling factors which are either of molecular nature (assuming the validity of stationary state hypothesis for active species in a curing reaction scheme, although there are several factors which considerably limit its application area) or located on higher architectural levels which in turn may influence the degree of diffusion-controlled processes; their course may be additionally complicated by inhomogeneities in the system itself, and also due to free volume when the volume occupied by the products of reaction diminishes the available volume increasing the 'local concentration' of the reactants and therefore the rate of reaction.

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