Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 1, 193–198

KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY-AMINE CURE REACTION
Part VII. Resorcinol diglycidylether–aniline

R. M. Vinnik[1] *and V. A. Roznyatovsky*[2*]

[1]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygina str. 4, Moscow 117334, Russia
[2]Chemistry Department, Moscow State University, Moscow 119899, GSP-3, Russia

A combination of kinetic method and DSC measurements was used to examine the system of resorcinol diglycidylether–aniline. The purpose of this study is to obtain information about linear polycondensation in epoxy-amine system. The reaction of resorcinol diglycidylether (RDGE) with aniline falls into the family of epoxy-amine reaction mixtures, within of which the functional groups varies only. The molar heats and the rate constants for the three pathways were evaluated by nonlinear regression analysis of the data assuming that reaction mechanism proposed for simple molecular epoxy-amine system such as phenylglycidylether–aniline would be operative in the reaction between resorcinol diglycidylether and aniline.

A feature of the present reaction system is that it proceed through the structural changes occurred with the heat effect. The loss of catalytic activity by the molecules of the reaction product was used as indicator for the structure forming in the reaction medium.

Keywords: *aniline, DSC, epoxy-amine, kinetic calorimetry, linear polycondensation, resorcinol diglycidylether, solventless systems*

Introduction

Thermochemistry of the reactions of amines with epoxides is believed to be governed primarily by the exothermic effect of the reaction of the epoxy ring opening. Therefore a convenient way to follow these reactions is by measurements of the rate of the heat release. In the case of some epoxy-amine reactions this approach has proved particularly informative [1]. However, a major difficulty in the quantitative treatment of the reactions of amines with epoxides is the lack of knowledge of their chemical nature, since the successful application of thermokinetic method to analytical problem is facilitated by understanding reaction mechanism involved. Only a careful analysis of data from various viewpoints can provide useful indications regarding the molecular mechanism of the processes. Thus, the first step is to select some kinetic scheme representing reaction mechanism. The next important step is a molecular interpretation of the mechanism of the process at the molecular level.

In reactions involving two large molecules it can hardly can be expected that every collisions having the necessary energy will lead to reaction, since there must inevitably be steric or orientation factors tending to reduce the rate. In this case, there must be a factor producing an enhanced rate. Such a factor may be the complex formation between the reagents which became stable and obtains reactivity under action of catalyst. If the reaction occurs within the complex, the translations motions of the reactants are reduced, increasing the probability of an encounter, and their molecular geometry is altered to facilitate the chemical transformation by optimally locating functional groups.

According to kinetic analysis the product (OH-groups) is formed from the reaction between epoxy- and NH-groups via two pathways, with non-catalytic and catalytic. In catalytic reaction all the runs showed first order behaviour both with respect to glycidylether units and with respect to the product molecules [2]. The basic assumption in the proposed catalytic reaction scheme is, in essence, that the reaction does not proceed through free reacting groups. The course of the catalytic reaction is formulated as

$$\mathrm{AE}+\mathrm{X}\leftrightarrows\mathrm{AEX}^{*}\rightarrow\mathrm{P} \qquad (1)$$

where AE is the complex between the reagents, AEX* is the 'activated' complex, which gives rise to the reaction products P.

Because here AE is equivalent to C_0, the initial number of moles of the reagent in deficiency, occurrence of complex AE would lead to a kinetic rate equation:

$$\frac{\mathrm{d}C_{\mathrm{x2}}}{\mathrm{d}t}=k_{\mathrm{ef2}}(C_0-C_{\mathrm{p}})C_{\mathrm{p}} \qquad (2)$$

In early stages of the process, it was assumed that the reaction occurs with no interference of the

---

[*] Author for correspondence: vit.rozn@chem.msu.ru

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

catalytic reaction. During this period the reaction kinetics, which is of first order in both epoxide and amine, is represented by

$$\frac{\mathrm{d}C_{\mathrm{x1}}}{\mathrm{d}t} = k_{\mathrm{ef1}}(C_{\mathrm{A}} - C_{\mathrm{p}})(C_{\mathrm{E}} - C_{\mathrm{p}}) \tag{3}$$

where C_A and C_B are the initial concentrations of NH- and epoxy-groups in mol L^{-1} respectively, C_p is the concentration of the OH-functional groups which are formed in the course of the reaction.

Epoxy-amine model reactions mixtures provide the connection between reaction chemistry and product structure. However, the studies by calorimetry have largely been restricted to cure reactions. In previous paper [3], we determined kinetic data for simple molecular epoxy-amine reaction such as phenylglycidylether–aniline. In case of this reaction another factor shown to be important is the exothermic effect due to structural changes in the reaction medium. In order to explain the existence another exothermic process apart from exothermic effect of the reaction we proposed the idea of intermolecular aggregation when interactions between chains can lead to self-assembly and to phase separation [4]. Obviously, we need a good probe or indicator for the structure forming in the reaction medium before we can begin to analyse similar reactions. Such probe found was the loss of catalytic activity by the molecules of the reaction product. We proposed that the loss of the catalytic activity is directly related to the structure changes and that it can express itself through rate equations. It turned out that this sort of behaviour is simply equivalent to 'saturation effect', kinetically speaking.

As it is well-known, epoxy-amine cure reaction causes a significant increase in the viscosity. It must be noted that a tremendous amount of work has been dedicated to the correlation of reaction kinetics with the viscosity of the epoxy-amine reaction system through diffusion-limited reaction mechanism. However, this assumption has not so far, been proven experimentally. The values of the rate constants show that under chosen conditions the epoxy-amine model reaction [2, 3] takes place at rates that are order of magnitude slower than curing reaction. Meanwhile, in both epoxy-amine systems, the molar heat for catalyzed reaction reveals little or no variation with reaction temperature and initial reagent concentration. To obtain a unified explanation of these data, it is interesting to analyse the thermokinetics of one more epoxy-amine system. It is also evident that for simple molecular epoxy-amine system such as phenylglycidylether–aniline as well as the reaction between resorcinol diglycidylether and *m*-phenylenediamine alone are not in themselves adequate for determining the mechanism of the epoxy-ring opening by amine in the solventless reaction medium.

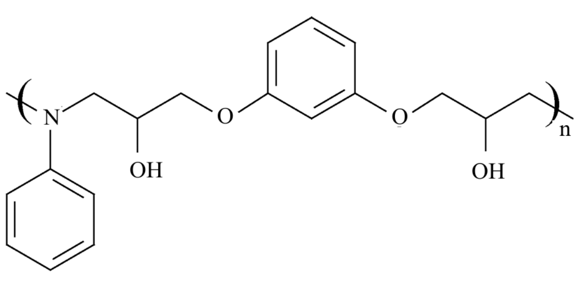

Fig. 1 Structural formula of the product of the reaction of resorcinol diglycidylether–aniline

The reaction of resorcinol diglycidylether (RDGE) with aniline falls into the family of epoxy-amine reaction mixtures, within of which the functional groups varies only (Fig. 1). Here the glycidylether unit is the reactive functional group of epoxide and the functional groups of amine are NH-groups. The addition of the amine group onto the epoxy ring results in the formation of linear polymer.

This reaction can be of some interest from the following point of view: it offers the possibility of performing the polycondensation in epoxy-amine system far above T_g (the glass transition temperature), whereas the study of the glass-forming reaction system showed that the reaction was too fast for the kinetic analysis even at the temperatures lower the glass transition temperature [2].

Previously [6], assuming the importance of prereaction binding in a catalyzed process, a kinetic study of this reaction was carried out in the simplified form to check the validity of Eq. (2). By measuring the heat release rate on the reaction time, the rate constant k_{ef} and molar reaction heat q were estimated graphically from a plot of W_t/Q_t *vs*. Q_t using the equation:

$$W_t/Q_t = k_{ef}C_0 - k_{ef}Q_t/q \tag{4}$$

where W_t and Q_t are the rate of the heat release and the reaction heat release at time t, respectively.

The data were analyzed by plotting the function W_t/Q_t *vs*. Q_t. The plot is shown in Fig. 2. The fact that this reaction shows second order rate behaviour is definite evidence in favour of association mechanism, where C_0 is the initial concentration of the complex in mol L^{-1}. It equals the concentration of the deficient reagent.

The linear portion of the curve was extrapolated to intercept Q_t, giving the value of q, the molar heat of the reaction. The slope of the linear portion of the curve was used to calculate the value of the rate constant for the reaction, k_{ef}. Beyond this region, the linear relationship did not hold and the values of Eq. (4) were higher than those expected from the linear relationship. During this time the reaction rate was described by the kinetics of the following form:

$$W_t = \mathrm{const} - k_{ef}(C_{OH})_s Q_t \tag{5}$$

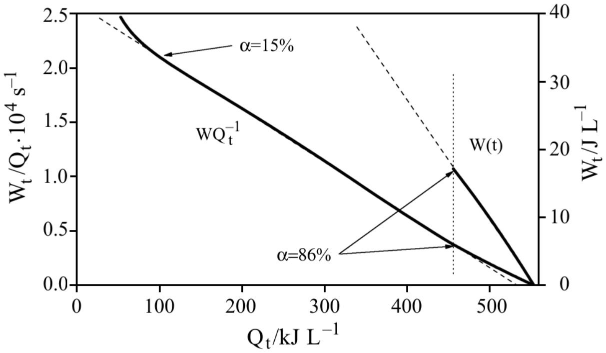

Fig. 2 Plot of the function W_t/Q_t *vs.* Q_t and plot of W_t *vs.* Q_t; the ratio of functional groups amine/epoxy equals 0.67 at 70°C

Because of quantity of the reaction product is determined by conversion the deficient reagent, in Fig. 2 the straight line plot continued up to the complete conversion of epoxide. In all rate measurements the plot of W_t *vs.* Q_t was straight line. The latter is also illustrated by Fig. 2.

Interpretation of these data would suggest the presence of some sort of 'saturation effect'. By 'saturation' condition is meant a situation where the reaction medium is saturated with OH-groups and newly formed OH groups leave the reaction region due to the structure forming. Such a hypothesis has been confirmed in agreement with Eq. (5) by plotting W_t *vs.* Q_t.

In examination of the applicability of Eq. (4) to the reaction of resorcinol diglycidylether (RDGE) with aniline, we found that an Eq. (4) was valid starting with about 15% of conversion. Equations (4) and (5) ignore the uncatalyzed reaction, which proceed to appreciable extent at the beginning of the reaction and initiates the catalytic reaction.

In order to make a more complete description of the experimental kinetic curves obtained by calorimetry, we report on the calculation of the whole curve of the heat realised rate.

Experimental

The reagents were distilled in the argon flow. Kinetic runs were performed at a various initial concentrations of the components using 0.25 g samples in sealed aluminium pans.

The measurements were carried out using differential scanning calorimeter DSC-111 ('Setaram', France). In all cases, the differential scanning calorimetry curves were recorded with heating rates of 5°C min^{-1}. The glass transition temperature was estimated as an intersection of the baseline and the rising part of the baseline shift. First-order transition temperatures were reported as the maxima at their endothermic peaks.

Kinetic measurements were carried out by varying the reagent concentration. The data were treated as previously described [3, 5]. The initial experimental points were obtained by the extrapolation to zero time. Within a given experiment mean deviation of the calculated from the observed kinetic curves was about 1.5%.

Assuming that reaction mechanism proposed for simple molecular epoxy-amine system such as phenylglycidylether–aniline would be operative in the reaction between resorcinol diglycidylether and aniline, the raw of the heat release rate which must be given by the Eq. (6).

$$W = Q_{mol1}k_{ef1}[E][A] + Q_{mol2}k_{ef2}[AE][P–P^{sat}] + \\ + Q_{mol3}k_{ef3}[(P–P\ sat) –P_{inactive}][P–P^{sat}] \qquad (6)$$

In this equation, AE is the current concentration of the stable complexes formed by the reagents, amine (A) and epoxide (E), in mol L^{-1}. W is the heat release rate, the reagent concentrations are represented in terms of the concentration of functional groups. Q_{mol1} and Q_{mol2} are the molar heats of the epoxy-ring opening for uncatalyzed reaction and catalyzed reactions respectively; k_{ef1} is a rate constant for uncatalyzed reaction; k_{ef2} is (observed) effective rate constant for the reaction catalyzed by OH-groups formed in the reaction. The later term represents the heat of the structure forming process. For this process, Q_{mol3} and k_{ef3} are the molar heat and a rate constant, respectively. $P_{inactive}$ is the concentration of OH-groups which takes part in the process of structure forming. The onset of this process corresponds to the concentration of the reaction product denoted as P^{sat}.

Results and discussion

Typical examples of the experimental curves obtained for the reaction of resorcinol diglycidylether with aniline are shown in Fig. 3. The agreement between the values of the experimental curve of the heat release rate and those calculated from Eq. (6) is illustrated in the same Fig. 3. The latter replies the validity of the raw of the heat release rate (6) in reaction medium under the chosen conditions. As is apparent from Fig. 3, with increasing amine content, reaction rate increases. This feature of the epoxy-amine reaction systems is common for epoxy-amine systems considered previously [2, 5].

The data indicates that the heat involved in the cause of the reaction is consistent with 100% conversion. The completion of the reaction described here is entirely accounted for by the prereaction binding of the reagents. It is quite possible that the reaction considered here concerns the high cyclization tendency. Recently, the high cyclization tendency in polycondensa-

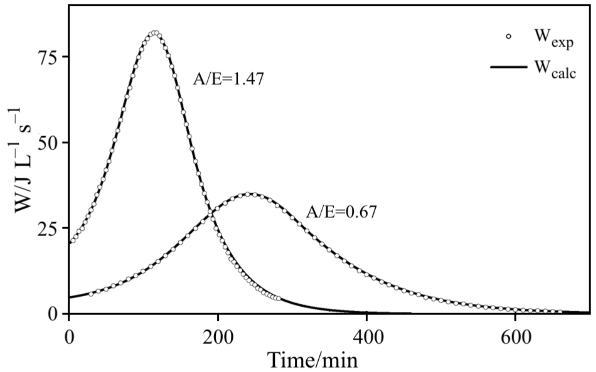

Fig. 3 Experimental rate curves on the reaction time with various of functional groups amine/epoxy at 70°C

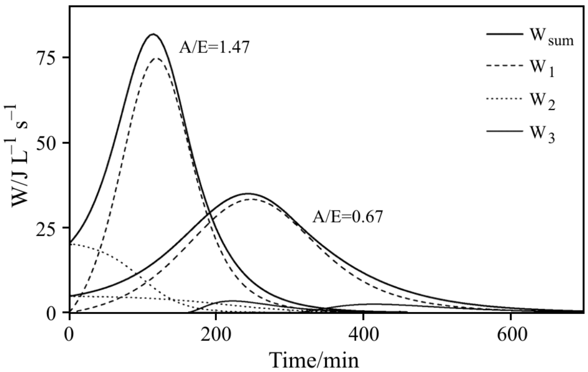

Fig. 4 The heat release rate on the reaction time in each of the three pathways, uncatalyzed, autocatalyzed and structure-forming process

tion processes has been reported as a feature polycondensation under kinetic control [7].

Quantitative evaluation of the molar heats Q_{mol1}, Q_{mol2}, Q_{mol3} and the rate constants for the three pathways k_{ef1}, k_{ef2}, k_{ef3} obtained at different reagent ratio were carried out by nonlinear regression analysis of the data according to the Eq. (6), and the values were collected in Table 1. The molar heats Q_{mol1} and Q_{mol2} are almost independent of reagent ratio as is observed (Table 1). The values of Q_{mol2} are always less than the values of Q_{mol1}. Within the frame of the kinetic model (Eq. (6)), the catalytic reaction differs from uncatalytic one in that the reagents are bonding into the stable complexes. Most likely that complex formation stability is given by the difference between molar heats Q_{mol1} and Q_{mol2}.

As above mentioned, our experiments are not precise enough to unambiguously determine Q_{mol1} and k_{ef1} depending upon reagent ratio. These values seem somewhat inconclusive due to the large amount of scatter in the data. However, as it is seen from Table 1, the value of k_{ef1} at least 100-fold smaller than k_{ef2}. The catalytic reaction differs from uncatalytic one in that the reagents are binding into the stable complexes.

As can be seen in Fig. 3, the experimental curves are well described by the sum of contributions of three variables as well as in other epoxy-amine systems [2, 3, 5]. In Fig. 4, as an example, the typical curves W are decomposed to show variation of the heat release rate in each of the three processes by itself. One can see that curves W_2 indicate the presence of an especially marked induction period. During the induction period epoxy ring opening occurs with no catalyse action on the initial rate.

The time dependence of the rate heat evolving in the third process has also long-continued induction period to the point denoted as $\mathrm{P}^{\mathrm{sat}}$ in Eq. (6), where the rate curve increases rapidly and reaches to the maximum, then decreases gradually. The values Q_{mol3} and k_{ef3} are also given in Table 1. These data indicate that some of the catalytic activity is lost after the point denoted as $\mathrm{P}^{\mathrm{sat}}$ in Eq. (6). This point is found to be in the region of 70% of conversion (Table 1). In the presence of NH-groups in twofold excess, the process represented by the curve W_3 is not observed. The same behaviour was observed in the case of the other epoxy-amine systems [2, 3].

Table 1 Summary of thermokinetic analysis of the reaction between diglycidylether and aniline at 70°C

A/E	$k_1/10^7$ L mol^{-1} s^{-1}	$k_2/10^5$ L mol^{-1} s^{-1}	$k_3/10^5$ L mol^{-1} s^{-1}	Q_{mol1}/kJ mol^{-1}	Q_{mol2}/kJ mol^{-1}	Q_{mol3}/kJ mol^{-1}	C^{sat}/%
0.48	8.25	5.39	14.9	135	87	16	68.4
0.67	5.74	5.31	14.3	205	91	25	70.4
0.75	6.73	5.41	10.8	225	86	29	69.3
0.93	8.23	5.66	7.62	190	82	42	71.0
1.09	10.2	6.07	9.06	200	88	39	73.1
1.28	12.5	7.35	14.2	240	96	28	75.6
1.47	15.3	8.11	23.3	235	96	18	77.2
1.62	11.9	8.54	95.4	245	92	6	89.9
2.11	6.87	10.0	–	365	95	–	–
3.16	9.16	12.2	–	315	91	–	–
4.07	15.2	11.1	–	185	87	–	–

The additional heat effect presumably reflects corresponding structural changes in the reaction medium resulting in 'saturation' condition due to the incompatibility between the polymer molecules entangled in different degrees and low-molecular mass molecules. Thus additional heat can be related to organisation of the polymer chains into the entangled structure. In other words, the entangled polymer is subjected to microphase separation because polymer–polymer contacts are more favourable than contacts of polymer with reaction medium [8].

Combining the kinetic results and DSC measurements made on the samples after the complete the reaction, one may receive further confirmation the validity of the interpretation of the experimental data. Scans were run as soon as possible after the complete the reaction and also on samples annealed at room temperature.

For a sample cooled into the glassy state, as can be seen in Fig. 5, the C_p curve exhibits a heat capacity jump due to the glass transition. This sample was initially rapidly cooled to 0°C in the DSC at cooling rate 5°C min^{-1} and the temperature was then raised at a heating rate of 5°C min^{-1}. As might be expected under these conditions, it is the absence of endothermic peak in the C_p curve. In unaged sample such picture is a feature of amorphous polymers [9]. As evident from Fig. 5, the differences between first and second scans appeared after aging at room temperature for 5 days. Such endothermic peak is a consequence of the structural relaxation process during heating run.

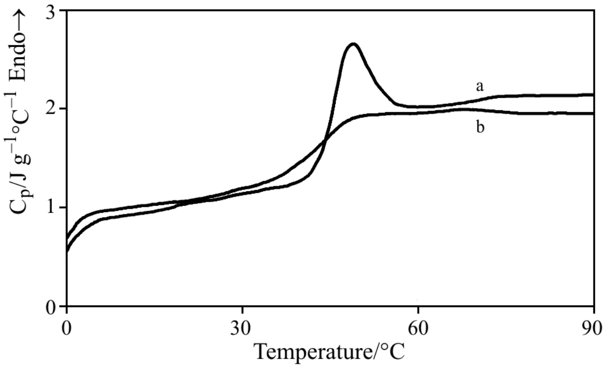

Fig. 5 DSC heating scan a – after the complete of the reaction and b – after of aging at room temperature for 5 days; The ratio of functional groups amine/epoxy equals 1.28

Figure 6 shows the first and second heating runs for sample that had been aged for four months. Two endothermic transitions are the main features of these DSC scans. That at the lower temperature is assigned to a glass transition. It noticed by a strong enthalpy relaxation endotherm, while the endotherm at the higher temperature has the appearance of a melting transition. The second scan shows that this endothermic effect nearly at 67°C has almost completely disappeared in the second DSC trace while the endotherm in heat capacity jump is still present. Before starting second scan, the sample was kept at room temperature for one month. The enhanced endothermic peak in heat capacity jump at a temperature immediately above T_g during the first and second scans indicates that a great degree of relaxation occurred during annealing. In comparison with this endothermic peak, the endotherm in the region of 60–70°C corresponds to the melting of the ordered structure that appears with annealing. The latter indicates that some kind of order is appearing in the sample after long annealing time.

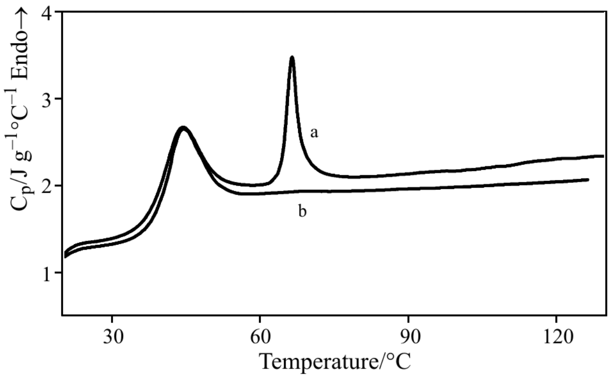

Fig. 6 DSC curves of the sample with the ratio of functional groups amine/epoxy equalled 0.67; a – the first run of the sample aged for four months at room temperature and b – the second run

One can appreciate from Figs 5 and 6 that in contrast with the transition of relaxation origin, the second peak location is the same irrespective of the glass transition temperature, it almost independent of the reagent ratio. Since the peak temperature for all mixtures is observed at essentially at the same position independent of the reagent ratio, this implies that it is possible for the reaction system to form ordered regions. This is consistent with our previous studies [3, 5]. We propose that the endotherm in the region of 60–70°C reflects that some kind of order is appearing in the sample after long annealing time. It is well-established the presence of ordered regions in amorphous polymers [10, 11]. From the above, it may be supported that such samples are composed of both crystalline and amorphous components.

Unlike the cross-linked resorcinol diglycidylether-diamine samples [12], the glass-forming ability even under fast cooling makes the samples of resorcinol diglycidylether–aniline is of interest as a model in the investigation of the capability of the glass-forming system to exhibit a strong enthalpy relaxation.

If the polymer molecules aggregates or coil up, would be observed the deviation of the experimental points from the rate raw Eq. (6), since this equation takes into account the total concentration of the polymer molecules. Entanglement of polymer molecules coiled up in different degrees can be a cause of the loss of catalytic activity by the polymer molecules. In this case, most probably those OH-groups assisted reaction become difficult of access. Thus, the loss of catalytic activity by the molecules of the reaction product serves as indicator for the occurrence the process of structure-forming during the kinetic analysis.

Previous reports [2, 3, 5], studying interaction epoxy- and NH-groups pointed out the importance of association between the reagents. The uncatalyzed pathway is presumed to give rise to a catalytic reaction in the observed rate of epoxy ring opening. In the catalyzed reaction, due to the formation of the stable complexes under action of catalyst, the electron donating ability of NH-group is further enhanced, resulting in further decrease in the electrophilicity of the C undergoing addition.

Thus the epoxy-amine reactions illustrate the ability of functional groups in solventless system to realise the catalyzed reaction by the formation of stable complexes. The latter are assumed to assist the formation of the reactive intermediates and propagate the polymerisation process over a long reaction time.

The melting point of the ordered phase is not influenced by the polymer concentration. Hence, it seems reasonable to account for the melt-like peak in the heating scans after long annealing time as the resulting from the short-range ordering of the molecules relative to each other. For example, annealing studies performed within the glassy state and at various temperatures for various times revealed that annealed glass is able to crystallize and the degree of crystallinity increased with increasing annealing time [13].

The linear polycondensation in epoxy-amine system, reported herein bears a close similarity to the simple molecular epoxy-amine system such as phenylglycidylether–aniline [3]. The increasing information from kinetic picture of the linear polycondensation in epoxy-amine system may lead to further experiments, resulting in a better understanding of the mechanism of structure forming during the epoxy-amine reactions.

Conclusions

By using calorimetry the behaviour of the epoxy-amine linear polycondensation system has been investigated explicitly. Resorcinol diglycidylether was polycondensed with aniline. Here we used a way of checking the reaction mechanism contained the comparison of the heat realised rates determined experimentally with those calculated from the experimental points.

Analysis of the experimental curves was used to show that the results are consistent with the physical model of the reaction outlined in Eq. (6). This model incorporates both uncatalyzed and autocatalyzed pathways as well as includes structural transformation in the reaction medium. Then additional exothermic effect during the present reaction was interpreted by considering this heat effect as a result of the structural changes in the reaction medium occurring at longer times of the reaction. At the beginning of the reaction, only uncatalyzed reaction proceeds to appreciable extent. The latter is strongly exothermic as compared to the catalyzed one. Similar thermokinetic behaviour has been observed with the system of phenylglycidylether–aniline [3]. The explanation of the differences in molar heats for the uncatalyzed and catalyzed reactions lies in the prereaction binding in a catalyzed pathway.

Our results indicate that structure-forming processes can be also identified by thermokinetic studies. The elucidation of the mechanism of the structure-forming process in epoxy-amine systems, however, requires further studies.

References

1 H. B. Mark and G. A. Rechnitz, Kinetics in Analytical Chemistry, Wiley, New York 1968.
2 R. M. Vinnik and V. A. Roznyatovsky, J. Therm. Anal. Cal., 71 (2003) 819.
3 R. M. Vinnik and V. A. Roznyatovsky, J. Therm. Anal. Cal., 75 (2003) 753.
4 J. T. Kindt and W. M. Gelbart, J. Chem. Phys., 114 (2001) 1432.
5 R. M. Vinnik and V. A. Roznyatovsky, J. Therm. Anal. Cal., 73 (2003) 531.
6 M. I. Vinnik, R. M. Vinnik, V. E. Grinev and S. W. Pilyugaitseva, Russ. Chem. Bull., 42 (1993) 843.
7 H. R. Kricheldorf, M. Rubenshtein, M. Mascos and M. Schmidt, Macromolec., 34 (2001) 71.
8 E. Dormidontova and G. ten Brinke, Macromol., 31 (1998) 2649.
9 L. C. E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier Scientific: Amsterdam, Oxford, New York 1978.
10 G. S. Y. Yeh, J. Macromol. Sci., B 6 (1972) 465.
11 V. A. Kargin, J. Polym. Sci., 30 (1958) 247.
12 R. M. Vinnik and V. A. Roznyatovsky, J. Therm. Anal. Cal., 74 (2003) 29.
13 I. Alig, D. Braun, R. Langendorf, M. Voit and J. H. Wendorf, J. Non-Cryst. Solids, 221 (1997) 261.

Received: February 18, 2005
In revised form: April 26, 2006

DOI: 10.1007/s10973-005-6955-6