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KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY–AMINE CURE REACTION
Part V. Phenyl glycidyl ether–aniline

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Abstract

Using calorimetric method to reaction kinetics in solventless system, the quantitative aspects of the epoxy ring opening in the reaction between phenyl glycidyl ether and aniline have been discussed. Using the Mangelsdorf method we have found that this reaction system gives fairly clean kinetics through whole process. The kinetic picture of this reaction system is akin to diepoxy–diamine cure mechanism.

It was detected kinetically, apart from exothermic effect of the reaction of the epoxy ring opening, the existence another exothermic process at the last stages of the reaction. The latter also contributes to the total heat. The contribution of this thermal effect to the total heat is found to be dependent on the reactant ratio.

The data for the reaction between phenyl glycidyl ether and aniline could not be fitted well if uncatalyzed mechanism was ignored. Thus, the reaction of epoxy ring opening by aniline occurs by two concurrent pathways: one is uncatalyzed and the other, the main, is autocatalyzed.

Keywords: aniline, DSC, epoxy–amine thermokinetics, Mangelsdorf's method, phenyl glycidyl ether, reaction kinetics in solventless systems

Introduction

The preceding series of papers described the thermokinetic measurements of epoxy–amine cure system [1–4]. Epoxy–amine cure kinetics has long been a subject of considerable scientific interest, but the mechanism of this process is still not adequately understood. The interest in cure reactions is prompted by their commercial importance. The term 'cure' is used to name the overall transformation from liquid to glassy solid due to chemical reaction. The classical but still most popular explanation for the epoxy–amine cure reactions is their interpretation in terms of the diffusion rate limitation. In this connection much of the experimental works on cure mechanism have been con-

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cerned with fitting kinetic data into diffusion rate limitation scheme. The correct interpretation of the thermokinetic curves is in contradiction to the diffusion rate limitation scheme in the mechanism of epoxide ring opening by amine. That is to say, diffusion process plays a crucial role in diffusion not reagents but reaction product. It has been reported that cure reaction actually takes place in the molten phase, though this type of reaction systems outwardly appear to be solid.

Since epoxide ring opening produces very high thermal powers, experimental kinetic data are commonly obtained using calorimetry. Data published on analytical application of physical methods indicate that the validity of the results obtained by calorimetry depends on the correctness of the kinetic treatment [5]. Kinetic method by using calorimetry to mechanism of epoxy–amine cure reaction requires knowledge of the molar heat of the epoxy ring opening during the cure reaction. As a rule, for this kind of analysis, kinetic parameters are determined with the assumption that the heat evolved at any time during the cure reactions directly proportional to the extent of conversion. The ratio of the heat produced at given time to the heat produced at infinite time is a measure of the extent of conversion. When carrying out kinetic studies it is frequently difficult to measure the heat evolved at the start of a reaction. Moreover, this approach takes no account the occurrence of additional processes, thermal effects, for example, thermal effect of the phase transition.

Using the Mangelsdorf method described in [6] we have reinvestigated the cure of an epoxy–amine system, and in so doing have found a completely different experimental results. It permit the evaluation of the both the rate constants and the molar heat of the epoxy ring opening during the cure reaction. In essence this method represents a ‘kinetic investigation’ approach to reaction mechanism. It turned out that the reaction of resorcinol diglycidyl ether (RDGE) with *m*-phenylenediamine (MPDA) gives fairly clean kinetics through whole process. Moreover the reaction was also assistance through a preassociation mechanism in which the reactants are assembled before bond-breaking step occurs, and does not proceed through free reacting groups. Therefore, the reaction of epoxy ring opening is not sensitive to the viscosity of the reactive medium. The preassociation mechanism provides a lower-energy pathway than a mechanism that proceeds through free reactants. An example of such stabilization, by hydrogen bonding, is found in general acid catalysis of the cleavage of carbamates formed from weakly basic amines [7].

The preassociation plays a significant if not the dominating role in the kinetics of the network formation. The preassociation may explain the fact observed in previous papers that the reaction is not diffusion-controlled. In other words, the association of molecules precludes the necessity for molecules to undergo diffusion-controlled collision before reaction can take place. Unfortunately, these supramolecular features have not obtained the deserved attention in the study the cure of epoxy–amine systems.

To gain information about the mechanism, in the present study we have extended previous work [1–4] by determining kinetic data for simple molecular epoxy–amine reaction such as phenyl glycidyl ether–aniline that has not been intensively studied by using calorimetry. Another reason for this study stems from our desire to apply the Mangelsdorf approach to the study of epoxy–amine model reaction.

Experimental

Purification of the reagents was conducted by distillation in the argon flow. Differential scanning calorimeter DSC-111 ('Setaram', France) was used to obtain the extent of reaction during the isothermal reactions of epoxy–amine systems. A mixture of epoxide and aniline (ca. 0.25 g) of known composition was sealed in aluminium pans and subjected to isothermal reaction at different reagent ratios.

When the reactions were run to completion, the samples were annealed and a dynamical run was conducted at heating rate of 5°C min^{-1}.

Results

The values of molar heat of the epoxy ring opening were evaluated by 'kinetic investigation' approach to reaction mechanism. Scheme 1 depicts the reaction now accepted for the epoxy ring opening by amine.

$$2\ \underset{O}{H_2C\text{-}CH}-R + R'-NH_2 \longrightarrow R\text{-}\underset{OH}{CH}-CH_2\text{-}\underset{R'}{N}\text{-}CH_2\text{-}\underset{OH}{CH}-R$$

Scheme 1

Typical kinetic curves of the rate of the heat release are shown in Fig. 1. The reaction rate increases as the reaction advances and passes through a maximum. Such maximum is typical of many epoxy–amine reactions, and is indicative of catalytic action of the hydroxyl groups formed during the course of epoxy–amine reaction [8, 9]. However, from Fig. 1 it is apparent that in early stage of the reaction, contribution

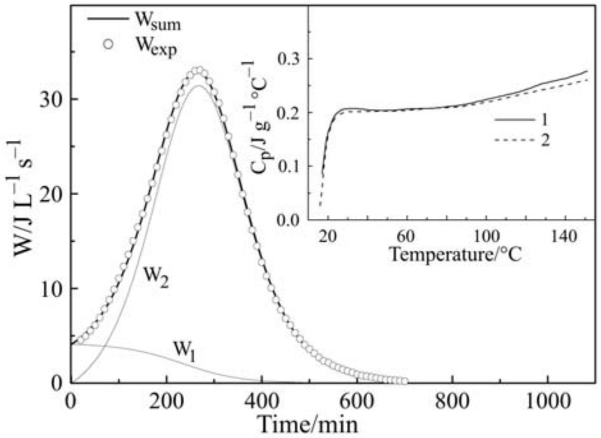

Fig. 1 The result of computer treatment of the kinetic curve of the heat release rate *vs.* time for the isothermal reaction between phenyl glycidyl ether and aniline: ○ – experimental data, — – calculated curve. The curing temperature is 70°C and the ratio of functional groups amine/epoxy equals 1.9; upper right-hand inset: DSC heating scan of the reacted sample with a large excess of amine: 1 – first scan; 2 – second scan

from the uncatalyzed reaction plays an important part. We assume that uncatalyzed reaction proceeds through free reagents unlike autocatalyzed pathway where preassociation mechanism exists.

The treatment of experimental kinetic curves is based on the analogy between the model and cure reaction. In agreement with the conclusions of earlier work [1], noncatalytic mechanism is expressed in the form:

$$\frac{\mathrm{d}C_{\mathrm{x1}}}{\mathrm{d}t}=k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}}) \tag{1}$$

where $\mathrm{d}C_{\mathrm{x1}}/\mathrm{d}t$ is the reaction rate in uncatalyzed reaction; C_{x} is the total concentration of OH groups for both reactions formed to a given time; C_{E} is the initial concentration of functional groups of epoxide in mol L^{-1}; C_{A} is the initial concentration of NH-groups in mol L^{-1}, k_{ef1} is a rate constant for uncatalyzed reaction.

To describe catalytic process we introduced equation:

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

where k_{ef2} is effective rate constant for the reaction catalyzed by OH groups formed in the reaction, an observed rate constant k_{ef2} takes into account the complex formation between the molecules amine and epoxide [1]; C_0 is the initial concentration of the complex in mol L^{-1} (it should be noted the concentration of the complex equals the concentration of the deficient reagent); $(C_0–C_{\mathrm{x}})$ is the current concentration of the complex in mol L^{-1}.

The catalytic activity was described as due to mechanism involving the complex formation between reagents [2]. The function of this complex is to hold a nucleophile within the critical distance of an electrophile for a sufficient length of time.

After much discussion in the literature of reactivity of the primary and the secondary amine hydrogen atoms in the course of the epoxy ring opening, the strongest consequence comes from the kinetic study to mechanism underlying the reaction between amine- and epoxy-groups [2]. As judged by reaction mechanism [2], the same lone pair electrons on nitrogen atom of NH_2-group attacks and open an epoxide ring in the course of the reaction. The latter implies absence of substitution effect.

A simple expression relating the heat releasing rate W to the reaction rate $\mathrm{d}C_{\mathrm{x}}/\mathrm{d}t$ may be written as:

$$W=Q_{\mathrm{mol}}\frac{\mathrm{d}C_{\mathrm{x}}}{\mathrm{d}t} \tag{3}$$

where Q_{mol} is the molar heat of epoxy ring opening (kJ mol^{-1}).

The kinetic equation in the terms of the molar heat of epoxy ring opening for the two reaction pathways: uncatalyzed and autocatalyzed can thus be given by equation:

$$W=W_1+W_2=\frac{\mathrm{d}Q}{\mathrm{d}t}=Q_{\mathrm{mol1}}k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})+Q_{\mathrm{mol2}}k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})C_{\mathrm{x}} \tag{4}$$

From Fig. 1, it can be seen that the excellent agreement found in this experiment between the calculated curves of the rate of the heat release and the experimental data. The experimental points follow closely the calculated curve. The contribution from the two processes namely, W_1, W_2 involved in the reaction kinetics is also shown in Fig. 1. DSC heating scans of the reacted sample are shown in the inset of Fig. 1.

By combination of both mechanisms, uncatalyzed and autocatalyzed, the reaction kinetics can be described over the entire conversion range in reaction mixtures only containing more than about two-fold excess of amine with respect to the reacting functional groups. However, in mixtures having stoichiometric composition the relationship (4) held up to about 70% of conversion after which there was a considerable increase in the rate of heat release.

In order to provide a basis for understanding these results, after the kinetic measurements when all reagents have reacted, we carried out the DSC heating scans. DSC scans of the reacted samples with different composition are displayed in Fig. 2. After the first heating run, from 20 to 150°C, the samples were annealed and a second heating run was performed. Curves of Fig. 2 represent the first and the second heating scans of the samples after the completion of the reaction. The line (1) is the first scan, and the line (2) represents the second scan taking right after cooling from the initial one. A characteristic feature of these curves is the endotherms arising during the first scans. These endotherms are quite broad, starting at 45°C and ending at 80°C. All endothermic peaks show a maximum at about 65°C. Their value is directly dependent on the reagent ratio, though substantial variation in the shape of the transition is apparent. Endothermic enthalpies ΔH in J g^{-1} are listed also in Table 1.

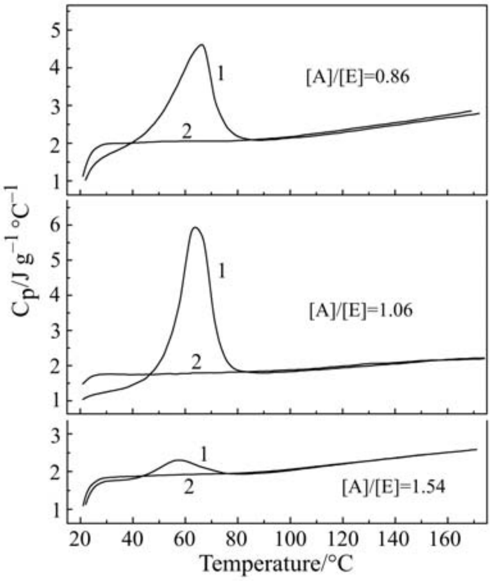

Fig. 2 1 – The first and 2 – the second DSC heating scan of the reacted samples with different reactant ratios

Table 1 Summary of thermokinetic analysis of the reaction between phenyl glycidyl ether and aniline at 70°C

	$[A]/[E]$								
	0.52	0.72	0.86	1.06	1.28	1.54	1.9	3.1	4.5
Q_{mol1}/kJ mol^{-1}	335.6	169.6	152.8	204.3	204.3	377.2	201.3	322.5	258.7
Q_{mol2}/kJ mol^{-1}	89.86	92.95	84.57	85.83	97.97	99.23	107.2	86.08	93.78
Q_{mol3}/kJ mol^{-1}	14.72	26.75	46.47	38.1	26.13	25.96	0	0	0
$k_1 \cdot 10^7$/L mol^{-1} s^{-1}	2.98	3.81	6.17	4.12	5.76	4.12	4.93	4.5	8.96
$k_2 \cdot 10^5$/L mol^{-1} s^{-1}	3.01	2.95	3.22	3.16	3.79	4.76	5.41	8.53	9.92
C^{sat}/%	73.2	69	63.5	69.8	74.2	76.3	100	100	100
Q_{sum}/kJ L^{-1}	367	455	535	577	594	571	526	430	355
Q_1/%	20.0	9.9	9.9	9.4	11.7	16.7	11.3	29.2	28.6
Q_2/%	78.3	84.8	75.6	80.1	82.8	83.3	88.7	70.8	71.4
Q_3/%	2.5	5.2	14.5	10.5	5.6	4.9	0	0	0
ΔH/J g^{-1}	–28.6	–45.9	–57.3	–67.7	–	–2.07	0	0	0

Perhaps the most obvious explanation of these results is that in this system the product molecules tend to organize, leading to the formation of molecular microaggregates. This corresponds to a situation where the reaction region is saturated with OH-groups and newly formed OH groups leave the reaction region. This view led us to an attempt to include term for saturation kinetics in the kinetic Eq. (4). This term was applied in the form:

$$\frac{\mathrm{d}C_{x3}}{\mathrm{d}t}=k_{ef3}[(C_x-C_x^{sat})-C_{x3}](C_x-C_x^{sat}) \tag{5}$$

where C_x^{sat} is the saturated concentration OH groups in the reaction volume. k_{ef3} is a rate constant for this process; C_{x3} is the concentration of OH groups which escape from the reaction medium.

At the present stage of research the mechanism of product structuring is mostly unknown, and thus, possible mathematical model for the calculation of the thermokinetic curve can be deduced only by phenomenological assumption. In a previous Part [1] non-linear Eq. (5) was also applied for the case of the epoxy–amine cure reaction in the vitrificated reaction mixture to describe the reaction kinetics in structure forming reaction medium.

The rate of heat evolution W_3 is equal:

$$W_3=Q_{mol3}\frac{\mathrm{d}C_{x3}}{\mathrm{d}t} \tag{6}$$

where Q_{mol3} is the molar heat of the third process. The net rate of heat evolution W can be written in the following form:

$$W=W_1+W_2+W_3=Q_{mol1}k_{ef1}(C_A-C_x)(C_E-C_x)+$$
$$+Q_{mol2}k_{ef2}(C_0-C_x)(C_x-C_{x3})+Q_{mol3}k_{ef3}[(C_x-C_x^{sat})-C_{x3}](C_x-C_x^{sat}) \tag{7}$$

Kinetic expression (7) describes the whole course of the reaction. Some typical kinetic curves for several reagent ratios are illustrated in Fig. 3. It should be noted that the agreement between the observed and the calculated curves was estimated by the mean square deviation, which did not exceed 1.5%.

The rate constants for catalyzed k_{ef2} and uncatalyzed k_{ef1} pathways are reported in Table 1 which also includes the molar heat of the epoxy ring opening for autocatalyzed reaction, Q_{mol2} calculated according to Eq. (4). The procedure used for determining these parameters has been described previously [1]. It is apparent that the molar heat of epoxy ring opening for autocatalyzed reaction independents of epoxy–amine composition.

As well as autocatalyzed reaction W_2, the curve W_3 represents exothermic process which contributes to the overall thermal effect. It is interpreted in terms of the kinetics of the formation of intermolecular associates with subsequent tend to the phase transition.

When the degree of conversion approaches C_x^{sat} the increasing in the rate of evolving of the heat due to the onset of additional exothermic process is obvious. The values of C_x^{sat} are given in Table 1. As one can see from Table 1, these values are not significantly different from one another.

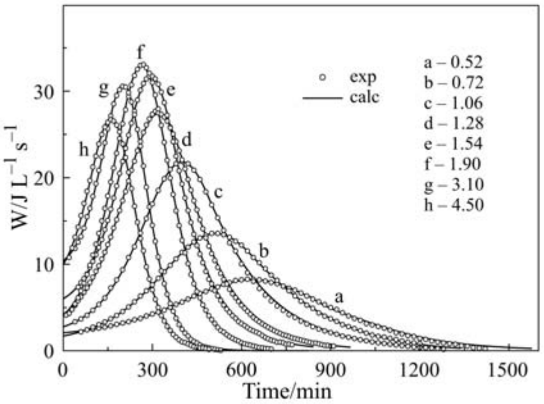

Fig. 3 Isothermal rate curves of the heat release for the reaction phenyl glycidyl ether–aniline with different reagent ratios at 70°C

Additional exothermic effect we associated with the leaving of the newly formed OH groups (C_{x3}) from the reaction region. Q_{mol3} is the molar heat of this process. The values of Q_{mol3} are listed in Table 1.

In percentage terms, the contribution from the three processes involved in the reaction kinetics to the integral value of the reaction heat is also represented in Fig. 5. Comparison of these values depending on excess of amine shows that the magnitude of uncatalyzed reaction is the least not far from stoihiometry, while the curve Q_3 demonstrates the contrary tendency. Under the conditions of the considerable excess of one of the reagents the process represented by the curve Q_3 is not observed.

As is apparent from Fig. 3, whereas excess of epoxide caused a decrease in rate in comparison with the stoichiometric content, the same excess of amine caused an increase in reaction rate. In Fig. 4, we have plotted the rate constant *vs.* excess of amine over epoxide and it is seen that on the whole, there exists a fairly good linear correlation between them.

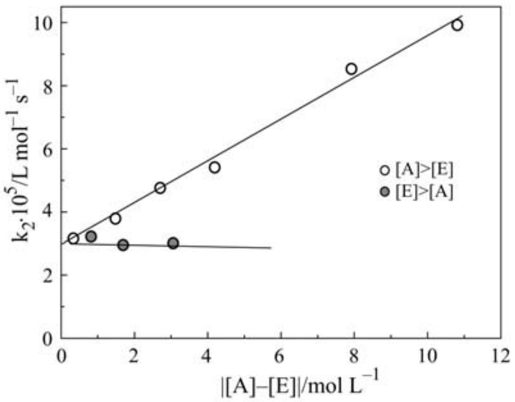

Fig. 4 Dependence an effective rate constant k_{ef2} on the amine excess, 70°C

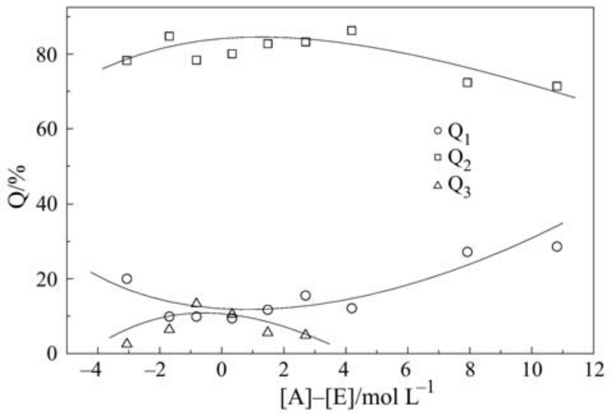

Fig. 5 Dependence the contribution from Q_1, Q_2 and Q_3 process on the aniline excess, 70°C

$$k_{\mathrm{ef2}}=k_{\mathrm{amine}}(C_{\mathrm{A}_0}-C_{\mathrm{E}_0})+k_{\mathrm{ef2(A=E)}} \tag{8}$$

The k_{amine} term describes catalytic activity of excess of amine; $k_{\mathrm{ef2(A=E)}}$ is the apparent rate constant of the stoichiometric composition; ($C_{\mathrm{Ao}}-C_{\mathrm{Eo}}$) is excess of amine over epoxide, mol L^{-1}. Whereas clear straight line from Fig. 4 indicates that reaction rate for autocatalyzed reaction independent of reagent ratio in the case excess of epoxide.

Discussion

One of the earliest attempts to study kinetics of the reaction between phenyl glycidyl ether and aniline was made in [10]. These authors applied thermolecular interaction mechanism first proposed by Smith for catalysed reaction [8]. From this work it is obvious that the kinetic picture of this reaction is not consistent with Smith's proposed mechanism. The third-order kinetics (first order in both the epoxy and amine and catalyst) holds at approximately 20% conversion.

The results obtained from spectroscopic studies on the reaction under consideration have been reported in [11]. One of the outstanding features found on this work, is the existence of a phenomenon of diffusion rate limitation arising in viscous medium. Obviously, this simple explanation is not valid because under the same conditions the reaction kinetics was analyzed by back titration with silver nitrate as far as 100% completion in [10]. Thus, no evidence of a diffusion limiting off was found.

If Eq. (7) is correct, reaction rate constant for autocatalyzed reaction should be independent of the composition of the reaction mixture. It is apparent that in the presence of epoxy in excess, rate constant for autocatalyzed reaction independent of reagent ratio (Table 1). However, this behavior is hold only in the presence of epoxy in excess. While, as above mentioned, in the presence of aniline in excess, reaction rate increases with increasing amine content due to catalytic activity of excess of amine. This finding supports an interpretation of the kinetics in terms of the preassociation mechanism. In the reaction under consideration, catalytic activity of excess of amine is an indication of the presence of the reactant association.

The effect of catalytic activity of excess of amine agrees with observations emerging from the epoxy–amine cure process [2].

The data for this reaction could not be fitted well if uncatalyzed pathway was ignored. Uncatalyzed reaction W_1 plays an important part up to about 50% conversion as seen in Fig. 1. However, as the first points of the kinetic curves are subject to some error, there is clearly scatter in thermokinetic parameters determined by calculation. Since the experimental values are not of precision, these data are not the subject of the discussion.

The important feature to be noted is that the kinetic results represent the same trend as those described previously [2, 3] in the case of formation of epoxy–amine glassy polymer. However, the reaction of aniline with phenyl glycidyl ether is markedly slower than that of resorcinol diglycidyl ether (RDGE) with *m*-phenylenediamine thus suggesting that bifunctional origin of the reactants and not a viscosity of the reaction mixture is responsible for the high rate of epoxy ring opening by amine. It is conceivable that the key to the mechanism of epoxy–amine ring opening by amine lies in the role of the reactant association. As compared with cure reaction, in the case of the reaction under consideration, side-reactions involving the etherification reactions appear to be absent.

The kinetic form described by Eq. (5) is interpreted as arising from the considerable increase in the reaction rate of heat release during the last part of the reaction. The latter may be considered as an initial stage of aggregation of the reaction product with subsequent phase transition. In this case, endotherm observed during the DSC heating run may be considered as a melt-like transition. In the case of a large excess of amine, according to the kinetics (Fig. 1), there is no evidence for product structuring and no endothermic peak were also observed during the DSC heating runs.

Perhaps, these molecular associates are created including hydrogen bonding between OH groups. The results reported in [12], where the reaction of aniline with phenyl glycidyl ether was studied by near infrared spectroscopy, also point to structuring of the molecules through H-bonding.

Not much has been found in the literature to indicate the molar heat of the epoxy ring opening during the epoxy–amine model reaction. One value repeatedly cited is that 110 kJ mol^{-1}.

Direct calorimetric measurement of the enthalpy for the reaction mixture phenyl glycidyl ether–aniline containing two-fold excess of amine with respect to the reacting functional groups was carried out in [10, 13]. On the whole, for this reaction ratio, a fairly good linear correlation between the heat estimated from the area under the isothermic kinetic curve and conversions based on the titration was obtained. Indeed, the molar heat of the epoxy ring opening during the epoxy–amine model reaction was determined as 110 kJ mol^{-1}. The heat of this reaction was also determined from combustion experiments [13, 14]. This value has been reported as 113 kJ mol^{-1}. As it can be seen from Table 1, for autocatalyzed reaction, there was no observable light variation in the molar heat of epoxy ring opening within a broad range of reagent ratio. Aggregation in the course of the reaction can be solely the precursor of melt-like transitions observed in DSC heating scans. A possible explanation for the endothermic observed during DSC heating runs may lie in the fact that interaction between the aromatic rings also contributes to molecular aggregates (cluster) formation. More detailed interpretation into the nature of melt-like transitions will be discussed in connection with a more comprehensive experimental study.

Conclusions

Quantitative information on the kinetics of the simple molecular epoxy–amine system, such as phenyl glycidyl ether–aniline was obtained by analysing the thermokinetic curves taken at various reagent ratios using the Mangelsdorf approach. At that the calorimetric method represents a simple and convenient technique for the study reaction kinetics in solventless systems.

The kinetics of the system phenyl glycidyl ether–aniline shows the close similarity to epoxy–amine cure mechanism. The kinetic picture of this reaction is akin to epoxy–amine cure mechanism. From the results it is evident that the reaction between phenyl glycidyl ether and aniline occurs by two parallel reaction paths: one is uncatalyzed and the other, the main, is autocatalyzed.

Working in the presence of an excess of aniline, we found the increasing the reaction rate as the amine content increases. It was reported in earlier part [2] that an excess of amine has the same trends in epoxy–amine cure reaction. From these results it is clear that the influence of an excess of amine on the rate is characteristic for reactions between epoxide and amine.

A possible explanation for a considerable increase in the reaction rate of heat release during the reaction at the last stages is that under these conditions the behavior of the reaction system is governed by the product structuring. Thus, for correct simulation of the thermokinetic curves, during the last part of the reaction, we included the saturation kinetics. At present stage we are not able to provide a detailed explanation concerning the reason for phase transitions observed in DSC scans. Meanwhile this kind of study could be useful in the investigation of the capability of small molecules to give rise to the structures, via non-covalent bonding. Thus, further experiments are required in order to find out the structure forming mechanism.

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