Kinetics of multifunctional thiol-epoxy click reactions studied by differential scanning calorimetry: Effects of catalysis and functionality

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ABSTRACT

Isothermal reaction kinetics of thiol-epoxy (multifunctional thiol-difunctional epoxy) reactions with and without external catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were studied using differential scanning calorimetry (DSC). Autocatalytic behavior is observed both without DBU and with DBU, which is attributed to autocatalysis effects of hydroxyl products of the reaction. The isothermal curing kinetics are well described by the Kamal autocatalytic model, which is expressed as $d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n$ (α: fractional conversion; $d\alpha/dt$: apparent rate of reaction). Parameters of the reaction, including reaction orders m and n, apparent rate parameters k_1 and k_2, and activation energies are determined by fitting the experimental data to the Kamal model. For the thiol-epoxy reaction without DBU, the overall reaction order ($m + n$) is approximately 3 (with $m \approx 2$ and $n \approx 1$) but decreases to 2 (with $m \approx 1$ and $n \approx 1$) upon addition of DBU. Based on the most commonly described mechanism for nucleophilic thiol-epoxy reactions in the literature, new reaction schemes are proposed by incorporating the hydroxyl autocatalysis effect as well as the effect of external catalyst DBU on apparent reaction order. The proposed reaction schemes allow for excellent fits to reaction kinetics for thiol-epoxy reactions with and without DBU. In contrast to the strong effect of external DBU catalyst on reaction kinetics, changing the thiol monomer functionality leads to relatively small changes in apparent rate parameters and no change in the order of reaction or reaction mechanism.

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1. Introduction

The thiol-epoxy reaction (or mercaptan-epoxy reaction [1], also called the thiol-epoxy "click reaction" [2–4]) is used to synthesize polymers for applications associated with adhesives and high-performance coatings [5–9]. There has been growing interest in the thiol-epoxy coupling reaction as an effective synthetic tool because of its efficiency and robustness. For example, thiol-epoxy reactions have been extensively used to synthesize a new family of reactive polymers called poly(β-hydroxythio-ether)s, which are typically high molecular weight, linear polymers with reactive hydroxyl groups that easily allow for post-polymerization modification [10–19]. Thiol-epoxy reactions have also been used in surface modification [20,21], nanoparticle functionalization [22],

synthesis of hybrid polymer networks [23–27] and shape memory polymer foams [28], and biomedical [29,30] and other applications [31–37].

Base catalysts, including regular amine base catalysts (e.g., triethylamine) or stronger bases such as 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) and LiOH, are commonly used to catalyze thiol-epoxy reactions [7,10–14,17,18,21–23]; other catalysts like Lewis acids [29,30,38] and photobase generators [25,26,39] have also exhibited effectiveness in catalyzing this reaction. As depicted in Scheme 1, the generally accepted mechanism for the base-catalyzed thiol-epoxy reaction is a simple nucleophilic ring-opening reaction [2–4,23]. Base catalysts deprotonate thiols to generate thiolate anions, which then undergo a nucleophilic ring-opening coupling reaction with epoxide groups to form alcoholate anions. The protonation of the alcoholate anions via either the base catalyst (Scheme 1a) or the thiol (Scheme 1b) results in thiol-epoxy reaction products [2].

In order to test the mechanism in Scheme 1, several studies [5–7,34,36] have focused on detailed, multifunctional curing kinetics

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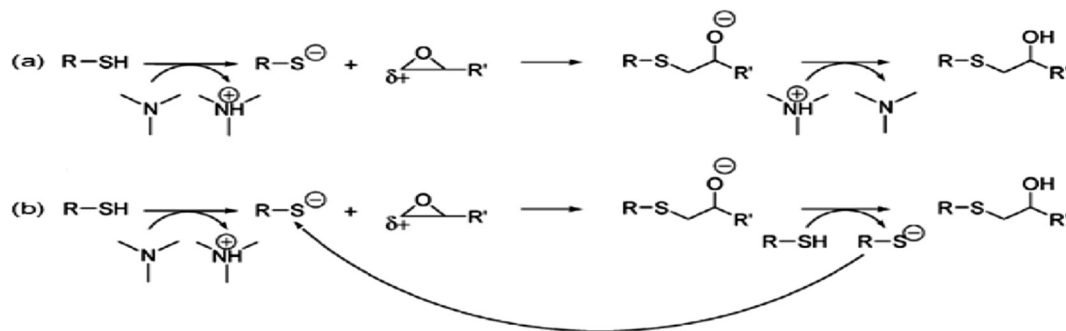
Scheme 1. Proposed mechanism for base-catalyzed thiol—epoxy reactions (adapted from Ref. [2]).

of base-catalyzed thiol-epoxy reactions. Lu et al. [5] studied the isothermal reaction kinetics of an epoxy/nitrogen-containing thiol system, bis[3-(2,3-epoxypropylthio)phenyl]-sulfone (BEPTPhs)/tri-mercaptothioethylamine (TMTEA), where the tertiary nitrogen in the TMTEA thiol molecule can act as a base catalyst. They found that the BEPTPhs/TMTEA reaction followed autocatalytic kinetics [5,40—43] and attributed the autocatalytic behavior to hydroxyl-group-containing species formed during reaction. (Autocatalytic behavior due to hydroxyl products has been well studied in amine-epoxy curing kinetics [41—43].) The potential autocatalysis effect of hydroxyl products on reaction kinetics is not included in the generally accepted mechanism for base-catalyzed thiol-epoxy reactions shown in Scheme 1. Thus, there is a need to revisit that mechanism.

Here, we report on the isothermal reaction kinetics of multi-functional thiol-epoxy reactions with and without external catalyst DBU. We chose DBU as catalyst for two reasons. First, because of its enhanced basic character [44], there has been interest in DBU as an effective organocatalyst for reactions such as the Michael addition reaction [44—46]. While DBU is commonly described as a "non-nucleophilic strong base", there are reports demonstrating that DBU also possesses significant nucleophilic character and shows effectiveness in catalyzing the Baylis—Hillman reaction [47,48]. Second, previous studies have shown that DBU exhibits superior effectiveness and efficiency for base-catalyzed thiol-epoxy re-actions [7,19,21,49] over a number of other amine base catalysts including triethylamine. Using differential scanning calorimetry (DSC) to characterize the reactions, we show that isothermal thiol-epoxy reactions with and without DBU exhibit autocatalytic behavior. We also demonstrate that the curing kinetics data fit well to the Kamal autocatalytic model [40,41] and describe the effects of DBU catalyst on reaction order, rate parameters, and activation energies. We further consider the effect of thiol monomer func-tionality on curing kinetics. To adequately account for effects made evident by our DSC experiments, we modify the thiol-epoxy reac-tion mechanism shown in Scheme 1 in order to account for both an autocatalytic effect of hydroxyl products as well as for the change in apparent reaction order in going from reactions without external DBU catalyst to DBU-catalyzed thiol-epoxy reactions.

2. Experimental

2.1. DSC sample preparation

Difunctional epoxy D.E.R.™ 383 (DER), a homologue of bisphenol A diglycidyl ether with an epoxy equivalent molecular weight (M_{eq}) of 180 g mol^{-1}, was provided by The Dow Chemical Company. Trime-thylolpropane tris(3-mercaptopropionate) (SH_3, $M_{eq} = 133$ g mol^{-1}), a trifunctional thiol, and pentaerythritol tetrakis(3-mercapto propionate) (SH_4, $M_{eq} = 122$ g mol^{-1}), a tetrathiol, and the catalyst

DBU were from Sigma-Aldrich. All reactants were used as received. Stoichiometric amounts of thiol and epoxy components were mixed in a high-speed mixer (FlackTek, DAC 150.1 FVZ-K) at 3500 rpm at room temperature. ~10 mg of the liquid monomer mixture was then immediately transferred into an aluminum DSC pan and placed into the DSC sample holder for isothermal reaction kinetics measurement. Within error, no weight loss was observed with a DSC sample before and after reaction. For DBU-catalyzed SH_3-DER reactions, the DBU loading was maintained at 0.17% mol DBU/mol thiol groups in the reactant mixture. A loading of 0.10% mol DBU/mol thiol groups was used for DBU-catalyzed SH_4-DER reactions. (These DBU catalyst loadings were chosen in order to minimize the potential for reaction at room temperature during sample preparation while maintaining the reaction timescales at curing temperatures in a reasonable range for DSC characterization.)

2.2. DSC isothermal reaction

Isothermal thiol-epoxy reaction kinetics were studied by monitoring the heat flow evolution during reaction using a Mettler-Toledo DSC822e differential scanning calorimeter. The isothermal runs were performed at temperatures ranging from 160 to 200 °C for thiol-epoxy reactions without DBU and from 60 to 100 °C for DBU-catalyzed thiol-epoxy reactions. A DSC sample pan was inserted into the sample holder which had been equilibrated at the desired curing temperature for ~10 min. The heat flow changes during isothermal reaction were collected until no detectable de-viation from the final baseline was observed. The detectable heat of reaction at each curing temperature for a sufficiently long reaction time, ΔH_t, was determined by integrating the heat flow evolved within the polymerization time. After isothermal reaction, the sample was rapidly cooled to −20 °C at a 40 °C min^{-1} cooling rate, and the residual heat of reaction, ΔH_r, was measured during the following heating scan (at 10 °C min^{-1} heating rate) to a much higher temperature (300 and 200 °C for reactions without and with DBU, respectively) in order to ensure complete conversion. The total heat of reaction (or enthalpy of reaction), ΔH_0, is the sum of ΔH_t and ΔH_r. In this study, $\Delta H_r = 0$ for all reactions of interest, i.e., all reactions achieved full conversion after isothermal curing at each curing temperature for a sufficiently long reaction time and $\Delta H_0 = \Delta H_t$. A similar ΔH_0 value was determined from a 10 °C min^{-1} heating scan of a sample from −20 °C to a sufficiently high tem-perature at which no further reaction was evident [41,50]. This result indicates that the isothermal curing approach used here led to full, attainable conversion. (See Supplementary materials.) Within error, the complete conversion of the system after isothermal curing was confirmed via Fourier transform infrared spectroscopy (FTIR) (Bruker, Tensor 37) by the disappearance of the thiol peak at ~2570 cm^{-1} [7].

The glass transition temperatures (T_gs) of fully cured samples

(previously heated to a higher temperature to ensure full conversion) were obtained from the second heating ramp at 10 °C min^{-1} after cooling to −20 °C with a 40 °C min^{-1} cooling rate. The T_gs obtained during the first heating scan (immediately after isothermal curing) and the second heating scan were identical within experimental error, which is also consistent with complete conversion of the reaction after isothermal curing for a sufficient amount of time. (See Supplementary materials).

3. Results and discussion

This section is divided into two main subsections. The first subsection compares the isothermal reaction kinetics of thiol-epoxy reactions with and without DBU as characterized by DSC. The second describes a new reaction scheme for thiol-epoxy reactions based on modifying the most common mechanism in the literature [2] by incorporating the effects of both hydroxyl-based autocatalysis and the external catalyst DBU on apparent reaction order.

3.1. Isothermal curing kinetics characterized by DSC

Differential scanning calorimetry has been widely used to study reaction kinetics of different kinds of curing systems, including amine-epoxy curing [41–43,50–52], free radical polymerizations in bulk and/or confined geometries [53–56], among others [57–59]. Kinetic parameters can be determined from dynamic [50–52, 57–61] or isothermal [41–43,52–56] DSC heat flow data by taking advantage of the fact that the exothermic heat evolved during the reaction is proportional to the extent of monomer conversion through the enthalpy of reaction, ΔH_0. It is widely accepted that isothermal experiments generate more reliable kinetic parameters than dynamic experiments; thus, we have performed isothermal DSC studies of reaction kinetics for both thiol-epoxy reactions with and without DBU.

3.1.1. Isothermal curing kinetics of SH_3-DER reactions without DBU

Fig. 1a shows isothermal heat flow curves as a function of reaction time for SH_3-DER reactions without DBU at curing temperatures ranging from 160 to 200 °C. The reacting system consists of a stoichiometric mixture of a trifunctional thiol (SH_3) and a difunctional epoxy (DER) without DBU. Integration of the heat flow curve under the baseline to a particular isothermal reaction time, t,
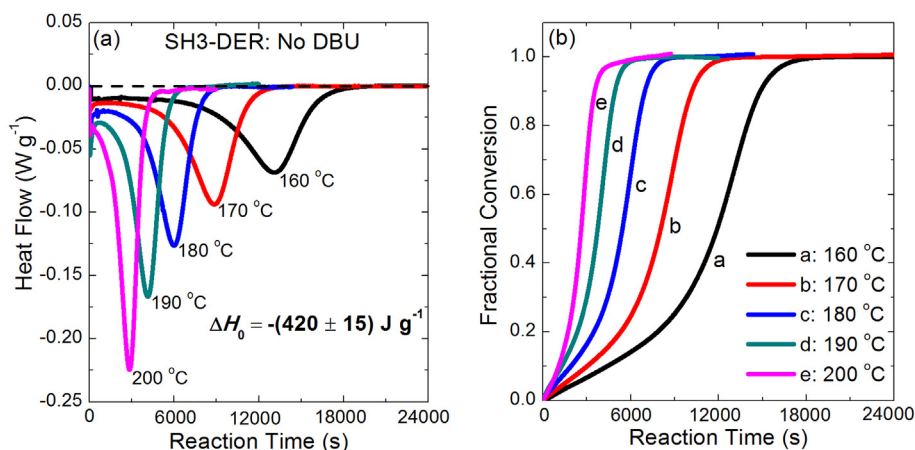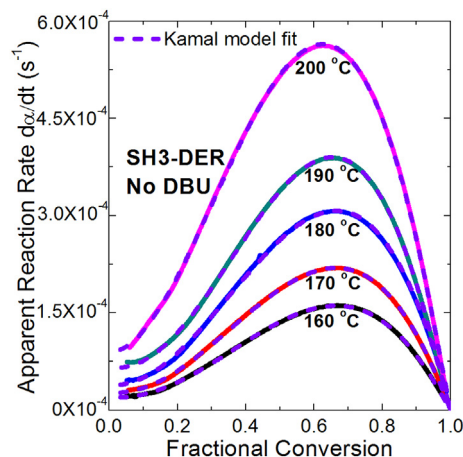

Fig. 2. Apparent reaction rate, $d\alpha/dt$, as a function of fractional conversion for isothermal SH_3-DER reactions without DBU (stoichiometric amounts) at temperatures ranging from 160 to 200 °C, along with Kamal model fits (dotted curves) to the experimental data (solid curves). (Note: Dotted curves and solid curves overlap almost perfectly.)

results in the heat flow generated within reaction time t at that curing temperature, ΔH_t. The fractional conversion at t, $\alpha(t)$, is given by the ratio $\Delta H_t/\Delta H_0$. (A plot of $\alpha(t)$ is shown in Fig. 1b.) ΔH_0 for the thiol-epoxy reaction here is determined to be -420 ± 15 J g^{-1}. This ΔH_0 value is close to values reported for similar thiol-epoxy curing systems in previous studies [6,34].

Fig. 2 shows the apparent reaction rate, $d\alpha/dt$, for SH_3-DER reactions without DBU as a function of fractional conversion based on $\alpha(t)$ curves in Fig. 1b. As shown in Fig. 2, the apparent reaction rate is relatively low at low fractional conversion and increases with increasing conversion until reaching a maximum value at 60–70% conversion, consistent with results by Lu et al. [5]. Such autocatalytic behavior has been observed in amine-epoxy curing reactions [41–43] and has been attributed to hydroxyl-containing products autocatalyzing the reaction according to a scheme first proposed by Horie and coworkers [42]. Autocatalytic behavior in thiol-epoxy reactions can be caused by a similar autocatalysis effect of hydroxyl products.

The Kamal model [40,41] is the most commonly used model to describe isothermal curing kinetics with autocatalytic behavior and

Fig. 1. (a) DSC heat flow as a function of reaction time for isothermal SH_3-DER reactions without DBU (bulk, stoichiometric amounts) at temperatures ranging from 160 to 200 °C; (b) Corresponding conversion, α, curves for these reactions obtained by normalizing the integrated heat flow at a given reaction time to the total heat flow of reaction.

is expressed in equation form as follows:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (1)$$

where $d\alpha/dt$ is the apparent rate of reaction, k_1 and k_2 are apparent rate constants with different activation energies (E_{a1} and E_{a2}, respectively) and apparent pre-exponential factors. The Kamal model as expressed in the form of Eq. (1) has been used in the literature to model curing kinetics of many systems as characterized by DSC, including bulk amine-epoxy and thiol-epoxy reactions [5,41–43]. (We note that with Eq. (1) both apparent reaction rate and apparent rate parameters have units of s^{-1} while conventional reaction rate and rate parameters have units that reflect molar concentrations (e.g., a conventional reaction rate has units of mol L^{-1} s^{-1}). Here, we employ apparent reaction rate (rate of fractional conversion) and the Kamal model in the form of Eq. (1) because the goal of our study is to investigate issues related to how the presence of external catalyst and thiol monomer functionality affect reaction mechanism and activation energy rather than absolute values of reaction rates and rate parameters.)

For the reaction kinetics shown in Fig. 2 (without DBU catalyst), k_1 is the apparent rate coefficient for the reaction catalyzed by catalytic impurities, and k_2 is the apparent rate coefficient for the reaction catalyzed by the hydroxyl products formed during the curing reaction. The reaction orders are given by the exponents m (hydroxyl-catalyzed reaction) and n (impurity-catalyzed reaction). For the SH$_3$-DER reaction without DBU, the experimental kinetics data can be fit very well to the Kamal model over the entire conversion range, with no deviation at high conversion due to diffusion limitations [42]. (The dashed-line model fits overlap very well with the curves representing experimental results.) The absence of diffusion limitations can be explained by the fact that the T_g of the curing system at all conversions is below the curing temperature, so the reacting mixture never approaches vitrification.

As obtained by fitting experimental data to the Kamal autocatalytic model, Table 1 lists the apparent reaction orders and other kinetic parameters of SH$_3$-DER reactions without DBU at various temperatures. The overall reaction order ($m + n$) of SH$_3$-DER reactions without DBU approximates to 3 with $m \approx 2$ and $n \approx 1$, which is consistent with observations by Lu et al. [5]. These results differ from other curing systems showing autocatalytic kinetics such as amine-epoxy [42,43] and anhydride-epoxy [63,64] systems, where $n > m$.

Fig. 3a shows Arrhenius plots associated with k_1 and k_2 values of SH$_3$-DER reactions without DBU, from which activation energies E_{a1} and E_{a2} and pre-exponential factors A_1 and A_2 can be determined. As shown in Table 1, $E_{a1} > E_{a2}$. This result may be explained by a hydroxyl group formed during the reaction partly protonating the oxygen atom in the epoxy group, thereby facilitating the ring-opening reaction and leading to a lower activation energy barrier for reaction between thiol and epoxy groups [5]. Both E_{a1} and E_{a2} values determined here are greater than those reported by Lu et al. [5], which can be rationalized by the fact that the catalytic nitrogen atom within the monomer used in their study can facilitate the reaction and lower activation energies. The apparent activation energy, E_a, of the SH$_3$-DER reaction without DBU can be estimated from the slope of the logarithmic plot of time to reach a characteristic event (or a given degree of conversion), e.g., time at which the apparent rate of reaction reaches a maximum (t_p), as a function of reciprocal temperature [41,43,62] as shown in Fig. 3b. As shown in Table 1, the apparent activation energy of the SH$_3$-DER reaction without DBU is equal within error to E_{a1}.

As shown by comparing Table 2 to Table 1, similar values of m, n, E_{a1}, E_{a2}, and E_a are obtained for SH$_4$-DER reactions and SH$_3$-DER reactions without DBU, with k_1 and k_2 values being slightly enhanced for the SH$_4$-DER reactions. These results are consistent with the reaction mechanism being independent of thiol functionality. The difference in k_1 and k_2 values may be caused by SH$_3$ and SH$_4$ having different pK$_a$ values, which would affect rate parameters [46]. The difference in k_1 values may also be caused by differences in catalytic impurity levels in SH$_3$ and SH$_4$.

3.1.2. Isothermal curing kinetics of DBU-catalyzed thiol-epoxy reactions

Fig. 4 shows the apparent reaction rate, $d\alpha/dt$, as a function of fractional conversion for DBU-catalyzed SH$_3$-DER reactions. With 0.17% mol DBU/mol thiol groups, the thiol-epoxy reaction occurs at vastly lower temperatures due to the catalytic effect of external catalyst DBU. DBU-catalyzed thiol-epoxy reactions show autocatalytic behavior and exhibit a maximum in apparent reaction rate at ~50% conversion (vs. ~60–70% conversion for the thiol-epoxy reaction without DBU). The difference in conversion level at the maximum apparent reaction rate for thiol-epoxy reactions with and without DBU indicates that the reaction mechanism may be altered by the addition of external catalyst DBU.

As shown in Table 3, the effect of hydroxyl autocatalysis is greater than that of the catalytic effect of external catalyst DBU on the apparent reaction rate ($k_2 >> k_1$). This is consistent with the observation in SH$_3$-DER reactions without DBU that $k_2 >> k_1$, meaning that the autocatalysis effect by the hydroxyl group is much greater than the effect of the catalytic impurity. According to Fig. 5 and Table 3, $E_{a1} > E_{a2}$ in the DBU-catalyzed thiol-epoxy reaction, similar to the case without DBU. However, compared to the thiol-epoxy reaction without DBU, there is an increase in both activation energies and pre-exponential factors with the addition of external catalyst DBU, e.g., the apparent activation energy of the overall reaction increases from 64 ± 2 to 71 ± 2 kJ mol^{-1} upon addition of DBU [65].

According to Table 3, the overall reaction order ($m + n$) of the DBU-catalyzed thiol-epoxy reaction is approximately 2 with $m \approx 1$ and $n \approx 1$, which is different than the reaction without DBU ($m \approx 2$ and $n \approx 1$). This result indicates that the reaction mechanism changes with addition of the external catalyst DBU. The incorporation of external catalyst has been known to alter the reactions mechanisms of other curing systems [66,67]. For example, Karkanas et al. [66] investigated the reaction kinetics of amine-epoxy curing reactions with and without external catalyst and found that the catalyst can mask the autocatalytic behavior under certain conditions and lead to general nth order kinetics ($d\alpha/dt = k(1-\alpha)^n$) as commonly observed in step-growth polymerizations [68]. To our best knowledge, no detailed study has focused on the effect of the external catalyst on the reaction mechanism of the thiol-epoxy curing kinetics. The effect of DBU catalysis on the thiol-epoxy reaction will be discussed in the following section.

Table 1
Kinetic parameters for isothermal SH$_3$-DER reactions without DBU (stoichiometric amounts) obtained by fitting the experimental data to the Kamal model.

Temperature (°C)	160	170	180	190	200
k_1 ($\times 10^{-5}$ s^{-1})	2.0	2.7	3.9	6.7	9.2
k_2 ($\times 10^{-3}$ s^{-1})	1.2	1.6	2.1	3.1	3.9
m	2.2	2.2	2.1	2.2	1.9
n	1.1	1.0	1.0	1.1	1.1
A_1 (s^{-1})	7.9				
A_2 (s^{-1})	7.2				
E_{a1} (kJ mol^{-1})	66 (±5)				
E_{a2} (kJ mol^{-1})	50 (±3)				
E_a (kJ mol^{-1})	64 (±2)				

Note: k_1 and k_2 are apparent rate parameters because the units do not reflect the reaction order. (Value of k_1 at 160 °C is 2.0×10^{-5} s^{-1}).
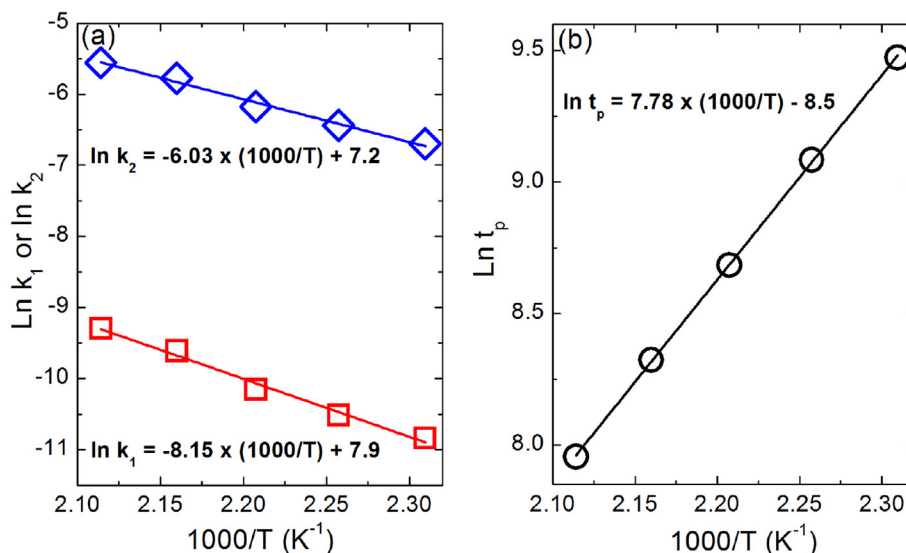
Fig. 3. Arrhenius plots of (a) apparent rate parameters k_1 (s^{-1}) and k_2 (s^{-1}), and (b) the time for reaching the maximum apparent reaction rate, t_p (s), of isothermal SH$_3$-DER reactions without DBU (bulk, stoichiometric amounts).

Table 2
Kinetic parameters for isothermal SH$_4$-DER reactions without DBU (stoichiometric amounts) obtained by fitting the experimental data to the Kamal model.

Temperature (°C)	160	170	180	190	200
k_1 ($\times 10^{-5}$ s^{-1})	3.1	4.9	7.3	9.7	15
k_2 ($\times 10^{-3}$ s^{-1})	1.7	2.3	3.4	4.1	5.7
m	2.2	2.2	2.2	2.0	2.0
n	1.1	1.1	1.2	1.1	1.2
A_1 (s^{-1})	7.6				
A_2 (s^{-1})	7.9				
E_{a1} (kJ mol^{-1})	65 (±5)				
E_{a2} (kJ mol^{-1})	52 (±3)				
E_a (kJ mol^{-1})	64 (±2)				

Note: k_1 and k_2 are apparent rate parameters because the units do not reflect the reaction order. (Value of k_1 at 160 °C is 3.1×10^{-5} s^{-1}).

We also note that similar kinetic parameters (m, n, E_{a1}, E_{a2}, and E_a), except for slightly enhanced rate parameters (k_1 and k_2), are obtained for DBU-catalyzed SH$_4$-DER reactions (see supplementary materials). Thus, compared to the addition of external catalyst DBU,

change of the thiol monomer functionality has a minor effect on the kinetics of the thiol-epoxy reaction.

3.2. Proposed thiol-epoxy reaction mechanisms

As shown above, the overall reaction order for the thiol-epoxy reaction without DBU approximates to 3 with $m \approx 2$ and $n \approx 1$, consistent with observations in another thiol-epoxy curing system without external catalyst studied by Lu et al. [5] This result indicates that thiol-epoxy reactions without the addition of external catalyst may follow the same reaction mechanism. We further observe that the overall reaction order decreases to ~2 upon addition of external catalyst DBU, which indicates that the thiol-epoxy reaction mechanism is changed by DBU catalysis.

We note that a very recent study by Loureiro et al. [69] has focused on a monofunctional thiol-epoxy reaction catalyzed by a tertiary amine. In their study, they observed that the system underwent a fast autocatalytic reaction step after a relatively long induction period. They modeled the reaction kinetics by assuming
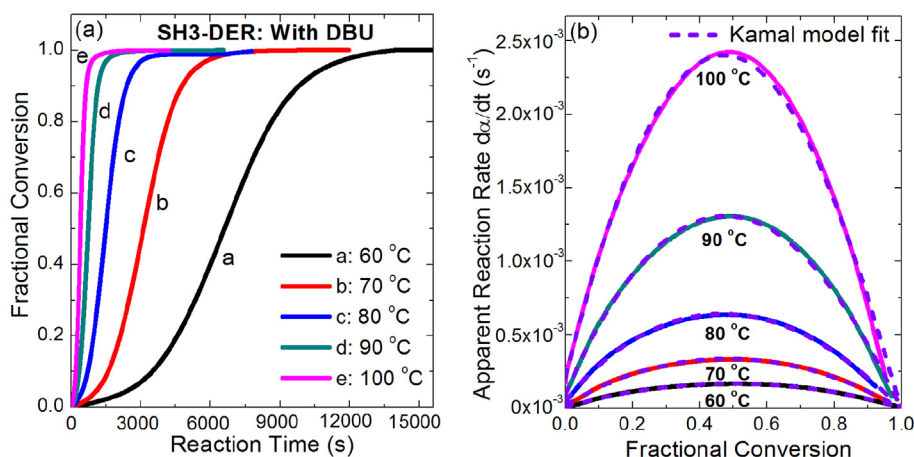

Fig. 4. (a) Fractional conversion as a function of reaction time for isothermal DBU-catalyzed SH$_3$-DER reactions (stoichiometric amounts) at temperatures ranging from 60 to 100 °C; (b) Apparent reaction rate, $d\alpha/dt$, as a function of fractional conversion for reactions at temperatures ranging from 60 to 100 °C along with Kamal model fits (dotted curves) to the experimental data (solid curves). (Note: Dotted curves and solid curves overlap almost perfectly.)

Table 3
Kinetic parameters for isothermal DBU-catalyzed SH_3-DER reactions (stoichiometric amounts with a catalyst loading of 0.17% mol DBU/mol thiol groups) obtained by fitting the experimental data to the Kamal model.

Temperature (°C)	60	70	80	90	100
k_1 ($\times 10^{-5}$ s^{-1})	0.77	1.7	4.6	9.4	21
k_2 ($\times 10^{-3}$ s^{-1})	0.65	1.3	2.4	5.1	9.8
m	1.0	1.0	0.9	1.0	1.1
n	1.0	1.0	1.0	1.1	1.1
A_1 (s^{-1})	19.2				
A_2 (s^{-1})	17.9				
E_{a1} (kJ mol^{-1})	82 ($\pm$6)				
E_{a2} (kJ mol^{-1})	70 ($\pm$3)				
E_a (kJ mol^{-1})	71 ($\pm$2)				

Note: k_1 and k_2 are apparent rate parameters because the units do not reflect the reaction order. (Value of k_1 at 60 °C is 0.77×10^{-5} s^{-1}).
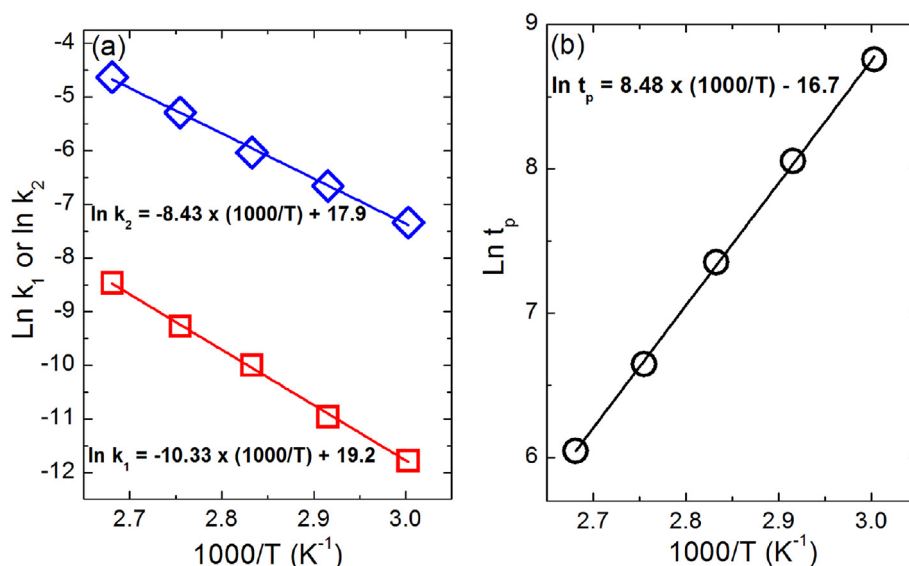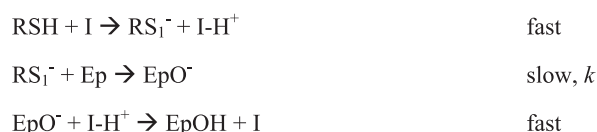
autocatalysis effect, we propose a reaction scheme for thiol-epoxy reactions without DBU, Scheme 2, which is a modification of the mechanism shown in Scheme 1.

In Scheme 2, RSH, Ep, and EpOH represent thiol, epoxide, and hydroxyl products formed via addition reaction between thiol and epoxide, respectively. I is a catalytic impurity, which initiates the thiol-epoxy reaction by deprotonating the thiol. EpO^- is an alcolate anion formed via the nucleophilic coupling reaction between a thiolate anion (RS^-) and an epoxide group, which can further deprotonate thiols. Thus, thiol deprotonation by catalytic impurities (RS_1^-) or by EpO^- (RS_2^-) can generate thiolate anions in the thiol-epoxy reaction without DBU.
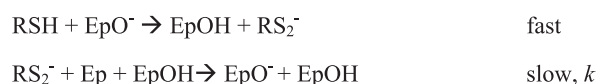
We define s and e to be the concentrations of RSH and Ep at time t, respectively, s_0 and e_0 their initial concentrations, respectively, I_0

Fig. 5. Arrhenius plots of (a) apparent rate parameters k_1 (s^{-1}) and k_2 (s^{-1}), and (b) the time for reaching the maximum apparent reaction rate, t_p (s), of isothermal DBU-catalyzed SH_3-DER reactions (bulk, stoichiometric amounts).

that thiolate anions were slowly generated during the induction period and then initiated a fast autocatalytic propagation/proton transfer reaction. Attempts to use the model proposed by Loureiro et al. [69] to fit the experimental data obtained for the multifunctional thiol-epoxy reactions here did not lead to good fits of the data. (The poor fit of their model to our data is not unexpected given the difference in basicity and nucleophilicity of DBU, the catalyst used here, and the catalyst benzyldimethylamine used in Ref. [69]. For further discussion, see Ref. [70].) Moreover, their model fails to rationalize the overall reaction order change of the thiol-epoxy (multifunctional system) reactions due to the DBU catalysis effect observed in our study. In consideration of the effect of external catalyst DBU on apparent reaction order as well as the hydroxyl autocatalysis effect, new reaction schemes based on both the commonly described mechanism in the literature [2] and the Kamal model are proposed, as described below.

3.2.1. Proposed mechanism for thiol-epoxy reactions without external catalyst DBU

With the Kamal autocatalytic model, one part of the curing reaction is catalyzed by catalytic impurities and the other part by reaction products, which are hydroxyl groups in the case of thiol-epoxy reactions. In consideration of the hydroxyl group

the initial concentration of impurity I, α the conversion of Ep at time t, and α_1 and α_2 the conversion of Ep at time t caused by the external catalysis effect and the autocatalysis effect, respectively. In the reaction catalyzed by catalytic impurities (part 1 of the overall reaction), the concentration of the formed thiolate anions, $[RS_1^-]$, is dictated by the concentration of the impurity I, i.e., $[RS_1^-] \cong I_0$. According to the proposed reaction scheme, the rate of

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Catalytic impurities effect

$RSH + I \rightarrow RS_1^- + I\text{-}H^+$	fast
$RS_1^- + Ep \rightarrow EpO^-$	slow, k
$EpO^- + I\text{-}H^+ \rightarrow EpOH + I$	fast

Hydroxyl autocatalysis effect

$RSH + EpO^- \rightarrow EpOH + RS_2^-$	fast
$RS_2^- + Ep + EpOH \rightarrow EpO^- + EpOH$	slow, k'

Scheme 2. Proposed reaction scheme for thiol-epoxy reactions without external catalyst DBU.

consumption of epoxide at time t due to the effect of catalytic impurities is given by

$$d\alpha_1/dt = k\left[RS_1^-\right][Ep] = kI_0e_0(1-\alpha) = k_1(1-\alpha) \qquad (2)$$

where $k_1 = kI_0e_0$, and k_1 is the overall rate constant of the consumption of epoxide catalyzed by catalytic impurities in the system.

In the reaction due to the hydroxyl autocatalysis effect (part 2 of the overall reaction), the concentration of the thiolate anions $[RS_2^-]$ is proportional to the concentration of EpO$^-$ which can be taken as αe_0. The rate of consumption of epoxide at time t due to the hydroxyl autocatalysis effect is then be given by

$$d\alpha_2/dt = k'\left[RS_2^-\right][Ep][EpOH] = k'e_0^3\alpha^2(1-\alpha) = k_2\alpha^2(1-\alpha) \qquad (3)$$

where $k_2 = k'e_0^3$, and k_2 is the rate parameter for the consumption of epoxide due to the hydroxyl autocatalysis effect. The overall rate of consumption of epoxide or the apparent rate of reaction at time t can then be represented by

$$d\alpha/dt = d\alpha_1/dt + d\alpha_2/dt = k_1(1-\alpha) + k_2\alpha^2(1-\alpha) \qquad (4)$$

this expression is a particular form of the Kamal model with $m = 2$ and $n = 1$. Thus, the observed kinetics of thiol-epoxy reactions without DBU can be rationalized by Scheme 2. The experimental kinetics data can also be fit reasonably well to the Kamal model with common reactions orders of $m = 2$ and $n = 1$, resulting in similar rate parameters for thiol-epoxy reactions without DBU. (See Supplementary materials.)

3.2.2. Proposed mechanism for DBU-catalyzed thiol-epoxy reactions

The overall DBU-catalyzed thiol-epoxy reaction is assumed to consist of two parts, one catalyzed by the external catalyst DBU and the other by hydroxyl products. With the overall DBU-catalyzed reaction, it is assumed that thiols are effectively deprotonated only by DBU because of its superior basic character [44]. Scheme 3 shows the proposed reaction scheme for DBU-catalyzed thiol-epoxy reactions.

In Scheme 3, RSH, RS$^-$, Ep, EpOH, and EpO$^-$ have the same meanings as in the thiol-epoxy reaction without DBU. Since thiol is assumed to be deprotonated only by the highly active external catalyst DBU, the concentration of the formed thiolate anions $[RS^-]$ is dictated by the concentration of the catalyst DBU, d_0, i.e.,

DBU catalysis effect	
RSH + DBU → RS⁻ + DBU-H⁺	fast
RS⁻ + Ep → EpO⁻	slow, k''
EpO⁻ + DBU-H⁺ → EpOH + DBU	fast
Hydroxyl autocatalysis effect	
RSH + DBU → RS⁻ + DBU-H⁺	fast
RS⁻ + Ep + EpOH → EpO⁻ + EpOH	slow, k'''
EpO⁻ + DBU-H⁺ → EpOH + DBU	fast

Scheme 3. Proposed reaction scheme for DBU-catalyzed thiol-epoxy reactions.

$[RS^-] \cong d_0$. The rate of consumption of epoxide at time t due to the external catalysis effect of DBU is then given by

$$d\alpha_1/dt = k''\left[RS^-\right][Ep] = k''d_0e_0(1-\alpha) = k_1'(1-\alpha) \qquad (5)$$

where $k_1' = k''d_0e_0$, and k_1' is the overall rate constant of the consumption of epoxide catalyzed by DBU. The rate of consumption of epoxide at time t due to the hydroxyl autocatalysis effect is

$$d\alpha_2/dt = k'''\left[RS^-\right][Ep][EpOH] = k'''d_0e_0^2\alpha(1-\alpha) = k_2'\alpha(1-\alpha) \qquad (6)$$

where $k_2' = k'''d_0e_0^2$, and k_2' is the overall rate constant of the consumption of epoxide due to the hydroxyl autocatalysis effect. Thus, the overall rate of consumption of epoxide or the apparent rate of reaction at time t is

$$d\alpha/dt = d\alpha_1/dt + d\alpha_2/dt = k_1'(1-\alpha) + k_2'\alpha(1-\alpha) \qquad (7)$$

Eq. (7) is a particular form of the Kamal model with $m = 1$ and $n = 1$. Thus, the observed curing kinetics of DBU-catalyzed thiol-epoxy reactions are well described by the proposed reaction scheme shown in Scheme 3. The experimental kinetics data can also be fit reasonably well to the Kamal model with common reactions orders of $m = 1$ and $n = 1$, resulting in similar rate parameters for thiol-epoxy reactions with DBU. (See Supplementary materials.)

3.2.3. Catalytic impurities/DBU catalysis effect vs. hydroxyl autocatalysis effect

For both thiol-epoxy reactions with and without external catalyst DBU, at any stage of reaction the overall reaction is caused by the combination of the external catalyst DBU/catalytic impurities effect and the hydroxyl autocatalysis effect. It is reasonable that a competition between these two effects exists throughout the whole reaction. Fig. 6a plots the calculated percentage of the reaction contributed from the hydroxyl autocatalysis in terms of the overall reaction, $(d\alpha_2/dt)/(d\alpha/dt)$, as a function of conversion for both SH$_3$-DER reactions with and without DBU. As shown in Fig. 6a, the percentage of reaction from hydroxyl autocatalysis increases from ~30% up to ~100% with increasing conversion for SH$_3$-DER reactions without DBU, which indicates that the hydroxyl autocatalysis effect predominates at higher conversion whereas it contributes less to the overall reaction compared to the external catalysis effect at lower conversions. However, for the DBU-catalyzed case, the hydroxyl autocatalysis effect is already dominant at relatively low conversion, e.g., ~80% of the overall reaction is caused by the hydroxyl autocatalysis effect at 10% conversion and only a slight increase is observed in the percentage of the reaction from the hydroxyl autocatalysis effect with increasing conversion.

The overall activation energy of the reaction at any conversion can be obtained from an Arrhenius plot of apparent reaction rate, $d\alpha/dt$, at a particular fractional conversion α. (see Supplementary materials.) Fig. 6b shows the determined overall activation energy as a function of conversion for SH$_3$-DER reactions with and without DBU. The overall activation energy of the thiol-epoxy reaction without DBU exhibits a continuous decrease from ~69 kJ mol^{-1} (identical within error with the E_{a1} value which is 66 ± 5 kJ mol^{-1}) to ~48 kJ mol^{-1} (identical within error to the observed E_{a2} value which is 50 ± 3 kJ mol^{-1}) with increasing conversion. The decrease in overall activation energy with increasing conversion is due to the fact that the hydroxyl products can facilitate ring-opening reactions associated with epoxide and lower the activation energy barrier. This effect increases with increasing hydroxyl product concentration (or conversion) for the thiol-epoxy
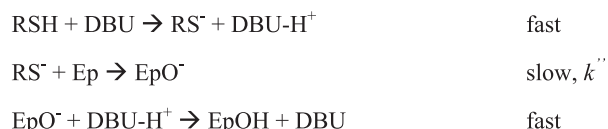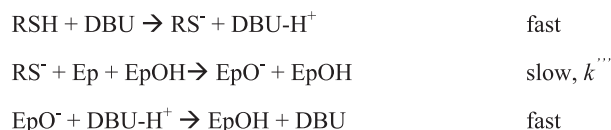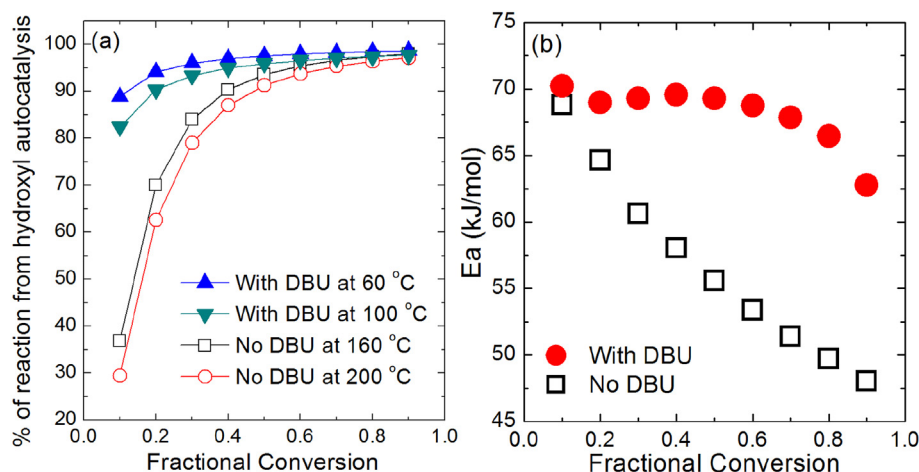
Fig. 6. (a) Percentage of reaction contributed by hydroxyl autocatalysis effect in terms of the overall reaction; (b) Activation energy of the overall reaction, E_a, as a function of fractional conversion for isothermal SH$_3$-DER reactions with and without DBU (stoichiometric amounts).

reaction without DBU, which results in the hydroxyl autocatalysis effect predominating at higher conversions. In contrast to the reaction without DBU, as shown in Table 3 the DBU-catalyzed case exhibits an overall activation energy (71 ± 2 kJ mol^{-1}) that is within error equal to E_{a2} (70 ± 3 kJ mol^{-1}) even at low conversion. The difference between reactions with and without DBU can be explained by the fact that at low conversion the hydroxyl autocatalysis effect predominates over the external catalysis effect in the DBU-catalyzed thiol-epoxy reaction but plays a minor role in the case without DBU, as shown by Fig. 6a. The overall activation energy of the DBU-catalyzed SH$_3$-DER reaction remains nearly unchanged up to ~70% conversion and decreases only slightly at higher conversion.

4. Conclusion

The isothermal reaction kinetics of multifunctional thiol-epoxy reactions with and without external catalyst DBU are studied using isothermal DSC methods. Autocatalytic curing kinetics are observed in both cases, which is attributed to the autocatalysis effect of the hydroxyl products formed during the reaction. The Kamal autocatalytic model with a overall order of reaction $m + n = 3$ (with $m \approx 2$ and $n \approx 1$) is applied to describe the isothermal curing kinetics of the thiol-epoxy reaction without DBU; the same model with an overall reaction order of 2 ($m \approx 1$ and $n \approx 1$) is used for the DBU-catalyzed case. New reaction schemes for thiol-epoxy reactions are proposed based on the most commonly described mechanism in the literature by incorporating the hydroxyl autocatalysis effect as well as the effect of external catalyst DBU on apparent reaction order. The observed reaction kinetics for both thiol-epoxy reactions with and without DBU are well described by the proposed reaction schemes. Further analysis based on the Kamal autocatalytic model indicates that there is a competition between the catalytic impurity/DBU catalysis effect and the hydroxyl autocatalysis effect at all levels of conversion. For the thiol-epoxy reaction without DBU, the effect of catalytic impurities governs the early-stage reaction whereas the autocatalysis effect predominates at higher conversions. However, for the DBU-catalyzed case, the hydroxyl autocatalysis effect which contains DBU as a reactive component outweighs the catalysis effect caused by DBU alone, even at relatively low conversions, e.g., 10% conversion. In contrast to the significant effect of external catalyst DBU on apparent reaction mechanism, a change in thiol monomer

functionality from trithiol to tetrathiol has only a minor effect on rate parameter values and no effect on reaction mechanism.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.10.068.

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