

Research Article

Cure Kinetics of an Optical Polythiourethane with Amine Catalyst by IR Analysis

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An optical polythiourethane based on *m*-xylylene diisocyanate (XDI) and 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol (BES) has been studied. Triethylamine was adopted as a catalyst, and the solid-state isothermal cure reaction was carried out using FTIR spectroscopy, in the temperature range of 75°C-105°C. The -NCO absorption band of XDI was used to monitor the conversion of diisocyanate into polythiourethane. The reaction rate enhanced with an increase in the content of the catalyst, and the gel time determined by swelling test was shorter for the system with higher catalyst content. Kinetic parameters were calculated from the infrared spectrum data, and the results showed that the curing reaction of polythiourethane accords with first-order kinetic characteristics. The activation parameters obtained from the evaluation of kinetic data were $\Delta H^* = 97.22 \text{ kJ mol}^{-1}$, $\Delta S^* = -6.77 \text{ J K}^{-1} \text{ mol}^{-1}$, and $E_a = 100.23 \text{ kJ mol}^{-1}$. The observed negative entropy of activation value supported the formation of a transition state in the cure reaction.

1. Introduction

It is generally known that polyurethanes have increasingly attracted attention because of their outstanding properties and wide applications in foams, plastics, rubber, and coatings [1–3]. As a member of the polyurethane family, polythiourethanes (PSU) are formed by a reaction of isocyanates or isothiocyanate with polyols, polythiols, water, and amines containing an active hydrogen atom [4, 5]. The sulfur element can be from either of the reactants or two of them. The refractive index of polythiourethanes can be as high as 1.71 or even higher due to the addition of the sulfur element in the polyurethane structure [6–9]. Polythiourethanes with high refractive index and low chromatic dispersion have replaced traditional eyeglass lenses and are popular among people, due to their lightness, good impact strength, and good processability [10–14].

The curing of optical polythiourethane involves the formation of a crosslinking network from multifunctional isocyanates and thiols, in which at least one of them is trifunctional or more [15]. The thiourethane linkage

(-NHCOS-) is a result of the reaction between an isocyanate group (-NCO) of isocyanate and a thiol group (-SH) of polythiol. During the three-dimensional crosslinked network forming, the viscosity increased rapidly and molecular weight reached infinity.

The curing reaction of the polyurethane system plays an important role in the manufacturing process as well as the properties of final products [16–18]. The kinetic reaction and mechanism of the cure reaction determine the physicochemical properties and mechanical performance of the cured product [19–21]. Several factors are involved in the formation of urethanes, such as chemical structure and concentration of reagents, reaction medium, and catalyst. Some reports have been published to describe the polymerization kinetics of thermoset polymers [22, 23].

A large number of characterization methods have been used to monitor the kinetics of polymerization reactions, such as titration methods, ultrasonic waves, microcalorimetry, differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) measurements [24–29]. FTIR is known as a

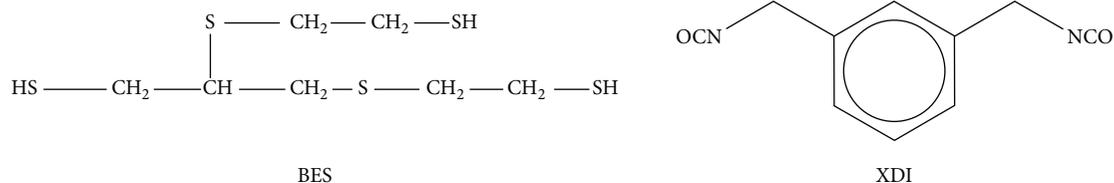


FIGURE 1: Chemical structure of BES and XDI.

very rapid and reliable method well suited for monitoring the curing process of the PU formation [24, 30].

As far as we know, there have been few studies concerning the kinetics of the optical polythiourethane thermoset process [21, 30]. In this study, the cure kinetics of the polythiourethane formation between *m*-xylylene diisocyanate (XDI) and 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol (BES) were researched by using the quantitative FTIR spectroscopy. As one of the important raw materials for commercial high refractive index PSU materials, the kinetics of XDI participating in the curing reaction of polythiourethane have not been studied. Triethylamine (TEA) was used as the catalyst to speed up the polythiourethane formation, and the effect of the catalyst concentration on the reaction kinetics was also investigated. Kinetic and thermodynamic parameters were calculated using normalized conversion curves. The results will provide references for the curing process of optical polythiourethane, such as PSU coatings, films, or lens productions.

2. Materials and Methods

2.1. Materials. 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol (BES, 99%) and *m*-xylylene diisocyanate (XDI, 98%) were provided by Mitsui Chemicals. The chemical structures are shown in Figure 1. The phosphate mold release agent was provided by Shanghai Longxu Chemicals. Triethylamine (TEA, 99%) and dimethylformamide (DMF, 99%) were purchased from Aladdin. All the chemicals were used without further purification.

2.2. Crosslinking of Polythiourethane. The PSU thermoset system was prepared from the reaction of BES and XDI. The two reactants for crosslinking were mixed in a molar ratio of 1:1. Two drops of phosphate mold release agent and proper TEA were mixed under stirring for 10 min and degassed under vacuum for 20 min. All operations were carried out in a glove box at 5°C and N₂ gas protection to avoid the reaction between H₂O and XDI. The polythiourethane reaction system was prepared freshly for FTIR measurements.

2.3. FTIR Spectroscopy Measurements. A Nicolet 6700 FTIR spectrophotometer using the OMNIC program was used to monitor the curing process of optical polythiourethane, within a range of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹. The absorbance spectra were recorded at proper time intervals, measuring the progressive decrease of the NCO band at 2260 cm⁻¹. The temperature of the sample oven was controlled by a thermoregulator. Isothermal polymerization

kinetic parameters were evaluated at 75°C, 90°C, and 105°C, respectively. CH₂ stretching at 2920 cm⁻¹ was chosen as an internal standard because it remained practically unaffected throughout the curing reaction. The normalized data were used to calculate the kinetic and thermodynamic parameters for the cure reaction.

2.4. Thermodynamic Parameters. Thermodynamic parameters were determined using the Arrhenius law (Equation (1)), and the Eyring relationship (Equation (2)) was used to determine the activation enthalpy (ΔH^*) and entropy (ΔS^*),

$$k = Ae^{-E_a/RT}, \quad (1)$$

$$\ln \frac{k}{T} = \ln \frac{R}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}, \quad (2)$$

where k is the kinetic constant, A is the frequency factor, E_a is the activation energy, R is the universal gas constant, T is the temperature, N is Avogadro's constant, and h is Planck's constant.

2.5. Swelling Measurements. The gel time was measured using a solubility method, where the time when the insoluble polymer first appears in the dimethylformamide (DMF) solvent was measured at room temperature. Under the isothermal conditions, several unreacted samples (W1) were placed in the oven. After a certain interval, a sample was removed and immersed into the DMF solvent at room temperature for a week until swollen equilibrium was obtained. Then, the solvent was vaporized and the dry sample weighted as W2. The percentage of the insoluble portion of the initial sample gave the gel fraction (G). Measurements were repeated at least for three parallel samples in each case and the results were averaged.

$$\text{Gel fraction } (G) = \frac{W2}{W1} \times 100\%. \quad (3)$$

3. Results and Discussion

3.1. FTIR Analysis. The polythiourethane formation can be depicted in a simple manner, as seen in Figure 2.

Theoretically, nucleophilic reaction could occur between isocyanate and any compound with active hydrogen. Due to the induction effect, the carbon atom and the oxygen atom in the -NCO group form an electrophilic center and a nucleophilic center, respectively. When isocyanates react with thiols, the oxygen atoms in the -NCO group accept the hydrogen atoms in the -SH group to form carbonyl groups.

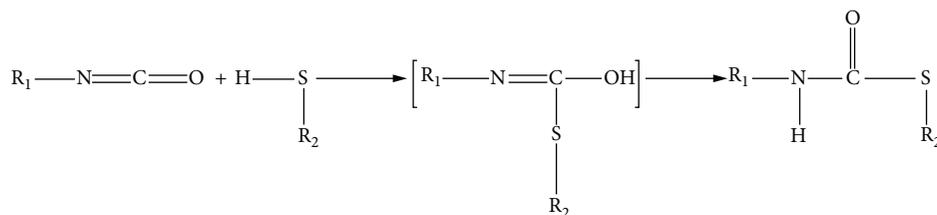
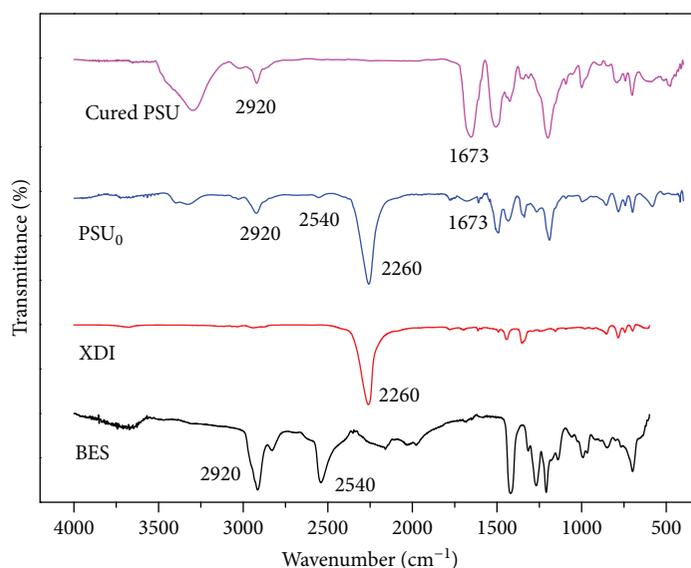


FIGURE 2: A diagram of polythiourethane formation.

FIGURE 3: FTIR spectra of the BES, XDI, PSU₀ and cured PSU.

Because of the instability of hydroxyls on the unsaturated carbon atoms, the structure undergoes intramolecular rearrangement and the -NH-COS- group is formed.

Figure 3 gives the FTIR spectra of the BES, XDI, PSU₀ (mixture of BES and XDI just after preparation), and the cured PSU. The details of the FTIR bands are presented in Table 1. The absorption band for the NCO stretching of XDI is at around 2260 cm⁻¹, which can be used to monitor the isocyanate group conversion during polymerization [28]. On the other hand, the characteristic bands of C=O at 1673 cm⁻¹ and NH at 3510–3100 cm⁻¹ were clearly observed in the spectra of the cured sample, which also proved the formation of polythiourethane [28, 31]. The absorption at 2540 cm⁻¹ is due to -SH of BES [32].

Quantification is based on the Lambert-Beer law. Assuming that no obvious side reactions occur in the polymerization reaction [15], the decrease of the intensity of the 2260 cm⁻¹ band was used to monitor the conversion of the -NCO group with -CH₂ stretch absorbance (2920 cm⁻¹) as the internal standard.

The cure reaction between the BES and XDI can be followed by means of quantitative FTIR spectroscopy. Figure 4 shows the IR spectra taken in the course of the PSU formation between BES and XDI at 105°C with 150 ppm TEA in the system. The absorbance peak of the isocyanate at 2260 cm⁻¹ decreased due to the reaction between

TABLE 1: Principal peak assignments in the FTIR spectra of BES, XDI, PSU₀, and cured PSU.

Observed peaks (cm ⁻¹)	Peak assignments
3510–3100	-NH stretching vibrations
2920	-CH ₂ stretching vibration
2540	-SH stretching vibration
2260	-NCO stretching vibration
1673	-C=O stretching vibration of PSU

the -SH of BES and the -NCO of XDI. As can be seen, NCO stretching bands at 2260 cm⁻¹ disappeared gradually and the C=O stretching band at 1673 cm⁻¹ increased simultaneously, which indicate the conversion of isocyanate to polythiourethane.

3.2. Influence of Temperature on Isocyanate Conversion. Using peak height to represent peak intensity, isocyanate conversion p can be expressed as [33, 34]

$$\text{NCO conversion } (p) = 1 - \frac{A_t/A_{It}}{A_0/A_{I0}} \quad (4)$$

where A_0 and A_t correspond to the peak intensity of absorbance (2260 cm⁻¹) at the initial time and specified time

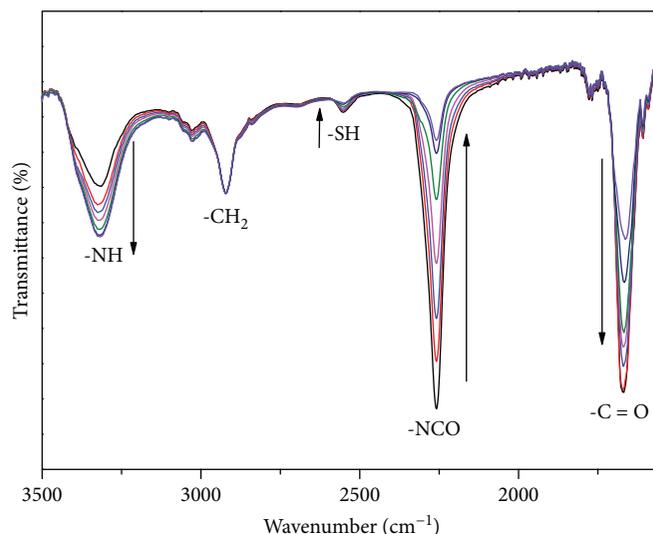


FIGURE 4: FTIR spectra of PSU with 150 ppm TEA at 105°C at different curing times. (curing time from bottom to top is 5, 7, 10, 15, 20, 30, and 40 min).

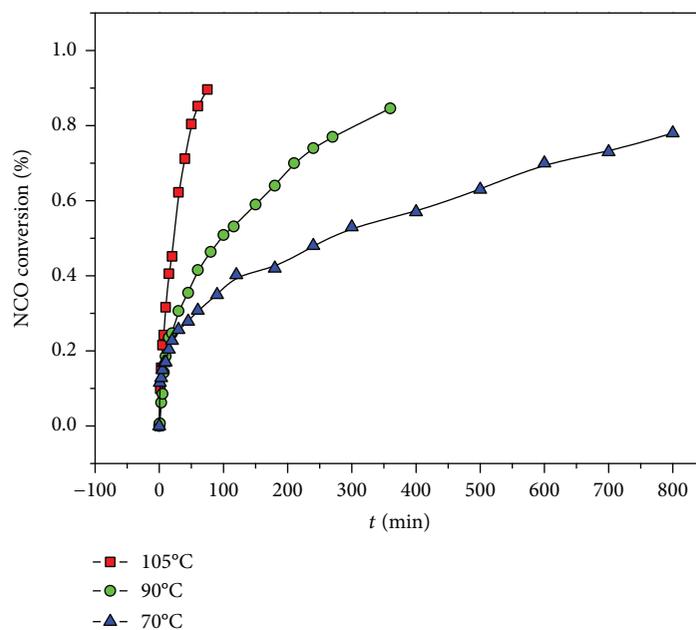


FIGURE 5: Isocyanate conversion versus curing time of PSU at 75°C, 90°C, and 105°C with 150 ppm TEA.

during the curing, respectively. A_{I0} and A_{It} are the peak intensity of absorbance (2920 cm^{-1}) which is assigned to the internal standard. Many papers have used the isocyanate conversion p to research the curing process of thermosetting systems. Pradip et al. [33] have researched the curing of polyurethane prepolymers with three hyperbranched polyols and found that all polyurethane formations in their study followed the second-order kinetics. In our previous work [34], rheological measurements and FTIR spectroscopy were used to investigate the curing of XDI and BES system with dibutyltin dichloride as the catalyst. The isocyanate conversion was calculated and the conversion vs. time was observed.

Figure 5 shows the results of -NCO conversion of XDI with the -SH group of BES at 75°C, 90°C, and 105°C. Apparently, the conversion increased with time until -NCO was consumed completely. The conversion rate increased with the increase of temperature. At 105°C, the conversion reached about 90% within 75 min, while it took 6 h for the conversion to reach 85% at 90°C. For 75°C, the polymerization occurred more slowly and the -NCO conversion was only around 80% even if it has been reacting for 14 h.

3.3. Curing Kinetics. The understanding of the mechanism and kinetics of the curing is very important in the

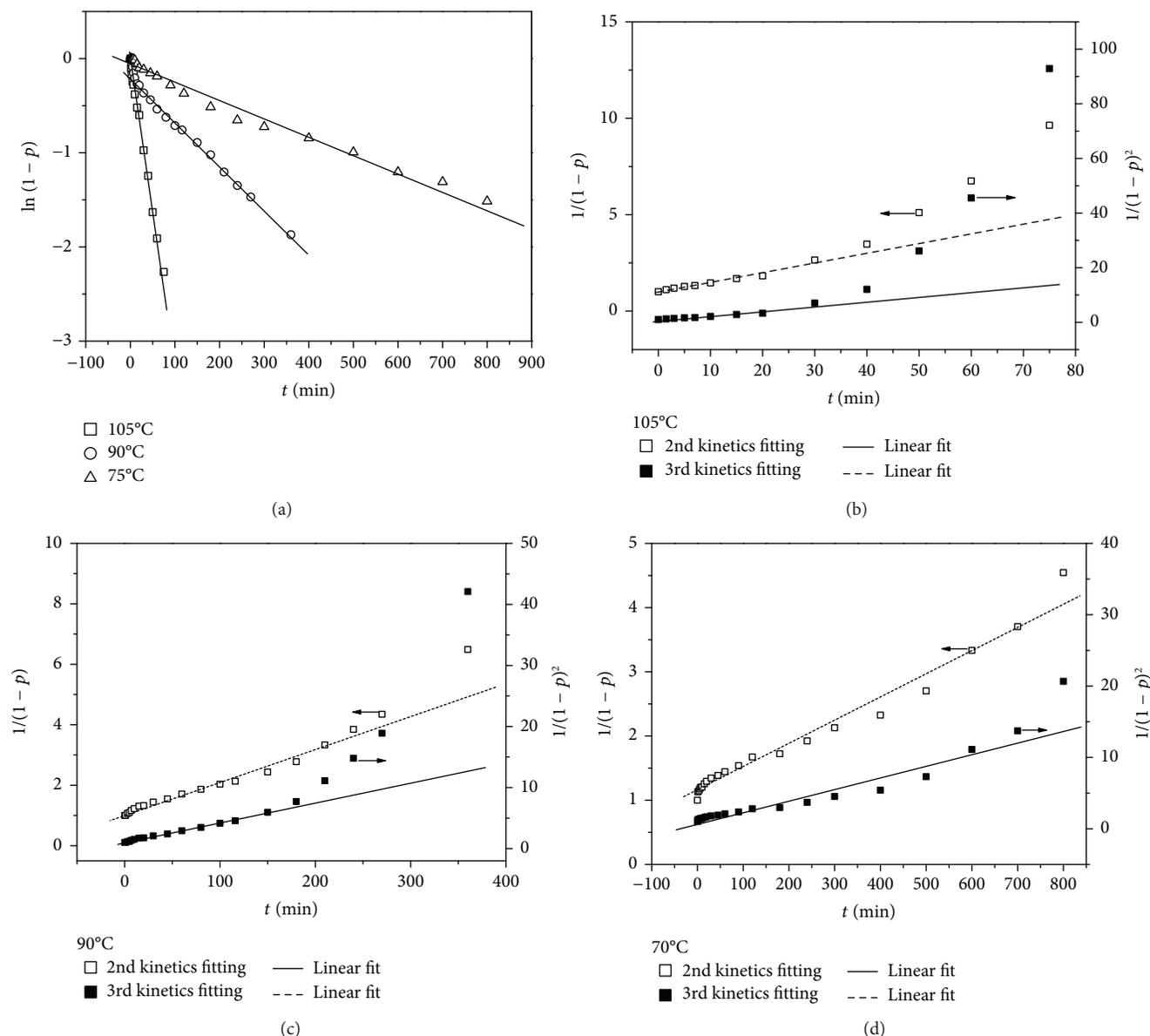


FIGURE 6: First-order rate law for PSU with 150 ppm TEA at different temperature (a). Second-order rate law and third-order rate law for PSU with 150 ppm TEA at 105°C (b), 90°C (c), and 75°C (d).

evaluation of structure–morphology–property relationships of a material. Kinetic mechanisms describing polythiourethane formation between thiols and isocyanates are not well understood. The following rate law was adopted to describe the polymerization reaction:

$$\frac{d[\text{NCO}]}{dt} = -k[\text{NCO}]^a[\text{SH}]^b, \quad (5)$$

where k is the rate constant and $[\text{NCO}]$ and $[\text{SH}]$ are the concentrations of isocyanate and thiol, respectively. Similarly, the exponents a and b represent the order of reaction with respect to isocyanate and thiol, respectively. $n = a + b$ is the overall order of reaction.

The empirical schemes, n th order, is widely used for modelling the cure kinetics for thermosetting materials [15, 35]. The n th-order kinetics can be expressed as

$$\frac{dp}{dt} = k(1-p)^n. \quad (6)$$

Here p is the degree of cure (isocyanate conversion), and k is the constants related to the rate constants, which depends on the temperature. The parameter n is related to the reaction order. Here we used the n th-order approach for modelling the curing kinetics of PSU. If the curve $\ln(1-p)$ plotted against time is a straight line, the mechanism of this reaction follows a first order. If the

TABLE 2: First-order kinetic parameters and thermodynamic parameters of PSU curing process with 150 ppm TEA.

Temperature (K)	1st-order equation		E_a (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹)
	K (min ⁻¹)	R^2			
348	0.0019	0.988			
363	0.0051	0.981	100.23	97.22	-20.13
378	0.0301	0.997			

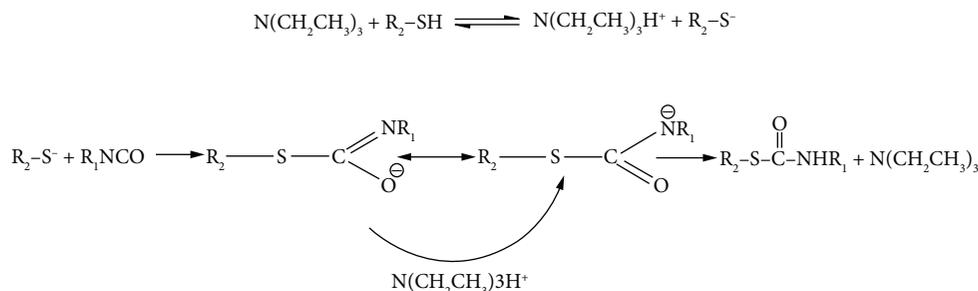


FIGURE 7: Mechanism of nucleophilic addition between isocyanate and thiol catalyzed by TEA.

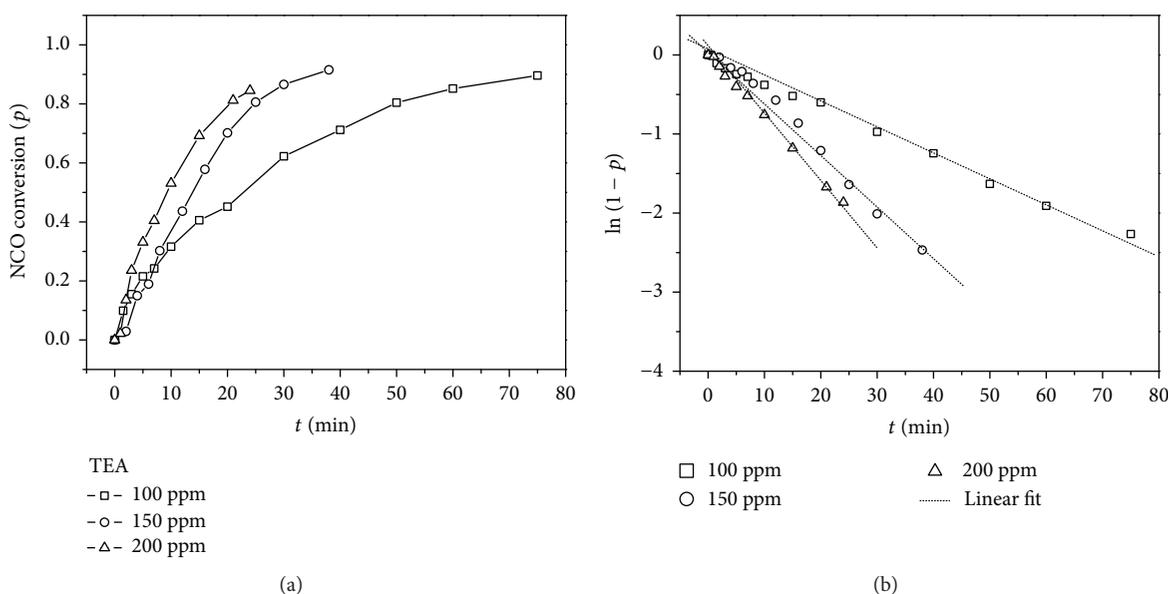


FIGURE 8: Isocyanate conversion versus curing time of PSU with different TEA content at 105°C (a) and the corresponding first-order rate law.

curve $(1/(1-p))$ plotted against time is a straight line, the mechanism of this reaction follows a second order. And so on.

$$\text{If } n = 1, \ln(1-p) = -kt + C.$$

$$\text{If } n = 2, 1/(1-p) = kt + C.$$

If $n = 3$, $1/(1-p)^2 = kt + C$, where C is the integration constant.

The polythiourethane formation between BES and XDI with 150 ppm TEA was conducted at three different temperatures in the range of 75-105°C to determine the kinetics parameters of the reaction. The curves to which the three equations are applied for the PSU are shown in Figure 6. Comparing the results, it is evident that PSU polymerization is a typical first-order reaction, because only the plots of \ln

TABLE 3: First-order kinetic parameters of PSU curing process at 105°C with different TEA content.

Temperature (K)	Catalyst content (ppm)	1st-order equation	
		K (min ⁻¹)	R^2
378	100	0.0301	0.997
378	150	0.0688	0.991
378	200	0.0790	0.998

$(1-p)$ versus time were found to be linear (Figure 6(a)). The rate constants k from the slope of the linear fit line are listed in Table 2 for different curing temperatures. From the experimental results, it can be seen that the curing reaction rate constant rises notably at higher temperature, which

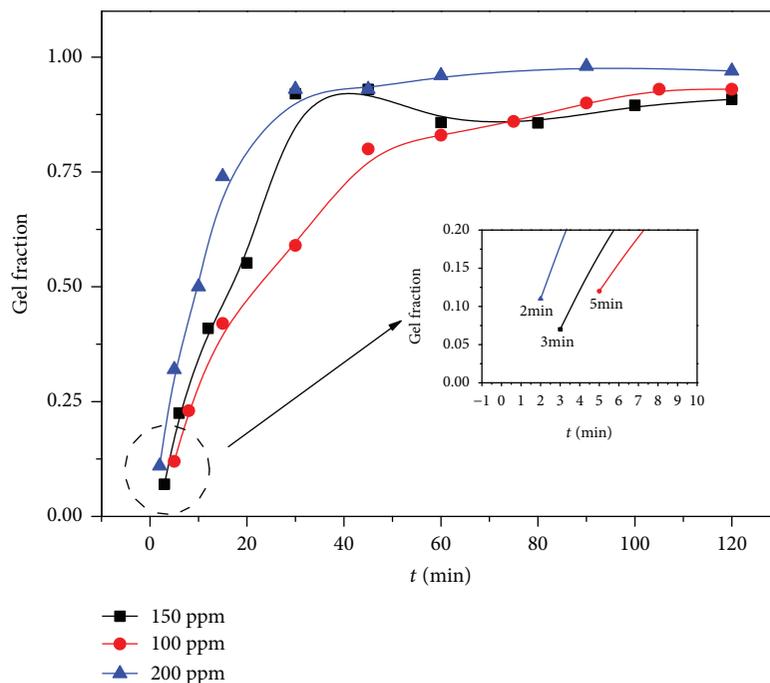


FIGURE 9: Gel time with different TEA content at 105°C.

means the polymerization reaction between BES and XDI is accelerated with the increase of temperature.

3.4. Influence of the Catalyst on the Cure Reaction Rate. The amine catalysts are known to be the most suitable catalysts for the urethane formation [36, 37]. Triethylamine (TEA) was selected in this work to be used as a catalyst for the polythiourethane formation between -SH and -NCO. The reaction mechanism of nucleophilic addition between thiol and NCO catalyzed by TEA is shown in Figure 7. First, an anionic thiol is formed by TEA, and then the anionic thiol is attacked by isocyanate to form a complex. Finally, the proton is transferred to the complex and the NHCOS is obtained [36].

Active catalysts allow a rapid reaction of the PSU system. The polythiourethane formation between BES and XDI was carried out in the presence of a catalyst with different concentrations at 105°C, as shown in Figure 8, and the first-order kinetic parameters are listed in Table 3. During the curing reactions of PSU, a three-dimensional crosslinking network is formed and -NCO groups are consumed gradually. The conversion rate of -NCO is larger with a higher catalyst concentration. -NCO groups converted 92% taking 28 minutes with a 200 ppm catalyst, while taking 38 minutes with a 150 ppm catalyst. When the catalyst concentration is as low as 100 ppm, it spent over 75 min for the -NCO conversion to 90%.

When a crosslinked polymer is immersed in an appropriate solvent, the polymer imbibes the solvent and undergoes swelling. When the insoluble polymer first appears, the gel and the crosslinked network form. Gelation times with different catalyst contents were determined through swelling measurement and are shown in Figure 9. No gel was formed at the beginning, but after an induc-

tion period, a gel was formed and the gel fraction increased very quickly as the cure proceeded. Obviously, the gel with a high catalyst content appeared earlier, indicating a faster reaction. This is consistent with the conclusion we mentioned above.

Although it seems to be applicable, the n th-order approach has some limits as the reaction process is very complex. In a polymerization process, the liquid reactants slowly become solid as the reaction proceeds, and obviously, the reaction mechanisms are changing. Many reports have shown that the curing reaction is controlled by the diffusion in the last part of the reaction [38, 39]. Even so, this approach has proved to be able to reflect the process to a great extent.

3.5. Calculation of the Activation Energy, Activation Enthalpy, and Entropy. Activation energy of the PSU formation was determined according to equation (1), as listed in Table 2. E_a is 100.23 kJ mol⁻¹, a comparatively large value, indicating that the curing reaction of PSU must have occurred in the presence of a catalyst and/or heating to some extent.

Activation enthalpy (ΔH^*) and entropy (ΔS^*) gained from the Eyring relationship are very useful to understand the reaction mechanism. The Eyring relationship (equation (2)) was used to determine the values and ΔH^* and ΔS^* are presented in Figure 9 and Table 2.

The Eyring plot for the thermal curing reaction between BES and XDI is illustrated in Figure 10, which gives a straight line. In curing processes, thermodynamic parameter values are the actual indicators for practical applications. The activation enthalpies and entropies can be obtained from the evaluation of the Eyring plot. The activation enthalpy was found to be $\Delta H^* = 97.22$ kJ mol⁻¹ and the activation entropy can be found to be $\Delta S^* = -20.13$ J K⁻¹ mol⁻¹.

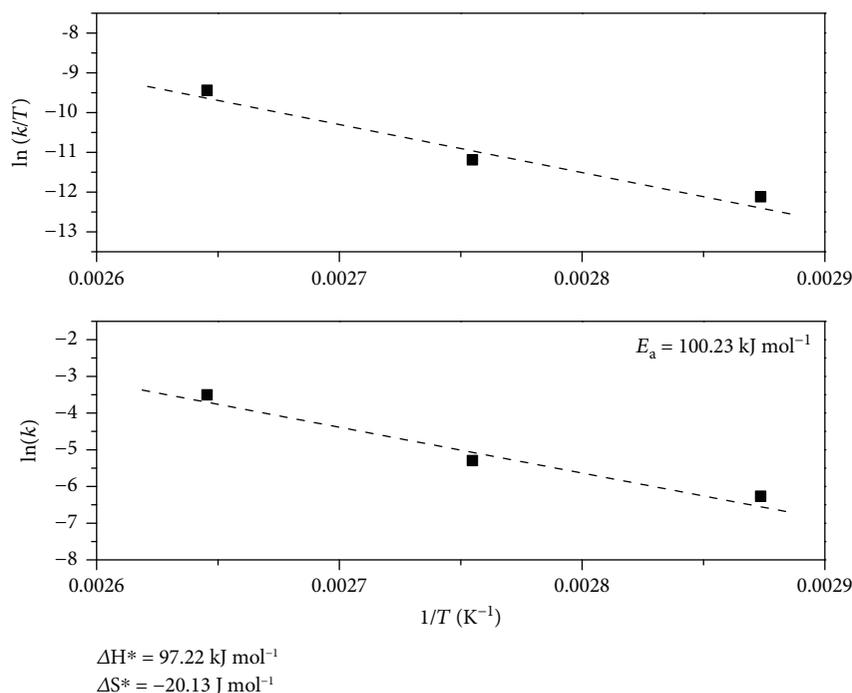


FIGURE 10: $\ln(k)$ and $\ln(k/T)$ versus reciprocal of curing temperature of PSU.

As shown in Table 2, the positive ΔH^* value indicates that the curing process is endothermic in nature. This is consistent with the above results where the isocyanate conversion increased with the increasing temperature. In addition, high values for the activation enthalpies were found, indicating that strong associations between the hydroxyl groups were present for polyurethane systems [40]. These could be considered similar to those present in thiol groups in BES-XDI systems, according to ΔH^* values (Table 2). The value for the activation entropy was negative, which attested to an associative mechanism in the transition state [40]. Support for this assignment of an associated mechanism in the transition states for the polythiourethane formation between BES and XDI comes from comparison of the activation enthalpies with the bond energies of the S-H and C=N bonds (363 kJ/mol for S-H and 615 kJ/mol for C=N), which were broken in the reaction. The activation enthalpy was much smaller than the bond energy.

4. Conclusions

The kinetic studies on the optical polythiourethane formation have been performed by means of quantitative FTIR spectroscopy. *m*-Xylylene diisocyanate (XDI) and 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol (BES) were used as the key raw materials. The curing reaction of the optical polythiourethane exhibits first-order kinetics. Triethylamine added as a catalyst can significantly accelerate the reaction process, probably due to the formation of the intermediate transition state. The negative value of the activation entropy, as well as the comparison between the activation enthalpy and the dissociation energies of the breaking

bonds, confirms that transition states may be formed during the curing process.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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