

Research Article

Kinetic Analysis of the Reaction between Tannic Acid (TA) and L-Lysine Diisocyanate (LDI) Systems

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The kinetics of the synthesis of green polyurethane from the reaction between tannic acid (TA) and L-lysine diisocyanate (LDI) were investigated using the differential scanning calorimeter (DSC) technique and dynamic rheological tests. The evaluation of the reaction behavior of the prepared samples was carried out using nonisothermal conditions at dynamic heating rates of 5, 10, 15, and 20°C/min. The evolution of the activation energy with conversion was computed through the five isoconversional methods of Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose (KAS), the Ozawa-Flynn-Wall method (OFW), Friedman (FR), Starink, and Vyazovkin. The average activation energy calculated from these methods was estimated at 46.5, 46.8, 47.2, 47.3, and 51.4 KJ/ mol, respectively. The preexponential factor was evaluated at 5.04×10^5 1/s. The overall reaction order (n + m) was also found to be around 1.8912. The results of the combination of the model-free method and model-fitting approach exhibited that the reaction mechanism was an autocatalytic type, implying the autocatalytic effect of the urethane groups formed during the reaction. The obtained kinetic for TA/LDI was verified through its good agreement with the experimental data. Moreover, the results found from the isothermal rheological test show that with increasing temperature, the gelation time decreases.

1. Introduction

Green polyurethane refers to a type of polyurethane material that is produced using environmentally friendly or sustainable methods and incorporates renewable or recycled resources. It is characterized by its reduced environmental impact compared to traditional polyurethane materials, which often rely on fossil fuels and nonrenewable resources. Green polyurethane can be developed through various approaches, such as biobased polyols, recycled content, green chemistry principles, and life cycle considerations [1–3]. The kinetic behavior of the reaction in green polyurethane refers to the study of the rate at which chemical reactions occur during the formation of the polyurethane material using environmentally friendly or sustainable methods. It involves understanding the reaction mechanisms, reaction rates, and factors that influence the reaction kinetics. The reaction kinetics in green polyurethane can be influenced by several factors, including catalysts, reactant ratios, temperature, mixing, and agitation, as well as the nature of the raw materials.

Understanding the kinetic behavior of the reaction is crucial for optimizing the synthesis process, controlling the reaction rate, and achieving desired polyurethane properties in terms of curing time, mechanical strength, and other performance parameters. Experimental techniques, such as monitoring the reaction progress over time, measuring reaction rates, and analyzing reaction intermediates, can be employed to study the kinetic behavior of the reaction in green polyurethane [4, 5]. In this regard, the development of polyurethanes prepared from biocompatible reagents has become one of the most attractive research fields [6]. It is also one of the most suitable applications of polyurethane in the field of tissue engineering. Therefore, a wide range of polyurethanes have been studied and used in medical and pharmaceutical applications due to their special properties such as biostability, biodegradability, and tunability, and the availability of a wide range of reagents makes it possible to synthesize polyurethanes with different properties. The first step in the development of strong and durable green polyurethanes is the production of polyols with biological value [7, 8]. The synthesis of biocompatible materials from renewable resources is of great importance for two reasons: First off, it is thought to be an option to use less oil in the synthesis of different polymers, and secondly, biobased raw materials hold promise as ecofriendly resources for the manufacture of polymers [9–12].

One of the most important chemicals in this respect is tannic acid (TA), a cheap and easily accessible plant polyphenolic compound that has been taken into account in several studies in the creation of biodegradable multiarm star branching aqueous polyurethane by Shun Luo et al. [5] and also in the preparation of polyurethane/tannic acid hydrogel by Jie Wen et al. [4]. In addition, the structure of TA is similar to that of branched polyester due to the presence of branches, the presence of a phenol-type hydroxyl functional group, the pyranose heterocycle, and the presence of ester bonds, which make them special and unique. Accordingly, the phenolic hydroxyl groups of the TA molecule can interact with isocyanate (-NCO) to produce dynamic phenol-carbamate linkages in the polyurethane chains. This is based on the molecular structure of TA that was previously introduced. The introduction of these tannic acid structures, which have several phenolic structures, will be prepared to increase the mechanical properties of polyurethane.

The next step to achieving a greener polyurethane formulation is the use of potentially biobased di, tri, or polyisocyanates [15]. Furthermore, the use of biocompatible isocyanates also has a special place [16]. So, green polyols have good reactivity with conventional diisocyanates and can also induce mechanical strength, biodegradability, and biocompatibility in the produced PUs, but the use of these carbohydrates is still limited in the synthesis of PUs and has not been widely studied. The use of these carbohydrates in polyurethane networks has been reported as a crosslinking agent, a reactive agent with isocyanate groups, or as a filler [17, 18]. For example, produced polyurethanes based on castor oil grafted with starch, which have excellent mechanical properties [19]. In reports, carbohydrates, such as cellulose nanocrystals or starch nanocrystals, have been used as valuable fillers in PUs [20]. While the majority of bio-diisocyanate monomer synthesis routes still require phosgene gas as a reagent for petroleum, there are commercial isocyanates with high source availability, such as isocyanates containing fatty acids or amino acids [21, 22]. Diisocyanates based on the drug L-lysine have been used for biomedical PUs in the past several years as drug delivery systems, hydrogels, and implant materials [15, 16]. For this purpose, this isocyanate has been used in several recent events, where L-lysine diisocyanate (LDI) based on L-lysine was compared with diisocyanate monomers produced on petroleum such as hexamethylene diisocyanate and diisocyanate isocyanate in terms of reactivity and final properties of the produced PU and using from that [16, 18,

23-25]. Also, a fully verifiable poly (urea urethane ester) thermoplastic was synthesized using this isocyanate [26]. However, one of the rare cases in this case has been the investigation of the reaction kinetics of these two monomers [11, 27-29]. Knowing the kinetics and the parameters related to the reaction can determine an optimal process in the design and synthesis of high-performance structures based on polyurethane in various fields of application such as medicine, pharmaceutical, biological, and other cases [27]. In kinetic studies, first, the rate of conversion against time is determined, and finally, a suitable model is presented to predict the behavior of the reaction [30, 31]. The study of the kinetic behavior of the reaction in green polyurethane is an active area of research, and while significant progress has been made, there are still gaps and challenges that need to be addressed. Some of the key gaps in our understanding of the kinetic behavior of green polyurethane reactions include the following: (i) Limited data on specific green polyurethane systems: The availability of comprehensive kinetic data for specific green polyurethane formulations is often limited. Many studies focus on traditional polyurethane systems, and there is a need for more research dedicated to understanding the kinetics of reactions specifically tailored for green polyurethane materials. (ii) Optimization of reaction parameters: The optimization of reaction parameters, such as catalyst type and concentration, reactant ratios, and processing conditions, for green polyurethane systems is an ongoing challenge. Further investigation is needed to determine the ideal conditions that maximize reaction rates and produce polyurethane materials with the desired properties. (iii) Mechanistic understanding: While general reaction mechanisms in polyurethane formation are well-established, there is a need for a better mechanistic understanding of the reactions involved in green polyurethane systems. This includes understanding the influence of biobased polyols, recycled content, and other green chemistry principles on the reaction kinetics. (iv) Standardization of testing methods: There is a lack of standardized testing methods and protocols for evaluating the kinetic behavior of green polyurethane reactions. Establishing consistent testing methodologies would facilitate comparison and reproducibility of results across different studies.

(v) Scale-up considerations: The kinetics of polyurethane reactions can be influenced by the scale of production. It is important to investigate the scalability of green polyurethane synthesis processes and understand any potential changes in the reaction kinetics at larger scales. Addressing these gaps in the study of the kinetic behavior of green polyurethane reactions will contribute to a deeper understanding of the synthesis process, facilitate process optimization, and ultimately enable the development of high-performance and sustainable polyurethane materials

In these investigations, the amount of activation energy and the amount of released heat (if the reaction is exothermic) are also determined, and in this way, useful information is obtained in the field of industrial applications of polymers [17, 32]. Here, modeling the TA/LDI reaction using curing behavior and rheometric analysis is studied using a simple and efficient method.



SCHEME 1: The mechanism of the reaction between TA and LDI.

2. Experimental

2.1. Materials. L-Lysine diisocyanate (LDI), methyl ethyl ketone (MEK) as solvent, and tannic acid (TA) were purchased from Sigma and used without further purification.

2.2. Sample Preparation and Measurements. In this research, polyurethanes were obtained by the reaction between a polyol and a 3% molar excess of LDI in MEK as solvent (Scheme 1) without any special catalyst and accelerator. Initially, samples are kept in a 4°C refrigerator until they are analyzed. These samples were examined using the DSC analysis (Mettler Toledo Star, Swiss) with rates of 5, 10, 15, and 20°C/min in the temperature range of 20-180°C under a nitrogen atmosphere. The kinetic behavior of prepared samples was analyzed using four different heating rates according to ICTAC recommendations [17]. In addition, the rheological behavior of the samples was assessed by the use of a HAAKE MARS 2 rheometer (Thermo Fisher Scientific, Karlsruhe, Germany). For this purpose, first of all, the samples were heated to a temperature stability of ±0.1°C using a heating furnace. Also, the research and calculations related to the isothermal baking process in the temperature range of 30 to 80°C with a strain of 1% and a frequency of 1 Hz have been done, and finally, the evolution of dynamic viscosity (η^*) and storage and loss modulus (G', G'') with reaction time were evaluated (ATR-FTIR of the final sample is given in Figure S01).

3. Reaction Kinetic Modeling

The following Equation (1) can describe the kinetic behavior of a reaction.

$$\frac{d\alpha}{dt} = k(T) \times f(\alpha). \tag{1}$$

where $f(\alpha)$ is a fractional conversion-related function connected to the reaction mechanism. Equation (2) illustrates

k(T), a temperature-dependent reaction rate constant that follows the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right).$$
 (2)

For a dynamic heating schedule $d\alpha/dt = \beta d\alpha/dT$, in which the constant heating rate is $(\beta = dT/dt)$.

In a DSC analysis, the conversion (α) is defined as the ratio of the released reaction heat at time *t* to the total amount of heat produced throughout the reaction in a non-isothermal heating process, namely, $\alpha = \Delta H_t / \Delta H$ [33].

The kinetic triplet parameters, i.e., activation energy (E_a) , reaction model $(f(\alpha))$, and the preexponential factor (A)should be evaluated to understand the kinetic behavior of a reaction correctly. In a nonisothermal mode, E_a values are determined easily using the methods suggested by ASTM E 698-79 [10, 19]. Therefore, to calculate the activation energy, the correlation between heating rate (β) and temperature (T_p) can be utilized and evaluated without the intervention of the kinetic model.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{g(\alpha)A.R}{E}\right) - \frac{E}{R.T_p}.$$
 (3)

Figure 1 shows the plot of $\ln (\beta/T_p^2)$ against $1/T_p$ in which the activation energy can be calculated from slope = $-E_a/R$; $E_a = 48.5$ KJ/mol.

However, many reactions/curing processes are complicated and multistep, and constant activation energy can no longer be considered with temperature and conversion during the curing reaction. Therefore, isoconversional or model-free methods can overcome such difficulties and take into account the dependence of the activation energy E_a on temperature and reaction conversion.



FIGURE 1: Kissinger's method for activation energy determination for TA/LDI system.

3.1. Isoconversional Techniques for E_a Evaluation. In general, isoconversional methods can be divided into two groups, which include differential methods and integral methods. Friedman's technique falls within the category of differential methods, whereas the integral methods include Kissinger-Akahira-Sunose (KAS), the Ozawa-Wall-Flynn method (OWF), Vyazovkin, and the approximation of Starink. Without the use of the kinetic model, any of these techniques may determine the correlation between the conversion and reaction activation energies (E_a) [16, 18, 23]. To examine how the activation energy of the TA/LDI polymerization changes with conversion, all five models are used (see Table 1).

The activation energy may be determined from the slope of the fitted line by graphing the *y*-axis versus the *x*-axis for four heating rates while taking a constant conversion (α) value into consideration.

Vyazovkin describes another approach in [34]. By applying numerical integration and minimizing the following equation to solve the temperature integral $I(E_a, T_{\alpha,i})$, one can get the activation energy for a specific value of the conversion.

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j\neq 1}^n \frac{I(E_a, T_{\alpha,i})\beta_j}{I(E_a, T_{\alpha,j})\beta_i}.$$
(4)

3.2. Model-Fitting Approach for $f(\alpha)$ Finding. The reaction type, $f(\alpha)$, represents the dependency of the reaction rate on conversion and can be treated as a mathematical description of the reaction mechanism. There are a lot of functions to mathematically describe different reaction mechanisms. The functions most commonly used can be classified into two categories: The *n*-order (Equation (14)) and the autocatalytic model (Equation (6)) [35].

$$n^{\text{th}} \text{order model} \coloneqq k(T)(1-\alpha)^n,$$
 (5)

TABLE 1: Model parameters.

Models	<i>y</i> -axis	<i>x</i> -axis	Slope
FR	$\ln\left(\frac{d\alpha}{dt}\right)$	$\frac{1}{T}$	$\frac{E_a}{R}$
KAS	$\ln \frac{\beta}{T^2}$	$\frac{1}{T}$	$\frac{E_a}{R}$
OFW	$\ln eta$	$\frac{1.052}{T}$	$\frac{E_a}{R}$
Starink	$\ln \frac{\beta}{T^{1.92}}$	$\frac{1}{T}$	$\frac{E_a}{R}$



FIGURE 2: DSC thermograms of the TA/LDI at various heating flows (all curves are corrected by linear baseline).

The autocatalytic model :=
$$k(T)\alpha^m (1-\alpha)^n$$
, (6)

where the reaction's orders are m and n.

4. Results and Discussion

4.1. Reaction Kinetic Analysis

4.1.1. Nonisothermal Curing Reactions of TA/LDI System. For the investigation of reaction behavior, the nonisothermal scanning calorimetry test was used at different heating rates. The results related to the nonisothermal reaction analysis are reported in Figure 2. The results confirm the existence of a common exothermic peak in the temperature range of 409.46-449.68 K for all the prepared samples. Another intriguing finding is that as the heating rate has increased, the typical temperatures of the exothermic peaks of the initial curing temperature (T_f) have moved to higher values.

As can be seen from Table 2, the final Tg is independent of the heating rate and is about 132 K. By plotting the temperature against the heating rate and fitting lines separately on T_i ,

$\beta/(C \min^{-1})$	T_i (k)	T_p (k)	T_f (k)	ΔH (J/g)	Tg _{init} (k)	Tg (k)	CR%*
5	345.7	409.5	429.3	30.1	-23.1	131.7	94.2
10	349.8	426.5	510.0	63.2	-21.9	133.6	95.4
15	351.9	440.8	521.6	82.5	-19.5	129.5	92.8
20	359.4	449.7	535.9	102.8	-17.3	132.5	94.6

TABLE 2: Temperature-related data of TA/LDI at different heating rates.



FIGURE 3: The characteristic temperatures $(T_i, T_p, \text{ and } T_f)$ of TA/LDI against heating rate (β).

 T_p , and T_f values at different heating rates and extrapolating to $\beta = 0$ (the intercept of the fitting line), the characteristic temperatures of static curing conditions can be calculated [36]. The T- β fitting lines are plotted in Figure 3, and the intersections are determined as $T_i = 18.7^{\circ}$ C, $T_p = 53.4^{\circ}$ C, and $T_f = 135.5^{\circ}$ C. This reaction temperature is relatively high, implying that the reaction rate between TA and LDI is low. In the following, the area under the DSC curve between T_i and T_f at different heating rates can be computed to obtain the total enthalpy of the reaction. The conversion of the reaction can be determined by dividing the partial area by the total enthalpy of the reaction. A plot of the trend of conversion against temperature is shown in Figure 4.

A sudden increase in conversion can be attributed to the enhanced reaction rate and autoacceleration in urethane formation. Under nonisothermal circumstances, the simultaneous changes in k(T) and $f(\alpha)$ result in a sigmoidal α -*T* curve.

For further investigation, the plot of the reaction/curing rate $d\alpha/dt$ versus conversion α is also shown in Figure 5. As can be seen, all curves have the same shape, and the conversion at the maximum reaction rate, α_p , is about 0.42. As the α_p at all heating rates is almost the same, the Kissinger method was applied as an initial estimation for the activation energy of the reaction.

Figure 1 shows the best-fitting line obtained according to Kissinger's method, by which the activation energy can be determined as 49.91 KJ/mol. However, as mentioned before,



FIGURE 4: Curves for the evolution of conversion against temperature at various heating rates for TA/LDI.



FIGURE 5: The change of $d\alpha/dt$ versus temperature for the TA/LDI system.

this method can only give a single value for activation energy. So, isoconversional techniques (differential and integral) are employed to determine the activation energy and assess the potential change in activation energy with conversion. The cure status of TA/LDI polyurethane samples can be specified by the cure index (CI) which in turn is calculated by the glass transition temperature (Table 2). The reaction rate is slow, and the reactive moieties have adequate time to participate in the urethane formation reaction, as shown in Table 2, which results in high CI at low heating rates ($\beta = 5$ and 10°C/min). On the other side, high β (20°C/min) reduces reaction time but boosts molecular kinetic energy, which boosts the likelihood of molecular collisions to enhance the curing state.

4.2. Isoconversional Methods. The correlation of reaction rate $(d\alpha/dt)$ and conversion can be obtained using the modelfree kinetic method. Also, the E_a values of the reaction between TA and LDI at different conversions were estimated by FR (Figure S2), KAS (Figure S3), OFW (Figure S4), Starink (Figure S5), and Vyazovkin. It can be evident that the E_a values calculated by the OFW, KAS, Starink, and Vyazovkin methods show a similar evolution, changing somewhat in the range of 45-50 KJ/mol at conversion between 5 and 95%. In contrast, the rate of change of the E_a values calculated by the Friedman method is higher at the entire conversion range. This is because the FR method is very sensitive in the reason of the presence of the term of the reaction rate values $(d\alpha/dt)$ in the calculation [37]. In contrast to multistep reactions, which exhibit many trends for E_a vs. conversion, single-step reactions have a constant E_a throughout a range of conversion or temperature.

As seen in Figure 6, three different trends are observed over the curing/reaction. As seen in Figure 6, the reaction process is split into three different stages: (1) $\alpha < 0.2$ stage I, the E_a value decreases with conversion. At the beginning of the polymerization process, during a kinetic control reaction, monomers gradually convert into intermediate components and form urethane and carbamate groups, which can play a catalytic role in the reaction. The urethane group autocatalysis mechanism is given in the following Scheme 2.

(2) $0.2 < \alpha < 0.85$ stage II, the E_a value remained at a constant value (level off) with conversion [38]. At this stage, the intermediate components will grow successively into macromolecules, and the reaction gradually becomes diffusion control, which is expected to increase activation energy. Conversely, the autocatalytic reaction increases due to the formation of more urethane and carbamate groups. The balance between these two opposite effects causes the E_a value to remain unchanged. (3) $\alpha > 0.85$ stage III, the E_a value shows the increase in viscosity, and the diffusion-controlled mechanism of reaction in the system explains an upward trend, the increase in activation energy. Additionally, the rise in molecular weight, the crosslinking density, and the noticeably lower number of reactive groups should be primarily blamed for the increase in apparent activation energy in the final stage for the TA/LDI systems. In general, the reaction between polyols and isocyanates to form polyurethane is an exothermic reaction that proceeds through a step called ure-



FIGURE 6: The activation energy (E_a) value against the degree of reaction.

thane formation. The activation energy for this step typically ranges from tens to a few hundred kilojoules per mole (KJ/mol). It is important to note that the activation energy can be influenced by factors such as the type and structure of the polyol and isocyanate, the presence of catalysts or additives, temperature, and reaction conditions.

From a kinetic point of view, the detailed examination of the curing behavior of a system depends on all parameters of kinetic triplets. Therefore, other key terms, including reaction model $f(\alpha)$ and preexponential factor A, should be estimated. These two kinetic parameters were calculated using M'alek's model fitting [19]. Two models are used to determine reaction model $f(\alpha)$ and preexponential factor A: $y(\alpha)$ (Equation (7)) and $z(\alpha)$ (Equation (8)).

$$y(\alpha) = \frac{d\alpha}{dt}e^x,\tag{7}$$

$$z(\alpha) = \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} P(x).$$
(8)

The temperature integral is expressed as $\pi(x)$, where $x = E_a/RT$ is the reduced activation energy. Of course, an approximation is taken into account here by applying the fourth rational expression of Senum and Yang as follows:

$$p(x) = \frac{(E_a/\text{RT})^3 + 18(E_a/\text{RT})^2 + 88(E_a/\text{RT}) + 96}{(E_a/\text{RT})^4 + 20(E_a/\text{RT})^3 + 120(E_a/\text{RT})^2 + 240(E_a/\text{RT}) + 120}.$$
(9)

Here, E_a is the average value calculated from the five mentioned isoconversional methods in the conversion range



SCHEME 2: Reaction mechanism between the isocyanate and hydroxyl groups in LDI and TA components, respectively.

of 0.1 and 0.9. The functions of $y(\alpha)$ and $z(\alpha)$ were normalized by their maximum values within (0, 1) intervals, namely:

$$Y_{s}(\alpha) = \frac{y(\alpha)}{\operatorname{Max}(y(\alpha))},$$

$$Z_{s}(\alpha) = \frac{z(\alpha)}{\operatorname{Max}(z(\alpha))}.$$
(10)

The highest conversions, α_M and a_p^{∞} , respectively, coincided with the peaks of the $y(\alpha)$ and $z(\alpha)$ functions, which suggests the choice of the most appropriate kinetic model for the examined curing/reaction process. Figure 7 depicts, respectively, how the $y(\alpha)$ and $z(\alpha)$ functions change as a result of conversion. The values of α_p , α_M , and a_p^{∞} that were identified as the maximum points in DSC curves are presented in Table 3. As the values of α_M and a_p^{∞} are independent of β , it can be concluded that the same reaction mechanism is governed at all heating rates. It is found that the Malek method will be applicable for nonisothermal kinetic data when the heating rate effect on the reaction kinetics is ignorable. In this investigation, the autocatalytic model represented by Equation (6) may be used as the kinetic model of the urethan production reaction since $0 < \alpha_M < a_p^{\infty}$ and $a_p^{\infty} \neq 0.623$.

After the kinetic model $(f(\alpha))$ has been established, the average value of E_a may be used to calculate further kinetic parameters, such as the preexponential factor and the kinetic exponents.

$$A = \frac{\beta X_p}{Tf'(\alpha_p)} \times \exp x_p.$$
(11)

This corresponds to the conversion α_p , the maximum on the DSC curve. Additionally, p is the DSC curve's maximum, and $f'(\alpha_p)$ is the kinetic model's differential form $(df(\alpha)/d\alpha)$. To fit the kinetic model, the following assumptions have been used: n-type order and autocatalytic kinetics. Using the five isoconversion methods stated above, the average activation energy was computed with $\alpha = 0.1 - 0.9$. The kinetic parameters can be calculated by adjusting the reaction rate with experimental data at a specified reaction temperature and time. The *n*-order and autocatalytic models are used to initially fit the experimental data to determine the kinetic model function. The *n*th-order reaction model's



FIGURE 7: The change of $Y_s(\alpha)$ and $Z_s(\alpha)$ function relative to α .

TABLE 3: The values of α_p , α_M , and a_p^{∞} evaluated for the reaction of the TA/LDI system.

β (C min ⁻¹)	α_p	$lpha_M$	a_p^∞
5	0.529	0.5013	0.520
10	0.498	0.5155	0.537
15	0.505	0.5262	0.540
20	0.509	0.5155	0.537

Equation (12) model may be simplified as follows:

$$\ln\left(Af(\alpha) = \ln\left(\frac{d\alpha}{dT}\varphi\right) + \frac{E_a}{\mathrm{RT}} = \ln\left(A\right) + n\ln\left(1-\alpha\right).$$
(12)

The graph of $\ln [Af(\alpha)]$ against $\ln (1 - \alpha)$ illustrated in Figure 8 demonstrates the considerable departure of experimental data from the *n*th-order reaction model. For the *n* th-order cure mechanism, a straight line should appear when $\ln (Af(\alpha))$ was plotted vs. $\ln (1 - \alpha)$, whose slope is the reaction order (*n*). According to Figure 9, there is a notable discrepancy, notably in the lower conversion range between 0.1 and 0.5, which rejects the conformity of the reaction mechanism with the *n*-order model. The development of a



FIGURE 8: ln $(d\alpha/dt) + E_a/RT$ vs. ln $(1 - \alpha)$ with different heating rates along with the preliminary results of the fitting.

maximum in the curve of $\ln [Af(\alpha)]$ against $\ln (1 - \alpha)$ is common for autocatalytic processes. Assuming the autocatalytic model, the kinetic model can be considered as follows:

$$\ln\left(Af(\alpha) = \ln\left(\frac{d\alpha}{dT}\varphi\right) + \frac{E_a}{RT} = \ln\left(A\right) + n\ln\left(1 - \alpha\right) + m\ln\left(\alpha\right).$$
(13)

A two-parameter autocatalytic kinetic model of Sestak-Berggren's may be used to compute the kinetic parameters of the autocatalytic model [35]. The average value of (α_M) , α_{mav} , was used to calculate the kinetic parameters *m*, *n*, and *A*. According to M'alek, the general kinetic model may be recast in terms of the ratio of reaction order, $\gamma = m/n$ [39]

$$\ln\left(\frac{d\alpha}{dT}\beta e^{E_a/\mathrm{RT}}\right) = \mathrm{Ln}A + n\ln\left(\alpha^{\gamma}(1-\alpha)\right),\tag{14}$$

$$\gamma = \frac{m}{n} = \frac{\alpha_{\rm mav}}{1 - \alpha_{\rm mav}}.$$
 (15)

The preexponential factor (A) and the orders of nonand autocatalytic processes (*n* and *m*, respectively) were determined by graphing $\ln (d\alpha/dT\beta e^{E_a/RT})$ against $\ln (\alpha^{\gamma}$ $(1-\alpha))$, the results of which are presented in Figure 9. These findings suggest that the experimental data and the model fitting curve are identical. In addition to the above, it has been shown that the experimental results and the autocatalytic model agree well over the whole conversion spectrum. As a consequence, it can be shown from this result's analysis that the TA/LDI system's response rate peaks at α_p after a certain period of time



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FIGURE 9: Validation of the autocatalytic model by comparing simulation results with experimental data of TA/LDI reaction at different heating rates.

TABLE 4: Calculated parameters for *n*-order mode and autocatalytic model.

β (C min ⁻¹)	п	т	$A \times 10^{-5}$
5	1.40	0.41	4.49
10	1.36	0.43	4.63
15	1.50	0.44	5.36
20	1.60	0.47	5.69

and then steadily declines. In the case of polyurethane formation, the reaction between a polyol and an isocyanate typically proceeds through an initial nucleophilic addition of the polyol to the isocyanate, forming an intermediate known as an isocyanate-terminated prepolymer. This intermediate can then react with additional polyol molecules, leading to chain extension and the formation of the polyurethane polymer.

In some cases, the isocyanate-terminated prepolymer can act as an autocatalyst, meaning it accelerates the reaction by catalyzing the further reaction between the polyol and isocyanate. This autocatalytic behavior can result in a rapid increase in the reaction rate as the concentration of the isocyanate-terminated prepolymer increases.

Autocatalysis in polyurethane reactions can be influenced by factors such as the type and concentration of the isocyanate, the nature of the polyol, the reaction temperature, and the presence of catalysts or additives. It is important to note that not all polyurethane reactions exhibit autocatalytic behavior, and the occurrence of autocatalysis can vary depending on the specific system and reaction conditions.

The MATLAB code was used to fit the reaction process, and the relevant findings are shown in Table 4.



FIGURE 10: Curves for viscosities—temperature relation and G' and G'' against time (isothermally reacted/cured at 35°C).

The results indicated that the autocatalytic type results agree with the experimental data of the reaction between TA and LDI. The autocatalytic model based on relevant results can be written as follows:

$$\frac{d\alpha}{dt} = 5.0425 \times 10^5 e^{-E_a/\text{RT}} \alpha^{0.4357} (1-\alpha)^{1.4555} (0.1 < \alpha < 0.9).$$
(16)

Also, to be more sure of the selected model, the autocatalyst model was used for fitting reaction conversion and temperature, and the results were compared with experimental data (Figure 9).

Therefore, it can be said that the kinetic model created and considered in this research is suitable and reliable. Therefore, based on the results obtained so far, a mechanism for this reaction has been proposed in such a way that the presence of the urethane groups can catalyze the TA/LDI reaction process. In the first range, the autocatalytic reaction causes isocyanates to react with the hydroxyl groups on TA chains; after a short induction period along with an exothermic reaction, the reaction rate has increased [36].

4.3. Rheology Study. For further investigation, the viscosity evolution of the TA/LDI system within the reaction/curing process was recorded and reported in Figure 10. The findings show that viscosity gradually increases along a declining trend. The data also demonstrate that the reaction time increases with increasing temperature, taking 31.7 minutes at 35°C, 28.9 minutes at 45°C, and only 17.4 minutes at 65°C. The key takeaway from this discussion of rheological behavior is that the crosspoints of the storage and loss modulus curves are regarded as reliable indicators of the gelation point. Therefore, it can be seen that with the passage of time, the loss and storage modulus have increased slowly, and after a short induction period, they have shown an increasing trend. The continuation of the curing reaction, due to the increase in connections and entanglements, has caused a decrease in molecular movements, which results in a shortening of the intersection time between the loss modulus and the storage



FIGURE 11: ln $(d\alpha/dt) + E_a/RT$ vs. ln $(1 - \alpha)$ with different heating rates along with the preliminary results of the fitting.

modulus. Consequently, this also implies that Figure 10 illustrates the transformation of a viscous fluid into a solid gel at 35° C due to sufficient intermolecular contact of polymer chains, G'. The Arrhenius law can also be used to explain how the temperature increase has sped up gelation [40].

$$k' = k'_0 \exp\left(\frac{-E_a}{\mathrm{RT}}\right),\tag{17}$$

$$k' \equiv \frac{1}{t_{\rm gel}},\tag{18}$$

$$\ln t_{\text{gael}} = -\ln k_0' + \frac{E_a}{\text{RT}}.$$
(19)

So, gel time changes are inversely proportional to temperature under isothermal conditions. The fact that the activation energy acquired from the two DSC and rheological approaches differs significantly is another extremely important point that needs to be made in this context. This may be because the rheological method is viewed from an isothermal point of view, whereas the DSC method is viewed from a nonisothermal point of view. The system freezes quickly in isothermal circumstances, but in nonisothermal conditions, viscosity is initially reduced, allowing for greater mobility. Heating the system then facilitates reactions in the viscoelastic state seen in Figure 11.

5. Conclusion

The polyurethane production kinetics of the TA/LDI system were investigated using nonisothermal DSC measurements, which are a part of green chemistry. By employing a combination of the isoconversional method and the model-fitting technique, the researchers gained an understanding of the reaction mechanism. Various isoconversional techniques like Chatterjee-Conrad, Friedman, KAS, OFW, Starink, and Vyazovkin were employed, along with single and multiple heating rate techniques, to analyze the fluctuation of activation energy with conversion.

The mean activation energy (E) was determined to be 48.5 KJ/mol. It should be noted that the KAS method showed a deviation from the other methods, but all approaches were consistent in their ability to predict cure kinetic parameters for the TA/LDI system. The results indicated that the autocatalytic model effectively describes the reaction mechanism across the entire conversion range. The model's predictions were validated, showing a favorable agreement with the experimental data.

The overall reaction order (m + n) was found to be 1.8912. Additionally, the relationship between polymerization progress and rheological behavior was assessed. It was observed that viscosity is temperature-dependent, and as the temperature increases, the gel time decreases.

Data Availability

The MATLAB code of the article is available in the support information.

Conflicts of Interest

All authors declare that they have no conflicts of interest.

Authors' Contributions

Ali Karbasi and AmirHossein Enayati Gerdroodbar provided substantial contributions to the investigation, data curation, and writing of the original draft. Reza Darvishi was responsible for the conceptualization, methodology, and supervision. Ghasem Payam contributed to the writing—review and editing.

Supplementary Materials

The corresponding author will provide any findings and information necessary to support. Also, other raw/processed data with several figures are available in the Supporting Information. The data in the supporting information includes several MATLAB codes and five figures. Supporting information.docx: ATR-FTIR and output figures from running MATLAB code. f.txt: m-file for Equation (13) in the manuscript. rk455, rk451, and rk45.txt: m-file for rungekutta function for solving first order differential equation. programvyam.txt, programvya.txt, and Vay2.tex: m-file used for the Vyazovkin method. minii.txt: m-file for minimizing Equation (4) in the manuscript. (*Supplementary Materials*)

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