

Bulk Polymerization Kinetics of Hydroxyl Terminated Polybutadiene and Toluene Diisocyanate with Infrared Spectroscopy

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ABSTRACT

A study on bulk polymerization kinetics of Hydroxy Terminated Polybutadiene (HTPB) and Toluene Diisocyanate (TDI) with infrared (IR) spectroscopy has been conducted. The investigations included the molar ratio of 2,4-TDI to 2,6-TDI isomers, the initial molar ratio of isocyanate group to a hydroxyl group, and the reaction temperature. The polymerization rate constant was calculated based on the decrease rate of TDI. Kinetics model had been evaluated through the following reaction steps: (1) 2,4-urethane production, (2) 2,6-urethane production, (3) the reaction between 2,4-urethane and the isocyanate group of 2,4-TDI, (4) the reaction between 2,4-urethane and the isocyanate group of 2,6-TDI, (5) the reaction between 2,6-urethane and isocyanate group of 2,4-TDI, and (6) the reaction between 2,6-urethane and the isocyanate group of 2,6-TDI. Those reaction steps were assumed to be the first order reaction with the reaction rate constants k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 , respectively. The reaction rate constants obtained at molar ratio of 2,4-TDI to 2,6-TDI of 80:20, isocyanate group to hydroxyl group ($R_{NCO/OH}$) initial molar ratio of 1:1, and reaction temperature of 40 °C were 6.2×10^{-5} , 5.8×10^{-5} , 3.1×10^{-5} , 2.8×10^{-5} , and 2.5×10^{-5} L.mole⁻¹.min⁻¹ for k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 , respectively, with the activation energy of 1152, 952, 1001, 656, and 1001 kJ/mole for reaction (1)–(6), respectively. The results showed that the polymerization reaction rate-determining step was the reaction of 2,6-urethane and isocyanate group of 2,6-TDI (reaction (6)).

Keywords: bulk polymerization; kinetics; hydroxy terminated polybutadiene; toluene diisocyanate

ABSTRAK

Penelitian ini mempelajari kinetika polimerisasi langsung HTPB dengan TDI menggunakan spektroskopi infra merah. Variabel penelitian untuk menentukan data kinetika (tetapan kecepatan polimerisasi) adalah persentase komposisi isomer 2,4-TDI terhadap 2,6-TDI, perbandingan mol mula-mula gugus isosianat terhadap gugus hidroksil ($R_{NCO/OH}$), dan suhu reaksi. Tetapan kecepatan polimerisasi dihitung berdasarkan konsentrasi TDI. Model kinetika dievaluasi dengan tahapan reaksi termasuk: (1) pembentukan gugus 2,4-uretan, (2) pembentukan gugus 2,6-uretan, (3) gugus isosianat dari 2,4-TDI dan gugus 2,4-uretan, (4) gugus isosianat dari 2,4-TDI dan gugus 2,6-uretan, (5) gugus isosianat dari 2,6-TDI dan gugus 2,4-uretan, dan (6) gugus isosianat dari 2,6-TDI dan gugus 2,6-uretan. Setiap tahapan reaksi merupakan reaksi orde satu dan memiliki tetapan kecepatan polimerisasi k_1 , k_2 , k_3 , k_4 , k_5 , dan k_6 . Nilai tetapan kecepatan polimerisasi dihitung berdasarkan perhitungan model kinetik yang dikembangkan dapat diperoleh nilai k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 pada kondisi perbandingan mol isomer 2,4-TDI terhadap 2,6-TDI 80:20, perbandingan mol mula-mula gugus isocianat terhadap gugus hidroksil ($R_{NCO/OH}$) 1:1, dan suhu reaksi 40 °C diperoleh nilai $6,2 \times 10^{-5}$, $5,8 \times 10^{-5}$, $3,1 \times 10^{-5}$, $2,8 \times 10^{-5}$, dan $2,5 \times 10^{-5}$ L.mol⁻¹.men⁻¹ dan memiliki energi aktivasi 1152, 952, 1001, 656, and 1001 kJ/mol. Tahapan yang menentukan kecepatan reaksi polimerisasi adalah reaksi gugus isosianat dari 2,6-TDI dan gugus 2,6-uretan.

Kata Kunci: polimerisasi langsung; model kinetika; HTPB; TDI

INTRODUCTION

Hydroxy Terminated Polybutadiene (HTPB) and Toluene Diisocyanate (TDI)-based polyurethanes are recently applied for modern solid propellant binder because of their proper mechanical properties and relative pot life longevity [1-2]. This elastomer provides a

strong mechanical property, flexibility, cracking and deformation-free at the propellant burning and operational condition (-50 to 50 °C). Additionally, elastomer should have long pot life (operational viscosity) to have homogeneous composite constituents in the mixing process [3]. All processes starting from mixing and ending with casting usually

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have minimum pot life of two hours [4]. The mechanical properties can be controlled by adjusting the molar ratio of HTPB to TDI [5].

Recent research issues of polyurethane formation from HTPB-TDI are focused on (1) kinetics study of the polymerization, (2) finding the new derivatives of HTPB to provide a higher combustion energy, (3) optimization of the mechanical properties, and (4) the control of the pot life of the elastomer [6-7].

Polyurethane from HTPB and TDI have mechanical properties in large areas due to the presence of TDI isomers in equilibrium [8]. TDI has two isomers, namely 2,4-TDI and 2,6-TDI [9-10]. The viscoelasticity behavior and the mechanical properties of produced elastomer are affected by the composition of the TDI isomers. The propellant binder is usually made of the mixture of two isomers with the initial molar ratio of 2,4-TDI to 2,6-TDI of 80:20 (%). However, during the mixing process the composition changes to 40:60 (%) [11-12]. The 2,4 and 2,6-TDI isomer mixture is unstable, which depends on the temperature and the age. The TDI isomer composition causes the change of polyurethane pot life and mechanical properties of elastomer. Therefore, the effect of TDI isomer composition on elastomer properties is important to find the binder's formula.

There are two approaches to study polymerization kinetics of HTPB and TDI. First, the kinetics of polymerization based on the product concentration. The kinetics is observed from the change of product concentration of a simple reaction between the NCO and OH group. This approach is applied in most of rheological study to predict the pot life due to the simplicity of the chemical equation. The polyurethane formation kinetic in bulk condition has been studied based on the change of polymer product properties such as viscosity [1,7-11], polymer weight [7-8], torque [13-14], and thermal properties [10-11,14-16]. However, this kinetic model cannot be applied for studying the effect of TDI isomers to their pot life since the reactivity of NCO groups in both 2,4 and 2,6-TDI isomers are indistinguishable. Recently the polymerization kinetics of TDI and HTPB in solution is studied using assumption that influence of the isomers of TDI is ignored [17]. The fact that isomers in TDI are in the equilibrium state and have significant reactivity differences [18].

Second, the kinetics of polymerization is based on the change of reactant concentration over time. This approach can explain competitive reaction of TDI isomers on the polyurethane formation [17,19]. The polyurethane formation in bulk condition has been studied by analysis of the characteristic functional group change based on infrared absorption data [5-6], viscosity change (rheology) [1,7-11], and magnetic resonance/NMR [20,21]. The reaction temperature affect on reaction rate constant and the TDI isomer equilibrium.

The relation of reaction temperature to reaction rate constant and isomer equilibrium usually follows Arrhenius equation

In the kinetics study on HTPB-TDI polymerization based on Flory's theory, hydroxyl groups react with isocyanate groups to form urethane groups [13-14]. Either their molecular weight or fluid viscosity does not affect their reactivity. Polymerization consists of several steps of reaction involving two hydroxyl groups in HTPB and two isocyanate groups in TDI. Polymerization will be terminated if all of the functional groups have reacted to form urethane groups. Ajithkumar et al. states that urethane groups can react with isocyanate groups to form allophanate groups as a branching reaction [15]. If isocyanate group concentration is less than hydroxyl group one, the hydroxyl group reacts with isocyanate group to form urethane group (the main reaction). The isocyanate reacts with urethane in the presence of excessive isocyanate. Wibowo et al. stated that the linear and branching reaction could occur simultaneously and competitively [19].

In this research, the polymerization kinetic study of HTPB and TDI isomers has been conducted using the infrared spectroscopy. The effect of molar ratio 2,4 to 2,6-TDI isomers and initial molar ratio of isocyanate group to hydroxyl group have been evaluated. Additionally, the activation energy was also determined.

EXPERIMENTAL SECTION

Materials

HTPB with hydroxyl number 40, average functionality of 1.9, and average molecular weight of 3000 g/mol produced from radical polymerization of butadiene. 2,4-TDI and 2,6-TDI were used as raw materials for TDI. The mixtures of TDI isomers were prepared from 2,4-TDI and 2,6-TDI with 2,4-TDI to 2,6-TDI molar ratio of 80:20, 65:35, and 35:65. The TDI isomers were directly used without prior purification.

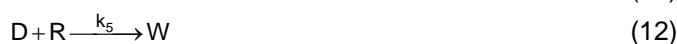
Instrumentation

Isocyanate concentration was measured with infrared spectrometer (infrared FTIR Hitachi IRPrestige Serial A210043). The polymer viscosity was measured with a digital viscometer operated at temperature of 25°C.

Procedure

HTPB was reacted with TDI in a one-liter autoclave for 60 min under inert nitrogen atmosphere and initial -NCO to -OH ($R_{\text{NCO/OH}}$) molar ratio of 1:1 and

Kinetics model is evaluated through reaction steps including (1) hydroxyl group and isocyanate group from 2,4-TDI to produce 2,4-urethane, (2) hydroxyl group and isocyanate group from 2,6-TDI to produce the 2,6-urethane, (3) 2,4-urethane and isocyanate group from 2,4-TDI, (4) 2,4-urethane and isocyanate group from 2,4-TDI, (5) 2,6-urethane and isocyanate group from 2,4-TDI, and (6) 2,6-urethane and isocyanate group from 2,6-TDI. Those reactions are shown in eq. 8–13.



The increase of reaction temperature enhances collision of reactant molecules leading to incline the reaction rate. The effect of temperature on reaction rate constant is presented with Arrhenius relation, shown in eq. 14, where k_i , A_i , E_i , R , and T were reaction rate constant in reaction step- i ($i = 1, 2, 3, 4, 5, 6$), collision factor in reaction step- i , activation energy in reaction step- i , ideal gas constant, and reaction absolute temperature, respectively. This equation is also valid for expressing the effect of temperature on isomer equilibrium constant (K) as presented in eq. 15, where A_k and E_k are collision factor and activation energy of equilibrium, respectively.

$$k_i = A_i e^{(-E_i/RT)} \quad (14)$$

$$K = A_k e^{(-E_k/RT)} \quad (15)$$

RESULTS AND DISCUSSION

As mentioned above that reaction of HTPB and TDI produces polyurethane. Bulk polymerization kinetics of HTPB and TDI has been evaluated based on the infrared absorbance at 2270 cm^{-1} , a specific absorption for isocyanate group. The NCO concentration is presented as intensity at 2270 cm^{-1} measured with infrared spectroscopy [15,25]. The decrease of the intensity every ten minutes of reaction is shown in Fig. 2.

For study on kinetic model, the isocyanate concentration equivalent to absorbance at 2270 cm^{-1} is plotted to the time and expressed in Fig. 2. Based on steps of reaction in eq. 1 to 6 and curve isocyanate concentrations every 10 min in Fig. 1, polymerization kinetics cannot describe the effect of 2,4-TDI/2,6-TDI ratio and it is predicted via steps eq. 7 to 13. If the polymerization reaction follows the eq. 7 to 13, the equation of kinetic model may be described in eq. 14 to 18.

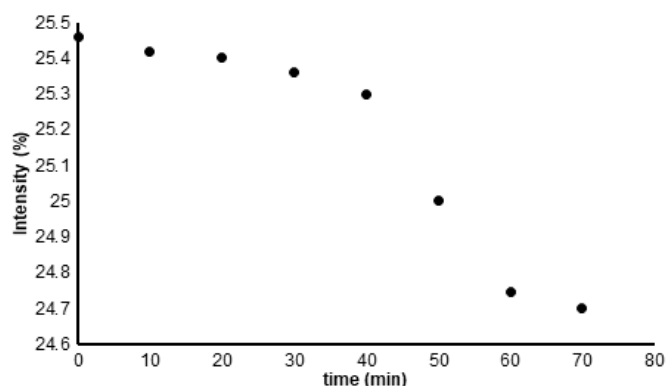


Fig 2. The decreasing of isocyanate concentration was measured from intensity of infrared spectroscopy at 2270 cm^{-1}

Mole balance of hydroxyl groups (A) and isocyanate groups (B and D) at certain time of reaction is shown in eq. 16–18, where C_{A_0} , C_{B_0} , and C_{D_0} are initial concentration of A, B, and D, respectively.

$$C_{A_0} = C_A + C_R + C_S + C_U + C_V + C_W + C_X \quad (16)$$

$$C_{B_0} = C_B + C_R + 2C_U + C_V + C_W \quad (17)$$

$$C_{D_0} = C_D + C_S + C_V + 2C_X + C_W \quad (18)$$

Each step is assumed to fit the first order reaction with the rate constant of k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 . The concentration decreasing rate of A, B, D, R, and S groups are shown in eq. 19–23. Those simultaneous differential equations need three known variables to solve. If geometric structure of V is assumed to be the same as W, then the reaction rate constant of k_4 is the same as k_5 . This assumption is taken from the same as the attraction force of atoms if the structure geometry of neighbor atoms is the same [21]. By this assumption, this models needs only one known variable, i.e. total NCO concentration.

$$\frac{-dC_A}{dt} = k_1 C_A C_B + k_2 C_A C_D \quad (19)$$

$$\frac{-dC_B}{dt} = k_1 C_A C_B + k_3 C_B C_R + k_4 C_B C_S \quad (20)$$

$$\frac{-dC_D}{dt} = k_2 C_A C_D + k_5 C_D C_R + k_6 C_D C_S \quad (21)$$

$$\frac{-dC_R}{dt} = k_1 C_A C_B - k_3 C_B C_R - k_5 C_D C_R \quad (22)$$

$$\frac{-dC_S}{dt} = k_2 C_A C_D - k_4 C_B C_S - k_6 C_D C_S \quad (23)$$

The kinetic model can be evaluated by solving the simultaneous equations in eq. 19–23 using Runge-Kutta methods [12]. From the calculation, the reaction rate constant of k_1 , k_2 , k_3 , k_4 , k_5 and k_6 are 6.2×10^{-5} , 5.8×10^{-5} , 3.1×10^{-5} , 2.8×10^{-5} , and $2.5 \times 10^{-5} \text{ L.mol}^{-1}.\text{min}^{-1}$, respectively. Plotting NCO concentration versus time is shown in Fig. 3. This kinetics model is better fitted than Flory's model applied by Ajithkumar [15].

The calculated methods are then applied for all of variables. In the reaction of HTPB and pure 2,4-TDI isomer, urethane concentration (D) is zero. The reaction rate equation is simpler by only using eq. 8 and 10. Calculation of reaction rate constant generates k_1 and k_3 of 6.2×10^{-4} and 4.5×10^{-4} L.mol⁻¹.min⁻¹. Value of $k_1 \gg k_3$ that the branch bonding formation rate is smaller than the linear bonding one. At initial reaction mechanism, the NCO and OH groups are available in sufficient quantities. The value of k_1 represents the rate constant of simpler reaction approach of HTPB and TDI reported by Ajithkumar et al. [15] and Wibowo et al. [5], in which the polymerization rate constant in solution at ambient temperature with initial mole ratio of NCO to OH ($R_{\text{NCO/OH}}$) 1:1 is 6.0×10^{-4} L.mol⁻¹.min⁻¹.

Polymerization of HTPB and pure 2,6-TDI through reaction steps of A and D produces S, and S and D produces V, shown in eq. 8 and 10, respectively. The calculation of reaction rate constant generates k_2 and k_4 of 5.4×10^{-4} and 1.3×10^{-4} L.mol⁻¹.min⁻¹, respectively. The value $k_2 \gg k_4$ represents branch bonding formation rate is less than linear bonding one. Generally, the reactivity of isomer 2,4-TDI is higher than isomer 2,6-TDI. The structure of 2,4-TDI is more regular than 2,6-TDI where NCO groups are far away from each other. The negative partial charge of atom N of NCO on 2,4-TDI is higher than 2,6-TDI, so 2,4-TDI is more reactive than 2,6-TDI isomer.

The overall polymerization rate is complex reaction, but for simplifying the kinetics model, the overall polymerization rate constant is defined the value of as the determining polymerization rate. The determining polymerization rate is the lowest step reaction rate. Based on the Table 1, the determining polymerization rate is sixth step with the lowest reaction rate constant (2.5×10^{-4} L.mol⁻¹.min⁻¹).

Effect of Initial Mole Composition of Isomers

The reaction rate constants k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 calculated using eq. 13–21 for different initial mole composition of isomers are presented in Table 1. This result represents that no difference reaction rate if the reaction steps are the same. It means that the different mole ratio of isomers does not change reaction rate constant of each step. Isomers of TDI cannot be

assumed as new compound. The different composition of isomers is assumed in the equilibrium. The polymerization of HTPB and pure 2,4-TDI only gives reaction rate constant k_1 and k_3 because there is no D groups. The polymerization of HTPB and pure 2,6-TDI only results in reaction rate constant k_2 and k_6 because of no B groups. The value of k_4 or k_5 is real representation of isocyanate reactivity difference of isomer TDI of 2,4-TDI and 2,6-TDI. Value k_4 or k_5 significantly influences to the reaction rate.

Based on the calculation of value k_1 to k_6 , the decrease of isocyanate concentration at various values of initial mole composition of isomers can be plotted versus time as presented in Fig. 4. The kinetics model developed has average error of 2.4% in comparison to experimental data, so the kinetics model represents real kinetics for different TDI isomer composition. Increasing percentage of isomer 2,4-TDI leads to increase of reaction rate because reactivity of 2,4-TDI is higher than 2,6-TDI.

Effect of $R_{\text{NCO/OH}}$

The higher $R_{\text{NCO/OH}}$ means the more number of isocyanate groups, so the reaction of branch bonding formation, eq. 5, shifts to right side. The more branch bonding formation leads to produces rigid structure. This

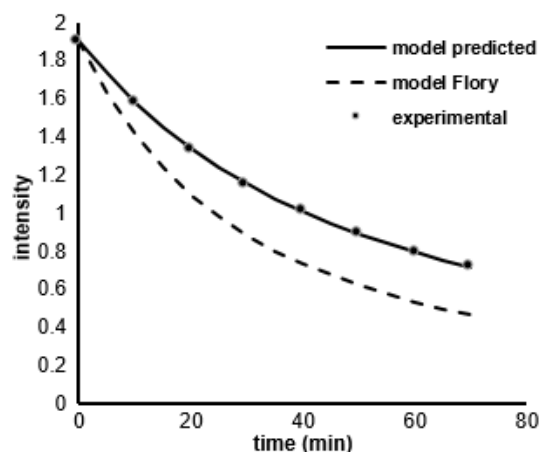


Fig 3. Curve of isocyanate concentration versus time of polymerization at temperature 40 °C, $R_{\text{NCO/OH}} = 1:1$, and initial mole percentage ratio of 2,4-TDI to 2,6-TDI 80:20

Table 1. Polymerization rate constants of HTPB and TDI with various initial mole composition of isomers at temperature 40 °C, and $R_{\text{NCO/OH}} = 1:1$

Reaction rate constant ($\times 10^5$ L.mol ⁻¹ .men ⁻¹)	$R_{2,4/2,6}$ isomer of TDI				
	0:100	35:65	65:35	80:20	100:0
k_1	6.2	6.2	6.2	6.2	0
k_2	0	5.8	5.8	5.8	5.8
k_3	3.1	3.1	3.1	3.1	0
$k_4 = k_5$	0	2.8	2.8	2.8	0
k_6	0	2.5	2.5	2.5	2.5

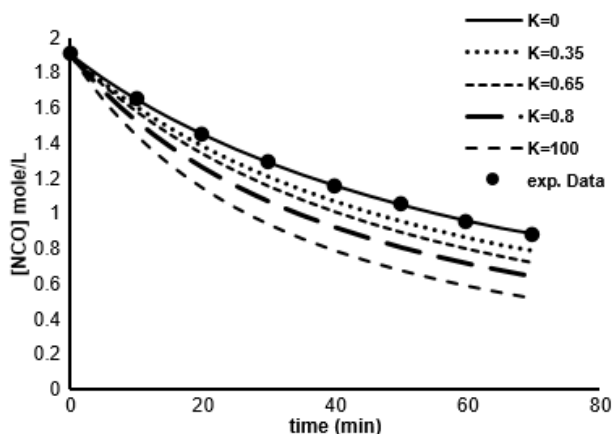


Fig 4. Curve of decreasing isocyanate concentration versus time at various values of initial mole composition of isomers isomer TDI at temperature 40 °C, and $R_{NCO/OH} = 1:1$

phenomenon is similar to effect of $R_{NCO/OH}$ on pot life, because more branch bonding formed increases the viscosity of slurry. This phenomenon has no effect to reaction rate. The initial mole ratio isocyanate to hydroxyl means initial mole ratio of isocyanate and hydroxyl group concentration, and the value does not change for all time of reaction. Based on the reaction steps, the $R_{NCO/OH}$ does not affect to reaction rate constant, but it changes the shift of the reaction equilibrium to right side or more product side. This assumption is evaluated on the curve of the decrease of isocyanate concentration rate versus time as shown in Fig. 5. The increase of $R_{NCO/OH}$ does not change reaction rate constant.

Effect of Reaction Temperature

Reaction temperature significantly affects to isomer equilibrium and polymerization rate following Arrhenius equation, as presented in eq. 14 and 15. The effect of reaction temperature to reaction rate constants or isomer equilibrium can be evaluated based on value of their collision frequency factor and reaction activation energy. For calculating collision frequency factor and reaction activation energy, polymerization of HTPB and TDI has been conducted at various temperatures (40, 50, 60, and 70 °C) with other conditions constant. After reaction rate constants (k_i) being calculated, then $\ln(k_i)$ was plotted versus $(1/T)$ as can be seen in Fig. 6. According to the Arrhenius equation, the intercept is $\ln(A)$ and the slope is $(-E_a/R)$. The collision frequency factor and reaction activation energy for each reaction rate constants are presented in Table 2.

Value of k_1 is close to k_3 , indicating the reaction of HTPB with 2,4-TDI and 2,6-TDI is similar to reaction of linear bonding formation. The value of k_3 is close to k_6

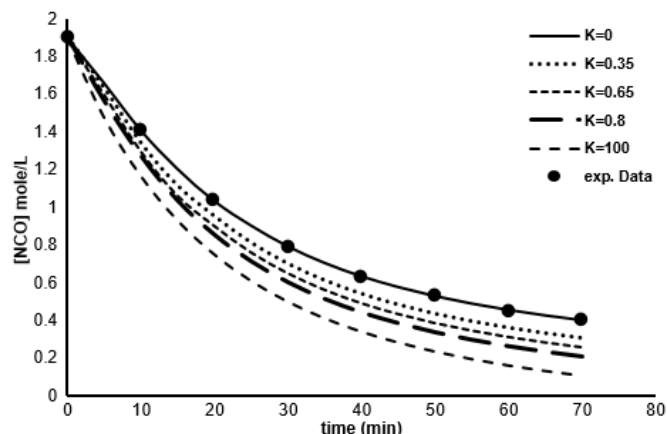


Fig 5. Decreasing isocyanate concentration at various $R_{NCO/OH}$ at temperature 40 °C and initial mole composition of isomers 80:20

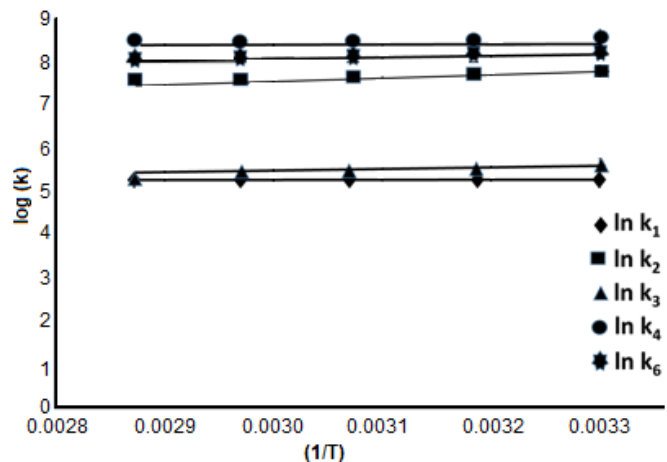


Fig 6. Plot of $\ln(k_i)$ versus $1/T$ for reaction HTPB and TDI with $R_{NCO/OH} = 1:1$, and initial mole composition of isomers 80:20

Table 2. Value of rate constant representing collision frequency factor and reaction activation energy of HTPB-TDI reaction

Reaction rate constant	E_a (kJ/mol)
K	576
k_1	1152
k_2	952
k_3	1001
k_4	656
k_6	1001

revealing that both 2,4-TDI and 2,6-TDI isomers react with HTPB and formation of branch bonding occurs. The difference of reaction rate of HTPB-TDI reaction is determined by the fourth or fifth step that lower than k_1 or k_3 . The activation energy of reaction for fourth and fifth steps is low, and the effect of reaction temperature is small. The reaction temperature affects significantly

branch-bonding formation from both 2,4-TDI and 2,6-TDI isomers.

Value of k_1 is 10–50 times higher than that of k_3 . The initial reaction of linear bonding formation occurs more than branch bonding one. This phenomenon is supported with the lower value of activation energy. The lower activation energy of linear bonding formation shows that the branch bonding formation rate is faster than linear bonding one. It is in agreement with the earlier research of the polyurethane behavior [26]. The effect of reaction temperature is more significant for branch bonding rather than linear bonding formation, although it has lower reaction rate constant.

The activation energy of each reaction step shows the effect of reaction temperature on the reaction rate constant. The first reaction needs higher energy than third and sixth reaction, and then third reaction is higher activation than second one, and the second reaction gives higher activation than fourth one. The third reaction has the same energy as the sixth reaction. Based on Table 2, the first reaction is most sensitive to the change of reaction temperature, but this reaction is not the determining reaction. These data show that the reactivity of reaction step can change if reaction temperature increases. For example, the determining reaction step is first step at 40 °C, but the determining reaction step was third step if the polymerization conducted at 70 °C. The high gain of activation energy each step may change the highest value of reaction rate constants. The activation energy of isomers equilibrium is 576 kJ/mole, which is the lowest activation energy. The isomer equilibrium is less sensitive to temperature than the other reactions.

CONCLUSION

The effect of TDI isomers on pot life of polyurethane produced from HTPB and TDI has been examined by observing the decrease of isocyanate concentration using infrared spectroscopy. Calculation of the reaction rate constants using the kinetics model developed at percentage mole ratio of 2,4-TDI to 2,6-TDI isomer 80:20, initial mole ratio of isocyanate to hydroxyl group 1:1, and reaction temperature 40 °C generated give k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 values of 6.2×10^{-5} , 5.8×10^{-5} , 3.1×10^{-5} , 2.8×10^{-5} , and 2.5×10^{-5} L.mol⁻¹.min⁻¹ and activation energy of those steps of 1152, 952, 1001, 656, and 1001 kJ/mole, respectively. This model was developed based on the reactivity of NCO group in the different geometric structure. This determining step of this polymerization is 2,6-urethane and NCO group from 2,6-TDI with activation energy of 656 kJ/mol. This model presents that isomer equilibrium plays an important role to polymerization kinetics. The data is expected to be

applied in reactor design and to predict the operational viscosity for tailoring composite, and adhesive.

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