

## Kinetic Study of HTPB (Hydroxyl Terminated Polybutadiene) Synthesis Using Infrared Spectroscopy

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**Abstract:** A kinetic study of HTPB synthesis by radical polymerization of butadiene with hydrogen peroxide initiator was conducted using infrared spectroscopy. HTPB conversion was determined based on the conjunction termination rate constant, and all polymerization kinetics were evaluated to identify the constant. All polymerization steps (decomposition, initiation, propagation, conjunction, and proportional termination) can be evaluated based on polymer conversion and functionality from data provided by infrared spectroscopy. The investigation variables included the initial molar ratio of initiator to monomer ( $H_2O_2$ /butadiene) and the reaction temperature. These steps were assumed as the first-order reactions, giving constant reaction rates of  $k_{d_1}$ ,  $k_{d_2}$ ,  $k_p$ ,  $k_t$ ,  $k_{tc}$ , and  $k_{td}$ . The reaction rates obtained for these constants were  $4.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $8.9 \times 10^{-4}$ ,  $7.7 \times 10^3$ ,  $8.5 \times 10^7$ ,  $3.2 \times 10^7$  and  $5.3 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ , respectively, with activation energy of 7608, 14188, 2247, 105, 87 and 135  $\text{kJ mol}^{-1}$ , respectively. The determining step of the reaction rate was identified as the initiation reaction. HTPB conversion can be measured if all polymerization kinetics constants have been evaluated.

**Keywords:** polymerization; HTPB; butadiene

### ■ INTRODUCTION

Polyurethane based on hydroxyl-terminated polybutadiene (HTPB), in recent years, has been used as a solid propellant binder for satellite-launcher-motor boosters and ICBM (intercontinental ballistic missile) motors [1-2], because it has good mechanical properties at rocket operating temperatures. Polyurethane based on HTPB is synthesized by copolymerization of HTPB and isocyanates, such as toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI). Research into polyurethane based on HTPB as a propellant binder has been conducted since 1945 [3]. Initially, this research focused on HTPB/isocyanate composition related to its mechanical and viscous-elasticity properties. Subsequent research has focused on the effect of HTPB structures such as chain length, isomers, hydroxyl value, and molecular weight distribution. In the last ten years, research into polyurethane based on HTPB has looked at increasing the energetic properties of the binder by

substituted HTPB with nitro, azide, and oxy functional groups [4-7]. HTPB is a polybutadiene with two chains of hydroxyl groups that have been particularly studied in its use in propellant materials. HTPB can be synthesized by ionic, ionic-coordination, and radical polymerization of butadiene. HTPB produced by ionic and ionic-coordination polymerization has narrow molecular distribution weight, but this type of production requires a highly complex reaction, which is expensive to carry out [3-5]. In contrast, HTPB produced by radical polymerization has broad molecular weight distribution, but its formation reaction is simple and cheap. HTPB is, therefore, generally produced by radical polymerization of butadiene using a hydrogen peroxide initiator [3,8].

The synthesis mechanism for HTPB by radical polymerization of butadiene with hydrogen peroxide initiator is (1) decomposition of hydrogen peroxide producing hydroxyl radicals, (2) monomer initiation by hydroxyl radicals producing radical monomers, (3) propagation of radical monomer growth with

monomers producing radical polymers, (4) termination of radical polymers producing 'dead polymers' [9-10]. Termination steps are simultaneous mechanisms involving both conjunction and disproportional reactions. Conjunction termination would produce HTPB, while disproportional termination would produce mono hydroxyl polybutadiene (HPB) [4]. Given this mechanism, the study of the kinetics of HTPB synthesis requires at least two data sets to be retrieved. The initiation and termination steps are fast reactions [8], and data kinetics are limited by polymer weight and average molecular weight. Therefore, the difficulty is encountered in data retrieval, given the fast reaction rate of the process. For this reason, it is assumed that in the kinetics of HTPB synthesis, termination and initiation rates are the same, and simultaneous conjunction and disproportional termination are ignored [10].

This approach resembles the olefin polymerization kinetics for rubber applications [7-8]. The kinetic of radical polymerization of butadiene and other diene compounds and olefins for rubber applications has been explored since 1940 [11-12]. The polybutadiene in rubber applications has hydrogen-ended functional groups, and polymerization usually uses a peroxide initiator, a redox system, and other strong oxidizers. Wibowo assumes that the ratio of HTPB and mono hydroxyl polybutadiene (HPB) conversion is constant, but this data cannot be satisfied statically [13]. The aim of this research is to explore all the kinetic steps of HTPB synthesis using at least three sets of data retrieved in a manner suitable for fast reaction rates.

The kinetics of radical polymerization can be evaluated based on the presence of increased polymers or decreased monomers. Decreased monomers can be observed from their pressure [14-15], while increased polymers can be evaluated from their weight and chain extent or molecular weight. Unfortunately, decreased monomers and increased polymers cannot be simultaneously identified. The polymer molecular weight can be evaluated via colligative property measurement, viscosity, light scattering, size exclusion chromatography and gel permeation chromatography [16-18]. The polymer extent of a reaction can also be identified by

infrared spectrometry, based on double bond absorption and type of isomer (cis, trans and vinyl isomers) [12,14,19]. Kinetic study of HTPB synthesis by infrared spectroscopy is the most commonly used method because it is fast, cheap and simple to perform.

Infrared spectrometry using adsorption infrared spectra at wavenumber  $2250\text{ cm}^{-1}$  can be applied to determine hydroxyl value and functionality of polybutadiene and HTPB [20-22]. The functionality of HTPB is a ratio of average hydroxyl chain to polybutadiene structure. Based on this functionality, the ratio of mono hydroxyl polybutadiene and hydroxyl terminated polybutadiene (HTPB) can be estimated and infrared analysis of polybutadiene can be used to determine the extent of reaction and functionality. All of the constant reaction steps in HTPB synthesis should be evaluated using at least two kinetic data items, and this research, therefore, includes the conjunction and disproportional steps in studying the kinetics of HTPB synthesis via infrared spectroscopy to describe HTPB conversion, average functionality, and molecular weight distribution. Through this approach, all kinetic data for HTPB synthesis can be explored.

In HTPB synthesis by radical polymerization of butadiene using a hydrogen peroxide initiator, butadiene is radically polymerized via initiation, propagation and termination stages [6-7]. The initiation stage involves the dissociation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to produce hydroxyl radicals ( $\text{OH}^\bullet$ ) which then react with t monomer butadiene ( $\text{C}_4\text{H}_6$ ), producing radical monomer chains with hydroxyl groups ( $\text{HO}-\text{C}_4\text{H}_6^\bullet$ ). The propagation stage involves the growth of the polymer. The active radical monomers ( $\text{HO}-\text{C}_4\text{H}_6^\bullet$ ) react with other monomers to produce radical active dimers ( $\text{HO}-(\text{C}_4\text{H}_6)_2^\bullet$ ). Polymer activity develops by the addition of monomer butadiene to produce higher polymer radical actives ( $\text{HO}-(\text{C}_4\text{H}_6)_n^\bullet$ ). The growth activity of the polymer radicals is terminated by reactions between polymer radicals producing dead polymers, via the active polymer radical ( $\text{HO}-(\text{C}_4\text{H}_6)_x$ ) reacting with the other active radical polymers ( $\text{HO}-(\text{C}_4\text{H}_6)_y^\bullet$ ). The termination can proceed by combinatorial-type reactions producing HTPB with two

end hydroxyl chains ( $\text{HO}-(\text{C}_4\text{H}_6)_{x+y}-\text{OH}$ ) or proportional-type reactions producing two dead polymers,  $\text{HO}-(\text{C}_4\text{H}_6)_x$  and  $\text{HO}-(\text{C}_4\text{H}_6)_y$ , with one of the dead polymers having a double bond. Functionality is identified as the total of dead polymers of both two-hydroxyl-chained (HTPB) and one-hydroxyl-chained (mono hydroxyl polybutadiene) types. Based on the enthalpy of formation, disproportional-type reactions need higher energy than combinatorial-type reactions [8-9]. By means of this kinetic model, all of the kinetic data (rate constants), including the combinatorial and proportional steps, can be effectively evaluated.

## ■ EXPERIMENTAL SECTION

### Materials

Butadiene 98% used in this research was produced by Aneka Gas Co Ltd., Jakarta, Indonesia and was distilled to remove tert-butylcatechol. The hydrogen peroxide used was in pure analysis grade, and the solvent used was toluene.

### Instrumentation

The reactor used was an autoclave of 1-L capacity equipped with a stirrer and hot fluid control. A closed FTIR cuvette was connected to the reactor and the solution from the reactor was continuously circulated to it.

The in-situ HTPB product was identified by FTIR (Fourier transform infrared spectrometry). FTIR outputs were measured at ambient conditions at the wavenumber range of  $400\text{--}4000\text{ cm}^{-1}$  using an FT-IR spectrometer (Prestige-21). HTPB was identified at wavenumber of  $3500, 1700, 710, 790,$  and  $910\text{ cm}^{-1}$  for specific absorption of hydroxyl and CH, and cis, trans and vinyl isomers [6]. HTPB was observed for absorption bending vibrations (wagging) of the CH groups in the cis-HTPB unit at a wavenumber of  $730\text{ cm}^{-1}$ , for out-of-plane (wagging) vibrations of the  $\text{CH}_2$  groups near the double bond of the vinyl-HTPB units at  $910\text{ cm}^{-1}$ , and for out-of-plane (wagging) vibrations of the CH groups near the double bonds in trans-HTPB units at  $970\text{ cm}^{-1}$ .

The polymer concentration was measured for absorbance at wavenumber  $1750\text{ cm}^{-1}$  via bending

vibrations (wagging) of the CH groups, then extrapolated to a standard curve using Beer's law [12]. The standard solution was HTPB in toluene at concentrations of  $1.0 \times 10^{-5}, 5.0 \times 10^{-5}, 1.0 \times 10^{-4}, 5.0 \times 10^{-4}$  and  $1.0 \times 10^{-3}\text{ mol L}^{-1}$ .

The hydroxyl number of HTPB was determined by observing FTIR uptake values at wavenumber  $3450\text{ cm}^{-1}$  as specific uptake for hydroxyl groups [1]. The absorbance of hydroxyl groups was then extrapolated with standard alcohol 1,4-butanediol and 1-butanol. In this research, standard alcohol was a mixture of 1,4-butanediol and 1-butanol (mol/mol) at 1.0, 1.1, 1.2, 2.0. The functionality of 1-butanol is 1 and 1,4-butanediol is 2.

### Procedure

Butadiene was reacted with hydrogen peroxide in a 1-L autoclave for 60 min in inert nitrogen conditions. The reaction was isothermal and conducted at  $100\text{ }^\circ\text{C}$  and 25 bar pressure. The extent of the reaction and functionality was measured by FTIR spectroscopy at wavenumber of  $3450, 730, 790$  and  $910\text{ cm}^{-1}$  [1,4,7]. Reaction parameters were initiator and reaction temperatures.

The effect of the initiator on polymerization kinetics was studied by adjusting the initial  $\text{H}_2\text{O}_2$ /butadiene ratio (mol/mol) to 10, 20, 30 and 32%, and the reaction was carried out at  $100\text{ }^\circ\text{C}$ , 25 bar, and stirrer speed of 100 rpm. The initial butadiene concentration was 1 M. The effect of reaction temperature on polymerization kinetics was studied by adjusting the reaction temperature to 100, 110 and  $118\text{ }^\circ\text{C}$  at a pressure of 25 bar, initial  $\text{H}_2\text{O}_2$ /butadiene ratio of 10%, and stirrer speed of 100 rpm.

### Kinetic model

The polymerization of butadiene with hydrogen peroxide initiator occurs through free radical mechanisms [8]. The reaction is started by the dissociation of hydrogen peroxide to form a pair of hydroxyl radicals ( $\text{OH}^\bullet$ ) with dissociation rate constant of  $k_d$ . The reaction of hydroxyl radical ( $\text{OH}^\bullet$ ) and monomer butadiene ( $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ ) produces the radical-ended monomer  $^\bullet\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$  with

adding monomer reaction rate of  $k_a$ . The initiation step, therefore, comprises the dissociation of hydrogen peroxide and the adding of monomer reaction. The propagation reaction is started by radical-ended dimer  $\bullet(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_2\text{OH}$  production from radical-ended monomer  $\bullet\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$  and another monomer. The radical-ended dimer then reacts with another monomer to form radical-ended trimer  $\bullet(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_3\text{OH}$ . These propagation reactions occur repeatedly so that the radical-ended polymer acquires a longer chain length  $\bullet(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_x\text{OH}$ . The propagation rate is constant at steady-state and radical-ended polymer reactivity in the chain growth is the same. Individual propagation reactions are identified as  $rp_1, rp_2, \dots, rp_i$ , following the extent of the reaction. These propagation reaction steps have the same reaction rates because the activity of the radicals is the same (their activity is not affected by the size of the molecule). The radical-ended polymer reactivity in chain growth is the same. Therefore, all propagation stages can be characterized using the same reaction rate constant of  $k_p$  [8-10]. The termination step occurs in simultaneous combinatorial and proportional reactions [7].  $\bullet\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_x-\text{OH}$  and other polymer-ended radicals produce mono hydroxyl polybutadiene with a double bond,  $\text{H}_2\text{C}-\text{C}=\text{H}-\text{CH}=\text{CH}_2(\text{H}_2\text{C}-\text{C}=\text{H}-\text{CH}-\text{CH}_2)_x-\text{OH}$ , and another mono hydroxyl polybutadiene with a single bond  $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_2(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_x-\text{OH}$ . The junction or combinatorial reaction is a covalent bond reaction of the radical-ended polymer  $\bullet(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_x-\text{OH}$  and the other radical-ended polymer  $\bullet(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_y-\text{OH}$  to produce HTPB,  $\text{HO}(\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2)_{x+y}-\text{OH}$ . The combinatorial and proportional termination rate constants are  $k_{tc}$  and  $k_{td}$ .

The initiator decomposition, initiation, propagation and termination reactions in the radical polymerization of butadiene are simplified as presented in Equations 1 to 5. Compound I is the initiator, R and A are butadiene monomers,  $\text{RP}_i$  are active polymers with chain length  $i$ , and  $\text{RP}_i$  and  $\text{RP}_j\text{R}$  are stable polymers bound to hydroxyl groups R with chain length  $j$ . The initiator decomposition reaction rate constant is  $k_d$ , the monomer adding rate

constant is  $k_a$ , the propagation rate constant is  $k_p$  and the termination rate constant is  $k_t$ . The combinatorial reaction rate constant in the termination reaction is  $k_{td}$  and the disproportional reaction rate constant in the termination reaction is  $k_{tc}$ . These polymerization kinetics are the assumed first order:



The reaction rate equation of initiator dissociation is expressed in Eq. (6). The reaction rate equations of the polymerization steps (initiation, propagation, and termination) are expressed in Eq. (6) to Eq. (10). Polymer concentration comprises all polymers with chain extent from  $j = 0$  to  $j = n$ ,  $[\text{P}]_0 = \sum_{j=0}^n \text{P}_j$ . The active radical concentration  $[\text{M}]_0$  comprises all radical polymers with chain extent from  $j = 0$  to  $j = n$ ,  $[\text{M}]_0 = \sum_{j=0}^n \text{RP}_j$ . The termination rate constant is the sum of combination and disproportion rate constants ( $k_t = k_{tc} + k_{td}$ ).

$$R_d = -\frac{d[\text{I}]}{dt} = 2fk_d[\text{I}] \quad (6)$$

$$R_i = -\frac{d[\text{A}]}{dt} = k_a[\text{A}][\text{P}_1] \quad (7)$$

$$R_p = -\frac{d[\text{A}]}{dt} = k_a[\text{A}][\text{P}_1] + k_p[\text{A}][\text{P}_0] \quad (8)$$

$$R_{ap} = \frac{d[\text{P}]_0}{dt} = R_i - 2k_a[\text{P}]_0 \quad (9)$$

$$R_t = -\frac{d[\text{M}]_0}{dt} = (2k_{tc} + k_{td})[\text{P}]_0^2 \quad (10)$$

Monomer A is initiated by hydroxyl radicals forming radical-ended monomers followed by continuous propagation with polymer radicals growing their size/length of chain. Through polymer radical growth, radical concentration is constant (steady-state) until the rate of radical forming is zero ( $R_{ap} = 0$ ). Eq. (9) would express in Eq. (11).

$$[P]_0 = \left( \frac{fk_d[I]}{k_t} \right)^{1/2} \quad (11)$$

The equation of propagation rate would be expressed by substituting Eq. (11) into Eq. (7) to form Eq. (12).

$$R_p = \left( \frac{k_p}{k_t^{1/2}} \right) \left( fk_d[I]^{1/2} \right) [A] \quad (12)$$

Eq. (6) is merged with Eq. (9) then integrated with  $\beta = (k_{tc}/k_t)$  and  $\alpha = (-k_{td}t)$  to express initial monomer concentration  $[A]_0$ , expressed in Eq. (13) where  $M_A$  is the molecular formula of monomer butadiene [11]. Monomer conversion is  $X = [A]/[A]_0$ .

$$[A]_0 = (2 - \beta)f[I]_0(1 - \alpha) \quad (13)$$

$$M_n = \frac{([M]_0 - [M])M_A}{([P]_0 + [M]_0)} \quad (14)$$

$$M_n = \frac{A_0XM_A}{([P]_0 + [M]_0)} \quad (15)$$

Eq. (16) is formed from merging Eq. (10), (12) and (15) and would apply to the calculation of the termination rate constant  $k_t$ . The values of  $k_t$  and  $\beta$  can be evaluated based on each change of average molecular weight and weight of the polymer.

$$\left( \frac{([A]_0XM_A)/M_n}{[I]_0\alpha} \right)^{1/2} = \left( \frac{fk_d}{k_t} \right)^{1/2} + (2 - \beta)(1 - \alpha) \left( \frac{[I]_0}{\alpha} \right)^{1/2} \quad (16)$$

The propagation rate constant  $k_p$  is calculated from Eq. (6). The constant  $(k_p/k_t^{1/2})$  is calculated as the slope of plotting  $R_p$  to  $R_i$  or  $R_p$  to  $(fk_d[I]_0^{1/2}[A]_0)$ .

Polymer functionality ( $f_{OH}$ ) is the equivalent total of hydroxyl groups bonded in the polymer (polybutadiene). Polymers are a mixture of mono hydroxyl polybutadiene ( $RM_i$ ) and hydroxyl terminated polybutadiene ( $RM_iR$ ) [9]. The functionality of the polymer is expressed in Eq. (17).

$$f_{OH} = \frac{2[RM_i] + [RM_iR]}{([RM_i] + [RM_iR])} \quad (17)$$

The total polymer produced is  $P$  with  $P = 2[RM_i] + [RM_iR]$ .  $RM_i$  is eliminated from Eq. (17) to become Eq. (18).

$$[RM_i] = 1 - \frac{P}{f_{OH}} \quad (18)$$

The combinatorial termination rate is the increasing rate of polymer  $RM_iR$  expressed by Eq. (19). Eq. (20) is the integration of Eq. (19) with the initial condition  $[RM_iR]_0 = 0$  and HTPB concentration at time  $t$  of  $[RM_iR]$ .

$$\frac{d[RM_iR]}{dt} = k_{td}[RM_iR] \quad (19)$$

$$\ln[RM_iR] = k_{td}t + \text{constants} \quad (20)$$

Eq. (18) is to be substituted into Eq. (20) to form Eq. (21), which is the relationship equation of the polymer produced (HTPB) and the functionality of the polymer as the time of reaction. The disproportional termination rate constant  $k_{td}$  is the slope of plotting  $\ln(1 - P/f_{OH})$  as time  $t$ . The conjunction termination rate constant  $k_{tc}$  is the deviation of  $k_t$  and  $k_{td}$  ( $k_{tc} = k_t - k_{td}$ ).

$$\ln\left(1 - \frac{P}{f_{OH}}\right) = k_{td}t \quad (21)$$

The polymer concentration was determined by the absorbance of polymers at wavenumber  $910 \text{ cm}^{-1}$  at the time of reaction.

## RESULTS AND DISCUSSION

HTPB was identified by infrared spectroscopy at wavenumber  $400\text{--}4000 \text{ cm}^{-1}$  and its infrared spectrum is shown in Fig. 1. The HTPB compound was identified based on infrared absorption at  $3450, 1730, 710, 910,$  and  $970 \text{ cm}^{-1}$ , a specific absorption for the hydroxyl group, C-C bond, and C=C bond with cis, trans, and vinyl isomers [12-13]. The presence of a hydroxyl group indicates that the polybutadiene has hydroxyl groups. The

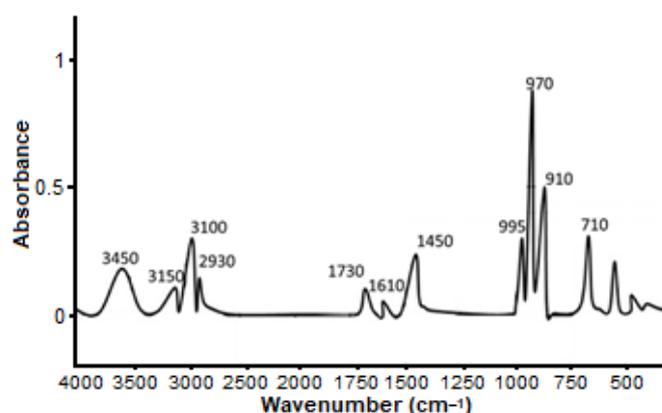


Fig 1. Infrared spectra of polybutadiene

absorbance at wavenumber 710, 910, and 970  $\text{cm}^{-1}$  were sharp and strong. The absorption at 930  $\text{cm}^{-1}$  implied increasing HTPB. The functionality of HTPB was observed at wavenumber 3450  $\text{cm}^{-1}$ .

The absorbance of polybutadiene infrared spectra every ten minutes was observed at wavenumber 910 and 3450  $\text{cm}^{-1}$  (Table 1). The HTPB concentration was linear to absorbance (Beer's law) [12]. The HTPB concentration was calculated based on absorbance at 910  $\text{cm}^{-1}$  ( $A_{910}$ ) using Beer's law in Eq. (22) [12]. The functionality of the polymer was measured based on absorbance at 3450  $\text{cm}^{-1}$  ( $A_{3450}$ ) using Eq. (23). The  $\epsilon$  and  $b$  are molar attenuating coefficient or absorptivity of the attenuating species and the optical path length, respectively

$$P = \frac{A_{910}}{\epsilon b} \quad (22)$$

$$[\text{RM}_i] = \frac{A_{3450}}{\epsilon b} \quad (23)$$

The HTPB concentration and functionality every ten minutes are shown in Table 1. Initial condition was

$[\text{A}]_0 = 0.00023 \text{ mol L}^{-1}$  and  $[\text{I}]_0 = 0.00002 \text{ mol L}^{-1}$ . The polymer produced ( $\text{XM}_A$ ) was calculated from the absorbance of the infrared spectra at 1750  $\text{cm}^{-1}$ .

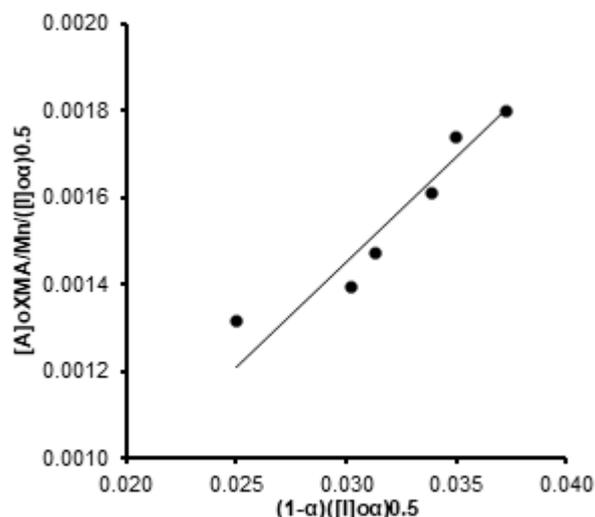
To study the kinetic model, the  $([\text{A}]_0 \text{XM}_A / M_n) / ([\text{I}]_0 \alpha)^{1/2}$  was plotted to the  $(1-\alpha)([\text{I}]_0 / \alpha)^{1/2}$  and expressed in Fig. 2 based on Eq. (16). The value of  $(2-\beta)$  is the slope of this curve. The value of  $(fk_d/k_t)^{1/2}$  is the intercept of this curve. The value of  $\beta$  ( $k_{tc}/k_t$ ) and  $(fk_d/k_t)^{1/2}$  are 12,001 and  $8.5 \times 10^7 \text{ mol L}^{-1} \text{ sec}^{-1}$ . The value of  $fk_d$  was calculated from the decomposition data of hydrogen peroxide in the various solvents [17]. The dissociation rate constant of hydrogen peroxide in toluene is  $4.2 \times 10^{-5} \text{ sec}^{-1}$  [15].

The propagation rate constant  $k_p$  was calculated from Eq. (6). The constant  $(k_p/k_t^{1/2})$  was calculated as the slope of plotting  $R_p$  to  $R_i$  or  $R_p$  to  $(fk_d[\text{I}]_0^{1/2}[\text{A}]_0)$  as expressed in Fig. 3. The value of  $(k_p/k_t^{1/2})$  is 4.62 and the value of  $k_p$  is  $7.7 \times 10^3 \text{ mol L}^{-1} \text{ sec}^{-1}$ .

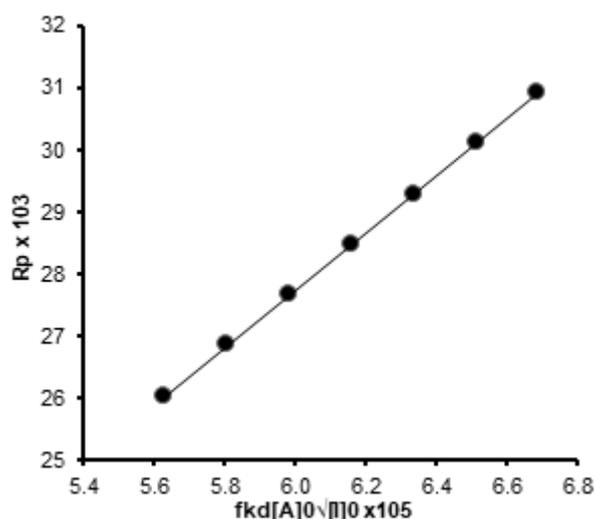
The disproportional termination rate constant ( $k_{td}$ ) is the slope of curve  $\ln(1-P/f_{OH})$  as time  $t$  as expressed in

**Table 1.** HTPB concentration and functionality at 100 °C and pressure of 25 bar

Time (min)	Absorbance at 910 $\text{cm}^{-1}$	Absorbance at 3450 $\text{cm}^{-1}$	$C_p$ (mol $\text{L}^{-1}$ )	$f_{OH} = [\text{RMR}]/[\text{RM}]$
10	0	0	0	1
20	0.23	0.05	0.00023	1.11111
30	0.35	0.16	0.00035	1.35556
40	0.48	0.31	0.00048	1.68889
50	0.58	0.41	0.00058	1.91111
60	0.62	0.42	0.00062	1.93333



**Fig 2.** Curve  $([\text{A}]_0 \text{XM}_A / M_n) / ([\text{I}]_0 \alpha)^{1/2}$  versus  $(1-\alpha)([\text{I}]_0 / \alpha)^{1/2}$



**Fig 3.** The curve of  $R_p$  to  $(fk_d[\text{I}]_0^{1/2}[\text{A}]_0)$

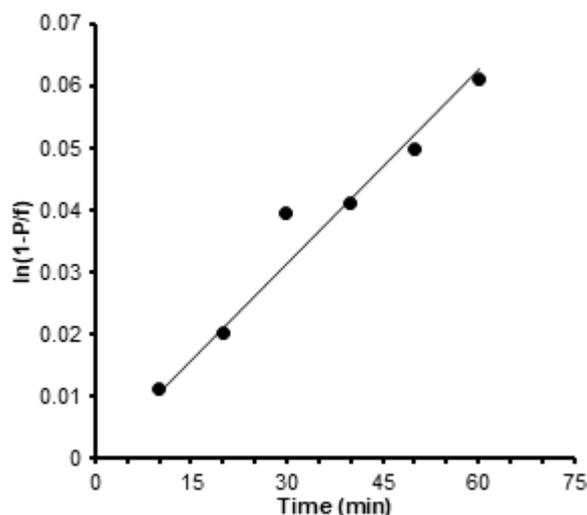


Fig 4. Plotting  $\ln(1-P/f_{OH})$  as time  $t$

Fig. 4. The value of  $(k_t/k_{td})$  is 2.5. The conjunction termination rate constant  $k_{tc}$  is the deviation of  $k_t$  and  $k_{td}$ . The value of  $k_t$ ,  $k_{td}$ , and  $k_{tc}$  are  $8.5 \times 10^7 \text{ mol L}^{-1} \text{ sec}^{-1}$ ,  $3.2 \times 10^7$ , and  $5.3 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ .

Based on the radical polymerization mechanism and the value of their rate constant, value of  $k_d = 4.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $k_i = 8.9 \times 10^{-4} \text{ L mol}^{-1} \text{ sec}^{-1}$ ,  $k_p = 7.7 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$ ,  $k_t = 8.5 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ ,  $k_{td} = 3.2 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ , and  $k_{tc} = 5.3 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ . The determining polymerization rate is the lowest step reaction rate. Therefore, the determining polymerization rate is the initiation reaction which has the lowest reaction rate constant ( $2.5 \times 10^{-4} \text{ L mol}^{-1} \text{ sec}^{-1}$ ).

The monomer radical forming rate is faster than the initiator decomposition ( $k_i > k_d$ ) indicating that the monomer radical forming step determines the initiation rate. Every hydroxyl radical formed directly reacts with a butadiene monomer to produce a monomer radical. This phenomenon corresponds to Flory's statement that the speed of initiation in radical polymerization is represented by the reaction of the formation of a radical monomer [13,16].

The  $k_p$  value is almost equal to  $k_i$ , indicating a competitive reaction, each forming of a monomer radical being followed by the growth of the polymer radical. The overall polymerization reaction rate is an exponential curve as shown in Fig. 4. Initially, the polymerization reaction grows rapidly with the formation of monomer

radicals. When the monomer radical formation reaction is complete, the growth of the polymer will decrease [16-17].

The  $(k_p/k_t^{1/2})$  value of 2.56 indicates that the propagation rate is faster than the termination rate. On polymerization, at 100 °C and a pressure of 350 psi the polybutadiene formed has a long chain. The reaction at 90 °C and a pressure of 350 psi obtained  $(k_p/k_t^{1/2}) = 0.07$ , indicating that the polymer is not formed because all of the growing polymer radicals will directly become dead polymers. Thus, the requirement for polybutadiene formation is a minimum temperature of 100 °C at a pressure of 350 psi.

The value of  $k_{td}$  is higher than  $k_{tc}$  indicating that more HTPB is produced than monofunctional polybutadiene. The value of  $k_{td}/k_{tc}$  of 1.6 indicates that polymer functionality is 1.6. HTPB formation is faster than the formation of mono functional polybutadiene. The results show that the functionality of polymer can be used to study the termination reactions of both disproportional and combinatorial termination in the radical polymerization of butadiene. This result refines the study of butadiene polymerization kinetics by using average molecular weight data and conversion based only on the termination rate [15,17].

According to Eq. (13) and Fig. 2, the polymerization rate ( $R_p$ ) is directly proportional to  $\exp(-k_d t/2)$ ,  $[A][I]_0^{1/2}$ , and  $k_p/k_t^{1/2}$ . The polymerization rate is proportional to  $\exp(-k_d t/2)$  indicating that the decomposition rate decreases exponentially as more initiators are used for polymerization. The polymerization rate is directly proportional to  $[A][I]_0^{1/2}$ , indicating that the polymerization rate is directly proportional to the initial initiator and initial monomer concentration. The overall polymerization rate is directly proportional to the initial initiator concentration. This value is the same as that for the radical polymerization of both olefin and styrene [14]. The polymerization rate is proportional to  $(k_p/k_t^{1/2})$  indicating that polymerization will occur if the value of  $(k_p/k_t^{1/2})$  is greater than one, so propagation will take place before termination occurs. The calculation results show that the value of  $(k_p/k_t^{1/2})$  is 2.56, and so maintained polymerization will take place.

**Table 2.** Polymerization rate constants of HTPB and TDI

Reaction rate constant	Initial H <sub>2</sub> O <sub>2</sub> /butadiene ratio (%mol/mol)			
	10%	20%	30%	32%
$k_d$ (sec <sup>-1</sup> )	$4.2 \times 10^{-5}$	$4.2 \times 10^{-5}$	$4.2 \times 10^{-5}$	$4.2 \times 10^{-5}$
$k_a$ (L mol <sup>-1</sup> sec <sup>-1</sup> )	$8.9 \times 10^{-4}$	$8.9 \times 10^{-4}$	$8.9 \times 10^{-4}$	$8.9 \times 10^{-4}$
$k_p$ (L mol <sup>-1</sup> sec <sup>-1</sup> )	$7.7 \times 10^3$	$7.7 \times 10^3$	$7.7 \times 10^3$	$7.7 \times 10^3$
$k_t$ (L mol <sup>-1</sup> sec <sup>-1</sup> )	$8.5 \times 10^7$	$8.5 \times 10^7$	$8.5 \times 10^7$	$8.5 \times 10^7$
$k_{tc}$ (L mol <sup>-1</sup> sec <sup>-1</sup> )	$5.3 \times 10^7$	$5.3 \times 10^7$	$5.3 \times 10^7$	$5.3 \times 10^7$
$k_{td}$ (L mol <sup>-1</sup> sec <sup>-1</sup> )	$3.2 \times 10^7$	$3.2 \times 10^7$	$3.2 \times 10^7$	$3.2 \times 10^7$

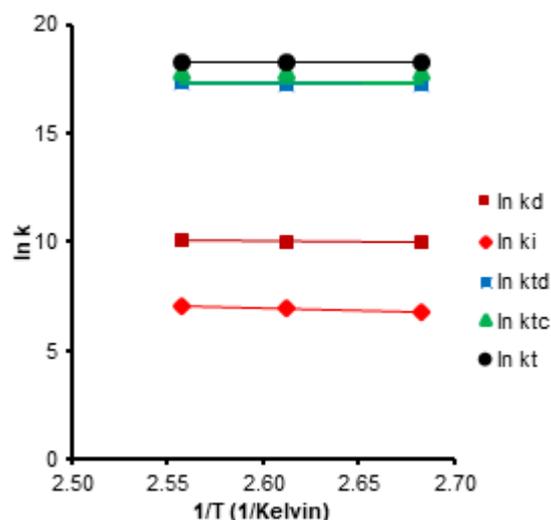
### Effect of Initiator

The reaction rate constants  $k_d$ ,  $k_a$ ,  $k_p$ ,  $k_t$ ,  $k_{tc}$ , and  $k_{td}$  were calculated using Eq. (16) for different initial H<sub>2</sub>O<sub>2</sub>/butadiene ratios and the results are presented in Table 2. These results indicate that there is no difference in the polymerization rate if the polymerization steps are the same and that the different initial H<sub>2</sub>O<sub>2</sub>/butadiene ratio does not change the polymerization rate constants of each step. Based on the calculation of the values of  $k_d$ ,  $k_a$ ,  $k_p$ ,  $k_t$ ,  $k_{tc}$ , and  $k_{td}$ , the developed kinetic model had an average error of 1.9% in comparison to experimental data, so the model represents real kinetics for different initial H<sub>2</sub>O<sub>2</sub>/butadiene ratios. Therefore, the increasing initial concentration of the initiator significantly increases the reaction rate.

### Effect of Reaction Temperature

Reaction temperature significantly affects polymerization, following the Arrhenius equation, as presented in Eq. (14). The effect of reaction temperature on polymerization rate constants can be evaluated based on collision frequency factor and reaction activation energy. To calculate these variables, polymerization of butadiene was conducted at various reaction temperatures (100, 110 and 118 °C). After reaction rate constants were calculated,  $\ln(k_i)$  was plotted versus  $(1/T)$ , as can be seen in Fig. 5. According to the Arrhenius equation, the intercept is  $\ln(A)$  and the slope is  $(-E_i/R)$ . The collision frequency factor and reaction activation energy for each reaction rate constant is presented in Table 3.

The activation energy of each reaction step shows the effect of reaction temperature on the reaction rate constant. The initiation reaction needs higher energy than the other reactions. Based on Table 3, the initiation reaction can be

**Fig 5.** The plot of  $\ln(k)$  versus  $1/T$ **Table 3.** The activation energy for polymerization of butadiene

Reaction steps	$E_a$ (kJ/mol)
Dissociation	7608.1414
Initiation	14188.6724
Propagation	2247.2742
Termination	105.5878
Conjunction termination	87.2970
Disproportional termination	135.5182

identified as the most sensitive to the change of reaction temperature and is, therefore, the determining reaction. This data confirms that the rate of reaction was affected by the reaction temperature increase.

### CONCLUSION

The termination of radical polymerization of butadiene using hydrogen peroxide initiator was examined by observing the increase of polymer conversion and functionality. Polymerization of

butadiene was carried at an initial H<sub>2</sub>O<sub>2</sub>/butadiene ratio of 10%, with hydrogen peroxide 25%, and a reaction temperature of 100 °C. The kinetic constants of polymerization were  $4.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $8.9 \times 10^{-4} \text{ L mol}^{-1} \text{ sec}^{-1}$ ,  $7.7 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$ ,  $8.5 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ ,  $3.2 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$ , and  $5.3 \times 10^7 \text{ L mol}^{-1} \text{ sec}^{-1}$  for  $k_D$ ,  $k_a$ ,  $k_p$ ,  $k_t$ ,  $k_{tc}$ , and  $k_{td}$ , respectively, with activation energy of 7608, 14188, 2247, 105, 87, and 135 kJ/mol, respectively. The determining step of this polymerization was the initiation reaction. This kinetic model shows that the conversion of difunctional polybutadiene (HTPB) had been affected by the reaction temperature.

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