MECHANISM AND KINETICS OF CHAIN TRANSFER AND BACK-BITING REACTIONS IN POLYETHYLENE ADDITION

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ABSTRACT

The paper introduces new a researching method to study the mechanism and kinetics of the reactions in the polymerisation of ethylene by computer with the aids of GAUSSIAN 98 softwares. Calculation using density functional theory with the popular B3LYP at the 6-31g(d) was suitable for the research. Free radical ethyl and ethylene were good enough for modelling the propagation in the addition of polyethylene. The rate of propagation depending on temperature was an exponent function with the activative energy of 28 kJ/mole. The termination by chain tranfer using propanal was mainly the abstraction of hydrogen of carbonyl group. The calculated percentage of product was around 85 % at 220°C that was in good agreement with the experimental results. At 300°C, the efficient of termination by chain transfer of propanal was 90, 5% in comparison to 1,8 % of propane, 34,9 % of propene and 49, 4% of butene-1. The mechanism and kinetics of back-bitting of polyethylene radical were investigated. The branches of butyl and pentyl were obtained with the distribution of 4-5 branches per 1000 C of polyethylene at 300°C.

1. INTRODUCTION

Computational chemistry has been known as an efficient method having a wide contribution in explaining and clarifying the reaction mechanism and predicting of the products of the reactions those are conducted in the extreme conditions (high pressure, temperature etc.)[3,5]. The polyethylene addition by the free radical chain reaction has being interested by the chemists, technologists and manufaturers [6,16,17,18]. The current researches focus in the technology to achieve high quality products with the required polymerization degree, average molecular weigh, and especially the lowest branching degree of the polyethylene[18]. One of these research directions is to search for the best chain transfer agent in the termination of the polyethylene addition, especially for light density polyethylene (LDPE).

Low molecular weight compounds such as propane, butane, hexane, propene, 1-buten and 1-hexene are used as chain transfer agents in the termination of polymerisation of ethylene[6]. However, the their transfer chain abilities are limited due to the dificulties in process control to give LDPE with required average degree of polymerisation (DP). In addition, the formed LDPE has the high branching degree (BD). When using transfer chain agent, DP depends greatly on the ratio of chain transfer rate constant/ propagation rate constant, thus controlling and selecting suitable temperature in termination by chain transfer agents lead to control requried $\overline{DP}$ [10,12,16,18].

$$\frac{1}{\overline{DP_{tr}}} \approx \frac{1}{\overline{DP}} + \frac{k_{tr}}{k_p}\frac{[S]}{[M]}$$

$\overline{DP_{tr}}$ and $\overline{DP}$ are the average degree of polymerisation with and without chain transfer agent, respectively.

K_{tr} : chain transfer rate constant

K_p: propagation rate constant

[S]: concentration of chain transfer agent

[M]: concentration of monomer.

Recently, in 2000 the DSM company from Holand has been using propanal as a chain transfer agent in LDPE addition. The experimental results found that different from the other chain transfer agents, propanal reacted as efficient chain transfer agent when lowering temperature. In the other hand, the experimental results also gave that chain transfer reaction of propanal was predominantly hydrogen abstraction at carbonyl group (84%) (Fig.1).
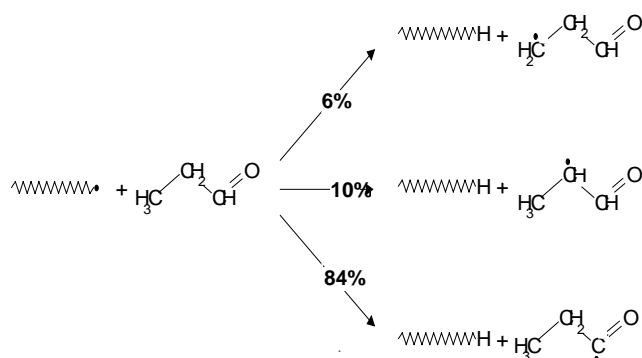
Fig.1. Proposal mechanism of chain transfer of propanal at 200°C and 2000 at.

The research by computer is the best method to contribute in clarifying the mechanism and kinetics of chain transfer by propanal[4,5,15].

The other problem in polymerisation of ethylene is the branching which is unwanted and leads to lower the polymer quality. One of the proposal mechanisms of branching is back-bitting in LDPE addition (Fig.2).
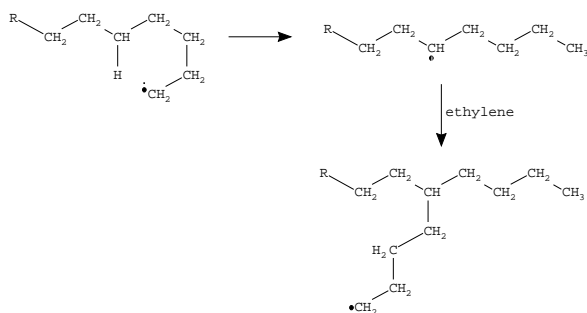
**Fig.2.** Proposal mechanism of branching by back-biting in LDPE polymerisation.

Analysis of LDPE by ^{13}C-NMR shows that butyl branches are present in the highes quantities, followed by ethyl short chain branches. Butyl branches are formed via 6-mebered rings (Fig.2).

Using computational method, our objectives are aimed at:

- Investigating the mechanism and kinetics of chain transfer by propanal in comparison with propan, propene, 1-butene in LDPE polymerisation.
- Clarifying the mechanism and kinetics of LDPE branching by back-biting
- .

2. METHODOLOGY

2.1 Computatinal scheme
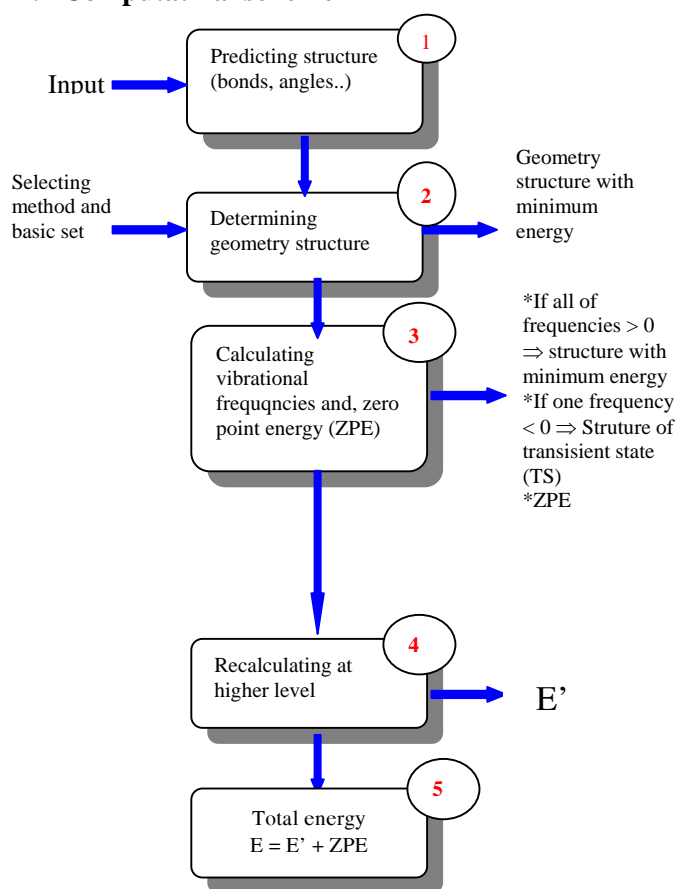
2.2 Computational methods

All of the electronic structure calculations were carried out using the program package GAUSSIAN 98 [14]. Geometries, frequencies and total energies of reactants, transition states, and products were optimized at the several level of theory with several basis sets as follows (ranking by more acuracies):[13,19,22,23]

- B3LYP/6-31g* // B3LYP/6-31g*
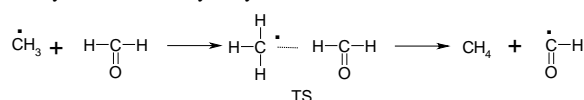- B3/6-311++g**// B3/6-311++g**
- MP2/6-311++g** // MP2/6-311++g**

- CCSD(T)/6-31g*// B3LYP/6-31*
- CCSD(T)/6-311++g** // B3LYP/6-31*
- CCSD(T)/6-311++g** // CCSD(T)/6-311++g**
- CCSD(T)/6-31++g (3df,2p) // B3LYP/6-31*

3. RESULTS AND DISCUSSIONS
3.1 Selecting calculation method

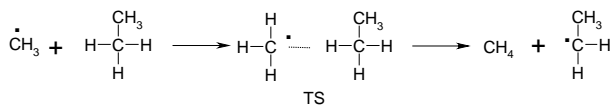Investigation was carried out on the simplest model of radical methyl and formaldehyde (Table 1)[15,20,21].

Table 1. Activative energy (Ea) of chain transfer of radical methyl and formaldehyde by different calculation methods.

$$\dot{C}H_3 + H-\overset{\overset{\displaystyle |}{O}}{\underset{}{C}}-H \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle H}{C}}\cdot\cdots H-\overset{\overset{\displaystyle |}{O}}{\underset{}{C}}-H \longrightarrow CH_4 + \overset{\overset{\displaystyle |}{O}}{\underset{}{\dot{C}}}-H$$

TS

No.	Method	Ea (KJ/mol)
01	B3LYP/6-31g* // B3LYP/6-31g*	21.267
02	B3/6-311++g**// b3/6-311++g**	26.649
03	MP2/6-311++g** // MP2/6-311++g**	57.315
04	CCSD(T)/6-31g*// B3LYP/6-31*	53.860
05	CCSD(T)/6-311++g** // B3LYP/6-31*	45.552
06	CCSD(T)/6-311++g** // CCSD(T)/6-311++g**	N/A
07	CCSD(T)/6-31++g (3df,2p) // B3LYP/6-31*	N/A

N/A: undetermined because of very long calculation time.

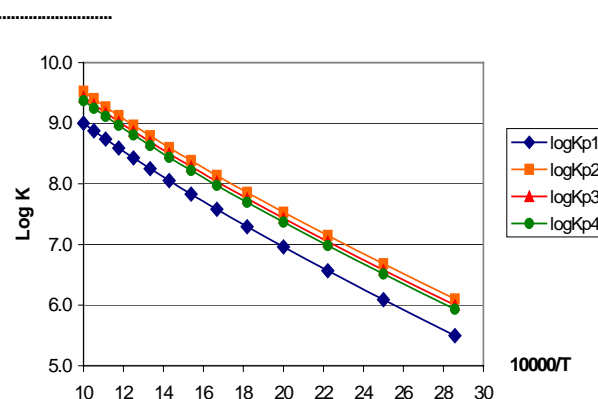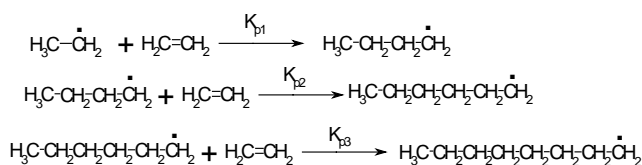**Table 2.** Rate reaction constant of radical methyl and ethane by experiments and by calculation using B3LYP/6-31g*.

$$\dot{C}H_3 + H-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\displaystyle H}{C}}-H \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle H}{C}}\cdot\cdots H-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\displaystyle H}{C}}-H \longrightarrow CH_4 + \overset{\overset{\displaystyle CH_3}{|}}{\underset{\displaystyle H}{\dot{C}}}-H$$

TS

T(°K)	K calculation [cm³.mol⁻¹.s⁻¹] Ktt	K experiment [cm³.mol⁻¹.s⁻¹] Ktn	Ktt/Ktn
350	1.07×10^5	4.64×10^4	2.31
400	9.68×10^5	3.06×10^5	3.16
450	5.56×10^6	1.45×10^6	3.84
500	2.32×10^7	5.35×10^6	4.33
550	7.66×10^7	1.65×10^7	4.64
600	2.12×10^8	4.41×10^7	4.81
650	5.12×10^8	1.05×10^8	4.86
700	1.11×10^9	2.29×10^8	4.84
750	2.20×10^9	4.63×10^8	4.75
800	4.06×10^9	8.80×10^8	4.62
850	7.08×10^9	1.58×10^9	4.47
900	1.17×10^{10}	2.72×10^9	4.31
950	1.86×10^{10}	4.50×10^9	4.13
1000	2.84×10^{10}	7.18×10^9	3.95

When comparing the calculation results with the experimental results, method B3LYP/6-31g* is the best in good agreement with experimental data (Table 2)[1,2]. The

tunnel effect of hydrogen can be neglected because of self error cancel and B3LYP/6-31g* method can be used for the investigating the mechanism and kinetics of LDPE polymerisation. Propagation rate constants and activative energies (28 KJ/mol) do not change so much when adding one monomer ethylene (Fig.3, Table 3). Thus model of radical ethylene and ethylene is good enough for modelling the propagation in LDPE polymerisation.

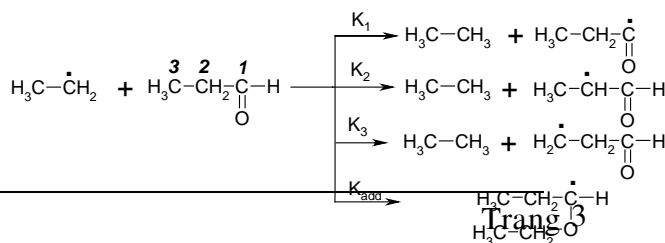### 3.2 Mechanism and kinetics of propagation in LDPE polymerisation

$$H_3C-\dot{C}H_2 + H_2C=CH_2 \xrightarrow{K_{p1}} H_3C-CH_2-CH_2-\dot{C}H_2$$

$$H_3C-CH_2-CH_2-\dot{C}H_2 + H_2C=CH_2 \xrightarrow{K_{p2}} H_3C-CH_2-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$H_3C-CH_2-CH_2-CH_2-CH_2-\dot{C}H_2 + H_2C=CH_2 \xrightarrow{K_{p3}} H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\dot{C}H_2$$

....

Equation	R²
Log K_{p1} = - 0.1895 (10000/T) + 10.805	0.9972
Log K_{p2} = - 0.1852 (10000/T) + 11.288	0.9970
Log K_{p3} = - 0.1856 (10000/T) + 11.196	0.9970
Log K_{p4} = - 0.1858 (10000/T) + 11.137	0.9970

Fig.3. Effect of length of carbon skeleton on propagation rate constants [cm³.mol⁻¹.s⁻¹]

**Table 3**: Actvative energy (kJ/mol) of reaction between radical 1-alkyl and ethylene using B3LYP/6-31g*

Radical 1-alkyl	Methyl	Ethyl	1-Propyl	1-Butyl	1-Pentyl	1-Hexyl
Ea (kJ/mol)	27.4	29.7	28.1	28.0	28.0	27.8

3.3 Mechanism and kinetics of chain transfer by propanal

$$H_3C-\dot{C}H_2 + H_3C-CH_2-\overset{\overset{1}{\underset{\displaystyle ||}{|}}}{\underset{\displaystyle O}{C}}-H$$

$$\xrightarrow{K_1} H_3C-CH_3 + H_3C-CH_2-\dot{C}\overset{}{\underset{\displaystyle ||}{}}_{O}$$

$$\xrightarrow{K_2} H_3C-CH_3 + H_3C-\dot{C}H-\overset{}{\underset{\displaystyle ||}{C}}-H$$

$$\xrightarrow{K_3} H_3C-CH_3 + \dot{H}_2C-CH_2-\overset{}{\underset{\displaystyle ||}{C}}-H$$

$$\xrightarrow{K_{add}} H_3C-CH_2-\overset{\displaystyle \dot{C}}{\underset{\displaystyle H_3C-CH_2-O}{}}-H$$

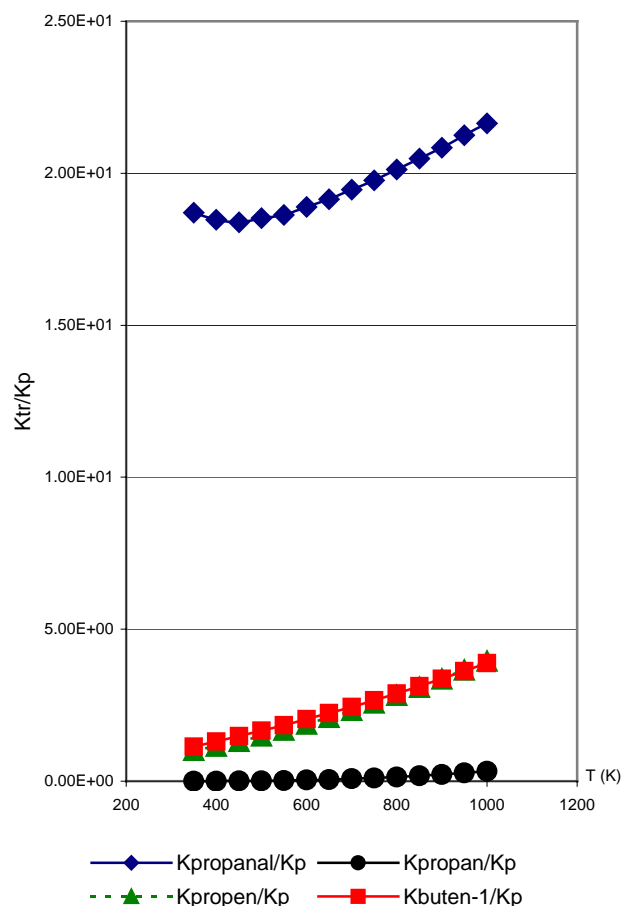|				
% product by experiment*	85	14	1	N/A

* : Source from DSM company from Holand

Chain transfer rate of propanal are exponel and a function of temperature (Fig.4).

The product percentage of reaction between propanal and radical ethyl shows that at 300°C hydrogen astraction at C1 reached to 85.5 % is in agreement with eperiments conducted by DSM com pany from Holland (Table 4).

Propanal acts as a chain transfer agent because of its chain tranfer constant is highest among those of the other chain transfer agents at the seme temperature. Chain tranfer rate of propene is similar to that of 1-butene, but chain transfer of propan is lowest (Fig.5).

Chain transfer of LPDE can be operated still efficiently at low temperature (450°K) when using propanal.

Model of radical ethyl and propanal respresents to chain transfer. Reactions between radical ethyl and propanal are paralell.

Chain transfer reactions of propanal are conducted by hydrogen abstraction at C1, C2, C3, and by addition to C=O group.
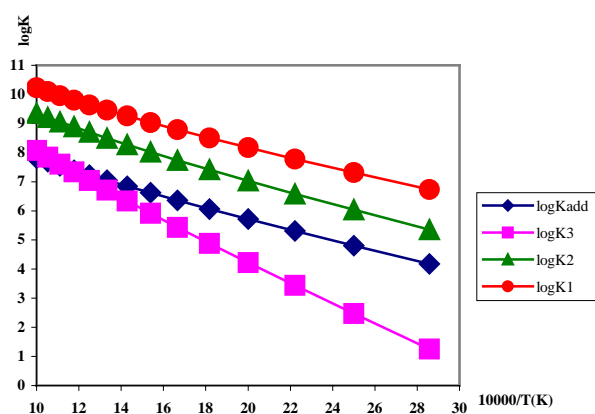
Equation	R^2
Log K_1 = - 0.1891 (10000/T) + 12.009	0.9962
Log K_2 = - 0.2156 (10000/T) + 11.401	0.9971
Log K_3 = - 0.3678 (10000/T) + 11.643	0.999
Log K_{add} = - 0.1960 (10000/T) + 9.6875	0.9977

Fig.4. Effect of temperature on chain transfer rates constants [$cm^3.mol^{-1}.s^{-1}$] of propanal.
K_1, K_2, and K_3 : chain transfer constants of hydrogen abstraction at C_1, C_2, and C_3 respectively
Kadd: chain transfer constant of addition to carbonyl group.

Table 4. Absolute reaction rate constanxt and % product of propanal and radical ethyl at 300°C .

Reaction	H abstra-ction at C1	H abstra-ction at C2	H abstra-ction at C3	Addd-tion at C=O
Absolute reaction rate constanxt [$cm^3.mol^{-1}.s^{-1}$]	5.12 x 10^8	4.35 x 10^7	1.67 x 10^5	1.86 x 10^6
Relative reaction rate constanst	3065.9	260.5	1	11.1
% product by calculation	85.1	14.5	< 0.1	< 0.3

Fig.5. Effect of temperature on chain transfer ratio Ktr/Kp using propanal, propane, propene and butene-1 as chain transfer agents.

3.4 Mechanism and kinetics of branching by back-bitting

Using 1-octyl representing for LDPE radical for reseaching mechanism and kinetics of branching by back-bitting.
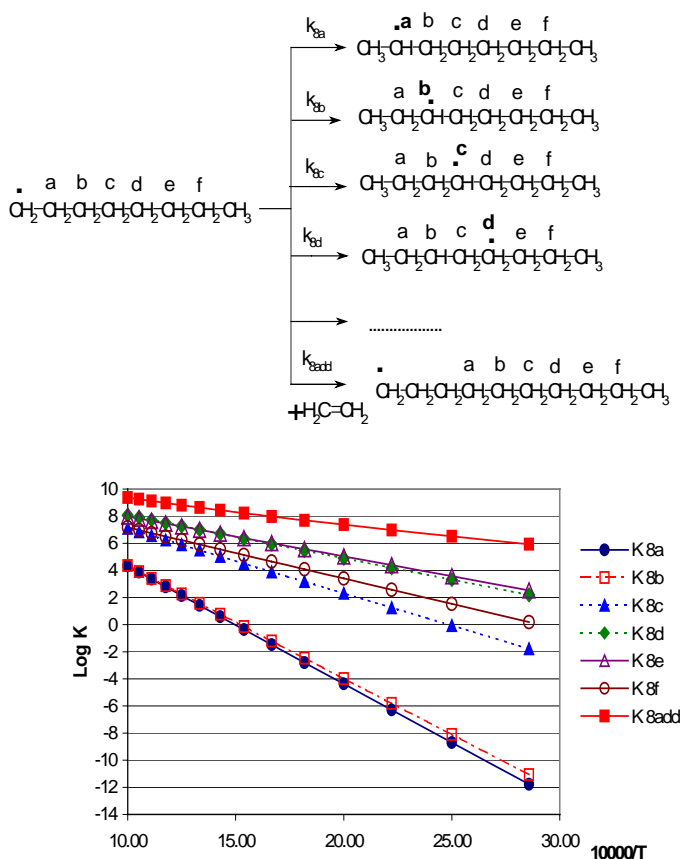
Fig.6. Effect of temperature on branching by back-bitting in LDPE polymerisation.

Back-bitting of 1-octyl radical occurred most easily at positions d and e because reaction constants at these are bigger than those at the other positions. Thus LDPE radical will be branched with the 4C-branches or 5C-branches.

Braching ratio for 1000 CH_2 units by back-bitting is caculated by the formula:

$$r_{bb} = 500 \frac{r_b}{r_p [M]}$$

r_{bb}: branching ratio by back-bitting.
r_b: back-bitting rate
r_p: propagation rate (equivalent to K_{add})
[M]: concentration of monomer (usually taken as 1 unit).

Table 5: Effect of temperature on the formation of butyl and pentyl branches per 1000 units of CH_2 group by branching by back-bitting in LDPE polymerization.

T (°K)	K_{8d} [cm^3.mol^{-1}.s^{-1}]	K_{8e} [cm^3.mol^{-1}.s^{-1}]	K_{8add} [cm^3.mol^{-1}.s^{-1}]	Butyl branch	Pentyl branch
350	1.54 x 10^2	3.40 x 10^2	8.57 x 10^5	0.1	0.2
400	2.07 x 10^3	3.77 x 10^3	3.27 x 10^6	0.3	0.6
450	1.56 x 10^4	2.44 x 10^4	9.59 x 10^6	0.8	1.3
500	7.83 x 10^4	1.08 x 10^5	2.33 x 10^7	1.7	2.3
550	2.94 x 10^5	3.69 x 10^5	4.94 x 10^7	3.0	3.7
600	8.87 x 10^5	1.02 x 10^6	9.46 x 10^7	**4.7**	**5.4**
650	2.26 x 10^6	2.43 x 10^6	1.66 x 10^8	6.8	7.3
700	5.06 x 10^6	5.12 x 10^6	2.74 x 10^8	9.2	9.3
750	1.02 x 10^7	9.77 x 10^6	4.30 x 10^8	11.9	11.4
800	1.88 x 10^7	1.72 x 10^7	6.43 x 10^8	14.7	13.4
850	3.24 x 10^7	2.84 x 10^7	9.27 x 10^8	17.5	15.3
900	5.26 x 10^7	4.46 x 10^7	1.30 x 10^9	20.3	17.2
950	8.15 x 10^7	6.67 x 10^7	1.77 x 10^9	23.1	18.9
1000	1.21 x 10^8	9.59 x 10^7	2.35 x 10^9	25.6	20.4

4. CONCLUSION

Calculation using density functional theory with the popular B3LYP at the 6-31g(d) was suitable for the research.

Free radical ethyl and ethylene were good enough for modelling the propagation in the addition of polyethylene. The rate of propagation depending on temperature was an exponent function with the activative energy of 28 kJ/mole.

The mechanism and kinetics of termination of the polyethylene addition by using propanal as a chain transfer agent were investigated. The rate of propagation depending on temperature was also exponent function. The termination by chain tranfer using propanal was mainly the abstraction of hydrogen of carbonyl group. The calculated percentage of product was around 85 % at 220°C that was in good agreement with the experimental results conducted by DSM Co. from Holland.

Propanal was shown as the most efficient chain transfer agent among propanal, propane, propene and butene-1. At 300°C, the efficient

of termination by chain transfer of propanal was 90, 5% in comparison to 1,8 % of propane, 34,9 % of propene and 49, 4% of butene-1.

The mechanism and kinetics of back-bitting of polyethylene radical were investigated. The branches of butyl and pentyl were obtained with the distribution of 4-5 branches per 1000 C of polyethylene at 300°C.

The results have partly distributed to the explanation and clarification of the chain transfer role of propanal as well as its excellent property in comparison to the other chain transfer agents such as propane, propene and butene-1 in the polyethylene addition by free radical mechanism. The results have also partly distributed to the clarification of the branch formation by back-bitting of polyethylene radical and the prediction of the branching dregee.

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