J. of the Korean Oil Chemists' Soc.,
Vol. 28, No. 1. March, 2011. 22~28

Effect of the Organometallic Catalyst in the Preparation of Polybutylenesuccinate

Keun-Ho Park†

†*Dept. of Chemical Engineering, Changwon National University*
Changwon, Gyeongnam, 641-773, Korea
(Received December 17, 2010 ; Accepted January 8, 2011)

Abstract : Esterification reaction between succinic acid[SA] and 1,4-butanediol [BD} was kinetically investigated in the presence of organometallic catalysts (ESCAT- 100Ag18, MBTO) at 150~180℃. The reaction followed from the measurement of the quantity of water which was distilled from the reaction vessel. The esterification reaction was carried out under the first order kinetics with respect to the concentration of reactants and catalyst, respectively. The overall reaction order was 2nd. From the examination of relationship between apparent reaction rate constants and reciprocal absolute temperature, the activation energy has been calculated as 146.70 kJ/mol(ESCAT-100Ag18) and 87.57 kJ/mol(MBTO), respectively.

Keywords : esterification, succinic acid, 1,4-butanediol, organometallic catalysts, activation energy.

1. Introduction

The preparation of poly(butylenesuccinate) (PBS) is usually carried out by the esterification reaction. These can be formed by the esterification of SA with BD. The esterification process is generally preferred[1-3]. In the theory of the polyesterification reaction developed by Flory [4] based on the reaction of diacid and glycol, the reaction was known to be acid catalyzed.

Knowledge of the kinetics of the esterification reaction of SA with BD is important for the industry[5-9]. A few reports on such investigations have been published previously but they do not account completely for experimental observations [10,11]. In the present study improvements have been made, and good agreement between an experimental data and an appropriate rate expression is obtained over a wide conversion range. Gold-Schmidt, Rolfe and Hinshelwood reported that in the absence of an externally added strong acid, the diacid monomer acts as its own catalyst for the esterification reaction. This reaction is the third-order overall with the second-order dependence on the carboxyl concentration, which comprises two first-order dependencies: one for the carboxyl as reactants and the other as the catalyst.

In this paper, the kinetic study of the esterification of succinic acid with

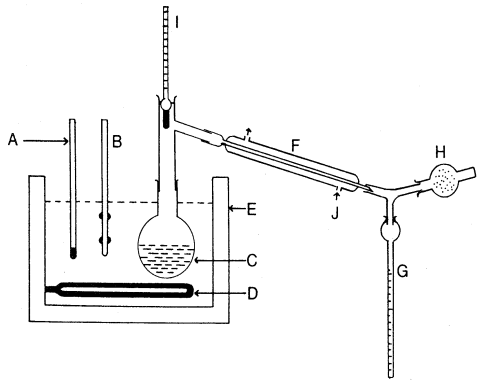
† Corresponding author
(E-mail : khopark@changwon.ac.kr)

1.4-butanediol was investigated by applying the results to the various catalysts. In addition, the effect of molar ratio of SA and BD on the kinetics was also investigated.

2. Experimental

2.1 Apparatus

The apparatus used in this work is shown in Figure 1. For the kinetic study on the esterification reaction. It is important to prevent water formed in this reaction from being retained and to make it distill smoothly. Therefore, we have paid special attention to the following points: (i) nitrogen was made to flow through the reaction vessel at a steady rate of 60 mL/min: (ii) the length of tube was reduced as far as possible in ordre to shorten the response time of the acceptor(a micromass cylinder).



A : Thermoregulator B : Stirrer
C : Distilling flask D : Heater
E : Oil bath F : Condenser
G : Micromass cylinder
H : Calcium chloride tube
I : Thermometer
J : Cooling water

Fig. 1. Esterification reaction apparatus.

2.2 Reagents

Succinic acid was purchased from Junsei Chemical Co. Ltd(special grade), 1,4-Butanediol was purchased from Daejung (experimental grade) and used without further purification.

ESCAT-100Ag18 and MBTO were purchased from Saeho company and used as catalysts. Commercial products(catalysts) were also used without further purification.

2.3 Esterification

Into the reaction vessel 0.5 mol SA, 1.0 mol EG and an adequate amount of catalyst were introduced. The reaction was carried out by stirring under the nitrogen atmosphere.

The temperature of the reaction mixture heated with the BD bath was measured with a thermocouple detector and was confirmed to be 180℃.

The reaction was considered to have started at the time when the water first condensed in the acceptor. After that, the progress of the reaction was fellowed by measuring the quantity of water corrected in the acceptor.

3. Results and discussion

3.1 Kinetic treatment

The mode of the esterification of SA with BD is shown as below in a simplified form, which water and poly(butylenesuccinate) (PBS) are formed:

$$\underset{S}{HOOCCH_2CH_2COOH} + 2\ \underset{B}{HO(CH_2)_4OH} \xrightarrow{\text{Catalyst}} \underset{P}{HO(CH_2)_4OOCCH_2CH_2COO(CH_2)_4OH} + 2\ \underset{W}{H_2O} \quad \text{-----(1)}$$

In the rate equation (1), noting that the amount of BD that has reacted at any time t is two times as much as amount of *SA,* we may write $2C_{Ao}X_A = C_{Bo}X_B$. Because the volume of reacting system varies linearly

with conversion, moles (N_A, N_B) of reactants A and B are $N_A = N_{Ao}(1 - X_A)$, $N_B = N_{Bo}(1 - X_A)$, respectively.

We assumed that the rate determining step is equation 1, the reduced rate of SA can be written as follows[12]:

$$-Y_S = -\frac{1}{V}\frac{dN_S}{dt} = kCsC_BC_k = k\frac{N_SN_BN_W}{V^3} \quad \text{----------} \quad (2)$$

Chang and Karalis[13] assumed the third-order for the uncatalyzed reaction and the second-order for the catalyzed reaction that is contributed from the external catalyst. Since the by-product of water is distilled from the reaction system, the total volume of the mixture decreases with time. In correcting concentration of reactants, the removal of formed water is accompanied by a decrease in volume, so that we apply such a correction to this model. The properties of catalyst are usually kept constantly in quality during the reaction. We consider the change of volume in catalyst term(C_k), Ns, N_B, N_W and V of the rate equation (2) can be written as follows:

$$Ns = Ns_0(1-Xs) \quad \text{----------} \quad (3)$$
$$N_B = N_{B0} - 2Ns_0Xs \quad \text{----------} \quad (4)$$
$$N_W = 2Ns_0Xs \quad \text{----------} \quad (5)$$
$$V = V_O - v \cdot Nw = 2vNs_OXs \quad \text{------} \quad (6)$$

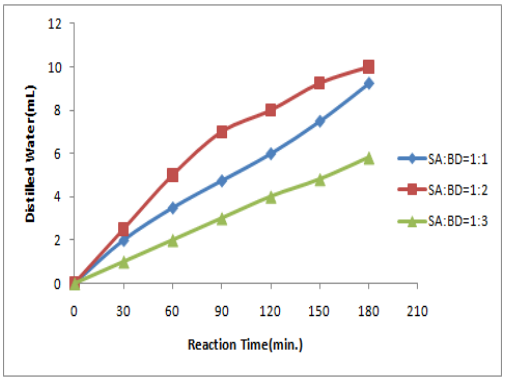
Substituting equation (3), (4), (5) and (6) into equation (2) and rearranging give the next equation.

$$\frac{dX_S}{dt} = k \cdot \frac{N_k \cdot (1-X_S) \cdot (N_{B0} - 2N_{S0} \cdot X_S)}{(V_0 - 2vN_{S0} \cdot X_S)} \quad \text{----------} \quad (7)$$

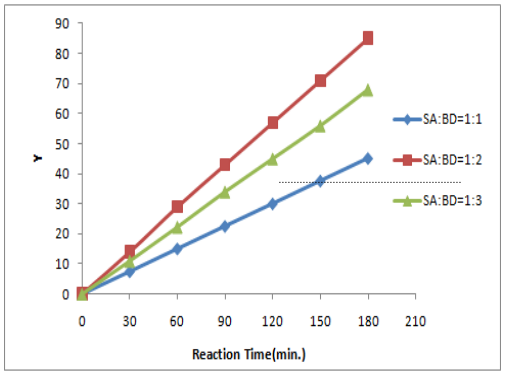
In equation (7), considering the noting that the mole concentration of BD is two times as much as mole concentration of *SA*, we can write equation (8) and then kinetic value, *Y*, is obtained as follows:

$$Y = W + (V_0 - 2vN_{S0})\ln\left(\frac{1}{1-(W/2vN_{S0})}\right) = k' \cdot N_k \cdot t \quad \text{----------} \quad (8)$$

Fig. 2 shows the relationship of the esterification reaction with changing molar ratio M (1-3) of BD and SA. As shown in Fig. 2, the reactivity increases as molar ratio up to 2.0. However, the molar ratio is larger than 2.0, the reactivity decreases with the increase of molar ratio.



(a)



(b)

Fig. 2. Relationship of molar ratio between (a) Distilled water and reaction time, and (b) Y and reaction time in the esterification reaction of SA and BD(reaction temperature 160 ℃, ESCAT-100Ag18 catalyst).

By using the equation (8), the data in Fig. 2(a) is replotted in Fig. 2(b). As shown in

Fig. 2(b), the linear relationship of Y against reaction time except initial step proves the suitability of the proposed kinetic treatment.

3.2 Catalyzed Esterification Reaction

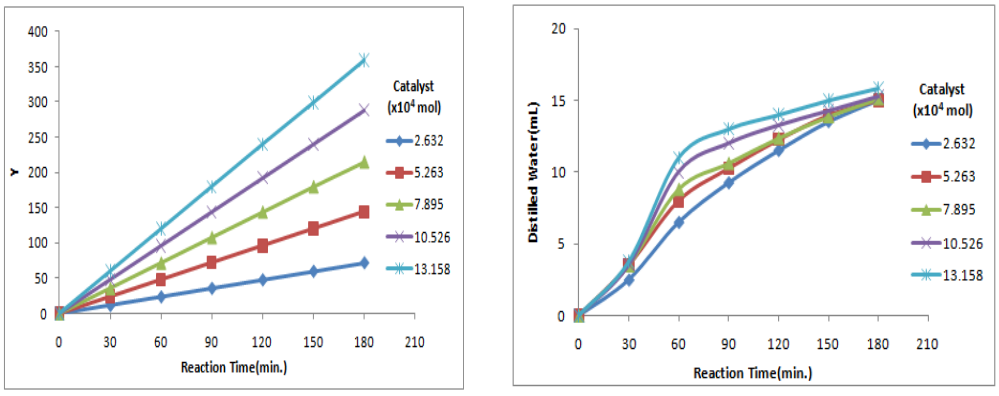
3.2.1 Effect of ESCAT-100Ag18 Catalyst

Fig. 3(a) shows the correlation between extent of reaction and time at various concentrations of ESCAT-100Ag18 as a catalyst in the esterification reaction. The results replotted data of Fig. 3(b) according to equation (8) showed the high linearity. The rate constant *(k')* was calculated from the slope in the plot of Y against time, and was shown against concentration of catalyst in Fig. 3(b). The rate constant values of MBTO catalyst are higher than those of ESCAT-100Ag18 catalyst. In a series of metal compound as catalysts, the catalyzed reaction on the polycondensation is largely influenced by the mutual relation between the metal compound of catalysts and the negatively charged carbonyl oxygen of the ester group.

Table 1 shows that the apparent rate constant, K', which is obtained from the slope of Flg. 3(b). From the obtained results, we can conclude that the rate constant values of the esterification reaction increase with catalysts.

3.2.2 The Effect of Temperature Dependence

The results of esterification of SA and BD at 150-180 °C in the presence of ESCAT-100Ag18 as a catalyst are shown in Fig. 4. The rate of reaction increases with the increase of temperature, and it is faster in the catalyzed reaction than in the uncatalyzed reaction. The time required for 50% completion of the reaction was 130 min at 160 °C. 60 min at 170 °C, and 45 min at 180 °C. Thus, the reactivity increases 1.3-2.1 times faster with increasing reaction temperature. The data of Fig. 4(a) *is* replotted in Fig. 4(b) by employing equation(8). As shown in Fig. 4(b), the linear relationship of Y against reaction time except initial step proves the suitability of the proposed treatment.

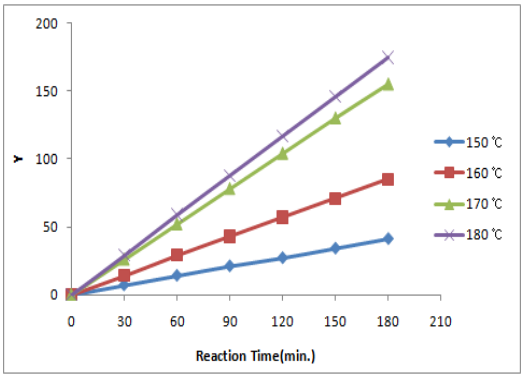


(a) (b)

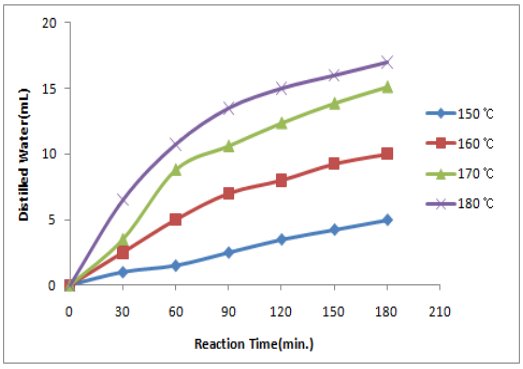
Fig. 3. Relationship between (a) Distilled water and reaction time, and (b) Y and reaction time in the esterification reaction of SA and BD(molar ratio 1:2) with ESCAT-100Ag18 catalyst. (reaction temperature 170 ℃).

Table 1. Apparent Reaction Rate Constant (k′) in the Esterification Reaction between SA and BD with ESCAT-100Ag18 and MBTO Catalysts(Molar Ratio 1:2)

Amount of catalyst (x 10^4 mol)	Apparent rate constant (k‘x10^3 mL/mol · min.)	
	MBTO	ESCAT-100Ag18
2.632	390.642	398.980
5.263	781.135	797.809
7.895	1,171.777	1,196.789
10.526	1,562.270	1,595.618
13.158	1,952.912	1,994.599



(a)



(b)

Fig. 4. Relationship between (a) Distilled Water and reaction time, and (b) Y and reaction time in the esterification reaction of SA and BD(molar ratio 1:2) at various temperature (ESCAT-100Ag18 catalyst).

Table 2. Apparent Reaction Rate Constant (k′) in the Esterification Reaction between SA and BD(molar ratio 1:2) with Organometallic Catalysts

Temperature(℃)	Apparent rate constant (k‘, mL/mol · min.)	
	MBTO	ESCAT-100Ag18
150	242	285
160	296	596
170	1,286	1,092
180	1,335	1,227

Table 2 shows that apparent rate constant, K′, which is obtained from the slope of Fig. 4(b). From the obtained results, we can conclude that the activity of catalyst increases with temperature.

The apparent rate constant, *K‘*, against reciprocal of absolute temperature is logarithmically plotted in Fig. 5. The apparent activation energy, *E* is calculated from the slope in the plot of In *K′*, against 1/T. The apparent activation energy for formation of PBS with using ESCAT-100Ag18 as a catalyst is 146.7 KJ/mol, and using MBTO as a catalyst is 123.41 KJ/mol, whereas the value of uncatalized reaction is slightly higher (149 KJ/mol)[12]. From the result, it can be seen that the formation of PBS in the

presence of catalysts occurs easily than that of uncatalyzed reaction.

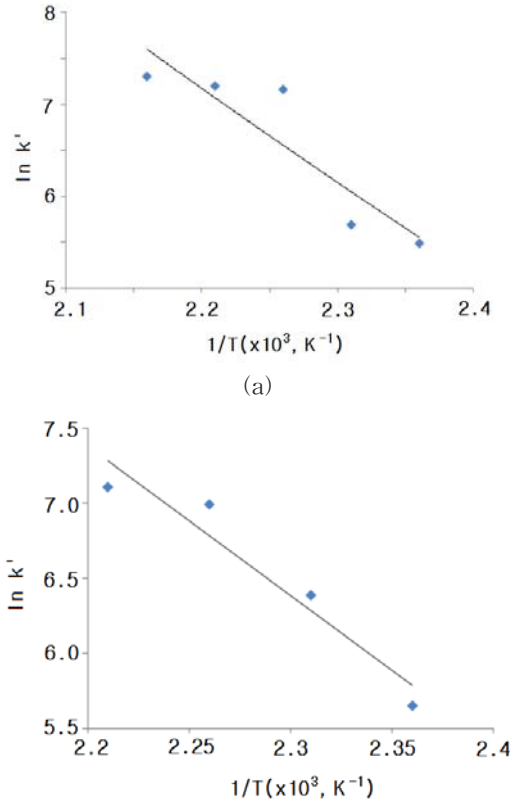


Fig. 5. Arrhenius plot of the esterification reaction of SA between BD with (a) MBTO and (b) ESCAT-100Ag18 Catalysts.

4. Conclusions

Effect of the esterification reaction between succinic acid and 1,4-butanediol was kinetically investigated in the presence of organic metal catalysts (alkyl-silver oxide (ESCAT-100Ag18, MBTO).

1. The esterification reaction was carried out under the first-order conditions with respect to the concentration of reactants, respectively. The overall reaction order was 2nd.
2. The activation energy has been calculated as 146.70 kJ/mol (ESCAT-100Ag18) and 123.41 kJ/mol (MBTO), respectively.

Nomenclature

Cs : Concentration of SA for reaction time
C_B : Concentration of BD for reaction time
C_M : Concentration of catalyst
N_{SO} : Initial mole number of SA
N_{BO} : Initial mole number of BD
Ns : Mole number of SA for reaction time
N_B : Mole number of BD for reaction time
N_k : Mole number of catalyst
V : Volume of reactants
N_W : Mole number of distilled water
V_0 : Initial volume of reactants SA and BD
X_s : Fraction of reactant SA
k : Rate constant
k' : Apparent rate constant
T : Temperature
t : Reaction time

REFERENCES

1. Y. X. Xu, J. Xu, D. Liu, B. Guo, and X. Xie, Synthesis and Characterization of Biodegradable Poly(butylene Succinate-co-Propylene Succinate)s, *J. Appl. Polym. Sci.*, **109(3)**, 1881 (2008).
2. B. Belhalfaoui, A. Aziz, E. H. Elandaloussi, M. S. Ouali, and L. C. De Menorval, Succinate-bonded cellulose: A regenerable and powerful sorbent for cadmium-removal from spiked high-hardness groundwater, *J. hazard. mater.* **169(1)**, 831 (2009).
3. B. D. Ahn, S. H. Kim, Y. H. Kim, and J. S. Yang, Synthesis and characterization of the biodegradable copolymers from succinic acid and adipic acid with 1,4-butanediol, *J. Appl. Polym. Sci.,*

82(11), 2808 (2001).
4. E. H. Woo, J. W. Barlow. and D. R. Paul, Phase behavior of blends of aliphatic polyesters with a vinylidene chloride/vinyl chloride copolymer, *J. Appl. Polym. Sci.,* **32**, 3889 (1986).
5. R. Bacaloglu, M. Fisch, and K. Biesiada, Kinetics of polyesterification of adipic acid with 1,3-butanediol, *Polymer Eng. Sci.,* **38(6)**, 1014 (1998).
6. S. S. Park and J. S. Choi, Kinetics of the Formation of Poly(ethylene-co-1,4-cyclohexylenedimethylene) Terephthalate Oligomer by Various Catalysts, *Korean Chem. Eng. Res.,* **42(3)**, 326 (2004).
7. K.H. Park and D. S. Kim, Effect of Monobutyl Tinoxde Catalyst in Esterification Reaction between Succinic Acid and 1,4-Btanediol, *J. Kor. Oil Chem. Soc.,* **26(3)**, 362 (2009).
8. K. H. Park and N. H. Kim, A Study on the Transesterification Reaction between Dimethylphthalate and 1,4-butanediol, *Transaction of the institute of industry and technology*, **13**, 211 (1999).
9. K. H. Park, Effect of Chloride Catalysts in Transesterification Reaction between Dimethylphthalate and Ethylene Glycol, *Transac. insti. indus. tech.,* **12**, 307 (1998).
10. A. K. Kolah, N. S. Asthana, D. T. Vu, C. T. Lira, and D. J. Miller, Reaction Kinetics for the Heterogeneously Catalyzed Esterification of Succinic Acid with Ethanol, *Ind. Eng. Chem. Res.*, **47**, 5313 (2008).
11. J. H. Clark, V. Budarin, T. Dugmore, R. Luque, D. J. Macquarrie, and V. Strelko, Catalytic performance of carbonaceous materials in the esterification of succinic acid, *Catalysis Communications*, **9(8)**, 1709 (2008).
12. S. S. Park, H. W. Jun, and S, S, Im, Kinetics of Forming Poly(Butylene Succinate) (PBS) Oligomer in the Presence of MBTO Catalyst, *Polymer Eng. Sci.,* **38(6)**, 905 (1998).
13. W. L. Chang, T. Baranowski, and T. Karalis, Role of functionality in MDI-based elastomer preparation, *J. Polym. Chem. Ed.* **51(6)**. 1077 (1993).