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°C. 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
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 order to shorten the response time of the acceptor (a micromass cylinder).

![Fig. 1. Esterification reaction apparatus.](image)

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°C.

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 followed 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:

\[
\text{HOOCCH}_2\text{CH}_2\text{COOH} + 2 \text{HO(CH}_2\text{)}_4\text{OH} \rightarrow \text{HO(CH}_2\text{)}_4\text{OOCCH}_2\text{CH}_2\text{COO(CH}_2\text{)}_4\text{OH} + 2 \text{H}_2\text{O}
\]

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 \( 2C_A \dot{X}_A = C_B \dot{X}_B \). Because the volume of reacting system varies linearly