Kinetic Study and Simulation of the Precopoly transesterification Step in the Copoly(Ethylene-Polyoxyethy lene Terephthalate) Production Process

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The kinetics of the precopoly transesterification step for the production process of the copoly(ethylene-polyoxyethylene terephthalate), COPEPOET, has been analyzed. The prepolyl transesterification step involves two competitive parallel reactions generating the same by-product, ethylene glycol: 1. Prehomopoly transesterification reaction of bis (2-hydrox ylylene terephthalate), BHET, with itself and 2. Precopoly transesterification reaction of BHET with poly(oxyethylene), POE. The kinetic constants of both reactions, BHET with BHET and BHET with POE, were calculated. The analysis was made as follows: 1. A kinetic model was developed in order to calculate the kinetic constants k_H and k_c of the prehomopoly transesterification and precopoly transesterification reactions; 2. The simulation of the precopoly transesterification step was carried out by integrating the differential equations, which describe the prepolyl transesterification step. A fourth-order Runge-Kutta method was used for this integration. Several values that fall within the interval of 0.05 to 1.5 were assigned to the rate constant ratio k_H/k_c. For each k_H/k_c value, a set of k_H and k_c values were obtained. The parameters of the Arrhenius equation A and E were evaluated by means of a multiple regression analytical method; and 3. By comparison between theoretical and experimental data the best k_H/k_c value was obtained. The k_H value was found to be several times smaller than that of k_c.

INTRODUCTION

Elastomeric copolymers are a group of high performance polymers that exhibit properties of both, a thermoplastic as well as an elastomer. They were commercialized, in 1972, under the trademark Hytrel [name given at the elastomeric copolyester formed by the hard segment, TMT, and soft segment, POTM] by DuPont, as has been reported by Legge et al. and Herman et al. (1, 2). The successful commercialization of these elastomeric copolymers prompted research directed toward the understanding of their structure, morphology, and chemistry. Many structural variations have been studied, and numerous blends with other polymers have been reported. These materials are of great commercial importance as engineering thermoplastic elastomers. The elastomeric copolyester possesses a structure of two phases, one hard and the other soft, and it is considered to be a copolyester formed by these randomly joining hard and soft segments, according to Cella and Walker et al. (3, 4). The hard phase (short part of the chain) contributes to the polymer strength and the soft phase supplies its elastomeric character. The hard or crystallizable segments consist of sequences of alkylene terephthalate units and the soft elastomeric segments are long-chain polyalkylene oxide glycols. Poly(ethylene terephthalate), PET, and poly(butylene terephthalate), PBT, plants can be used for the production of elastomeric copolymers through changes in equipment and process, as has been proposed by Herman et al. (2).
The elastomeric copolyester copolymer(ethylene-polyoxyethylene terephthalate), COPEPOET, is manufactured by means of three steps as in PET production process according to Ravindranath et al. [5, 6]: 1. Transesterification of dimethyl terephthalate, DMT, with ethylene glycol, EG. 2. Precopolytransesterification of bis(2-hydroxyethyl) terephthalate), BHET, with poly(oxyethylene), POE, and 3. Copolytransanesterification of PET and COPEPOET oligomers. The structure of the resulting copolyester, COPEPOET, is shown below:

\[
\begin{align*}
\text{soft segment} & \quad \text{hard segment} \\
\end{align*}
\]

where, \( m = 23 \), approximately.

The precopolytransesterification step kinetic model takes into account the system of two competitive parallel reactions, as has been considered by Mathew et al. and Yamanis et al. [7, 8]. The method is capable of determining \( k_1 \) and \( k_2 \), the prehomopolytransesterification and precopolytransesterification reaction constants, based on the non-isothermal reaction of BHET and POE. It also establishes the bases for the simulation of the precopolytransesterification step. Besides, and in agreement with Flory's equal reactivity hypothesis [9], \( k_1 \) and \( k_2 \) are considered to be the same as that of the homopolytransesterification and copolytransesterification reactions, which occur in the final stage of the copoly(ethylene-polyoxyethylene terephthalate) production process.

**REACTION SCHEME**

BHET is a monomer previously obtained by transesterification of dimethyl terephthalate, DMT, with ethyleneglycol, EG, as shown below. Two reactions are occurring in a series-parallel fashion in the transesterification step: Ester interchange between \( E_m \) and \( F_m \), reaction 1, and transesterification between \( E_m \) and \( E_g \), reaction 2.

\[
\begin{align*}
\text{Ester interchange reaction} \\
E_m + F_m & \rightleftharpoons E_g + F_m \\
\end{align*}
\]

\[
\begin{align*}
\text{Transesterification reaction} \\
E_m + \text{EG} & \rightleftharpoons E_g + \text{EG} \\
\end{align*}
\]

The chemical reactions 3 and 4 shown below take place irreversibly in the precopolytransesterification step and lead to the production of \( Z \) and \( C_m \), which are PET and COPEPOET oligomers. \( Z \) and \( C_m \) are copolymerized to produce the elastomeric copolyester copolymer(ethylene-polyoxyethylene terephthalate), COPEPOET. Table 1 explains the symbols used for the transesterification, 1 and 2, and precopolytransesterification, 3 and 4, step reactions.

This paper describes the precopolytransesterification step only, since the transesterification step has been already described in a previous paper [10]. Two competitive parallel reactions, generating the same by-product, ethyleneglycol, are occurring in the precopolytransesterification step. The reactions are:

1. Prehomopolytransesterification of bis(2-hydroxyethyl) terephthalate), BHET, with itself and 2. Precopolytransesterification of BHET and poly(oxyethylene), POE.

**EXPERIMENTAL PROCEDURE**

**Equipment.** A three-liter stirred glass reactor provided with a distillation column, a condenser, a collector tank, a heating mantle and a temperature indicator was used to carry out the precopolytransesterification reactions. Figure 1 illustrates the reaction equipment.

**Materials.** For the laboratory reactions, BHET obtained from the transesterification of DMT with EG, reactions 1 and 2, and pure POE were used to produce the copoly(ethylene-polyoxyethylene terephthalate), POE was provided by the Mexican Company Polioles, S. A. The catalyst tetrabutyl titanate, TBT, was TYZOR® TBT from DuPont.

**Synthesis of COPEPOET.** BHET and POE are fed to the reactor at a molar ratio of \( E_g / F_g \) equal to 5.67. The reactive mixture (BHET and POE) is heated to about 215°C. At this temperature and under agitation, 0.47 gram of TBT is loaded to the reactor (OR). It has been observed that the ethylene glycol begins to be removed from the reactive mixture at 220°C. Therefore, the authors determined that the TBT catalyst could be loaded at the temperature of 215°C. The temperature was increased gradually from 215°C to 240°C, at a heating rate of 90°C per hour and at a pressure of 1 x 105 Pa, for about 30 minutes. The ethylene glycol generated from the precopolytransesterification reactions 3 and 4 leaves the reactor (OR) through the distillation column (DC). EG is condensed in C and collected in a graduated container (GC).
**KINETIC MODEL**

The kinetic model presented here evaluates the \( A \) and \( E \) kinetic parameters of the prehomopolytransesterification reaction 3 and precopolytransesterification reaction 4 reactions and simulates the precopolytransesterification step in the copoly(ethylene-polyoxyethylene terephthalate) production process.

By considering the precopolytransesterification reactions 3 and 4, a three ordinary differential equations system is proposed:

\[
\frac{d[\text{E}_g]}{dt} = \frac{-k_H \cdot [\text{E}_g]^2 - k_r \cdot [\text{E}_g] \cdot [\text{P}_g]}{V} \tag{5}
\]

\[
\frac{d[\text{P}_g]}{dt} = -k_r \cdot [\text{E}_g] \cdot [\text{P}_g] \quad \text{V} \tag{6}
\]

\[
\frac{d[\text{g}]}{dt} = \frac{k_H \cdot [\text{E}_g]^2 + k_r \cdot [\text{E}_g] \cdot [\text{P}_g]}{V} \tag{7}
\]

where \( \text{E}_g \) is the hydroxyethyl ester end group equivalents of unreacted BHET, \( \text{P}_g \) is the non-reacted POE moles in the reactor, and \( \text{g} \) is the ethylene glycol moles evolved from the reactor.

The volume of the reaction mixture, \( V \), increases as the temperature is increased and it decreases as ethylene glycol leaves the reaction system. According to above explanation and Laubriet et al. (11), it is assumed that the concentration of the catalyst remains constant during all reaction time and has no significance for the kinetic model. An expression of \( V \), as a function of the temperature, \( T \), and ethylene glycol \( g \), is shown as follows:

\[
V = (V_{\text{DMT}})(n_{\text{DMT}}) + (V_{\text{EG}})(g) - (V_{\text{m}})(m) +
\]

\[
(V_{\text{POE}})(m_{\text{POE}}) - (V_{\text{EG}})(g) \tag{8}
\]

where: \( V_{\text{m}} \) and \( m \) are the volume and the moles of methanol after the transesterification reaction of DMT.

**Table 1. Symbol Explanation.**

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{COOH}_2)</td>
<td>Methyl ester end group</td>
</tr>
<tr>
<td>(-\text{COOCH}_2\text{CH}_3\text{OH})</td>
<td>Hydroxyethyl ester end group</td>
</tr>
<tr>
<td>(\text{HOCH}_2\text{CH}_2\text{OH})</td>
<td>Moles of ethylene glycol</td>
</tr>
<tr>
<td>(\text{CH}_3\text{OH})</td>
<td>Moles of methanol</td>
</tr>
<tr>
<td>(-\text{COOCH}_2\text{CH}_2\text{OOC}\cdot\text{H})</td>
<td>Diester group</td>
</tr>
<tr>
<td>(-\text{CO}(\text{CH}_2\text{CH}_2\text{O})_n\cdot\text{OH})</td>
<td>Moles of poly(oxyethylene)</td>
</tr>
<tr>
<td>(-\text{CO}(\text{CH}_2\text{CH}_2\text{O})_n\cdot\text{OH})</td>
<td>Hydroxypolyoxyethyl ester end group</td>
</tr>
</tbody>
</table>

---

**Fig. 1. Precopolytransesterification reactor.** OR is the reaction vessel, DC the distillation column, C the condenser, and GC the EG collector.
with EG, reactions 1 and 2. g is the ethylene glycol generated from precopolymerization reactions 3 and 4. The molar volumes for DMT, EG and POE are obtained from the following expressions:

$$V_{DMT} = 191.5 (1 + 0.0014 (T - 413))$$

$$V_{eg} = 60.6 (1 + 0.0014 (T - 413))$$

$$V_{Pog} = \frac{1000}{1.163 + 6.87 \cdot 10^{-5} \cdot T - 8.46 \cdot 10^{-7} \cdot T^2}$$

The Carothers equation is given by the average degree of polymerization, DPn, as a function of the functional group conversion, p, as follows:

$$\bar{DP} = \frac{1}{1 - p}$$

Where:

$$p = \frac{(Eg_0 + P_0g) - (Eg + Pg)}{(Eg_0 + P_0g)}$$

and

$$(Eg_0 + P_0g) - (Eg + Pg) = 2 \cdot g$$

A mole of ethylene glycol is formed when two hydroxyl or carboxyl, -OH or -COOR, end groups have taken part in the reaction. Therefore, we have the following expression for p:

$$p = \frac{2 \cdot g}{Eg_0 + P_0g}$$

On the other hand, \(\bar{DP}_n\) is equal to the ratio of functional groups present initially to the total number at any particular time, i. in the polymerization process as shown below:

$$\bar{DP}_n = \frac{Eg_0 + P_0g}{Eg + Pg}$$

Combining this expression with the Carothers equation and solving for Eg, we have:

$$Eg = Eg_0 + P_0g - 2 \cdot g - Pg$$

Equations 5 and 6 give the following differential equation:

$$\frac{dEg}{dPg} = \frac{-k_4 [Eg]^3 - k_5 [Eg] \cdot [Pg]}{-k_4 \cdot [Eg] \cdot [Pg]}$$

$$\frac{dEg}{dPg} = \frac{k_2 / k_5 [Eg]}{[Pg]} = 1$$

Where \(r_c = k_4 / k_5\), then

$$\frac{dEg}{dPg} = r_c \cdot \frac{Eg}{[Pg]} = 1$$

The solution of Eq 15 gives a mathematical expression for Eg as a function of Pg and \(r_c\) as follows:

$$Eg = \left[ \frac{Eg_0}{[Pg]^c} \right] \cdot [Pg]^c - \left[ \frac{1}{1 - r_c} \right] \cdot [(Pg_0)^c \cdot [Pg]^c - Pg]$$

By substitution of Eg from Eq 16 in Eq 14, a function f(Pg, r_c) is obtained:

$$f(Pg, r_c) = \left[ \frac{Eg_0}{[Pg_0]^c} \cdot [Pg]^c - \left[ \frac{1}{1 - r_c} \right] \cdot [(Pg_0)^c \cdot [Pg]^c - Pg] - (Eg_0 + P_0g) - 2 \cdot g - Pg)$$

The rate Eq 5 and 6 take the following form:

$$\int (Pg, r_c) = \int \frac{V}{V_{Pog}} = \frac{-k_4 t}{k_5}$$

The Arrhenius parameters \(A_c\) and \(E_c\) for \(k_c\) were determined by multiple regression by using Eq 20 shown below:

$$k(Pg, r_c) = A_c \cdot e^{-E_c / R T} \cdot t$$

Equation 20 corresponds to the following mathematical expression:

$$Y = b_0 + b_1 X_1 + b_2 \cdot X_2$$

where: X1 and X2 are different.

**SIMULATION OF THE REACTION SYSTEM**

**Numerical Procedure.** The above described kinetic model works following the next steps: i) The experimental data reaction-evolved EG vs time are obtained by carrying out reactions 3 and 4. ii) Several values for \(r_c\) are assumed in the interval of 0.01 to 1.5. iii) With data from the two previous steps and the initial values for Eg and Pg, substituted in Eq 16 a Pg value is obtained for each experimental point. iv) The kinetic constant \(k_c\) as a function of (Pg, r_c) and time is calculated through Eq 18. v) With Eq 20, the Arrhenius equation parameters are obtained for \(k_c\). v) Differential Equations 5 to 7 are simultaneously solved. And vii) A value for \(r_c\) is obtained by comparison of the experimental and the calculated EG according to Yamans et al. (8). This mathematical procedure is shown in Fig. 2.

By a numerical integration of Eq 19 and by following the same calculation procedure used above to obtain \(k_c\), the Arrhenius equation parameters A and E for the kinetic constant \(k_4\) are also obtained.
RESULTS AND DISCUSSION

Table 2 shows the amount of reactants, POE and BHET, charged to the reactor (OR) and the amount of products, oligomer and EG, obtained from the prepoly transesterification reactions 3 and 4. Experimental EG data used in the present work were generated from the non-isothermal prepoly transesterification re-

<table>
<thead>
<tr>
<th>Reagents</th>
<th>POE</th>
<th>BHET</th>
<th>Oligomer*</th>
<th>EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles</td>
<td>0.45</td>
<td>3</td>
<td>—</td>
<td>0.992</td>
</tr>
<tr>
<td>Equivalents</td>
<td>—</td>
<td>6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Grams</td>
<td>450</td>
<td>762</td>
<td>1150.5</td>
<td>61.5</td>
</tr>
</tbody>
</table>

*It contains 0.04 wt% of TBP catalyst.
were compared with experimental ethylene glycol data, as shown in Fig. 4. In Fig. 4, it is observed that an \( r_c \) value of 0.1 gives the best fit of experimental data. The results of the simulation are shown in Fig. 5, these described the behavior of products and reactants for \( r_c = 0.1 \). In Fig. 5, \( \text{EG} \) is the hydroxyl end groups of unreacted BHE, calculated through Eq 5. \( \text{FP} \) is the moles of nonreacted POE calculated through Eq 6, and \( g \) is the moles of reacted EG calculated through Eq 7.

The \( A \) and \( E \) values of the Arrhenius equation, for both prehomopolytransesterification and precopolytransesterification reactions, which were found by multiple regression, are reported in Table 3.

Two mathematical expressions have been found for the kinetic constants, \( k_c \) and \( k_H \), which are shown below, Eq 24 and 25. These mathematical expressions will predict the \( k_c \) and \( k_H \) values at different temperatures for the oligomerization reactions 3 and 4, involved in the copoly (ethylene-polyoxyethylene terephthalate) production process.

\[
\ln k_c = - \frac{9844}{T} + 21.52
\]

\( T \)[\( K \)]  

\[
\ln k_H = - \frac{9755.4}{T} + 19.03
\]

The kinetic constants \( k_c \) and \( k_H \) are represented in Fig. 6 as functions of the average degree of polymerization, which was calculated by means of Eq 12. It is
important to clarify that neither the degree of polymerization, $D_{n}$, nor the molecular weight, $M_{n}$, have any importance to the kinetic predictions for the following reason: The polyoxyethylene, POE, of molecular weight of about 1500 plays an important role in the immiscibility of both hard and soft segments. Nevertheless, this kinetic study used a POE of molecular weight of 1000, that is, much smaller than 1500, and a level in the final oligomer of about 39 wt%. This last formulation guarantees the miscibility of the soft segment into the hard segment amorphous phase according to Legge et al. and Cellà (1, 3).

The behavior of the number-average degree of polymerization, $D_{n}$, as a function of the reaction time was determined and is shown in Fig. 7.

CONCLUSIONS

The kinetic parameters $A$ and $E$ of the oligomerization reactions were determined by using the kinetic model developed here. The simulation of the differential Equations 5–7 predicts the evolution of ethylene glycol (EG), polyoxyethylene glycol (POE) and bis (2-hydroxyethylene terephthalate) (BHET) and consequently the average degree of polymerization, $D_{n}$, in the copoly (ethylene-polyoxyethylene terephthalate) production process. The reactivity ratio, $r_{c}$, was determined by minimizing the variation between theoretical and experimental amounts of ethylene glycol produced. The kinetic constant, $k_{n}$, of the homo-oligomerization reaction, between two BHET molecules, was found to be several times smaller than the kinetic constant, $k_{c}$, of the co-oligomerization reaction, between BHET and POE. The $A$ and $E$ values of the co-oligomerization reaction that best fit experimental data were found, by multiple regression, to be $2.22 \times 10^{5}$ cm$^{3}$/mole-min and $8.194 \times 10^{4}$ J/mole, respectively. A possible molecular explanation proposed by the authors is the following: As the polyoxyethylene, POE, is less viscous than the bis (2-hydroxyethyleneterephthalate), BHET, its molecules possess greater mobility, and as both have about the same ratio by weight, POE can be reacted since the beginning. Therefore, the kinetic constant of the copolycondensation reaction, $k_{c}$, is larger than that of the homopolycondensation reaction, $k_{n}$.

NOMENCLATURE

COPEPOET copoly(ethylene-polyoxyethylene terephthalate)
POE poly(oxytheylene)

**Table 3. Values of A and E Obtained by Multiple Regression.**

<table>
<thead>
<tr>
<th>Deviation</th>
<th>$r_{c}$</th>
<th>$A$, cm$^{3}$/mole-min</th>
<th>$E$, J/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>0.01</td>
<td>$3.95 \times 10^{2}$</td>
<td>$1.1142 \times 10^{6}$</td>
</tr>
<tr>
<td>0.003</td>
<td>0.1</td>
<td>$2.22 \times 10^{6}$</td>
<td>$6.194 \times 10^{4}$</td>
</tr>
<tr>
<td>0.075</td>
<td>0.5</td>
<td>$9.02 \times 10^{6}$</td>
<td>$6.244 \times 10^{4}$</td>
</tr>
<tr>
<td>0.211</td>
<td>1.5</td>
<td>$3.72 \times 10^{6}$</td>
<td>$6.214 \times 10^{4}$</td>
</tr>
</tbody>
</table>

**Fig. 5.** Generated EG and unreacted BHET and POE versus reaction time for $r_{c}$ equal to 0.1.

**Fig. 6.** Kinetic constants as a function of the degree of polymerization.
Fig 7. Degree of polymerization, $DP_n^w$, as a function of the reaction time.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{EG}$</td>
<td>molar volume of EG</td>
</tr>
<tr>
<td>$V_{POE}$</td>
<td>molar volume of POE</td>
</tr>
<tr>
<td>$V_{mf}$</td>
<td>final volume of methanol</td>
</tr>
<tr>
<td>$m_f$</td>
<td>final moles of methanol</td>
</tr>
<tr>
<td>$E_g$</td>
<td>moles of EG generated from the oligomerization reactions</td>
</tr>
<tr>
<td>$r_c$</td>
<td>reactivity ratio $k_h/k_c$</td>
</tr>
<tr>
<td>$n_{DMT}$</td>
<td>initial number of moles of DMT</td>
</tr>
<tr>
<td>$R$</td>
<td>universal constant of the gases</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$DP_n$</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>$p$</td>
<td>degree of conversion of functional groups</td>
</tr>
</tbody>
</table>

Subscript "0" denotes moles or equivalents taken initially.

REFERENCES