Polycondensation Rate of Poly (ethylene terephthalate) at Reduced Pressure

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In the ethylene glycol terephthalate (EGT) polycondensation process, the reaction product removal rate affects the progress of the reaction, because the polycondensation rate of poly (ethylene terephthalate) (PET) is slow and its equilibrium constant is small. In order to study the rate of this reaction separately from that of product removal, the main reactions which lead to the formation of PET, the side reactions which result in polymer degradation and influence the reaction product removal rate under reduced pressure are considered in this paper.

Using an open system experimental apparatus, the relation between time and degree of polymerization is investigated. Polycondensation process experiments were carried out under a reduced pressure of 0.6 Torr at 275°C, 280°C and 285°C and continuous stirring at 40 rpm.

The number-average degree of polymerization is calculated from the relative and intrinsic viscosities at 20°C.

The rate of polycondensation reaction was then calculated using a computer and the frequency factor, which is a function of catalyst concentration, and activation energy were investigated. These values are of great asset in the understanding of polycondensation reactions.

1. Introduction

Plants with a production capacity of 60 t/day of poly(ethylene terephthalate) (PET) have already been constructed, and plants of still larger production capacity can be constructed, but the construction costs are prohibitive now. Thus, before a large, viable PET plant can be constructed, the polycondensation reaction rate, which is a function of temperature, nature and concentration of the catalyst, must more accurately be determined. However, because the polycondensation rate of PET is slow and its equilibrium constant is small, and because the reaction product removal rate, or the diffusion mass transfer rate, affects the progress of the reaction, no investigator have been able to cope with these problems under industrial conditions yet.

In order to calculate the rate constant of polycondensation reaction from the experimental results, the influence of mass transfer must be taken into account by use of a combined model of chemical reaction and mass transfer. The diffusion rate of the reaction products is expressed as a function of the configuration of the reactor, the mixing element, the surface area of diffusion, the viscosity of reaction mixture and others.

Challa7) calculated the rate of polycondensation reaction at temperatures where the degradation reactions did not exist in a closed system. Kobayashi3) and Tomita5) calculated the rates in an open system, but taking into account the degradation reactions, however, their experimental conditions were steady thin film state. Pell4) calculated the reaction rate and the diffusion rate of the reaction product in thin film state in an open system, but the degradation reactions were not considered.

Accordingly, the results they obtained were not of sufficient accuracy to warrant their use under industrial conditions.

In this paper, experiments of PET polycondensation reaction were carried out, with continuous stirring, in an open system in a stainless steel batch reactor in the pressure of a Sb2O3 catalyst and a stabilizer, (C6H5O)3PO, and the rate of polycondensation was more rigorously calculated by taking into account of the diffusion rate of the reaction products and the degradation reactions in a simulated polycondensation process.

2. Experimental

2.1 Apparatus and Procedure

The PET polycondensation experimental apparatus used is shown in Fig. 1. The apparatus consists of a 1.0 l stainless steel vessel type reactor with an internal thermocouple well and a spiral, ribbon shaped mixing element. The stirring shaft
is sealed with O-rings made of biton. Constant temperature was maintained with an electrical heater, a thermocouple and an on-off controller. Pressure was controlled at 0.6 Torr with a magnetic valve, vacuum pump and cold trap. Since the viscosity increases with increase in the degree of polymerization, the stirring was held constant at 40rpm, and a torque meter was attached to the stirring shaft. The readings on the torque meter could be used to approximate the absolute viscosity value of the polymer.

2.2 Reagent

Bis-β-hydroxyethyl-terephthalate (BHET), monomer of PET, was furnished by a commercial supplier. Pure BHET was prepared by dissolving the material in water and drying repeatedly and finally by crystallization.

Polycondensation was carried out with Sb$_2$O$_3$ and (C$_6$H$_5$O)$_3$PO. Both materials were of commercial extra-pure grade and were used without further purification.

2.3 Polycondensation

Three hundred grams of BHET, the catalyst and the stabilizer were packed in the vessel and the air was purged with dry nitrogen. After about 10 minutes, when the reaction temperature had attained 150°C and the BHET had melted completely in the nitrogen atmosphere, stirring and reduction of the vessel pressure were started. After about 15 minutes, when a steady state had been attained, sampling of the reaction mixture was started and continued at regular intervals.

2.4 Analysis

The number-average degree of polymerization (DP) was calculated from the following equation.

$$[\eta] = 7.55 \times 10^{-4}(192\bar{P}_n + 62)^{0.685}$$

The intrinsic viscosity $[\eta]$ was calculated from the relative viscosity, which was determined with a 0.5% solution at 20°C, using a phenol-tetrachloroethane (1:1 w/w) mixture as a solvent. $[\eta] = (1/1+1.4(\eta_r-1.0)-1.0)/0.35$

The relation between relative viscosity and DP is shown in Fig. 2.

3 Results and Discussion

3.1 Experimental Results

Fig. 3 shows the relation between time and DP for various concentrations of catalyst. Other conditions were constant, i.e., stabilizer, 0.06% w/w BHET; temperature, 280°C; pressure, 0.6 Torr;
stirring, 40 rpm. On each curve in Fig. 3, the DP attains a maximum at certain reaction time, which is different for different catalyst concentration. But the range of the DP maximum is small. This shows the effect of stabilizers, because it is a common knowledge that a curve reaches a maximum earlier and DP is less in those cases where no stabilizers are used.

Fig. 4 also shows the relation between time and DP for various degrees of reaction temperature, but in Fig. 4, 0 on the time axis is aligned with 100 on the DP axis. As in Fig. 3, other conditions are kept constant. A comparison of Figs. 3 and 4 shows that the effect of the catalyst was larger than that of the temperature.

3.2 Calculation of Reaction Rate

From available information, the chemical reaction of PET including the degradation reactions, can be written as follows:

Main reaction

\[
\begin{align*}
2(\text{-COOCH}_2\text{CH}_2\text{OH}) & \rightleftharpoons k_1 k_2 \text{PET} + \text{EG} \\
& \text{(ethylene glycol)} \\
\text{-COOCH}_2\text{CH}_2\text{OH} + \text{-COOH} & \rightleftharpoons k_3 k_4 \text{PET} + \text{H}_2\text{O} \\
\end{align*}
\]

(1)

Side reaction

\[
\begin{align*}
\text{-COOCH}_2\text{CH}_2\text{OH} & \rightleftharpoons k_5 k_6 \\
\text{-COOH} + \text{CH}_3\text{CHO} & \rightleftharpoons k_7 k_8 \text{PET} + \text{CH}_3\text{CHO} \\
& \text{(5)}
\end{align*}
\]

Diffusion of the reaction product

\[
\frac{dC_t}{dt} = f\left(\frac{dC_{\text{OH}}}{dt}, \frac{dC_{\text{COOH}}}{dt}, N, P, \mu, S, P^*, C_l, K_D\right)
\]

Equation (6) has already been investigated and confirmed in batch and continuous process applications in small and large scale plants. The details will be mentioned elsewhere. Reactions (1), (2) and (5) are second-order and (3) and (4) are first-order reactions. The terminal-vinyl group of Eq. (4) behaves like an ethyl-ester end-group of Eq. (1), so that a model of the reaction rate of an ethyl-ester end-group can be constructed as in the following equation.
\[ \frac{dCOH}{dt} = k_4 COH - k_5 COH \cdot CDES - \frac{dCOOH}{dt} + k_6 COH - k_7 CDES \] (7)

Similarly, the reaction rate and material balance equations for each component were constructed, and each rate constant was determined with experimental data by computer calculations that followed the flow chart shown in Fig. 5. But it was too complicated to calculate all the values of \( k_1 \sim k_{10} \) by trial and error. Thus, under reduced pressure at 275°C, the following assumptions were made from the available information\(^3\),\(^10\) and the result of adaption of the experimental data\(^11\).

\[ k_1 = k_2, \quad k_1 = 0.25k_3, \quad k_3 = 4.0k_4 \]
\[ k_5 = k_6, \quad k_7 = k_8, \quad k_5 = 180k_7 \] (8)

Similar assumptions, that is, the coefficients were changed, were also made by considering the activation energy\(^3\),\(^11\) at 280°C and 285°C. The reaction rate constant \( k_1 \) can be expressed by

\[ k_1 = k_{1,cat} + k_{1,non} \] (9)

Arrhenius plots of the reaction rate constant are shown in Fig. 6. Which indicated the existence of satisfactory linear relations. The activation energy was calculated from the slopes of these lines.

\[ E_{1,cat} = 18.5 \text{ kcal/mol} \] (10)
\[ E_{1,non} = 40.0 \text{ kcal/mol} \] (11)

This value of Eq. (10) lies between the values obtained by Tomita\(^5\) and Kobayashi\(^3\), because in this study, the rate constant of polycondensation reaction was calculated by separating the diffusion rate from the reaction products.

Using Eqs. (10), (11), and the Arrhenius equation, frequency factor \( A \) could be calculated. Plots of \( A \) vs. catalyst concentration are shown in Fig. 7. Using Fig. 7, frequency factors of \( k_{1,cat} \) were represented by the following linear relation.

\[ A \times 10^{-8} = 84.5 \cdot C \] (12)

According to Arrhenius’s equation, the rate of polycondensation reaction was represented, using Eqs. (9), (10), (11) and (12), by

\[ k_1 = 84.5 \cdot C \cdot 10^{8} \cdot e^{-18,500/RT} + 4.0 \cdot 10^{16} \cdot e^{-40,000/RT} \] (13)

Fig. 8 shows deviations of the calculated value of DP from the experimental data which were account within ±9%.

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Nomenclature

\[ A = \text{frequency factor} \quad (\text{mol}^{-1}\text{mol}^{-1}\text{hr}^{-1}) \]

\[ C_x = \text{weight per cent of catalyst in BHET} \quad (\%) \]

\[ C_i = \text{concentration of } i \text{ component in reaction mixture} \quad (\text{mol}^{-1}\text{m}^{-3}) \]

\[ E_1 = \text{activation energy} \quad (\text{cal} \text{mol}^{-1}) \]

\[ K_d = \text{diffusion constant} \quad (\text{mol} \text{m}^{-3} \text{hr}^{-1}) \]

\[ k_1, k_2, k_3, \ldots k_9, k_{10} = \text{polycondensation reaction rate constant} \quad (\text{mol}^{-1}\text{mol}^{-1}\text{hr}^{-1}) \]

\[ N = \text{number of revolutions} \quad (\text{rpm}) \]

\[ P = \text{pressure of reaction} \quad (\text{Torr}) \]

\[ P_n = \text{number of average DP} \quad (\text{-}) \]

\[ P_i = \text{saturated vapor pressure of component } i \quad (\text{Torr}) \]

\[ R = \text{gas constant} \quad (1.987 \text{cal} \text{mol}^{-1}\text{K}^{-1}) \]

\[ S = \text{surface area of diffusion} \quad (\text{m}^2) \]

\[ T = \text{temperature} \quad (\text{K}) \]

\[ [\eta] = \text{intrinsic viscosity} \quad (\text{cm}^2\text{g}^{-1}) \]

\[ \eta_r = \text{relative viscosity} \quad (\text{-}) \]

\[ \mu = \text{melting viscosity} \quad (\text{poise}) \]

Subscript

\[ \text{OH} = \text{ethyl-ester end-group} \]

\[ \text{COOH} = \text{carboxyl end-group} \]

\[ \text{DES} = \text{di-ester radical in polymer} \]

\[ \text{exp} = \text{experimental value} \]

\[ \text{cal} = \text{calculated value} \]

\[ \text{cat} = \text{with catalyst} \]

\[ \text{non} = \text{without catalyst} \]

References

5) Tomita, K., Polymer, 14, 50 (1973).

要 旨

減圧下におけるポリエチレンテレフタラートの重総合反応速度

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ポリエチレンテレフタラートの重総合反応は、速度定数および平衡定数が小さいため副生物の拡散速度が反応の進行に大きく影響する。本研究では純粋な化学反応速度を求めるために実験および解析を行った。実 験 設 置（Fig. 1）は約 1.0 l の SUS 製で触媒に三酸化アンチモン、安定剤にリン酸トリフェニルを用い280℃、0.6 Torr、40 rpm、安定剤濃度 0.06% (w/w) な らびに触媒濃度を 0.01、0.03、0.06 および 0.09% (w/w)（モノマー）での実験を行った（Fig. 3）。さらに無触媒の場合と触媒濃度 0.06%、0.6 Torr、40 rpm、安定剤濃度 0.06% で280℃、275℃、285℃ での各温度条

本報を「重総合反応に関する研究」第2報とする。

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Keyword

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