Modeling of Semibatch Direct Esterification Reactor for Poly(ethylene terephthalate) Synthesis

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SYNOPSIS

A comprehensive kinetic model for a semibatch direct esterification reactor has been developed. The solid–liquid equilibrium of terephthalic acid was considered in the modeling. Effects of the monomer feed ratio, reaction temperatures, and oligomer addition on the conversion, degree of polymerization, and the formation of diethylene glycol were studied. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is an important material for the production of synthetic fibers, films, beverage bottles, and molded plastic parts. The first step in the synthesis of PET is the esterification process in which the main reaction is the direct esterification of terephthalic acid (TPA) with ethylene glycol (EG). Generally, catalysts are not used for the esterification process, because acid end groups of TPA can catalyze the reactions. In this process, bis(hydroxyethyl)terephthalate (BHET) and some linear oligomers are prepared, and water is evolved as a condensation byproduct. The products (BHET and its oligomers) usually have a degree of polymerization (DP) of 2–5, and they are polymerized to higher molecular weight polymers in the further stages usually with a metal catalyst. In the semibatch esterification process, the temperature of the reaction mixture (TPA and EG) is increased gradually, and the vapors emerging from the reactor are passed through a distillation column. The condensation byproduct, water, is separated from EG in the column, and the glycol is refluxed to the reactor. The main purpose here is to provide useful information for the direct esterification process in a semibatch reactor.

Two of the main objectives in operating an esterification reactor are to achieve a high conversion of TPA in short reactor residence time and to minimize the amount of byproducts such as diethylene glycol (DEG) from undesirable side reactions. It is very useful to predict the optimum reactor conditions for this kind of process by a computer simulation. Although many simulation studies[1–4] have been made to develop mathematical models for the continuous esterification process, little has been reported on the modeling of the semibatch esterification process. There are some modeling works[5–8] on the semibatch transesterification of dimethyl terephthalate with EG, which is another route to synthesize PET. Modeling of semibatch esterification of TPA with EG, however, is complicated because of the extremely low solubility of TPA. In this study, we develop a comprehensive kinetic model for the acid-catalyzed reactions in a semibatch esterification reactor using the polymer segment approach[9] that is a kind of functional group model. The effect of key operating variables on the reactor performance is investigated.

ASSUMPTIONS AND MODELING

Polymer Segment Approach

In a polymerization process, polymers of varying chain lengths are formed. A modeling approach that properly accounts for varying chain lengths is important to establish the framework for representing polymers in the reaction kinetics. There are two kinds of modeling approaches: molecular species

Table I   Molecular Structures of Components Considered

Symbol	Descriptions	Molecular Structure
TPA	Terephthalic acid	$HOOC$—◯—$COOH$
EG	Ethylene glycol	$HOCH_2CH_2OH$
W	Water	H_2O
tEG	EG end group	$HOCH_2CH_2O$—
tTPA	TPA end group	$HOOC$—◯—CO—
bEG	EG repeat units	—OCH_2CH_2O—
bTPA	TPA repeat units	—OC—◯—CO—
bDEG	Diethylene glycol repeat unit	—$OCH_2CH_2OCH_2CH_2O$—

models and functional group models. Generally speaking, molecular species models are more comprehensive than functional group models in providing the information of product composition. However, molecular species models require more time to calculate a result, because each unique polymer molecule is tracked as an independent component. In this study, the polymer segment approach,[9] a functional group approach, is used to establish the overall reaction network.

Polymerization reactions can be regarded as reactions between two reactive functional groups. All components considered in the reaction scheme are listed in Table I. Here, we define five different oligomeric segments: tEG, tTPA, bEG, bTPA, and bDEG ("t" and "b" represent "terminal functional group" and "bound monomer repeating units," respectively).

Using the polymer segment approach, the number-average DP of the oligomers produced can be written as

$$DP = \frac{\{[tEG] + [bEG] + [tTPA] + [bTPA] + [bDEG]\}}{\{[tEG] + [tTPA]\}}. \quad (1)$$

Reaction Scheme

The complete set of reactions considered here is shown in Table II. In this table, k_i ($i = 1\text{--}6$) are the "effective" rate constants (L/mol·min) and K_i ($i = 1\text{--}5$) are the equilibrium constants. Reactions 1–4 are the esterification reactions, and reaction 5 is the polycondensation reaction. It is known that DEG is formed in the esterification stage and in the beginning of the polycondensation stage, whereas acetaldehyde, acid end groups, and vinyl end groups are formed mainly in the final stages of polycondensation.[10] Reaction 6 is a side reaction leading to the DEG formation. Although several reaction mechanisms have been proposed to describe the DEG formation reaction, the possibility of reaction 6 is considered only. The intermolecular acidolysis and alcoholysis are not explicitly accounted for in the reaction scheme because in these reactions, the chain length is redistributed but the segments are conserved.

In the direct esterification process, the limited solubility of TPA in EG might bring in mass transfer limitation due to the slow rate of TPA dissolution. In this study, the process is assumed to be controlled by the rate of the reactions.

Mathematical Model

Assuming that functional group reactivity does not depend on the polymer chain length, material balance equation of each component in a semibatch reactor can be written as

Table II   Reaction Scheme of Esterification Process Considered in this Work

No.	Reactions	Rate Constants (forward, reverse)
1	EG + TPA ⇌ tEG + tTPA + W	k_1, k_1/K_1
2	EG + tTPA ⇌ tEG + bTPA + W	k_2, k_2/K_2
3	tEG + TPA ⇌ bEG + tTPA + W	k_3, k_3/K_3
4	tEG + tTPA ⇌ bEG + bTPA + W	k_4, k_4/K_4
5	tEG + tEG ⇌ bEG + EG	k_5, k_5/K_5
6	tEG + tEG → bDEG + W	k_6

$$d[\text{TPA}]/dt = V\{-R_1 - R_3\} \tag{2}$$

$$d[\text{EG}]/dt = V\{-R_1 - R_2 + R_5\} \tag{3}$$

$$d[\text{tEG}]/dt = V\{R_1 + R_2 - R_3$$
$$- R_4 - 2R_5 - 2R_6\} \tag{4}$$

$$d[\text{tTPA}]/dt = V\{R_1 - R_2 + R_3 - R_4\} \tag{5}$$

$$d[\text{bEG}]/dt = V\{R_3 + R_4 + R_5\} \tag{6}$$

$$d[\text{bTPA}]/dt = V\{R_2 + R_4\} \tag{7}$$

$$d[W]/dt = V\{R_1 + R_2 + R_3 + R_4 + R_6\} \tag{8}$$

$$d[\text{bDEG}]/dt = V\{R_6\} \tag{9}$$

where V is the liquid volume of the reaction mixture. R_i (i = 1–6) are the reaction rates for reactions 1–6 and are shown in Table III. Here, [TPA] is the mole number of TPA dissolved in the liquid phase. At the equations above, the assumptions of perfect mixing and constant melt density are used.

For the calculation of the concentrations of volatile components (EG and water) in the liquid and in the vapor phases, a quasi-steady state assumption is used for the vapor–liquid equilibrium in small increments of time. No vapor phase calculations of the polymer are considered because the polymer is not volatile. The vapor phase is assumed to follow the ideal gas law

$$p_i = p_t y_i \tag{10}$$

where p_t is the total pressure of the reactor and p_i and y_i the partial pressure and the mole fraction of component i in the vapor phase. Using the Raoult's law, the partial pressure of volatile components is given by

$$p_i = p_i^* x_i \tag{11}$$

where p_i^* is the saturated vapor pressure of volatile component i and x_i the mole fraction of component i in the liquid phase. The vapor pressure data of water and EG are obtained from a pure component databank.[11]

As indicated in Table II, reactions 1–4 are essentially reversible. In industrial practice, the condensation byproduct, water, is distilled off continuously from the reactor to promote the forward reactions. Thus, the concentration of water should be updated by subtracting the equivalent mole number of the condensed water removed from the reactor.

Because the solubility of TPA in EG is extremely low and the esterification is occurring in the liquid

Table III Reaction Rates of Reactions Defined in Table II

$R_1 = \{4\, k_1\, [\text{EG}]\, [\text{TPA}] - (k_1/K_1)\, [\text{tTPA}]\, [W]\}/V^2$
$R_2 = \{2\, k_2\, [\text{EG}]\, [\text{tTPA}] - 2\, (k_2/K_2)\, [\text{bTPA}]\, [W]\}/V^2$
$R_3 = \{2\, k_3\, [\text{tEG}]\, [\text{TPA}] - (k_3/K_3)\, [\text{tTPA}]\, [W]\}/V^2$
$R_4 = \{k_4\, [\text{tEG}]\, [\text{tTPA}] - 2\, (k_4/K_4)\, [\text{bTPA}]\, [W]\}/V^2$
$R_5 = \{k_5\, [\text{tEG}]\, [\text{tEG}] - 4\, (k_5/K_5)\, [\text{bEG}]\, [\text{EG}]\}/V^2$
$R_6 = \{k_6\, [\text{tEG}]\, [\text{tEG}]\}/V^2$

k_i, the effective rate constants (L/mol·min); [ ], the mole number in the liquid phase.

phase, the solid–liquid equilibrium of TPA should be considered to calculate the concentration of the dissolved TPA in the liquid phase. Assuming that the solubility of TPA in water is negligible, the mean solubility of TPA in the reaction mixtures can be given by[2]

$$\alpha = \alpha_{\text{EG}} W_{\text{EG}} + \alpha_{\text{BHET}} W_{\text{OLG}} \tag{12}$$

where α_{EG} and α_{BHET} are the temperature dependences of the solubility of TPA in EG and in BHET, respectively, and W_{EG} and W_{OLG} are the weight fractions of EG and of oligomers, respectively. The experimental data by Yamada et al.[2] are used for the calculation of α_{EG} and α_{BHET}.

In trying to calculate the concentration of each component with reaction time, the material balance equations and the equilibrium equations for volatile components and solid TPA should be solved simultaneously. Also, one must consider the change in reaction volume due to the continuous removal of water and the dissolution of solid TPA into liquid TPA that can participate the reactions.

A numerical procedure can be used to solve the material balance equations and the equilibrium equations simultaneously. In this study, the fourth-order Runge–Kutta method is used. The numerical values used are summarized in Table IV.

Acid-Catalyzed Reactions

The rate constants are dependent of temperature, catalyst type, and catalyst concentration. According to the previous works,[12,13] it can be assumed that the rate constants for the acid-catalyzed esterification and polycondensation are written as

$$k_i\ (i = 1\text{--}5) = A_i C_{\text{acid}} \exp(-E_i/RT) \tag{13}$$

where A_i is the preexponent factor (L^2/mol^2·min), E_i is the activation energy, R is the gas constant, T is the temperature in K, and C_{acid} is the total acid

Table IV Numerical Values Used for the Calculation

1) Temperature dependences of solubility of TPA in EG and in BHET
   α_{EG} = 9062 exp ($-4877/T$) (TPA moles in 1 kg EG)
   α_{BHET} = 374 exp ($-3831/T$) (TPA moles in 1 kg BHET)
   (T is in the absolute temperature)
2) Vapor pressures of EG and water
   For EG, ln p = 79.3 + ($-10105/T$) + ($-7.5 \times$ ln T) + $7.3e^{-19} \times T^6$
   For W, ln p = 73.6 + ($-7259/T$) + ($-7.3 \times$ ln T) + $4.2e^{-6} \times T^2$
   (p is vapor pressure in Pa)
3) Density of TPA: ρ = 1.371 (g/mL)
4) System pressure (p_t) = 1.5 (atm)

concentration (mol/L). In this study, C_{acid} can be defined as

$$C_{acid} = \{2[TPA] + [tTPA]\}/V \qquad (14)$$

where V is the volume of the liquid phase. Acid catalysis influences both the forward and the reverse reactions. Acid catalysis is not considered for the DEG formation reaction in the model.

EXPERIMENTAL

The direct esterification experiments were carried out using a pilot plant reactor with a reaction volume of 12 L. The pilot plant was designed to resemble an industrial reactor system. A distillation column was attached to the reactor to distill off the reaction byproduct, water. The column was maintained at approximately 100–140°C throughout the reaction. The water vapor was condensed and collected in a graduated vessel, and the rate of water evolution was used to monitor the progress of esterification.

The reactor was charged with the predetermined amount of TPA powder (fiber grade, Samsung Petrol. Chem. Co.) and EG (Amoco Co.). The mixture was first rapidly heated from 140 to 230°C for 70 min approximately and then gradually heated up to 250°C (or 240°C) with heating rate of 4.8°C/h (or 2.4°C/h). The reactor temperature is controlled accurately (±2°C) by a PID temperature controller. The reactor was pressurized at 1.5 atm throughout the reaction.

RESULTS AND DISCUSSION

Estimation of Kinetic Parameters

For a simulation study, the rate constants k_i (i = 1–6) and the equilibrium constants K_i (i = 1–5) should be determined. It is very surprising to note that only relatively few experimental data in the open literature can be used in developing a simulation model for the semibatch direct esterification process. In this study, we try to estimate the rate constants by fitting the model results against our experimental data.

From the previous works,[1,7,8,10] it can be assumed that the reactivity of acid end group on TPA is equivalent to the reactivity on oligomer chain (tTPA), whereas the reactivity of hydroxyl end group on EG is twice of the reactivity on half-esterified EG (tEG), i.e., $k_1 = k_2 = 0.5k_3 = 0.5k_4$. In reverse esterifications, water attacks an ester link, splitting the polymer molecule into two smaller molecules. Similarly, it can be assumed that $(k_1/K_1) = (k_2/K_2)$ and $(k_3/K_3) = (k_4/K_4)$.

Polycondensation reactions occur when a hydroxy end group (tEG) attacks an ester link near the end of a oligomeric chain, releasing free EG or DEG as a byproduct. In comparison of the polycondensation reactions with the esterification reactions between hydroxy end group (tEG) and carboxyl end group (tTPA), both have a very similar reaction mechanism. The nucleophiles and electropiles of the two reactions are the same as each other. The only difference in the reaction mechanism is the leaving group: EG in the polycondensation and water in the esterification. Hence, we assume in this study that the rate constants of the two reactions are same, i.e., k_3 ($=k_4$) = k_5, and they have the same activation energy value. This assumption is useful to simplify the determination of the kinetic parameters, although accurate kinetic parameters are essential to the development of a rigorous process model.

The equilibrium constants for the main reactions have been examined in a number of studies, and it is generally accepted that K_1 ($=K_2$), K_3 ($=K_4$), and K_5 are 2.50, 1.25, and 0.5, respectively.[5] No experimental result for the rate constant for the DEG formation has been published. For the estimation of k_6, we use the kinetic parameters used in a simulation study of Ravindranath and Mashelkar.[1]

In this study, once we adjusted the value of k_1 to match the experimental data, all of the main reaction rates, k_i (i = 1–5), could be determined. In Figure 1, the model results are fitted against four experimental data sets. Here, the adjusted rate con-
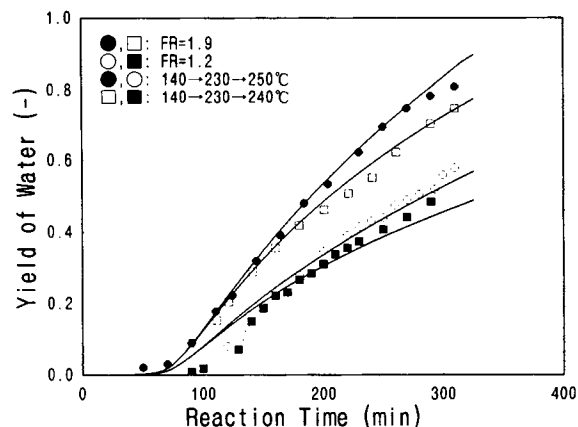
Figure 1 Estimation of the reaction rate constants by fitting the model results against the experimental results. The solid lines are calculated by the model using the kinectic parameters shown in Table V.

stant of the reaction 1 is $k_1 = 5.62 \times 10^4 \exp(-18,000/RT)$ $(L/mol)^2/min$, and all of rate constants used are summarized in Table V. It is noted that the model fits the experimental data very well for high monomer feed ratio cases, but there is a considerable deviation for low monomer feed ratio cases. The deviation might be arising from the mass transfer limitation of TPA from the solid phase to the liquid phase. In the following sections, we investigate the influence of different operating variables on the reactor performance using the reaction rate constants fitted against the experimental data.

Overall Aspect of Esterification Process

Figure 2 shows the normalized weight fraction of each component in the reaction mixture with reaction time at a constant temperature. For the calculation, it is assumed that the monomer feed ratio (FR = $[EG]_0/[TPA]_0$) is 1.9, reaction temperature 250°C, and reactor pressure 1.5 atm, which are very close to the operating conditions used in many industrial processes. ($[EG]_0$ and $[TPA]_0$ are the total mole numbers of EG and TPA in the feed, respec-

tively.) Because the amounts of DEG produced and water in the mixture under the given condition are relatively low, the profiles for DEG and water cannot be seen in this figure. From this figure, one can see that the solid TPA keeps dissolving in the reaction melt as reaction proceeds and then it completely disappears at a certain time (t = 130 min). It is interesting to note that the amount of the liquid TPA is almost unchanged until the complete dissolution of solid TPA is reached. This implies that the solid TPA acts as a reservoir supplying the liquid TPA molecules, which will be consumed by the esterification reactions.

Figure 3 shows variation in the liquid volume of the reaction melt with reaction time. As shown in this figure, the dissolution of the solid TPA increases the volume of the liquid phase. After the complete dissolution of TPA, however, the volume of the liquid phase slightly decreases due to the continuous removal of water vapor.

Effect of Monomer Feed Ratio

First, we examine the effect of the monomer feed ratio (FR) on the conversion of TPA, the number-average chain length of the oligomers produced, and the DEG formation. Figure 4 shows how mole number of the undissolved solid TPA varies with reaction time at four different monomer feed ratios. It is found that the solid TPA is completely dissolved at a shorter reaction residence time as the ratio is increased. The use of large quantity of EG is useful to enhance the solubility of TPA. Moreover, the enhanced solubility of TPA accelerates the TPA consumption reactions, because the acid end groups of the dissolved TPA catalyze the reactions.

Figure 5 shows the effect of the monomer feed ratio on the fractional conversion of total acid end groups with reaction time. As reported for similar system (e.g., transesterification of DMT with EG in a semibatch reactor[7]), the conversion gradually increases as the ratio of EG to TPA increases. This indicates that more EG is available for the esteri-

Table V **Kinetic Parameters Used**

Reaction No.	Preexponent Factor (A_i)	Activation Energy (E_i)	Equilibrium Constant (K)
1, 2	5.62×10^4, $(L/mol)^2/min$	18.00, kcal/mol	2.50
3, 4	2.81×10^4, $(L/mol)^2/min$	18.00, kcal/mol	1.25
5	2.81×10^4, $(L/mol)^2/min$	18.00, kcal/mol	0.50
6	1.35×10^8, $(L/mol)/min$	29.80, kcal/mol	—

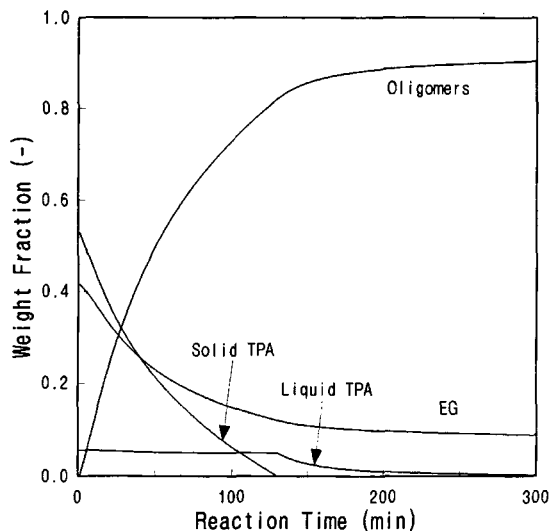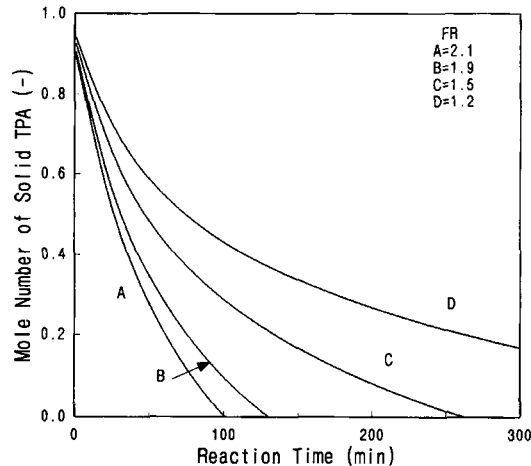**Figure 2** The weight fraction of each component in the reaction mixture with reaction time (FR = 1.9 and T = 250°C).

Figure 4 Effect of monomer feed ratio on the concentration profile of the undissolved solid TPA with time (T = 250°C). The mole numbers are nondimensionalized with respect to [TPA]$_0$.

fication reactions. It is also shown that the higher the ratio, the higher the equilibrium conversion. However, more EG hinders the polycondensation reactions and lowers the number-average chain length at a fixed conversion of acid end groups, as seen in Figure 6.

Figure 7 shows mole number of DEG produced with reaction time varying monomer feed ratio. As expected, DEG increases as the monomer feed ratio increases.

Effect of Reaction Temperature

When the monomer feed ratio is kept constant, the reaction temperature can also influence the reaction

rate. In industrial practice, the reaction temperature is gradually increased from about 100°C to about 250°C. Generally, the temperature of the reaction mixture is first rapidly increased for a shorter time and then slowly increased throughout the process. Hence, we consider two cases: constant temperature operation and nonisothermal operation with a relatively lower heating rate, which are very close to the industrial practice.

As shown in Figure 8, higher reaction temperature is useful to increase the solubility of TPA at the beginning of the process and to increase the rates of TPA consumption reactions. From Figure 9, it is shown that the fractional conversion of total acid
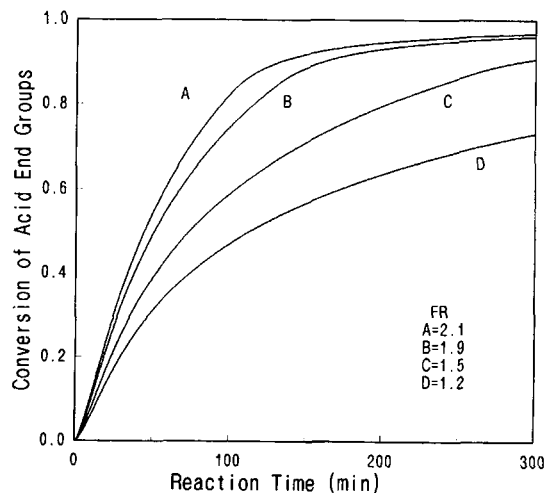

Figure 3 Variation in the liquid phase volume with reaction time. The volume is nondimensionalized with respect to the initial volume of the reaction mixture (FR = 1.9 and T = 250°C).

Figure 5 Effect of monomer feed ratio on the conversion of the acid end groups (T = 250°C).
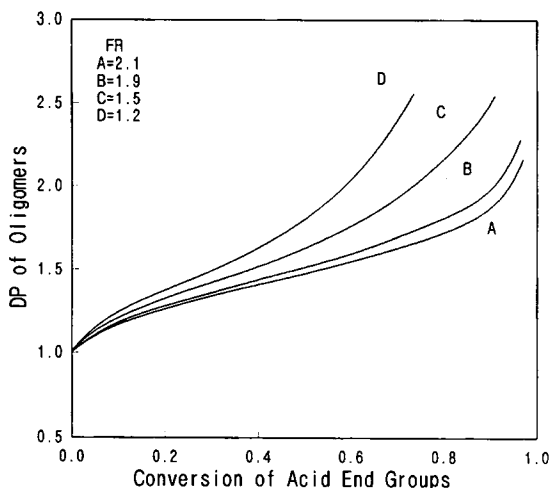
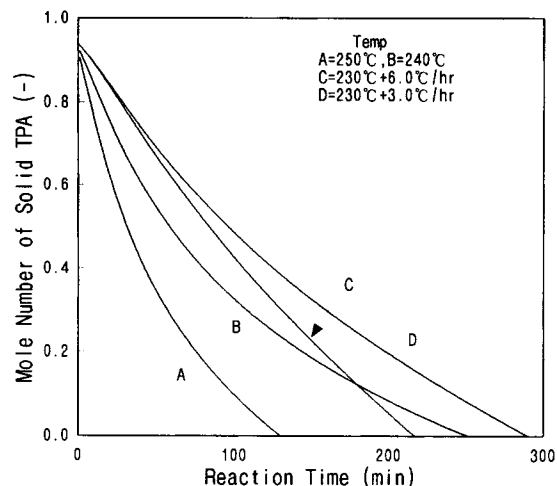**Figure 6** Effect of monomer feed ratio on the number-average chain length of the oligomers produced (T = 250°C).

Figure 8 Effect of reaction temperature on the concentration profile of the undissolved solid TPA with reaction time (FR = 1.9).

end groups increases as reaction temperature increases. Figure 10 shows the concentration profile of DEG produced with reaction time varying reaction temperature. As expected, DEG increases as the reaction temperature increases.

Effect of Adding Oligomers to the Feed

Low TPA solubility in EG requires the use of large quantities of EG, but that will not be economical in terms of the large energy requirement for EG vaporization and condensation. In an industrial process, a portion of the products from the esterification reactor is recycled to the feed, and the recycled

products are used as starting materials for the next batch to enhance the solubility of TPA in the reaction melt. Now, we examine the effect of adding oligomers to the feed on the esterification process.

The products recycled consist of mainly BHET and its linear oligomers and they may also contain unreacted TPA, EG, and water. The following molar composition for the recycled products is used in our model simulation: 1.3% TPA, 6.3% EG, 31.4% tEG, 4.8% tTPA, 19.2% bEG, 34.6% bTPA, 2.1% bDEG, and 0.3% water, which were calculated at FR = 1.5, T = 250°C and t = 300 min.

As shown in Figures 11 and 12, the addition of oligomers to the feed is useful to enhance the solubility of TPA at the beginning of the process and
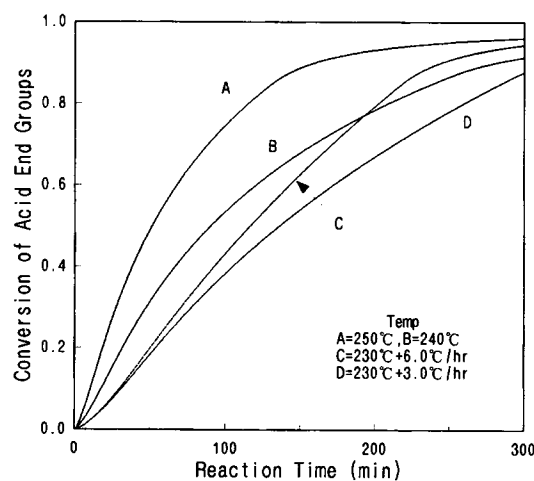

Figure 7 Effect of monomer feed ratio on the DEG formation (T = 250°C). The mole numbers are nondimensionalized with respect to [TPA]$_0$.

Figure 9 Effect of reaction temperature on the conversion of the acid end groups (FR = 1.9).
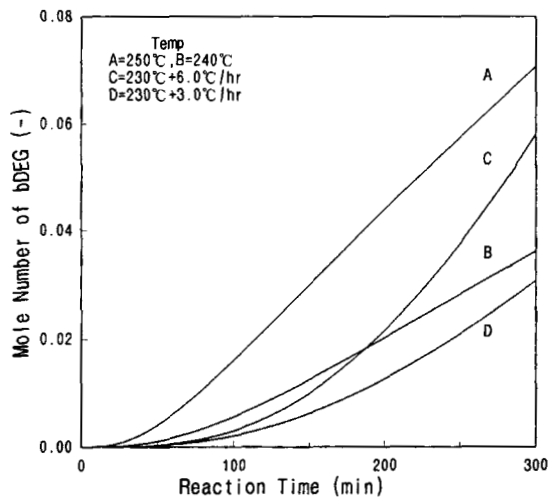
Figure 10 Effect of reaction temperature on the DEG formation (FR = 1.9).

Figure 12 Effect of adding oligomers to the feed on the conversion of acid end groups (FR = 1.5 and T = 250°C).

to increase the conversion of the reaction. The addition of oligomers, however, does not make a big difference in the equilibrium conversion at the final stage of the process, due to the considerations of chemical and phase equilibrium. As expected, the addition of oligomers increases the DEG formation as shown in Figure 13.

CONCLUSIONS

We developed a mathematical model to simulate the direct esterification process in a semibatch reactor.

The solid–liquid equilibrium of TPA was considered in our modeling, and the model simulation indicates that the solubility of TPA is one of the key factors determining the overall aspect of the reactions. The influence of various operation variables such as the monomer feed ratio, reaction temperature, and the addition of oligomers to the feed was investigated. It was found that higher ratio of EG to TPA in the feed, higher reaction temperature, and larger amount of the oligomers added are useful to enhance the solubility of TPA and to increase the conversion of the reaction. However, they also increase the amount of DEG produced. Thus, there must be an optimum value for the operating conditions at which the res-
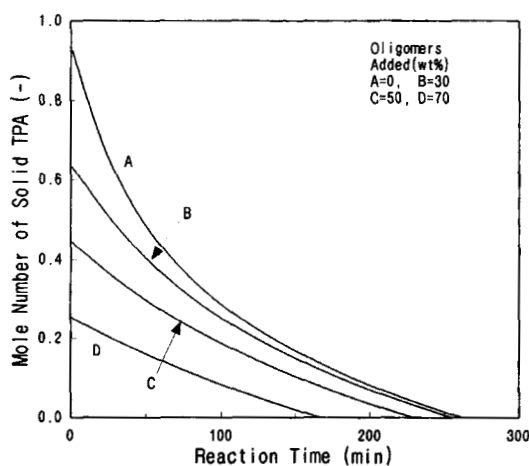

Figure 11 Effect of adding oligomers to the feed on the concentration profile of the undissolved solid TPA with reaction time. The mole numbers are nondimensionalized with respect to the total mole number of TPA units at the feed (FR = 1.5 and T = 250°C).
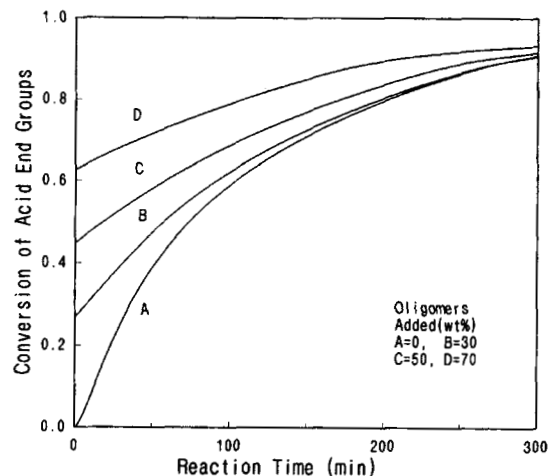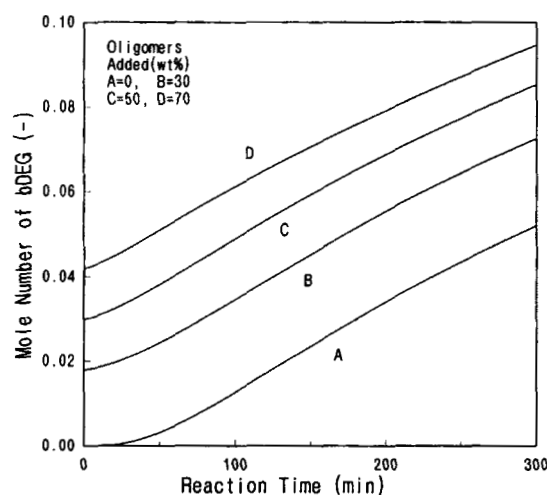

Figure 13 Effect of adding oligomers to the feed on the DEG formation. The mole numbers are nondimensionalized with respect to the mole number of TPA units at the feed (FR = 1.9 and T = 250°C).

idence time is minimum within an acceptable DEG content, and the optimum operating conditions can be easily examined by this kind of simulation study.

REFERENCES

1. K. Ravindranath and R. A. Mashelkar, *Polym. Eng. Sci.*, **22**, 610 (1982).
2. T. Yamada, Y. Imamura, and O. Makimura, *Polym. Eng. Sci.*, **25**, 788 (1985).
3. T. Yamada and Y. Imamura, *Polym. Eng. Sci.*, **28**, 385 (1988).
4. T. Yamada, *J. Appl. Polym. Sci.*, **51**, 1323 (1994).
5. K. Ravindranath and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **26**, 3179 (1981).
6. A. Kumar, V. K. Sukthankar, C. P. Vaz, and S. K. Gupta, *Polym. Eng. Sci.*, **24**, 185 (1984).
7. K. Y. Choi, *Polym. Eng. Sci.*, **27**, 1703 (1987).
8. G.-D. Lei and K. Y. Choi, *Ind. Eng. Chem. Res.*, **31**, 769 (1992).
9. T. L. Mock, C.-C. Chen, D. L. Phipps, Jr., and R. A. Greenberg, AIChE Spring National Meeting, 1988.
10. K. Ravindranath and R. A. Mashelkar, *Chem. Eng. Sci.*, **41**, 2197 (1986).
11. ASPENPCD (Pure Component Data Bank of AspenPlus™), Aspen Technology, Inc.
12. H. K. Reimschuessel and B. T. Debona, *J. Poly. Sci., Polym. Chem. Ed.*, **17**, 3241 (1979).
13. J. Otton and S. Ratton, *J. Poly. Sci., Polym. Chem. Ed.*, **26**, 2183 (1988).