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Analysis of the Esterification Process for Poly(ethylene terephthalate)

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Abstract: The first esterification reactor in the continuous polymerization of poly(ethylene terephthalate) has been analyzed by solving the material balances for the two-phase system with respect to the solubility of terephthalic acid. The Newton-Raphson method was used to solve the material balance equations instead of the Simplex method that is frequently used for finding a minimum point of a residual rather than a solution of an equation. A solution for the material balance equations, with the constraint of non-zero liquid phase fraction, could not be obtained with the solubility data of Yamada *et al.*, but could be obtained with solubilities over a minimum value that is larger than their data. Thus, the solubility data of Yamada *et al.* are considered to be too small. On the other hand, the solubility data of Baranova and Kremer are so large that they gave a solution with the liquid phase only. Based on our results, several typical solubility curves satisfying the constraint of a non-zero liquid phase fraction are suggested in this study; we studied the reaction characteristics of the system using these curves. A higher temperature and a lower pressure are preferred for reducing the content of diethylene glycol.

Keywords: esterification, PET, solubility, modeling, analysis.

Introduction

Poly(ethylene terephthalate) is made from esterification and polycondensation reactions between terephthalic acid and ethylene glycol. Side reactions produce diethylene glycol (DEG), which is an impurity. Modelling of the polymerization has been used to determine how to reduce the amount of diethylene glycol produced, and many investigators have used computer simulations of the process to investigate the reaction characteristics for specific process conditions.[1-10]

The polymerization process of poly(ethylene terephthalate) consists of esterification and polycondensation processes. Esterification takes place in a continuous flow stirred tank reactor while polycondensation takes place in a rotating disk reactor. The former usually consists of three reactors in series, in which the esterification reaction occurs in the early stage of the polymerization reaction. The latter consists of two reactors in series, which produce a polymer that has the appropriate properties for use in downstream applications.

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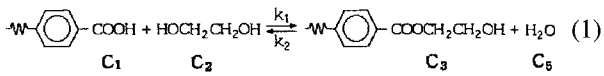
The reaction mechanisms are basically the same in both reactors, but the major reactions are determined by the stage of conversion and the process characteristics. That is, in the continuous flow stirred tank reactor, the major reaction is esterification, whereas in the rotating disk reactor the major reaction is polycondensation. By using different types of reactors in each process one can maximize the efficiency of the polymerization because control of the water content becomes easier.

The purpose of this research is to analyze the characteristics of the first esterification process in a continuous stirred tank reactor by mathematical modelling and simulation. Modelling and simulation of the esterification process have been attempted by many investigators including Ravindranath and Mashelkar[1-4] and Yamada *et al.*[5-10] The reaction mechanisms suggested by the two major research groups conform in the mechanisms of the esterification and polycondensation reactions, but differ in the mechanisms of the side reactions that produce diethylene glycol. The mechanisms of the side reactions are not yet clearly identified, so well designed and better experiments are needed. Another difference between the two research groups is the way they obtain the vapor pressures and mole fractions of water and ethylene glycol. Ravindranath and Mashelkar[1] fixed the concentration of acid end-group based on the observation by Kemkes.[11] On the other hand, Yamada *et al.*[5] took into account the solubility of terephthalic acid and introduced the fraction of liquid phase in the two-phase system. The accuracy of the solubility data and reaction rate constants have to be improved in the latter, however, and more effort should be devoted to improving the data in the future. In this study, based on the work of Yamada *et al.*, problems that might be encountered in modelling and simulating the esterification process in a continuous flow stirred tank reactor (CSTR) were discussed and some suggestions to improve the results were made.

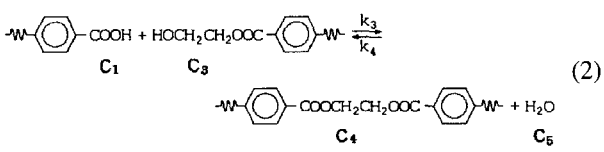
Mathematical Modelling

Various reactions involved in the polymerization of poly (ethylene terephthalate) are summarized as follows. Here, C_i is the concentration of component i in the liquid phase, and $k_1 \sim k_9$ are the reaction rate constants.

① Esterification



(1)



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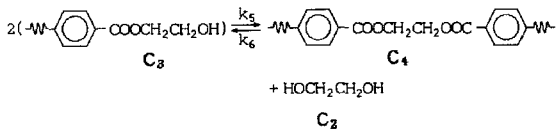
② Polycondensation



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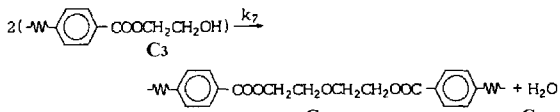
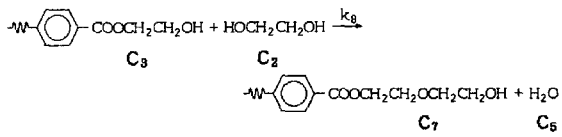
③ Side reactions leading to the formation of diethylene glycol



(4)



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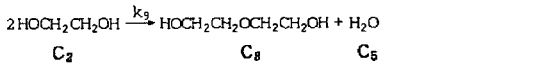

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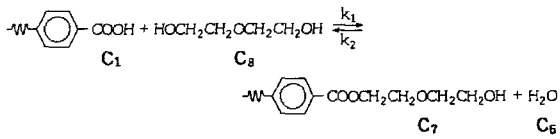

(7)

For the reactions above, the following assumptions are introduced in order to establish rate equations.

① Reactions take place in the liquid phase only. Terephthalic acid partly dissolves into the reaction mixture, and the dissolved terephthalic acid participates in the reaction.

② The rate of dissolution of terephthalic acid is very rapid. Therefore, the rate determining step is the reaction of terephthalic acid, not the dissolution of terephthalic acid.

③ The material that consists of the solid component in the heterogeneous system is the undissolved terephthalic acid.

④ All acidic functions entail carboxylic end-groups.

⑤ The concentration of diethylene glycol(DEG) is given by the sum of C_6, C_7 and C_8.

⑥ The pressure in the reactor is given by the sum of the partial pressures of ethylene glycol and water. The partial pressure of diethylene glycol is lower than those of ethylene glycol and water.

⑦ All the non-volatile components in the reaction mixtures are defined as oligomers.

⑧ Since the degree of polymerization is not very high in the esterification stage, the reactivity of functional groups does not depend on the polymer chain length.

⑨ In the formation of diethylene glycol, the reactivity of each hydroxyl end-group is the same. That is, $k_8 = 2k_7$ and $k_9 = 4k_7$.

Since esterification reaction between terephthalic acid and

ethylene glycol seems to take place only in the liquid phase, the weight fraction of the liquid phase plays an important role in developing the esterification model. The weight fraction of the liquid phase, designated as β, is related to the carboxylic end-group concentration by Eq. (8). Here, AV_a is the concentration of carboxylic acid end-groups (including undissolved terephthalic acid) in the reaction mixture, and AV is the concentration of carboxylic end-groups based on the weight of the reaction mixture, excluding ethylene glycol and water.

$$AV_a = AV(1-\beta w_{EG}-\beta w_{H_2O}) \tag{8}$$

In this equation, w_{EG} and w_{H_2O} are the weight fractions of ethylene glycol and water respectively in the liquid phase of the reaction mixture. When there is no undissolved TPA in the reaction mixture ($\beta = 1$), the Eq. (8) reduces to Eq. (9).

$$\begin{aligned}(AV_a)_{\beta=1} &= \zeta \\ &= AV[1-(w_{EG}+w_{H_2O})] = AVw_{OLG}\end{aligned} \tag{9}$$

Here, w_{OLG} is the weight fraction of oligomers, and w_{EG}, w_{H_2O} and w_{OLG} satisfy the following equation.

$$w_{EG}+w_{H_2O}+w_{OLG} = 1 \tag{10}$$

In the liquid phase of the reaction mixture, the following relations are established when the average solubility of terephthalic acid is designated as α.

① $AV_a > \alpha$ (when undissolved TPA remains in the reaction mixture)

$$\alpha\beta = AV_a - \eta_{TPA}(1-\beta) \tag{11}$$

Putting Eq. (8) into Eq. (11) gives

$$\beta = \frac{AV-\eta_{TPA}}{\alpha+AV(w_{EG}+w_{H_2O})-\eta_{TPA}} \tag{12}$$

The concentration of carboxylic end-groups in the liquid phase of the reaction mixture, C_1, is given by α. The equivalent concentration of TPA, η_{TPA}, is the equivalent of carboxylic end-groups per unit mass of pure TPA. (η_{TPA} = 12.039 → -COOH equiv/kg TPA)

② $AV_a \leq \alpha$ (when there is no undissolved TPA in the reaction mixture)

$$\beta = 1 \text{ and } C_1 = \zeta \tag{13}$$

Here, α is given by the equivalent mole of carboxylic end-group of TPA dissolved per unit mass of the liquid phase of the reaction mixture.

In the following Equations, the ratio of the hydroxyl end-group to the total end-groups, φ; the number average molecular weight, M_n; the number average degree of polymerization, P_n; the saponification value, SV; the degree of esterification, E_s; and the percentage of DEG based on bound TPA, d, are expressed in terms of the equivalent of carboxylic end-groups, AV, and the equivalent of hydroxyl end-groups, OHV, in the oligomers.

$$\varphi = OHV/(AV+OHV) \tag{14}$$

$$M_n = 2000/(AV+OHV) \tag{15}$$

$$P_n = \frac{M_n(1+e)+26.03+70.09e-\varphi(88.10+176.20e)}{192.17+236.23e} \tag{16}$$

$$SV = 2000P_n/M_n \tag{17}$$

$$E_s = (SV-AV)/SV \tag{18}$$

$$d = 100[(P_n+2\varphi-1)/P_n]\,[e/(e+1)] \tag{19}$$

where, e is the ratio of DEG to bound EG in the dried oligomer.

If q_{EG} and q_{H_2O} are the amounts of ethylene glycol consumed and water produced in the reaction with TPA, respectively, then the following Equations are established.

$$q_{EG} = \frac{62.07}{166.13} F_{TPA}\left(\frac{P_{nf}+2\varphi_f-1}{P_{nf}} - \frac{P_{ni}+2\varphi_f-1}{P_{ni}}\right) \tag{20}$$

$$q_{H_2O} = \frac{2\times 18.02}{166.13} F_{TPA}\left(\frac{P_{nf}+\varphi_f-1}{P_{nf}} - \frac{P_{ni}+\varphi_i-1}{P_{ni}}\right) \tag{21}$$

where, F_{TPA} is the flow rate of TPA, and the subscripts i and f denote initial and final values, respectively.

The material balances of EG and water are as follows.

$$F^i_{EG} = Q_{EG} + \beta F_P \cdot w_{EG} + q_{EG} \tag{22}$$

$$F^i_{H_2O} + q_{H_2O} = Q_{H_2O} + \beta F_P\ w_{H_2O} \tag{23}$$

And, the total material balance is

$$F^i = F_P + Q_{EG} + Q_{H_2O} \tag{24}$$

Here, F^i_{EG} is the inlet flow rate of ethylene glycol, $F^i_{H_2O}$ is the inlet flow rate of water, Q_{EG} is the vapor flow rate of ethylene glycol, Q_{H_2O} is the vapor flow rate of water, F^i is the total inlet flow rate of feed and F_P is the outlet flow rate of reaction mixture from the reactor.

Combining Eqs. (22), (23), and (24) gives

$$Q_{EG} = \frac{(F^i_{EG}-q_{EG})(1-\beta w_{H_2O})-\beta w_{EG}(F^i-F^i_{H_2O}-q_{H_2O})}{1-\beta w_{H_2O}-\beta w_{EG}} \tag{25}$$

$$Q_{H_2O} = \frac{F^i_{H_2O} + q_{H_2O} - \beta w_{H_2O}(F^i - Q_{EG})}{1 - \beta w_{H_2O}} \quad (26)$$

With the assumption that the total pressure in the reactor be obtained by adding the partial pressures of EG and water, the mole fractions of EG and water in the gas phase are obtained by the following equations.

$$y_{EG} = \frac{Q_{EG}/62.07}{Q_{EG}/62.07 + Q_{H_2O}/18.02} \quad (27)$$

$$y_{EG} + y_{H_2O} = 1 \quad (28)$$

$$x_{EG}\,\gamma_{EG}\,P_{EG} = y_{EG}\,P \quad (29)$$

$$x_{H_2O}\,\gamma_{H_2O}\,P_{H_2O} = y_{H_2O}\,P \quad (30)$$

$$x_{H_2O} + x_{EG} + x_{OLG} = 1 \quad (31)$$

where y_{EG} and y_{H_2O} denote mole fractions of ethylene glycol and water in the vapor phase, respectively. x_{EG}, x_{H_2O}, and x_{OLG} are the liquid phase mole fractions of ethylene glycol, water, and oligomers. γ_{EG} and γ_{H_2O} denote the activity coefficients of ethylene glycol and water; P_{EG} and P_{H_2O} are the vapor pressures of ethylene glycol and water, and P is the total pressure.

The activity coefficients are given by the Van Laar equations.

$$\ln\gamma_{EG} = \frac{A}{\left(1 + \frac{A}{B}\frac{x_{EG}}{x_{H_2O}}\right)^2} \quad (32)$$

$$\ln\gamma_{H_2O} = \frac{B}{\left(1 + \frac{B}{A}\frac{x_{H_2O}}{x_{EG}}\right)^2} \quad (33)$$

And, the vapor pressures are expressed as follows.

$$\log P_{EG} = 7.8808 - \frac{1957}{t + 193.8} \quad (34)$$

$$\log P_{H_2O} = 7.9668 - \frac{1668.2}{t + 228} \quad (35)$$

where P_{EG} is the vapor pressure (mmHg) of ethylene glycol at the reaction temperature, P_{H_2O} is the vapor pressure (mmHg) of water at the reaction temperature, and t is the reaction temperature (°C). Eqs. (27) through (35) will give the mole fractions in the liquid or vapor phase.

The rates of formation for components C_1 through C_8 can be described from Eqs. (1) through (7) as follows.

$$\frac{dC_1}{d\theta} = -k_1C_1C_2 + k_2C_3C_5 - k_3C_1C_3 + k_4C_4C_5 - k_1C_1C_8 + k_2C_5C_7 \quad (36)$$

$$\frac{dC_2}{d\theta} = -k_1C_1C_2 + k_2C_3C_5 + k_5C_3^2 - k_6C_2C_4 - k_8C_2C_3 - 2k_9C_2^2 \quad (37)$$

$$\frac{dC_3}{d\theta} = k_1C_1C_2 - k_2C_3C_5 - k_3C_1C_3 + k_4C_4C_5 - 2k_5C_3^2 + 2k_6C_2C_4 - 2k_7C_3^2 - k_8C_2C_3 \quad (38)$$

$$\frac{dC_4}{d\theta} = k_3C_1C_3 - k_4C_4C_5 + k_5C_3^2 - k_6C_2C_4 \quad (39)$$

$$\frac{dC_5}{d\theta} = k_1C_1C_2 - k_2C_3C_5 + k_3C_1C_3 - k_4C_4C_5 + k_7C_3^2 + k_8C_2C_3 + k_9C_2^2 + k_1C_1C_8 - k_2C_5C_7 \quad (40)$$

$$\frac{dC_6}{d\theta} = k_7C_3^2 \quad (41)$$

$$\frac{dC_7}{d\theta} = k_8C_2C_3 + k_1C_1C_8 - k_2C_5C_7 \quad (42)$$

$$\frac{dC_8}{d\theta} = k_9C_2^2 - k_1C_1C_8 + k_2C_5C_7 \quad (43)$$

where $k_8 = 2k_7$, $k_9 = 4k_7$.

The material balances for each component in a CSTR are as follows.

Carboxylic end-groups

$$F^iC_{10} - F_PAV_a + \beta W(dC_1/d\theta) = 0 \quad (44)$$

Hydroxyl end-groups

$$F^iC_{30} - \beta F_PC_3 + \beta W(dC_3/d\theta) = 0 \quad (45)$$

Diester groups

$$F^iC_{40} - \beta F_PC_4 + \beta W(dC_4/d\theta) = 0 \quad (46)$$

Diethylene glycol

$$F^i(C_{60} + C_{70} + C_{80}) - \beta F_P(C_6 + C_7 + C_8) + \beta W(dC_6/d\theta + dC_7/d\theta + dC_8/d\theta) = 0 \quad (47)$$

Water

$$F^iC_{50} - \beta F_PC_5 - Q_{H_2O}\eta_{H_2O} + \beta W(dC_5/d\theta) = 0 \quad (48)$$

Ethylene glycol

$$F^iC_{20} - \beta F_PC_2 - Q_{EG}\eta_{EG} + \beta W(dC_2/d\theta) = 0 \quad (49)$$

where C_{K0} is the inlet concentration of component K; η_{H_2O} and η_{EG} are equivalent concentrations of water and ethylene glycol, respectively, expressed as moles per unit mass (η_{H_2O} = 55.494 mole/kg, η_{EG} = 16.111 mole/kg); W is the total weight of reaction mixture in the reactor.

The relation between mole fraction and weight fraction is

$$w_i = x_i M_i / \sum_{j=1}^{N} x_j M_j \tag{50}$$

where x_i and x_j are the liquid phase mole fractions of components i and j; w_i is the liquid phase weight fraction of component i; N is the number of components; M_i and M_j are the weights per mole of components i and j.

In the liquid phase including ethylene glycol and water the number average molecular weight of oligomer, M_{OLG}, is given by

$$M_{OLG} = \frac{2000\beta w_{OLG}}{\beta C_1 + OHV[1-\beta(w_{EG}+w_{H_2O})]} \tag{51}$$

The computational procedure for the concentration of each component in the liquid phase involved the following iterative method and its flowsheet is described in Figure 1.

1. Assume *AV, OHV* and *e*.
2. Calculate q_{EG} and q_{H_2O} from Eqs. (14), (15), (16), (20) and (21).
3. Guess initial values of x_i and M_{OLG}.
4. Compute w_i given by Eq. (50) and β given by Eqs. (12) and (13).
5. Compute new M_{OLG} ($M_{OLG,N}$) given by Eq. (51). If the difference between M_{OLG} and ($M_{OLG,N}$) is small enough (less than ε_1), then proceed to the next step. If not, substitute $M_{OLG,N}$ for M_{OLG} and return to step 4.
6. Compute Q_{EG} and Q_{H_2O} given by Eqs. (25) and (26), and y_{EG} given by Eq. (27).
7. Compute new x_i ($x_{i,N}$) given by Eqs. (28) through (35). If the difference between $x_{i,N}$ and x_i is small enough (less than ε_2), then proceed to the next step. If not, substitute $x_{i,N}$ for x_i and return to step 4.
8. Compute the solutions (C_1~C_8) of the material balances given by Eqs. (44) through (49).
9. From the solutions, calculate AV_N, OHV_N and e_N. If the differences between AV_N and *AV*, OHV_N and *OHV*, e_N and *e* are small enough (less than ε_3), then finish the computation. If not, substitute AV_N, OHV_N and e_N for *AV*, *OHV* and *e*, respectively and return to step 2.
10. Print the results.

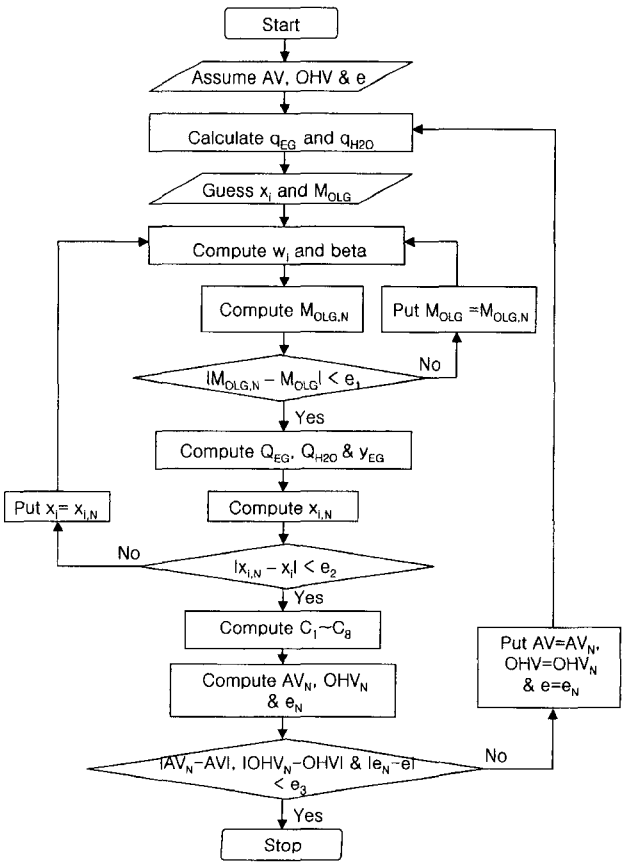

Figure 1. Flowsheet of the computational procedure.

The formulation in this work is basically the same as Yamada *et al.*'s,[5] but there are several differences between them. One is related to the solution method. In step 8, this study employed a Newton-Raphson iteration method to solve the simultaneous nonlinear equations, while Yamada *et al.*'s[6,7] employed the Simplex method. The Newton-Raphson iteration method leads to a solution that satisfies the given equations within a tolerance limit of 10^{-9}. On the other hand, the Simplex method, which was developed by J. A. Nelder and R. Mead,[12] provides an algorithm to search for the minimum points of given functions that are closest to zero. Therefore, the Simplex method leads to a solution that does not necessarily satisfy the given equations. The other one is related to how to obtain the values of *AV, OHV* and *e*. In this study these variables were computed numerically, while experimentally measured values were used for these variables in Yamada *et al.*'s work.[5-7] Therefore, with Yamada *et al.*'s approach one cannot get a solution for the equations without previously measured values of these variables. In this work, however, these variables were computed numerically for the given process conditions along with the other variables including the concentrations of components. Consequently, it is not necessary to measure these variables in advance.

The following values of the reaction rate constants obtained by Yamada *et al.*[7,9,10] were used in the computation.

$$k_1 = 1.5657 \times 10^9 \exp(-19640/RT) \tag{52}$$

$$k_2 = 1.5515 \times 10^8 \exp(-18140/RT) \tag{53}$$

$$k_3 = 3.5165 \times 10^9 \exp(-22310/RT) \tag{54}$$

$$k_4 = 6.7640 \times 10^7 \exp(-18380/RT) \tag{55}$$

$$k_5 = 7.7069 \exp(-2810/RT) \tag{56}$$

$$k_6 = 6.2595 \times 10^6 \exp(-14960/RT) \tag{57}$$

$$k_7 = 2.0583 \times 10^{15} \exp(-42520/RT) \tag{58}$$

When we compute the weight fraction of liquid phase, β, it is necessary to know the solubility of terephthalic acid, α. Yamada *et al.*[5] performed an experiment to obtain the solubility of terephthalic acid in the reaction mixture using ethylene glycol and bis-hydroxyethyl terephthalate (BHET). The solubilities of terephthalic acid in these solvents show temperature dependence as follows.

$$\alpha_{EG} = 18124\exp(-9692/RT) \tag{59}$$

$$\alpha_{BHET} = 748\exp(-7612/RT) \tag{60}$$

where R is the gas constant of 1.987 cal/mol · K and T is the absolute temperature.

Then, the solubility of terephthalic acid in the reaction mixture is calculated as follows.

$$\alpha = \alpha_{H_2O} w_{H_2O} + \alpha_{EG} w_{EG} + \alpha_{OLG} w_{OLG} \tag{61}$$

If the amount of terephthalic acid dissolved in the water is very small and the solubility in the oligomer is equal to that in the BHET, the solubility α is given by

$$\alpha \fallingdotseq \alpha_{EG} w_{EG} + \alpha_{BHET} w_{OLG} \tag{62}$$

The solubility of terephthalic acid in the BHET differs in several works; that is, the data obtained by Yamada *et al.*[5] are smaller than those by Baranova and Kremer[13] at temperatures below 300 °C. In view of the oligomers that compose most of the liquid phase of the reaction mixture, it can be said that the solubility in BHET is more important than that in ethylene glycol. Especially in the practical temperature range of 240~260 °C, the solubility data by both groups have a large difference. In this temperature range, Ravindranath and Mashelkar[1] assumed the solubility of terephthalic acid in the reaction mixture, α, to be constant at 1.2048 equiv/kg. This value is closer to the data by Baranova and Kremer[13] than to those by Yamada *et al.*[5] Since the chemical component that participates in the reaction is the dissolved terephthalic acid, the solubility of terephthalic acid in the reaction mixture is a very important factor in understanding the characteristics of the process.

Results and Discussion

In our computer calculation, we tried the solubility data expressed by the Eqs. (59) and (60), which were obtained by Yamada *et al.*,[5] and found that the fraction of liquid phase in the reaction mixture, β, converged to zero and the concentration of carboxylic end-group, C_1, converged to the solubility α. This means that there remains no liquid phase, but solid phase only. This is unreasonable because the reaction cannot occur in solid phase and also it is not the real situation in the reactor. In Eq. (12), β is given as a function of AV and α. Since the weight fractions of ethylene glycol and water are very small and α is smaller than AV, β would be less than 1. If α becomes smaller, β would also become smaller. However, AV is obtained by

$$AV = \frac{C_1\beta + \eta_{TPA}(1-\beta)}{1-\beta w_{EG} - \beta w_{H_2O}} \tag{63}$$

Here, if β becomes smaller, AV approaches to η_{TPA}. Then, according to Eq. (12), the value of β would in turn lead to zero. In this way, with solid phase only, C_1 readily converges to α. Thus, the value of α plays an important role in determining the weight fraction of liquid phase. If it is too small, the liquid phase fraction becomes zero. In the previous section, it was discussed that the solubility data by Yamada *et al.*[5] are relatively small compared to those by Baranova and Kremer,[13] and even to those assumed by Ravindranath and Mashelkar.[1] Thus, with the Yamada *et al.*'s solubility data one cannot get a solution that satisfies the material balance equations having non-zero liquid phase fraction. However, if one uses the Simplex method as used by Yamada *et al.*,[6,7] one may get a rough solution with such a small solubility data, since the method searches for the minima of residuals of the material balance equations.

Therefore, in this study, an attempt has been made to search for the minimum required value of the solubility that gives rise to a solution satisfying the material balance equations with a constraint of non-zero liquid phase fraction. The solubility α in Eq. (12) was replaced by the carboxylic end-group concentration C_1, and for a specific temperature the value of AV was controlled to get a solution C_1 that is closest to the Yamada *et al.*'s solubility data, but still satisfying the material balance Eqs. (44)~(49) with a constraint of non-zero liquid phase fraction. The computation was performed for a reaction system in which the process conditions were selected such as the reaction mass of 250 kg, the residence time of 5 hrs, the molar EG to TPA ratio of 2, and the pressure of 760 mmHg. The temperature range was spanned from 240 to 295 °C.

The minimum required values of carboxylic end-group concentration C_1 thus obtained were plotted in Figure 2 over the given temperature range and compared with the solubility data by Yamada *et al.* and data by Baranova and Kremer. In this Figure the carboxylic end-group concentration is expressed as [-COOH]. It was found that the minimum required carboxylic end-group concentrations are larger than the solubility data by Yamada *et al.*, while they are smaller than those by Baranova and Kremer. It is clear from this Figure that the minimum required concentrations of carboxylic end-group are closer to the solubility data by Baranova and Kremer at high temperature region while they are closer to the data by Yamada *et al.* at low temperature region. Using these minimum required concentrations of the carboxylic end-group, we obtained the values for the other process variables and summarized them in Table I. In this table, we can see that

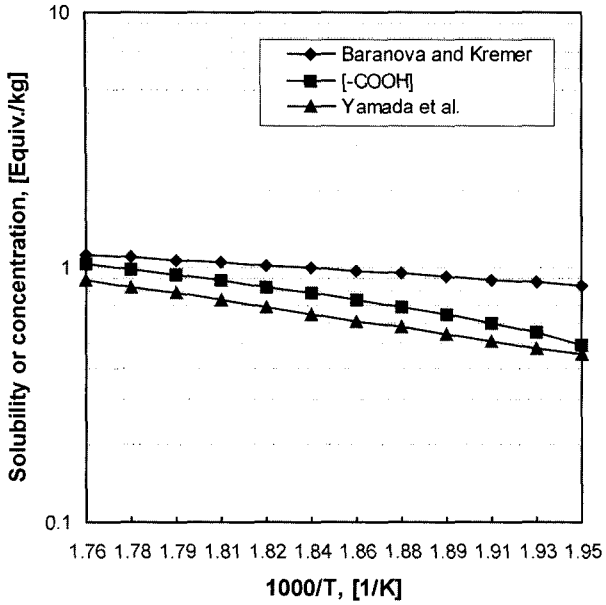

Figure 2. Comparison of the solubility data of TPA in the literatures with the minimum required concentrations of carboxylic end-group.

the fraction of liquid phase, β, increases monotonically from ~0.3 to ~0.8 as the temperature increases from 240 to 295 °C.

Thus, in order to get a solution for the mass balance equations with a constraint of non-zero liquid phase fraction, we should have a solubility at least larger than these minimum required concentrations of carboxylic end-group, which were found to be greater than the solubility data by Yamada *et al.* Therefore, in this study, we tried to draw several linear curves over the minimum required concentration curve and obtained two typical solubility curves and named them Curve-I and Curve-II, respectively. Those are:

Curve-I

$$\alpha_{BHET} = 200 \exp(-5957/RT) \quad (64)$$

Curve-II

$$\alpha_{BHET} = 457 \exp(-6797/RT) \quad (65)$$

Curve-I was drawn tangent to the minimum required concentration curve of carboxylic end-group at the temperature of ~295 °C and, then, it gives somewhat higher value than the minimum required concentration of carboxylic end-group at low temperature region. On the other hand, Curve-II was drawn to closely approach to the solubility data curve by Baranova and Kremer at temperature of ~295 °C and to approach to Curve-I at low temperature region. Thus, at high temperature region, Curve-I lies close to the minimum required concentration curve of carboxylic end-group while Curve-II lies close to the solubility data curve by Baranova and Kremer. At low temperature region, both curves lie in between two limiting curves of Baranova and Kremer and the minimum concentration curve. Considering the solubility data suggested by Ravindranath and Mashelkar[1] that are closer to the data by Baranova and Kremer than to those by Yamada *et al.* and the results shown in Figure 2, the solubility data curve by Baranova and Kremer is favorable at high temperature region while the minimum required concentration curve of carboxylic end-group is favorable at low temperature region. In this context, Curve-II would be preferred to Curve-I.

In order to study the feasibility of the two suggested solubility curves computations were performed again for the reaction systems selected. Both curves successfully gave

Table I. Calculated Results for the First Esterification Reactor with the Minimum Required Concentration of Carboxylic End-group (p = 760 mmHg)

t	P	EG/TPA	W	τ	AV	OHV	e	d	ϕ	M_n	P_n	M_{OLG}	SV	E_s	w_{EG}	w_{H_2O}	w_{dH_2O}	Q	β
240	760	2.0	250	5.0	8.3487	0.7013	0.01645	0.5229	0.0775	221	1.2484	741	11.298	0.2611	0.02677	0.0001	0.0840	19.3	0.3260
245	760	2.0	250	5.0	7.1195	0.7434	0.01442	0.6061	0.0945	254	1.4138	872	11.116	0.3595	0.01724	0.0001	0.1185	18.8	0.4328
250	760	2.0	250	5.0	6.2062	0.6913	0.01262	0.6219	0.1002	290	1.5961	1019	11.009	0.4363	0.01166	0.0001	0.1458	18.6	0.5132
255	760	2.0	250	5.0	5.6276	0.5931	0.01109	0.5930	0.0953	322	1.7624	1170	10.963	0.4867	0.00838	0.0001	0.1635	18.5	0.5653
260	760	2.0	250	5.0	5.2729	0.4875	0.00974	0.5429	0.0846	347	1.9010	1317	10.951	0.5185	0.00634	0.0001	0.1743	18.5	0.5983
265	760	2.0	250	5.0	5.0152	0.3939	0.00853	0.4885	0.0728	370	2.0239	1450	10.947	0.5419	0.00497	0.0000	0.1821	18.5	0.6231
270	760	2.0	250	5.0	4.7759	0.3178	0.00747	0.4391	0.0624	393	2.1479	1559	10.941	0.5635	0.00402	0.0000	0.1894	18.5	0.6466
275	760	2.0	250	5.0	4.5097	0.2583	0.00656	0.3981	0.0542	419	2.2913	1640	10.925	0.5872	0.00332	0.0000	0.1978	18.4	0.6728
280	760	2.0	250	5.0	4.2352	0.2116	0.00582	0.3653	0.0476	450	2.4520	1690	10.904	0.6116	0.00281	0.0000	0.2066	18.4	0.7000
285	760	2.0	250	5.0	3.8772	0.1756	0.00517	0.3394	0.0433	493	2.6815	1715	10.867	0.6432	0.00240	0.0000	0.2185	18.3	0.7350
290	760	2.0	250	5.0	3.4421	0.1474	0.00460	0.3186	0.0411	557	3.0138	1719	10.818	0.6818	0.00206	0.0000	0.2334	18.1	0.7773
295	760	2.0	250	5.0	3.0000	0.1245	0.00413	0.3015	0.0398	640	3.4457	1705	10.766	0.7213	0.00179	0.0000	0.2491	18.0	0.8207

solutions for the mass balance equations over the broad range of temperature satisfying the non-zero liquid phase constraint. The results were summarized in Tables II~III and shown in Figure 3. Under the pressure of 760 mmHg, Curve-I gave the liquid phase fraction of 0.8~0.9 over the temperature range of 240~295 °C. The solubility generally increases monotonically with temperature and thus the same monotonic increase is expected for the liquid phase fraction, too. However, as shown in Table II and Figure 3, this one showed a slight fluctuation in the liquid phase fraction over the temperature range of 255~275 °C. This phenomenon might be attributed to the effect of material balance in the process system. As the temperature was increased, the effect of increased solubility was thought to be cancelled out by the evaporation of EG and water. It is clear from Table II that the vapor flow rate of EG and water increases rapidly from 17.1 to 17.7 kg/hr as temperature was increased from 255 to 275 °C. This was a substantial increase compared to the cases of the minimum required concentration of carboxylic end-groups and the Curve-II, where the vapor flow rates were almost standstill in this temperature range. In Table III and Figure 3, the Curve-II, which has solubilities closer to those by Baranova and Kremer at high temperature region, showed the liquid phase fractions of ~1 at temperatures above 275 °C and those of < 1 at temperatures below 275 °C. For this curve the liquid phase fraction increased monotonically with temperature, as expected from the increased solubility.

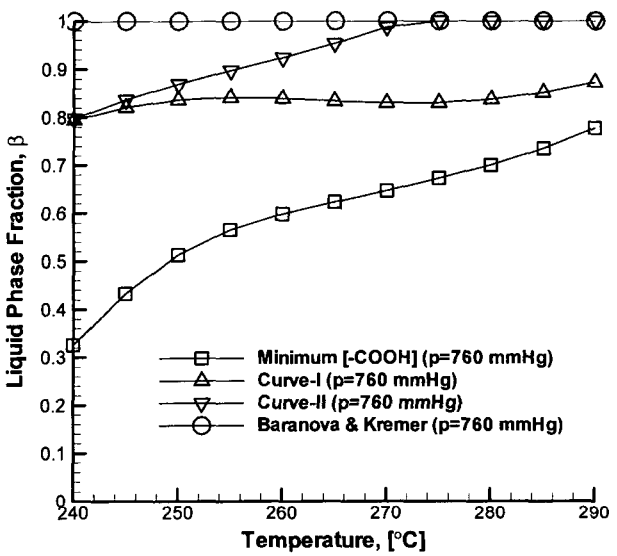

Figure 3. Profiles of the fraction of liquid phase, β, expressed as functions of temperature for the different solubility curves.

For the purpose of comparison, we tried the solubility data by Baranova and Kremer in computation for the same process system and summarized the results in Table IV and Figure 3. It was shown that the liquid phase fraction reached ~1.0 over the broad temperature range of 240~295 °C under the pressure of 760 mmHg since the solubility data by Baranova and Kremer were sufficiently large to obtain a non-zero liquid phase fraction. However, their data can be considered as too large since there remained no solid phase even at such a low temperature as 240 °C under the atmospheric pressure. In the real processes under atmospheric pressure, the solid particles of undissolved TPA are commonly found at low temperature.

The concentration of carboxylic end-groups, *AV*, based on the weight of the reaction mixture excluding EG and water was expressed as a function of temperature in Figure 4. The profiles were quite opposite to the profiles of the liquid phase fraction. With less liquid phase fraction we had more undissolved TPA that contributed to the increase in *AV*. When there was not any undissolved TPA remained in the reaction mixture ($\beta = 1$, Baranova and Kremer), *AV* showed values in between 0.7 and 1 in an increasing order as the

Table II. Calculated Results for the First Esterification Reactor with the Solubility of Curve-I **(p = 760 mmHg)**

t	P	EG/TPA	W	τ	AV	OHV	e	d	ϕ	M_n	P_n	M_{OLG}	SV	E_s	w_{EG}	w_{H_2O}	w_{dH_2O}	Q	β
240	760	2.0	250	5.0	2.9562	1.1417	0.00617	0.5065	0.2786	488	2.5445	987	10.427	0.7165	0.01056	0.0001	0.2658	16.7	0.7949
245	760	2.0	250	5.0	2.6763	0.9946	0.00646	0.5386	0.2709	545	2.8428	1092	10.436	0.7435	0.00811	0.0001	0.2745	16.8	0.8211
250	760	2.0	250	5.0	2.5256	0.8395	0.00655	0.5461	0.2495	594	3.1100	1207	10.465	0.7587	0.00637	0.0001	0.2778	16.9	0.8364
255	760	2.0	250	5.0	2.4954	0.6896	0.00645	0.5308	0.2165	628	3.2998	1326	10.510	0.7626	0.00514	0.0001	0.2764	17.1	0.8415
260	760	2.0	250	5.0	2.5503	0.5557	0.00620	0.5002	0.1789	644	3.4002	1441	10.561	0.7585	0.00424	0.0001	0.2721	17.3	0.8393
265	760	2.0	250	5.0	2.6415	0.4435	0.00587	0.4625	0.1438	648	3.4395	1543	10.611	0.7511	0.00358	0.0001	0.2668	17.5	0.8340
270	760	2.0	250	5.0	2.7201	0.3536	0.00549	0.4244	0.1150	651	3.4653	1626	10.651	0.7446	0.00307	0.0000	0.2625	17.6	0.8299
275	760	2.0	250	5.0	2.7486	0.2734	0.00509	0.3897	0.0935	660	3.5221	1686	10.679	0.7426	0.00266	0.0000	0.2604	17.7	0.8303
280	760	2.0	250	5.0	2.7044	0.2292	0.00471	0.3600	0.0781	682	3.6443	1723	10.691	0.7470	0.00233	0.0000	0.2614	17.7	0.8374
285	760	2.0	250	5.0	2.5837	0.1874	0.00434	0.3351	0.0676	722	3.8572	1737	10.689	0.7583	0.00205	0.0000	0.2653	17.7	0.8515
290	760	2.0	250	5.0	2.3914	0.1548	0.00400	0.3146	0.0608	785	4.1919	1733	10.674	0.7760	0.00182	0.0000	0.2721	17.7	0.8723
295	760	2.0	250	5.0	2.1575	0.1290	0.00369	0.2976	0.0564	875	4.6580	1714	10.651	0.7974	0.00162	0.0000	0.2807	17.6	0.8972

Table III. Calculated Results for the First Esterification Reactor with the Solubility of Curve-II **(p = 760 mmHg)**

t	P	EG/TPA	W	τ	AV	OHV	e	d	ϕ	M_n	P_n	M_{OLG}	SV	E_s	w_{EG}	w_{H_2O}	w_{dH_2O}	Q	β
240	760	2.0	250	5.0	2.9205	1.1425	0.00612	0.5049	0.2812	492	2.5651	989	10.422	0.7198	0.01049	0.0001	0.2673	16.7	0.7980
245	760	2.0	250	5.0	2.4993	0.9970	0.00623	0.5301	0.2852	572	2.9778	1,100	10.411	0.7599	0.00786	0.0001	0.2818	16.7	0.8369
250	760	2.0	250	5.0	2.1575	0.8431	0.00609	0.5289	0.2810	667	3.4710	1,223	10.415	0.7928	0.00599	0.0001	0.2930	16.8	0.8695
255	760	2.0	250	5.0	1.8756	0.6950	0.00573	0.5051	0.2704	778	4.0554	1,350	10.425	0.8201	0.00465	0.0001	0.3019	16.9	0.8972
260	760	2.0	250	5.0	1.6143	0.5639	0.00523	0.4680	0.2589	918	4.7895	1,470	10.433	0.8453	0.00369	0.0001	0.3104	16.9	0.9237
265	760	2.0	250	5.0	1.3289	0.4548	0.00468	0.4265	0.2550	1,121	5.8477	1,572	10.430	0.8726	0.00298	0.0001	0.3202	16.9	0.9527
270	760	2.0	250	5.0	0.9866	0.3671	0.00413	0.3864	0.2712	1,477	7.6922	1,647	10.413	0.9053	0.00244	0.0001	0.3331	16.9	0.9872
275	760	2.0	250	5.0	0.8825	0.2970	0.00380	0.3577	0.2518	1,696	8.8369	1,696	10.423	0.9153	0.00210	0.0001	0.3361	16.9	1.0000
280	760	2.0	250	5.0	0.9186	0.2410	0.00360	0.3357	0.2078	1,725	9.0074	1,725	10.446	0.9121	0.00187	0.0000	0.3333	17.0	1.0000
285	760	2.0	250	5.0	0.9559	0.1967	0.00343	0.3169	0.1707	1,735	9.0802	1,735	10.466	0.9087	0.00169	0.0000	0.3307	17.1	1.0000
290	760	2.0	250	5.0	0.9944	0.1616	0.00328	0.3009	0.1398	1,730	9.0684	1,730	10.483	0.9051	0.00154	0.0000	0.3284	17.1	1.0000
295	760	2.0	250	5.0	1.0349	0.1335	0.00316	0.2875	0.1143	1,712	8.9851	1,712	10.498	0.9014	0.00142	0.0000	0.3261	17.2	1.0000

Table IV. Calculated Results for the First Esterification Reactor with the Solubility of Baranova and Kremer **(p = 760 mmHg)**

t	P	EG/TPA	W	τ	AV	OHV	e	d	ϕ	M_n	P_n	M_{OLG}	SV	E_s	w_{EG}	w_{H_2O}	w_{dH_2O}	Q	β
240	760	2.0	250	5.0	0.7091	1.1415	0.00378	0.3925	0.6168	1,081	5.4717	1,081	10.126	0.9300	0.00698	0.0002	0.3659	15.8	1.0000
245	760	2.0	250	5.0	0.7120	0.9914	0.00424	0.4335	0.5820	1,174	5.9725	1,174	10.174	0.9300	0.00571	0.0001	0.3612	16.0	1.0000
250	760	2.0	250	5.0	0.7266	0.8390	0.00450	0.4532	0.5359	1,277	6.5306	1,277	10.224	0.9289	0.00470	0.0001	0.3562	16.2	1.0000
255	760	2.0	250	5.0	0.7501	0.6940	0.00456	0.4514	0.4806	1,385	7.1147	1,385	10.274	0.9270	0.00389	0.0001	0.3513	16.4	1.0000
260	760	2.0	250	5.0	0.7796	0.5649	0.00445	0.4341	0.4202	1,488	7.6760	1,488	10.320	0.9245	0.00326	0.0001	0.3468	16.5	1.0000
265	760	2.0	250	5.0	0.8125	0.4561	0.00426	0.4091	0.3595	1,577	8.1674	1,577	10.360	0.9216	0.00277	0.0001	0.3427	16.7	1.0000
270	760	2.0	250	5.0	0.8470	0.3676	0.00403	0.3826	0.3026	1,647	8.5580	1,647	10.394	0.9185	0.00239	0.0001	0.3392	16.8	1.0000
275	760	2.0	250	5.0	0.8825	0.2970	0.00380	0.3577	0.2518	1,696	8.8369	1,696	10.423	0.9153	0.00210	0.0001	0.3361	16.9	1.0000
280	760	2.0	250	5.0	0.9187	0.2410	0.00360	0.3357	0.2078	1,725	9.0074	1,725	10.446	0.9121	0.00187	0.0000	0.3333	17.0	1.0000
285	760	2.0	250	5.0	0.9559	0.1967	0.00343	0.3169	0.1707	1,735	9.0802	1,735	10.466	0.9087	0.00169	0.0000	0.3307	17.1	1.0000
290	760	2.0	250	5.0	0.9944	0.1616	0.00328	0.3009	0.1398	1,730	9.0684	1,730	10.483	0.9051	0.00154	0.0000	0.3284	17.1	1.0000
295	760	2.0	250	5.0	1.0349	0.1335	0.00315	0.2875	0.1143	1,712	8.9851	1,712	10.498	0.9014	0.00142	0.0000	0.3261	17.2	1.0000

temperature was gradually increased from 240 to 295 °C. For the case of Curve-II, the equivalent of carboxylic end-group, *AV*, showed a gradual decrease from 2.9205 to 0.8825 as the temperature was gradually increased from 240 to 275 °C, along with an increase in β from 0.7980 to 1. Then, *AV* showed a slight increase up to 1.0349 as the temperature was gradually increased from 275 to 295 °C, without any solid phase remained.

The polymerization reaction occurs in the liquid phase. TPA must be dissolved in the reaction mixture as much as possible in order to obtain polymers of high molecular weight. The degrees of polymerization for the cases were expressed as functions of temperature in Figure 5. Here, we can see that the greater the solubility data used, the higher the degree of polymerization obtained. Also, the higher temperature led to a higher degree of polymerization as was expected from the fact that the solubility become greater as temperature is increased. The polymerization reaction mostly produces water as a byproduct and the water thus produced behaves as a hydrolyzer in the reverse reactions, which reduces the degree of polymerization. Therefore, the water must be removed from the reactor in order to increase the degree of polymerization. An increased temperature helped remove EG and water from the reaction mixture as shown in Tables II~IV. As the reaction temperature was increased, the vapor flow rate, Q, was increased and the weight fractions of EG and water, w_{EG} and w_{H_2O}, were decreased. In Table III, for the case of Curve-II, the number average degree of polymerization gradually increased from 2.5651 to 9.0802 and the number average molecular weight increased from 492 to 1735 as the reaction temperature was increased from 240 to 285 °C. However, they decreased slightly as the temperature

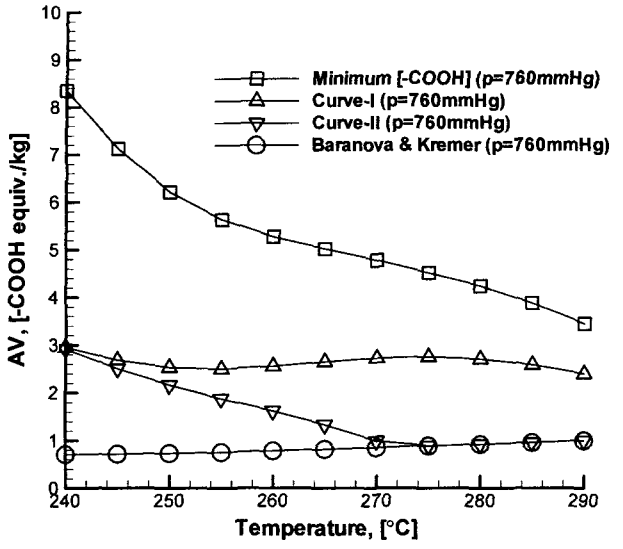

Figure 4. Profiles of the concentration of carboxylic end-groups, *AV*, based on the weight of the reaction mixture excluding EG and water expressed as functions of temperature for the different solubility curves.

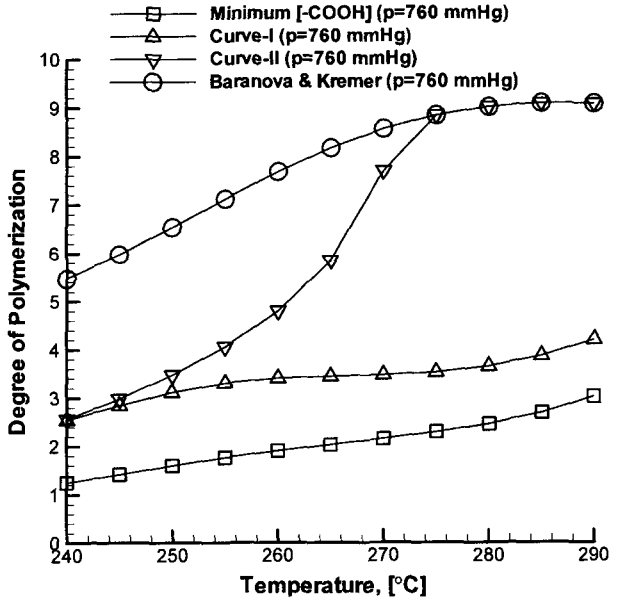

Figure 5. Profiles of the degree of polymerization expressed as functions of temperature for the different solubility curves.

was further increased up to 295 °C. For the oligomers in the liquid phase, the number average molecular weight of the oligomers, M_{OLG}, was 989 at the reaction temperature of 240 °C and it gradually increased up to 1735 as the temperature was increased up to 285 °C. Then, it also slightly decreased to 1712 as the temperature further increased up to 295 °C. This was caused by the reduced concentration of EG resulted from the increased vapor flow rate of EG at the high temperature.

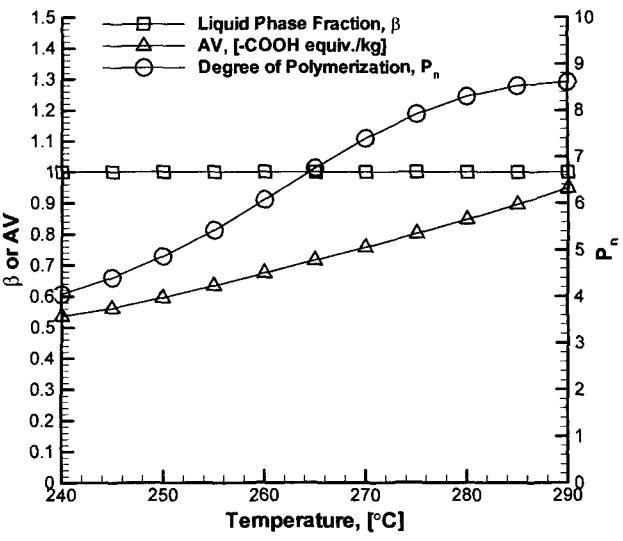

Figure 6. The effects of higher pressure on the reaction characteristics for the case of Curve-II.

The degree of esterification increased from 0.7198 to 0.9153 as the temperature was increased from 240 to 275 °C, along with the fraction of liquid phase. When the fraction of liquid phase reached ~1, there remained no solid TPA in the reaction mixture and the degree of esterification decreased gradually as the temperature was increased up to 295 °C.

Some other calculated results for the Curve-II were summarized in Table III. The equivalent of hydroxyl end-group, *OHV*, was 1.1425 and showed a monotonic decrease to 0.1335 as the temperature was increased up to 295 °C. The content of diethylene glycol (DEG) is considered critical since it has a relatively high melting temperature that it may behave as a defect in polymer processes like fiber spinning. The content of DEG based on bound TPA was 0.5049% at 240 °C and 0.2875% at 295 °C and showed a linear decrease in between. Therefore, a higher temperature is preferred to obtain a lower content of DEG.

The effects of higher pressure on the reaction characteristics were investigated using Curve-II and summarized in Table V and shown in Figure 6. When the pressure was increased to 1,520 mmHg, the system showed liquid phase only over the broad range of temperature without leaving any undissolved TPA. Thus, higher pressure is preferred to make solid TPA completely dissolved in the reaction mixture. As the temperature was increased from 240 to 295 °C, *AV* showed gradual increase from 0.5352 to 1.0050 while *OHV* showed gradual decrease from 1.8994 to 0.2167. The degree of polymerization also increased from 4.0418 to 8.6073 and the number average molecular weight of oligomers increased from 821 to 1650 as the temperature was increased from 240 to 290 °C. Then, they decreased a little bit as the temperature was increased further, which was similar phenomenon to the case of atmospheric pressure. The content of DEG based on

Table V. Calculated Results for the First Esterification Reactor with the Solubility of Curve-II **(p=1,520 mmHg)**

t	P	EG/TPA	W	τ	AV	OHV	e	d	ϕ	M_n	P_n	M_{OLG}	SV	E_s	w_{EG}	w_{H_2O}	w_{dH_2O}	Q	β
240	1520	2.0	250	5.0	0.5352	1.8994	0.01036	1.1675	0.7802	821	4.0418	821	9.840	0.9456	0.01805	0.0005	0.4059	14.4	1.0000
245	1520	2.0	250	5.0	0.5604	1.6926	0.01211	1.3335	0.7513	888	4.3970	888	9.906	0.9434	0.01502	0.0004	0.3952	14.8	1.0000
250	1520	2.0	250	5.0	0.5945	1.4623	0.01333	1.4295	0.7110	972	4.8538	972	9.983	0.9405	0.01239	0.0003	0.3844	15.2	1.0000
255	1520	2.0	250	5.0	0.6334	1.2238	0.01376	1.4365	0.6590	1,077	5.4195	1077	10.065	0.9371	0.01014	0.0003	0.3742	15.5	1.0000
260	1520	2.0	250	5.0	0.6741	0.9970	0.01342	1.3667	0.5966	1,197	6.0710	1197	10.145	0.9336	0.00827	0.0002	0.3650	15.9	1.0000
265	1520	2.0	250	5.0	0.7154	0.7979	0.01259	1.2532	0.5273	1,322	6.7517	1322	10.217	0.9300	0.00679	0.0002	0.3573	16.1	1.0000
270	1520	2.0	250	5.0	0.7575	0.6337	0.01156	1.1294	0.4555	1,438	7.3881	1438	10.279	0.9263	0.00565	0.0001	0.3508	16.4	1.0000
275	1520	2.0	250	5.0	0.8012	0.5036	0.01057	1.0158	0.3860	1,533	7.9164	1533	10.329	0.9224	0.00479	0.0001	0.3455	16.6	1.0000
280	1520	2.0	250	5.0	0.8470	0.4026	0.00971	0.9205	0.3222	1,601	8.2994	1601	10.370	0.9183	0.00416	0.0001	0.3410	16.7	1.0000
285	1520	2.0	250	5.0	0.8957	0.3245	0.00901	0.8440	0.2659	1,639	8.5269	1639	10.404	0.9139	0.00369	0.0001	0.3370	16.8	1.0000
290	1520	2.0	250	5.0	0.9480	0.2639	0.00846	0.7841	0.2178	1,650	8.6073	1650	10.432	0.9091	0.00333	0.0001	0.3333	16.9	1.0000
295	1520	2.0	250	5.0	1.0050	0.2167	0.00805	0.7380	0.1774	1,637	8.5586	1637	10.456	0.9039	0.00306	0.0001	0.3298	17.0	1.0000

bound TPA was 1.1675% at 240 °C and decreased linearly to 0.7380% as the temperature was increased to 295 °C. These are much higher than those in the case of atmospheric pressure. Therefore, a lower pressure is preferred to reduce the DEG content.

Conclusions

The first esterification reactor in a continuous polymerization process of poly(ethylene terephthalate) was analyzed by solving the mass balance equations in two-phase system and for the analysis several parametric expressions for the solubility of terephthalic acid in the reaction mixture were tested. In solving the material balance equations we adopted the Newton-Raphson method instead of the Simplex method since the Newton-Raphson method gives accurate solutions for the material balance equations. It was found that there is a minimum required concentration of carboxylic end-groups to obtain a solution to the material balance equations with the constraint of non-zero liquid phase fraction and therefore, the solubility of terephthalic acid should be larger than this minimum concentration. Computational results showed that the solubility data suggested by Yamada *et al.* cannot give a solution satisfying the constraint of non-zero liquid phase fraction since their solubility data are too small compared to this minimum concentration. On the other hand, the solubility data suggested by Baranova and Kremer led to a solution satisfying the constraint, but they were considered relatively large. Based on the results, several typical solubility curves were suggested in this research and the performance of the first esterification reactor of poly (ethylene terephthalate) was discussed using them. A higher temperature and a lower pressure are preferred to reduce the content of DEG.

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