

Influence of Water on Esterification Reaction between Terephthalic Acid and Ethylene Glycol

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Synopsis

Examples of simulation in the first reactor for the direct continuous esterification were shown to predict the effects of water added into the reactor ($\delta_{\text{H}_2\text{O}}$) on the reactions by a computer. From the simulation results, the followings were confirmed: Although the higher $\delta_{\text{H}_2\text{O}}$ gives the worse results, i.e., the main reaction rates become lower, it brings about the better results, i.e., the side reactions of diethylene glycol (DEG) formation is suppressed; the clearing point where solid (undissolved) terephthalic acid begins not to exist in the reaction mixtures, $\beta = 1$, is the point of $AV = 0.6$ eq/kg, which coincides with the point obtained from the experimental observation, independently of reaction conditions.

INTRODUCTION

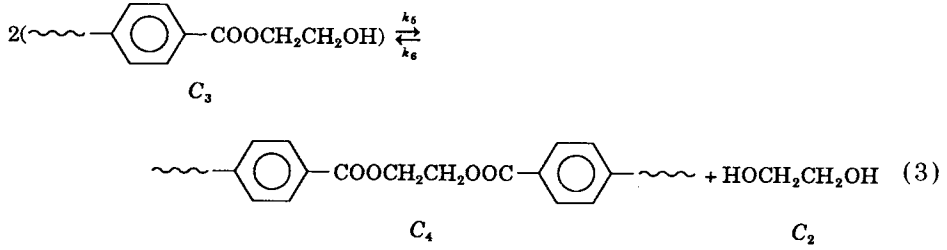
When manufacturing poly(ethylene terephthalate) (PET) continuously, numerous conditions, such as the charge rates of raw and auxiliary materials, temperatures, pressures, etc., are involved and the product, PET, quality or production rate are more or less dependent on each of these conditions.

The simulation model of continuous esterification reaction proposed by Yamada et al.¹ has been utilized to conduct an integrated analysis of the effects of each individual condition and ascertain the optimum manufacturing conditions in the production plant. In other words, it is a computer software to estimate the combination of conditions such as rates of raw and auxiliary materials, concentrations, reaction temperatures, reaction pressures, etc. in the esterification reactors for continuous manufacturing of PET through simulating actual situations by a computer. The present model gives useful information on the continuous esterification reaction shown as follows.

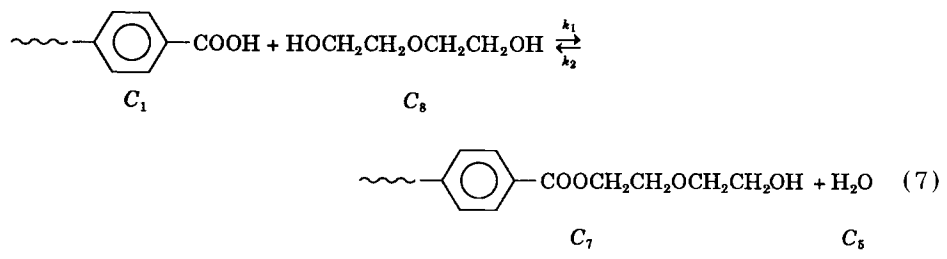
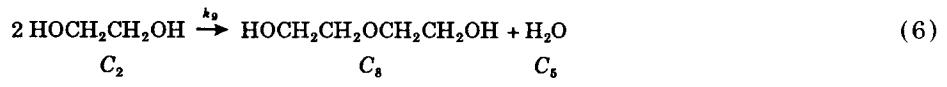
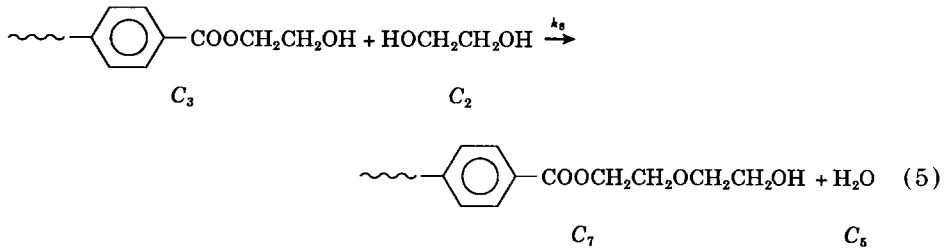
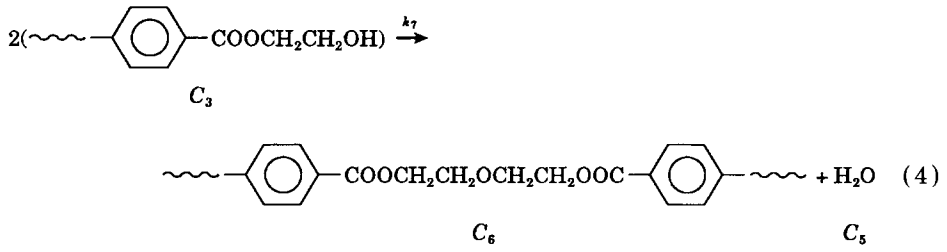
Input Data (Operational Conditions)

1. Reaction temperature: t ;
2. Reaction pressure: P ;
3. Throughput based on PET: F_p ;
4. Total weight in the reactor: W (or mean residence time: τ);
5. Molar ratio of ethylene glycol (EG) to terephthalic acid (TPA), which fed to the first reactor: E/T ;
6. Number of reactors: n ;
7. Flow rate of EG added anew to the reactor per 1 kg/h of throughput based on PET polymer: δ_{EG} ;
8. Flow rate of water added anew to the reactor per 1 kg/h of throughput based on PET polymer: $\delta_{\text{H}_2\text{O}}$.

2. Polycondensation reactions



3. Side reactions leading to the formation of diethylene glycol (DEG) in the oligomer



where C_i is the concentration of component i in the liquid phase and k_1 to k_9 are the reaction rate constants, and there are the relations $k_8 = 2k_7$ and $k_9 = 4k_7$ (see Appendix A).

REACTION RATE EQUATIONS

The reaction rate equations of C_1 to C_8 are given as follows.

$$(dC_1/d\theta) = -k_1C_1C_2 + k_2C_3C_5 - k_3C_1C_3 + k_4C_4C_5 - k_1C_1C_8 + k_2C_5C_7 \quad (8)$$

$$(dC_2/d\theta) = -k_1C_1C_2 + k_2C_3C_5 + k_5C_3^2 - k_6C_2C_4 - k_8C_2C_3 - 2k_9C_2^2 \quad (9)$$

$$(dC_3/d\theta) = k_1C_1C_2 - k_2C_3C_5 - k_3C_1C_3 + k_4C_4C_5 - 2k_5C_3^2 + 2k_6C_2C_4 - 2k_7C_3^2 - k_8C_2C_3 \quad (10)$$

$$(dC_4/d\theta) = k_3C_1C_3 - k_4C_4C_5 + k_5C_3^2 - k_6C_2C_4 \quad (11)$$

$$(dC_5/d\theta) = k_1C_1C_2 - k_2C_3C_5 + k_3C_1C_3 - k_4C_4C_5 + k_7C_3^2 + k_8C_2C_3 + k_9C_2^2 + k_1C_1C_8 - k_2C_5C_7 \quad (12)$$

$$(dC_6/d\theta) = k_7C_3^2 \quad (13)$$

$$(dC_7/d\theta) = k_8C_2C_3 + k_1C_1C_8 - k_2C_5C_7 \quad (14)$$

$$(dC_8/d\theta) = k_9C_2^2 - k_1C_1C_8 + k_2C_5C_7 \quad (15)$$

where $k_8 = 2k_7$ and $k_9 = 4k_7$, and θ denotes the reaction time.

MATHEMATICAL MODEL FOR CONTINUOUS REACTORS

Assumptions for Modeling

Assumptions for modeling of direct esterification are given as follows.

1. Reactions occur only in the liquid phase. TPA is partly dissolved in the reaction mixtures and this dissolved TPA participates in the reaction.
2. The rate of dissolution of TPA is very fast. The rate-determination step, therefore, is not the dissolution of TPA, but the reaction of TPA.
3. Only undissolved TPA forms the solid component of the heterogeneous system.
4. All acidic functions entail carboxyl end groups.
5. The concentration of DEG is given by the sum of C_6 , C_7 , and C_8 .
6. The pressure in the reactor is given only by the sum of partial pressures of EG and water existing in it. The partial pressure of DEG is lower than those of EG and water.
7. All the nonvolatile components in reaction mixtures are defined as oligomer.
8. Reactivity of functional group does not depend on the polymer chain length as it can be assumed that the degree of polymerization is not very high in the esterification step.
9. In the formation of DEG the reactivity of each hydroxyl end group will be assumed to be the same. That is, $k_8 = 2k_7$ and $k_9 = 4k_7$.

Liquid Weight Fraction in Reaction Mixtures (β)

Since the esterification of TPA with EG is considered to occur only in the liquid phase, unaffected by any undissolved TPA, the weight fraction of this phase has been selected a principal parameter in the development of our simulation model.

The weight fraction of liquid phase, β , in the reaction mixtures is related to the concentration of carboxyl end groups in the system by eq. (16), where AV_a represents the total concentration of carboxyl end groups in the reaction reaction mixtures and AV represents their concentration based upon the weight of the mixtures excluding that of both EG and water.

$$AV_a = AV \cdot (1 - \beta w_{EG} - \beta w_{H_2O}) \quad (16)$$

When there is no undissolved TPA in reaction mixtures ($\beta = 1$), eq. (16) reduces to eq. (17)

$$(AV_a)_{\beta=1} = \zeta = AV \cdot \{1 - (w_{EG} + w_{H_2O})\} = AV \cdot w_{OLG} \quad (17)$$

where w_{EG} = weight fraction of EG in the liquid phase of reaction mixtures, w_{H_2O} = weight fraction of water in the liquid phase of reaction mixtures, and w_{OLG} = weight fraction of oligomer in the liquid phase of reaction mixtures.

w_{EG} , w_{H_2O} and w_{OLG} satisfy the following equation.

$$w_{EG} + w_{H_2O} + w_{OLG} = 1 \quad (18)$$

When the mean solubility of TPA in the liquid phase of reaction mixtures is represented by α , the following relationships results.

1. $\zeta > \alpha$ (when insoluble TPA remains in reaction mixtures)

$$\alpha\beta = AV_a - \eta_{TPA} \cdot (1 - \beta) \quad (19)$$

Substitution of eq. (16) into eq. (19) gives

$$\beta = \frac{AV - \eta_{TPA}}{\alpha + AV \cdot (w_{EG} + w_{H_2O}) - \eta_{TPA}} \quad (20)$$

where η_{TPA} = equivalents of carboxyl end groups per 1 kg pure TPA (i.e., $\eta_{TPA} = 12.039$ —COOH equiv/kg TPA).

The concentration of carboxyl end groups in the reaction mixtures, C_1 , is given by α .

2. $\zeta \leq \alpha$ (no undissolved TPA in reaction mixtures)

$$\beta = 1 \quad \text{and} \quad C_1 = \zeta \quad (21)$$

where α is given as equivalent moles of carboxyl end groups of dissolved TPA in 1 kg liquid phase of reaction mixtures.

Mean Solubility of TPA (α)

The temperature dependences of the solubility of TPA in EG, α_{EG} , and that in BHET, α_{BHET} , are given as follows¹

$$\alpha_{EG} = 18124 \cdot \exp(-9692/RT) \quad (22)$$

$$\alpha_{BHET} = 758 \cdot \exp(-7612/RT) \quad (23)$$

where

$$\begin{aligned} \alpha_{EG} &= \text{solubility of TPA in EG;} \\ \alpha_{BHET} &= \text{solubility of TPA in BHET;} \\ R &= \text{gas constant, } R = 1.987 \text{ cal/mol} \cdot \text{ }^\circ\text{K;} \\ T &= \text{absolute temperature, } T = t + 273.15. \end{aligned}$$

The mean solubility of TPA in reaction mixtures containing EG and water can be calculated by the following equation

$$\alpha = \alpha_{H_2O} \cdot w_{H_2O} + \alpha_{EG} \cdot w_{EG} + \alpha_{OLG} \cdot w_{OLG} \quad (24)$$

where α_{H_2O} = solubility of TPA in water and α_{OLG} = solubility of TPA in oligomer.

If the amount of dissolved TPA in the water component of reaction mixtures is negligible because of the very little amount of water in them and the solubility of TPA in oligomer, α_{OLG} , is equivalent to that in BHET, α_{BHET} , α is given by

$$\alpha \approx \alpha_{EG} \cdot w_{EG} + \alpha_{BHET} \cdot w_{OLG} \quad (25)$$

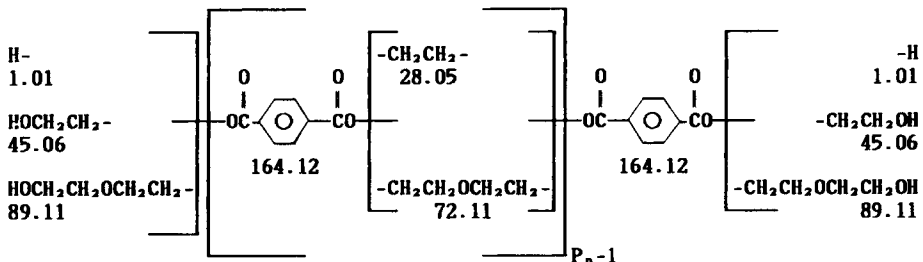
Relations among Oligomer Properties

The relations among oligomer properties are given in the following equations

$$\phi = OHV/(AV + OHV) \quad (26)$$

$$M_n = 2000/(AV + OHV) \quad (27)$$

The chemical structure of oligomer with P_n of polymerization degree can be expressed as follows



where atomic weights of carbon, hydrogen, and oxygen are 12.011, 1.008 and 15.999, respectively.

The relation between M_n and P_n can be given by eq. (28)

$$M_n = (P_n - 1)(164.12 + 28.05)/(1 + e) + (P_n - 1)(164.12 + 72.11)e / \\ (1 + e) + 164.12 + 2(1 - \phi) \times 1.008 \\ + 2\phi\{45.05/(1 + e) + 89.11e/(1 + e)\} \quad (28)$$

By rearrangement of eq. (28), P_n can be expressed by eq. (29)

$$P_n = \{M_n(1 + e) + 26.03 + 70.09e - \phi(88.10 + 176.20e)\} / \\ (192.17 + 236.23e) \quad (29)$$

$$SV = 2000 \cdot P_n / M_n \quad (30)$$

$$E_s = (SV - AV) / SV \quad (31)$$

As the sum of EG linkages and ether linkages (DEG) can be expressed as $(P_n - 1 + 2\phi)$, if the number of ether linkages is represented by x , x is found by the following relation

$$(1 + e) : e = (P_n - 1 + 2\phi) : x, \text{ i.e., } x = (P_n - 1 + 2\phi)e / (1 + e) \quad (32)$$

As the number of TPA units is equal to P_n , d is found by $100 \cdot x / P_n$.

$$d = 100[(P_n + 2\phi - 1) / P_n] \cdot [e / (1 + e)] \quad (33)$$

where ϕ = ratio of hydroxyl end groups to total end groups, M_n = number average molecular weight, P_n = number average degree of polymerization, SV = saponification value, E_s = esterification degree, e = molar ratio of DEG to bound EG, and d = percentage of DEG content based on TPA.

The value of e is measured by a gas chromatographic analysis after methanolysis of oligomer.

PREDICTION OF MELTING POINTS

The following equation reported by Yamada et al.^{5,6} can give the prediction of melting points.

$$1/T_m = 0.111049 \times 10^{-3} \cdot OHV^2 - 0.200468 \times 10^{-4} \cdot OHV^3 - 0.298614 \\ \times 10^{-3} \cdot \exp(-OHV) - 0.196193 \times 10^{-2} \cdot AV / (P_n + OHV) \\ + 0.605210 \times 10^{-3} \cdot AV^2 / (P_n + OHV)^2 - 0.971548 \times 10^{-2} \cdot AV / \\ (P_n + OHV)^2 + 0.980871 \times 10^{-3} \cdot OHV / (P_n + OHV)^2 + 0.142510 \\ \times 10^{-3} \cdot \exp\{AV / (P_n + OHV)\} - 0.655692 \times 10^{-4} \cdot \ln(P_n) \\ + 0.415790 \times 10^{-2} \quad (34)$$

where T_m is the melting points of oligomer.

MATERIAL BALANCE IN CONTINUOUS STIRRED TANK REACTOR (CSTR)

Determination of Mole Fractions of EG and Water in the Vapor or Liquid Phases

If q_{EG} and q_{H_2O} represent, respectively, the amount of EG consumed in reaction with TPA and water generated in the reaction, then for the case of a continuous stirred tank reactor (CSTR) the following equations may be written

$$q_{EG} = \frac{62.07}{166.13} \cdot F_{TPA} \cdot [(P_{nf} + 2\phi_f - 1)/P_{nf} - (P_{ni} + 2\phi_i - 1)/P_{ni}] \quad (35)$$

$$q_{H_2O} = \frac{2 \times 18.02}{166.13} \cdot F_{TPA} \cdot [(P_{nf} + \phi_f - 1)/P_{nf} - (P_{ni} + \phi_i - 1)/P_{ni}] \quad (36)$$

where F_{TPA} is the throughput based on TPA and subscripts i and f show the input and output, respectively. The derivation of eqs. (35) and (36) is given in Appendix B.

Material balances of EG and water in a CSTR are given as follows

$$F_{EG}^i = Q_{EG} + \beta F_P w_{EG} + q_{EG} \quad (37)$$

$$F_{H_2O}^i + q_{H_2O} = Q_{H_2O} + \beta F_P w_{H_2O} \quad (38)$$

Total material balance is

$$F^i = F_P + Q_{EG} + Q_{H_2O} \quad (39)$$

where

F_{EG}^i = input rate of EG,

Q_{EG} = vapor flow rate of EG,

F^i = total input rate,

$F_{H_2O}^i$ = input rate of water,

Q_{H_2O} = vapor flow rate of water, and

F_P = output rate of reaction mixtures.

Combining eqs. (37), (38), and (39) gives

$$Q_{EG} = \{ (F_{EG}^i - q_{EG})(1 - \beta w_{H_2O}) - \beta w_{EG}(F^i - F_{H_2O}^i - q_{H_2O}) \} / (1 - \beta w_{H_2O} - \beta w_{EG}) \quad (40)$$

$$Q_{H_2O} = \{ F_{H_2O}^i + q_{H_2O} - \beta w_{H_2O}(F^i - Q_{EG}) \} / (1 - \beta w_{H_2O}) \quad (41)$$

On the assumption that the total pressure in a reactor is obtained by the sum of the partial pressures of EG and water, the vapor phase mole fractions of EG and water are given by the following equations.

$$y_{EG} = \frac{Q_{EG}/62.07}{Q_{EG}/62.07 + Q_{H_2O}/18.02} \quad (42)$$

$$y_{EG} + y_{H_2O} = 1 \quad (43)$$

$$x_{EG} \cdot \gamma_{EG} \cdot P_{EG} = y_{EG} \cdot P \quad (44)$$

$$x_{H_2O} \cdot \gamma_{H_2O} \cdot P_{H_2O} = y_{H_2O} \cdot P \quad (45)$$

$$x_{EG} + x_{H_2O} + x_{OLG} = 1 \quad (46)$$

where

x_{EG} , x_{H_2O} , x_{OLG} = liquid phase mole fraction of EG, water, oligomer;

y_{EG} , y_{H_2O} = vapor phase mole fraction of EG, water;

P_{EG} , P_{H_2O} = vapor pressure of EG, water;

P = total pressure (reaction pressure); and

γ_{EG} , γ_{H_2O} = activity coefficient of EG, water.

The activity coefficients are given by Van Laar equation

$$\ln \gamma_{EG} = \frac{A}{(1 + A \cdot x_{EG}/B \cdot x_{H_2O})^2} \quad (47)$$

$$\ln \gamma_{H_2O} = \frac{B}{(1 + B \cdot x_{H_2O}/A \cdot x_{EG})^2} \quad (48)$$

The vapor pressures are expressed by

$$\log P_{EG} = 7.8808 - 1957/(t + 193.8) \quad (49)$$

$$\log P_{H_2O} = 7.9668 - 1668.2/(t + 228) \quad (50)$$

where

A , B = constants of Van Laar equation,

P_{EG} , P_{H_2O} = vapor pressures of EG or water at a reaction temperature (mm Hg), and

t = reaction temperature ($^{\circ}\text{C}$).

The use of eqs. (42)–(50) gives the liquid phase or vapor phase mole fractions and the weight fraction of each component can be obtained from the following relation.

$$w_i = x_i M_i / \sum_{j=1}^N x_j M_j \quad (51)$$

where subscripts of i and j represent water, EG, and oligomer;

x_i, x_j = liquid phase mole fraction of component i, j ;
 w_i = liquid phase weight fraction of component i ;
 N = number of components; and
 M_i, M_j = molecular weight of component i, j .

The number average molecular weight of oligomer (M_{OLG}) in the liquid phase containing EG and water and excluding undissolved TPA is estimated by

$$M_{\text{OLG}} = \frac{2000\beta w_{\text{OLG}}}{\beta C_1 + \text{OHV}[1 - \beta(w_{\text{EG}} + w_{\text{H}_2\text{O}})]} \quad (52)$$

The derivation of eq. (52) is given in Appendix C.

Material Balance in a CSTR

The material balance of each component in the J th reactor of CSTR is as follows.

Carboxyl end groups

$$F_P^{J-1} \cdot C_{10} - F_P^J \cdot AV_a + \beta W (dC_1/d\theta) = 0 \quad (53)$$

Hydroxyl end groups

$$F_P^{J-1} \cdot C_{30} - \beta F_P^J \cdot C_3 + \beta W (dC_3/d\theta) = 0 \quad (54)$$

Diester groups

$$F_P^{J-1} \cdot C_{40} - \beta F_P^J \cdot C_4 + \beta W (dC_4/d\theta) = 0 \quad (55)$$

DEG

$$F_P^{J-1} \cdot (C_{60} + C_{70} + C_{80}) - \beta F_P^J \cdot (C_6 + C_7 + C_8) + \beta W (dC_6/d\theta + dC_7/d\theta + dC_8/d\theta) = 0 \quad (56)$$

Water

$$F_P^{J-1} \cdot C_{50} + \delta_{\text{H}_2\text{O}} \cdot F_S \cdot \eta_{\text{H}_2\text{O}} - \beta F_P^J \cdot C_5 - Q_{\text{H}_2\text{O}} \cdot \eta_{\text{H}_2\text{O}} + \beta W (dC_5/d\theta) = 0 \quad (57)$$

EG

$$F_P^{J-1} \cdot C_{20} + \delta_{\text{EG}} \cdot F_S \cdot \eta_{\text{EG}} - \beta F_P^J \cdot C_2 - Q_{\text{EG}} \cdot \eta_{\text{EG}} + \beta W (dC_2/d\theta) = 0 \quad (58)$$

where

C_{K0} = input concentration of component K into J th reactor;
 F_P^J = output rate of reaction mixtures from the J th reactor;

$$F_S = \text{throughput based on PET polymer}; F_S = \frac{166.23}{192.17} \cdot F_{\text{TPA}};$$

W = total weight of reaction mixtures in the J th reactor;

$\delta_{\text{EG}}, \delta_{\text{H}_2\text{O}}$ = flow rates of EG and water added anew to the J th reactor per 1 kg/h of throughput based on PET polymer;

$\gamma_{\text{EG}}, \eta_{\text{H}_2\text{O}}$ = equivalent concentrations of EG and water; $\eta_{\text{EG}} = 16.111 \text{ mol/kg (EG)}, \eta_{\text{H}_2\text{O}} = 55.494 \text{ mol/kg (H}_2\text{O)}$.

PROCEDURE FOR ESTIMATION OF CONCENTRATION OF EACH COMPONENT IN LIQUID PHASE

The concentration of each component is determined with given values for AV , OHV , and e by the procedure shown in Figure 1 entailing:

Step 1. q_{EG} and $q_{\text{H}_2\text{O}}$ are given by eqs. (26), (27), (29), (35), and (36).

Step 2. x_i and M_{OLG} are assumed as an initial value.

Step 3. w_i is given by eq. (51), and β is given by eqs. (20), (21), and (25).

Step 4. New M_{OLG} ($M_{\text{OLG},N}$) is given by eq. (52)—If the difference between $M_{\text{OLG},N}$ and M_{OLG} is very small (less than ϵ_1), the calculation proceeds to the next step after $M_{\text{OLG},N}$ is replaced by M_{OLG} . If not so, the calculation returns to Step 3 after $M_{\text{OLG},N}$ is replaced by M_{OLG} .

Step 5. Q_{EG} and $Q_{\text{H}_2\text{O}}$ are given by eqs. (40) and (41). y_{EG} is given by eq. (42).

Step 6. New x_i ($x_{i,N}$) is given by eqs. (43)–(50).—If the difference between $x_{i,N}$ and x_i is very small (less than ϵ_2), x_i is determined after $x_{i,N}$ is replaced by x_i . If not so, the calculation returns to Step 3 after $x_{i,N}$ is replaced by x_i .

Step 7. $x_i, y_i, w_i, M_{\text{OLG}}, Q_{\text{EG}}, Q_{\text{H}_2\text{O}}$, and β are determined as results.

EFFECT OF DIANTIMONY TRIOXIDE AND TITANIUM DIOXIDE ON REACTION RATE CONSTANTS

The reaction rate constants (k_i) of the reaction scheme for the direct esterification between TPA and EG are related to the reaction temperature and the concentrations of diantimony trioxide and titanium dioxide as follows.^{4,7}

$$k_1 = (3.75 \times 10^{-4} \cdot \text{Sb}^{3+} + 1) \times 1.5657 \times 10^9 \cdot \exp(-19640/RT) \quad (59)$$

$$k_2 = (4.75 \times 10^{-4} \cdot \text{Sb}^{3+} + 1) \times 1.5515 \times 10^8 \cdot \exp(-18140/RT) \quad (60)$$

$$k_3 = (6.25 \times 10^{-4} \cdot \text{Sb}^{3+} + 0.1[\text{TDO}] + 1) \times 3.5165 \times 10^9 \cdot \exp(-22310/RT) \quad (61)$$

$$k_4 = (4.50 \times 10^{-4} \cdot \text{Sb}^{3+} + 1) \times 6.7640 \times 10^7 \cdot \exp(-18380/RT) \quad (62)$$

$$k_5 = (3.50 \times 10^{-4} \cdot \text{Sb}^{3+} + 0.08[\text{TDO}] + 1) \times 7.7069 \cdot \exp(-2810/RT) \quad (63)$$

$$k_6 = (1.75 \times 10^{-4} \cdot \text{Sb}^{3+} + 0.04[\text{TDO}] + 1) \times 6.2595 \times 10^6 \cdot \exp(-14960/RT) \quad (64)$$

$$k_7 = (3.75 \times 10^{-4} \cdot \text{Sb}^{3+} + 0.085714[\text{TDO}] + 1) \times 2.0583 \times 10^{15} \cdot \exp(-42520/RT) \quad (65)$$

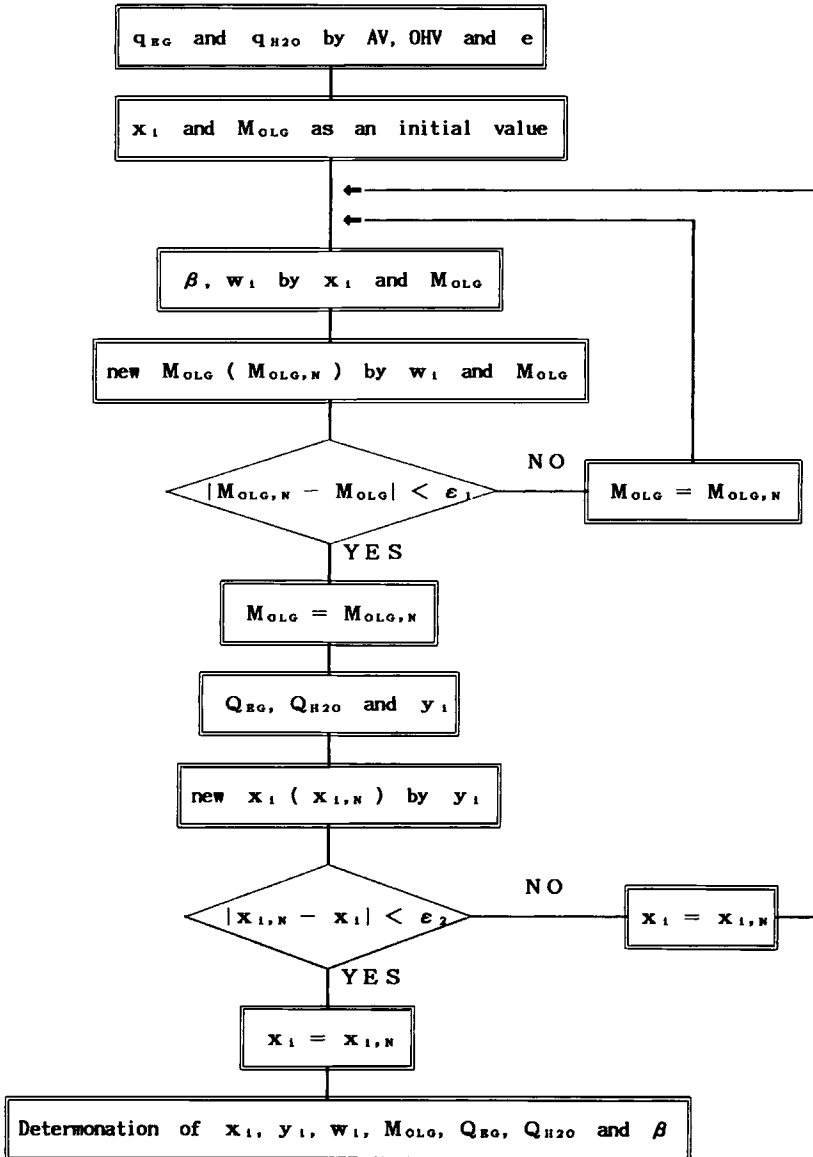


Fig. 1. Determination procedure of x_i , y_i , w_i , M_{OLG} , Q_{EG} , Q_{H_2O} , and β in use of AV, OHV, and e.

where Sb^{3+} is the mole number of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 moles of TPA; [TDO] is the weight percent of charged titanium dioxide against PET; R is the gas constant; T is the absolute temperature.

RESULTS AND DISCUSSION

Table I lists the simulation results at various concentrations of water (δ_{H_2O}) added the first esterification reactor under the conditions of $P = 0, 0.5$

and $1.0 \text{ kg/cm}^2\text{G}$, $E/T = 2.0$, $\tau = 5.0 \text{ h}$, concentration of antimony trioxide (Sb^{3+}) = $400 \mu\text{mol/TPAmol}$, and concentration of titanium dioxide ($[\text{TDO}]$) = 0.5 wt \% /PET . Figures 2-7 show the relations of the amount of water added to the first reactor ($\delta_{\text{H}_2\text{O}}$) and the dried oligomer properties (AV , ϕ , P_n , M_n , E_S , d) at $P = 0 \text{ kg/cm}^2\text{G}$ with the simulation results tabulated in Table I. In general, these figures suggest that the higher the $\delta_{\text{H}_2\text{O}}$ is, the lower the reaction rates become and then the higher the reaction temperature is, the higher the degree of decrease in the reaction rates becomes. This is due to why the higher $\delta_{\text{H}_2\text{O}}$ brings about the higher decrease of EG dissolved in the reaction mixtures by the vapor-liquid equilibrium relation in the reactor: Although the higher $\delta_{\text{H}_2\text{O}}$ gives the worse results, the main reaction rates become lower, as shown in Figures 2-6; on the other hand, it brings the better results that the side reaction of diethylene glycol (DEG) formation is suppressed, as shown in Figure 7.

Figure 8 shows the relation between $\delta_{\text{H}_2\text{O}}$ and the weight fraction of water in the vapor phase (distillate), $w_{\text{H}_2\text{O}}^d$. In spite of addition of water, $w_{\text{H}_2\text{O}}^d$ becomes lower as $\delta_{\text{H}_2\text{O}}$ becomes higher. From this figure that is considered why EG in the reaction mixtures decreases so as to satisfy the vapor-liquid equilibrium by adding water to the reactor, so that EG removed from the reaction mixtures brings its increase in the vapor phase. This fact means that by the adequate addition of water polymer of low DEG content can be produced.

Figure 9 shows the relation between AV and β . From this figure, it is confirmed that this relation can be expressed by a fixed curve, independent of $\delta_{\text{H}_2\text{O}}$ and reaction temperature. This figure suggests that the clearing point where solid TPA begins not to exist in the reaction mixtures, that is the point of $\beta = 1$, is the point of $AV = 0.6 \text{ eq/kg}$. This gives almost the same result as that obtained from our experimental observation of the pilot plant. The agreement of the estimated and observed results suggests support of the validity of the present model; the mathematical model, solubilities of TPA, assumption of vapor-liquid equilibrium as ideal solution, and so on.

CONCLUSION

The computer simulation was carried out to predict the effect of water in EG added into a reactor and on the esterification reactions. From the simulation results, it has been quantitatively understood that the addition of water brings about the undesirable effect of the decrease in main reactions in the esterification process, but on the other hand it gives the desirable effect of the suppression of side reactions (DEG formation reactions). It has also been shown that the reaction pressure has a great influence on their reactions.

The good agreement of the clearing point between estimated and observed results supports the validity of the present model.

APPENDIX A: DERIVATION OF $k_8 = 2k_7$ AND $k_9 = 4k_7$

Considering that the reaction rate constants of k_7 , k_8 , and k_9 correspond to the encounter probability of each hydroxyl end group, the probability where one end group reacts with the others is proportional to the number of combinations for each end group given below.

TABLE I
 Simulation Results for First Esterification Reactor at

t (°C)	P (kg/cm ² G)	τ (h)	E/T	δ_{EG}	δ_{H_2O}	AV (eq/kg)	OHV (eq/kg)	ϕ	E_s	M_n	P_n
240	0.0	5.0	2.0	0.00	0.00	4.583	1.294	0.220	0.568	340	1.804
240	0.0	5.0	2.0	0.00	0.01	5.155	1.216	0.191	0.519	314	1.681
240	0.0	5.0	2.0	0.00	0.02	5.785	1.128	0.163	0.465	289	1.565
240	0.0	5.0	2.0	0.00	0.03	6.499	1.025	0.136	0.407	266	1.456
240	0.0	5.0	2.0	0.00	0.04	7.384	0.894	0.108	0.336	242	1.343
240	0.0	5.0	2.0	0.00	0.05	8.750	0.676	0.072	0.231	212	1.207
250	0.0	5.0	2.0	0.00	0.00	2.447	1.186	0.327	0.763	550	2.847
250	0.0	5.0	2.0	0.00	0.01	2.897	1.149	0.284	0.722	494	2.575
250	0.0	5.0	2.0	0.00	0.02	3.373	1.108	0.247	0.679	446	2.343
250	0.0	5.0	2.0	0.00	0.03	3.884	1.063	0.215	0.633	404	2.139
250	0.0	5.0	2.0	0.00	0.04	4.434	1.013	0.186	0.585	367	1.959
250	0.0	5.0	2.0	0.00	0.05	5.052	0.955	0.159	0.531	333	1.794
260	0.0	5.0	2.0	0.00	0.00	0.600	0.930	0.608	0.941	1306	6.648
260	0.0	5.0	2.0	0.00	0.01	0.961	0.914	0.488	0.906	1067	5.457
260	0.0	5.0	2.0	0.00	0.02	1.338	0.897	0.401	0.870	895	4.603
260	0.0	5.0	2.0	0.00	0.03	1.707	0.879	0.340	0.835	773	4.001
260	0.0	5.0	2.0	0.00	0.04	2.148	0.858	0.286	0.794	665	3.463
260	0.0	5.0	2.0	0.00	0.05	2.583	0.837	0.245	0.753	585	3.063
240	0.5	5.0	2.0	0.00	0.00	2.357	1.874	0.443	0.767	473	2.389
240	0.5	5.0	2.0	0.00	0.01	2.739	1.821	0.399	0.731	439	2.232
240	0.5	5.0	2.0	0.00	0.02	3.135	1.765	0.360	0.694	408	2.092
240	0.5	5.0	2.0	0.00	0.03	3.558	1.704	0.324	0.655	380	1.962
240	0.5	5.0	2.0	0.00	0.04	4.005	1.639	0.290	0.615	354	1.844
240	0.5	5.0	2.0	0.00	0.05	4.482	1.567	0.259	0.573	331	1.735
250	0.5	5.0	2.0	0.00	0.00	0.481	1.607	0.770	0.952	958	4.758
250	0.5	5.0	2.0	0.00	0.01	0.687	1.575	0.696	0.931	884	4.409
250	0.5	5.0	2.0	0.00	0.02	1.014	1.550	0.604	0.899	780	3.911
250	0.5	5.0	2.0	0.00	0.03	1.350	1.522	0.530	0.866	696	3.509
250	0.5	5.0	2.0	0.00	0.04	1.702	1.493	0.467	0.832	626	3.173
250	0.5	5.0	2.0	0.00	0.05	2.066	1.461	0.414	0.797	567	2.891
260	0.5	5.0	2.0	0.00	0.00	0.394	1.421	0.783	0.960	1102	5.490
260	0.5	5.0	2.0	0.00	0.01	0.415	1.372	0.768	0.958	1119	5.590
260	0.5	5.0	2.0	0.00	0.02	0.436	1.326	0.752	0.956	1135	5.681
260	0.5	5.0	2.0	0.00	0.03	0.458	1.281	0.737	0.954	1150	5.765
260	0.5	5.0	2.0	0.00	0.04	0.480	1.240	0.721	0.952	1163	5.840
260	0.5	5.0	2.0	0.00	0.05	0.503	1.201	0.705	0.950	1173	5.905
240	1.0	5.0	2.0	0.00	0.00	1.383	2.280	0.622	0.859	546	2.686
240	1.0	5.0	2.0	0.00	0.01	1.684	2.236	0.570	0.830	510	2.523
240	1.0	5.0	2.0	0.00	0.02	1.996	2.191	0.523	0.799	478	2.376
240	1.0	5.0	2.0	0.00	0.03	2.320	2.142	0.480	0.768	448	2.243
240	1.0	5.0	2.0	0.00	0.04	2.657	2.091	0.440	0.736	421	2.121
240	1.0	5.0	2.0	0.00	0.05	3.003	2.037	0.404	0.704	397	2.011
250	1.0	5.0	2.0	0.00	0.00	0.418	2.020	0.828	0.957	820	4.009
250	1.0	5.0	2.0	0.00	0.01	0.436	1.967	0.819	0.955	832	4.077
250	1.0	5.0	2.0	0.00	0.02	0.454	1.917	0.808	0.954	843	4.140
250	1.0	5.0	2.0	0.00	0.03	0.473	1.869	0.798	0.952	854	4.200
250	1.0	5.0	2.0	0.00	0.04	0.587	1.857	0.760	0.941	819	4.036
250	1.0	5.0	2.0	0.00	0.05	0.751	1.800	0.706	0.924	784	3.881
260	1.0	5.0	2.0	0.00	0.00	0.337	1.838	0.845	0.966	919	4.502
260	1.0	5.0	2.0	0.00	0.01	0.352	1.782	0.835	0.964	937	4.599
260	1.0	5.0	2.0	0.00	0.02	0.368	1.730	0.825	0.963	954	4.692
260	1.0	5.0	2.0	0.00	0.03	0.384	1.679	0.814	0.961	969	4.780
260	1.0	5.0	2.0	0.00	0.04	0.400	1.631	0.803	0.960	985	4.866
260	1.0	5.0	2.0	0.00	0.05	0.417	1.586	0.792	0.958	999	4.945

$$F_s = 100 \text{ kg/h, Sb}_2\text{O}_3 = 400 \text{ } \mu\text{mol, T}_1\text{O}_2 = 0.5 \text{ wt } \%$$

Various Amounts of Water Charged into Reactor

100e (%)	d (%)	w_{EG}	w_{H_2O}	$w_{H_2O}^d$	Q (kg/h)	F_P (kg/h)	F_P^0 (kg/h)	β	T_m (°C)	βw_{EG}
0.891	0.609	0.0158	0.0004	0.205	51.9	99.1	98.1	0.646	226	0.0102
0.936	0.586	0.0164	0.0004	0.199	53.9	98.1	97.1	0.597	224	0.0098
0.986	0.556	0.0171	0.0004	0.191	56.0	97.0	96.1	0.543	215	0.0093
1.055	0.522	0.0180	0.0004	0.182	58.2	95.8	95.0	0.482	—	0.0087
1.162	0.478	0.0194	0.0004	0.170	60.7	94.4	93.6	0.406	—	0.0079
1.385	0.396	0.0223	0.0004	0.146	63.9	92.1	91.5	0.288	—	0.0064
0.922	0.802	0.0072	0.0003	0.287	49.9	101.1	100.5	0.831	229	0.0060
0.959	0.791	0.0075	0.0003	0.281	51.6	100.4	99.8	0.793	231	0.0059
1.000	0.777	0.0077	0.0003	0.276	53.4	99.6	99.0	0.752	234	0.0058
1.050	0.762	0.0080	0.0003	0.269	55.2	98.8	98.3	0.708	238	0.0057
1.107	0.744	0.0083	0.0003	0.262	57.1	98.0	97.4	0.660	241	0.0055
1.179	0.722	0.0087	0.0003	0.254	59.0	97.0	96.5	0.607	240	0.0053
0.830	0.850	0.0035	0.0002	0.363	48.5	102.5	102.1	0.996	237	0.0035
0.858	0.847	0.0035	0.0002	0.359	50.1	102.0	101.6	0.964	234	0.0034
0.892	0.847	0.0036	0.0002	0.354	51.6	101.4	101.0	0.932	233	0.0034
0.918	0.837	0.0037	0.0002	0.351	53.2	100.9	100.5	0.900	232	0.0033
0.965	0.837	0.0038	0.0002	0.344	54.8	100.2	99.9	0.861	233	0.0033
1.011	0.834	0.0039	0.0002	0.339	56.5	99.6	99.2	0.824	236	0.0032
1.074	1.011	0.0201	0.0008	0.309	46.4	104.6	102.8	0.838	215	0.0168
1.109	0.998	0.0205	0.0008	0.304	48.1	103.9	102.1	0.805	216	0.0165
1.149	0.984	0.0211	0.0008	0.300	49.9	103.1	101.4	0.772	216	0.0163
1.192	0.967	0.0217	0.0008	0.295	51.7	102.3	100.7	0.736	217	0.0160
1.245	0.950	0.0224	0.0008	0.289	53.5	101.5	99.9	0.698	217	0.0156
1.301	0.928	0.0232	0.0008	0.283	55.4	100.6	99.0	0.657	216	0.0152
1.124	1.237	0.0090	0.0006	0.391	45.5	105.6	104.5	1.000	225	0.0090
1.124	1.210	0.0090	0.0006	0.392	46.9	105.1	104.1	0.983	224	0.0088
1.159	1.207	0.0092	0.0006	0.388	48.5	104.6	103.6	0.955	223	0.0088
1.199	1.205	0.0094	0.0006	0.384	50.0	104.0	103.0	0.926	222	0.0087
1.240	1.199	0.0097	0.0006	0.379	51.6	103.4	102.5	0.896	222	0.0087
1.285	1.194	0.0099	0.0006	0.374	53.2	102.8	101.9	0.865	223	0.0086
1.834	1.987	0.0061	0.0004	0.388	46.3	104.7	104.0	1.000	229	0.0061
1.718	1.851	0.0059	0.0004	0.398	47.5	104.5	103.8	1.000	230	0.0059
1.612	1.727	0.0056	0.0004	0.408	48.8	104.3	103.7	1.000	231	0.0056
1.514	1.614	0.0054	0.0004	0.418	50.0	104.1	103.5	1.000	231	0.0054
1.426	1.512	0.0052	0.0004	0.427	51.1	103.9	103.3	1.000	232	0.0052
1.346	1.420	0.0050	0.0004	0.435	52.3	103.7	103.2	1.000	232	0.0050
1.305	1.406	0.0252	0.0014	0.373	42.8	108.2	105.6	0.921	209	0.0232
1.341	1.397	0.0257	0.0014	0.370	44.5	107.6	105.0	0.896	210	0.0230
1.381	1.389	0.0263	0.0014	0.366	46.1	106.9	104.4	0.870	210	0.0229
1.423	1.378	0.0269	0.0014	0.362	47.8	106.3	103.8	0.842	210	0.0226
1.469	1.367	0.0275	0.0014	0.358	49.4	105.6	103.1	0.814	210	0.0224
1.518	1.353	0.0282	0.0014	0.354	51.1	104.9	102.5	0.785	210	0.0221
1.762	2.015	0.0138	0.0010	0.411	43.4	107.6	106.1	1.000	218	0.0138
1.675	1.905	0.0132	0.0009	0.421	44.7	107.4	105.8	1.000	218	0.0132
1.595	1.803	0.0126	0.0009	0.431	45.9	107.1	105.6	1.000	219	0.0126
1.521	1.711	0.0121	0.0009	0.440	47.2	106.8	105.5	1.000	220	0.0121
1.472	1.638	0.0120	0.0009	0.445	48.4	106.6	105.2	0.992	220	0.0119
1.487	1.620	0.0118	0.0009	0.446	49.9	106.1	104.8	0.978	220	0.0115
3.015	3.375	0.0096	0.0007	0.406	44.4	106.6	105.5	1.000	222	0.0096
2.845	3.169	0.0092	0.0007	0.416	45.7	106.4	105.3	1.000	222	0.0092
2.689	2.981	0.0087	0.0007	0.426	46.9	106.1	105.1	1.000	223	0.0087
2.544	2.807	0.0083	0.0007	0.435	48.2	105.9	104.9	1.000	224	0.0083
2.410	2.646	0.0080	0.0007	0.444	49.4	105.7	104.7	1.000	225	0.0080
2.287	2.500	0.0076	0.0007	0.453	50.6	105.4	104.6	1.000	226	0.0076

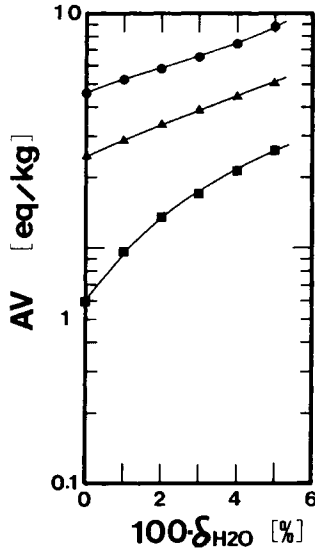
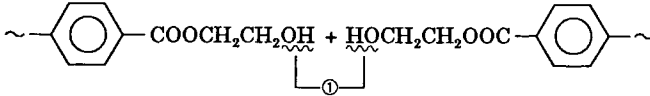


Fig. 2. Influence of added water (δ_{H_2O}) on AV under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

For k_7 in eq. (4), its combination number is one from the following expression



For k_8 in eq. (5), its combination number is two from the following expression

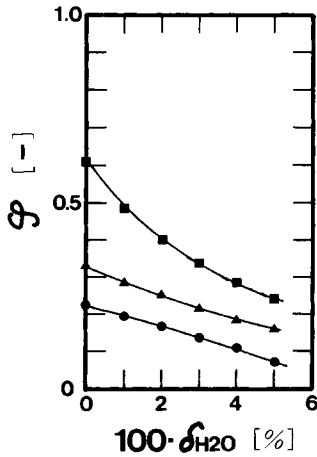
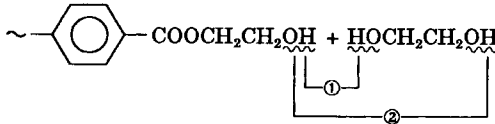


Fig. 3. Influence of added water (δ_{H_2O}) on ϕ under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

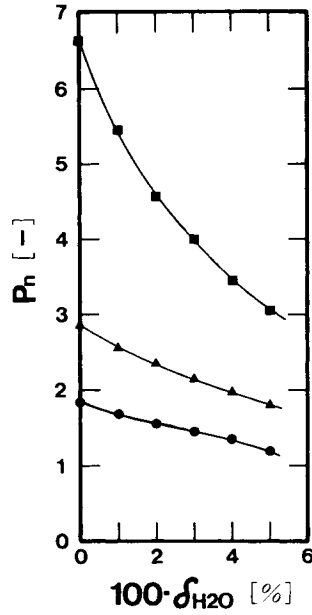


Fig. 4. Influence of added water (δ_{H_2O}) on P_n under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

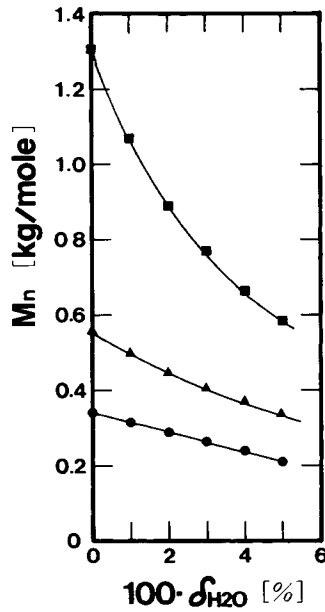


Fig. 5. Influence of added water (δ_{H_2O}) on M_n under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

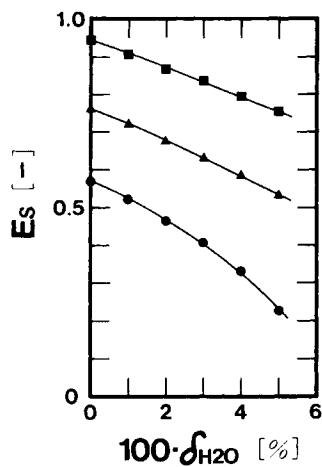
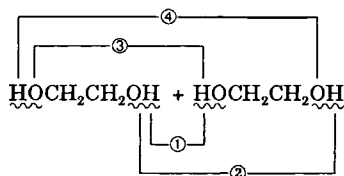


Fig. 6. Influence of added water (δ_{H_2O}) on E_S under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

For k_9 in eq. (6), its combination number is four from the following expression



If the hydroxyl end groups have the same reactivity, it can be derived from the above combinations that $k_8 = 2k_7$ and $k_9 = 4k_7$.

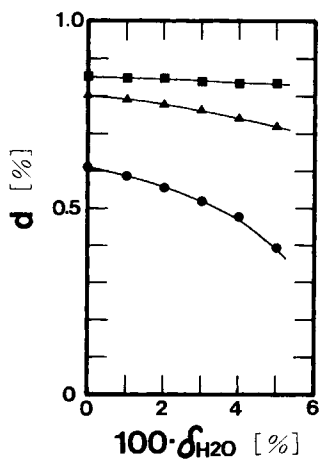


Fig. 7. Influence of added water (δ_{H_2O}) on d under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

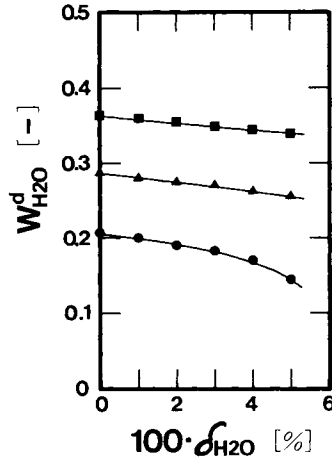


Fig. 8. Relation between added water (δ_{H_2O}) and weight fraction of water in the vapor phase ($w_{H_2O}^d$) under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

APPENDIX B: DERIVATION OF EQS. (35) AND (36)

Derivation of Eq. (35) (q_{EG})

We consider a molecule of oligomer of poly(ethylene terephthalate) (PET) with the polymerization degree of P_n . The amount of ethylene glycol (EG) bound into the polymer chain is given by $(P_n - 1)/(1 + e)$, and that of the end group given by $2\phi/(1 + e)$. Then the amount of EG due to ether (DEG) linkage bound into the polymer chain is given by $2(P_n - 1)e/(1 + e)$, and that of the end group given by $4\phi e/(1 + e)$.

The ratio of bound EG to a polymer chain linkage is given by $[(P_n - 1)/(1 + e) + 2\phi/(1 + e) + 2(P_n - 1)e/(1 + e) + 4\phi e/(1 + e)]/P_n$.

From the above, the changed amount of bound EG (q_{EG}) from the polymerization degree of P_{ni} to P_{nf} , which is equal to that consumed by the reactions shown in eqs. (1)–(7), is expressed by the following equation

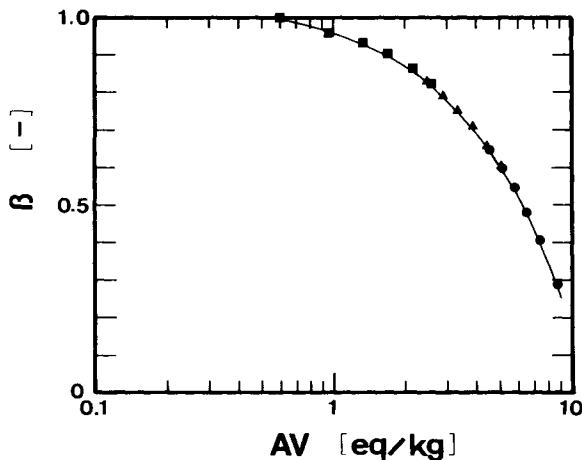


Fig. 9. Relation between AV and weight fraction of liquid phase (β) under $P = 0 \text{ kg/cm}^2\text{G}$. ●, 240°C; ▲, 250°C; ■, 260°C.

$$q_{EG} = F_{TPA} (M_{EG}/M_{EG}) \{ [(P_{nf} - 1)/(1 + e) + 2\phi_f/(1 + e) + 2(P_{nf} - 1)e/(1 + e) + 4\phi_f e/(1 + e)]/P_{nf} - [(P_{ni} - 1)/(1 + e) + 2\phi_i/(1 + e) + 2(P_{ni} - 1)e/(1 + e) + 4\phi_i e/(1 + e)]/P_{ni} \} \quad (66)$$

where M_{EG} = molecular weight of EG, $M_{EG} = 62.07$; and M_{TPA} = molecular weight of TPA, $M_{EG} = 166.13$.

Judging from the DEG content in oligomer of a few percents, the influence of DEG on q_{EG} is negligible. If so ($e = 0$), eq. (66) reduces to eq. (35).

Derivation of Eq. (36) (q_{H_2O})

After the manner of the derivation of q_{EG} , we consider a molecule of PET oligomer with the polymerization degree of P_n . When a polymer chain linkage is formed by the reactions shown in eqs. (1) and (2), two molecules of water are generated. Therefore, for the formation of the oligomer with the polymer chain linkages of $(P_n - 1)$, the water molecules of $2(P_n - 1)$ are generated. Then, as the formation of a hydroxyl end group brings about the generation of a molecule of water, the water molecules of 2ϕ are generated for the formation of the oligomer with the hydroxyl end group ratio of ϕ .

On the other hand, for the formation of an ether (DEG) linkage bound into the polymer chain, three molecules of water are generated from eq. (4); for the formation of the DEG end group, two molecules are generated from eqs. (5)–(7). An oligomer with the polymerization degree of P_n comprises the polymer chains with the EG linkages of $(P_n - 1)/(1 + e)$ and DEG linkages of $(P_n - 1)e/(1 + e)$, and the bifunctional end groups with the carboxyl end groups of $2(1 - \phi)$ and hydroxyl endgroups of 2ϕ ; the hydroxyl end groups comprise EG molecules of $2\phi/(1 + e)$ and the DEG molecules of $2\phi e/(1 + e)$.

From the above results, the amount of water (q_{H_2O}) generated by the reactions is expressed by the following equation after the manner of the derivation of q_{EG} .

$$q_{H_2O} = F_{TPA} (M_{EG}/M_{EG}) \{ [2(P_{nf} - 1)/(1 + e) + 2\phi_f/(1 + e) + 3(P_{nf} - 1)e/(1 + e) + 4\phi_f e/(1 + e)]/P_{nf} - [2(P_{ni} - 1)/(1 + e) + 2\phi_i/(1 + e) + 3(P_{ni} - 1)e/(1 + e) + 4\phi_i e/(1 + e)]/P_{ni} \} \quad (67)$$

Judging from the DEG content in oligomer of a few percents, the influence of DEG on q_{H_2O} is negligible. If so ($e = 0$), eq. (67) reduces to eq. (36).

APPENDIX C: DERIVATION OF EQ. (52)

Now, we consider the reaction mixtures of W kg which consist of the liquid phase (βW kg; oligomer without undissolved TPA and with dissolved TPA, EG, and water) and the solid phase ($(1 - \beta)W$ kg; undissolved TPA).

As the weight of oligomer in the liquid phase is $\beta W w_{OLG}$ kg, the number of molecules of oligomer with the number average molecular weight of M_{OLG} in the liquid phase is expressed by $\beta W w_{OLG}/(M_{OLG}/1000)$. On the other hand, the number of the oligomer molecules can be also given by $\{\beta W C_1 + OHV[1 - \beta(w_{EG} + w_{H_2O})]\}/2$. From the above results, we can obtain the following relation.

$$\beta W w_{OLG}/(M_{OLG}/1000) = \{\beta W C_1 + OHV[1 - \beta(w_{EG} + w_{H_2O})]\}/2 \quad (68)$$

Rearrangement of eq. (68) gives eq. (52).

NOMENCLATURE

AV	concentrations of total carboxyl end groups in dried oligomer, eq/kg; $AV = C_T / \{ T_S + W_e [1 - (w_{EG} + w_{H_2O})] \}$
AV_a	concentration of total carboxyl end groups in the reaction mixtures, eq/kg; $AV_a = C_T / (T_S + W_e)$
C_1	concentration of carboxyl end groups in the liquid phase of reaction mixtures, eq/kg
C_2	concentration of EG in the liquid phase of reaction mixtures, mol/kg
C_3	concentration of hydroxyl end groups in the liquid phase of reaction mixtures, eq/kg
C_4	concentration of diester groups in the liquid phase of reaction mixtures, mol/kg
C_5	concentration of water in the liquid phase of reaction mixtures, mol/kg
C_6, C_7, C_8	concentration of free and bound DEG in the liquid phase of reaction mixtures, mol/kg
C_{k0}	input concentration of component k , eq/kg or mol/kg
C_T	total amount of carboxyl end groups, equiv.
$dC_i/d\theta$	reaction rate of component i , eq/kg·h or mol/kg·h
d	percentage of DEG content in dried oligomer based on bound TPA, 10^{-2} mol/mol (TPA)
e	molar ratio of DEG content to bound EG in dried oligomer, mol/mol (bound EG)
E_S	esterification degrees of dried oligomer
E/T	molar ratio of EG to TPA of the slurry, which fed to the first reactor
F_P	actual output rates of reaction mixtures discharged from the reactor, kg/h
F_P^J	actual output rates of reaction mixtures discharged from the J th reactor, kg/h
F_S	throughput based on PET, kg/h
F_{TPA}	throughput based on TPA, kg/h
k_1 to k_9	reaction rate constants as defined in eqs. (1)–(7)
M_n	number average molecular weight of oligomer, g/mol
M_{OLG}	number average molecular weight of oligomer in the liquid phase free from undissolved TPA defined as eq. (52), g/mol
n	number of reactors
OHV	concentrations of hydroxyl end groups in 1 kg dried oligomer, eq/kg
P	total pressures (= reaction pressures), mm Hg or Torr
P_n	number average degree of polymerization of oligomer
Q	total vapor flow rate, kg/h; $Q = Q_{EG} + Q_{H_2O}$
Q_{EG}	vapor flow rate of EG, kg/h
Q_{H_2O}	vapor flow rate of water, kg/h
Sb^{3+}	mole number of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 moles of TPA, $\mu\text{mol}/\text{TPAmol}$
SV	saponification value calculated from eq. (30), eq/kg
t	reaction temperatures, °C
T_m	melting point of dried oligomer, °C
[TDO]	weight percent of charged titanium dioxide against PET, wt %
w_{EG}	weight fraction of EG in the liquid phase of reaction mixtures free from undissolved TPA
w_{H_2O}	weight fraction of water in the liquid phase of reaction mixtures free from undissolved TPA
w_{EG}^d	weight fraction of EG in the vapor phase
$w_{H_2O}^d$	weight fraction of water in the vapor phase
w'_{EG}	weight fraction of EG in the reaction mixtures containing undissolved TPA; $w'_{EG} = \beta \cdot w_{EG}$
w'_{H_2O}	weight fraction of water in the reaction mixtures containing undissolved TPA; $w'_{H_2O} = \beta \cdot w_{H_2O}$
W	total weights of reaction mixtures in the reactor, kg
W_e	weight of liquid phase in the reaction mixtures, kg

Greek Symbols

β	weight fraction of liquid phase in the reaction mixtures; $\beta = W_e/(W_e + T_S)$
δ_{EG}	flow rate of EG added anew into the reactor per 1 kg/h throughput based on PET polymer, (kg/h)/(kg/h)(PET)
δ_{H_2O}	flow rate of water added anew into the J th reactor per 1 kg/h throughput based on PET polymer, (kg/h)/(kg/h)(PET)
η_{EG}	equivalent concentration of EG, $\eta_{EG} = 16.111$ mol/kg(EG)
η_{H_2O}	equivalent concentration of water, $\eta_{H_2O} = 55.494$ mol/kg(H ₂ O)
θ	reaction time, h
τ	mean residence time defined by W/F_S , h
ϕ	ratio of hydroxyl end groups to total end groups of dried oligomer; $\phi = OHV/(AV + OHV)$

Subscripts

EG	ethylene glycol
H ₂ O	water
TPA	terephthalic acid

Superscripts

d distillate (vapor phase)

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