Effect of Titanium Dioxide on Direct Esterification between Terephthalic Acid and Ethylene Glycol

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SYNOPSIS

Experiments at various concentrations for A and B kinds of titanium dioxide were made in the pilot plant, and the effect of titanium dioxide on continuous esterification between terephthalic acid and ethylene glycol was obtained. Reaction rate constants of the reaction scheme reported by Yamada et al. (1985) were determined to fit with the experimental data obtained. It was found that titanium dioxide ([TDO]) does not exert an influence on the reaction rate constants of k_1, k_2, and k_4 but does on the reaction rate constants of k_3, k_5, k_6, and k_7 as follows:

$$k_1 = 1.5657 \times 10^9 \exp(-19{,}640/RT)$$

$$k_2 = 1.5515 \times 10^8 \exp(-18{,}140/RT)$$

$$k_3 = (0.10[TDO] + 1) \times 3.5165 \times 10^9 \exp(-22{,}310/RT)$$

$$k_4 = 6.7640 \times 10^7 \exp(-18{,}380/RT)$$

$$k_5 = (0.08[TDO] + 1) \times 7.7069 \exp(-2{,}810/RT)$$

$$k_6 = (0.04[TDO] + 1) \times 6.2595 \times 10^6 \exp(-14{,}960/RT)$$

$$k_7 = (0.60[TDO] + 1) \times 2.0583 \times 10^{15} \exp(-42{,}520/RT) \text{ for B kind}$$

$$k_7 = (0.085714[TDO] + 1) \times 2.0583 \times 10^{15} \exp(-42{,}520/RT) \text{ for A kind}$$

Applying these reaction rate constants, simulation of continuous esterification in the first tank reactor was made and the following results were obtained: (1) The acceleration effect of titanium dioxide on the esterification reaction is minor, and there is hardly any difference in the effect on the esterification due to kinds of titanium dioxide. (2) The amount of diethylene glycol formation largely varies with kinds of titanium dioxide.

INTRODUCTION

The effect of polycondensation catalysts, potassium titanium oxyoxalate, and diantimony trioxide on the direct esterification between terephthalic acid (TPA) and ethylene glycol (EG) in a continuous process, which is one of the manufacturing methods of poly(ethylene terephthalate) (PET) and adopted recently worldwide for the purpose of cost reduction, were already reported.[1,2]

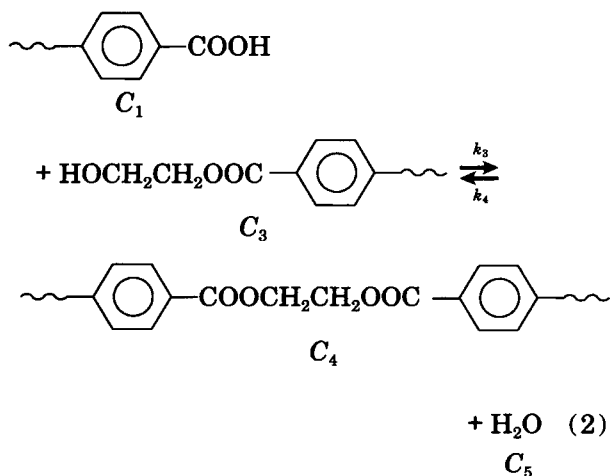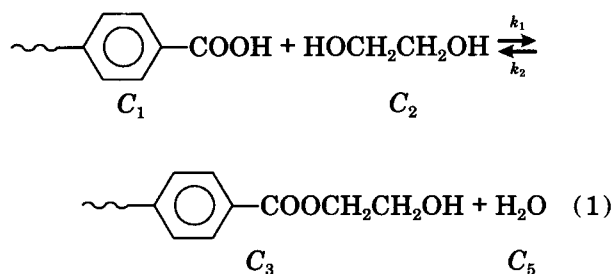On the other hand, when manufacturing synthetic fiber, film, etc. from PET, for making it dull or improving the spinability or "slipperability," it is customary that titanium dioxide (TiO_2) is added in PET. In order to secure better dispersion, is preferable to introduce the additive (titanium dioxide) at the stage, i.e., as earlier as possible, in the process. When titanium dioxide is introduced at the initial stage of the process, for example, at the esterication stage, there is a certain possibility that titanium dioxide may exert a certain influence on the esterification; therefore, it becomes important for industrial PET manufacturing to know the influence quantitatively.

To this author's knowledge, there is hardly any report on the influence of titanium dioxide on the esterification reaction between TPA and EG, and there are only a few patents by York[3] dealing with the item. In these patents the influence of titanium dioxide on the esterification is dealt only qualitatively, and as far as this author could find there is no literature dealing with the influence quantitatively. In the present study the quantitative analysis results of the influence of titanium dioxide on the esterification reaction between TPA and EG is reported.
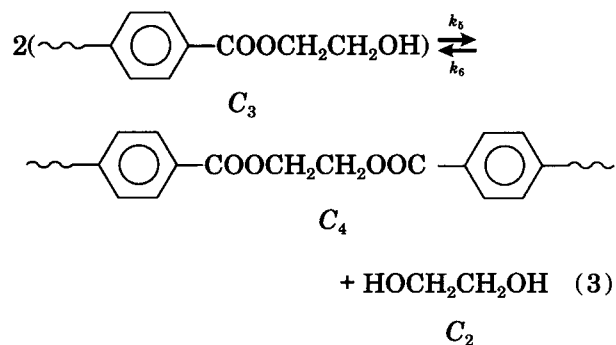
REACTION SCHEME FOR DIRECT ESTERIFICATION

Various reactions occurring in an reactor are given as follows.[4]
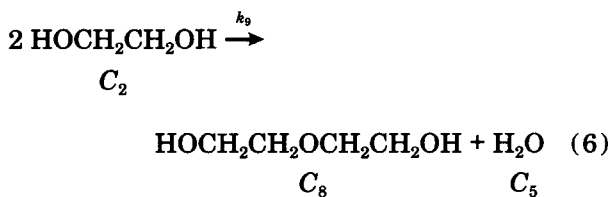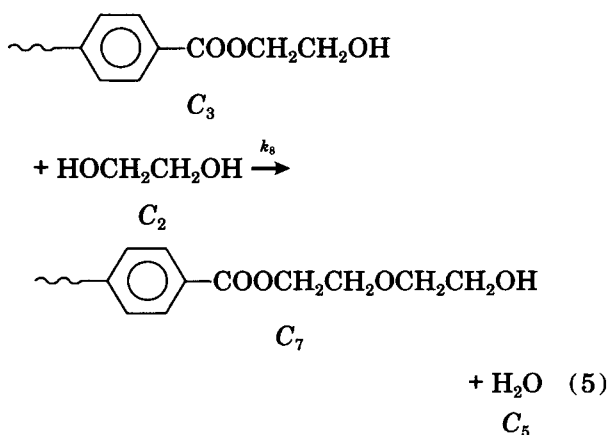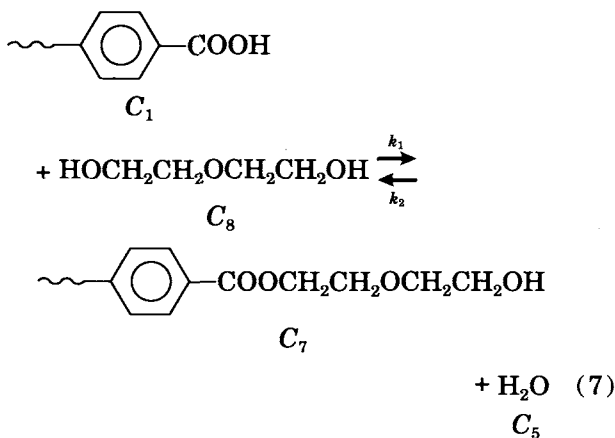
Esterification Reactions

$$\sim\!\!\!\langle\bigcirc\rangle\!\!-\!COOH + HOCH_2CH_2OH \underset{k_2}{\overset{k_1}{\rightleftarrows}}$$
$$\quad\quad C_1 \quad\quad\quad\quad C_2$$

$$\sim\!\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OH + H_2O \quad (1)$$
$$\quad\quad C_3 \quad\quad\quad\quad\quad C_5$$

$$\sim\!\!\!\langle\bigcirc\rangle\!\!-\!COOH$$
$$\quad\quad C_1$$

$$+ HOCH_2CH_2OOC\!\!-\!\!\langle\bigcirc\rangle\!\!\sim \underset{k_4}{\overset{k_3}{\rightleftarrows}}$$
$$\quad\quad\quad C_3$$

$$\sim\!\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OOC\!\!-\!\!\langle\bigcirc\rangle\!\!\sim$$
$$\quad\quad\quad C_4$$

$$+ H_2O \quad (2)$$
$$\quad C_5$$

Polycondensation Reactions

$$2(\sim\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OH) \underset{k_6}{\overset{k_5}{\rightleftarrows}}$$
$$\quad\quad C_3$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OOC\!\!-\!\!\langle\bigcirc\rangle\!\!\sim$$
$$\quad\quad C_4$$

$$+ HOCH_2CH_2OH \quad (3)$$
$$\quad C_2$$

Side Reactions Leading to the Formation of Diethylene Glycol (DEG) in the Oligomer

$$2(\sim\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OH) \overset{k_7}{\rightarrow}$$
$$\quad\quad C_3$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OCH_2CH_2OOC$$
$$\quad\quad C_6$$

$$\langle\bigcirc\rangle\!\!\sim + H_2O \quad (4)$$
$$\quad C_5$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OH$$
$$\quad\quad C_3$$

$$+ HOCH_2CH_2OH \overset{k_8}{\rightarrow}$$
$$\quad C_2$$

$$\sim\!\!\langle\bigcirc\rangle\!\!-\!COOCH_2CH_2OCH_2CH_2OH$$
$$\quad\quad C_7$$

$$+ H_2O \quad (5)$$
$$\quad C_5$$

$$2\, HOCH_2CH_2OH \overset{k_9}{\rightarrow}$$
$$\quad C_2$$

$$HOCH_2CH_2OCH_2CH_2OH + H_2O \quad (6)$$
$$\quad\quad C_8 \quad\quad\quad\quad\quad C_5$$

$$\sim\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-COOH$$

$$C_1$$

$$+ HOCH_2CH_2OCH_2CH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$$

$$C_8$$

$$\sim\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-COOCH_2CH_2OCH_2CH_2OH$$

$$C_7$$

$$+ H_2O \quad (7)$$

$$C_5$$
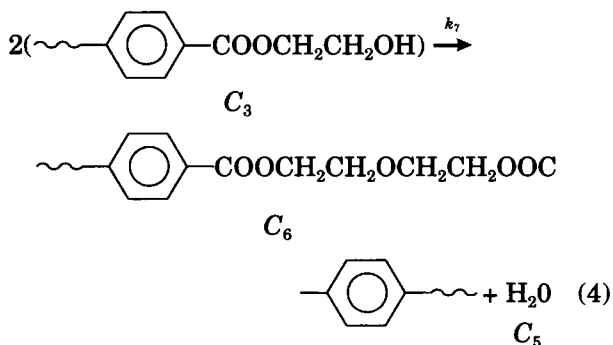
where C_i is the concentration of component i in the liquid phase and k_1 to k_9 are the reaction rate constants, and there are the relations $k_8 = 2k_7$ and $k_9 = 4k_7$ (refer to Appendix A).

REACTION RATE EQUATIONS

The reaction rate equations of C_1 to C_8 are obtained from the reaction scheme mentioned earlier as follows.[4]

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

$$\frac{dC_2}{d\theta} = -k_1C_1C_2 + k_3C_3C_5 + k_5C_3^2$$
$$- k_6C_2C_4 - k_8C_2C_3 - 2k_9C_2^2 \quad (9)$$

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

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

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

$$\frac{dC_6}{d\theta} = k_7C_3^2 \quad (13)$$

$$\frac{dC_7}{d\theta} = k_8C_2C_3 + k_1C_1C_8 - k_2C_5C_7 \quad (14)$$

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

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

MATHEMATICAL MODEL FOR ESTERIFICATION REACTIONS OF TPA WITH EG

Assumptions for Modeling

Assumptions for modeling of direct esterification are given as follows.[4]

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 $k_9 = 4k_7$.

Determination of Weight Fraction of Liquid Phase (β) in Reaction Mixtures

By the preceding assumptions, the weight fraction of the liquid phase in the reaction mixtures, β, and carboxyl end group concentration in the liquid phase, C_1, are derived.[4]

When undissolved TPA remains in the reaction mixtures (the solid phase exists in the reaction mixtures),

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

$$C_1 = \alpha \qquad (16)$$

where AV = concentration of total carboxyl end groups in dried oligomer; α = the mean solubility of TPA in the liquid phase of reaction mixtures, which is estimated from $\alpha = 18,124 \exp(-9692/RT)w_{EG} + 758 \exp(-7612/RT)w_{OLG}$ [see Eqs. (18) to (21)]; R = gas constant; T = absolute temperature; η_{TPA} = equivalents of carboxyl end groups per 1 kg of pure TPA (i.e., $\eta_{TPA} = 12.039$ —COOH equiv./kg TPA); 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.

When all TPA is dissolved in the reaction mixtures (the solid phase exists in the reaction mixtures),

$$\beta = 1 \quad \text{and} \quad C_1 = \zeta \qquad (17)$$

where ζ = concentration of carboxyl end groups in the reaction mixtures without undissolved TPA, which is defined by $\zeta = AV \cdot w_{OLG}$; w_{OLG} = weight fraction of oligomer in the liquid phase of reaction mixtures.

Mean Solubility of TPA (α)

The temperature dependencies of the solubility of TPA in EG, α_{EG}, and that in BHET, α_{BHET}, are given as follows.[4]

$$\alpha_{EG} = 18,124 \exp(-9692/RT) \qquad (18)$$

$$\alpha_{BHET} = 758 \exp(-7612/RT) \qquad (19)$$

where α_{EG} = solubility of TPA in EG
   α_{BHET} = solubility of TPA in BHET
   R = gas constant, R = 1.987 cal/mol K
   T = absolute temperature, $T = t$
      + 273.15

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

$$\alpha = \alpha_{H_2O}w_{H_2O} + \alpha_{EG}w_{EG} + \alpha_{OLG}w_{OLG} \qquad (20)$$

where α_{H_2O} = solubility of TPA in water, 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

$$\alpha \fallingdotseq \alpha_{EG}w_{EG} + \alpha_{BHET}w_{OLG} \qquad (21)$$
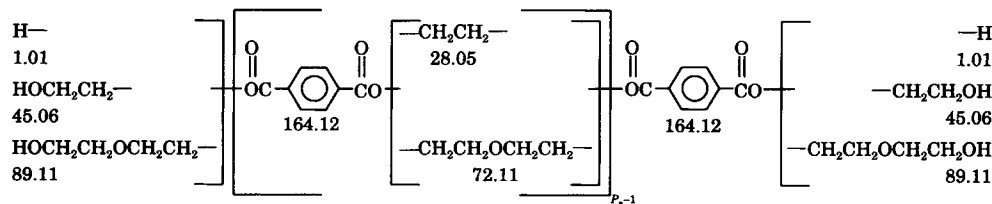
Relations among Oligomer Properties

The relations among oligomer properties are given in the following equations.[2]

$$\phi = \frac{OHV}{AV + OHV} \qquad (22)$$

$$M_n = \frac{2000}{AV + OHV} \qquad (23)$$

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. (24):

$$M_n = \frac{(P_n - 1)(164.12 + 28.05)}{1 + e}$$

$$+ \frac{(P_n - 1)(164.12 + 72.11)e}{1 + e} + 164.12$$

$$+ 2(1 - \phi) \times 1.008 + 2\phi \left[\frac{45.06}{1 + e} + \frac{89.11e}{1 + e} \right] \qquad (24)$$

By rearrangement of Eq. (24), P_n can be expressed by Eq. (25).

$$P_n = \frac{[M_n(1 + e) + 26.03 + 70.09e - \phi(88.10 + 176.20e)]}{192.17 + 236.23e}$$ (25)

And then, SV and E_s are given by the following relations:

$$SV = \frac{2000 P_n}{M_n}$$ (26)

$$E_s = \frac{SV - AV}{SV}$$ (27)

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:

$$(1 + e){:}e = (P_n - 1 + 2\phi){:}x;$$

$$\text{i.e., } x = (P_n - 1 + 2\phi)e/(1 + e)$$ (28)

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

$$d = 100\left[\frac{(P_n + 2\phi - 1)}{P_n}\right]\left(\frac{e}{1 + e}\right)$$ (29)

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 melting points of oligomer, T_m, can be predicted from the following equation.[5,6]

$$\frac{1}{T_m} = 0.111049 \times 10^{-3} \cdot OHV^2 - 0.200468$$

$$\times 10^{-4} \cdot OHV^3 - 0.298614 \times 10^{-3} \exp(-OHV)$$

$$- \frac{0.196193 \times 10^{-2} \cdot AV}{P_n + OHV} + \frac{0.605210 \times 10^{-3} \cdot AV^2}{(P_n + OHV)^2}$$

$$- \frac{0.971548 \times 10^{-2} \cdot AV}{P_n + OHV)^2}$$

$$+ \frac{0.980871 \times 10^{-3} \cdot OHV}{(P_n + OHV)^2} + 0.142510$$

$$\times 10^{-3} \exp \frac{AV}{P_n + OHV} - 0.655692 \times 10^{-4} \ln(P_n)$$

$$+ 0.415790 \times 10^{-2}$$ (30)

Estimation of Vapor Flow Rates of EG and Water (Q_{EG}, Q_{H_2O}) from a CSTR

The vapor flow rates of EG and water from a continuous stirred tank reactor (CSTR) shown in Figure 1, where the slurry of TPA and EG as raw materials is fed and EG with water is fed anew in order to adjust the reactions or is inevitably returned from the bottom of a distillation tower attached to the reactor, Q_{EG} and Q_{H_2O}, can be estimated from the following equations.[3]

$$Q_{EG} = \frac{[(F_{EG}^i - q_{EG})(1 - \beta w_{H_2O}) - \beta w_{EG}(F^i - F_{H_2O}^i - q_{H_2O})]}{1 - \beta w_{H_2O} - \beta w_{EG}}$$ (31)
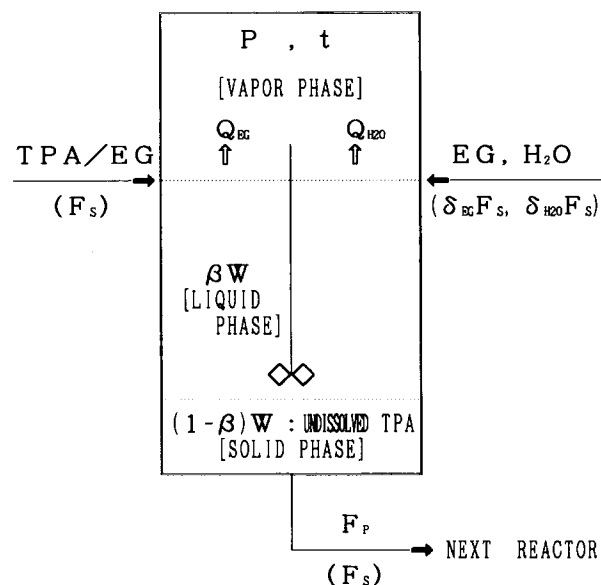
Figure 1 Continuous esterification process in steady state: P = reaction pressures; t = reaction temperature; W = weights of reaction mixtures; β = weight fraction of liquid phase (dissolved TPA and oligomer, EG, water) in the reaction mixtures; F_S = throughput based on PET polymer; F_P = actual discharge flow rates from the reactor; δ_{EG} = flow rate of EG added anew into the reactor per 1 kg/h of throughput based on PET polymer; δ_{H_2O} = flow rate of water added anew into the reactor per 1 kg/h of throughput based on PET polymer.

$$Q_{H_2O} = \frac{[F^i_{H_2O} + q_{H_2O} - \beta w_{H_2O}(F^i - Q_{EG})]}{1 - \beta w_{H_2O}} \quad (32)$$

where q_{EG} represents the amount of EG consumed by the esterification reaction in a CSTR defined as

$$q_{EG} = \frac{62.07}{166.13} F_{TPA}$$

$$\times \left(\frac{P_{nf} + 2\phi_f - 1}{P_{nf}} - \frac{P_{ni} + 2\phi_i - 1}{P_{ni}} \right) \quad (33)$$

q_{H_2O} represents the amount of water generated by the reaction in a CSTR defined as

$$q_{H_2O} = \frac{2 \times 18.02}{166.13} F_{TPA}$$

$$\times \left(\frac{P_{nf} + \phi_f - 1}{P_{nf}} - \frac{P_{ni} + \phi_i - 1}{P_{ni}} \right) \quad (34)$$

and F_{TPA} is the throughput based on TPA and subscripts i and f show the input and output, respectively (refer to Appendix B); and then

$$F^i_{EG} = \text{input rate of EG}$$

$$F^i_{H_2O} = \text{input rate of water}$$

$$Q_{EG} = \text{vapor flow rate of EG}$$

$$Q_{H_2O} = \text{vapor flow rate of water}$$

$$F_i = \text{total input rate}$$

Estimation of Concentration of Each Liquid Phase Component in a CSTR

The total pressure in a reactor is given by the sum of the partial pressures of EG and water; the vapor phase mole fractions of EG and water can be expressed as follows.[4]

$$y_{EG} = \frac{Q_{EG}/62.07}{Q_{EG}/62.07 + Q_{H_2O}/18.02} \quad (35)$$

$$y_{EG} + y_{H_2O} = 1 \quad (36)$$

$$x_{EG}\gamma_{EG}P_{EG} = y_{EG}P \quad (37)$$

$$x_{H_2O}\gamma_{H_2O}P_{H_2O} = y_{H_2O}P \quad (38)$$

$$x_{EG} + x_{H_2O} + x_{OLG} = 1 \quad (39)$$

where x_{EG}, x_{H_2O}, x_{OLG} = liquid phase mole fractions of EG, water, and oligomer; y_{EG}, y_{H_2O} = vapor phase mole fractions of EG and water; P_{EG} = vapor pressure of EG at a reaction temperature (mmHg), which is expressed by log P_{EG} = 7.8808 − 1957/(t + 193.8); P_{H_2O} = vapor pressure of water at a reaction temperature (mmHg), which is expressed by log P_{H_2O} = 7.9668 − 1668.2/(t + 228); P = total pressure (reaction pressure); γ_{EG}, γ_{H_2O} = activity coefficients of EG and water; t = reaction temperature (°C).

As the vapor–liquid equilibrium can be expressed by Raoult's law with little problem of practical use,[4] the activity coefficients (γ_{EG}, γ_{H_2O}) can be considered as one.

The weight fraction of each component (w_i) can be calculated from the following equation:

$$w_i = \frac{x_i M_i}{\sum\limits_{j=1}^{N} x_i M_j} \quad (40)$$

where 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

M_i, M_j = molecular weight of component i, j

and subscripts of i and j represent water, EG and oligomer.

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

$$M_{OLG} = \frac{2000\beta w_{OLG}}{\beta C_1 + \text{OHV}[1 - \beta(w_{EG} + w_{H_2O})]} \quad (41)$$

The derivation of Eq. (41) is given in Appendix C.

From these equations, all the concentration of each component (C_i) can be determined by using AV, OHV, and e.

Material Balance in a CSTR

The material balance of each component in the Jth reactor of CSTR is as follows.[4]

The material balance of carboxyl end groups is

$$F^{J-1}_P C_{10} - F^J_P \text{AV}_a + \beta W \left(\frac{dC_1}{d\theta} \right) = 0 \quad (42)$$

The material balance of hydroxyl end groups is

$$F_P^{J-1}C_{30} - \beta F_P^J C_3 + \beta W\left(\frac{dC_3}{d\theta}\right) = 0 \quad (43)$$

The material balance of diester groups is

$$F_P^{J-1}C_{40} - \beta F_P^J C_4 + \beta W\left(\frac{dC_4}{d\theta}\right) = 0 \quad (44)$$

The material balance of DEG is

$$F_P^{J-1}(C_{60} + C_{70} + C_{80}) - \beta F_P^J(C_6 + C_7 + C_8)$$

$$+ \beta W\left(\frac{dC_6}{d\theta} + \frac{dC_7}{d\theta} + \frac{dC_8}{d\theta}\right) = 0 \quad (45)$$

The material balance of water is

$$F_P^{J-1}C_{50} + \delta_{H_2O}F_S\eta_{H_2O} - \beta F_P^J C_5$$

$$- Q_{H_2O}\eta_{H_2O} + \beta W\left(\frac{dC_5}{d\theta}\right) = 0 \quad (46)$$

The material balance of EG is

$$F_P^{J-1}C_{20} + \delta_{EG}F_S\eta_{EG} - \beta F_P^J C_2$$

$$- Q_{EG}\eta_{EG} + \beta W\left(\frac{dC_2}{d\theta}\right) = 0 \quad (47)$$

where C_{EG} = input concentration of component K into Jth reactor

F_P^J = output rate of reaction mixtures from the Jth reactor

F_S = throughput based on PET polymer; F_S = 166.23/192.17(F_{TPA})

W = total weight of reaction mixtures in the Jth reactor

$\delta_{EG}, \delta_{H_2O}$ = flow rates of EG and water added anew to the Jth reactor per 1 kg/h of throughput based on PET polymer

η_{EG}, η_{H_2O} = equivalent concentrations of EG and water; η_{EG} = 16.111 mol/kg(EG), η_{H_2O} = 55.494 mol/kg(H2O)

EXPERIMENTAL

By using experimental results obtained from the pilot plant with about 50 kg/h throughput shown in Figure 2, the reaction rate constants in the reaction

scheme for the direct esterification of TPA with EG are determined for the first esterification reactor (RA-1). The outline of the pilot plant and its experimental procedure is as follows.

The first and second reactors (RA-1, RA-2) are esterification reactors, whose pressures were usually controlled under atmospheric or pressurized conditions. The third reactor (RA-3) is the prepolycondensation reactor, whose pressure was controlled at 20 to 100 torr. The fourth and fifth reactors (RA-4, RA-5) are polycondensation reactors. The RA-4 was usually controlled at 3–10 torr and is sometimes called the "medium polycondensation reactor." The RA-5 is usually called the "finisher" and was controlled at 2 torr and below.

After excess EG containing water was refined by the distillation towers (TW-1, TW-2), it was returned to the EG storage tank (EG-STK) and reused as raw material. TPA was fed through the mixing tank (MTK) at a fixed rate, which was controlled by the rotary feeder (RF), table feeder (TF), and impact line flowmeter (IPL). The gross weight of the mixing tank (MTK) involved with the slurry of TPA and EG was controlled by the weight controller (W) with the load cell.

The slurry of TPA and EG was continuously fed to the first reactor (RA-1) by the MONO-pump of screw type under the gross weight control of the mixing tank (MTK). Polycondensation catalyst and the other additives were usually fed to the first reactor (RA-1) at a fixed rate by the plunger pump. TPA reacts with EG in the first reactor (RA-1). During the reaction, water was evolved in the reactor. Excess EG containing water from the reactor was fed to the first distillation tower (TW-1) and refined through the distillation towers (TW-1, TW-2). Refined EG was returned to the EG storage tank (EG-STK). The pressure of the first reactor (RA-1) was controlled by the pressure controller and the control valves.

The amount of oligomer in the first reactor was controlled by the level controller and the control valve. The partially esterified oligomer was fed to the second reactor and the esterification of oligomer was continued. The pressure of the second reactor (RA-2) was controlled by the pressure controller and the control valves. The vapor of EG and water was fed to the first distillation tower (TW-1) and distilled by the TW-1 and TW-2. The esterified oligomer in the second reactor (RA-2) was fed to the prepolymerization reactor (RA-3) at a fixed rate by the gear pump, and the polycondensation reaction proceeded. Oligomer was sampled in a 1-L stainless steel flask under vacuum and cooled by liquid nitro-
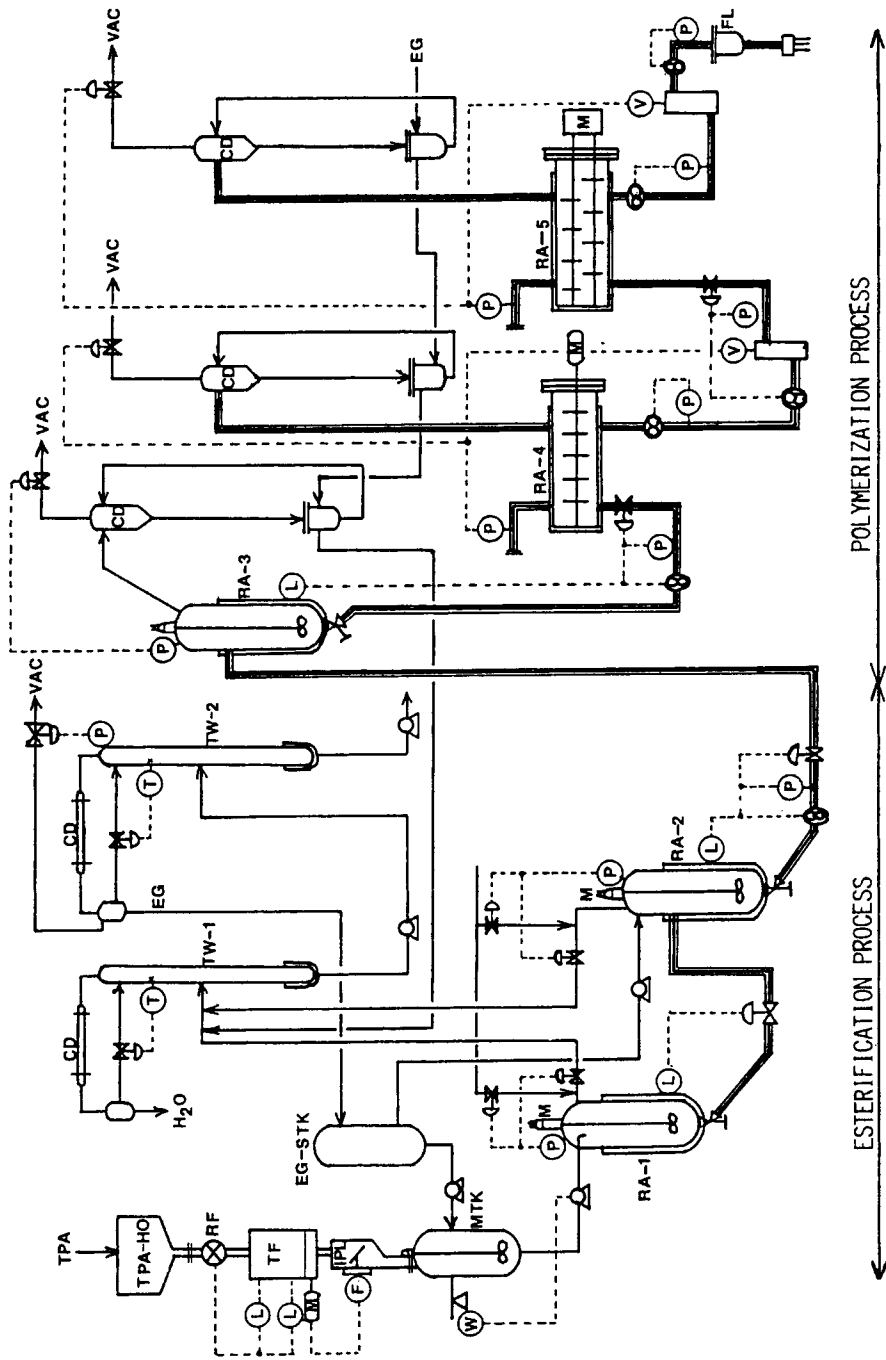
Figure 2 Process flow diagram of the pilot plant: TPA-HO, TPA hopper; RF, rotary feeder; IPL, impact line flow; MTK, mixing tank; MTK, mixing tank; EG-STK, EG storage tank; RA-1, first reactor; RA-2, second reactor; RA-3, third reactor; RA-4, fourth reactor; RA-5, fifth reactor; TW-1, first distillation tower; TW-1, second distillation tower; CD, condenser; FI, filter; M, motor; L, level controller; P, pressure controller; T, temperature controller; W, weight controller; VAC, vacuum.

Table I   Chemical Compositions of Titanium Dioxide (TiO₂) (wt %)

Kind of TiO₂	TiO₂	Dry Loss	Ignition Loss	SO₃	P₂O₅	SiO₂	K₂O	Na₂O	Fe	Al₂O₃	ZnO	Others
A	98.6	0.10	0.15	0.12	0.40	0.03	0.09	0.036	0.0007	—	0.0002	0.47
B	94.3	0.25	0.80	—	0.40	2.4	0.2	—	0.001	0.47	0.42	0.76

gen through the sampling valve installed at the bottom of the reactor.

With the pilot plant shown in Figure 2, experiments of continuous esterification reaction between TPA and EG were carried out at various concentra-

tions of two kinds of titanium dioxide (TiO₂), A and B listed in Table I.

Titanium dioxide dispersed in EG and diantimony trioxide dissolved in EG were mixed with TPA/EG slurry, and the mixture was fed to the

Table II   Analytical Procedure

The oligomer sampled from the reactor was ground to a powder in the hermetically sealed vessel for the purpose of the measurement of the following:

Determination of Carboxyl End Groups of the Oligomer (AV)

After the powdered oligomer was dried at 120°C for 24 h under vacuum, the dried oligomer sample of 0.5 g was weighed and then dissolved in warmed pyridine. After the solution was cooled at room temperature, the carboxyl end groups of the oligomer were titrated with $0.2N$ aqueous sodium hydroxide by the use of phenolphthalein as an indicator. The concentration of carboxyl end groups of the oligomer was determined by the titration, for which a correction was made by running a blank of a similar titration of pyridine without oligomer.

Determination of Hydroxyl End Groups of the Oligomer (OHV)

The hydroxyl end group concentration of the oligomer was determined according to a method of Ogg, Porter, and Willits.[7] The dried oligomer sample of 0.5 g was heated at 95°C for 1.5 h with the pyridine solution of acetic acid formed by the reaction titrated with $0.2N$ alcoholic sodium hydroxide by the use of phenolphthalein as an indicator.

Determination of Saponification Value of the Oligomer (SV_m)

A 0.5-g sample of the dried oligomer was dissolved by heating in 20 mL of EG. After dissolution of the oligomer 25 mL of $0.5N$ aqueous sodium hydroxide was added to the solution, and then it was heated for 1.5 h. The solution was titrated with $0.5N$ aqueous hydrochloric acid by the use of phenolphthalein as an indicator.

Determination of Diethylene Glycol Units in the Oligomer (e)

The concentration of DEG contained in the oligomer was determined by gas chromatographic analysis after methanolysis of the oligomer by a method reported by Yoda (1967).

Determination of Free EG Involved in the Reaction Mixtures (w'_{EG})

Free EG involved in the reaction mixtures was extracted in 500 mL of warm water from 200 g of the powdered oligomer. The concentration of free EG was determined by gas chromatography analysis. Diethylene glycol dimethyl ether was used as an internal standard substance. The weight fraction of EG in the reaction mixtures containing undissolved TPA, w'_{EG}, is related to that in the liquid phase of reaction mixtures free from undissolved TPA, w_{EG}, by the equation $w'_{EG} = \beta w_{EG}$.

Determination of Water Involved in the Reaction Mixtures (w'_{H_2O})

The Karl Fisher method was used for the determination of water involved in the reaction mixtures. The weight fraction of water in the reaction mixtures containing undissolved TPA, w'_{H_2O}, is related to that in the liquid phase of reaction mixtures free from undissolved TPA, w_{H_2O}, by the equation $w'_{H_2O} = \beta w_{H_2O}$.

Determination of Weight Fractions of EG or Water in the Distillate from the Reactor (w^d_{EG}, $w^d_{H_2O}$)

The vapor from the first reactor (RA-1) was condensed by the condenser installed at the vaportube between RA-1 and the distillation tower (TW-1). The condensate was called the "distillate" in this report. The weight fractions of EG or water in the distillate were determined by a gas chromatographic analysis. There is the relation between w^d_{EG} and $w^d_{H_2O}$;

$$w^d_{EG} + w^d_{H_2O} = 1.$$

Table III   Experimental Data at Various Concentrations of TiO$_2$

Run	[TOD] Kind	[TOD] wt %	AV (eq/kg)	OHV (eq/kg)	ϕ	M_n (g/mol)	P_n	E_s	100e (%)	d (%)
1	—	0	2.204	1.207	0.354	586	3.021	0.786	1.099	0.982
2	—	0	2.251	1.261	0.359	569	2.930	0.781	1.156	1.033
3	—	0	2.257	1.225	0.352	574	2.959	0.781	1.121	0.997
4	—	0	2.265	1.191	0.344	579	2.985	0.780	1.088	0.964
5	—	0	2.280	1.157	0.337	582	3.006	0.779	1.055	0.931
6	—	0	2.316	1.209	0.343	567	2.927	0.776	1.108	0.978
7	B	0.3	2.192	1.207	0.355	588	3.029	0.787	1.269	1.134
8	B	0.3	2.205	1.172	0.347	592	3.052	0.786	1.232	1.095
9	B	0.5	2.150	1.196	0.357	598	3.077	0.791	1.360	1.218
10	B	0.5	2.165	1.161	0.349	601	3.099	0.790	1.321	1.177
11	A	0.3	2.191	1.217	0.357	587	3.022	0.787	1.113	0.996
12	A	0.3	2.208	1.165	0.345	593	3.059	0.786	1.064	0.947
13	A	0.5	2.152	1.188	0.356	599	3.084	0.791	1.085	0.973
14	A	0.5	2.156	1.171	0.352	601	3.098	0.791	1.069	0.957

first esterification reactor (RA-1). Experiments were made under the conditions of t = 250°C, P = atmospheric pressure, E/T = 2.0, τ = 5.0 h, Sb^{3+} = 400 μmol/mol(TPA), where t is the reaction temperature, P is the reaction pressure, E/T is the molar ratio of EG and TPA fed to the first esterification reactor, τ is the mean residence time defined by τ = (total weight of the reaction mixtures)/ (throughput based on PET), Sb^{3+} is the mole number of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 moles of TPA.

Oligomer characteristics such as the carboxyl end group concentration (AV), hydroxyl end group

concentration (OHV), and molar ratio of diethylene glycol (DEG) to bound EG (e) were measured in accordance with the analytical methods described in Table II. Other oligomer characteristics were determined with the relations shown in Eqs. (22)–(29).

RESULTS AND DISCUSSION

Determination of Reaction Rate Constants

Two kinds of titanium dioxide, A and B, were used without further purification. In Table I chemical compositions of titanium dioxide used are given. In Table III experimental results at various concen-
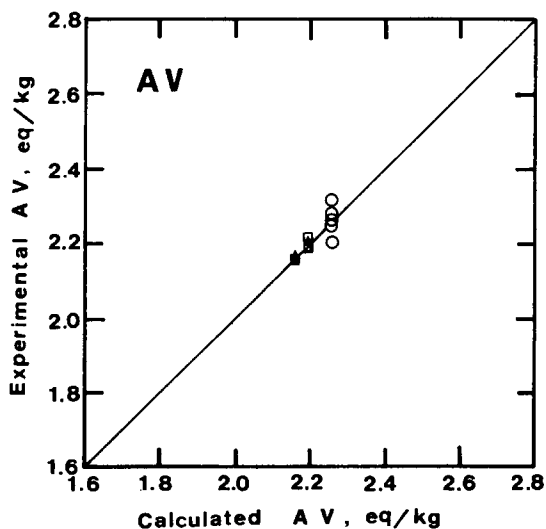

Figure 3   Correlation of experimental and calculated AV values: O, no TiO$_2$; △, B kind of TiO$_2$; □, A kind of TiO$_2$.

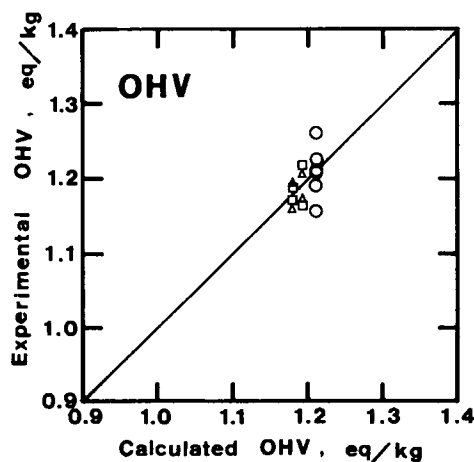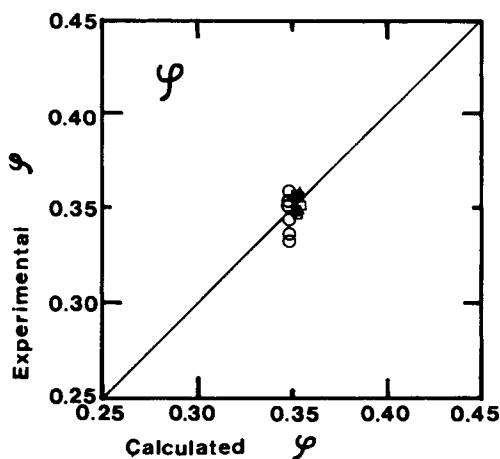**Figure 4**   Correlation of experimental and calculated OHV values: O, no TiO$_2$; △, B kind of TiO$_2$; □, A kind of TiO$_2$.

Figure 5 Correlation of experimental and calculated ϕ values: O, no TiO_2; $\triangle$, B kind of TiO_2; $\square$, A kind of TiO_2.

trations of A and B kinds of titanium dioxide are listed.

With the mathematical model proposed previously,[4,8] reaction rate constants in the reaction scheme mentioned above, where Eq. (7) is neglected because of no problem in practical use,[8] were determined to fit with experimental data in Table III. As a result, it became clear that, independently of the kinds of titanium dioxide, the reaction rate constants of main reactions, k_1 to k_6, are expressed by Eqs. (48) to (53), and the reaction rate constant of the side reaction of DEG formation, k_7, for B kind of titanium dioxide is expressed by Eq. (54), and that for A kind of titanium dioxide is expressed by Eq. (55), respectively.

$$k_1 = 1.5657 \times 10^9 \exp(-19,640/RT) \quad (48)$$

$$k_2 = 1.5515 \times 10^8 \exp(-18,140/RT) \quad (49)$$

$$k_3 = (0.1[TDO] + 1)$$
$$\times 3.5165 \times 10^9 \exp(-22,310/RT) \quad (50)$$

$$k_4 = 6.7640 \times 10^7 \exp(-18,380/RT) \quad (51)$$

$$k_5 = (0.08[TDO] + 1)$$
$$\times 7.7069 \exp(-2810/RT) \quad (52)$$

$$k_6 = (0.04[TDO] + 1)$$
$$\times 6.2595 \times 10^6 \exp(-14,960/RT) \quad (53)$$

For B kind of titanium dioxide,

$$k_7 = (0.60[TDO] + 1) \times 2.0583$$
$$\times 10^{15} \exp(-42,520/RT) \quad (54)$$

For A kind of titanium dioxide,

$$k_7 = (0.085714[TDO] + 1) \times 2.0583$$
$$\times 10^{15} \exp(-42,520/RT) \quad (55)$$

where [TDO] = weight percent of charged titanium dioxide against PET, R = gas constant, and T = absolute temperature.

Figures 3–8 show the comparison between experimental data and calculated values. It can be expected the agreement is almost within the experimental and analytical errors.

From Eqs. (48)–(55) the following is understood;

1. Titanium dioxide exerts no influence at all on the esterification reaction between TPA and EG.
2. The increase of the reaction rate constant, k_7, on DEG formation is more large with B kind of titanium dioxide than A kind. This is considered to be caused by the increase of DEG formation due to zinc oxide in B kind of titanium dioxide[9] and the suppression of DEG formation due to sodium oxide in A kind of titanium dioxide.[10]
3. The effect of titanium dioxide on the reaction rate constants in the first esterification reactor can be expressed as the following equation; $k_j = (c_j[TDO] + 1)A_j \exp(-E_j/RT)$. This suggests that titanium dioxide has an influence not on the apparent activation energy of reaction rate constant but on the frequency factor.
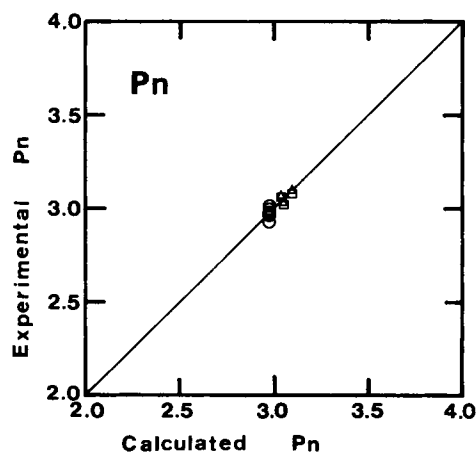
Figure 6 Correlation of experimental and calculated P_n values: O, no TiO_2; $\triangle$, B kind of TiO_2; $\square$, A kind of TiO_2.
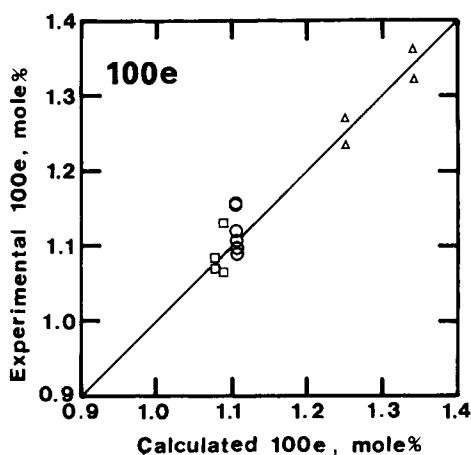
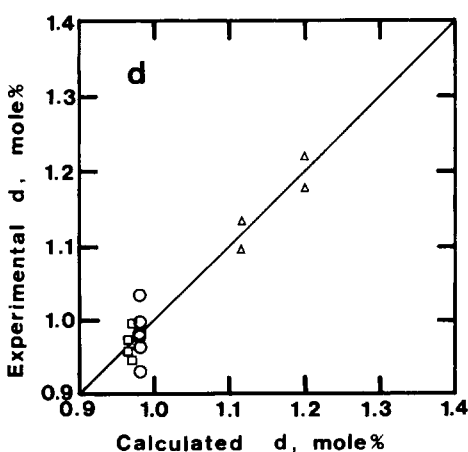**Figure 7**   Correlation of experimental and calculated 100e values: O, no TiO_2; △, B kind of TiO_2; □, A kind of TiO_2.

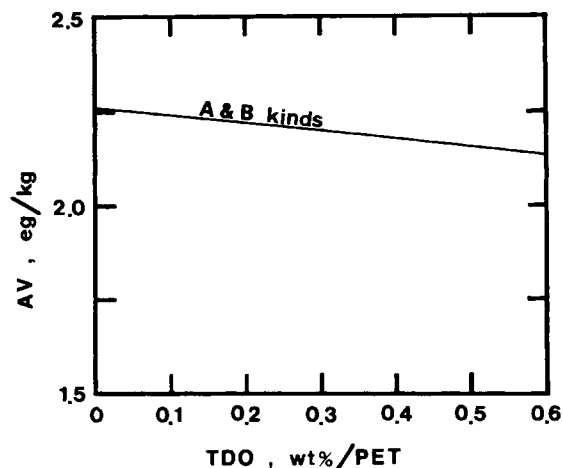**Figure 9**   Effect of titanium dioxide concentration of A kind or B on AV.

Relation between Titanium Dioxide Concentration and Oligomer Properties

Figures 9–14 give the relation between the titanium dioxide concentration and the oligomer properties (AV, OHV, ϕ, P_n, E_s, 100e, d) calculated by using Eqs. (48)–(55) under the conditions of $t = 250°C$, $P = 0$ kg/cm^2G, $E/T = 2.0$, and $\tau = 5.0$ h.

Figures 9–14 give the results that based on main reactions the oligomer properties slightly change with the concentration of titanium dioxide and have no difference between A and B kinds of titanium dioxide. For example, when the concentration of titanium dioxide varies from 0–0.5 wt %, the variation in AV is only about 0.1 eq/kg. Though this variation is minor, it cannot be neglected from the viewpoint of industrial production.
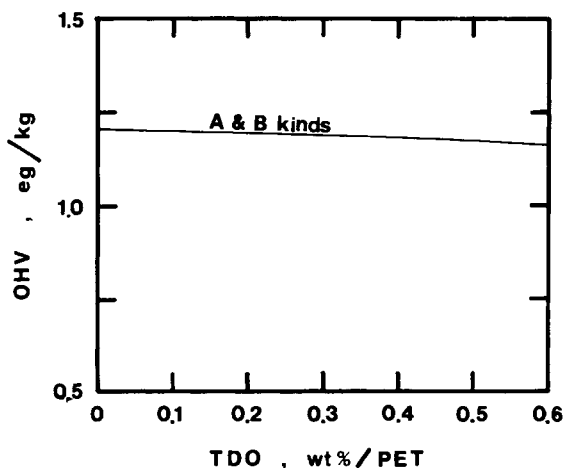
Figure 14 gives the results that, based on side reactions, DEG content fairly changes with the concentration of titanium dioxide and has the difference between kinds of titanium dioxide. It can be seen that the amount of DEG formation is higher with B kind of titanium dioxide than that with A kind of titanium dioxide. For example, at the concentration of titanium dioxide of 0.5 wt % with B kind, DEG content is about 0.25 mol % higher than with A kind. One of the causes of this difference is considered to be the conspiracy of the increase in DEG content due to zinc in B kind and the decrease in DEG content due to the suppression effect of sodium in A kind. In conclusion, in a continuous manufacturing process of PET starting from TPA and EG as raw materials, it was confirmed that the acceleration ef-

Figure 8   Correlation of experimental and calculated d values: O, no TiO_2; △, B kind of TiO_2; □, A kind of TiO_2.

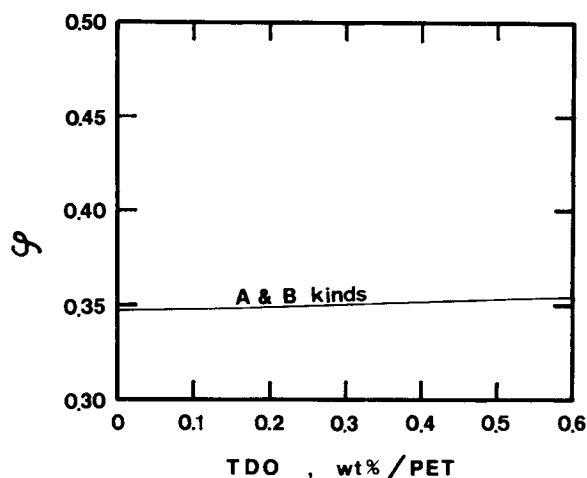**Figure 10**   Effect of titanium dioxide concentration of A kind or B on OHV.

Figure 11 Effect of titanium dioxide concentration of A kind or B on ϕ.

fect of titanium dioxide on the esterification reaction is minor, but it cannot be neglected in the industrial scale production. The amount of DEG formation was found to be largely different with the kind of titanium dioxide.

CONCLUSION

It was confirmed that titanium dioxide as an additive for making PET dull or improving the spinability has influence on side reactions rather than main reactions. Namely, in a continuous manufacturing process of PET starting from TPA and EG as raw materials, the acceleration effect of titanium dioxide on the esterification reactions is minor, but it cannot be neglected in industrial-scale production.
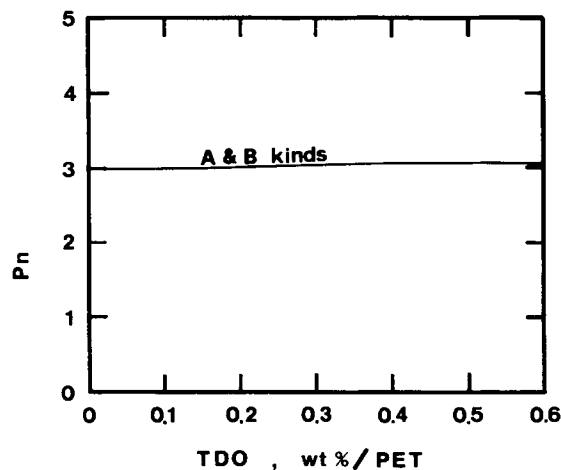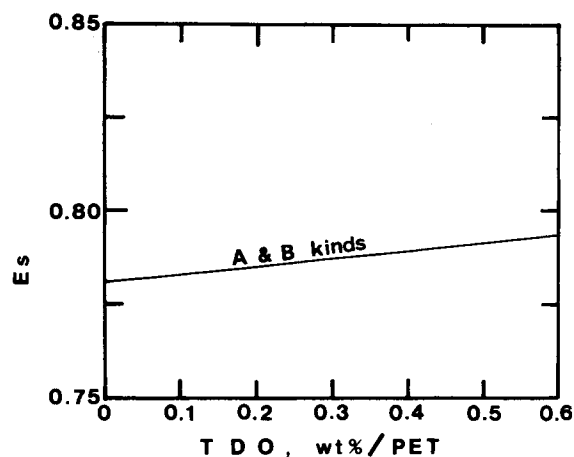

Figure 13 Effect of titanium dioxide concentration of A kind or B on E_S.

The amount of DEG formation was found to be largely different with kind of titanium dioxide. It was clear that the influence of titanium dioxide on reaction rate constants can be expressed in the following equation: $k_j = (c_j[\text{TDO}] + 1)A_j \exp(-E_j/RT)$, where [TDO] denotes the weight percent of titanium dioxide against PET.

From previous works[1,2] and present work, the reaction rate constants, k_j, can be expressed by $k_j = (a_jT_i + b_j\text{Sb}^{3+} + c_j[\text{TDO}])A_j \exp(-E_j/RT)$ for $j = 1 \sim 7$; where a_j, b_j, and c_j are constants, and T_i, Sb^{3+}, and [TDO] are the concentrations of potassium titanium oxyoxalate, diantimony trioxide, and titanium dioxide added in PET, respectively.

NOMENCLATURE

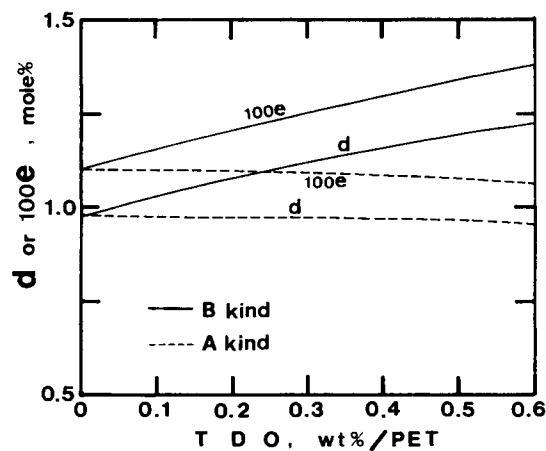AV = concentrations of total carboxyl end groups in dried oligomer, eq/kg; AV = C_T/

Figure 12 Effect of titanium dioxide concentration of A kind or B on P_n.

Figure 14 Effect of titanium dioxide concentration of A kind or B kind on DEG contents ($100e$, d).

$$[T_S + W_e\{1 - (w_{EG} + w_{H_2O})\}] = C_T/\{1 - \beta(w_{EG} + w_{H_2O})\}$$

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

$C_6, C_7,$ = concentration of free and bound DEG in
C_8 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 is fed to the first reactor

F^i = total input rate, kg/h

F_{EG}^i = input rates of EG, kg/h

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

F_P = actual output rates of reaction mixtures discharged from the 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) to (7)

M_{EG} = molecular weight of EG, g/mol; M_{EG} = 62.07

M_{H_2O} = molecular weight of water, g/mol; M_{H_2O} = 18.02

M_{PET} = molecular weight of a PET unit, g/mol; M_{EG} = 192.17

M_{TPA} = molecular weight of TPA, g/mol; M_{EG} = 166.13

M_i, M_j = molecular weight of component i, j, g/mol

M_n = number-average molecular weight, g/mol

M_{OLG} = number-average molecular weight of oligomer in the liquid phase free from undissolved TPA, g/mol

N = number of components

OHV = concentrations of hydroxyl end groups in 1 kg dried oligomer, eq/kg

P = total presures (= reaction pressures), mmHg or torr

P_{EG} = vapor pressure of EG at a reaction temperature, mmHg

P_{H_2O} = vapor pressure of water at a reaction temperature, mmHg

P_n = number-average degree of polymerization of oligomer

q_{EG} = amounts of EG bound in PET chain, kg/h

q_{H_2O} = amounts of water generated by the reaction, kg/h

Q_{EG} = vapor flow rate of EG, kg/h

Q_{H_2O} = vapor flow rate of water, kg/h

R = gas constant, R = 1.987 cal/mol K

Sb^{3+} = mole number of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 mole of TPA, μmol/TPAmol

SV = saponification value, eq/kg

t = reaction temperatures, °C

T = absolute temperature, $T = t + 273.15$, K

T_i = mole number of potassium titanium oxyoxalate supplied for 10^6 mol of TPA, μmol/TPAmol

T_m = melting point of dried oligomer, °C

T_S = weight of TPA undissolved, kg; $T_S = (1 - \beta)W$

[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_{OLG} = weight fraction of oligomer in the liquid phase of reaction mixtures free from undissolved TPA

W = total weights of reaction mixtures in the reactor, kg; $W = W_e + T_S$

W_e = weight of liquid phase in the reaction mixtures, kg; $W_e = \beta W$

x_{EG} = mole fraction of EG in the liquid phase of reaction mixtures free from undissolved TPA

x_{H_2O} = mole fraction of water in the liquid phase of reaction mixtures free from undissolved TPA

x_{OLG} = mole fraction of oligomer in the liquid phase of reaction mixtures free from undissolved TPA

y_{EG} = mole fraction of EG in the vapor phase

y_{H_2O} = mole fraction of water in the vapor phase

Greek Letters

α = mean solubility of TPA in the reaction mixtures expressed as equivalent moles of carboxyl end groups, eq/kg(reaction mixtures); $\alpha = (C_T - \eta_{\text{TPA}}T_S)/W_e = \{C_T - \eta_{\text{TPA}}(1 - \beta)W\}/\beta W$

α_{BHET} = solubility of TPA in BHET expressed as equivalent moles of carboxyl end groups, eq/kg(BHET)

α_{EG} = solubility of TPA in EG expressed as equivalent moles of carboxyl end groups, eq/kg(EG)

$\alpha_{\text{H}_2\text{O}}$ = solubility of TPA in water expressed as equivalent moles of carboxyl end groups, eq/kg(water)

α_{OLG} = solubility of TPA in oligomer expressed as equivalent moles of carboxyl end groups, eq/kg(oligomer)

β = weight fraction of liquid phase in the reaction mixtures; $\beta = W_e/(W_e/T_S) = W_e/W$

γ_{EG} = activity coefficient of EG in the liquid phase

$\gamma_{\text{H}_2\text{O}}$ = activity coefficient of water in the liquid phase

δ_{EG} = flow rate of EG added anew into the reactor per 1 kg/h of throughput based on PET polymer, (kg/h)/(kg/h)(PET)

$\delta_{\text{H}_2\text{O}}$ = flow rate of water added anew into the reactor per 1 kg/h of throughput based on PET polymer, (kg/h)/(kg/h)(PET)

ζ = concentration of carboxyl end groups in the reaction mixtures without undissolved TPA ($\beta = 1$), eq/kg

η_{EG} = equivalent concentration of EG, $\eta_{\text{EG}} = 16.111$ mol/kg(EG)

$\eta_{\text{H}_2\text{O}}$ = equivalent concentration of water, $\eta_{\text{H}_2\text{O}} = 55.494$ mol/kg(H$_2$O)

η_{TPA} = equivalent concentration of TPA expressed as equivalent moles of carboxyl end groups, $\eta_{\text{TPA}} = 12.039$ eq/kg(TPA)

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; $\phi = \text{OHV}/(\text{AV} + \text{OHV})$

Subscripts

BHET = bis-β-hydroxylethyl terephthalate

EG = ethylene glycol

H$_2$O = water

OLG = oligomer

P = at constant pressure or reaction mixtures

TPA = terephthalic acid

Superscripts

d = distillate (vapor phase)

EG = ethylene glycol

TPA = terephthalic acid

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 hyroxyl 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.
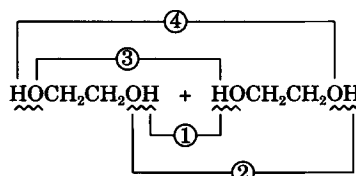
For k_7 in Eq. (4), its combination number is one from the following expression:
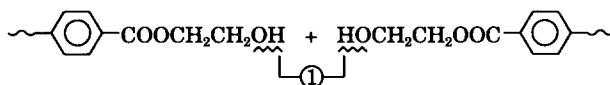
For k_8 in Eq. (5), its combination number is two from the following expression:
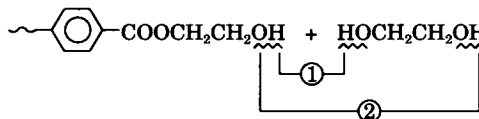
For k_9 in Eq. (6), its combination number is four from the following expression:

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

APPENDIX B: DERIVATION OF q_{EG} AND $q_{\text{H}_2\text{O}}$

Derivation of 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 this 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:

$$q_{EG} = F_{TPA}\left(\frac{M_{EG}}{M_{TPA}}\right)\left(\frac{(P_{nf} - 1)/(1 + e) + 2\phi_f/(1 + e) + 2(_{nf} - 1)e/(1 + e) + 4\phi_f e/(1 + e)}{P_{nf}}\right.$$

$$\left. - \frac{(P_{ni} - 1)/(1 + e) + 2\phi_i/(1 + e) + 2(P_{ni} - 1)e/(1 + e) + 4\phi_i e/(1 + e)}{P_{ni}}\right) \quad (B.1)$$

where M_{EG} = molecular weight of EG, M_{EG} = 62.07
M_{TPA} = molecular weight of TPA, M_{TPA} = 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. (B.1) reduces to the following equation:

$$q_{EG} = \frac{62.07}{166.13} F_{TPA}$$

$$\times \left(\frac{P_{nf} + 2\phi_f - 1}{P_{nf}} - \frac{P_{ni} + 2\phi_i - 1}{P_{ni}}\right)$$

Derivation of 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 of 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 of EG molecules of $2\phi/(1 + e)$ and the DEG molecules of $2\phi e/(1 + e)$.

From these 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}:

$$q_{H_2O} = F_{TPA}(M_{EG}/M_{TPA})[\{2(P_{nf} - 1)/(1 + e)$$

$$+ 2\phi_f/(1 + e) + 3(P_{nf} - 1)e/(1 + e)$$

$$+ 4\phi_f e/(1 + e)\}/P_{nf} - \{2(P_{ni} - 1)/$$

$$(1 + e) + 2\phi_i/(1 + e) + 3(P_{ni} - 1)e/$$

$$(1 + e) + 4\phi_i e/(1 + e)\}/P_{ni}] \quad (B.2)$$

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. (B.2) reduces to the following equation:

$$q_{H_2O} = \frac{2 \times 18.02}{166.13} F_{TPA}$$

$$\times \left(\frac{P_{nf} + \phi_f - 1}{P_{nf}} - \frac{P_{ni} + \phi_i - 1}{P_{ni}}\right)$$

APPENDIX C: DERIVATION OF M_{OLG}

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

As the weight of oligomer in the liquid phase is $\beta W w_{OLG}$ kilogram, 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 these results, we can obtain the following relation:

$$\frac{\beta W w_{OLG}}{(M_{nL}/1000)}$$

$$= \frac{\beta W C_1 + OHV[1 - \beta(w_{EG} + w_{H_2O}]}{2} \quad (C.1)$$

Rearrangement of Eq. (C.1) gives the following equation:

$$M_{OLG} = \frac{2000\beta w_{OLG}}{\beta C_1 + OHV[1 - \beta(w_{EG} + _{H_2O})]} \quad (C.2)$$

REFERENCES

1. T. Yamada and Y. Imamura, *Polym. Eng. Sci.*, **28**, 385 (1988).

2. T. Yamada, *J. Appl. Polym. Sci.*, **37**, 1821 (1989).

3. O. York, Jr., U.S. Pat. 2,906,737; *Chem. Abstr.*, **54**, 2274b; Brit. Pat. 807, 630; *Chem. Abstr.*, **53**, 12246a.

4. T. Yamada, Y. Imamura, and O. Makimura, *Polym. Eng. Sci.*, **25**, 788 (1985).

5. T. Yamada, Y. Mizuno, and Y. Imamura, *Polym. Eng. Sci.*, **28**, 377 (1988).

6. T. Yamada and Y. Imamura, *Polym. Eng. Sci.*, **28**, 381 (1988).

7. C.C. Ogg, W.L. Porter, and C.O. Willits, *Ind. Eng. Chem. Anal. Ed.*, **17**, 354 (1945).

8. T. Yamada, Y. Imamura, O. Makimura, and H. Kamatani, *Polym. Eng. Sci.*, **26**, 708 (1986).

9. K. Yoda, *Kobunshi Kagaku*, **24**, 472 (1967).

10. N. Munro and D. MacLean, Jap. Patent (registered), No. 255,007; *Chem. Abstr.*, **51**, 17237a; Brit. Pat., No. 777,628.