

# Influence of Reaction Temperature on Direct Esterifications in a Continuous Recycling Process Between Terephthalic Acid and Ethylene Glycol

TOSHIRO YAMADA

Toyobo Co., Ltd., Toyobo Research Institute, Film Research Laboratory, 10-24 Toyo-cho, Tsuruga, Fukui, 914 Japan

## SYNOPSIS

Simulations were carried out with a continuous recycle esterification model for the terephthalic acid–ethylene glycol (TPA–EG) system proposed previously. The influence of reaction temperatures, recycle ratios, and residence times on the oligomer characteristics was examined and the following results were obtained: (1) The main reactions proceed more under higher reaction temperatures, but the side reactions on diethylene glycol (DEG) proceed further than do the main reactions. (2) The higher residence time ratio of the first reactor to the total results in the proceeding of esterifications, which becomes remarkable as the temperature becomes high. (3) As the recycle ratio becomes high, the esterifications proceed, but in the very high degree of esterification, the tendency is reversed. (4) The characteristics of oligomer are almost the same at the same degree of esterification, independent of the reaction conditions. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

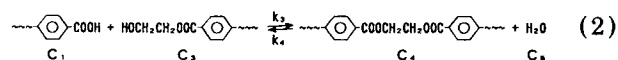
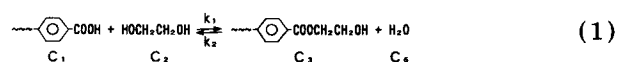
From a practical point of view, it is important to predict the optimum process for the production of poly(ethylene terephthalate) (PET) with a computer simulation. An esterification process in the terephthalic acid (TPA)–ethylene glycol (EG) route in PET manufacturing is of particular interest because of its complicated reactions. To examine what process is the best for the TPA–EG direct esterifications, the author<sup>1</sup> proposed a mathematical model for the recycling process. In this article, the simulated results for the recycling process are shown under various reaction temperatures, residence times, and recycle ratios. Of these, the influence of reaction temperatures on the oligomer characteristics will be discussed in detail.

## A MATHEMATICAL MODEL FOR A CONTINUOUS RECYCLE PROCESS BETWEEN TPA AND EG

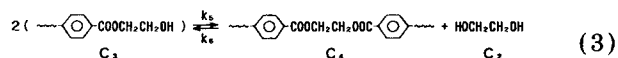
### Reaction Scheme for Direct Esterification

Various reactions occurring in a reactor are given as follows<sup>2</sup>:

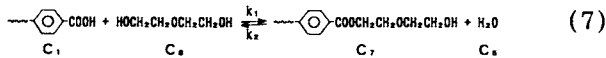
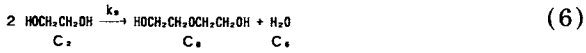
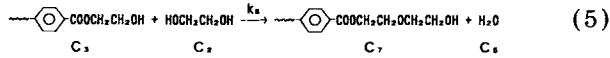
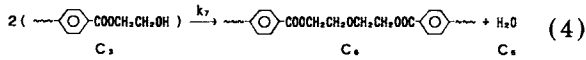
#### Esterification Reactions



#### Polycondensation Reactions



### 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  $k_1$ – $k_9$  are the reaction rate constants, where  $k_8 = 2k_7$  and  $k_9 = 4k_7$ .

### Reaction Rate Equations

The reaction rate equations of  $C_1$ – $C_8$  are obtained from the above reaction scheme as follows<sup>2</sup>:

$$\begin{aligned} (dC_1/d\theta) = & -k_1C_1C_2 + k_2C_3C_5 - k_3C_1C_3 \\ & + k_4C_4C_5 - k_1C_1C_8 + k_2C_5C_7 \quad (8) \end{aligned}$$

$$\begin{aligned} (dC_2/d\theta) = & -k_1C_1C_2 + k_2C_3C_5 + k_5C_3^2 \\ & - k_6C_2C_4 - k_8C_2C_3 - 2k_9C_2^2 \quad (9) \end{aligned}$$

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

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

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

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

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

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

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

### Assumptions for Modeling

Assumptions for the modeling of direct esterification are given as follows<sup>2</sup>:

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 a 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 a reactor is given only by the sum of the 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 being an oligomer.
8. Reactivity of the 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 can be assumed to be the same, i.e.,  $k_8 = 2k_7$  and  $k_9 = 4k_7$ .

### Determination of Weight Fraction of Liquid Phase ( $\beta$ ) in Reaction Mixtures

The authors<sup>2</sup> previously derived the weight fraction of the liquid phase in the reaction mixtures,  $\beta$ , and carboxyl end-group concentration in the liquid phase,  $C_1$ , on the assumptions mentioned above as follows:

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

$$\beta = \frac{AV - \eta_{\text{TPA}}}{\alpha + AV \cdot (w_{\text{EG}} + w_{\text{H}_2\text{O}}) - \eta_{\text{TPA}}} \quad \text{and} \quad C_1 = \alpha \quad (16)$$

where  $AV$  is the concentration of the total carboxyl end groups in the dried oligomer;  $\alpha$ , the mean solubility of TPA in the liquid phase of the reaction mixtures;  $R$ , the gas constant;  $T$ , the absolute temperature; and  $\eta_{\text{TPA}}$ , the equivalents of carboxyl end groups per 1 kg of pure TPA (i.e.,  $\eta_{\text{TPA}} = 12.039$  —COOH equiv/kg TPA). The  $w_{\text{EG}}$  and  $w_{\text{H}_2\text{O}}$  are the weight fractions of EG and water, respectively, in the liquid phase of the reaction mixtures.

When all TPA is dissolved in the reaction mixtures (the solid phase does not exist in the reaction mixtures),

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

where  $\zeta$  is the concentration of carboxyl end groups in the reaction mixtures free from undissolved TPA,

which is defined by  $\zeta = AV \cdot w_{OLG}$ ;  $w_{OLG}$  is the weight fraction of the oligomer in the liquid phase of the reaction mixtures.

### Mean Solubility of TPA ( $\alpha$ )

The temperature dependencies of the solubility of TPA in EG,  $\alpha_{EG}$ , and that in bis- $\beta$ -hydroxyethyl terephthalate (BHET),  $\alpha_{BHET}$ , are given as follows<sup>2</sup>:

$$\alpha_{EG} = 18124 \cdot \exp(-9692/RT) \quad (18)$$

$$\alpha_{BHET} = 748 \cdot \exp(-7612/RT) \quad (19)$$

where  $\alpha_{EG}$  is the solubility of TPA in EG;  $\alpha_{BHET}$ , the solubility of TPA in BHET;  $R$ , the gas constant, 1.987 cal/mol K; and  $T$ , the absolute temperature,  $t + 273.15$ .

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

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

where  $\alpha_{H_2O}$  is the solubility of TPA in water and  $\alpha_{OLG}$ , the solubility of TPA in the 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 the oligomer ( $\alpha_{OLG}$ ) is equivalent to that in BHET ( $\alpha_{BHET}$ ), an approximate of  $\alpha$  is given by

$$\alpha \approx \alpha_{EG} \cdot w_{EG} + \alpha_{BHET} \cdot w_{OLG} \quad (21)$$

### Relations Among Oligomer Characteristics

The relations among oligomer characteristics are given in the following equations<sup>1,2</sup>:

$$\phi = OHV/(AV + OHV) \quad (22)$$

$$M_n = 2000/(AV + OHV) \quad (23)$$

$$P_n = \{M_n(1 + e) + 26.03 + 70.09e - \phi(88.10 + 176.20e)\}/(192.17 + 236.23e) \quad (24)$$

$$SV = 2000 \cdot P_n/M_n \quad (25)$$

$$E_s = (SV - AV)/SV \quad (26)$$

$$d = 100 \{ (P_n + 2\phi - 1)/P_n \} \cdot \{ e/(1 + e) \} \quad (27)$$

where  $\phi$  is the ratio of hydroxyl end groups to total end groups;  $M_n$ , the number-average molecular weight;  $P_n$ , the number-average degree of polymer-

ization;  $SV$ , the saponification value;  $E_s$ , the esterification degree;  $e$ , the molar ratio of DEG to bound EG; and  $d$ , the percentage of DEG content based on TPA.

### Prediction of Melting Points

By the following equation,<sup>3,4</sup> we can predict the melting point,  $T_m$ , over a wide range of  $P_n$  from an oligomer to a polymer of PET:

$$\begin{aligned} 1/T_m = & 0.111049 \times 10^{-3} \cdot OHV^2 - 0.200468 \\ & \times 10^{-4} \cdot OHV^3 - 0.298614 \times 10^{-3} \cdot \exp(-OHV) \\ & - 0.196193 \times 10^{-2} \cdot AV/(P_n + OHV) \\ & + 0.605210 \times 10^{-3} \cdot AV^2/(P_n + OHV)^2 \\ & - 0.971548 \times 10^{-2} \cdot AV/(P_n + OHV)^2 \\ & + 0.980871 \times 10^{-3} \cdot OHV/(P_n + OHV)^2 \\ & + 0.142510 \times 10^{-3} \cdot \exp\{AV/(P_n + OHV)\} \\ & - 0.655692 \times 10^{-4} \cdot \ln(P_n) \\ & + 0.415790 \times 10^{-2} \quad (28) \end{aligned}$$

### Effect of Catalysts or Additive on Reaction Rate Constants

Yamada and Imamura<sup>5-7</sup> reported the effect of diantimony trioxide ( $Sb_2O_3$ ) and potassium titanium oxyoxalate [ $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ ], which are polycondensation catalysts, and titanium dioxide ( $TiO_2$ ), which is an additive on the esterification reactions between TPA and EG. The following equations were obtained:

$$k_1 = (3.75 \times 10^{-4} \cdot Sb^{3+} + 0.015 \cdot T_i + 1) \times 1.5657 \times 10^9 \cdot \exp(-19640/RT) \quad (29)$$

$$k_2 = (4.75 \times 10^{-4} \cdot Sb^{3+} + 9.1667 \times 10^{-3} \cdot T_i + 1) \times 1.5515 \times 10^8 \cdot \exp(-18140/RT) \quad (30)$$

$$k_3 = (6.25 \times 10^{-4} \cdot Sb^{3+} + 0.019167 \cdot T_i + 0.1[TDO] + 1) \times 3.5165 \times 10^9 \cdot \exp(-22310/RT) \quad (31)$$

$$k_4 = (4.50 \times 10^{-4} \cdot Sb^{3+} + 1.6667 \times 10^{-3} \cdot T_i + 1) \times 6.7640 \times 10^7 \cdot \exp(-18380/RT) \quad (32)$$

$$k_5 = (3.50 \times 10^{-4} \cdot Sb^{3+} + 0.015833 \times T_i + 0.08[TDO] + 1) \times 7.7069 \times \exp(-2810/RT) \quad (33)$$

$$k_6 = (1.75 \times 10^{-4} \cdot \text{Sb}^{3+} + 3.3333 \\ \times 10^{-3} \cdot T_i + 0.04[\text{TDO}] + 1) \\ \times 6.2595 \times 10^6 \cdot \exp(-14960/RT) \quad (34)$$

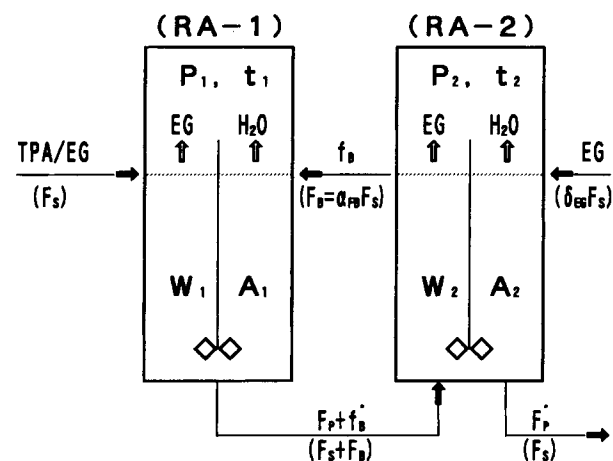
$$k_7 = (3.75 \times 10^{-4} \cdot \text{Sb}^{3+} + 0.0125 \cdot T_i \\ + 0.085714[\text{TDO}] + 1) \times 2.0583 \\ \times 10^{15} \cdot \exp(-42520/RT) \quad (35)$$

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

### Relation Between Actual Recycle Flow Rate and Recycle Flow Rate Based on PET

Figure 1 shows a schematic diagram<sup>1</sup> of a continuous recycle process in a steady state. In Figure 1, the actual recycle flow rates ( $f_B$ ,  $f'_B$ ) with EG and water are related to the recycle flow rate based on the PET polymer ( $F_B$ ) without EG and water as follows:

$$f_B = (F_B/M_{\text{PET}})/ \\ ((1 - \beta')/M_{\text{TPA}} + \beta'w'_{\text{OLG}}P'_{\text{nL}}/M'_{\text{nL}}) \quad (36)$$



**Figure 1** Continuous recycle esterification process in the steady state:  $P_1$ ,  $P_2$ , reaction pressures;  $t_1$ ,  $t_2$ , reaction temperature;  $W_1$ ,  $W_2$ , weights of reaction mixtures;  $A_1$ ,  $A_2$ , heat-transfer areas;  $F_S$ , throughput based on PET polymer;  $F_B$ , recycle flow rate based on PET polymer,  $F_B = \alpha_{\text{FB}}F_S$ ;  $F_P$ ,  $F_P'$ , actual discharge flow rates from reactor;  $f_B$ ,  $f'_B$ , actual recycle flow rates into which  $F_B$  and  $F'_B$  is converted;  $\alpha_{\text{FB}}$ , recycle ratio;  $\delta_{\text{EG}}$ , flow rate of EG added anew into RA-2 per 1 kg/h of throughput based on the PET polymer.

$$f'_B = (F'_B/M_{\text{PET}})/ \\ ((1 - \beta)/M_{\text{TPA}} + \beta w_{\text{OLG}}P_{\text{nL}}/M_{\text{nL}}) \quad (37)$$

where the superscript of prime (') represents RA-2 and no superscript represents RA-1;  $\beta$  is the weight fraction of liquid phase defined in eq. (16).  $M_{\text{PET}}$  and  $M_{\text{TPA}}$  are the molecular weight of PET polymer unit and TPA, respectively, i.e.,  $M_{\text{PET}} = 192.17$  and  $M_{\text{TPA}} = 166.13$ ;  $P_{\text{nL}}$  and  $M_{\text{nL}}$  are, respectively, the number-average degree of polymerization and the number-average molecular weight of oligomers in the liquid phase, free from undissolved TPA. Here,  $M_{\text{nL}}$  can be estimated by the relation of  $M_{\text{nL}} = 2000\beta w_{\text{OLG}}/[\beta C_1 + OHV\{1 - \beta(w_{\text{EG}} + w_{\text{H}_2\text{O}})\}]$  and  $P_{\text{nL}}$  can be obtained from eq. (24);  $w_{\text{OLG}}$  is the weight fraction of oligomer in the liquid phase free from undissolved TPA.

### Amount of EG Bound and Water Generated

#### Amount of EG Bound in PET Chain by the Reactions

The amount of bound EG can be obtained from the following equations for RA-1 and RA-2 by neglecting the effect of the DEG content:

1. For RA-1,

$$q_{\text{EG}} = (M_{\text{EG}}/M_{\text{PET}})F_B\{(P_n + 2\phi - 1)/P_n \\ - (P'_n + 2\phi - 1)/P'_n\} + (M_{\text{EG}}/M_{\text{PET}})F_S \\ \times (P_n + 2\phi - 1)/P_n \quad (38)$$

2. For RA-2,

$$q'_{\text{EG}} = (M_{\text{EG}}/M_{\text{PET}})(F_S + F_B)\{(P'_n + 2\phi' \\ - 1)/P'_n - (P_n + 2\phi - 1)/P_n\} \quad (39)$$

where  $M_{\text{EG}}$  is the molecular weight of EG ( $M_{\text{EG}} = 62.07$ );  $P_n$ , the number-average degree of polymerization of the dried oligomer,  $P_n = (M_n - 88.1\phi + 26)$  when ether linkage concentration (DEG content) is neglected;  $M_n$ , the number-average molecular weight of the dried oligomer,  $M_n = 2000/(AV + OHV)$ ;  $\phi$ , the ratio of hydroxyl end groups to total end groups of the dried oligomer,  $\phi = OHV/(AV + OHV)$ ;  $AV$ , the concentration of carboxyl end groups;  $OHV$ , the concentration of hydroxyl end groups; and  $F_S$ , the throughput based on PET polymer.

### Amount of Water Generated by the Reactions

The amount of water generated can be obtained from the following equations for RA-1 and RA-2 by neglecting the effect of DEG content:

1. For RA-1,

$$q_{H_2O} = (2M_{H_2O}/M_{PET})F_B\{(P_n + \phi - 1)/P_n - (P'_n + \phi' - 1)/P'_n\} + (2M_{H_2O}/M_{PET})F_S \times (P_n + \phi - 1)/P_n \quad (40)$$

or, alternatively, by use of the esterification degrees:

$$q_{H_2O} = (2M_{H_2O}/M_{PET})F_B(E_S - E'_S) + (2M_{H_2O}/M_{PET})F_S E_S \quad (41)$$

where  $M_{H_2O}$  is the molecular weight of water, i.e.,  $M_{H_2O} = 18.02$ ;  $E_S$  is the esterification degree defined as  $(SV - AV)/SV$ ;  $SV$  is the saponification value.

2. For RA-2 in the similar way as RA-1, the following relations are obtained:

$$q'_{H_2O} = (2M_{H_2O}/M_{PET})(F_S + F_B) \times \{(P'_n + \phi' - 1)/P'_n - (P_n + \phi - 1)/P_n\} \quad (42)$$

or, alternatively, by use of the esterification degrees

$$q'_{H_2O} = (2M_{H_2O}/M_{PET}) \times (F_S + F_B)(E'_S - E_S) \quad (43)$$

### Input Rates of EG, Water, and the Total

#### Input Rate of EG to Reactor

The input rates of EG ( $F_{EG}^i$ ,  $F_{EG}^{i'}$ ) into RA-1 and RA-2 can be obtained from eqs. (44) and (45), respectively:

1. For RA-1,

$$F_{EG}^i = (M_{EG}/M_{PET})F_S \cdot a + \beta' f_B w'_{EG} \quad (44)$$

where  $a$  is the molar ratio of EG against TPA charged into RA-1,  $a = E/T$ ; and  $w_{EG}$ , the

weight fraction of EG in the liquid phase free from undissolved TPA.

2. For RA-2,

$$F_{EG}^{i'} = \beta(F_P + f'_B)w_{EG} + \delta_{EG}F_S \quad (45)$$

where  $\delta_{EG}$  is the flow rate of EG added anew into RA-2 per 1 kg/h of  $F_S$ .

#### Input Rate of Water to Reactor

The input rates of EG ( $F_{H_2O}^i$ ,  $F_{H_2O}^{i'}$ ) into RA-1 and RA-2 can be obtained from eqs. (46) and (47), respectively:

1. For RA-1,

$$F_{H_2O}^i = \beta' f_B w'_{H_2O} \quad (46)$$

where  $w_{H_2O}$  is the weight fraction of water in the liquid phase free from undissolved TPA in RA-2.

2. For RA-2,

$$F_{H_2O}^{i'} = \beta(F_P + f'_B)w_{H_2O} \quad (47)$$

#### Total Input Rate to Reactor

The total input rates ( $F_T^i$ ,  $F_T^{i'}$ ) into RA-1 and RA-2 can be obtained from eqs. (48) and (49), respectively:

1. For RA-1,

$$F_T^i = F_S(M_{TPA} + M_{EG} \cdot a)/M_{PET} + f_B \quad (48)$$

2. For RA-2,

$$F_T^{i'} = F_P + f'_B + \delta_{EG}F_S \quad (49)$$

### Material Balances Around Reactors

#### Material Balance Around RA-1

The material balances of EG, water, and the total in RA-1 are given as follows:

1. For EG,

$$F_{EG}^i = Q_{EG} + q_{EG} + (F_P + f'_B)\beta w_{EG} \quad (50)$$

2. For water,

$$F_{H_2O}^i + q_{H_2O} = Q_{H_2O} + (F_P + f'_B)\beta w_{H_2O} \quad (51)$$

3. For the total,

$$F_T^i = Q_{EG} + Q_{H_2O} + F_P + f_B' \quad (52)$$

### Material Balance Around RA-2

The material balances of EG, water, and the total in RA-2 are given as follows:

1. For EG,

$$F_{EG}^{i'} = Q_{EG}' + q_{EG}' + (F_P' + f_B)\beta'w_{EG}' \quad (53)$$

2. For water,

$$\begin{aligned} F_{H_2O}^{i'} + q_{H_2O}' \\ = Q_{H_2O}' + (F_P' + f_B)\beta'w_{H_2O}' \end{aligned} \quad (54)$$

3. For the total,

$$F_T^{i'} = Q_{EG}' + Q_{H_2O}' + F_P' + f_B \quad (55)$$

The material balance of each component in RA-1 and RA-2 also is given as the previous report.<sup>1</sup>

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

By combining eqs. (50)–(52), the vapor (distillate) flow rates of EG and water ( $Q_{EG}$ ,  $Q_{H_2O}$ ) from RA-1 can be expressed as follows:

$$\begin{aligned} Q_{EG} = \{ (F_{EG}^{i'} - q_{EG}') (1 - \beta w_{EG}) \\ - \beta w_{EG} (F_T^i - F_{H_2O}^i - q_{H_2O}') \} / \\ \{ 1 - \beta (w_{EG} + w_{H_2O}') \} \end{aligned} \quad (56)$$

$$\begin{aligned} Q_{H_2O} = \{ (F_{H_2O}^{i'} + q_{H_2O}') - \beta w_{H_2O} (F_T^i - Q_{EG}') \} / \\ (1 - \beta w_{H_2O}') \end{aligned} \quad (57)$$

In the same manner as above, the vapor (distillate) flow rates of EG and water ( $Q_{EG}'$ ,  $Q_{H_2O}'$ ) from RA-2 can be expressed by eqs. (58) and (59):

$$\begin{aligned} Q_{EG}' = \{ (F_{EG}^{i'} - q_{EG}') (1 - \beta' w_{EG}') \\ - \beta' w_{EG}' (F_T^{i'} - F_{H_2O}^{i'} - q_{H_2O}') \} / \\ \{ 1 - \beta' (w_{EG}' + w_{H_2O}') \} \end{aligned} \quad (58)$$

$$\begin{aligned} Q_{H_2O}' = \{ (F_{H_2O}^{i'} + q_{H_2O}') - \beta' w_{H_2O}' (F_T^{i'} - Q_{EG}') \} / \\ (1 - \beta' w_{H_2O}') \end{aligned} \quad (59)$$

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

$$y_{EG} = (Q_{EG}/M_{EG}) / (Q_{EG}/M_{EG} + Q_{H_2O}/M_{H_2O}) \quad (60)$$

$$y_{EG}' = (Q_{EG}'/M_{EG}') / (Q_{EG}'/M_{EG}' + Q_{H_2O}'/M_{H_2O}') \quad (61)$$

As the vapor-liquid equilibrium in the esterification stage follows Rault's law with few problems for practical use,<sup>8</sup> we can determine the liquid-phase or vapor-phase mol fractions and the resultant weight fraction of each component.

## RESULTS AND DISCUSSION

The simulation was carried out as parameters of recycle ratios ( $\alpha_{FB} : \alpha_{FB} = 0, 0.5, 1.0, 1.5, 2.0, 2.5$ ), reaction temperatures ( $t_1, t_2 : t_1/t_2 = 250^\circ\text{C}/250^\circ\text{C}, 255^\circ\text{C}/255^\circ\text{C}, 260^\circ\text{C}/260^\circ\text{C}$ ), and residence times [ $\tau_1, \tau_2 : \tau_1/\tau_2$  (h/h) = 3/5, 4/4, 5/3, 6/2] under fixed conditions of reaction pressures ( $P_1, P_2 : P_1 = P_2 = 0 \text{ kg/cm}^2 \text{ g}$ ), and the molar ratio of EG to TPA fed to RA-1 ( $E/T : E/T = 2.0$ ), with no extra addition of EG to RA-2 ( $\delta_{EG} = 0$ ) and a total residence time ( $\tau_1 + \tau_2 = 8 \text{ h}$ ). These simulated results are illustrated in Figures 2–22, showing the typical characteristics of the oligomer ( $AV, \phi, P_n, E_S, d, T_m$ ). Table I shows the details of the simulated results for  $\tau_1/\tau_2 = 4 \text{ h}/4 \text{ h}$ . By the use of these figures and the table, the influence of these parameters on the oligomer characteristics will be discussed below.

### Influence of Reaction Conditions on Oligomer Characteristics

#### Influence on Carboxyl End Groups (AV)

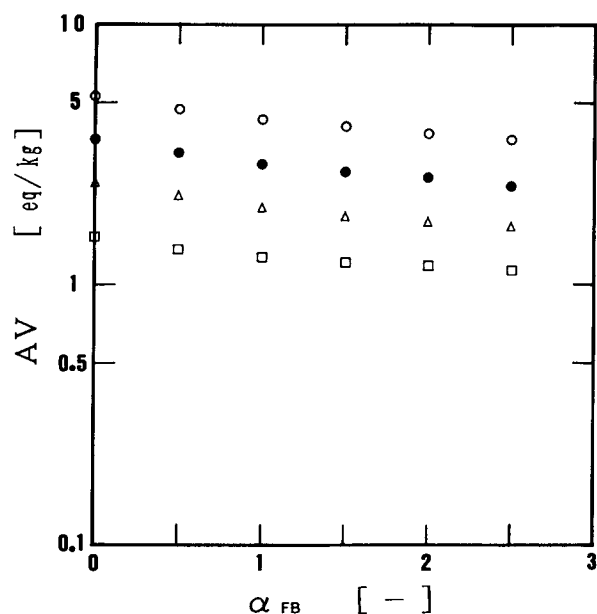
Figures 2–4 show the relation between  $\alpha_{FB}$  and AV as parameters of  $\tau_1/\tau_2$  and temperature. These figures lead to the following results:

When the total residence time of RA-1 and RA-2 is constant (i.e.,  $\tau_1 + \tau_2 = 8 \text{ h}$ ), the higher the ratio of  $\tau_1$  to  $\tau_2$  ( $\tau_1/\tau_2$ ), the more esterification reactions tend to proceed (AV becomes lower). Furthermore, the higher the temperature is, the more remarkable this tendency becomes.

The higher the recycle ratio ( $\alpha_{FB}$ ) is, the more esterification reactions tend to proceed (AV becomes lower). But, at lower AV (e.g., AV is lower than 0.2

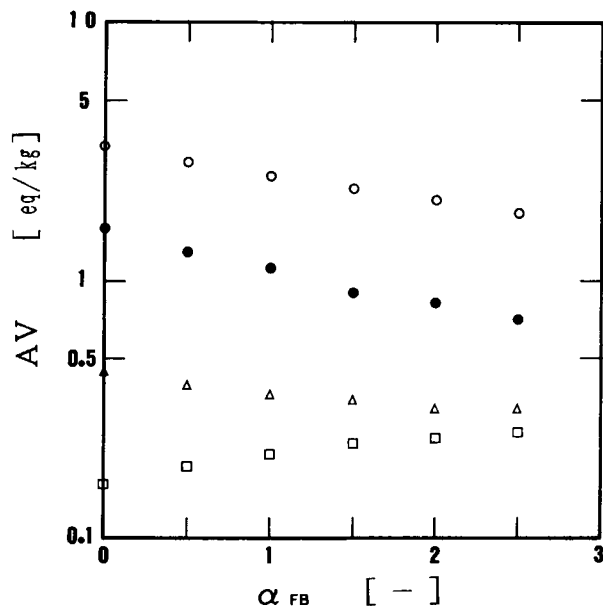
**Table I Simulation Results for a Continuous Recycle Esterification Process of TPA with EG under  $P_1 = P_2 = 0$  kg/cm<sup>2</sup> g,  $\tau_1 = \tau_2 = 4$  h,  $E/T = 2$ , and  $\delta_{EG} = 0$  ( $F_s = 100$  kg/h, No Addition of Catalysts and Fillers)**

	$t$ (°C)	$P$ (kg/ cm <sup>2</sup> g)	$\tau$ (h)	$E/T$	$\delta_{EG}$	$\alpha_{FB}$	$AV$ (equiv/kg)	$CHV$ (equiv/kg)	$\phi$	$E_s$	$M_n$	$P_n$	100e (%)	$d$ (%)	$w_{EG}$	$w_{H_2O}$	$Q$ (kg/h)	$F_P$ (kg/ h)	$F_P^0$ (kg/h)	$\beta$	$T_m$ (°C)
RA-1	250	0.0	4.0	2.0	—	0.0	4.597	1.254	0.214	0.567	342	1.814	1.183	0.801	0.0120	0.203	52.3	98.7	97.9	0.647	228
RA-2	250	0.0	4.0	—	0.00	0.0	3.652	0.367	0.091	0.661	498	2.680	1.240	0.852	0.0005	0.811	2.2	96.6	96.5	0.725	265
RA-1	250	0.0	4.0	2.0	—	0.5	4.082	1.278	0.238	0.613	373	1.966	1.120	0.813	0.0112	0.212	50.6	99.5	98.7	0.692	229
RA-2	250	0.0	4.0	—	0.00	0.5	3.242	0.475	0.128	0.697	538	2.874	1.185	0.868	0.0008	0.763	3.1	97.4	97.3	0.761	252
RA-1	250	0.0	4.0	2.0	—	1.0	3.682	1.290	0.259	0.649	402	2.108	1.071	0.817	0.0107	0.218	49.1	100.0	99.2	0.726	229
RA-2	250	0.0	4.0	—	0.00	1.0	2.918	0.556	0.160	0.725	576	3.054	1.136	0.873	0.0009	0.735	3.9	98.1	98.0	0.789	245
RA-1	250	0.0	4.0	2.0	—	1.5	3.384	1.295	0.277	0.676	427	2.231	1.022	0.809	0.0102	0.224	47.9	100.4	99.6	0.752	229
RA-2	250	0.0	4.0	—	0.00	1.5	2.689	0.623	0.188	0.745	604	3.188	1.084	0.863	0.0011	0.708	4.6	98.6	98.4	0.809	241
RA-1	250	0.0	4.0	2.0	—	2.0	3.180	1.293	0.289	0.695	447	2.328	1.007	0.816	0.0099	0.227	46.9	100.6	99.9	0.769	228
RA-2	250	0.0	4.0	—	0.00	2.0	2.551	0.681	0.211	0.758	619	3.255	1.069	0.870	0.0013	0.682	5.2	98.9	98.8	0.821	239
RA-1	250	0.0	4.0	2.0	—	2.5	2.974	1.288	0.302	0.714	469	2.437	0.993	0.823	0.0096	0.231	46.0	100.9	100.1	0.787	228
RA-2	250	0.0	4.0	—	0.00	2.5	2.385	0.718	0.231	0.773	645	3.380	1.050	0.874	0.0014	0.672	5.7	99.3	99.1	0.895	237
RA-1	255	0.0	4.0	2.0	—	0.0	3.573	1.208	0.253	0.659	418	2.194	1.217	0.931	0.0083	0.241	51.3	99.7	99.1	0.737	232
RA-2	255	0.0	4.0	—	0.00	0.0	2.559	0.299	0.105	0.760	700	3.724	1.234	0.960	0.0003	0.874	2.1	97.7	97.6	0.822	244
RA-1	255	0.0	4.0	2.0	—	0.5	3.069	1.214	0.283	0.705	467	2.432	1.119	0.910	0.0078	0.250	49.7	100.4	99.8	0.780	230
RA-2	255	0.0	4.0	—	0.00	0.5	2.183	0.387	0.151	0.793	778	4.111	1.162	0.953	0.0004	0.840	2.9	98.4	98.4	0.855	240
RA-1	255	0.0	4.0	2.0	—	1.0	2.748	1.210	0.306	0.735	505	2.621	1.088	0.917	0.0075	0.254	48.4	100.8	100.2	0.808	229
RA-2	255	0.0	4.0	—	0.00	1.0	1.946	0.457	0.190	0.815	832	4.373	1.143	0.970	0.0002	0.810	3.7	99.0	98.9	0.876	238
RA-1	255	0.0	4.0	2.0	—	1.5	2.459	1.207	0.329	0.762	546	2.820	1.035	0.900	0.0072	0.258	47.3	101.2	100.5	0.833	228
RA-2	255	0.0	4.0	—	0.00	1.5	1.718	0.514	0.230	0.836	896	4.685	1.088	0.952	0.0006	0.793	4.3	99.4	99.4	0.895	237
RA-1	255	0.0	4.0	2.0	—	2.0	2.246	1.202	0.349	0.782	580	2.991	1.009	0.898	0.0070	0.261	46.3	101.4	100.8	0.851	228
RA-2	255	0.0	4.0	—	0.00	2.0	1.563	0.565	0.265	0.850	940	4.899	1.057	0.946	0.0007	0.776	4.9	99.8	99.7	0.909	237
RA-1	255	0.0	4.0	2.0	—	2.5	2.105	1.191	0.361	0.796	607	3.124	1.034	0.933	0.0068	0.263	45.6	101.6	100.9	0.863	228
RA-2	255	0.0	4.0	—	0.00	2.5	1.482	0.607	0.291	0.858	958	4.979	1.089	0.986	0.0008	0.754	5.4	100.0	99.9	0.916	237
RA-1	260	0.0	4.0	2.0	—	0.0	2.562	1.114	0.303	0.753	544	2.824	1.159	0.986	0.0057	0.280	50.4	100.6	100.1	0.826	230
RA-2	260	0.0	4.0	—	0.00	0.0	1.599	0.233	0.127	0.848	1092	5.749	1.182	1.016	0.0001	0.923	1.9	98.7	98.7	0.908	242
RA-1	260	0.0	4.0	2.0	—	0.5	2.185	1.106	0.336	0.789	608	3.140	1.120	0.992	0.0055	0.285	49.1	101.1	100.6	0.859	229
RA-2	260	0.0	4.0	—	0.00	0.5	1.302	0.301	0.188	0.876	1248	6.533	1.158	1.035	0.0002	0.904	2.7	99.3	99.2	0.934	242
RA-1	260	0.0	4.0	2.0	—	1.0	1.920	1.091	0.362	0.814	664	3.421	1.088	0.990	0.0053	0.287	48.0	101.4	100.9	0.882	229
RA-2	260	0.0	4.0	—	0.00	1.0	1.123	0.359	0.242	0.892	1350	7.038	1.146	1.050	0.0002	0.873	3.0	99.7	99.6	0.950	243
RA-1	260	0.0	4.0	2.0	—	1.5	1.651	1.082	0.396	0.839	732	3.758	1.009	0.944	0.0051	0.291	46.9	101.7	101.2	0.905	229
RA-2	260	0.0	4.0	—	0.00	1.5	0.909	0.404	0.307	0.913	1524	7.912	1.052	0.990	0.0003	0.861	4.0	100.1	100.1	0.968	244
RA-1	260	0.0	4.0	2.0	—	2.0	1.496	1.074	0.418	0.854	778	3.988	1.047	0.994	0.0050	0.293	46.2	101.9	101.4	0.918	229
RA-2	260	0.0	4.0	—	0.00	2.0	0.824	0.451	0.354	0.921	1569	8.126	1.092	1.042	0.0004	0.828	4.5	100.4	100.3	0.976	244
RA-1	260	0.0	4.0	2.0	—	2.5	1.346	1.062	0.441	0.868	831	4.250	1.001	0.963	0.0049	0.294	45.4	102.0	101.5	0.931	230
RA-2	260	0.0	4.0	—	0.00	2.5	0.713	0.479	0.402	0.931	1677	8.668	1.046	1.011	0.0004	0.820	5.0	100.6	100.6	0.985	245

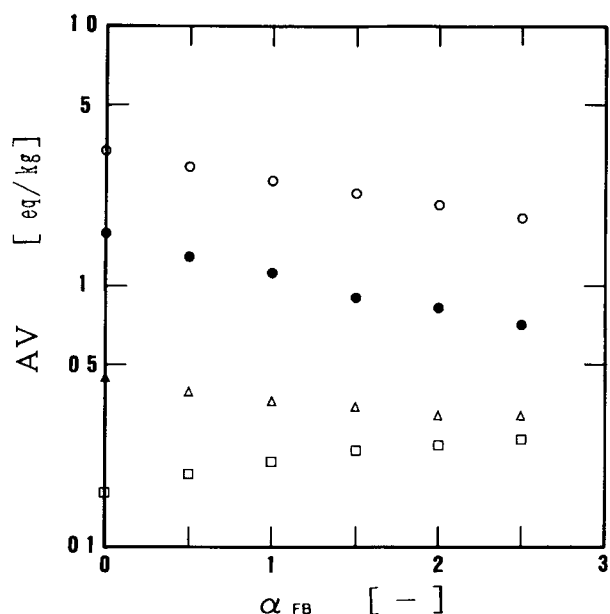


**Figure 2** Influence of  $\alpha_{FB}$  on AV in RA-2 under  $T_1 = 250^\circ\text{C}$ ,  $T_2 = 250^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

equiv/kg), the AV tends to increase with  $\alpha_{FB}$ . A plausible reason is that the reverse reactions also proceed due to the increase of water content in the recycle flow as esterification reactions proceed.



**Figure 3** Influence of  $\alpha_{FB}$  on AV in RA-2 under  $T_1 = 255^\circ\text{C}$ ,  $T_2 = 255^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



**Figure 4** Influence of  $\alpha_{FB}$  on AV in RA-2 under  $T_1 = 260^\circ\text{C}$ ,  $T_2 = 260^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

#### **Influence on Hydroxyl End-group Ratio ( $\phi$ )**

Figures 5–7 show the relation between  $\alpha_{FB}$  and  $\phi$  as parameters of  $\tau_1/\tau_2$  and temperature. From these figures, it can be seen that the higher the  $\alpha_{FB}$ , the higher the  $\phi$  that is observed.

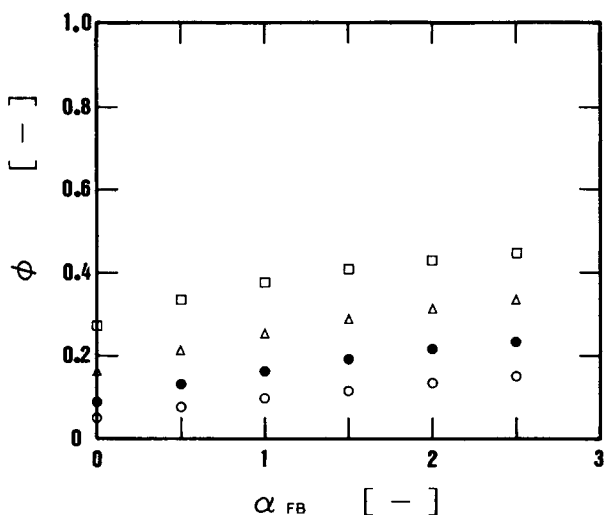
#### **Influence on Polymerization Degree ( $P_n$ )**

Figures 8–10 show the relation between  $\alpha_{FB}$  and  $P_n$  as parameters of  $\tau_1/\tau_2$  and temperature. Below a certain degree of  $P_n$  (less than 10 of  $P_n$ ),  $P_n$  increases with increasing  $\alpha_{FB}$ . This tendency becomes much clearer in higher temperatures. Above 10 of  $P_n$ , on the other hand, it shows the reverse tendency, whereby  $P_n$  becomes lower with the increase of  $\alpha_{FB}$ , presumably because esterification reactions occur more easily than do polycondensation reactions under given conditions.

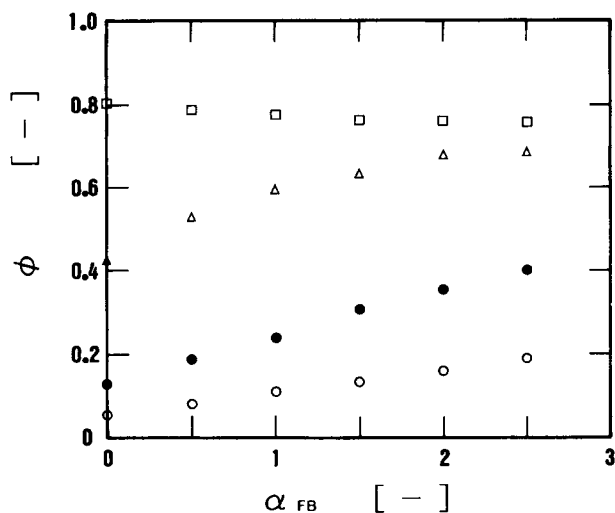
#### **Influence on Degree of Esterification ( $E_S$ )**

Figures 11–13 show the relation between  $\alpha_{FB}$  and  $E_S$  as parameters of  $\tau_1/\tau_2$  and temperature. These figures show that  $P_n$  has a similar tendency to that described for AV from a viewpoint of reactions except that the difference in the influence of  $(\tau/\tau')$  on  $P_n$  becomes smaller with higher temperatures contrary to that on AV. This could explain why the change in  $(AV/SV)$  becomes smaller the higher the  $E_S$  is, when reactions are proceeding vigorously.





**Figure 5** Influence of  $\alpha_{FB}$  on  $\phi$  in RA-2 under  $T_1 = 250^\circ\text{C}$ ,  $T_2 = 250^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



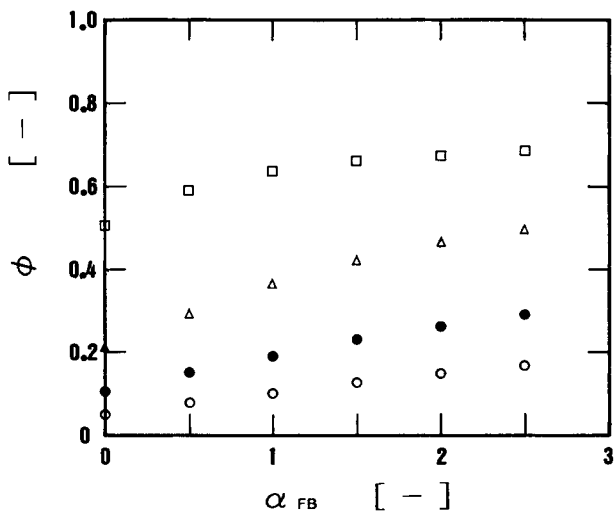
**Figure 7** Influence of  $\alpha_{FB}$  on  $\phi$  in RA-2 under  $T_1 = 260^\circ\text{C}$ ,  $T_2 = 260^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

**Influence on DEG Content (d)**

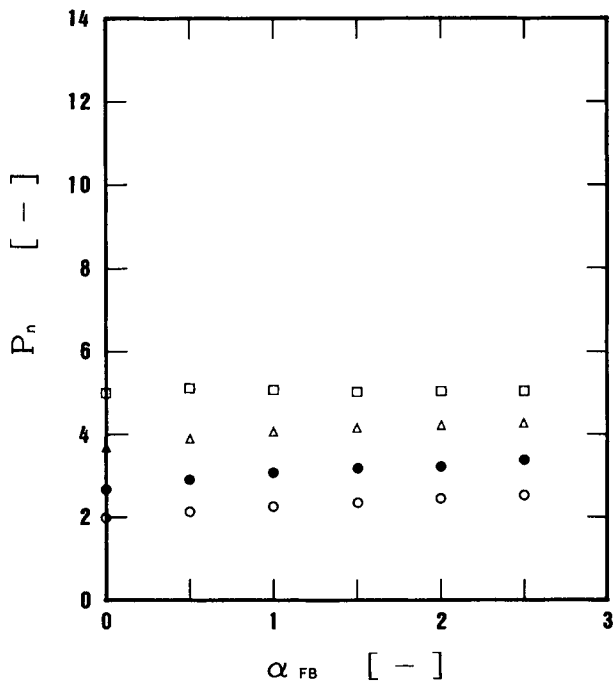
Figures 14–16 show the relation between  $\alpha_{FB}$  and  $d$  as parameters of  $\tau_1/\tau_2$  and temperature. It can be seen that a higher  $\alpha_{FB}$  tends to give a higher  $d$ . The effect of reaction temperature on the  $d$  is more prominent. With increasing the temperature, the  $d$  increases, because the activation energy calculated from the side reaction rate constant is higher than that for the main reaction.<sup>8</sup>

**Influence on Melting Point ( $T_m$ )**

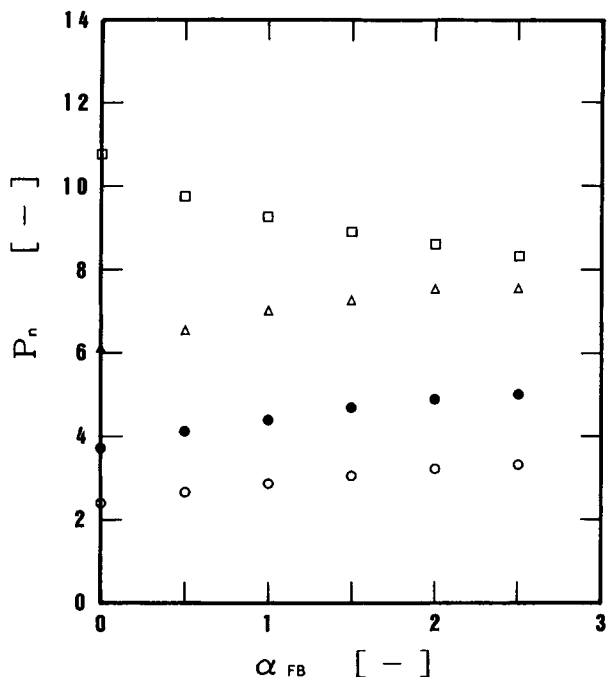
Figures 17–19 show the relation between  $\alpha_{FB}$  and  $T_m$  as parameters of  $\tau_1/\tau_2$  and temperature. These figures indicate that the higher the  $\alpha_{FB}$ , the lower



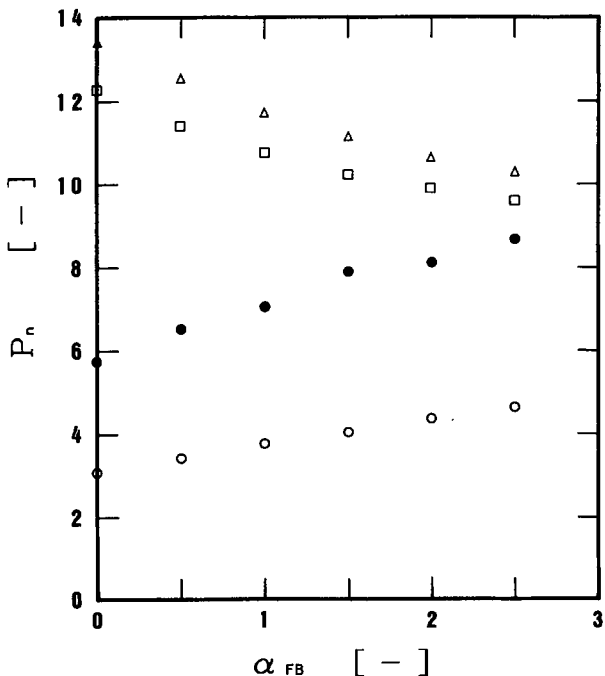
**Figure 6** Influence of  $\alpha_{FB}$  on  $\phi$  in RA-2 under  $T_1 = 255^\circ\text{C}$ ,  $T_2 = 255^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



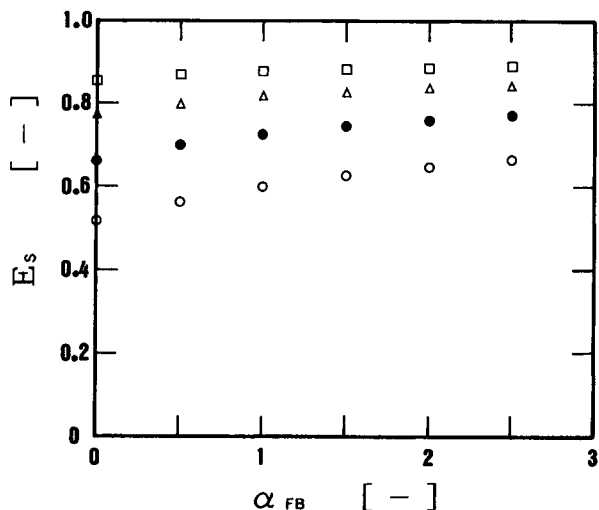
**Figure 8** Influence of  $\alpha_{FB}$  on  $P_n$  in RA-2 under  $T_1 = 250^\circ\text{C}$ ,  $T_2 = 250^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



**Figure 9** Influence of  $\alpha_{FB}$  on  $P_n$  in RA-2 under  $T_1 = 255^\circ\text{C}$ ,  $T_2 = 255^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



**Figure 10** Influence of  $\alpha_{FB}$  on  $P_n$  in RA-2 under  $T_1 = 260^\circ\text{C}$ ,  $T_2 = 260^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



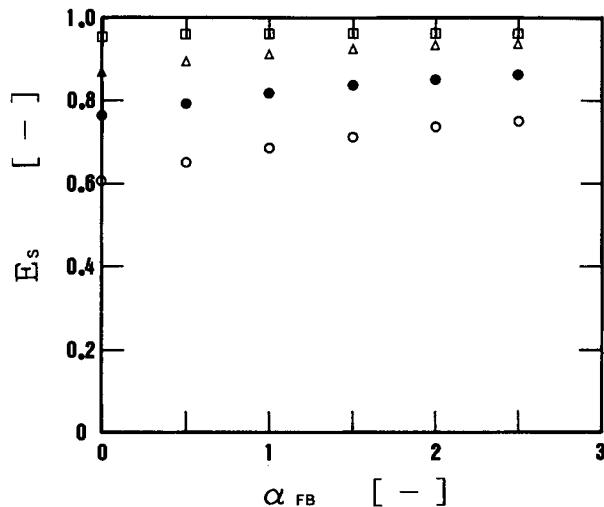
**Figure 11** Influence of  $\alpha_{FB}$  on  $E_S$  in RA-2 under  $T_1 = 250^\circ\text{C}$ ,  $T_2 = 250^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

is the  $T_m$ , which is more prominent in the low reaction temperature. At higher temperatures, however, this tendency is not always evident and the influence of  $\alpha_{FB}$  on  $T_m$  becomes obscure.

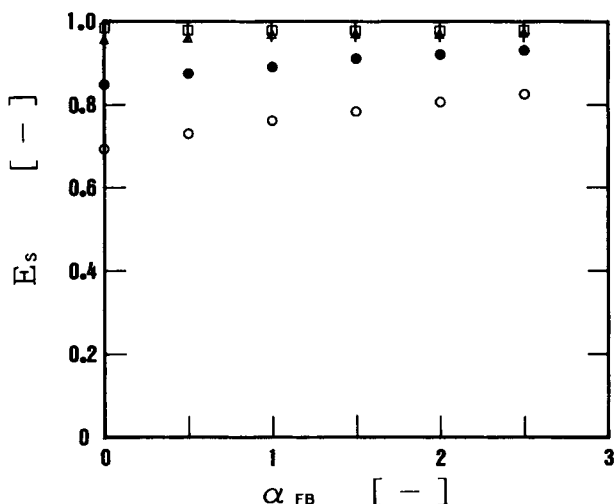
**Relationships Between Oligomer Characteristics**

**Relationship Between the Degree of Esterification ( $E_S$ ) and Carboxyl End Groups ( $AV$ )**

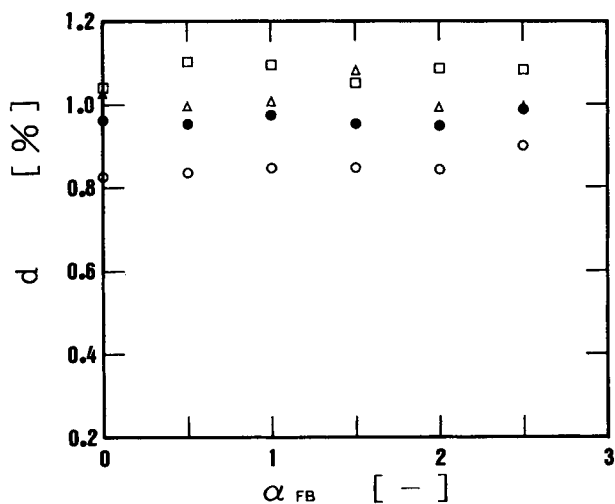
In Figure 20,  $AV$  is plotted as a function of  $E_S$  for various reaction temperatures and  $\tau_1/\tau_2$  values. It



**Figure 12** Influence of  $\alpha_{FB}$  on  $E_S$  in RA-2 under  $T_1 = 255^\circ\text{C}$ ,  $T_2 = 255^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



**Figure 13** Influence of  $\alpha_{FB}$  on  $E_S$  in RA-2 under  $T_1 = 260^\circ\text{C}$ ,  $T_2 = 260^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



**Figure 15** Influence of  $\alpha_{FB}$  on  $d$  in RA-2 under  $T_1 = 255^\circ\text{C}$ ,  $T_2 = 255^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

is clear that, independent of reaction conditions, the relationship between  $E_S$  and  $AV$  can be expressed as a single curve. This is the same result as that for a continuous esterification process of the cascade-type, reported previously.<sup>9</sup> A similar relation is found between  $E_S$  and  $P_n$  and  $E_S$  and  $d$ , as shown in Figures 21 and 22, respectively.

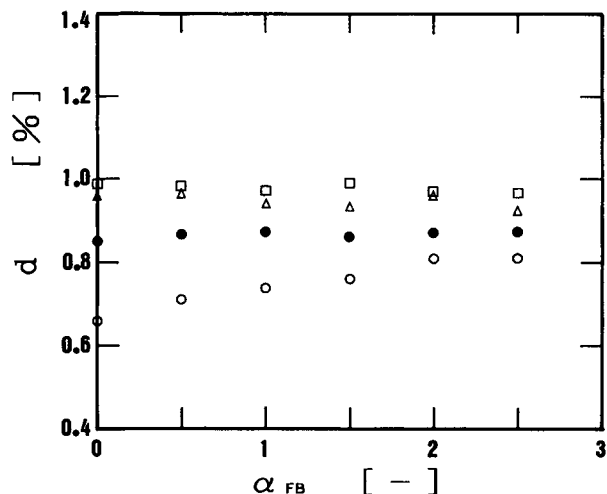
**Relationship Between the Degree of Esterification ( $E_S$ ) and the Degree of Polymerization ( $P_n$ )**

Figure 21 shows the relationship between  $E_S$  and  $P_n$ . It can be seen from Figure 21 that, independent

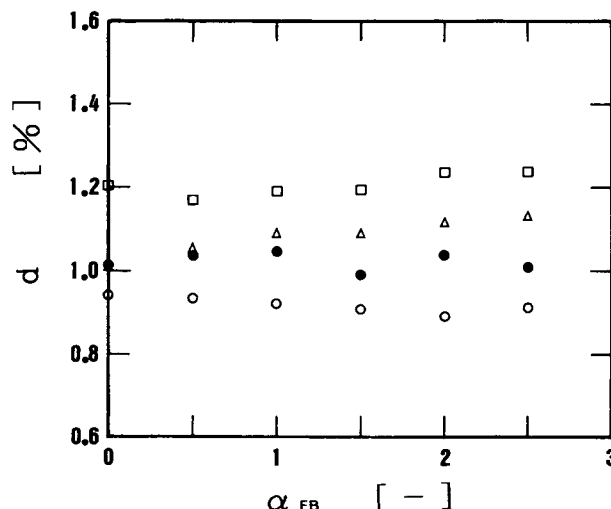
of reaction conditions, the approximate relationship between  $E_S$  and  $P_n$  can also be expressed as a certain curve.

**Relationship Between the Degree of Esterification ( $E_S$ ) and DEG Content ( $d$ )**

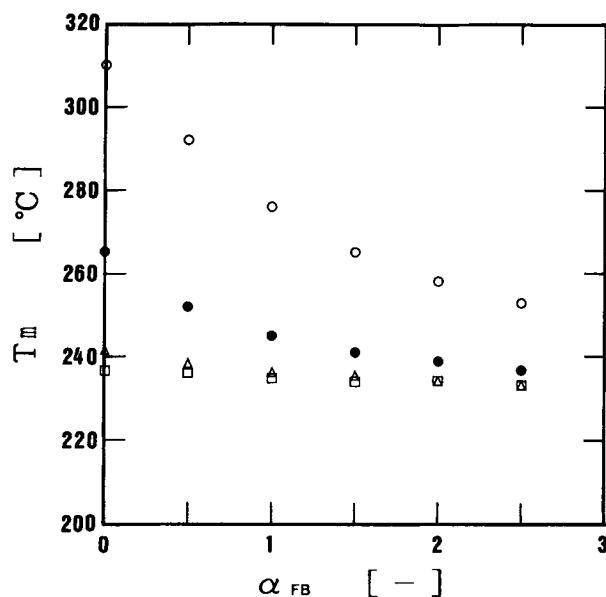
Figure 22 shows the relation between  $E_S$  and  $d$ . It can be seen from Figure 22 that, almost independent of reaction conditions, the relationship between  $E_S$  and  $d$  can also be expressed very roughly as a certain curve.



**Figure 14** Influence of  $\alpha_{FB}$  on  $d$  in RA-2 under  $T_1 = 250^\circ\text{C}$ ,  $T_2 = 250^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



**Figure 16** Influence of  $\alpha_{FB}$  on  $d$  in RA-2 under  $T_1 = 260^\circ\text{C}$ ,  $T_2 = 260^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (○)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; (△)  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; (□)  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

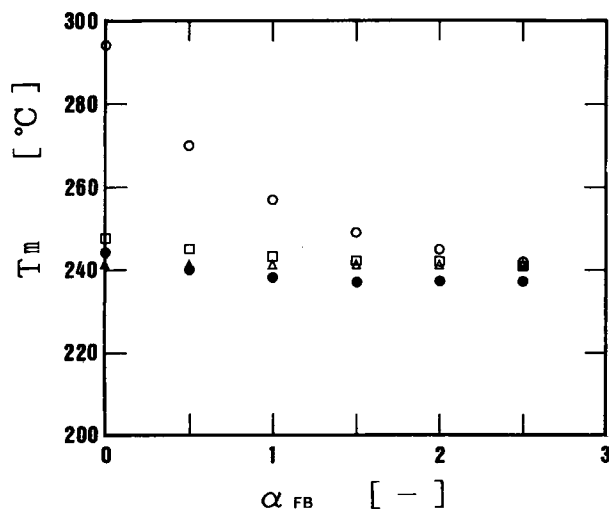


**Figure 17** Influence of  $\alpha_{FB}$  on  $T_m$  in RA-2 under  $T_1 = 250^\circ\text{C}$ ,  $T_2 = 250^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

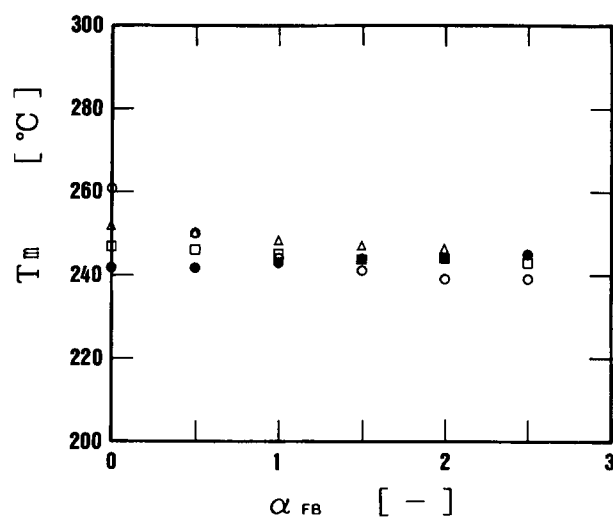
The above results suggest that where the degree of conversion ( $E_S$ ) is the same an oligomer corresponds with each of the other characteristics in roughly the same way.

## CONCLUSION

With increasing the reaction temperature, the main reactions in the esterifications proceed ( $AV$  becomes



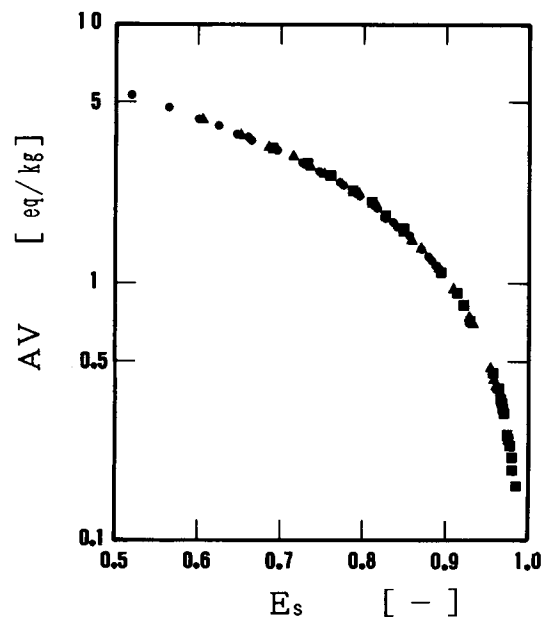
**Figure 18** Influence of  $\alpha_{FB}$  on  $T_m$  in RA-2 under  $T_1 = 255^\circ\text{C}$ ,  $T_2 = 255^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .



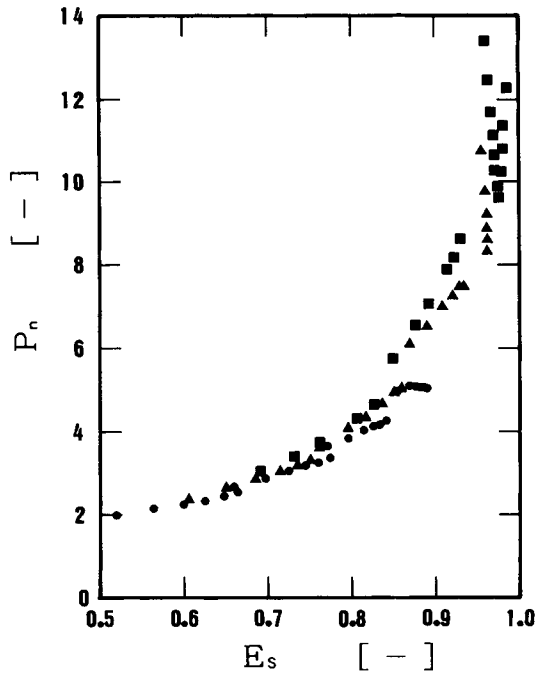
**Figure 19** Influence of  $\alpha_{FB}$  on  $T_m$  in RA-2 under  $T_1 = 260^\circ\text{C}$ ,  $T_2 = 260^\circ\text{C}$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (O)  $\tau_1 = 3 \text{ h}$ ,  $\tau_2 = 5 \text{ h}$ ; (●)  $\tau_1 = 4 \text{ h}$ ,  $\tau_2 = 4 \text{ h}$ ; ( $\Delta$ )  $\tau_1 = 5 \text{ h}$ ,  $\tau_2 = 3 \text{ h}$ ; ( $\square$ )  $\tau_1 = 6 \text{ h}$ ,  $\tau_2 = 2 \text{ h}$ .

lower) more easily and, simultaneously, the side reactions forming the DEG proceed rather than the main reactions. The reaction temperature affects the most on forming the DEG.

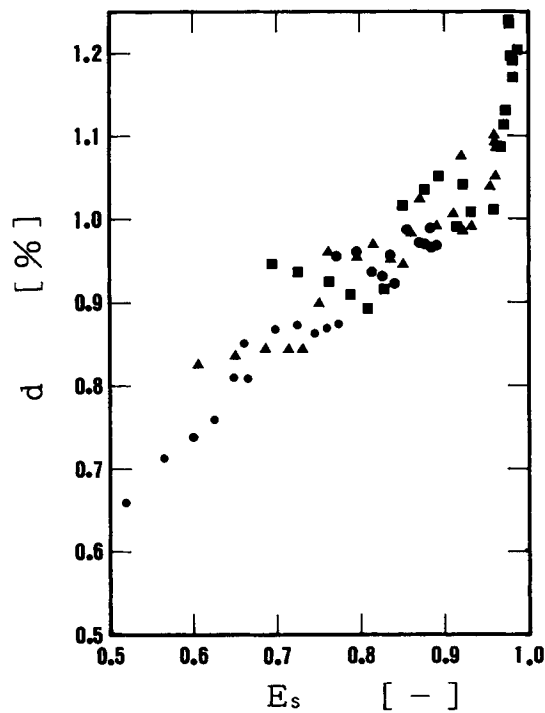
The higher the ratio of the residence time of the first reactor to the total time is, the esterification reactions tend to proceed. This tendency becomes remarkable at higher temperature.



**Figure 20** Relation between  $AV$  and  $E_S$  in RA-2 under  $\tau_1/\tau_2 (\text{h/h}) = 3/5, 4/4, 5/3, \text{ and } 6/2$ ,  $P_1 = P_2 = 0.0 \text{ kg/cm}^2 \text{ g}$ ,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (●)  $T_1 = T_2 = 250^\circ\text{C}$ ; ( $\blacktriangle$ )  $T_1 = T_2 = 255^\circ\text{C}$ ; ( $\blacksquare$ )  $T_1 = T_2 = 260^\circ\text{C}$ .



**Figure 21** Relation between  $P_n$  and  $E_s$  in RA-2 under  $\tau_1/\tau_2$ (h/h) = 3/5, 4/4, 5/3, and 6/2,  $P_1 = P_2 = 0.0$  kg/cm<sup>2</sup> g,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (●)  $T_1 = T_2 = 250^\circ\text{C}$ ; (▲)  $T_1 = T_2 = 255^\circ\text{C}$ ; (■)  $T_1 = T_2 = 260^\circ\text{C}$ .



**Figure 22** Relation between  $d$  and  $E_s$  in RA-2 under  $\tau_1/\tau_2$ (h/h) = 3/5, 4/4, 5/3, and 6/2,  $P_1 = P_2 = 0.0$  kg/cm<sup>2</sup> g,  $E/T = 2.0$ , and  $\delta_{EG} = 0.0$ . (●)  $T_1 = T_2 = 250^\circ\text{C}$ ; (▲)  $T_1 = T_2 = 255^\circ\text{C}$ ; (■)  $T_1 = T_2 = 260^\circ\text{C}$ .

The higher the recycle ratio is, the esterification reactions generally tend to proceed. But in the region of high degree of esterification (e.g.,  $AV < 0.2$  equiv/kg), the higher recycle ratio brings the lower degree of esterification (higher  $AV$ ). The oligomer characteristics are primarily determined by the degree of esterification, independent of the reaction conditions.

**NOMENCLATURE**

- $a$  molar ratio of EG against TPA charged into RA-1;  $a = E/T$
- $AV, AV'$  concentrations of total carboxyl end groups in dried oligomer (equiv/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 (equiv/kg);  $AV_a = C_T/(T_S + W_e)$
- $C_1$  concentration of carboxyl end groups in the liquid phase of reaction mixtures (equiv/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 (equiv/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  $k$  (equiv/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)]
- $E_s, E'_s$  esterification degrees of dried oligomer
- $E/T$  molar ratio of EG to TPA of the slurry, which fed to the first reactor;  $E/T = a$
- $f_B, f'_B$  actual recycle flow rates into which  $F_B$  is converted (kg/h)

$F^i$	total input rate (kg/h)
$F_B$	recycle flow rate based on PET polymer (kg/h); $F_B = \alpha_{FB} F_S$
$F_{EG}^i, F_{EG}^{i'}$	input rates of EG (kg/h)
$F_{H_2O}^i$	input rate of water (kg/h)
$F_P, F_P'$	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)–(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); $M_{EG} = 166.13$
$M_n$	number-average molecular weight (g/mol)
$M_{nL}$	number-average molecular weight of oligomer in the liquid phase free from undissolved TPA (g/mol)
$OHV, OHV'$	concentrations of hydroxyl end groups in 1 kg of dried oligomer (equiv/kg)
$P_1, P_2$	total pressures (= 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)
$P_n, P'_n$	number-average degree of polymerization of oligomer
$P_{nL}, P'_{nL}$	number-average degree of polymerization of oligomer in the liquid phase free from undissolved TPA
$q_{EG}, q'_{EG}$	amounts of EG bound in PET chain (kg/h)
$q_{H_2O}, q'_{H_2O}$	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
$Sb^{3+}$	mol number of antimony ion ( $Sb^{3+}$ ) in diantimony trioxide supplied for $10^6$ mol of TPA ( $\mu\text{mol}/\text{TPA mol}$ )
$SV$	saponification value (equiv/kg)
$t_1, t_2$	reaction temperatures ( $^{\circ}\text{C}$ )
$T$	absolute temperature, $T = t + 273.15$ (K)
$T_i$	mol number of potassium titanium oxyoxalate supplied for $10^6$ mol of TPA ( $\mu\text{mol}/\text{TPA mol}$ )

$T_m$	melting point of dried oligomer ( $^{\circ}\text{C}$ )
$T_s$	weight of TPA undissolved (kg)
[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
$W_1, W_2$	total weights of reaction mixtures in the reactor (kg)
$W_e$	weight of liquid phase in the reaction mixtures (kg)
$x_{EG}$	mol fraction of EG in the liquid phase of reaction mixtures free from undissolved TPA
$x_{H_2O}$	mol fraction of water in the liquid phase of reaction mixtures free from undissolved TPA
$x_{OLG}$	mol fraction of oligomer in the liquid phase of reaction mixtures free from undissolved TPA
$y_{EG}$	mol fraction of EG in the vapor phase
$y_{H_2O}$	mol fraction of water in the vapor phase

### Greek Letters

$\alpha$	mean solubility of TPA in the reaction mixtures expressed as equivalent moles of carboxyl end groups [equiv/kg (reaction mixtures)]; $\alpha = (C_T - \eta_{TPA} T_S) / W_e$
$\alpha_{BHET}$	solubility of TPA in BHET expressed as equivalent moles of carboxyl end groups [equiv/kg (BHET)]
$\alpha_{EG}$	solubility of TPA in EG expressed as equivalent moles of carboxyl end groups [equiv/kg (EG)]
$\alpha_{FB}$	recycle ratio defined as $\alpha_{FB} = F_B / F_S$
$\alpha_{H_2O}$	solubility of TPA in water expressed as equivalent moles of carboxyl end groups [equiv/kg (water)]
$\alpha_{OLG}$	solubility of TPA in oligomer expressed as equivalent moles of carboxyl end groups [equiv/kg (oligomer)]
$\beta$	weight fraction of liquid phase in the reaction mixtures; $\beta = W_e / (W_e + T_S)$
$\delta_{EG}$	flow rate of EG added anew into the reactor per 1 kg/h of throughput based on PET polymer [(kg/h)/(kg/h) (PET)]

$\epsilon_k$	calculated value of the left hand (residue) in each eqs. (73)–(84)
$\zeta$	concentration of carboxyl end groups in the reaction mixtures without undissolved TPA ( $\beta = 1$ ) (equiv/kg)
$\eta_{EG}$	equivalent concentration of EG, $\eta_{EG} = 16.111$ mol/kg (EG)
$\eta_{H_2O}$	equivalent concentration of water, $\eta_{H_2O} = 55.494$ mol/kg (H <sub>2</sub> O)
$\eta_{TPA}$	equivalent concentration of TPA expressed as equivalent moles of carboxyl end groups, $\eta_{TPA} = 12.039$ equiv/kg (TPA)
$\theta$	reaction time (h)
$\phi$	ratio of hydroxyl end groups to total end groups of dried oligomer; $\phi = OHV/(AV + OHV)$
$\tau_1, \tau_2$	residence time in the reactor defined as $\tau_1 = W_i/F_S$

### Subscripts

BHET	bis- $\beta$ -hydroxyethyl terephthalate
EG	ethylene glycol
H <sub>2</sub> O	water
OLG	oligomer
TPA	terephthalic acid
1, 2	RA-1 or RA-2

### Superscripts

$d$	distillate (vapor phase)
EG	ethylene glycol
TPA	terephthalic acid
' (prime)	RA-2

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