Effect of Diantimony Trioxide on Direct Esterification between Terephthalic Acid and Ethylene Glycol

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Synopsis

Experiments at various Sb_2O_3 concentrations were made in a pilot plant and the effect of Sb_2O_3 on continuous esterification between terephthalic acid (TPA) and ethylene glycol (EG) was obtained. Reaction rate constants of the previously reported reaction scheme were determined to fit with the experimental data obtained. It was found that the effect of Sb_2O_3 on reaction rate constant (k_i) can be expressed as follows.

$$k_1 = (3.75 \times 10^{-4}Sb + 1.0) \times 1.5657 \times 10^9 \exp(-19,640/RT)$$
$$k_2 = (4.75 \times 10^{-4}Sb + 1.0) \times 1.5515 \times 10^8 \exp(-18,140/RT)$$
$$k_3 = (6.25 \times 10^{-4}Sb + 1.0) \times 3.5165 \times 10^9 \exp(-22,310/RT)$$
$$k_4 = (4.50 \times 10^{-4}Sb + 1.0) \times 6.7640 \times 10^7 \exp(-18,380/RT)$$
$$k_5 = (3.50 \times 10^{-4}Sb + 1.0) \times 7.7069 \times \exp(-2810/RT)$$
$$k_6 = (1.75 \times 10^{-4}Sb + 1.0) \times 6.2595 \times 10^6 \exp(-14,960/RT)$$
$$k_7 = (3.75 \times 10^{-4}Sb + 1.0) \times 2.0583 \times 10^{15} \exp(-42,520/RT)$$

Simulation of esterification with these reaction rate constants at various Sb_2O_3 concentrations was made and the following results were obtained.

1. Sb_2O_3 accelerates the esterification reaction between TPA and EG.
2. Sb_2O_3 accelerates the main reaction and its effects on side reactions are minor. The higher the addition rate of Sb_2O_3, the lower the carboxyl end-group concentration (AV) and diethylene glycol content (DEG).
3. The comparison between simulation with potassium titanium oxyoxalate (PTO) in the previous report and with Sb_2O_3 in the present report shows that the acceleration of polycondensation reaction by Sb_2O_3 is higher. DEG formation rate is lower with PTO than Sb_2O_3.

INTRODUCTION

When *bis* β-hydroxyethyl terephthalate (BHET) and its low polymerization degree product, which is designated totally as oligomers, obtained by esterification are further heated, a high degree of polyethylene terephthalate (PET) is obtained. In selecting a polycondensation catalyst, the catalyst with high catalytic power, of course is preferable, but, at the same time, it is desirable that its solubility in the polymer is high and degradation of polymer, gel formation, coloration of polymer through side reactions and the formation of side products such as diethylene glycol (DEG) linkage, are lower.

Polycondensation catalysts reported by Wilfong[1] and Yoda[2] include antimonium, germanium, and titanium compounds. When manufacturing PET

through direct esterification of terephthalic acid (TPA) and ethylene glycol (EG), introducing polycondensation catalyst in esterification process, where the viscosity of reaction mixture is low is likely to give better dispersion of the catalyst in the polymer. Furthermore, when such polycondensation catalyst has an accelerating effect on the esterification reaction of TPA and EG, further improvement in the productivity and polymer quality can be expected by introducing such a polycondensation catalyst into the esterification process. However, the effect of polycondensation catalysts on esterification has not been studied extensively.

Yamada and Imamura[3] reported the effect of potassium titanium oxyoxalate (PTO; $K_2T_iO (C_2H_4)_2 \cdot 2H_2O$), as a polycondensation catalyst. Sb_2O_3 is widely used in industry as a polycondensation catalyst for the manufacture of PET. Stevenson and Nettleton[4] studied its effect on polycondensation reaction rate. However, the literature does not disclose the effect of Sb_2O_3 on the esterification reaction.

In this article the effect of Sb_2O_3 on the esterification reaction is reported.

EXPERIMENTAL

Experiments were made in the pilot plant described in the previous report by Yamada et al.[5] Sb_2O_3 dissolved in EG was added in the first tank reactor (RA-1) where the esterification reaction was carried out under the following conditions:

Reaction temperature (t): 250°C
Reaction pressure (p): atmospheric pressure
E/T: 2

where,

E/T is the molar ratio of EG over TPA fed to RA-1, EG charged as catalyst solution has to be included.
Mean residence time of reaction mixture (τ): 5 hrs

where,

$$\tau = \frac{\text{total weight of the reaction mixtures in RA-1}}{\text{throughput based on PET}} \tag{1}$$

ANALYTICAL

Oligomer characteristics, concentration of carboxyl end-groups (AV), concentration of hydroxyl end-groups (OHV), and concentration of DEG (e) are measured in methods used in the previous report by Yamada et al.[5]

RELATION AMONG OLIGOMER PROPERTIES

Relations among oligomer characteristics are given in the following formulae.

$$\phi = OHV/(AV + OHV) \tag{2}$$

$$M_n = 2000/(AV + OHV) \tag{3}$$

$$P_n = \frac{M_n(1 + e) + 26.5 + 70.09e - \phi(88.10 + 176.20e)}{192.17 + 236.23e} \tag{4}$$

$$SV = 2000\,P_n/M_n \tag{5}$$

$$E_s = (SV - AV)/SV \tag{6}$$

$$d = 100\left[(P_n + 2\phi - 1)/P_n\right] \cdot \left[e/(e + 1)\right] \tag{7}$$

where,

AV: concentration of carboxyl endgroups.
OHV: concentration of hydroxyl endgroups.
ϕ: ratio of hydroxyl endgroups to total endgroups.
M_n: number-average molecular weight.
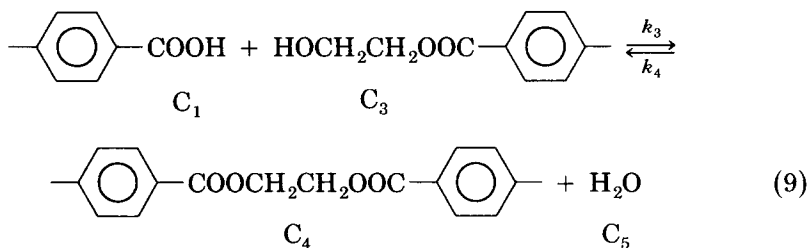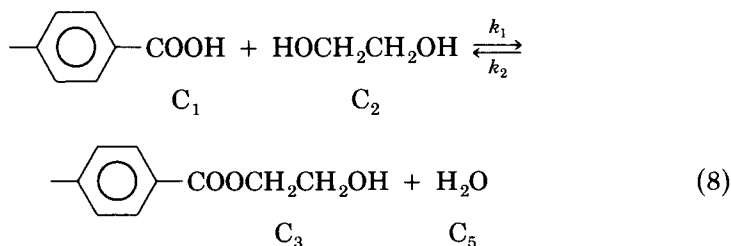P_n: number-average degree of polymerization.
SV: saponification value.
E_s: esterification degree.
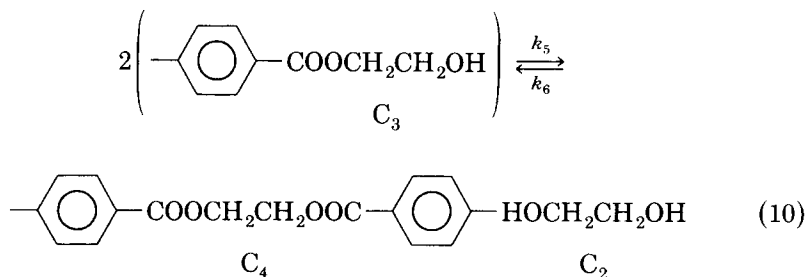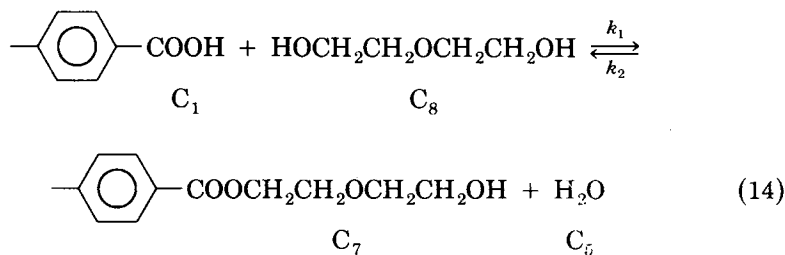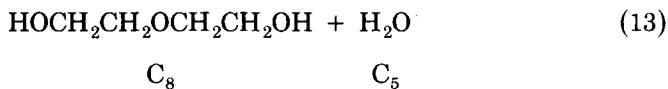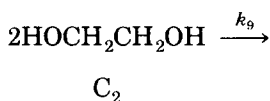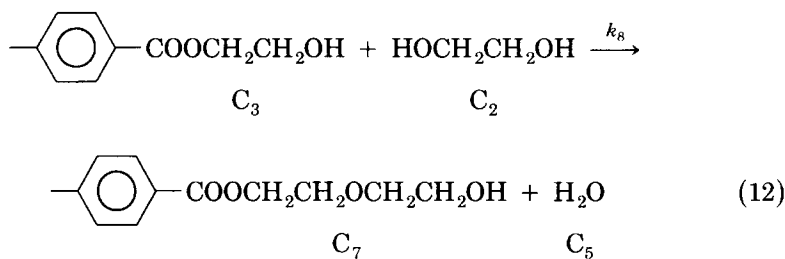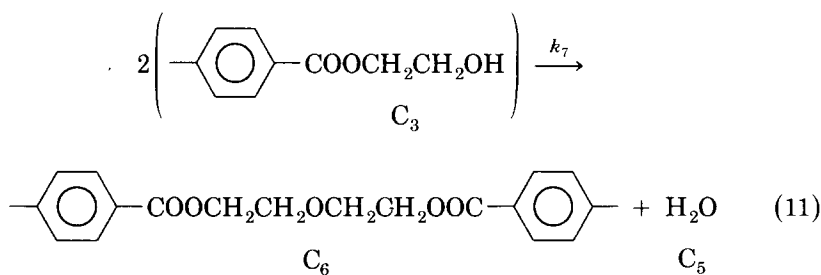e: molar ratio of DEG to bound EG.
d: percentage of DEG content based on TPA.

REACTION SCHEME

The reaction scheme for direct esterification is considered as shown in the previous report.

Esterification reaction

$$(8)$$

$$(9)$$

Polycondensation reaction

$$2\left(-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OH} \right) \underset{k_6}{\overset{k_5}{\rightleftharpoons}}$$

$$\text{C}_3$$

$$-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OOC}-\!\!\bigcirc\!\!-\text{HOCH}_2\text{CH}_2\text{OH} \qquad (10)$$

$$\text{C}_4 \qquad\qquad\qquad\qquad \text{C}_2$$

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

$$2\left(-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OH} \right) \xrightarrow{k_7}$$

$$\text{C}_3$$

$$-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OOC}-\!\!\bigcirc\!\!- + \text{H}_2\text{O} \qquad (11)$$

$$\text{C}_6 \qquad\qquad\qquad\qquad \text{C}_5$$

$$-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{OH} \xrightarrow{k_8}$$

$$\text{C}_3 \qquad\qquad\qquad \text{C}_2$$

$$-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \qquad (12)$$

$$\text{C}_7 \qquad\qquad\qquad \text{C}_5$$

$$2\text{HOCH}_2\text{CH}_2\text{OH} \xrightarrow{k_9}$$

$$\text{C}_2$$

$$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \qquad (13)$$

$$\text{C}_8 \qquad\qquad\qquad \text{C}_5$$

$$-\!\!\bigcirc\!\!-\text{COOH} + \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$$

$$\text{C}_1 \qquad\qquad\qquad \text{C}_8$$

$$-\!\!\bigcirc\!\!-\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \qquad (14)$$

$$\text{C}_7 \qquad\qquad\qquad \text{C}_5$$

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 of $k_8 = 2k_7$ and $k_9 = 4k_7$.

Yamada et al.[5] reported that neglecting Eq. (14) causes no practical problem. Therefore, in this report Eq. (14) is neglected.

RESULTS AND DISCUSSION

Reaction Rate Constants

Experimental data of characteristics of oligomer in RA-1 when continuous esterification reaction experiment was made under the conditions of t = 250°C, P = 0 kg/cm²G, E/T = 2.0, and τ = 5.0 h are summarized in Table I.

Reaction rate constants of the above reaction were determined to fit the experimental data in Table I by the mathematical model proposed by Yamada et al.[6] It was found that the effect of Sb_2O_3 on reaction rate constants are expressed as follows.

$$k_1 = (3.75 \times 10^{-4} Sb + 1.0) \times 1.5657 \times 10^9 \exp(-19640/RT) \tag{15}$$
$$k_2 = (4.75 \times 10^{-4} Sb + 1.0) \times 1.5515 \times 10^8 \exp(-18140/RT) \tag{16}$$
$$k_3 = (6.25 \times 10^{-4} Sb + 1.0) \times 3.5165 \times 10^9 \exp(-22310/RT) \tag{17}$$
$$k_4 = (4.50 \times 10^{-4} Sb + 1.0) \times 6.7640 \times 10^7 \exp(-22310/RT) \tag{18}$$
$$k_5 = (3.50 \times 10^{-4} Sb + 1.0) \times 7.7069 \exp(-2810/RT) \tag{19}$$
$$k_6 = (1.75 \times 10^{-4} Sb + 1.0) \times 6.2595 \times 10^6 \exp(-14960/RT) \tag{20}$$
$$k_7 = (3.75 \times 10^{-4} Sb + 1.0) \times 2.0583 \times 10^{15} \exp(-42520/RT) \tag{21}$$

where,

Sb: mole of antimonium in (Sb^{3+}) in Sb_2O_3 per 10^6 mole of supplied TPA.
R: gas constant
T: absolute temperature

The comparison of experimental data of oligomers and those calculated by applying reaction rate constants in formulae (15) to (21) are given in Figures 1-6.

From these figures it can be stated that the coincidence of experimentally obtained and calculated values is relatively satisfactory.

In other words, it is understood that in this way the effect of Sb_2O_3 on the continuous esterification of TPA and EG can be obtained with fair accuracy.

Simulation Results

In Figures 7-12, the results of simulation of the first continuous esterification tank reactor, with reaction rate constants are expressed in formulae (15)-(21), at various antimonium ion (Sb^{3+}) concentrations and the following reaction conditions:

t: 250°C
P: 0 kg/cm² g
E/T: 2.0
τ: 5 h

TABLE I
Experimental Data at Various Concentrations of Diantimony Trioxide

| Run	Sb^{3+} (μmol/TPA)	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	100	2.007	1.176	0.370	628	3.231	0.805	1.043	0.949
8	100	2.054	1.204	0.369	614	3.157	0.800	1.071	0.972
9	100	2.061	1.186	0.365	616	3.169	0.800	1.056	0.956
10	100	2.067	1.169	0.361	618	3.182	0.799	1.039	0.939
11	100	2.072	1.152	0.357	620	3.196	0.799	1.024	0.923
12	100	2.120	1.179	0.357	606	3.122	0.794	1.052	0.946
13	300	1.688	1.172	0.410	699	3.583	0.835	0.994	0.935
14	300	1.697	1.146	0.403	704	3.608	0.835	0.972	0.911
15	300	1.698	1.137	0.401	705	3.618	0.834	0.965	0.903
16	300	1.713	1.104	0.392	710	3.646	0.833	0.934	0.871
17	300	1.717	1.096	0.390	711	3.652	0.833	0.928	0.864
18	300	1.732	1.072	0.382	713	3.668	0.832	0.906	0.840
19	500	1.333	1.066	0.444	834	4.266	0.870	0.863	0.833
20	500	1.372	1.101	0.445	809	4.136	0.866	0.896	0.864
21	500	1.379	1.084	0.440	812	4.155	0.865	0.881	0.848
22	500	1.395	1.052	0.430	817	4.187	0.864	0.854	0.818
23	500	1.405	1.036	0.424	819	4.199	0.863	0.841	0.804
24	500	1.441	1.070	0.426	797	4.081	0.859	0.872	0.833
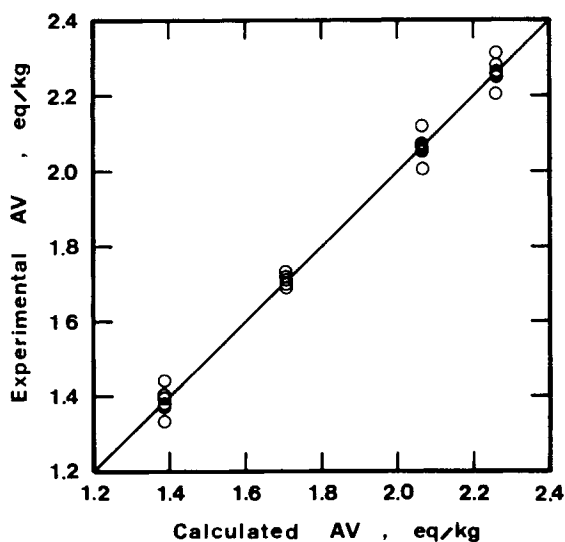
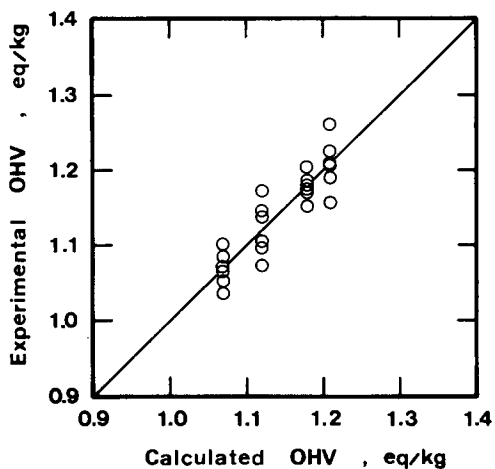Fig. 1.   Correlation of experimental and calculated AV.

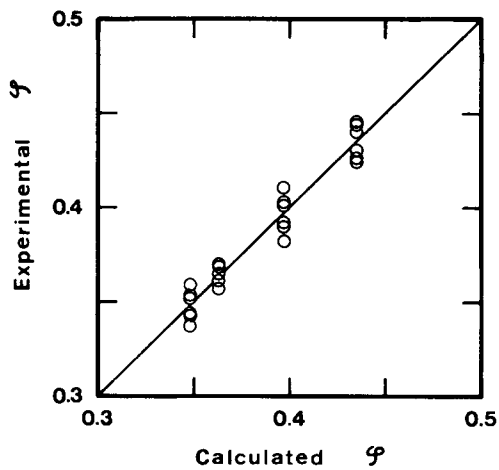Fig. 2. Correlation of experimental and calculated OHV.

Fig. 3. Correlation of experimental and calculated ϕ.
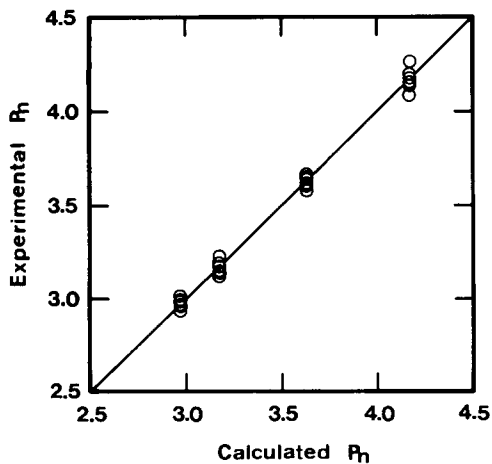
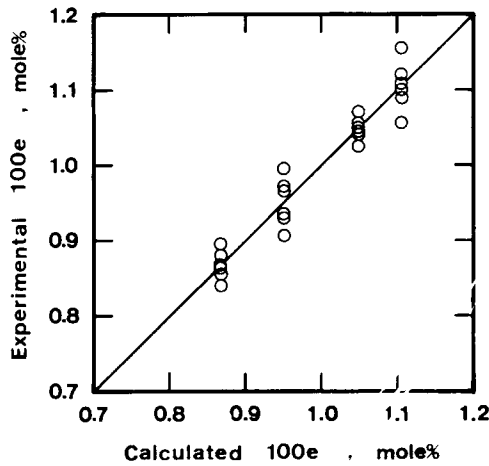Fig. 4. Correlation of experimental and calculated P_n.

Fig. 5. Correlation of experimental and calculated 100e.

In Figure 7, the relation between concentration of Sb_2O_3 (Sb^{3+}) and carboxylic endgroups (AV) is given. From this figure, it can be seen that as Sb_2O_3 concentration increases, AV decreases.

For instance, when $Sb^{3+} = 0$, Sb_2O_3 is not added, AV = 2.26 eq/kg, at $Sb^{3+} = 500$ μmol/TPA mol, AV = 1.39 eq/kg, and in this case, AV decreases as much as 0.87.

Also as seen from Figure 11, as Sb_2O_3 concentration increases, the esterification degree (Es) increases. From these figures, it is understood that Sb_2O_3 as a polycondensation catalyst also acts as an esterification catalyst.

In Figure 8, the relation between concentration of Sb_2O_3 and hydroxyl endgroups (OHV) is given. From this figure it is understood that as Sb_2O_3 concentration increases, OHV decreases gradually, but the degree of decrease is less than the decrease of AV in Figure 7. In Figure 9, as the concentration of Sb_2O_3 increases the ratio of OHV against total endgroups (ϕ) increases.
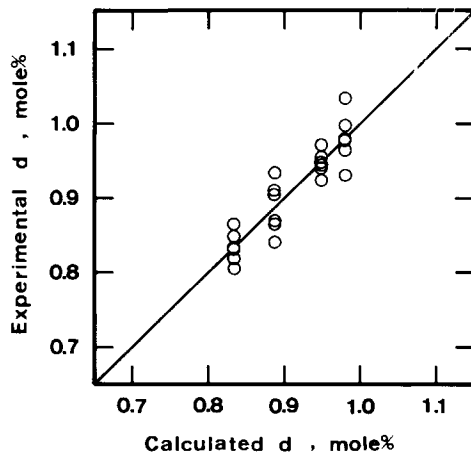
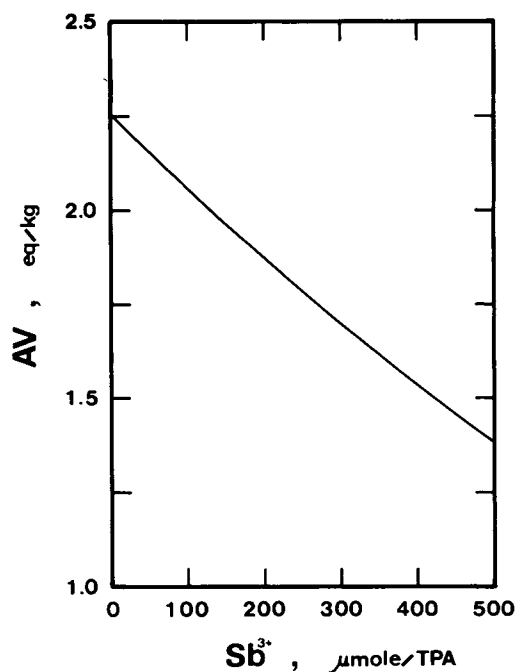Fig. 6. Correlation of experimental and calculated d.

Fig. 7. Relation between AV and antimony concentration.

In Figure 10, as Sb^{3+} increases the number-average molecular weight (P_n) increases gradually. For example, when Sb_2O_3 (Sb^{3+}) of 500 μmol/TPA is added, P_n increases by 1.2. The increases in OHV and P_n are minor in contrast with the degree of increase in AV.

In Figure 12, the relation between Sb_2O_3 concentration and DEG content (100e or d) in oligomers is given. The higher the Sb_2O_3 concentration, the lower the DEG content in oligomer. This phenomenon may be interpreted as
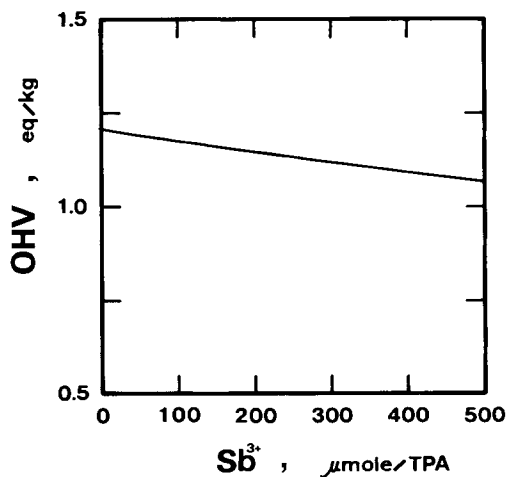
Fig. 8. Relation between OHV and antimony concentration.
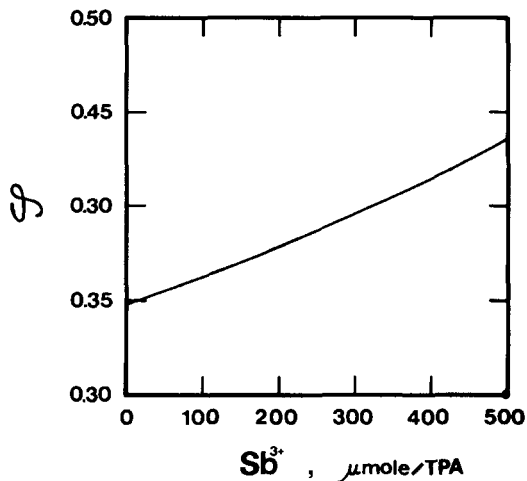
Fig. 9. Relation between ϕ and antimony concentration.

if Sb_2O_3 has the effect of suppressing the formation of DEG. However, since the rate constant of DEG formation reaction, k_7, expressed in formula (21) has the tendency to increase with an increase in Sb_2O_3, there is no suppressing effect on DEG formation reaction but rather an accelerating effect.

The phenomenon of decrease of DEG contents in oligomer along the increase of Sb_2O_3 concentration can be interpreted as being that (Fig. 8), as Sb_2O_3 concentration increases, OHV decreases and the degree of decrease in rate of DEG formation reaction given by formulae (11) and (12) is higher than the increase in the rate of DEG formation reaction due to the increase of reaction rate constant by formula (21). Apparently Sb_2O_3 seems to exert a suppressing effect on DEG formation reaction.

From the above phenomena a conclusion similar to the previous report by Yamada and Imamura[3] on potassium titanium oxyoxalate can be derived.
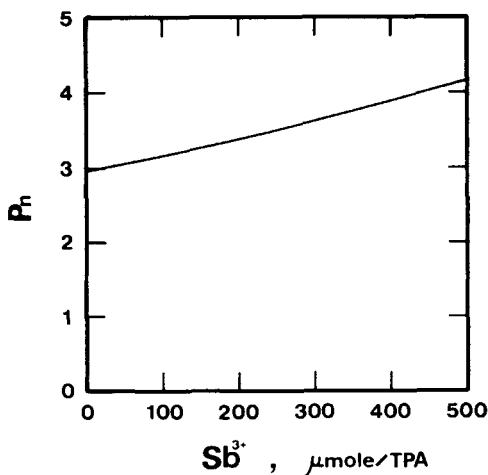

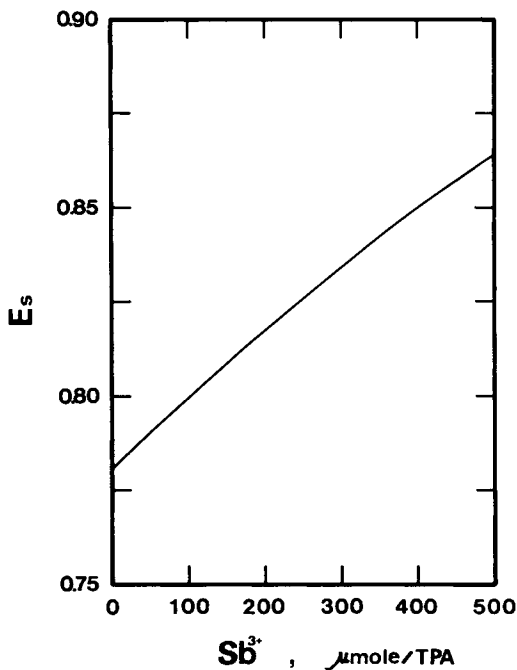Fig. 10. Relation between P_n and antimony concentration.

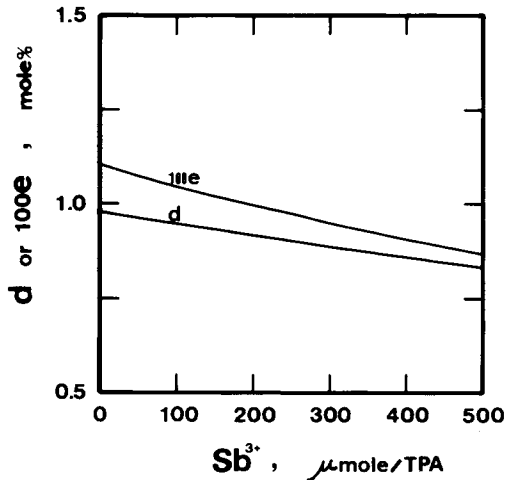Fig. 11.   Relation between E_s and antimony concentration.

Fig. 12.   Relation between DEG content (d or 100e) and antimony concentration.

1. When the reaction pressure is low, in the neighborhood of atmospheric pressure, the reduction of Sb_2O_3 catalytic power is minor and will cause no problems.

2. Under the reaction conditions detailed in the present report, Sb_2O_3 accelerates the esterification reaction.

3. Sb_2O_3 mainly accelerates the main reaction and its influence on side reactions is minor. The higher the addition rate of Sb_2O_3, the lower the

carboxylic endgroup concentration (AV) and DEG content. However, when considered from the viewpoint of plant operation, the higher the addition rate, the easier it agglomerates on the catalyst, this shortens the polymer, and therefore the higher addition rate of Sb_2O_3 is not always desirable for production.

Comparison of Diantimony Trioxide and Potassium Titanium Oxyoxalate

The comparison of the effect on the esterification by potassium titanium oxyoxalate (PTO) reported in the previous report by Yamada and Imamura[3] and that in the present report is made below by comparing other physical characteristics at a certain esterification degree (E_s) or carboxylic endgroup concentration (AV).

In Figure 13, the relation between the carboxylic endgroup concentration (AV) and the esterification degree (E_s) for both Sb_2O, and PTO are given. From this figure, it can be understood independent of the kind of catalysts, the relation between AV and E_s is, in this case, expressed in a certain fixed relation stating that in order to compare the effect on the esterification by Sb_2O_3 and PTD, comparing the relation between other physical characteristics with either E_s or AV, only one of them will do. Therefore, in the following, the comparison of the relation of a certain oligomer characteristics with AV for Sb_2O_3 and PTO will be made.

In Figure 14, the relations between AV and OHV are given. It can be seen that when Sb_2O_3 is used as the catalyst, higher OHV is obtained in comparison with PTO. The higher the addition rate of the catalyst or the higher the E_s, the difference becomes large. From the relations between AV and P_n in
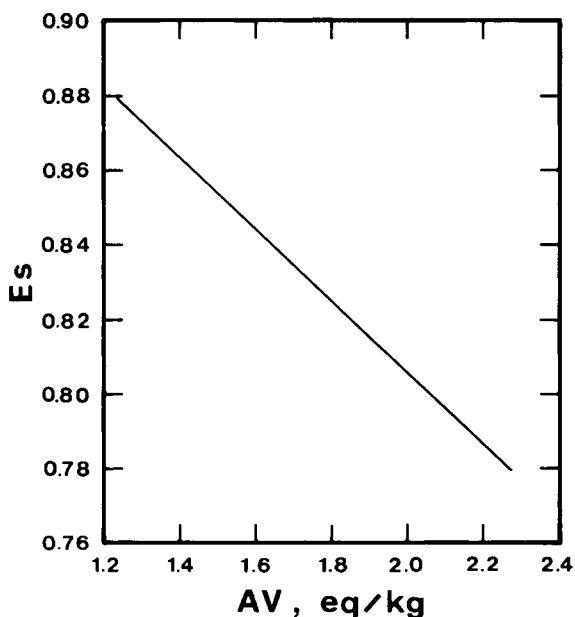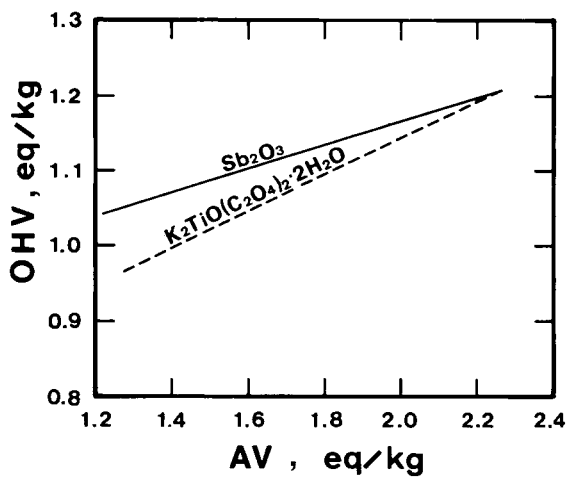
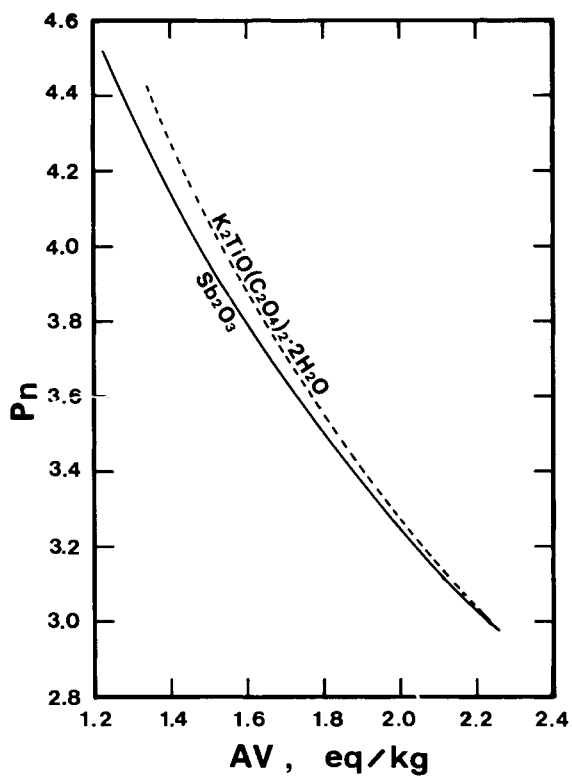Fig. 13. Relation between E_s and AV.

Fig. 14. Relation between OHV and AV.

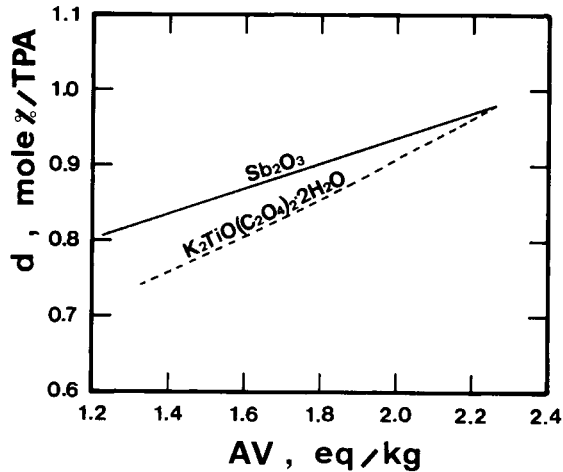Fig. 15. Relation between P_n and AV.

Fig. 16. Relation between d and AV.

Figure 15, it can be understood that P_n is lower for the case with Sb_2O_3 than that with PTO and the lower the AV, the greater the difference. From Figures 14 and 15, it can be seen that the effect of accelerating polycondensation reaction expressed in formula (10) is higher with PTO than with Sb_2O_3.

In Figure 16, the relation between AV and DEG content (d) based on TPA is shown. This figure shows that (d), when PTO is used as the catalyst, is lower than when Sb_2O_3 is used as the catalyst and the lower the AV, the greater the difference.

This means that, against Sb_2O_3, PTO exerts higher acceleration on the main reaction and less influence on side reactions. At the same AV, OHV is lower with PTO than with Sb_2O_3 (Fig. 14). The reaction rate of DEG formation reaction, expressed by formulae (11) and (12), is lower with PTO than with Sb_2O_3; this may be one of the reasons for this phenomenon. The above comparison can be concluded as the following: (1) The effect of accelerating the polycondensation reaction is higher with PTO than with Sb_2O_3. (2) In the case of PTO, the amount of DEG formation is less than in the case with Sb_2O_3.

CONCLUSION

In a continuous manufacturing process for PET starting from TPA and EG, it was confirmed that diantimony trioxide (Sb_2O_3) exerts polycondensation catalytic power as well as esterification catalytic power. From experimental data of the continuous esterification reaction at various Sb_2O_3 concentrations, reaction rate constants proposed by Yamada et al.[5,6] were obtained and it was found that the reaction rate constants (k_i) are expressed as

$$k_i = (b_1 \cdot Sb + 1)A_i \exp\left(-\frac{E_i}{RT}\right).$$

The influence of Sb_2O_3 on the esterification reaction was studied and the comparison with potassium titanium oxyoxalate (PTO) was made. It was

found that at the same reaction degree with PTO, oligomers of higher number-average molecular weight (P_n) and lower diethylene glycol (DEG) content are obtained.

References

1. R. E. Wilfong, *J. Polym. Sci.*, **54**, 385 (1961).
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