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Studies on the Formation of Poly(ethylene 2,6-naphthalate). 1. Polycondensation Catalyzed by Various Metal Compounds

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The polycondensations of bis(2-hydroxyethyl) naphthalate were kinetically investigated in the presence of various metallic compounds as catalysts at 295 °C. The effect of the catalyst nature in the polycondensation has been studied. The order of catalytic activity on the formation of poly(ethylene 2,6-naphthalate) was found to be related to the stability constants which are indicated in an index of the catalytic activity.

Introduction

The information concerning the role of the metal compounds as catalysts in the poly(ethylene 2,6-naphthalate) (PEN)[1-3] polymerization is very important to understand the catalytic activity.

The synthesis of PEN polymer is carried out in a two step process; that is, transesterification and polycondensation reaction. In the first step, dimethyl 2,6-naphthalate (DMN) reacts with ethylene glycol forming methanol and bis(2-hydroxyethyl) naphthalate (BHEN) oligomer. In the second step, the BHEN oligomer is converted to high molecular weight PEN polymer by elimilation of glycol between the hydroxyethyl ester end groups. In both reaction, various metallic compounds are used as the catalyst;

BHEN or oligomers

PEN molecules
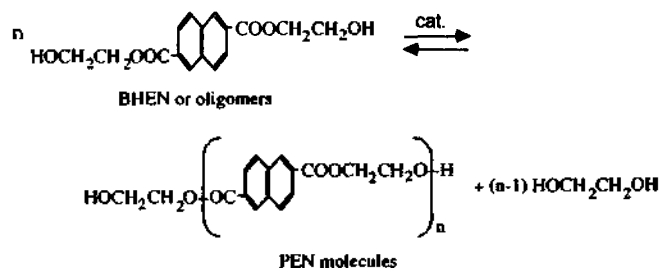
In general, the polycondensation of BHEN is subjected to temperatures from 285 to 300 °C. The rate of the propagation and degradation under these conditions depends largely upon the reaction temperature as well as on the kind and amount of metal compounds used as polycondensation catalysts.

The mechanism by which metal compounds act as poly-

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condensation catalysts for the formation of PEN polymer is still obscure. Many workers[4~7] have reported that in a series of metal compounds as catalysts, the catalyzed reactions on the polycondensation are largely influenced by the mutual relation between the metal compound of catalyst and the negatively charged carbonyl oxygen of the ester group.

Challa[4] previously has studied the forward and reverse reaction rates in the absence of catalyst. Stevenson and Nettleton[5] have suggested the effect of the side reaction on the propagation reaction in the presence of antimony trioxide as a catalyst, and they concluded that the observed propagation and degradation rates were very low but faster than rates of the uncatalyzed reaction studied by Challa.[4] Tomita and Ida[6] reported that the propagation and degradation reactions occur simutaneously by the same catalyst. Tomita[7] also reported that on the formation of poly(ethylene terephthalate), the order of catalytic activity has an excellent relation to the stability constant $(\log\beta_1)$[10] which is indicated in an index of the catalytic activity. On this problem, the authors[9] previously reported the ordering of catalytic activity on the transesterification of DMN and ethylene glycol with various metallic catalysts.

In this paper, kinetic aspects of propagation *vs.* degradation rate for the catalyzed polycondensation of BHEN in the presence of metal compounds as various catalysts were studied.

Experimental

bis(2-Hydroxyethyl)naphthalate (BHEN) was prepared by the reaction of dimethyl 2,6-naphthalate with ethylene glycol as described previously.[9] The catalysts were of commercial grade and were used without further purification.

BHEN (200 g) was introduced into a 500 mL polymerization tube. After BHEN had melted, the catalyst was added. Initially a low vacuum (760-1 mmHg) was applied to the system and after 30 min the vacuum was increased to a full pressure (about 0.2 mmHg). The reaction temperature was kept on at 295 °C during the required period of time. The polymer produced was then extruded into cold water (~5 °C).

The intrinsic viscosity was measured at 25 °C using *o*-chlorophenol as a solvent.[11] The carboxyl acid end group in PEN also was determined accoring to Pohl's method.[12] After 200 mg of PEN was rapidly dissolved in 20 mL of benzyl alcohol at 200 °C, the solution was kept up 135 °C and then titrated with a 0.02 N KOH solution in benzyl alcohol using phenolphthalein as a indicator.

Results and Discussion

Time Dependence on the Polycondensation Reaction. In commercial synthesis of poly(ethylene 2,6-naphthalate) (PEN), the polycondensation reaction would normally be carried out in a melt at about 295 °C, under reduced pressure and in an open system. The time dependence of the intrinsic viscosity value on the polycondensation reaction without catalyst was shown in Figure 1.

As shown in Figure 1, the intrinsic viscosity of PEN polymer increased with the reaction time for first 3 hours. After the maximum value reached, however, the intrinsic viscosity
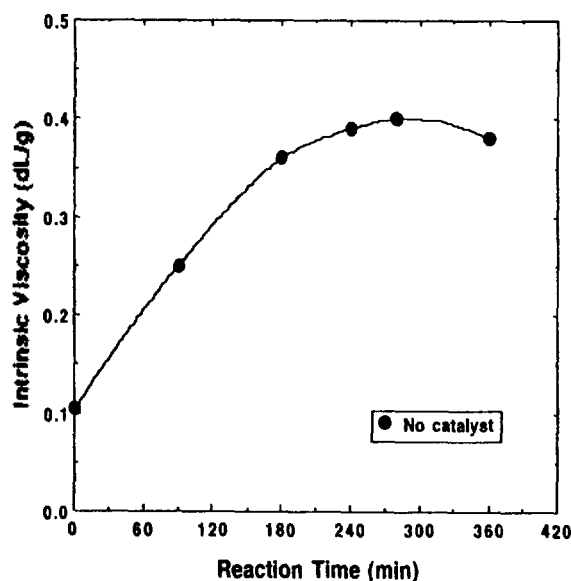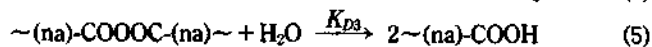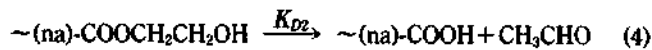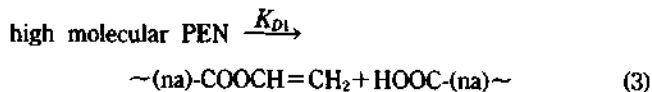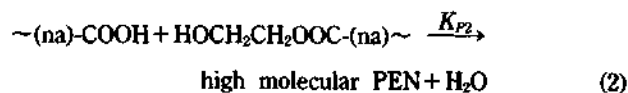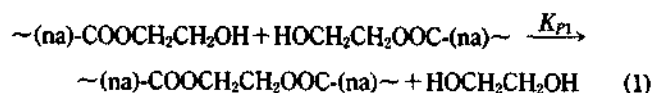

Figure 1. Time dependence of no-catalyst (conc; 1.5×10^{-6} mol/g BHEN) on the polycondensation of BHEN at 295 °C.

began to drop. These phenomenon suggest that the side reaction such as thermal degradation of polymer occured along with the polycondensation reaction. Tomita *et al.*[6] reported that these variations of intrinsic viscosities caused by the propagation and degradation reaction in the studies of poly (ethylene terephthalate) (PET).

Kinetics of the Polycondensation Reaction. The polycondensation reaction which leads to formation of PEN can be represented as follows;

$$\sim(na)\text{-COOCH}_2\text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{OOC-(na)}\sim \xrightarrow{K_{P1}}$$

$$\sim(na)\text{-COOCH}_2\text{CH}_2\text{OOC-(na)}\sim + \text{HOCH}_2\text{CH}_2\text{OH} \quad (1)$$

$$\sim(na)\text{-COOH} + \text{HOCH}_2\text{CH}_2\text{OOC-(na)}\sim \xrightarrow{K_{P2}}$$

$$\text{high molecular PEN} + \text{H}_2\text{O} \quad (2)$$

$$\text{high molecular PEN} \xrightarrow{K_{D1}}$$

$$\sim(na)\text{-COOCH}=\text{CH}_2 + \text{HOOC-(na)}\sim \quad (3)$$

$$\sim(na)\text{-COOCH}_2\text{CH}_2\text{OH} \xrightarrow{K_{D2}} \sim(na)\text{-COOH} + \text{CH}_3\text{CHO} \quad (4)$$

$$\sim(na)\text{-COOOC-(na)}\sim + \text{H}_2\text{O} \xrightarrow{K_{D3}} 2\sim(na)\text{-COOH} \quad (5)$$

where, $\sim(na)\sim$: a naphthalene ring ( )

Reactions, (1) and (2), contribute to propagation reaction of PEN. Carboxyl acid end groups can be reacted with hydroxyethyl end groups of PEN and increased the molecular weight of polymer. It is very important to determine the parameter of propagation rate. The reaction (1) proceeds by the nucleophillic attack of hydroxy end groups in BHEN, upon the ester carbonyl groups in BHEN. The reaction (2), of course, is of importance in the direct-esterification reaction between hydroxyethylester terminal groups and carboxyl end groups.

Considering this point, both of the reactions, (1) and (2) can be regarded as factors which change the molecular

weight of polymer, and the propagation rate constant (K_P) thus can be written as follows;

$$K_P = K_{P1} + K_{P2} \tag{6}$$

Degradation reactions occur during all the stage of PEN synthesis by the reaction of transesterification and polycondensation. The side reactions (3)-(5) seem to occur in same with the above-mentioned propagation reactions, (1) and (2). Very important side reaction (3) in polyester synthesis is the degradation of the repeating units by a molecular mechanism with random chain scission at ester links. Among thermally weak linkages, (i.e., the C-O bonds along the polymer chain) those located at β-scission from carbony groups most likely get subjected to the thermal cleavage forming carboxyl acid and vinyl end groups. The reaction (3) is very significant factor to determine the rate of degradation reaction.

In addition to the above side reaction (3), another side reactions, (4)-(5) also can be contribute to the degradation reaction, and the degradation rate constant (K_D), hence, can be definded as follows;

$$K_D = K_{D1} + K_{D2} + K_{D3} \tag{7}$$

The mole number (n) of a polymer can be written as following relation (8);

$$n = \frac{\text{repeat unit of PEN polymer}}{\text{molecular weight for a given time}} = \frac{242}{\text{Mn}} \tag{8}$$

where number average molecular weight (M_n) is represented as follows;[11]

$$M_n = \left(\frac{\text{IV}}{1.7 \times 10^{-4}} \right)^{1/0.830} \tag{9}$$

The value of n obtained also was thought to be composed of two components, the propagation mole number (n_P) and the degradation mole number (n_D), as expressed in equation (10).

$$n = n_p + n_D \tag{10}$$

As the n_P decrease and the n_D increase with the progress of the reaction, it can be suggested that the minimum value (dn/dt=0) should be existed at the time when the decreasing rate by propagation is equal to the increasing rate by degradation. Accordingly, the equation (11) can be obtained and represented as $dn_P/dt = -(dn_D/dt)$;

$$\frac{dn}{dt} = \frac{dn_P}{dt} + \frac{dn_D}{dt} = 0 \tag{11}$$

Assuming that propagation reaction on the formation of PEN obeys second order kinetics for the mole number (n_P) of the propagation reaction, the propagation rate on the polycondensation may be represented as $-(dn_P/dt) = K_P n_P^2$.

where K_P is a rate constant for the propagation reactions, (1) and (2). The integration of the above equation can be performed, and then the result of the integration was obtained as follows;

$$\frac{1}{n_P} - \frac{1}{n_{P0}} = K_P \, t \tag{12}$$

Assuming that the degree of polymerization of the BHEN is equal to 1, and that the initial mole number (n_{P0}) of poly-
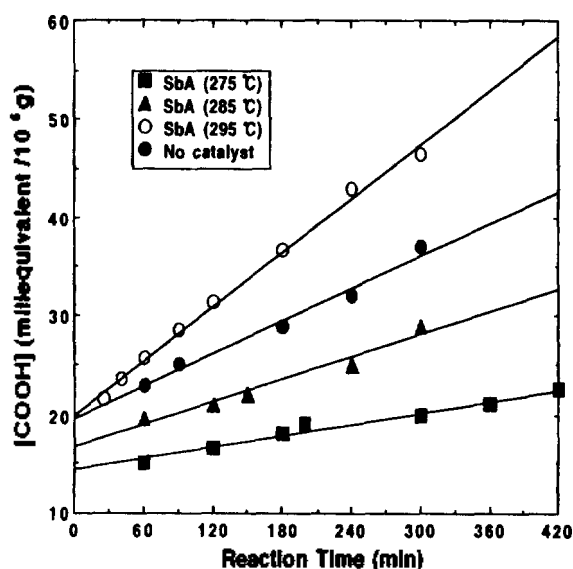

Figure 2. Dependence of rate of increase of carboxyl end groups during the polycondensation of BHEN at 295 °C without a catalyst and with antimony triacetate (conc; 1.5×10^{-6} mol/g BHEN) as a catalyst.

condensation reaction at the start point $(t=0)$ can be obtained as 1, the equation (12) thus may be rewritten by the equation (13);

$$n_P = \frac{1}{1 + K_P t} \tag{13}$$

In order to discuss the degradation rate, we investigated the change of carboxyl acid end group as well as the intrinsic viscosity during the reaction.

The extent of degradation was determined by measuring the changes in carboxyl group content. As shown in reactions (3), (4) and (5), the formations of the acids can be caused by the random b-scission in main chain of PEN molecules, the degradation of hydroxyethylester terminal group and the hydrolysis etc..

Figure 2 shows the changes of carboxyl acid end groups on the polycondensation of BHEN without a catalyst and in the presence of antimony triacetate as a catalyst. It can be seen that the rate of thermal degradation with a catalyst was more increased than that of without a catalyst, and also the degradation rate was largely accelerated by the increase the reaction temperature.

Whether or not the catalyst paticipated in the mechanism of the reaction, the trend of carboxyl groups in PEN polymer was appeared as a good linear relation.

Considering this point, it can be seen from the result of Figure 2 that the mole number (n_D) of degradation reaction was increased linearly with time. In other words, the degradation rate, $dn_D/dt = K_D$, can be written positively as zero-order reaction which is not depended upon any terms except for time for the polycondensation of BHEN. By solving this equation, the value of n_D was represented as the equation (14).
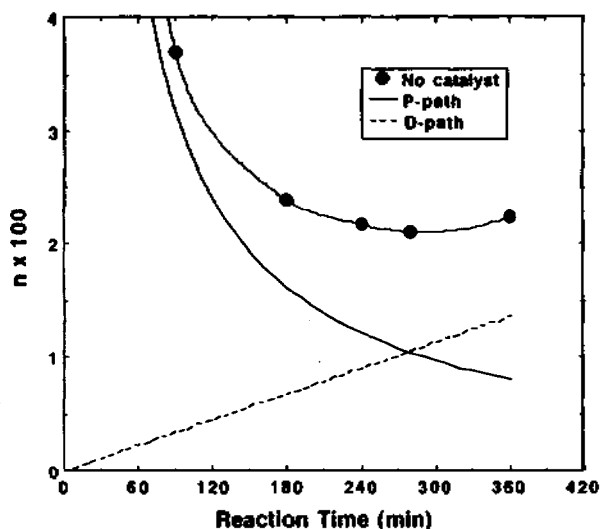
$$n_D = K_D \, t \tag{14}$$

Figure 3. Analysis of propagation and degradation path on the polycondensation of BHEN without catalyst.

From these equations (13) and (14), it can be possible to calculate K_P and K_D, the rate constants of propagation and degradation.

In order to calculate the propagation rate, we obtained by the form of dn_P/dt;

$$\frac{dn_P}{dt} = -K_P n_P^2 = -K_P\left(\frac{1}{1+K_P t}\right)^2 = -\frac{K_P}{(1+K_P t)^2} \qquad (15)$$

By inserting the equation (15) into the equation (11) and simplifying, we also get the degradation rate by dn_D/dt.

$$\frac{dn_D}{dt} = K_D = \frac{K_P}{(1+K_P t)^2} \qquad (16)$$

Experimentally, we can obtain the minimum number and the time at the minimum value, and take n_{min} and t_{min}. By subsitution of n_{min} and t_{min} into the equation (11) and simplifying, we get the equation (17).

$$n_{min} = (n_P)_{min} + (n_D)_{min}$$

$$= \frac{1}{1+K_P\ t_{min}} + K_D\ t_{min}$$

$$= \frac{1}{1+K_P\ t_{min}} + \frac{K_P}{(1+K_P\ t_{min})^2}\ t_{min} \qquad (17)$$

From the equation (17), we determined the value of K_P and K_D, as expressed in equation (18) and (19).

$$K_P = \frac{1}{t_{min}((1-n_{min})^{-0.5}-1)} \qquad (18)$$

$$K_D = \frac{K_P}{(1+K_P\ t_{min})^2} \qquad (19)$$

Because the values of the n_P and n_D from above mentioned equations are known, a graphical treatment permits the trends of n_P and n_D.

Accordingly, the applicability of equations, (13) and (14), to experimental values in Figure 1 is represented in Figure 3. We also expected that if the time (t_{min}) having minimum mole number (that is maximum viscosity) and the value of
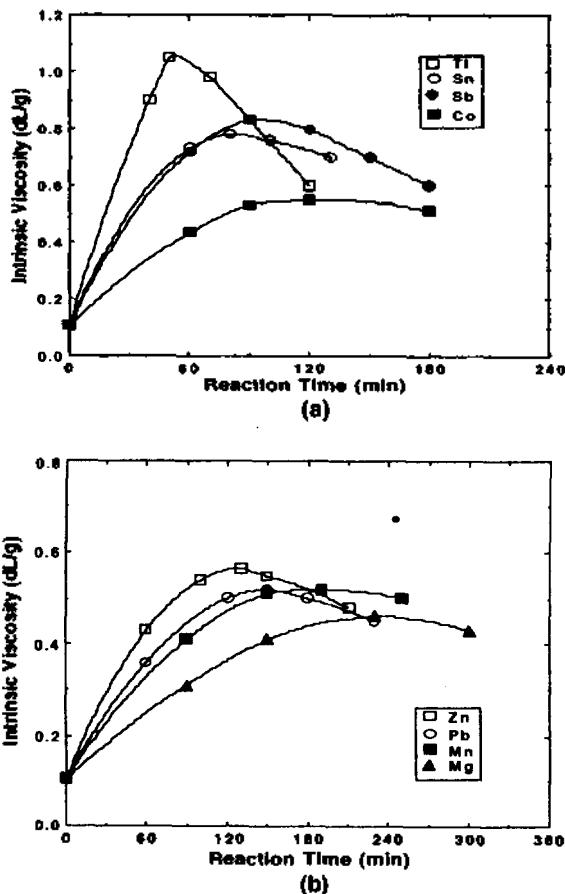

(a)

(b)

Figure 4. Effect of various catalysts (conc; 1.5×10^{-6} mol/g BHEN) on the polycondensation of BHEN at 295 ℃.

n_{min} at t_{min} can be known, the propagation rate constant (K_P) and the degradation rate constant (K_D) can be obtained from the slope of n_P and n_D.

Orders of Catalyst Activity Employed. The catalysis of the polycondensation is very similar to that of the transesterification with dimethyl 2,6-naphthalate and ethylene glycol.

Many workers[5~8] have reported that in a series of metal compounds as catalysts, the catalyzed reactions on the polycondensation are largely influenced to the mutual relation between the metal compound of catalyst and the negatively charged carbonyl oxgen of the ester group.

Syntheses of PEN are carried out with various catalysts of 1.5×10^{-6} mol/g BHEN at 295 ℃, and the results are given in Figure 4. Figure 4 shows the change of the molecular weight of the PEN polymer against reaction time. According to the type of catalyst employed, the maxium time to reach the maximum molecular weight was changed, as shown in Table 1.

The results in Table 1 indicate that the effective transesterification catalysts (that is; lead acetate, zinc acetate and cobalt acetate etc.) are the least effective in the polycondensation of BHEN.[5~7] The most active catalysts, on the contrary, were titanium isopropoxide, monobutyl tinoxide and antimony triacetate. From the results of Figure 4, we convinced that the variations of intrinsic viscosities give rise to the propagation and degradation rate of PEN polymer.

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Table 1. Relationship between maximum time, maximum molecular weight and mole number with various catalysts (conc.; 1.5×10^{-6} mol/g BHEN) at 295 ℃

Metal*	Max. time	Max. intrinsic viscosity	Molecular weight	Mole number ($n \times 100$)
	(min.)	(dL/g)	(Mn)	(242/Mn)
Ti(IV)	52	1.05	36,900	0.66
Sn(II)	84	0.78	25,800	0.94
Sb(III)	95	0.83	27,900	0.87
Co(II)	127	0.55	17,000	1.43
Zn(II)	128	0.57	17,500	1.38
Pb(II)	150	0.52	15,800	0.87
Mn(II) .	190	0.52	15,800	1.53
Mg(II)	235	0.46	13,700	1.78
None	277	0.40	11,600	2.09

*Ti(IV): titanium isopropoxide, Sn(II): monobutyltinoxide, Sb(III): antimony triacetate, Co(II): cobalt acetate, Zn(II): zinc acetate, Pb(II): lead acetate, Mn(II): manganese acetate and Mg(II): magnesium acetate.

Using the kinetic equations, (13) and (14), we also investigated the kinetic treatment for the catalyzed reaction of polycondensation of BHEN in the presence of various metal

Table 2. Comparison to rate constants, K_P and K_D, for the polycondensation of BHEN with various metal compounds as catalysts

Metal	Propagation rate constant	Degradation rate constant
	(K_P, mol^{-1} min^{-1})	($K_D \times 10^{-5}$, mol min^{-1})
Ti(IV)	5.84	6.29
Sn(II)	2.52	5.56
Sb(III)	2.41	4.55
Co(II)	1.09	5.60
Zn(II)	1.12	5.38
Pb(II)	0.86	5.08
Mn(II)	0.68	4.01
Mg(II)	0.47	3.75
None	0.34	3.76

compounds as catalysts. From the assumption that the propagation rate, K_P, is same with degradation rate, K_D, at the minimum value of mole number (n), we obtained the constant, K_P and K_D, of propagation rate and real degradation rate. By substitution of K_P and K_D into equations, (13) and (14), the values of propagation-degradation path analysis against reaction time were obtained.
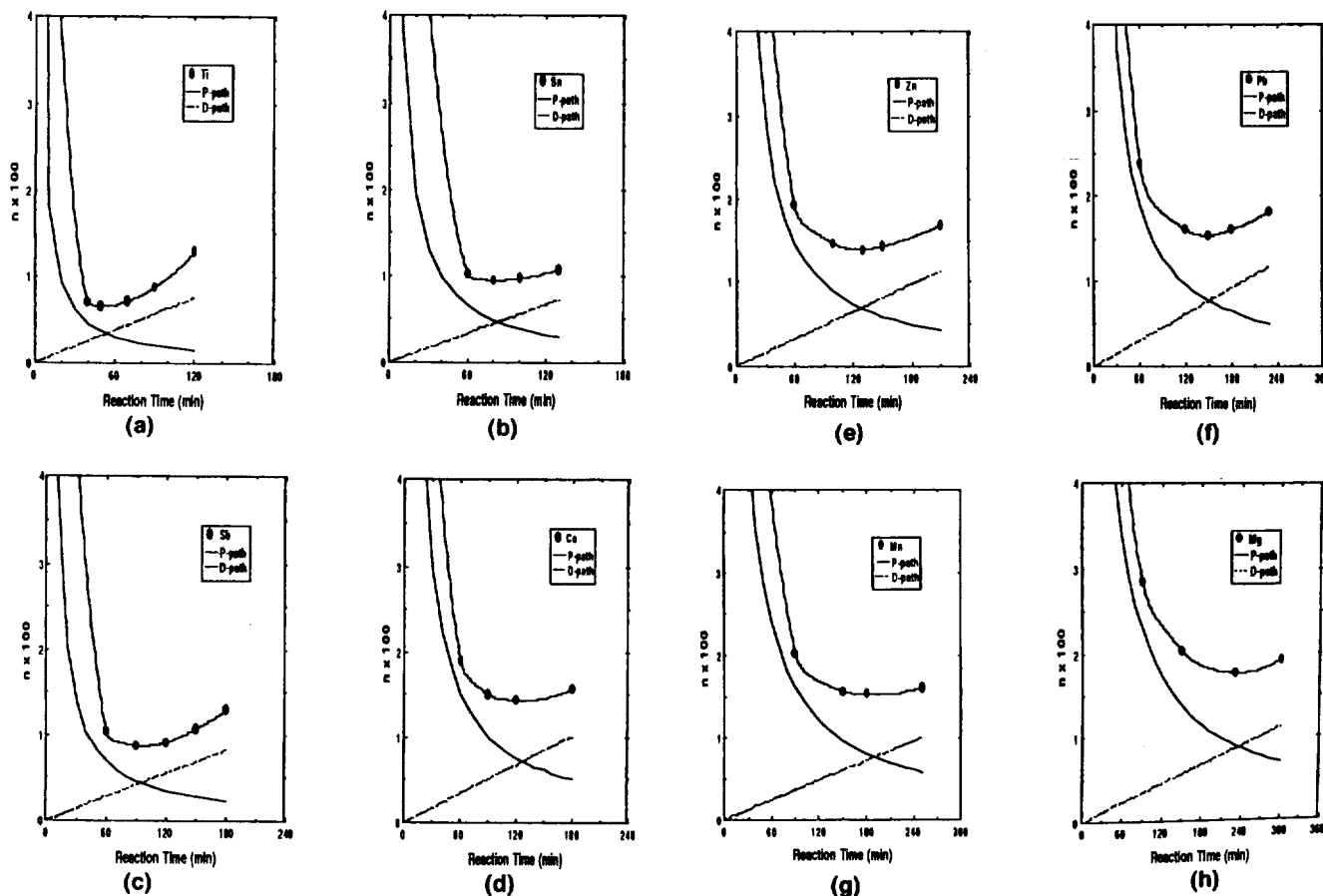

Figure 5. Analysis of propagation and degradation path on the polycondensation of BHEN with various metal compounds as catalysts.
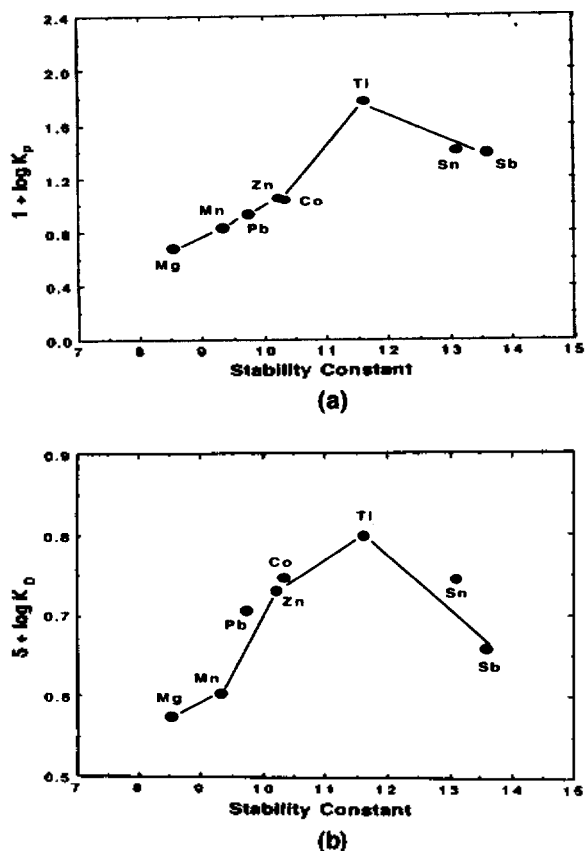
Figure 6. Dependence of apparent rate constant in the polycondensation of BHEN on the stability constant ($\log\beta_1$) of dibenzoyl methane complexes; (a) propagation rate, $1+\log K_P$, and (b) real degradation rate, $5+\log K_D$.
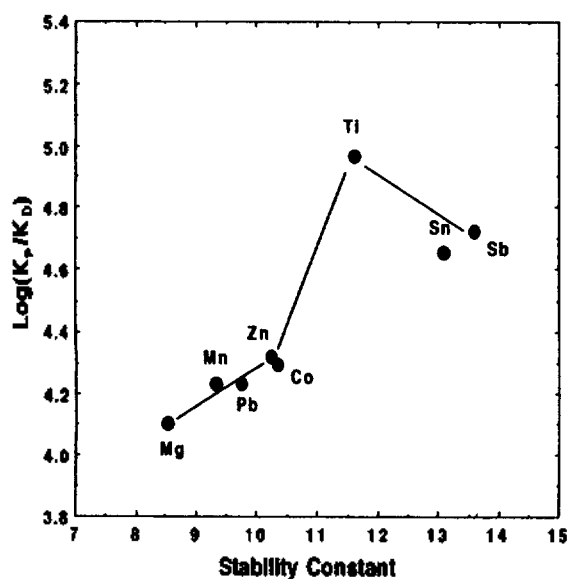

Figure 7. Effect of propagation rate to degradation rate against stability constant with various catalysts.

Using the above kinetic equations to data in Figure 4, the values of propagation-degradation path were obtained and then drawn separately, as shown in Figure 5. The results

of kinetic treatment to data in Figure 5 also were listed in Table 2.

Table 2 shows the values of rate constants, K_P and K_D, for the propagation and degradation rate. It can be seen, as shown in Table 2, that the titanium isopropoxide as a catalyst was very effective to the propagation and degradation rate than other catalysts.

The kinetics for the catalyzed polycondensation is known to be influenced greatly by the nature of catalyst employed. On this problem, Tomita[7] reported that on the formation of poly(ethylene terephthalate) the order of catalytic activity have an excellent relation to the stability constant which is indicated in an index of the catalytic activity.

Earlier, Tomita and Ida[6] showed that stability constants for the chelate compounds formed by a series of divalent metal ions with a group of β-diketons (e.g. benzoyl methane etc. proposed by Van Uitert *et al.*[10]) corresponded with the catalytic activity of a metal compounds in the polycondensation reaction. Using the results, we ordered the catalytic activity on the formation of poly(ethylene 2,6-naphthalate) polymer with various catalysts. Plots of $1+\log K_P$ and $5+\log K_D$ *vs.* stability constant ($\log \beta_1$) were obtained, as indicated in Figure 6. In Figure 6, we obtained a mountain-shaped relation, respectively.

In order to estimate the modifided catalytic activities by various catalysts, we also investigated the ratio of propagation to degradation rate, as shown in Figure 7. Except monobutyl tinoxide (Sn) catalyst, the result plotted was very similar to the tendency of propagation rate. The above orderings for the catalytic activity on the polycondensation catalysts were very similar to the kinetic treatments for the polycondensation of bis(2-hydroxyethyl) terephthalate.

Concluding Remarks

The kinetic rate associated with the rate constants of propagation and degradation reactions on the formation of poly (ethylene 2,6-naphthalate) in the presence of various metal compounds as catalysts were determined. It can be seen that the titanium catalyst is most active on the propagation reaction as well as the degradation reaction. The order of decreasing catalytic activity on the polycondensation also were found to be; Ti(IV)>Sn(II)>Sb(III)>Zn(II)>Co(II)>Mn(II)> Pb(II)>Mg(II), respectively.

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Studies on the Polycondensation Rate of Poly(ethylene 2,6-naphthalate). 2. Polycondensation by Antimony Catalysts

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The catalyzed polycondensations of bis(2-hydroxyethyl) naphthalate were kinetically investigated in the presence of various antimony compounds as a catalyst. The polymerization were investigated with various ligand types of antimony oxides, various concentrations of antimony triacetate and titanium/antimony mixed catalysts. The time to reach the maximum molecular weight was remarkably changed in each case. With increasing the concentration of antimony acetate, the propagation rate was largely increased, while the degradation rate was slightly decreased. It also can be seen that the propagation and degradation rate were larger influenced by the equimolecular titanium/antimony mixed catalyst than other mixed catalysts. The temperature dependence of bis(2-hydroxyethyl) naphthalate with antimony triacetate also has been studied. From the results, it was found that the propagation rate was less influenced by a temperature change than the degradation rate.

Introduction

The information concerning the role of the metal compounds as catalysts in the poly(ethylene 2,6-naphthalate) (PEN)[1~3] polymerization is very important to understand the catalytic activity. The authors[4,5] reported the ordering of catalytic activity on the formation of PEN with various metal compounds as catalysts. In the previous paper,[5] it was found that the more effective catalyst in the polycondensation reaction were titanium derivatives. However, titanium catalyst was caused the yellow formation of the polymer formed.

Considering this point, we tried to search the antimony compounds having an effective catalytic acivity except titanium catalyst. In the study of poly(ethylene terephthalate), many workers[6~10] have suggested the effect of the side reaction on the propagation reaction in the presence of antimony trioxide as a catalyst.

Maerov[11] studied the effectiveness of antimony catalyst with different numbers of hydroxyethyl ligands and found that the catalytic activity changed by the ligand numbers. However, the catalytic activity by which antimony compounds act as polycondensation catalysts for the formation of PEN polymer is still obscure.

In this paper, kinetic aspects for the catalyzed polycondensation of BHEN in the presence of antimony compounds as various catalysts were studied.

Experimental

bis(2-Hydroxyethyl)naphthalate (BHEN)[4] from the reaction

of dimethyl 2,6-naphthalate with ethylene glycol was prepared. Antimony catalysts, such as antimony triacetate, antimony trioxide, antimony tetroxide and antimony pentoxide, were of commercial products and were used without further purification. BHEN (200 g) was introduced into 500 mL polymerization tube. After BHEN had melted, the antimony catalyst was added. The reaction temperature at a full pressure (about 0.2 mmHg) was kept on at 295 ℃ during the required period of time. The polymer formed was then extruded into cold water (~5 ℃). The intrinsic viscosity was measured at 25 ℃ using o-chlorophenol as a solvent.[12]

Results and Discussion

Effect of Concentration with Antimony Catalyst.
The dependence of the rate of polycondensation reaction of BHEN on the catalyst concentration using antimony triacetate as a catalyst forms the subject of this part of investigation.

Syntheses of PEN polymer were carried out by three kinds of concentrations (range from 1.0×10^{-6} mol/g BHEN to 2.0 $\times 10^{-6}$ mol/g BHEN) at 295 ℃, as represented in Figure 1. The intrinsic viscosity of polymer formed was increased with the progress of reaction and reached the high molecular weight at a given time. As the catalyst concentration also was increased, the intrinsic viscosity were increased.

The values of maximum intrinsic viscosities with the concentrations of antimony triacetate were as follows; 1.0×10^{-6} mol/g BHEN; 0.76 dL/g at 95 minutes, 1.5×10^{-6} mol/g BHEN; 0.83 dL/g at 95 minutes and 2.0×10^{-6} mol/g BHEN; 0.87 dL/g at 98 minutes.

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