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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 activity except titanium catalyst. In the study of poly(ethylene terephthalate), many workers⁶⁻¹⁰ have suggested the effect of the side reaction on the propagation reaction in the presence of antimony trioxide as a catalyst.

Maerov¹¹ 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 °C during the required period of time. The polymer formed was then extruded into cold water (~5 °C). The intrinsic viscosity was measured at 25 °C 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 2.0×10^{-6} mol/g BHEN) at 295 °C, 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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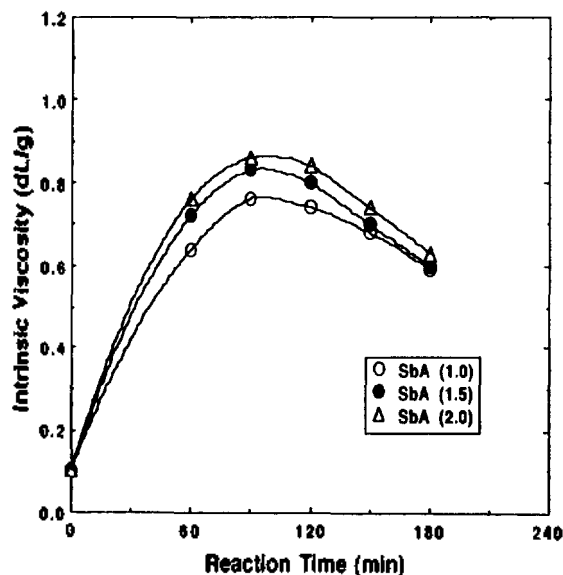


Figure 1. Effect of catalyst concentrations (conc; $1.0\text{--}2.0 \times 10^{-6}$ mol/g BHEN) with antimony triacetate on the polycondensation of BHEN at 295 °C.

Table 1. Comparison of rate constants, K_p with K_D , for the polycondensation of BHEN depending on the concentration of any-mony triacetate at 295 °C

Catalyst conc. ($\times 10^{-6}$, mol/ g BHEN)	Propagation rate constant	Degradation rate constant
	(K_p , $\text{mol}^{-1} \text{min}^{-1}$)	($K_D \times 10^{-5}$, $\text{mol} \text{min}^{-1}$)
1.0	2.17	5.05
1.5	2.41	4.55
2.0	2.45	4.22

After the maximum viscosity appeared, we can observe that the viscosity value begin to slow down. This fact suggests that side reactions such as the thermal degradation (e.g. random β -scission etc.) of PEN occurred during the reaction. The side reactions, in the previous paper,⁵ was confirmed by the formation of carboxyl acid end group. We also concluded that the variation of viscosity was caused by the relationship between the propagation rate and the degradation rate on the catalyzed polycondensation of BHEN.

In order to discuss the catalytic activity of antimony catalyst, the following kinetic equation was proposed in a previous paper.⁵ From the kinetic treatment, the mole number, n (a reciprocal of degree of polymerization), was thought to be composed of two components, n_p and n_D , as expressed by equation (1).

$$n = n_p + n_D \quad (1)$$

where n_p is the propagation mole number, $n_p = 1/(1 + K_p t)$ and n_D is the degradation mole number, $n_D = K_D t$. Here, the value of K_p and K_D also is apparent rate constant for the propagation and degradation reaction.

Using the kinetic equation (1) to data in Figure 1, the

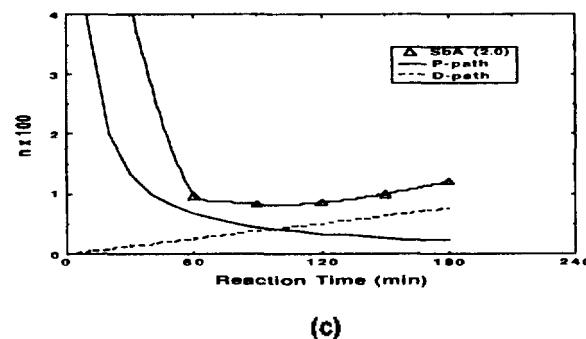
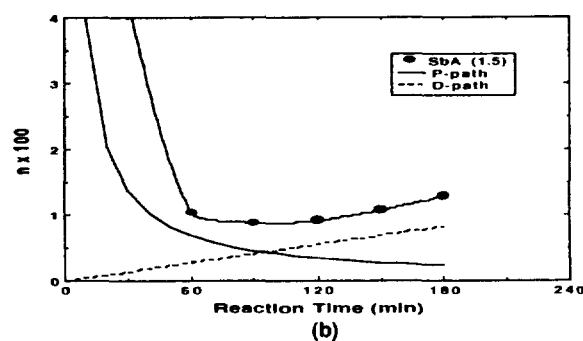
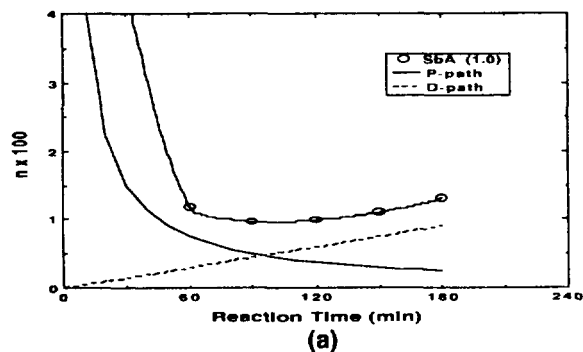


Figure 2. Analysis of propagation and degradation path on the polycondensation of BHEN with the concentration of antimony catalyst.

values of propagation-degradation path were obtained and then drawn separately as shown in Figure 2. From the slope of propagation/degradation path, the apparent rate constants (K_p and K_D) of the propagation and the degradation reaction were calculated and were listed in Table 1.

The values, K_p and K_D , obtained were logarithmically plotted as represented in Figure 3. The propagation rate constant, $1 + \log K_p$, was slightly increased as catalyst concentration increased. On the contrast, the degradation rate constant, $5 + \log K_D$, decreased very slightly.

In order to investigate the dependency of the propagation rate to the degradation rate, the ratio of the propagation rate to the degradation rate was estimated as shown in Figure 4. It can be seen that the catalytic activity of antimony triacetate was largely increased with increasing of the concentration of catalyst. From these interesting phenomenon, we can recognize that catalytic activity significantly depends on the concentration of catalyst.

Effect of Anionic Species for Antimony Oxides. In

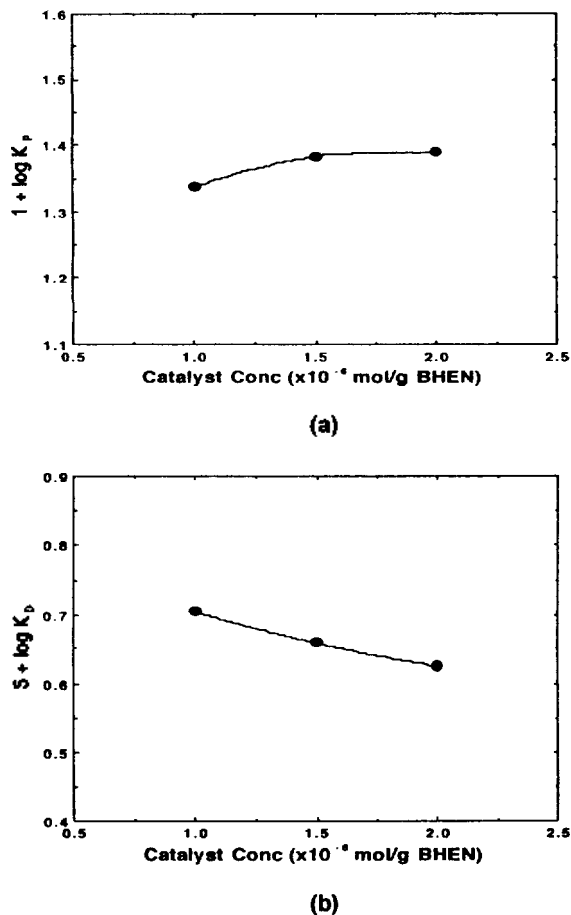


Figure 3. Plot of propagation and degradation rate constants against antimony triacetate as a catalyst.

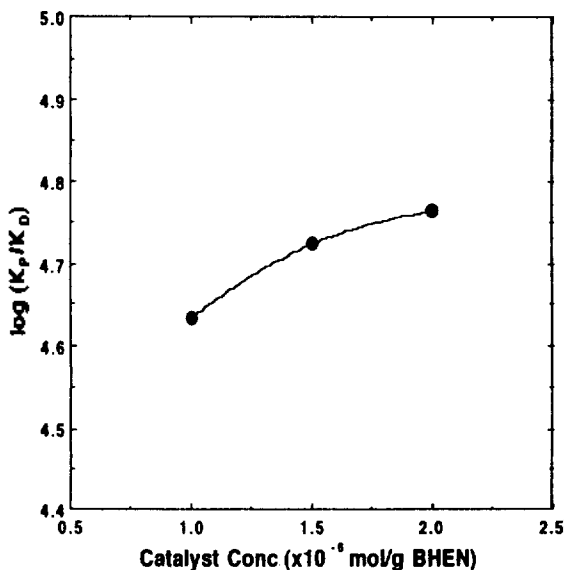


Figure 4. Effect of propagation rate to degradation rate with the concentration of antimony triacetate.

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

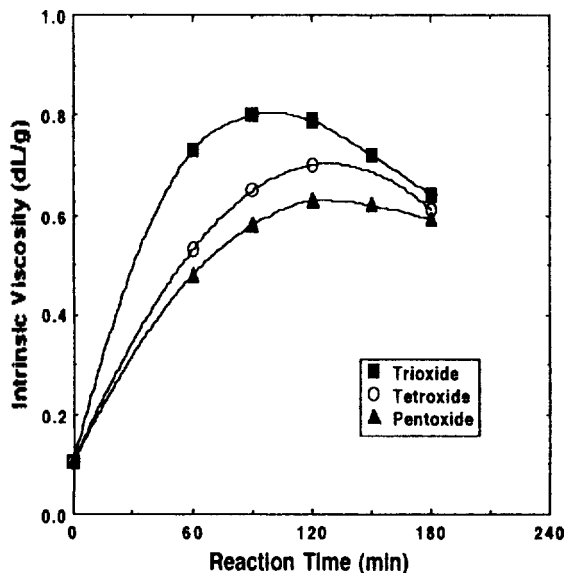


Figure 5. Effect of anionic species of antimony oxides as catalysts (conc; 1.5×10^{-6} mol/g BHEN) on the polycondensation of BHEN at 295 °C.

Table 2. Comparison of rate constants, K_p with K_d , for the polycondensation of BHEN depending on the oxygen numbers of anyimony oxides at 295 °C

Type*	Propagation rate constant	Degradation rate constant
	(K_p , mol ⁻¹ min ⁻¹)	($K_d \times 10^{-5}$, mol min ⁻¹)
Trioxide	2.20	4.50
Tetroxide	1.45	4.11
Pentoxide	1.31	4.82

*Trioxide: antimony trioxide, Tetroxide: antimony tetroxide and Pentoxide: antimony pentoxide.

the negatively charged carbonyl oxygen of the ester group.

In the previous work, Maerov¹¹ studied the effectiveness of antimony catalyst on the polycondensation reaction of BHET with varying numbers of hydroxy ethoxy ligands and found that the effectiveness change with the ligand number. Syntheses of PEN polymer were carried out by the ligand numbers of antimony-oxygen (Sb-O) in antimony catalysts (conc.; 1.5×10^{-6} mol/g BHEN) at 295 °C, and the results are plotted in Figure 5. The time to reach the maximum molecular weight were changed by the Sb-O employed. The maximum intrinsic viscosity values with ligands in antimony catalysts were as follows; antimony trioxide 0.805 dL/g at 100 minutes, antimony tetroxide 0.70 dL/g at 129 minutes and antimony pentoxide 0.63 dL/g at 125 minutes.

The results of kinetic treatment in Figure 5 were listed in Table 2. Table 2 shows the values of rate constant, K_p and K_d , for the propagation rate and the degradation rate. It can be seen that the propagation and the degradation rates are more influenced by antimony trioxide than only other catalysts. Of course, it can be seen that the catalytic activity of antimony triacetate is very similar to that of antimony

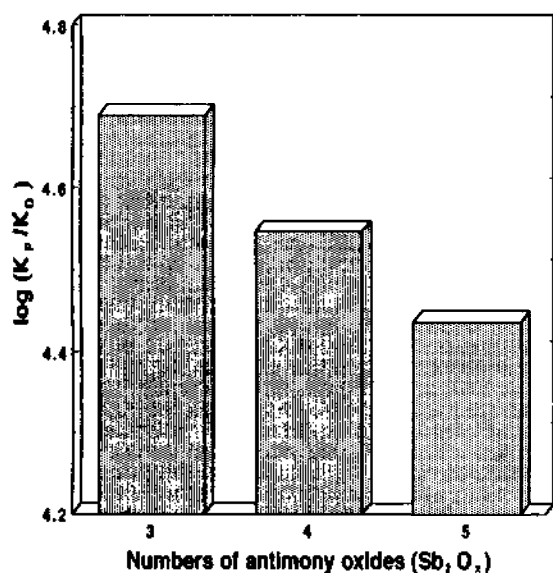


Figure 6. Effect of propagation rate to degradation rate with the anionic species of antimony oxides.

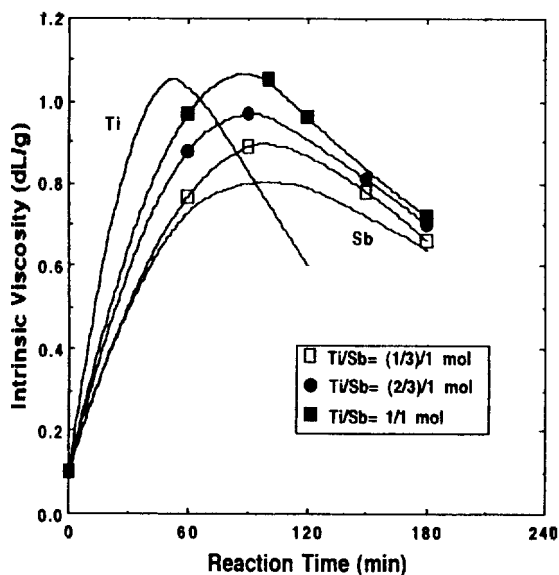


Figure 7. Effect of titanium concentration in the Ti/Sb mixed catalysts (conc.: 1.5×10^{-6} mol/g BHEN) on the polycondensation of BHEN at 295 °C.

trioxide. From this result, we could suggest that the catalytic activity was influenced on the ligands as well as the metal species in the same catalyst.

In order to appear the catalytic activity, we also investigated the ratio of the propagation rate to the degradation rate, as shown in Figure 6. It can be seen that the catalytic activities was largely decreased, when the ligand number of anionic species in antimony oxides as catalysts was increased.

Catalytic Activity for Antimony/Titanium Catalysts.

In order to investigate the catalytic activity of antimony/titanium catalysts on the polycondensation reaction, the time dependences on the polycondensation with the titanium/anti-

Table 3. Comparison of rate constants, K_p with K_d , for the polycondensation of BHEN with the concentration of titanium catalysts in antimony based catalysts (conc.: 1.5×10^{-6} mol/g BHEN) at 295 °C

Type of* catalyst	Propagation rate constant	Degradation rate constant
	(K_p , mol ⁻¹ min ⁻¹)	($K_d \times 10^5$, mol min ⁻¹)
Ti : Sb = (1/3) : 1	2.56	4.04
Ti : Sb = (2/3) : 1	3.00	3.91
Ti : Sb = 1 : 1	3.51	3.66

*Ti : Sb = (1/3) : 1 : titanium isopropoxide (conc.: 0.5×10^{-6} mol/g BHEN), Ti : Sb = (2/3) : 1 : titanium isopropoxide (conc.: 1.0×10^{-6} mol/g BHEN) and Ti : Sb = 1 : 1 : titanium isopropoxide (conc.: 1.5×10^{-6} mol/g BHEN).

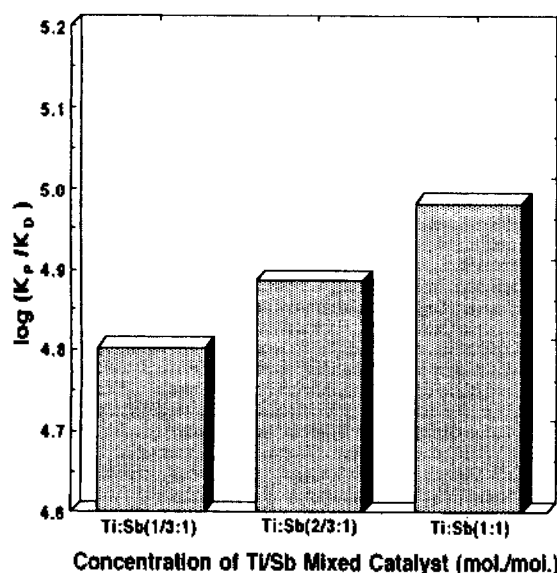


Figure 8. Effect of propagation rate to degradation rate with the titanium concentration in the Ti/Sb mixed catalysts.

mony (Ti/Sb) mixed catalyst were carried out at 295 °C, and the results of these experiments were plotted in Figure 7. The maximum intrinsic viscosity with the Ti/Sb mixed catalysts were as follows ; Ti : Sb = (1/3) : 1 ; 0.90 dL/g at 98 minutes, Ti : Sb = (2/3) : 1 ; 0.97 dL/g at 92 minutes and Ti : Sb = 1 : 1 ; 1.06 dL/g at 88 minutes.

When the mixed catalysts were compared with single titanium or antimony catalyst, the times to reach the maximum values were more extended. In the case of equimolecular mixed catalyst, the high intrinsic viscosity was obtained.

The kinetic treatment to data in Figure 7 was performed as listed in Table 3. Table 3 shows the values of rate constant, K_p and K_d , for the propagation and the degradation rate with the concentrations of titanium/antimony catalysts.

From this result, it also can be seen that the complex gives a greater catalytic influence than individual catalysts. When the ratio of titanium in the Ti/Sb mixed catalyst was increased, the propagation rate was gradually increased, but the degradation rate was rather decreased. The equimolecu-

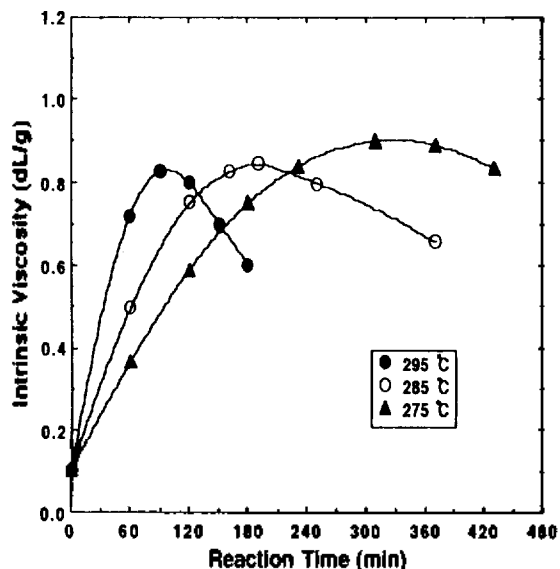


Figure 9. Effect of time dependence of BHEN with antimony triacetate (conc.; 1.5×10^{-6} mol/g BHEN).

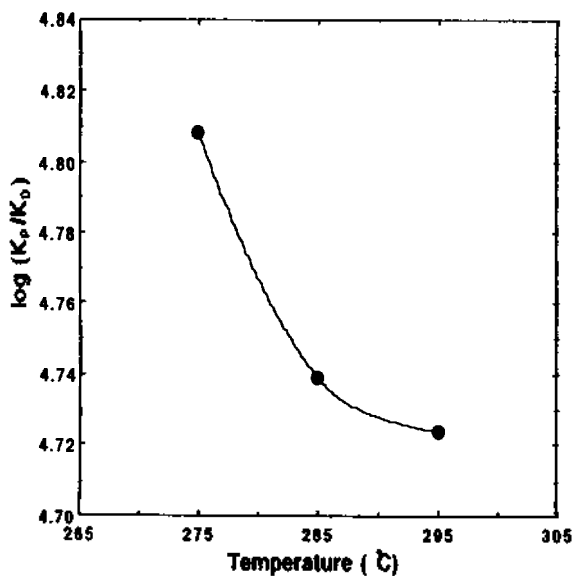


Figure 10. Effect of propagation rate to degradation rate with the change of temperature.

lar Ti/Sb mixed catalyst also was larger influenced on the propagation and degradation rate than another mixed catalysts.

In order to appear the catalytic activity, the ratio of the propagation rate to the degradation rate was represented in Figure 8. It can be seen that the catalytic activities was largely increased, when the ratio of titanium in the Ti/Sb mixed catalyst was increased.

Temperature Dependence with Antimony Triacetate. The temperature dependences of the intrinsic viscosity of the polymer were investigated with antimony triacetate (1.5×10^{-6} mol/g BHEN) used as a catalyst.

Figure 9 exhibits that raising the polymerization temperature shortens the reaction time to reach the maximum value

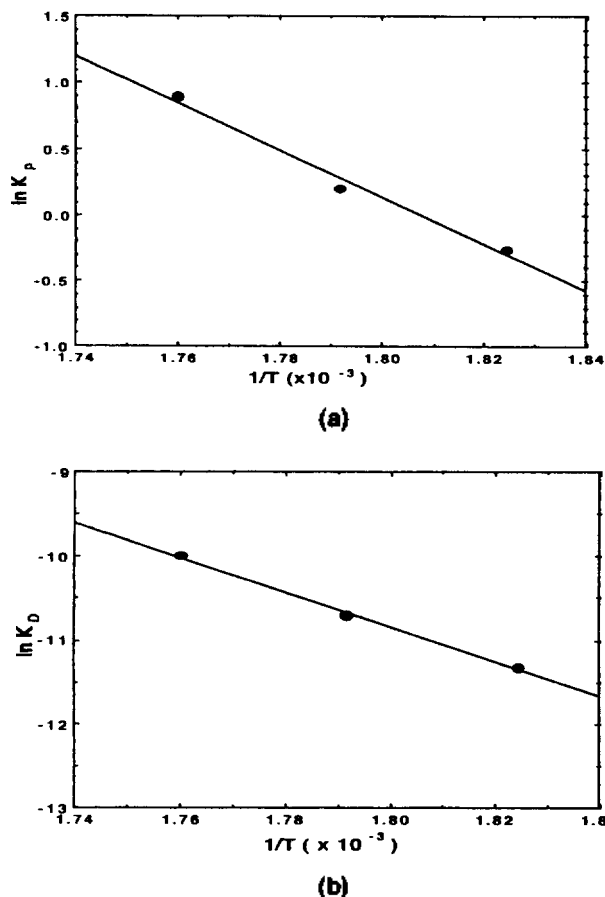


Figure 11. Arrhenius plots of antimony triacetate as a catalyst in the temperature dependence of BHEN in Table 4.

Table 4. Comparison of rate constants, K_p with K_d , for the polycondensation of BHEN in the temperature dependences of antimony triacetate as catalysts (conc.; 1.5×10^{-6} mol/g BHEN) at 295 °C

Temp. condition	Propagation rate constant	Degradation rate constant
	(K_p , mol ⁻¹ min ⁻¹)	($K_d \times 10^{-5}$, mol min ⁻¹)
275 °C	0.77	1.20
285 °C	1.22	2.23
295 °C	2.41	4.55

of the intrinsic viscosity of the formed polymer; *i.e.*, 328 min (0.90 dL/g) at 275 °C, 191 min (0.85 dL/g) at 285 °C and 95 min (0.83 dL/g) at 295 °C. The applications of P-D kinetic equations to data in Figure 11 were performed, as listed in Table 4.

Table 4 shows the values of rate constant, K_p and K_d , for the propagation and real degradation rate with the changes of reaction temperatures. In order to discuss the catalytic activity, the ratio of propagation rate to degradation rate was shown in Figure 10. It can be seen that the catalytic activities was largely decreased with raising the reaction temperature.

The Arrhenius plot was obtained by plotting both $\ln K_p$ and $\ln K_D$ against $1/T$ as shown in Figure 11. From these plots we obtained two apparent activation energies, E_p and E_D , of propagation and degradation, and their values were $E_p=148$ KJ/mol and $E_D=173$ KJ/mol, respectively. The apparent activation energy of determined by degradation rate is higher than that determined by the propagation rate. From this phenomenon, it can be seen that the degradation reaction is much more influenced by a temperature change than the propagation rate.

Concluding Remarks

The antimony catalyzed polycondensation on the formation of poly(ethylene 2,6-naphthalate) was investigated. The catalytic activities of antimony compounds were significantly influenced by the concentration of catalyst and the oxygen numbers of the antimony oxides as well as the metal species. Temperature was one of the most important factor to reduce the reaction time to reach the maximum value of the intrinsic viscosity of the formed polymer; the higher the temperature was, the faster the reaction rates were.

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Solvent Effects on Localized and Delocalized Cationic Charges in Solvolysis¹

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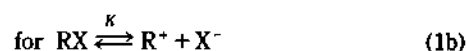
A measure of stabilities ($-\Delta H^{\circ}$) and resonance delocalization ($-\Delta q(C_a^+)$) for some carbocations has been estimated using the semiempirical AM1 method. The stability ($-\Delta H^{\circ}$) of carbocations can be correlated with the sensitivity (m) of localized cations to the solvent ionizing power scale Y, whereas the extent of resonance delocalization ($-\Delta q(C_a^+)$) can be correlated with the sensitivity (h) of delocalized cations to the solvent ionizing power scale I. It has been shown that two solvent ionizing power scales Y and I have in general opposite signs so that effects of electrostatic solvation are opposite for the localized and delocalized cationic charges. The use of two different solvent scales for a substrate with delocalizable cationic charge is not only prerequisite to the proper correlation of solvolysis rates but also is justified.

Introduction

Isolated carbocations, as those in the gas phase, are in general unstable unless the cationic charges are well delocalized; thus the instability of a carbocation in a given environment and at a given temperature is directly related to the degree to which the charge is localized. The unstable carbocations are stabilized either (i) by electrostatic solvation in solution or (ii) by delocalization of the cationic charge over relatively wide range as involved in resonance delocalization

of cationic charge into a benzene ring. The relative stability of a carbocation R^+ can be conveniently represented by the heat of formation (ΔH°) of the isolated ion pair² $R^+ + X^-$, as shown in eq (1a). By keeping

$$\Delta H^{\circ} = \Delta H_f(R^+) + \Delta H_f(X^-) - \Delta H_f(RX) \quad (1a)$$



the anion X^- constant, the relative stability of R^+ can be compared. An unstable carbocation is characterized by a la-