Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Acid-Base and Catalytic Properties of Metal Compounds in the Preparation of Polyethylene Terephthalate)

Jong Shik Chung[a]
[a] Department of Chemical Engineering, Pohang Institute of Science and Technology, Pohang, South Korea

To cite this Article Chung, Jong Shik(1990) 'Acid-Base and Catalytic Properties of Metal Compounds in the Preparation of Polyethylene Terephthalate)', Journal of Macromolecular Science, Part A, 27: 4, 479 — 490
To link to this Article: DOI: 10.1080/00222339009349570
URL: http://dx.doi.org/10.1080/00222339009349570

J. MACROMOL. SCI.—CHEM., A27(4), pp. 479–490 (1990)

ACID-BASE AND CATALYTIC PROPERTIES OF METAL COMPOUNDS IN THE PREPARATION OF POLY(ETHYLENE TEREPHTHALATE)

JONG SHIK CHUNG

Department of Chemical Engineering
Pohang Institute of Science and Technology
Pohang 790-600, South Korea

ABSTRACT

Catalytic activity of a metal complex for both the transesterification of DMT (dimethyl terephthalate) and the polycondensation of BHET (bis(2-hydroxyethyl terephthalate)) is described in terms of an acidity function formulated from the physical properties of the metal ion. Catalytic activity for both reactions is governed by the acidity of the metal ion, not by the type of anionic ligand. Maximum catalytic activity is observed with optimum bond strength between the metal ion and the double-bonded oxygen in the ester carbonyl group of DMT or BHET. Thus, a basic (less acidic) metal ion exhibits high catalytic activity for a more basic oxygen in the ester carbonyl of DMT, while a more acidic metal ions exhibits high catalytic activity for a less basic oxygen in the ester carbonyl of BHET. In the polycondensation reaction, a semiconductor metal ion shows higher activity than an insulator metal ion when compared at the same acidity value, but the former also catalyzes side reactions which can cause discoloration of the final poly(ethylene terephthalate) polymer. Discoloration is enhanced when a semiconductor metal ion has a redox couple during polycondensation.

INTRODUCTION

For the preparation of poly(ethylene terephthalate), DMT (dimethyl terephthalate) or TPA (terephthalic acid) was first esterified into BHET (bis(2-hydroxyethyl) terephthalate). Then subsequent polycondensation was carried out using BHET and its oligomer under vacuum. The esterification of TPA is usually carried out in the absence of any catalyst. However, the presence of a suitable metal complex greatly enhances the reaction rates of the transesterification of DMT and the polycondensation of BHET. Acetates of such metals such as Zn, Mn, and Mg were employed as catalysts for the transesterification reaction of DMT, while oxides of such metals as Sb and Ge were used for the polycondensation of BHET.

It is suggested that the catalytic activity of a metal complex is attributed to the ability for its metal ion to form a reaction intermediate with the ester carbonyl group in DMT or BHET, and that the reaction proceeds by nucleophilic attack of hydroxyl end groups upon ester carbonyl groups [1]. It has also been observed that for several metal salts the effect of the anionic species on catalytic activity is negligible [2, 3], probably because of the transformation of a metal salt into a stable metal complex in the reaction medium. In this case, the catalytic activity will be affected by the acidity (electronic state) of the metal ion for a given reactant (ester carbonyl group in DMT or BHET).

Attempts have been made to correlate the catalytic activity with the physical properties of a metal ion such as cation radius [5], electronegativity of the metal [6, 7], and the metal–oxygen bond strength [8]. No satisfactory result has been obtained, probably because there is no good measurement of the acidity of a metal ion with its physical properties.

In the present study the author reports a parameter which can be representative of the acidity of a metal ion, and which can be easily formulated from the physical properties of a metal ion. The correlation made between the catalytic activity and the acidity parameter of a metal ion yields some insight into the mode of catalysis in polyester synthesis reactions.

EXPERIMENTAL

Reagents

BHET was obtained from Polyscience Inc. and used without further purification. All catalysts were commercial products (guaranteed reagent grade) and used without further purification. Antimony trioxide, antimony pentachloride, and germanium(V) oxide were high purity grade from Aesar Co.. Ethoxides of aluminum, antimony, silicon, and magnesium, and isopropoxides of titanium and zirconium were products of Kojundo Chemical in Japan. Other metal ions were used in the acetate form and obtained from Aldrich.

Polycondensation

The polycondensation reaction was carried out in a semibatch open system with stirring at constant speed (80 rpm) under vacuum (0.3–0.4 torr). The reactor was equipped with nitrogen purge, stirrer with vacuum seal, and suction apparatus which consisted of condenser, cold trap, and vacuum pump. The reaction was carried out at 285°C with 0.8 mol BHET and 1×10^{-4} mol metal ion. The molecular weight of the product was monitored as a function of the reaction time by measuring the torque of the stirrer, since good correlation was obtained between motor torque and viscosity of PET polymer.

Measurement of Catalytic Activity

In order to measure the rate constant for polycondensation, the reaction rate was assumed to be second order with respect to the 2-hydroxyethyl ester group. The degree of polymerization has a linear relationship as a function of time [7];

$$DP = 1 + 2[E_0]kt = 1 + k_{\mathrm{eff}}t \tag{1}$$

where $[E_0]$ represents the initial concentration of the 2-hydroxyethyl ester group in the BHET monomer. A plot of DP vs t with experimental data gives a straight line except at the final stage of the reaction where the decomposition of polymer product and side reactions may be prominent.

Determination of Degree of Polymerization

The intrinsic viscosity was measured with *o*-chlorophenol as a solvent at 25°C with a Ubbelohde-type viscometer. This was converted to molecular weight by the Mark-Houwink equation [9];

$$[\eta] = 3.0 \times 10^{-4} M^{0.77} \tag{2}$$

The degree of polymerization was obtained from

$$M = 192DP + 62 \tag{3}$$

Melting Point

The melting point was measured by using a differential scanning calorimeter (Perkin-Elmer DSC-7).

RESULTS AND DISCUSSION

Acidity of Metal Ion

Tomita [2, 7], by using the stability constant (β_1) of dibenzoyl methane complex for metal species, found volcano-shaped correlations between log β_1 and catalytic activity for both transesterification and polycondensation reactions. However, it is not easy to obtain the stability constant for every metal ion, and it is more reasonable to use the acidity of a metal ion (Lewis acidity, tendency to accept an electron) for the reaction intermediate formed between a metal ion and the carbonyl oxygen in DMT or BHET.

Electronegativity is generally used to represent the acidity of a metal. However, it cannot follow the change of valency of a metal ion. There are several parameters that can follow the change of valency of metal ion:

Ionization potential, *IP* (+)
Valency of cation, *Z* (+)
Radius of cation, *R* (−)

where a plus sign indicates that the acidity increases with an increase in the value of the corresponding parameter. Because acidity is a tendency to attract electrons to form a covalent bond, a more acidic metal ion may increase its electron-withdrawing power or its ionization potential. As the valency of metal ion increases, it is more difficult to withdraw electrons (easier to accept electrons or more acidic). A smaller cation attracts electrons more strongly and becomes more acidic. Rather than using these parameters independently, it would be proper to combine them to represent the acidity of a metal ion. For simplicity, a linear combination of these parameters is used to define an acidity function, ϕ, for a metal ion:

$$\phi = \log\left((IP)(Z)/(R)\right) \quad (4)$$

where the unit of *IP* is the volt, and that of *R* is the Ångstrom.

Correlation of Acidity with Catalytic Activity

In Fig. 1, Tomita's rate constant data for various metal acetates in the transesterification of DMT with EG (ethylene glycol) are plotted as a function of ϕ. A curve similar to Tomita's volcano-shaped plot was obtained. Therefore, in addition to the complexing ability of dibenzoyl methane, the acidity function, ϕ, can also be used as a correlation factor for the catalytic activity of a metal ion in the

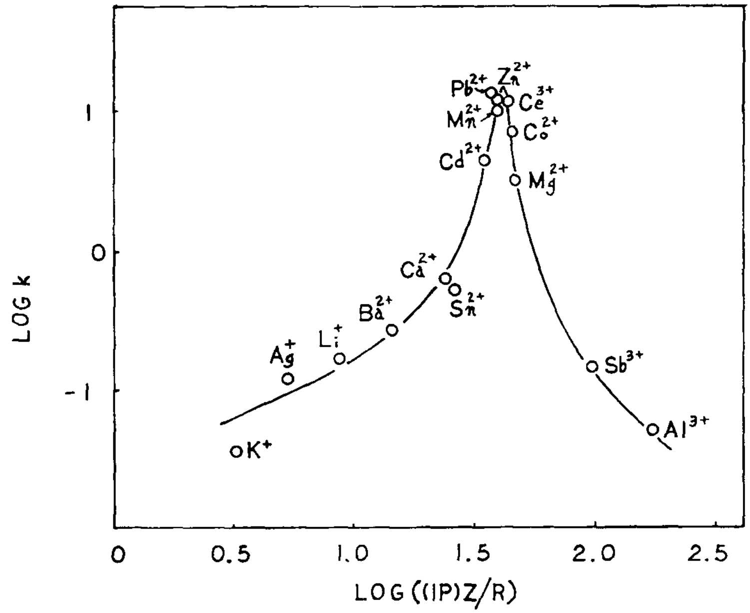


FIG. 1. Plot of catalytic activity with acidity function for the transesterification of DMT. Data were obtained from Tomita [2].

transesterification reaction. A group of metal ions having ϕ of about 1.6 is most active in the reaction.

For the polycondensation reaction of BHET, several sets of activity data are available as shown in Table 1. Because of different experimental conditions among investigators, the relative value of catalytic activity is obtained by setting the rate constant of antimony(III) to be 1.0. When only relative viscosity was measured as in the case of Maerov's data, the rate constant was assumed to be roughly proportional to $\eta^{1.3}$. The above relationship between rate constant and relative viscosity was obtained from Eqs. (1)–(3).

Maerov [4], who used antimony compounds with various numbers of hydroxyethoxy ligands, observed that catalytic activity was dependent on the number of hydroxyethoxy ligands in an antimony compound, and suggested the importance of the ligand geometric effect on catalytic activity. However, it should be noted that the change in the number of hydroxyethoxy ligand in an antimony compound also changes the effective charge of the remaining antimony cation complex. His results indicate that the phenyl ligand attached to an antimony ion is inactive for

TABLE 1. Relative Activities of Various Metal Ions in the Polycondensation Reaction

Metal ion	Energy band gap, eV	Maerov [4][a]	Rafler [5]	Tomita [7]	Present work
Sb^{5+}		0.92			1.15
Sb^{3+}	3.2–3.3	1.0	1.0	1.0	1.0[c]
Sb^{2+}		0.60[b]			
Sb^{+}		0.49[b]			
Ti^{4+}	3.2–3.5			2.76	1.53[c]
Sn^{2+}	2.4–3.7			1.17	1.41[c]
Mo^{6+}	2.8–3.5				0.69
Ge^{4+}	5.6–6.0		1.03		0.65
Ce^{3+}	5.5			0.85	
Zn^{2+}	3.2–3.4			0.72	0.73
Co^{2+}	0.5–0.7		0.67	0.67	0.64
Zr^{4+}	4.99				0.72
Al^{3+}	7.0–9.0		0.83	0.62	0.66
Si^{4+}	8.0–11.0				0.45
Pb^{2+}	2.6–3.6			0.55	0.52
Mn^{2+}	1.8–2.6		0.67	0.46	0.64
Mg^{2+}	7.8–7.4			0.46	0.40
Ca^{2+}	6.1–7.7		0.38	0.33	0.36
Ag^{+}	1.2–1.5		0.48		
Na^{+}	7.8				0.32
None				0.25	0.27

[a] The relative activity is based on the same amount of antimony.

[b] Corresponds to the effective charge of an antimony cation with a phenyl group attached to the antimony.

[c] Anion types tested for activity measurement are oxide, acetate, and ethoxide forms of antimony(III); and isopropoxide and acetate forms of titanium(IV) and tin(II). Data scattering was less than 15% among various anion salts for a metal ion.

exchange with the ester carbonyl group in BHET. In this case, the antimony valency of Maerov's data in Table 1 corresponds to the effective charge of the antimony cation complex, and is equal to the number of the hydroxyethoxy ligand in the antimony compound in Maerov's original data. The activity value of 0.6 for antimony(II) in Maerov's data is the average value calculated from four sets of relative activity data in Maerov's original data; 0.69 with monophenylantimony bis(2-hydroxyethoxide), 0.47 with triphenylantimonyoxide, and 0.62 with two sets of monophenylantimony bis(2-hydroxyethoxide).

Figure 2 shows a plot of the catalytic activities in Table 1 with the acidity function, ϕ. A good correlation between the logarithmic rate constant and ϕ exists,

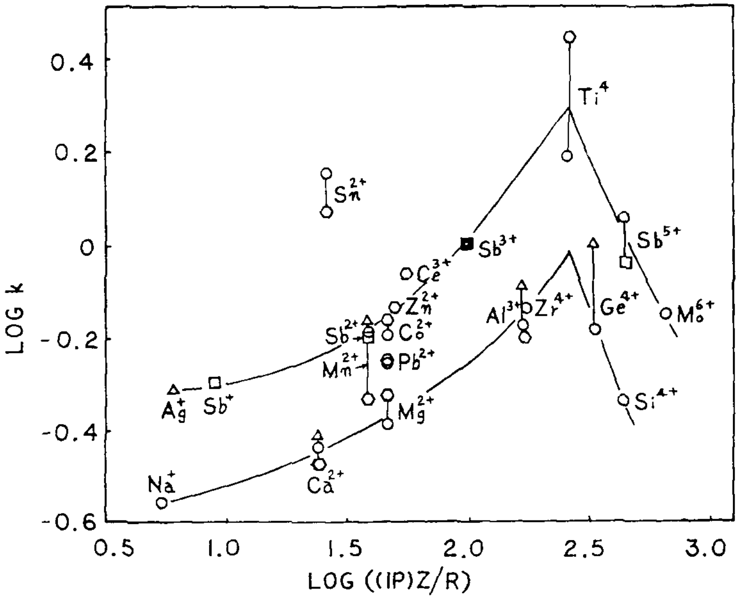


FIG. 2. Plot of catalytic activity with acidity function for the polycondensation of BHET. (□) Maerov [4]; (Δ) Rafler [5]; (○) Tomita [7]; (O) present work.

except for Sn(II). The author tested more than two different forms of anionic salt for antimony(III), titanium(IV), and tin(II) as shown in Table 1, and it was confirmed that metal ions with a different anionic salt gave almost the same activity. Therefore, activity change in the series of antimony ions tested by Maerov may be attributed to acidity changes due to the change in the charge of antimony cation complex, not to the ligand geometric effect. This is proved by the results in Fig. 2, where good correlation is observed between catalytic activity and acidity of the series of antimony ions. The result also supports the belief that the phenyl group attached to antimony is not involved in the exchange with the ester carbonyl group of BHET during the polycondensation reaction.

Among various metal compounds studied, only tin(II) showed a deviation from the plot. Tin(II) behaves as if it is oxidized into tin(IV) during the reaction since its activity, log k, corresponds to a ϕ value of about 2.1 which approaches the ϕ value of 2.35 of tin(IV). Although the polycondensation reaction occurs under high vacuum, trace of oxygen or water remaining in the reaction mixture may be involved in the oxidation. The unusual behavior of tin(II) is understandable if we

TABLE 2. Standard Electrochemical Potential of Some Metal Ions

Redox couple	Reduction potential, V
Ce^{4+}/Ce^{3+}	1.44
Sb^{5+}/Sb^{3+}	0.75
Sn^{4+}/Sn^{2+}	0.07
Ti^{4+}/Ti^{3+}	0.04
Mo^{6+}/Mo^{0}	0.0
Ni^{2+}/Ni^{0}	-0.28
Cr^{3+}/Cr^{2+}	-0.41
Zn^{2+}/Zn^{0}	-0.76
Ca^{2+}/Ca^{0}	-2.76

compare the standard electrochemical potential of tin(II) with those of other metal ions. Table 2 shows the standard reduction potential for selected metal ions. From the table it can be seen that Sn(II) can be more easily oxidized into Sn(IV) than Ce(III) is oxidized into Ce(IV) or Sb(III) into Sb(V).

The results in Fig. 2 shows that metal ions can be classified into two groups: one shows lower activity and the other shows higher activity when compared at the same acidity. Each group shows activity maximum at the same value of ϕ, about 2.4, in the polycondensation reaction of BHET.

The difference in the optimum value of ϕ between the transesterification of DMT and the polycondensation of BHET results from the difference in the basicity of oxygen in the ester carbonyl group. The electron density of ester carbonyl is lower with the 2-hydroxyethyl group than with the methyl group because of electron withdrawing and hydrogen bonding of terminal hydroxyl in the 2-hydroxyethyl group [7]. In other words, the double-bonded oxygen in the ester carbonyl group of BHET is less basic than that of DMT. The highest catalytic activity can be exhibited when bond strength between the carbonyl oxygen and the metal ion becomes optimum (neither too strong nor too weak). Therefore, high catalytic activity is observed with a more acidic metal ion for less basic carbonyl oxygen in BHET while a basic (less acidic) metal ion is needed for the more basic carbonyl oxygen in DMT.

Hovenkamp [10] observed that an esterification catalyst was poisoned by an acid end group such as benzoic acid but not poisoned by a hydroxyl group. This is reasonable in terms of the acid-base properties of a catalyst since the basic catalyst used for the transesterification of DMT can be poisoned by an acidic substance in the reaction mixture. Therefore, the direct esterification of TPA with

EG does not usually employ any catalyst because the basic catalyst can be poisoned by the acidic nature of TPA itself. In similar fashion, basic substance such as the hydroxyl group can poison the acidic catalyst used in the polycondensation of BHET, and this has been observed by Hovenkamp [10].

Effect of Semiconducting Properties on Polycondensation

Metal ions which show two different patterns of activity in Fig. 2 can be classified according to the semiconducting properties of the metal ions. In Table 1, the energy band gap for the corresponding metal oxide is shown. A material with an energy band gap in the 0–3 range or 4 eV is regarded as a semiconductor, while a material with a value larger than 4 eV is regarded as an insulator [11].

From the band gap data in Table 1 it is concluded that, when metal ions are compared at the same acidity value, the metal ions which show higher activities in Fig. 2 are semiconductors and the group of metal ions with lower activities are insulators. The activity difference between a semiconductor and an insulator can be explained if we consider the tendency of metal ions to form metal oxides. As shown in Fig. 3, the heat of formation of a metal oxide is generally higher in the

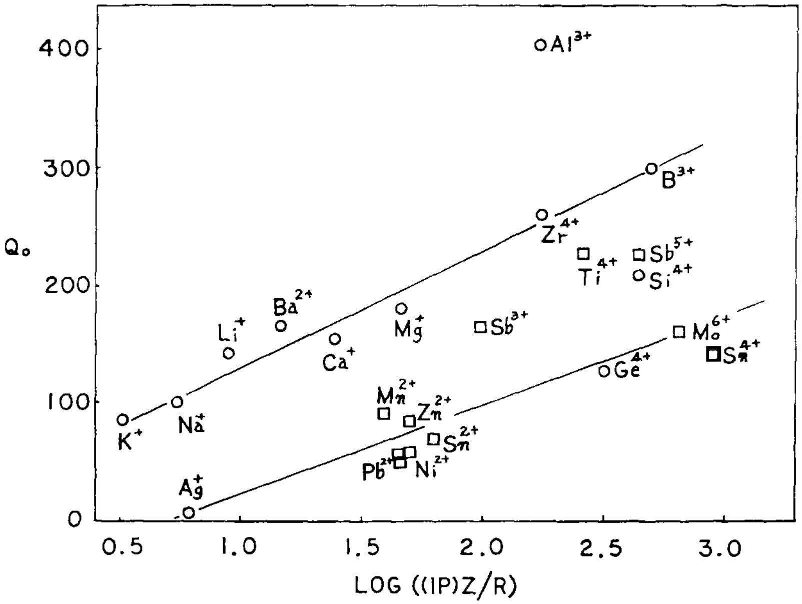


FIG. 3. Plot of heat of formation of oxide with acidity function. Data were obtained from Ref. 15. (○) Insulator, (□) semiconductor.

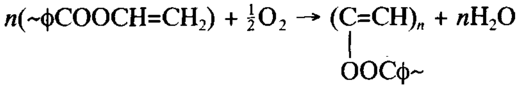
insulator group than in the semiconductor group. The high heat of formation of a metal oxide in the insulator group may promote the transformation of a metal ion into its corresponding oxide or hydroxide form, depressing the formation of an active reaction intermediate, the metal–ester carbonyl complex. Therefore, even in the case where the metal–oxygen bond strength (acidity value) in the metal ion–ester carbonyl complex is the same between semiconductor and insulator metal ions, the insulator will exhibit less activity than the semiconductor since the insulator metal ion forms a smaller number of active reaction intermediate than does the semiconductor metal ion.

The semiconducting properties of a metal species also affect the color characteristics of the final polymer. In general, the insulator group which shows lower activity in Fig. 2 does not induce any color formation in the final PET polymer. However, the semiconductor group results in discoloration of the PET polymer as shown in Table 3. Discoloration is more prominent when a metal ion has a variable valency, as in the cases of molybdenum, titanium, and tin.

It is known that discoloration results from the formation of polyacetylene from the vinyl group in PET polymer [12]. The vinyl group can be formed by the decomposition of PET polymer during the polycondensation reaction:

$$\sim\phi COOC_2H_4OOC\phi\sim \rightarrow \sim\phi COOCH{=}CH_2 + \sim\phi COOH \qquad (5)$$

Then free radical polymerization of the acetylene group proceeds in the presence of oxygen:



$$n(\sim\phi COOCH{=}CH_2) + \tfrac{1}{2}O_2 \rightarrow \underset{\substack{| \\ OOC\phi\sim}}{(C{=}CH)_n} + nH_2O \qquad (6)$$

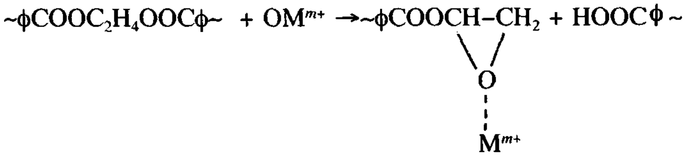
The initiator for free radical polymerization can be supplied by the carboxyl group:

$$\sim\phi COOH \rightarrow \sim\phi CO\cdot + \cdot OH \qquad (7)$$

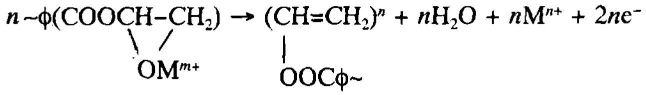
Reaction (7) can be catalyzed in the presence of a metal ion which has the ability to vary its valency and to form a redox couple, M^{m+}/M^{n+} [13].

$$\sim\phi COOH + M^{m+} \rightarrow \sim\phi CO^{-} + \cdot OH + M^{n+} \qquad (m < n) \qquad (8)$$

Otherwise, free radical polymerization can itself be a catalytic process if the metal ion has a redox couple and if the reaction proceeds by the formation of an ethylene oxide intermediate, as proposed for the decomposition of PET [14]. In this case, a semiconducting metal ion, which is able to chemisorb and dissociate dioxygen, will be effective for the reaction.



$$\sim\phi COOC_2H_4OOC\phi\sim + OM^{m+} \rightarrow \sim\phi COO\underset{\underset{M^{m+}}{\vdots}}{\underset{O}{CH-CH_2}} + HOOC\phi\sim \qquad (9)$$



$$n\sim\phi(COO\underset{OM^{m+}}{CH-CH_2}) \rightarrow (\underset{OOC\phi\sim}{CH}=CH_2)^n + nH_2O + nM^{n+} + 2ne^- \qquad (10)$$

$$M^{n+} + 2e^- + \tfrac{1}{2}O_2 \rightarrow OM^{m+} \qquad (11)$$

Therefore, the formation of color in the final PET polymer requires the presence of both oxygen and a semiconducting metal ion which is able to chemisorb oxygen. Moreover, the presence of a redox couple can accelerate discoloration either by creating more initiator for free radical polymerization or by catalyzing the discoloration reaction itself. In order to form a redox couple, a change of valency between higher value and lower one should be relatively easy, and this condition can be satisfied when the standard potential is near zero. Table 2 shows that the standard potentials for Mo, Ti, and Sn are near zero, and the results in Table 3 shows that the three compounds result in more severe discoloration of the final polymer than do others.

TABLE 3. Example of Semiconductor Metal Ions Which Produce Discolored PET Polymer

Catalyst[a]	Relative activity	mp, °C	Color
$Mo(CH_3COO)_6$	0.69	249	Dark brown
$Sn(CH_3COO)_2$	1.45	—	Brown
$Ti(i\text{-}C_3H_7O)_4$	1.53	259	Yellow
Sb_2O_3[b]	1.25	256	Yellowish-white
$Co(CH_3COO)_2$	0.64	259	Greyish-white
$Ni(CH_3COO)_2$	0.60	259	"
$Zn(CH_3COO)_2$	0.73	260	"

[a] Amount of catalyst used was 1×10^{-4} mol at 285°C, and the activity of Sb(III) was taken as 1.0.

[b] Catalyst concentration increased to 8×10^{-4} mol.

ACKNOWLEDGMENT

The author is grateful to Dr. Jung Y. Kim of KAIST for his financial support and encouragement for this work.

REFERENCES

[1] K. Yoda, *Kogyoku Kagaku Zasshi, 74,* 1476 (1971).
[2] K. Tomita and H. Ida, *Polymer, 16,* 185 (1975).
[3] H. Kamatani, S. Konagaya, and Y. Nakamura, *Ibid., 12,* 125 (1980).
[4] S. B. Maerov, *J. Polymer Sci., Polym. Chem Ed., 17,* 4033 (1979).
[5] G. Rafler, G. Reinish, and E. Bonatz, *Acta Chim. (Budapest), 81,* 253 (1974).
[6] K. Yoda, K. Kimoto, and T. Toda, *J. Chem. Soc., Jpn. Ind. Chem. Soc., 67,* 909 (1964).
[7] K. Tomita, *Polymer, 17,* 221 (1976).
[8] T. H. Shah, J. I. Bhatty, G. A. Gamlen, and D. Dollimore, *Ibid., 25,* 1333 (1984).
[9] W. R. Moore, *Ibid., 16,* 185 (1975).
[10] S. C. Hovenkamp, *J. Polym. Sci., Part A-1, 9,* 3617 (1971).
[11] W. H. Strehlow and E. L. Cook, *J. Phys. Chem. Ref. Data, 2,* 163 (1973).
[12] H. Zimmermann and E. Leibnitz, *Faserforch. Textiltech., 16,* 282 (1968).
[13] D. J. Williams, *Polymer Science and Engineering,* Prentice-Hall, Englewood Cliffs, New Jersey, 1971, p. 86.
[14] H. K. Reimschuessel, B. T. Debona, and A. K. S. Murthy, *J. Polym. Sci., Polym. Chem Ed., 17,* 3217 (1979).
[15] R. C. Weast, *Handbook of Chemistry and Physics,* CRC Press, 55th ed., 1974, p. D-45.

Received March 24, 1989
Revision received June 24, 1989