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NOTE

CORRELATION OF ACIDITY OF METAL ION WITH CATALYTIC ACTIVITY FOR THE FORMATION OF POLY(ETHYLENE TEREPHTHALATE)

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Abstract—For the transesterification of DMT (dimethyl terephthalate) and polycondensation of BHET [bis(2-hydroxyethyl) terephthalate)], catalytic activity of various metal complex can be correlated with acidity of metal ion, which is expressed as modified electronegativity. Based on correlations mode of catalysis for the formation of PET [poly(ethylene terephthalate] was suggested.

INTRODUCTION

For the preparation of PET, esterification of DMT or TPA (terephthalic acid) to prepare BHET monomer is subsequently followed by polycondensation of BHET under vacuum. The esterification of TPA is usually carried out in the absence of any catalyst. However, the presence of suitable metal complex is essential for the transesterification of DMT and for the polycondensation of BHET. Basic metal acetates such as Zn, Mn, and Mg are employed as catalyst for the transesterification reaction of DMT, while relatively acidic metal salts such as Sb and Ge are employed in the polycondensation of BHET.

It has been widely accepted that, for both esterification and polycondensation, catalyst transforms into a stable reaction intermediate with the ester carbonyl group in DMT or BHET, and that reaction proceeds by the nucleophilic attack of hydroxyl end groups upon the ester carbonyl groups [1-4]. This suggests us that the bond strength between metal ion and oxygen in the ester carbonyl group plays important role for the reactions. In this case, catalytic activity will be affected by the acidity of metal ion. Attempts have been made to correlate catalytic activity with physical properties of metal ion such as metal-oxygen bond strength [4], cation radius [5], and electronegativity of metal [3,6]. Correlations made with these parameters have not shown any satisfactory result yet.

In the present work, the author used a modified electronegativity, χ_i proposed by Tanaka [7], and found that there were good correlations between χ_i and catalytic activity of metal ion. Based on the correlations, the mode of catalysis in polyester synthesis reactions was explained.

EXPERIMENTAL

The polycondensation reaction was carried out in a semi-batch 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 consists of condenser, cold trap and vacuum pump. The reaction was carried out at 285°C with 0.8 mole BHET and 1×10^{-3} mole metal ion. Molecular weight of product was monitored as a function of reaction time by measuring torque of the stirrer, since a good correlation was obtained between motor torque and viscosity of PET polymer. In order to measure rate constant, k for the reaction, reaction rate was assumed to be second order with respect to 2-hydroxyethyl ester group [3].

RESULTS AND DISCUSSION

Tomita [2,3], using stability constant (β_1) of dibenzoyl methane complex of 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 is more reasonable to use acidity of metal ion (Lewis acidity, tendency to accept electron) for reaction intermediate of metal ion-ester carbonyl complex. Since acidity increases with increase in electronegativity, the modified electronegativity, χ_i can be indicative of acidity of a

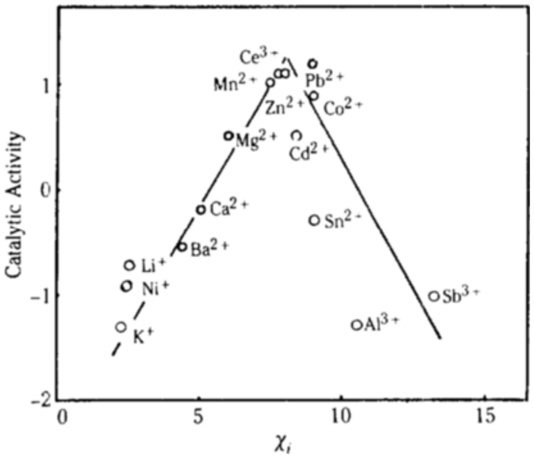


Fig. 1. Correlation of catalytic activity with χ_i in the transesterification of DMT.

Catalytic activity represents logarithmic rate constant (log k) for the reaction. All metal salts are in acetate form [2].

metal ion.

In Fig. 1 Tomita's data of catalytic activity for the transesterification are plotted as a function of χ_i. Similar curve as Tomita's volcano-shaped plot was obtained. Group of metal ion ranging in χ_i from 8 to 9 is most active in the reaction.

Figure 2 shows the same kind of plot done for the polycondensation of BHET. Because of different experimental conditions among investigators relative value on catalytic activity is obtained by setting rate constant of antimony (III) to be 1.0. Although there are some scatterings on activity data among investigators the result clearly shows that catalytic activity can be correlated with χ_i. Maximum in the activity was observed at the value of χ_i of about 13. The value of $\chi_{i,max}$ in the polycondensation of BHET is much higher than that observed in the transesterification of DMT.

The difference in the value of $\chi_{i,max}$ between transesterification and polycondensation results from the difference in the basicity of oxygen in the ester carbonyl group. Electron density of ester carbonyl is lower with 2-hydroxyethyl group than with methyl group, because of electron withdrawing by terminal hydroxyl in the 2-hydroxyethyl group [3]. Therefore, the double-bonded oxygen in the ester carbonyl group of BHET is less basic than that of DMT. The highest catalytic activity will be exhibited when bond strength between the carbonyl oxygen and metal ion becomes optimum (neither too strong nor too weak). As a matter of fact, less basic carbonyl oxygen in BHET requires more acidic metal ion, while more basic carbonyl oxygen in DMT does less acidic metal ion in order to get optimum bond strength.

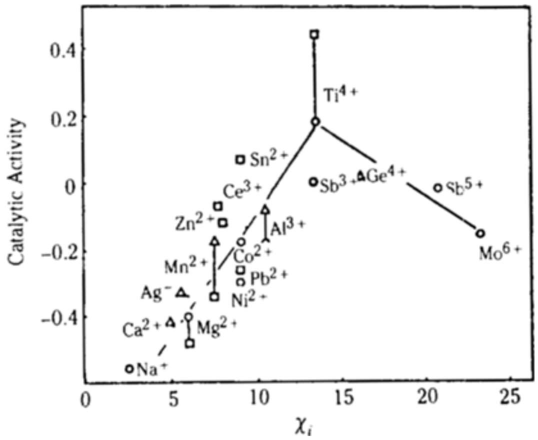
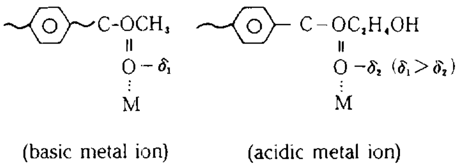


Fig. 2. Correlation of catalytic activity with in the polycondensation of BHET.

□, Tomita [3]; △, Rafler [5]; ○, Present work. Form of metal salt in the present work was ethoxide for Al(III), isopropoxide for Ti(IV), chloride dissolved in ethylene glycol for Mo(VI) and Sb(V), and acetates for other metal ions.



Hovenkamp [8] observed that esterification catalyst is poisoned by acid end group such as benzoic acid, but not poisoned by hydroxyl group. This is reasonable in terms of acid-base properties of catalyst, since basic catalyst used for the transesterification of DMT will be poisoned by acidic substance in reaction mixture. Therefore the direct esterification of TPA with EG does not usually employ any catalyst because basic catalyst will be poisoned by the acidic nature of TPA itself. In similar fashion basic substance such as hydroxyl group can poison acidic catalyst used in the polycondensation of BHET, and this has been observed by Hovenkemp [8].

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