Letters

Catalytic activity of metal compounds in the thermal decomposition of ethylene dibenzoate

As described in the previous paper[1], the thermal degradation of poly(ethylene terephthalate) (PET) is accelerated by metal compounds used as catalysts in the polycondensation reaction or the transesterification reaction. The author[1–3] found that the catalytic activity of metal compounds in the thermal degradation of PET could be evaluated from the *d*-value in the kinetic treatment (*p–d* analysis) of the polycondensation process of bis(2-hydroxyethyl)terephthalate (BHET).

In this Letter, the catalytic activity of metal compounds in the thermal decomposition of ethylene dibenzoate (EDB) was studied as a model for PET.

The catalytic effect of metal compounds on the thermal decomposition of EDB has been observed previously[4,5], in a semi-quantitative way and for limited catalyst types.

In this study, the catalytic activity of various metal compounds was followed by the quantitative method presented by the author[6].

EDB was synthesized from benzoyl chloride and ethylene glycol in acetone solution containing pyridine. The metal compounds used as the catalysts were the acetates and commercial products (guaranteed reagent grade) were used without further purification. Antimony (III) acetate was synthesized according to the method of Nerdel and Kleinwächter[7], and aluminium acetate by the method of Pande and Mehrotra[8].

The thermal decomposition of EDB in the presence of metal acetate (5 x 10^{-2} mol%) was carried out at 340°C in an ampoule sealed under reduced pressure. The extent of thermal-decomposition of EDB was determined by the author's method[6].

Figure 1 shows the variation of the time dependence of unreacted EDB with metal species. The slope corresponds to the rate constant of the thermal decomposition of EDB (see ref 6). *Figure 1* also shows the characteristics of each catalyst: e.g. titanium acetate markedly accelerates the reaction, while manganese acetate only has a slight effect, etc. This finding is consistent with the information obtained in *p–d* analysis of the polycondensation process of BHET[1].

The author[1,9] found that the stability constant of dibenzoyl methane (DBM) complex of each metal species was an excellent ordering factor of the catalytic activity of the metal compound in the transesterification of dimethyl terephthalate with ethylene glycol and in the polycondensation of BHET. As for the thermal degradation of PET, the logarithm of *d*-value was correlated by linear relationship (mountain-shaped) with the stability constant ($\log \beta_1$) of DBM complexes of the corresponding metal species[1].

The author attempted to apply $\log \beta_1$ to the ordering of catalytic activity of the metal compound in the thermal decomposition of EDB. The values of $\log \beta_1$ were shown in refs 1 and 9. The rate constants (k) after subtracting those for the reactions without catalyst[6] are plotted as $\log k$ against $\log \beta_1$ in *Figure 2*. A linear relationship (mountain-shaped) exists, and this relationship is quite similar to that between $\log d$ and $\log \beta_1$. This result supports the evaluation of catalytic activity of metal compounds in the thermal degradation of PET from *p–d* analysis.

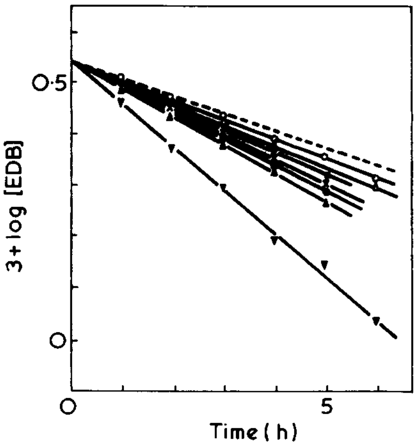

Figure 1 The thermal decomposition of EDB with various metal acetates as catalysts: O, Mn; △, Al; ▽, Sb; X, Pb; ●, Sn; ▲, Zn; ▼, Ti: — — —, without metal acetate (see ref 6)

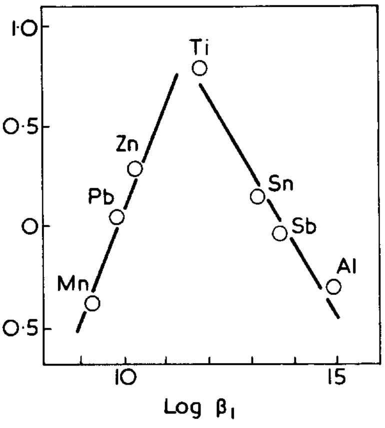

Figure 2 Rate constants of the thermal decomposition of EDB with various metal acetates as catalysts against stability constants of DBM complexes of the corresponding metal species

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