Studies on the formation of poly(ethylene terephthalate): 9. Thermal decomposition of ethylene dibenzoate as a model compound of poly(ethylene terephthalate)

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As a model compound for poly(ethylene terephthalate), the thermal decomposition of ethylene dibenzoate (EDB) was carried out at 330°–350°C. The EDB was determined from the ethylene glycol obtained on hydrolysis of the reaction mixture. The rate of decomposition, on the basis of the above determination, was found to obey first order kinetics. A comparison of the quantity of decomposed EDB with the quantity of benzoic acid suggested that usual approaches to the thermal decomposition of EDB on the basis of the determination of the quantity of benzoic acid were liable to error.

INTRODUCTION

In the polycondensation process of bis(2-hydroxyethyl) terephthalate (BHET) the thermal degradation of poly (ethylene terephthalate) (PET) occurs simultaneously. The author[1] found that this thermal degradation could be evaluated from the *d*-value in the kinetic treatment (*p–d* analysis) of the polycondensation process of BHET.

In the present study, the thermal decomposition of ethylene dibenzoate (EDB) was carried out as a model compound for PET.

The thermal decomposition of EDB has been studied by several researchers[2–4], and the products have been extensively identified. Among the many products benzoic acid (BA) was especially noted, and was used as an indication of the extent of thermal decomposition[4,5].

In the present study the thermal decomposition of EDB was followed by the measurement of the undecomposed EDB, and it was found that determination of BA was not a reliable method.

EXPERIMENTAL

Reagents

EDB was synthesised from benzoyl chloride and ethylene glycol in acetone solution containing pyridine.

Hydroquinone (HQ) and triphenyl phosphate (TPP) were commercial products (guaranteed reagent grade), and used without further purification.

Thermal decomposition

EDB was introduced into an ampoule, and dried at 50°C under reduced pressure for 20 h. The ampoule was sealed under reduced pressure, and left for a suitable time at 330°–350°C.

Determination of the quantity of undecomposed EDB

Excess NaOH (1N) was introduced into the reaction mixture dissolved in isopropanol, the solution refluxed for 30 min at 100°C, and titrated with 0.5 N HCl using phenolphthalein as an indicator. Excess $NaIO_4$ (0.02 M) was added to the solution, and after standing for 30 min at room temperature concentrated H_2SO_4 and 2 g of KI were added to the solution cooled with ice-cold water. After standing for 5 min the solution was titrated with 0.1 N $Na_2S_2O_3$.

Determination of the quantity of BA

It is difficult to determine the quantity of carboxylic acid in the mixture with carboxylic ester and carboxylic anhydride. The author found that the method proposed by Zimmermann and Leibnitz[4] was liable to give negative values for the carboxylic acid and that their procedure may lead to hydrolysis of the carboxylic ester.

The following method was found to be satisfactory. The sample was dissolved in acetone, and divided into two parts. One part was titrated with 0.1 N sodium methylate, and another, to which pyridine and water were added, with 0.1 N NaOH. The difference between the titres corresponded to the quantity of carboxylic anhydride, and the difference in titres between twice the former and the latter to the quantity of carboxylic acid.

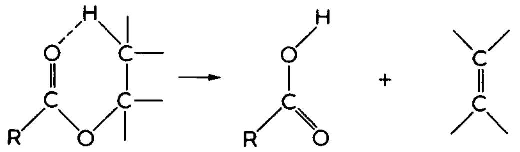
RESULTS AND DISCUSSION

Evaluation of the quantity of decomposed EDB

In previous studies[4,5] the extent of thermal decomposition of EDB was not evaluated from the quantity of decomposed EDB, but from the quantity of BA.

The quantity of carboxylic acid has been used as an indication for evaluating the extent of the thermal degradation of PET, and it was customary in the previous studies[6,7] to discuss the thermal degradation of PET on the basis of the quantity of carboxylic acid.

Usually, the thermal decomposition of carboxylic esters appears to be intramolecular in the following way:



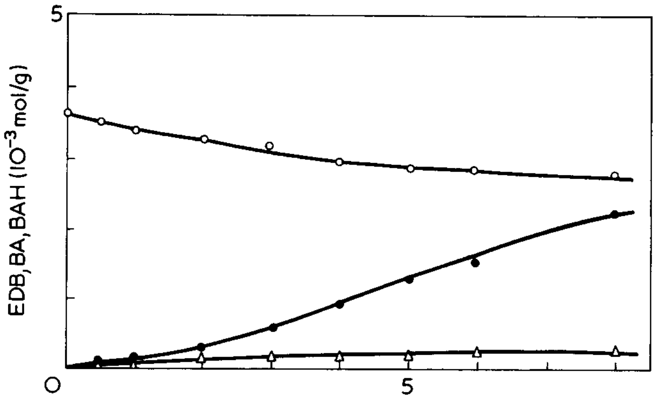


Figure 1 The thermal decomposition of EDB at 330°C: ○, EDB; ●, BA; △, BAH

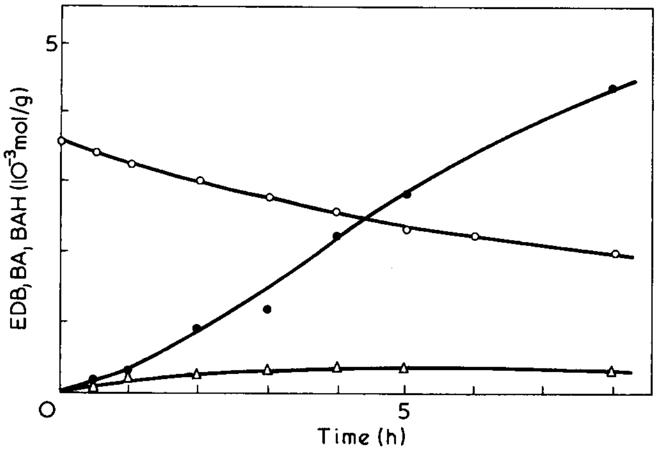


Figure 2 The thermal decomposition of EDB at 340°C: ○, EDB; ●, BA; △, BAH

This is a *cis* elimination reaction by E_i mechanism, and on this assumption, the thermal decomposition of EDB gives the corresponding acid (BA) and vinyl benzoate (VB).

Since there is some doubt that the determination of carboxylic acid directly corresponds to that of thermally decomposed EDB or degraded PET, the amount of thermally decomposed EDB was evaluated from the determination of the undecomposed EDB by measurement of the quantity of ethylene glycol obtained on hydrolysis of the reaction mixture, by the procedure described above.

Thermal decomposition of EDB

The thermal decomposition of EDB was carried out at 330°–350°C, and the quantities of undecomposed EDB, BA and benzoic anhydride (BAH)* formed are given in *Figures 1–3*.

If the thermal decomposition of EDB proceeds by E_i mechanism, the rate of decomposition should obey first order kinetics, viz.

$$\ln a_0/a = 2kt \tag{1}$$

where a is the concentration of EDB, k is a rate constant and 2 denotes that EDB has two ester bonds in its one molecule.

The linearity of the plot of log a against t (*Figure 4*) supports this assumption, and also indicates that the decomposed products do not autocatalytically accelerate the decomposition.

From *Figures 1–3*, the amount of BAH formed is small whilst the BA is formed in much larger quantities than corresponding to sample decomposition, and the yield time-course does not parallel that of the decomposition of EDB, but may be sigmoid. This result suggests that the de-

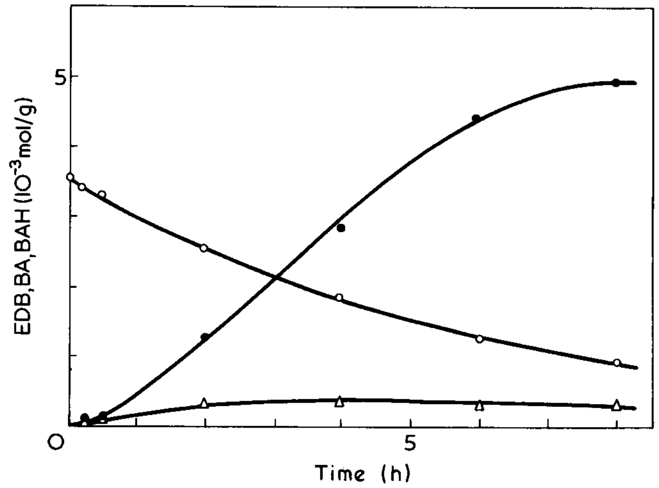


Figure 3 The thermal decomposition of EDB at 350°C: ○, EDB; ●, BA; △, BAH

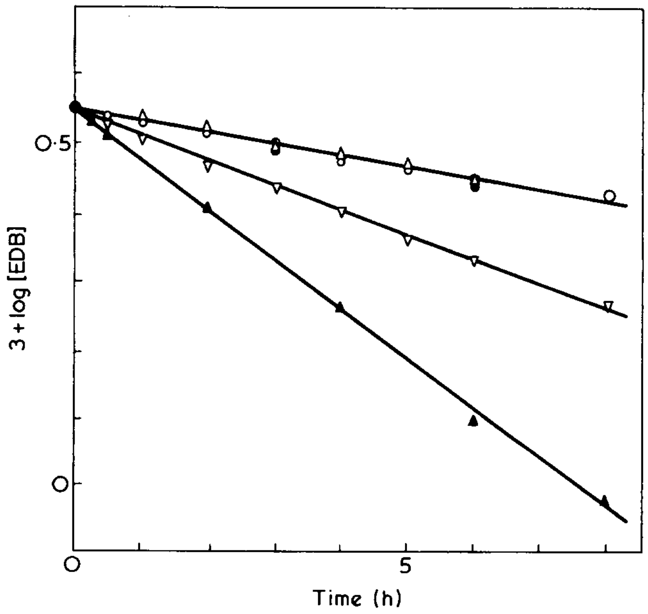


Figure 4 Application of equation (1) to the data for undecomposed EDB in *Figures 1–3* and *5*. Without additives: ○, 330°; ▽, 340°; ▲, 350°C. With additives at 330°C: ●, with triphenyl phosphate; △, with hydroquinone

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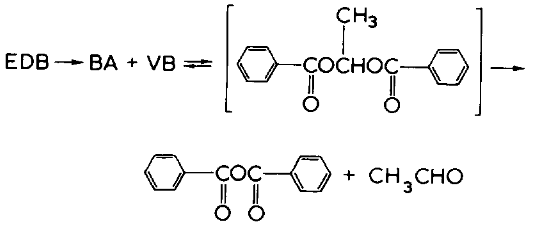
* BAH was reported to be formed as a result of Markownikoff addition of BA to VB, as shown below[2,4]:



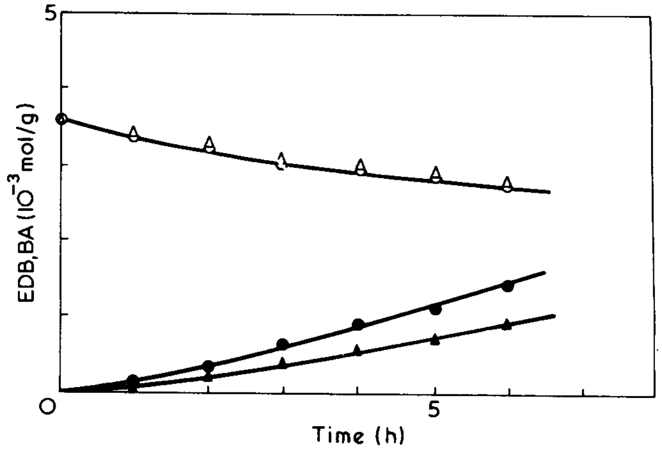


Figure 5 Effect of additives on the thermal decomposition of EDB at 330°C. With triphenyl phosphate: ○, EDB; ●, BA. With hydroquinone: △, EDB; ▲, BA

composition of EDB cannot be simply discussed from the quantity of BA.

Figures 4 and *5* represent the effect of additional TPP or HQ (5×10^{-2} mol%) on the thermal decomposition of EDB (330°C). These Figures show that the decomposition of EDB is little affected by either addition, but the quantity of BA is decreased by the addition of HQ (*Figure 5*). The result shows that HQ is not a stabilizer for the thermal decomposition of EDB and that measurement of the quantity of carboxyl group is unsatisfactory for the study of the thermal decomposition.

As described above, the direct method proposed must be adopted for the purpose of quantitative discussion of the thermal decomposition of EDB, the previous studies[3–5] based on the determination of BA must be accepted with caution.

The rate constants (k) in the thermal decomposition in *Figure 4* are: 330°C, 2.0×10^{-2} h^{-1}; 340°C, 4.3×10^{-2} h^{-1}; 350°C, 8.3×10^{-2} h^{-1} and the plots of log k against $1/T$ are linear and lead to an apparent activation energy E_a = 53.4 kcal/mol.

The apparent activation energy calculated by Goodings[3] from the quantity of distillates was 46.0 kcal/mol, whilst that of the thermal degradation of PET determined by the p–d analysis[1] of uncatalysed polycondensation of BHET, E_a = 49.5 kcal/mol. In view of *para*-substituents in PET molecules the activation energy for PET may be lower than for EDB[8], from this point of view, the value of E_a calculated by the author is more reasonable than that calculated by Goodings.

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