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THE USE OF THE RISING TEMPERATURE TECHNIQUE TO ESTABLISH THE KINETICS OF ACETALDEHYDE EVOLUTION DURING ATMOSPHERIC POLYMERIZATION OF BIS(HYDROXYETHYL)TEREPHTHALATE

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ABSTRACT

It is shown that the rising temperature method of establishing kinetic parameters can be applied to acetaldehyde evolution during the atmospheric polymerization of bis(hydroxyethyl)terephthalate. The Arrhenius parameters from the rising temperature method are $E = 190.8$ kJ mole^{-1} and $A = 8.0 \times 10^{11}$ s^{-1} and compare with those for the isothermal method of $E = 201$ kJ mole^{-1} and $A = 6.4 \times 10^{11}$ s^{-1}, both results obtained in the presence of the same catalyst. It is suggested that there is a direct relationship between the thermal degradation of poly(ethyleneterephthalate) and the formation of acetaldehyde. A first-order decay mechanism adequately describes the kinetic process.

INTRODUCTION

The preparation of poly(ethyleneterephthalate) (PET) is carried out by the polycondensation of bis(hydroxyethyl)terephthalate (BHET) or its oligomers at elevated temperatures and under reduced pressure. In spite of the high industrial production of PET, there is very little published information on the chemical reactions which are involved in its industrial synthesis [1–6]. More specifically, very little work has been published on the side reactions such as the thermal degradation of PET in the polycondensation of BHET.

Ritchie [7] concluded that PET breaks down thermally by a random primary chain scission. The resulting vinyl ester end groups are therefore destroyed in part by a series of competing secondary scissions, favoured by high temperatures, and in part by their readdition to carboxyl end groups to yield intermediate ethylene dicarboxylate units, which then form anhydride groups and acetaldehyde by disproportionation.

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According to Goodings [8], acetaldehyde is the major gaseous product of the thermal degradation of PET both at 283 and 306°C. Throughout the decomposition, it forms an approximately constant proportion (80%) of the gaseous products. In this study, the kinetics of acetaldehyde evolution during atmospheric polymerization of BHET are reported and rising temperature data are compared with the results from a series of isothermal experiments.

EXPERIMENTAL

Materials

All the materials used for polycondensation in this study were supplied by I.C.I. Fibres, Harrogate. Bis(hydroxyethyl)terephthalate was of industrial grade and was used without further purification. The catalysts employed were antimony oxide and a speciality catalyst (designated here catalyst X). Both catalysts were used without further purification. The 2,4-dinitrophenyl hydrazine and hydrochloric acid (2 M) used were obtained from normal suppliers and were of analytical grade. The acetaldehyde was determined by weighing the dried precipitate obtained from passing the exit gases from the polymerization through a saturated solution of 2-4 dinitrophenylhydrazine.

Polycondensation of bis(hydroxyethyl)terephthalate

The equipment used for the atmospheric polycondensation of bis(hydroxyethyl)terephthalate and the determination of the acetaldehyde formed is shown in Fig. 1. The polymerization tube was lowered into the liquid bath

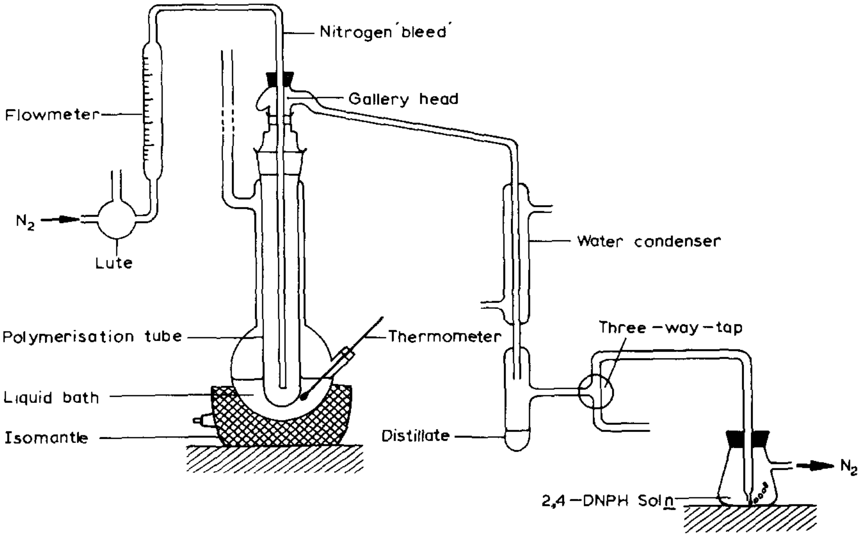


Fig. 1. Apparatus used for the atmospheric polycondensation of BHET and the determination of the acetaldehyde formed.

and 200 p.p.m. (0.06 g) of the appropriate catalyst was added to the monomer. When the monomer had melted, the nitrogen "bleed" was introduced and the nitrogen was passed through the melted mixture at a constant rate (100 ml min^{-1}). The procedure was repeated with the bath held at various constant temperatures in the presence of the catalyst. It was important to pass nitrogen at a constant rate because nitrogen, as well as stirring the reaction mixture, helps to "drive out" the acetaldehyde formed.

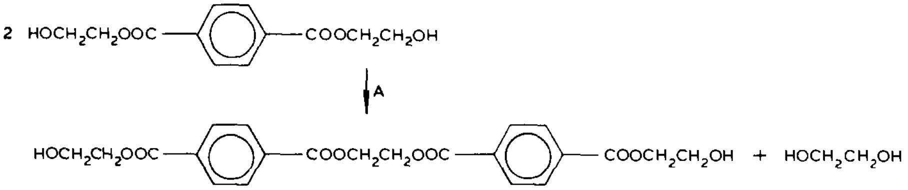
At the outlet, the acetaldehyde and nitrogen were passed through 30 ml of 2,4-DNPH solution. The yellow precipitate which formed was filtered off, dried and weighed. The amounts of precipitate formed over noted time intervals were determined at various temperatures (265, 270, 278, 282, 285 and 290°C).

The rising temperature polycondensation of BHET

The experimental procedure was exactly the same as that for the isothermal polymerization except that the temperature of the liquid bath was raised very slowly throughout the polycondensation. The temperature of the bath was raised by connecting the isomantle to an automatic heating device, which increased the temperature of the system at a constant rate (1.038×10^{-3} °C s^{-1}).

RESULTS AND DISCUSSION

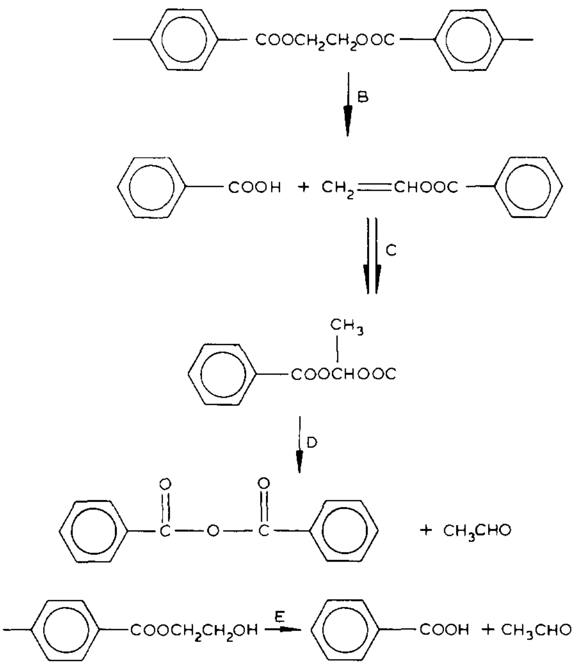
The polycondensation reaction which leads to the formation of poly(ethyleneterephthalate) can be represented as



During the polycondensation of BHET, the following side reactions are known to occur in parallel with the above main reaction [7,9].

The propagation reaction, which increases the molecular weight, and the degradation reaction, which decreases the molecular weight, occur simultaneously [9].

When the molecular weight of the polymer is increasing, the propagative reaction, A, is prevailing over the degradative reactions. The molecular weight starts to fall once the extent of degradation exceeds that of propagation.



Reactions B, D and E, which account for the formation of acetaldehyde during the polycondensation of BHET, are enhanced as the temperature of the reaction is raised. According to Tomita [9], the degradation reaction is much more influenced by a temperature change than the propagation reaction. Marshall and Todd [10] observed a fall in the melt viscosity of poly(ethyleneterephthalate) over the temperature range 282–320°C.

Figure 2 shows the formation of acetaldehyde (expressed as moles of acetaldehyde formed per mole of monomer) during the polycondensation of BHET in various constant temperature experiments. This can be expressed in terms of the concentration of monomer remaining in the melt (designated as *C* in Fig. 3). *C* can be regarded as the fraction of material undecomposed. If the fraction decomposed is represented by α, the *C* is represented by $1\text{-}\alpha$. Figure 4 shows a plot of $\ln 1/C$ against time, which shows a linear relationship for the data obtained at 265°C. Similar linear relationships between $\ln 1/C$ and time were established in the experiments carried out at 270, 278, 282, 285 and 290°C. The calculation of the specific reaction rate at these temperatures can be achieved on the basis that the isothermal kinetic mechanism is of the type

$$\frac{d\alpha}{dt} = K(1-\alpha)$$

i.e. a first-order process, when plots of $\ln(1/1-\alpha)$ against time should be linear as already noted (see Fig. 4). The Arrhenius plot from this isothermal data is shown in Fig. 5 from which the activation energy can be calculated as

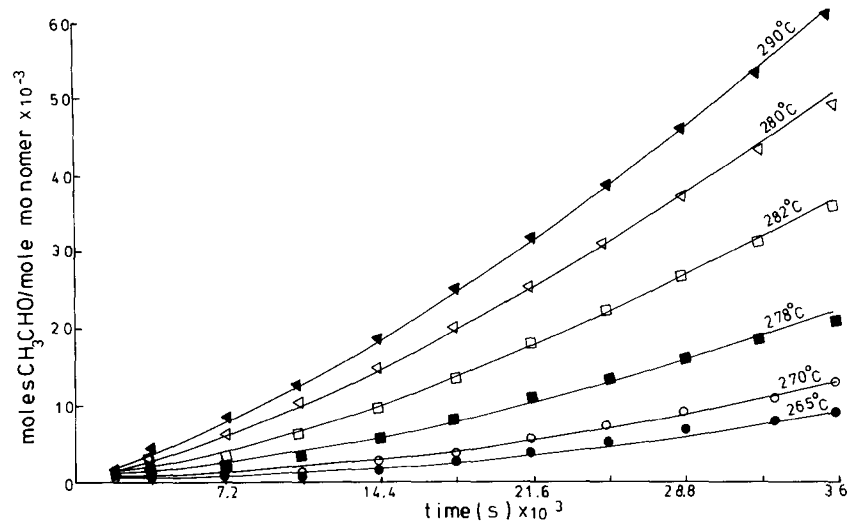


Fig. 2. Formation of acetaldehyde during polycondensation of BHET in various constant temperature experiments in the presence of catalyst X.

201 kJ mole^{-1} and the pre-exponential factor, *A*, as 6.4×10^{11} s^{-1}. These two parameters and the already noted first-order decay mechanism would seem to offer a complete description of the kinetic behaviour.

To study the formation of acetaldehyde kinetically, it was important to bubble the nitrogen gas through the molten mixture at a constant rate because Goodings [8] found from his work on the thermal degradation of PET from stirred polymer that the rate of evolution of acetaldehyde at

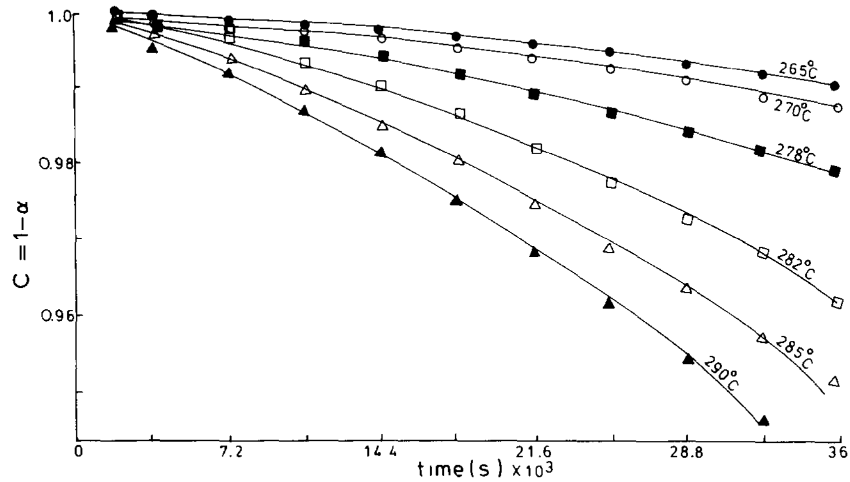


Fig. 3. The disappearance of monomer (C) from the reaction mixture with time (isothermal data).

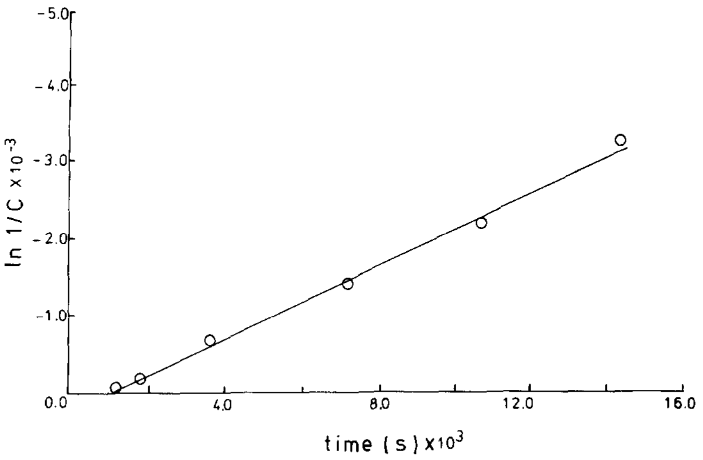


Fig. 4. Plot of ln $1/C$ against time at 265°C.

282°C was 1.7×10^{-3} moles/repeat unit h^{-1}, but when the polymer was unstirred, the rate was one tenth of this value or less. Goodings' value for the rate of evolution of acetaldehyde at 282°C agrees well with the one obtained from the data presented in this study, which is 3.4×10^{-3} moles/repeat unit h^{-1}. Goodings has also suggested that the activation energy of acetaldehyde (146 kJ mole^{-1}) obtained from the rate of fall of intrinsic viscosity and that for the process of acetaldehyde formation (149 kJ mole^{-1}) are very similar. It may therefore be reasonable to suggest that there is a direct relationship between the thermal degradation of PET and the formation of acetaldehyde. The activation energy calculated from our isothermal data was of the same order as Goodings', but somewhat higher.

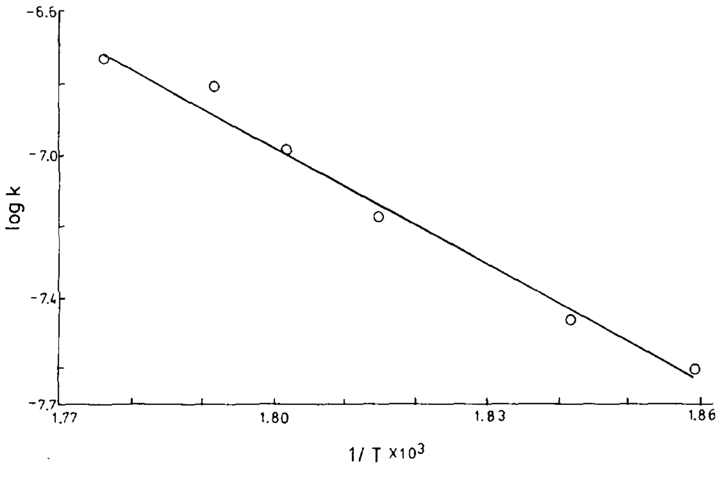


Fig. 5. Arrhenius plot from isothermal data using catalyst X.

The data for the reaction catalysed by antimony trioxide can be treated in a similar way. The Arrhenius plot obtained for this system is shown in Fig. 6 and this gives $E = 209.9$ kJ mole^{-1} and $A = 1.81 \times 10^{14}$. The first-order decay mechanism was again shown to be operative.

The rising temperature method of kinetic analysis can be used to establish the kinetic parameters with considerable saving of effort if a first-order decay mechanism can be presumed. This method, like others, uses the kinetic equation in the differential form. This avoids the difficulties of handling the integral of $e^{-E/RT}dT$ which presents several problems [11].

The method entails the use of the kinetic expression in the differential form

$$\frac{d\alpha}{dt} = Kf(\alpha) \tag{1}$$

where α is the fraction decomposed at time t, K is the rate constant to be used in the Arrhenius equation and $f(\alpha)$ is some function of α which describes the form of the kinetic expression.

To conform to the traditional practice, the kinetic expression should be similar to that utilized in homogeneous kinetics. Here the kinetic expression is of the form

$$\frac{dc}{dt} = Kf(c) \tag{2}$$

where c is the concentration at time t and K is the specific rate constant. In

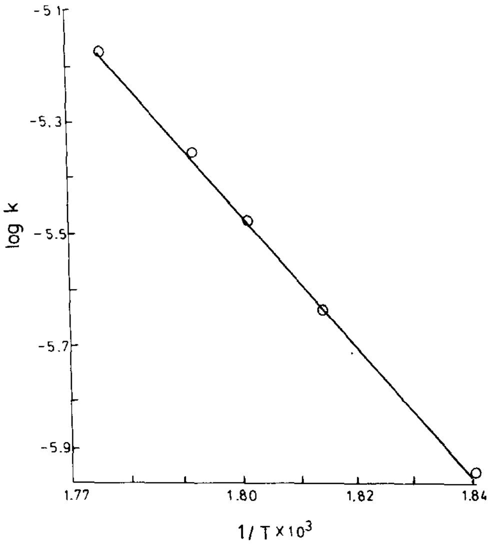


Fig. 6. Arrhenius plot from isothermal data using antimony oxide as catalyst.

this expression, as c tends to unity, then $f(c)$ tends to unity as well and

$$\frac{dc}{dt} = K$$

The Arrhenius equation then takes the form

$$K = A\, e^{-E/RT} \tag{3}$$

or

$$\log K = \log A - \frac{E}{RT} \tag{4}$$

where T is the temperature (in K), R the gas constant, E the activation energy and A the pre-exponential function. From these equations, it follows that K is the rate of the reaction at unit concentration and A is the specific rate constant at infinite temperature.

By the nearest analogy in eqn. (1) relating to solid state decomposition, it follows that as α tends to zero, c tends to unity, then $f(\alpha)$ must tend to unity for

$$\frac{d\alpha}{dt} = K$$

This happens if

$$f(\alpha) = (c)^n \tag{5}$$

but not if

$$f(\alpha) = [-\log(c)]\, p \tag{6}$$

or

$$f(\alpha) = (\alpha)^q \tag{7}$$

All three forms, i.e. eqns. (5)–(7), are found based on both experimental observation and theoretical models. Only those conforming to eqn. (5) adhere strictly to the principal definition which allows the constant K to be used in the Arrhenius equation.

In rising temperature experiments, a temperature programme is imposed on the system, i.e. a linear rise with time. The equation describing this is

$$T = T_0 - bt \tag{8}$$

where T_0 is the initial temperature and b the rate of rise of the temperature with time. It follows from eqns. (1) and (8) that

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} = \frac{K f(\alpha)}{b} \tag{9}$$

and

$$K = \frac{(d\alpha/dT)b}{f(\alpha)} \tag{10}$$

From the isothermal experiments, the acetaldehyde-forming reaction was determined to be first-order. Therefore, when a first-order function is used

$$f(\alpha) = (1 - \alpha) = C \tag{11}$$

$$K = \frac{(\mathrm{d}\alpha/\mathrm{d}T)b}{C} \tag{12}$$

An experiment similar to the isothermal experiments already reported was performed using catalyst X, but with a programmed temperature rise (as indicated in the experimental section). The calculation involves supposing that the $f(\alpha) = 1 - \alpha = C$, but this has already been shown to be true. Using eqn. (12), values of k for each temperature were calculated and these allowed a plot to be made of log k against $1/T$ from which the Arrhenius parameters may be determined (see Fig. 7).

The advantage of this simple direct method of utilising rising temperature data over methods is that, in the application of rising temperature experiments, investigators assume a single Arrhenius expression and seek to fit an accurate kinetic expression to the data. In this present approach, the analysis allows one to judge the Arrhenius parameters; the fact that $f(\alpha)$ may be an approximation does not affect by much the calculation of E and A. The Arrhenius parameters calculated, in this instance, from the rising temperature method on the basis of a first-order decay mechanism are $E = 190.8$ kJ mole^{-1} and $A = 8.1 \times 10^{11}$ s^{-1}. The activation energies obtained by both isothermal and rising temperature methods are seen to be very similar and in good agreement with the value reported in the literature [9] for the degradative reaction during the polycondensation of BHET.

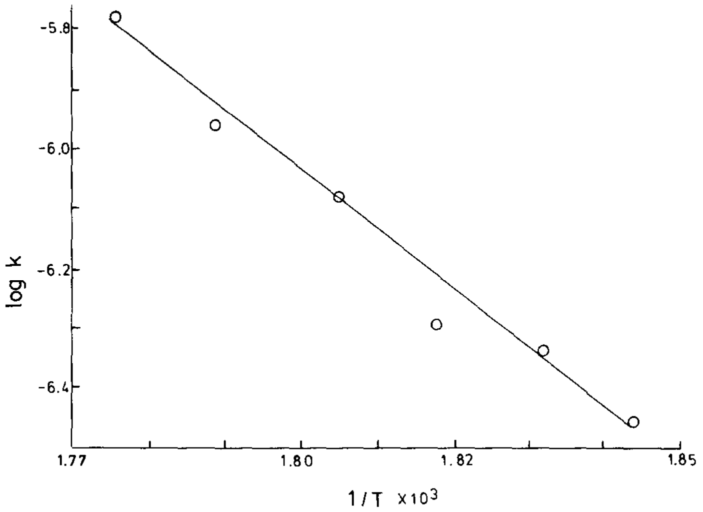


Fig. 7. Arrhenius plot calculated from rising temperature data using catalyst X.

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