

# A Study on the Polycondensation of Bis-Hydroxyethyl Terephthalate

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## Synopsis

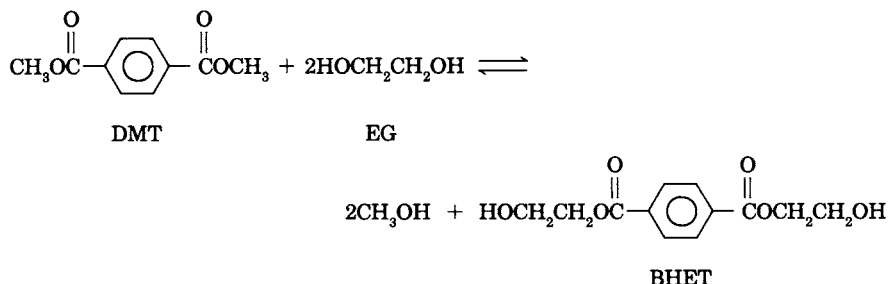
Poly(ethylene terephthalate) (PET) was synthesized from its monomer bis-hydroxyethyl terephthalate (BHET), in the presence of  $Sb_2O_3$  catalyst. A second order irreversible reaction model was developed, and the apparent rate constant was evaluated by observing the course of intrinsic viscosity change. At 278°C, the apparent rate constant in the presence of 0.025% (by weight) of  $Sb_2O_3$  was found to be 0.945 L/mol h.

## INTRODUCTION

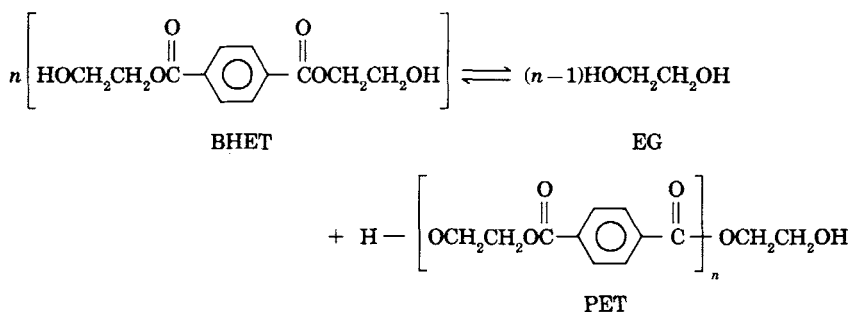
PET has been manufactured commercially either by the direct esterification of ethylene glycol and terephthalic acid or by the transesterification route in which dimethyl terephthalate is reacted with ethylene glycol usually in the presence of a catalyst. The kinetics of PET polycondensation via both these routes has received the attention of several investigators. However, very little has been written about the polycondensation of PET from its monomer BHET. Stevenson and Nettleton<sup>1</sup> assumed the polycondensation of PET in the presence of  $Sb_2O_3$  to be a reversible second-order reaction. When BHET trimer was polycondensed at 251°C in the presence of 0.025% (by weight) of  $Sb_2O_3$ , an equilibrium constant of 0.363 was obtained corresponding to a forward reaction rate constant of 0.28 L/mol h.

In this work, BHET obtained by the transesterification of dimethyl terephthalate (DMT) and ethylene glycol (EG) is separated from its oligomers by a process of recrystallization. The kinetics of polycondensation of pure BHET is then studied by observing the intrinsic viscosity change. The reactions involved in this study are as follows:

### 1. Ester interchange or transesterification:



## 2. Polycondensation:



## EXPERIMENTAL

## Synthesis of BHET

**Transesterification.** A round-bottom flask was charged with DMT and excess EG in the molar ratio 1:12 and zinc acetate (0.4 mmol/100 mL EG) was added to the mixture to act as a transesterification catalyst. Chloroacetic acid (1 mmol/100 mL EG) was added to inhibit the formation of catalyst-inhibiting substances. From this reaction mixture, methanol (boiling point 64.7°C) was removed by distillation until the head temperature of the column rose to 150°C. The reaction product consisting of BHET monomer, oligomer, and unreacted EG was allowed to cool to room temperature and then thoroughly agitated in distilled water. The mixture was now filtered to separate the monomer and oligomer from the unreacted EG which is highly water soluble. The white residue was then oven dried at 70°C for 24 h to remove all traces of EG or methanol.

**Purification of BHET.** The solid residue was added to distilled water and the mixture was brought to boil. The boiling solution was quickly filtered to separate the BHET oligomer from the monomer which has appreciable solubility in water at 100°C. The mother liquor was cooled to 10°C, and crystals of BHET monomer were recovered by filtration. This process was repeated until the monomer and oligomer were completely separated. The monomer crystals were then vacuum dried in an oven at 70°C for 24 h. A polarizing microscope was used to determine the melting point of BHET monomer. The monomer was observed to melt in the temperature range 107–109°C whereas the oligomer mixture melted between 170 and 175°C. As stated in the literature,<sup>2</sup> pure BHET melts in the temperature range 109–110°C, indicating that the BHET synthesized here was in the pure form.

## Synthesis of PET

Polycondensation of purified BHET was carried out in a test tube in the presence of  $\text{Sb}_2\text{O}_3$  catalyst (250 ppm). The reaction temperature was maintained at 278°C by immersing the test tube in a thermoregulator controlled  $\text{NaNO}_2$ – $\text{KNO}_3$  salt bath. A slow stream of nitrogen gas was bubbled through the melt for a period of 2 h, and the system pressure was then

reduced to 1.5 mm Hg. Polycondensation was now continued for 6 h with simultaneous removal of ethylene glycol and other volatiles by distillation. A sample of the polymer was removed every 2 h from the reaction tube to observe the course of polymerization by intrinsic viscosity measurements. During sampling, the polymer was first allowed to cool to room temperature under nitrogen to prevent degradation by oxidation.

### Solution Viscosity

Dilute solution viscosity of the polymer was measured using an Ubbelohde viscometer. The advantage of using this viscometer is that the measurement is independent of the amount of solution in the viscometer and measurement at a series of concentrations can easily be done by successive dilutions.

The polymer sample was accurately weighed and dissolved in a known volume of symmetric tetrachloroethane-phenol (1:1 vol). The solution was maintained at 130°C for 20–25 min to ensure the complete dissolution of the polymer into the solvent. The solution was then cooled to room temperature and filtered through a 0.45 mm cellulose filter paper. Using the method of successive dilutions, the relative viscosities were measured at 25°C. The solution concentration was restricted to the range that gave relative viscosities between 1.1 and 1.5. Relative viscosity data as a function of concentration was extrapolated to infinite dilution by means of the Huggins equation<sup>3</sup> to obtain the intrinsic viscosity  $[\eta]$ .

## THEORETICAL CONSIDERATIONS

### Kinetics of BHET Polycondensation

A simplified kinetic model was proposed based on the following assumptions:

1. The polycondensation reaction is almost completely irreversible. This assumption is justified by the fact that ethylene glycol is distilled off under reduced pressure from the reaction mixture, thereby causing the equilibrium to shift to the right.

2. The reaction is second order with respect to BHET alone.

3. The effect of side reactions on the rate equation can be neglected, assuming that only minimal amounts of side products are formed.

Based on these assumptions, the rate equation for monomer consumption can be written as

$$-\frac{dB}{dt} = 2kB^2$$

where  $B$  is the number of moles of particles having  $-\text{CH}_2\text{CH}_2\text{OH}$  end groups and  $k$  is the second-order reaction rate constant. Integration from initial to final condition yields

$$\bar{P}_n = \frac{B_0}{B} = 1 + 2kB_0t$$

where  $\bar{P}_n$  is the degree of polymerization and  $B_0$  is the initial number of moles of BHET.

Multiplying the above equation by  $M_0$ , the molecular weight of the repeating unit (192), and assuming the polymer to be sufficiently high molecular, we obtain

$$\bar{M}_n = 2kM_0B_0t \quad (1)$$

The number average molecular weight,  $\bar{M}_n$ , is related to the intrinsic viscosity by

$$[\eta] = K\bar{M}_n^a$$

where  $K$  and  $a$  are constants which are functions of the solvent as well as polymer type.

For PET as stated in literature,<sup>4</sup> in tetrachloroethanephenol (1:1 vol) at 25°C,

$$[\eta] = 2.1 \times 10^{-4}(\bar{M}_n^{0.82}) \quad (2)$$

Combining eqs. (1) and (2) yields

$$\log[\eta] = -3.678 + 0.82 \log(2kM_0B_0) + 0.82 \log t \quad (3)$$

If the second-order model assumption is valid, then a plot of  $\log[\eta]$  vs.  $\log t$  should yield a straight line whose intercept on the Y-axis can be used to calculate the reaction rate constant.

## RESULTS AND DISCUSSION

Viscosity data from three kinetic runs each conducted for 8 h was found to agree within  $\pm 5\%$ , indicating that the kinetic runs were fairly reproducible. Viscosities averaged over the three runs at each time interval were then used for studying the course of polycondensation. As shown in Figures 1 and 2, intrinsic viscosity and molecular weight of PET increased linearly with reaction time. At the end of 8 h of reaction, an intrinsic viscosity of 0.5369 dL/g was obtained corresponding to a molecular weight of 14,312.

The plot of  $\log[\eta]$  vs.  $\log t$  (Fig. 3) yielded a straight line of slope 0.8099 and intercept  $-1$ . The slope, which corresponds to the exponent  $a$  in the viscosity-molecular weight relationship, compared favorably with the value of 0.82 reported in the literature.<sup>4</sup> This validates the assumption of second-order kinetics for the polycondensation of PET. The rate constant was then calculated from eq. (3) and found to be 152.4/mol h. In terms of volume of polymer melt (assuming volume to be nearly constant), the rate constant can also be expressed as 0.945 L/mol h.

The reaction rate constant obtained in this study was observed to be slightly lower than that obtained by Stevenson and Nettleton,<sup>1</sup> for the polycondensation of linear ethylene terephthalate. On the basis of the derived activation energy of 29 kcal, the authors predicted a forward reaction rate constant of 1.28 L/mol h at 280°C.

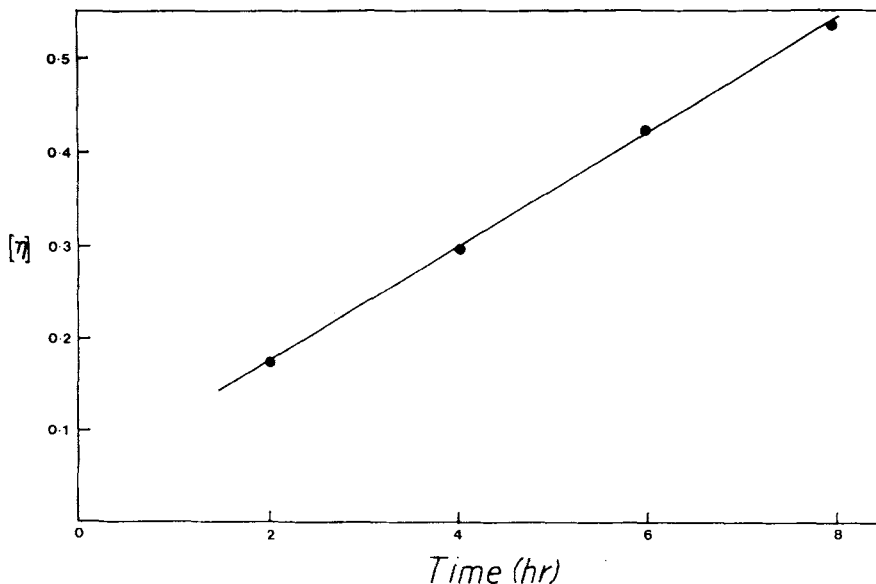


Fig. 1. Intrinsic viscosity vs. reaction time for PET.

One explanation for the lower reaction rate constant could be based on the theory given by Challa<sup>5</sup> that the hydroxyethyl end groups in a BHET oligomer or in PET are much more reactive than the hydroxyethyl end groups in a BHET monomer. Stevenson and Nettleton<sup>1</sup> developed a hypothesis that the BHET end groups compete successfully with oligomer end groups for antimony trioxide catalyst and that the BHET catalyst product is unreactive in polymerization. It would then follow that in the presence of a catalyst the polycondensation rate between two BHET oligomers or between a BHET oligomer and a BHET monomer is much faster than the

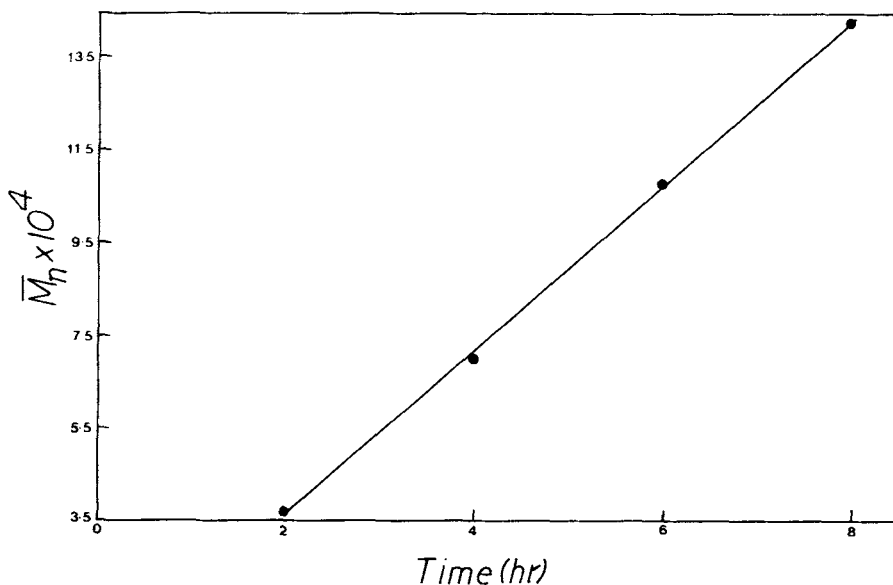


Fig. 2. Molecular weight vs. reaction time for PET.

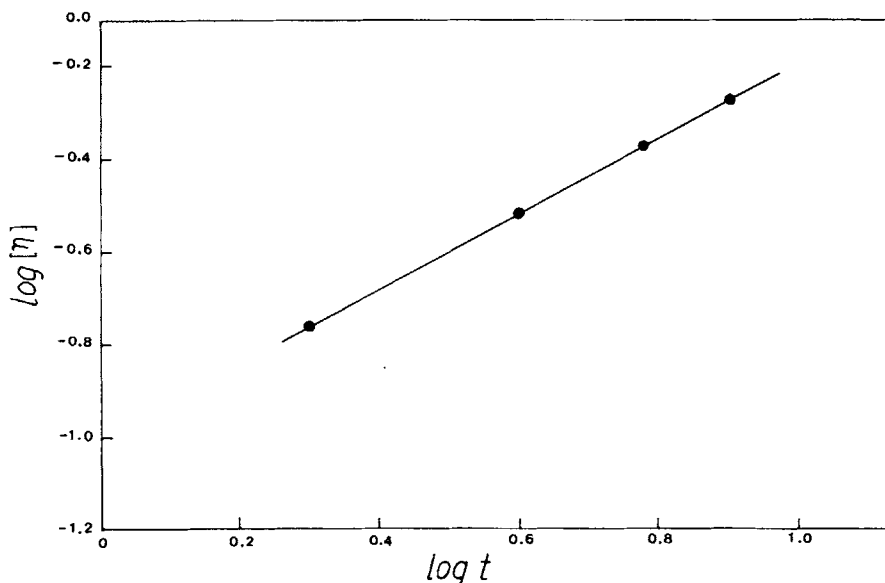


Fig. 3.  $\log[\eta]$  vs.  $\log t$  for PET.

polycondensation rate between two BHET monomers. Therefore, while polycondensing pure BHET, the initial reaction rate might be significantly suppressed. It should also be noted that while estimating the forward reaction rate constant, Stevenson and Nettleton took full account of the effect of the reverse reaction on the observed forward rate. By contrast, the second-order kinetic model proposed here was based on the assumption that the vacuum volatiles were completely removed from the system, thereby preventing the occurrence of any significant reverse reaction. However, it is likely that small quantities of glycol condensing along the sides of the reaction tube might trickle back onto the polymer melt and initiate a glycolysis reaction. If this occurred, the second-order kinetic model would have to be modified to take into account the reverse reaction, and the rate constant estimated here would represent a value significantly less than the true forward rate. However, the linear relationship between  $\log[\eta]$  and  $\log t$  indicates that the viscosity data fits the irreversible second-order model proposed here. Hence, the lower value of rate constant can be attributed solely to the possible deactivation of  $Sb_2O_3$  catalyst by the BHET monomer.

### SUMMARY AND CONCLUSIONS

Intrinsic viscosity data averaged over three kinetic runs was observed to fit the proposed kinetic model, indicating that the polycondensation of BHET was second order with respect to BHET alone. Removal of ethylene glycol and other volatiles under reduced pressure prevented the occurrence of any significant reverse reaction or side reactions. At 278°C, the apparent forward reaction rate constant for BHET polycondensation in the presence of  $Sb_2O_3$  catalyst was found to be 0.945 L/mol h. The polycondensation rate might have been suppressed by the initial deactivation of the  $Sb_2O_3$  catalyst by the BHET monomer as stated in literature by Stevenson and Nettleton.<sup>1</sup>

### References

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