

Aspects of the chemistry of poly(ethylene terephthalate): 5. Polymerization of bis(hydroxyethyl)terephthalate by various metallic catalysts

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(Received 6 September 1983; revised 11 January 1984)

Bis(hydroxyethyl)terephthalate (BHET) was polymerized to poly(ethylene terephthalate) (PET) in the presence of various metallic catalysts. The influence of the nature and concentration of these catalysts on the rate of polymerization has been investigated. The effect of the reaction temperature has also been studied. The order of decreasing catalytic influence of various metal ions, on the polymerization of BHET was found to be: $Ti > Sn > Mn > Zn > Pb > No$.

(Keywords: poly(ethylene terephthalate); polymerization; bis(hydroxyethyl)terephthalate; metallic catalysts)

INTRODUCTION

The preparation of poly(ethylene terephthalate) (PET) is usually carried out by polycondensation of bis(hydroxyethyl) terephthalate (BHET) at elevated temperatures and reduced pressures. In spite of high industrial production of PET only a few reports about the polycondensation reaction have been published¹⁻¹⁴.

Stevenson and Nettleton¹ studied the polycondensation of low-molecular weight PET over the temperature range in the presence of antimony trioxide catalyst, essentially paralleling Challa's earlier research² on the uncatalysed reactions. The catalysed reactions were faster, but the rate coefficient for polycondensation was relatively low even though the reverse reaction had been taken into account. It was considered that the vacuum volatile constituents of the reaction mixture were responsible for the deactivation of the catalysts, thus, slowing down the reaction. Antimony trioxide does not vigorously catalyse the polycondensation reaction of the pure monomer, bis(hydroxyethyl)terephthalate, and Stevenson and Nettleton concluded that the latter substance was responsible for the proposed deactivation of antimony trioxide, as a catalyst.

EXPERIMENTAL

Materials

The catalysts used in this study were commercial grade products and they were used without further purification. Bis(hydroxyethyl)terephthalate was supplied by the Im-

perial Chemical Industries Limited, Fibres Division, Harrogate and was also used without further purification.

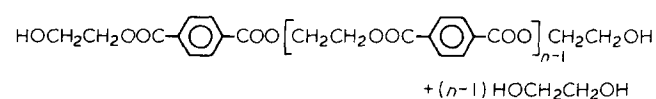
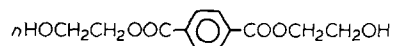
Polymerization of bis(hydroxyethyl)terephthalate

The polycondensation was carried out in a 250 ml polymerization tube, fitted with take off point for the by-products of the reaction. Bis(hydroxyethyl)terephthalate (50 g) was introduced into the polymerization tube and lowered into the dimethylphthalate vapour bath. After BHET had melted the appropriate catalyst was added and nitrogen was bubbled through the melt very slowly. An initially low vacuum was applied to the system and after 30 min the vacuum was increased to full value (0.1 mmHg). The polymerization was continued isothermally ($283^\circ + 1^\circ\text{C}$) for the required period of time. The polymer was then extruded into cold water.

The intrinsic viscosity of the polymer was determined in a capillary viscometer, using a mixture of phenol-tetrachloroethane (1:1 w/w) as a solvent, at 20°C .

RESULTS AND DISCUSSIONS

During the polycondensation of bis(hydroxyethyl)terephthalate, ethylene glycol is evolved and poly(ethyleneterephthalate) is formed;



The polycondensation of BHET has been studied by several workers in an attempt to determine the order of the reaction. However, contradictory results have been

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reported. According to Griehl and Schnoek³ the polycondensation is a first order reaction, whilst Korshak⁴ and Skwarski⁵ consider it to be a second order reaction.

The effect of catalyst nature

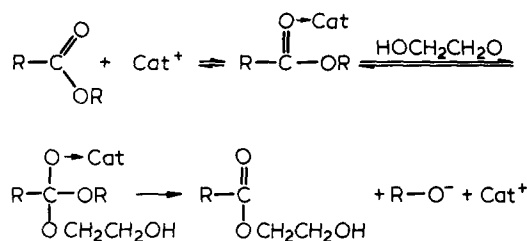
Bis(hydroxyethyl)terephthalate was polymerized to poly(ethylene terephthalate) using various catalytic systems, as the reaction proceeds very slowly in the absence of any catalyst. The rate of this reaction is influenced greatly by the nature of polycondensation catalyst. This effect was studied by polymerizing the monomer for a fixed period of time (60 min) using a catalyst concentration of 2×10^{-4} mol metal ion/mol BHET. At the end of the experiment the intrinsic viscosity of the polymer formed was determined and this was used as a guide to catalyst activity.

The results of these experiments are presented in *Table 1*. It can be seen that the titanium based catalyst (KTiOx) is the most active catalyst as far as the polymerization of BHET to PET is concerned. The disadvantage of using this catalyst commercially is that it imparts an undesirable yellow coloration to the polymer. The results show that antimony and tin based catalysts are less active than the titanium based catalysts but the polymer produced is of better quality.

The results in *Table 1* also indicate that the most effective transesterification catalysts⁶ namely, lead acetate, zinc acetate and manganese acetate are least effective in the polymerization of BHET, conversely potassium titanium oxalate, dibutyltin oxide and antimony trioxide are the least active transesterification catalysts.

Tomita⁷ has discussed the ordering factor for catalytic activity in some detail. According to his view the propagation reaction proceeds by the nucleophilic attack of hydroxyl end groups upon ester carbonyl groups in the 2-hydroxyethyl benzoate end groups. The reaction intermediate is regarded as a complex formed by the coordination of ester carbonyl groups to the metal species. This coordination lowers the electron density of the carbonyl atom and facilitates the nucleophilic attack of the hydroxyl group upon this positively polarized carbon atom. This reaction mechanism is very similar to that of the transesterification of dimethylterephthalate with ethylene glycol.

An electrophilic mechanism can also be formulated thus:



In this scheme a glycoxy anion is involved; it is difficult, however, to associate such a mechanism with solid phase polycondensation where no ionizing medium is present.

To be effective as a catalyst the metal ion must be able to form an intermediate (transition state) complex with the reacting molecules and the rate at which the metal is able to exchange molecules (the turn-over rate) appears to be one of the most important factors governing the activity of a catalyst.

The propagation and degradation reactions are both

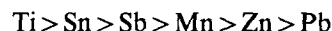
Table 1 Effect of the nature of the catalyst on the formation of PET at 290°C using catalyst concentration of 2×10^{-4} mol/mol BHET

Catalyst	Intrinsic viscosity of polymer
KTiOx	0.662
SnO(But) ₂	0.567
Sb ₂ O ₃	0.522
Mn-Acetate	0.490
Zn-Acetate	0.440
Pb-Acetate	0.435
No Catalyst	0.230

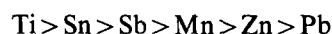
reported to occur simultaneously⁸ and they may be catalysed by the same catalyst. The extent to which these reactions are enhanced determines the suitability of any metal complex as a polymerization catalyst. A desirable catalytic system would be one which gives a high value for the ratio of propagation to degradation reaction.

Tomita⁸, from his analysis of the propagation and degradation reactions found that titanium acetate had such a favourable ratio in the polycondensation process but not in the transesterification reaction. This is most likely due to a difference in the bonding state of each reactant. For example, the comparison of BHET or its polycondensate to dimethylterephthalate in terms of their end groups suggests that the electron density of benzoate carbonyl group is lower in the 2-hydroxyethyl benzoate group than in the methyl benzoate group. This is a result of the terminal hydroxyl group being electron withdrawing and the hydrogen bond effect. Therefore the metal-methyl benzoate bond is stronger than the metal-2-hydroxyethyl benzoate bond.

If Tomita's approach is adopted it would at first seem reasonable to suggest that the strength of metal-reactant bond decreases in the following order:



However, as shown in *Table 1*, the activity of the polycondensation catalysts increases in the order



The above order of catalytic activity is very similar to that obtained by Nondek and Malek⁹ for the polycondensation of bis(hydroxyethyl)-isophthalate.

The metal oxygen bond lengths reported are not in agreement with the above assumption about the order of the bond strength, in fact they suggest an order of activity which is quite the reverse. Therefore, it is not possible to attribute the activity of the catalyst to the metal-oxygen interactions as outlined for the transesterification catalysis and so, some other explanation is required.

An attempt is made to explain the catalytic activity of the metal ions on the basis of 'hard' and 'soft' acids and bases. Ahrlund *et al.*¹⁵ concluded from their survey of relative affinities of ligand atoms for metal ions, that metal could be divided into two classes. In 'class a' are metals that form stable complexes with ligands whose donor atoms are first-row elements (N,O,F) while in 'class b' are metals that prefer to form bonds to ligands having second-row elements as donor atoms (P,S,Cl). They suggested that the degree of b-character of a metal is dependent on its oxidation state. In low oxidation states where the metal

possesses non-bonding electrons are capable of being used in bonding with the ligands, the degree of b-character is greater.

According to Ahrlund and co-workers titanium, tin, germanium, antimony and zinc are 'class a' metals because of their ability to form stable complexes with oxygen, whereas manganese and lead are classified as the borderline acceptors. This is in line with the metal-oxygen bond lengths discussed for the transesterification catalysts, but does not explain the different activities of the catalysts in the transesterification and the polycondensation reactions.

Other explanations for catalytic activity have been based on the chelate effect. But it would seem that a number of factors influence the degree of activity and because of this complexity no simple explanation has yet been described which satisfactorily accounts for the observed phenomenon.

The effect of catalyst concentration

The dependence of polycondensation rate on the catalyst concentration in the region of $5 \times 10^{-5} - 2.5 \times 10^{-4}$ mol metal ion/mol BHET, have been investigated. The results presented in Figure 1 show the effect of catalyst concentration on the intrinsic viscosity of the polymer formed.

Of the three catalysts used (titanium, antimony and tin) titanium catalyst has shown the greatest activity in the polymerization of BHET to PET and antimony trioxide has proved to be the least effective of the three catalysts. As the concentration of catalyst was increased the intrinsic viscosity (*IV*) of the polymer also increased for a fixed period (60 min) of polymerization, until a maximum value of *IV* was recorded. On increasing the catalyst concentration further a drop in the intrinsic viscosity was observed. This pattern of behaviour was demonstrated by each of the three catalysts employed.

Therefore, a region of optimum concentration was observed for each catalytic system under investigation. It was found (Figure 1) that the catalyst which enhanced the propagation reaction (the reaction which increases the molecular weight) to a greater extent also catalysed the degradation (the reaction which decreases the molecular weight) reaction more effectively. Our results show that potassium titanium oxalate (the most effective polycondensation catalyst used) caused the greatest fall in the intrinsic viscosity of the polymer on further addition of

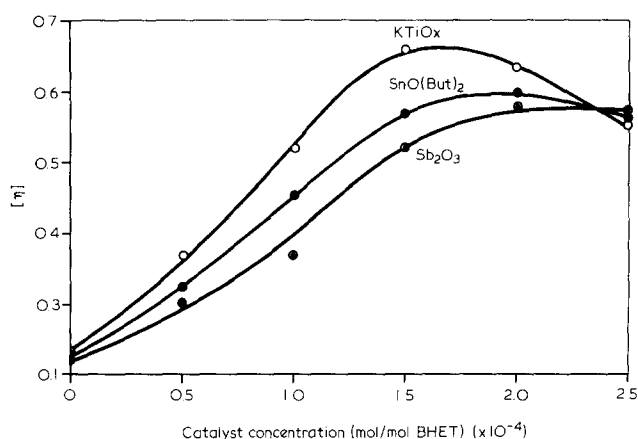


Figure 1 Effect of catalyst concentration on the polymerization of bis(hydroxyethyl)terephthalate

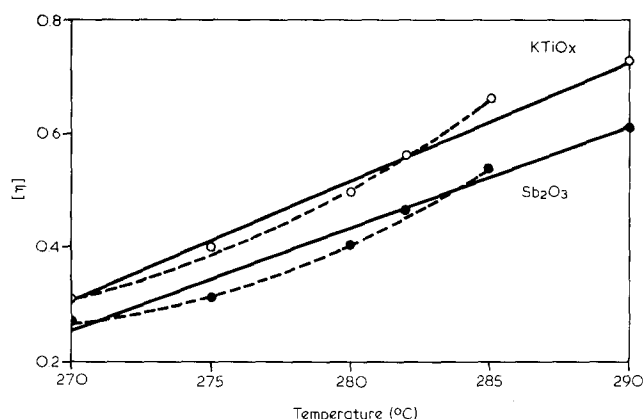


Figure 2 Effect of temperature on the polymerization of bis(hydroxyethyl)terephthalate

the catalyst beyond the optimum concentration region, conversely antimony trioxide (the least active of the three catalysts under investigation) did not cause any significant fall in the intrinsic viscosity of poly(ethylene terephthalate) as shown in Figure 1.

The dependence of optimum catalyst concentration is greatly influenced by the catalytic activity of the system employed. The approximate optimum concentration for KTiOx , $\text{SnO}(\text{But})_2$ and Sb_2O_3 are 1.5×10^{-4} mol metal catalyst/mol BHET, 2×10^{-4} mol/mol BHET and 2.4×10^{-4} mol/mol BHET, respectively. The fall in the intrinsic viscosity on the addition of catalyst beyond the optimum concentration implies that there is a competition for catalyst between the sites responsible for the polymerization reaction (largely end groups) and the sites on formed polymer which allow chain scission (e.g. ester oxygens). As the end group concentration falls and thus binds less of the metal ion catalyst, there is more metal ion available for the ester oxygen to complex as a preliminary to the scission reaction and, of course, the more polymer that has been formed the greater the number of ester oxygens which can compete with the end groups for the metal ion.

Thus, in the presence of 'excess' catalyst the degradation reaction is favoured. It follows that a mechanism for removing 'excess' catalyst as the reaction proceeds would allow the achievement of a higher molecular weight polymer in a shorter time.

The effect of temperature

The polycondensation of bis(hydroxyethyl)terephthalate was carried out at 270°, 275°, 280° and 295°C, using potassium titanium oxalate as catalyst. The results are plotted in Figure 2. These results show that the increase in intrinsic viscosity was linear with temperature. A closer analysis of the Figure suggests that if the points at 290°C were ignored, two curves may be obtained which are almost parallel to each other (shown by broken lines). This phenomenon may be explained by considering the degradation reaction which is much more influenced by a temperature change than the propagation reaction. As a result higher molecular weight polymer may be obtained by using lower temperatures and longer polymerization periods.

ACKNOWLEDGEMENTS

The authors wish to thank Mr A. A. B. Browne and Dr W.

Burns of the Imperial Chemical Industries Limited (Fibres Division, Harrogate) for their helpful discussions and suggestions on many scientific matters.

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