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THE DETERMINATION OF CATALYTIC ACTIVITY OF VARIOUS METALLIC COMPOUNDS IN THE POLYCONDENSATION OF BIS(HYDROXYETHYL)TEREPHTHALATE USING DSC AND TG TECHNIQUES

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ABSTRACT

The catalytic activities of various metal compounds in the polycondensation of bis(hydroxethyl)terephthalate to poly(ethyleneterephthalate) have been investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The peak maximum of the reaction peak in the DSC test (T_{max} in °C) gave values which corresponded well with the temperature at which the initial mass loss was observed in thermogravimetric analysis experiments (T_0 in °C). A comparison of T_{max} and T_0 at a fixed concentration with conventional methods shows good agreement. The order of catalytic activity obtained using both techniques is:

ZnAc > SnO(But)$_2$ > Sb$_2$O$_3$, KTiOx > Gegly.

The effect of the concentration of various catalysts on the polycondensation of BHET has also been investigated. These observations agree with data obtained by conventional methods but the techniques used here are judged to be more convenient.

INTRODUCTION

A method was developed by Wolf et al. [1] in 1978 to measure the catalytic activity of metal compounds in the metal-catalysed polycondensation of bis(hydroxyethyl)terephthalate (BHET) to give poly(ethyleneterephthalate) (PET). The method is based on differential scanning calorimetry (DSC) and offers a rapid, simple method for testing potential catalytic compounds. In this method BHET is mixed with the catalyst under investigation and a small sample is placed in the sample cell of the measuring head of the DSC, but the reference cell is left empty. The cells are subjected to a predetermined heating rate and the temperature of the measuring head (T) is plotted against the difference in temperature between the two cells (ΔT). The design of the equipment enabled different atmospheres to be used or a vacuum to be applied to the measuring head. In the experiments reported [1], a pressure of 40 Torr (53.3 mbar) was used.

In the studies reported by Wolf et al. [1] two endothermic peaks were observed: the first corresponds to the melting of BHET and the second corresponds to the polycondensation reaction. The peak maximum of the reaction peak (T_{max} in °C) was used as the ordering factor for the catalytic activity of polycondensation catalysts. A comparison of T_{max} at a fixed concentration with previously published kinetic measurements [2–7] showed that this value was lower for catalysts which gave faster reactions.

In the present study improvements in the DSC method are described and it is shown that thermogravimetric analysis (TG) could be used for the determination of catalytic activity in these polycondensation reactions. In this case the temperature at which the initial mass loss (T_0 in °C) occurred could also be used as the ordering factor for catalytic activity. These thermal analysis methods were therefore chosen in the present study to investigate the catalytic activity of various metal compounds.

EXPERIMENTAL

Materials

The BHET was supplied by ICI Fibres, Harrogate, and it was purified by recrystallization from hot water prior to its use. All the catalysts used were obtained from Hopkin and Williams. The BHET and the catalyst were ground and brushed through a 106 μm sieve to give fine loose powders.

Determination of catalytic activity

Thermogravimetric analysis was carried out using Du Pont 950 thermogravimetric analyser which was attached to the control unit of Du Pont 900 thermal analyser. The polycondensation was carried out by placing a 10 mg sample in a platinum pan hanging from the balance arm of the TG unit and heated by a 500 W quartz tubular furnace. A plot of mass loss versus temperature was obtained from which T_0 (onset temperature) can be determined (see Fig. 1).

Differential scanning calorimetry (DSC) experiments were carried out using a Du Pont 990 thermal analyser in conjunction with the Du Pont 910 differential scanning calorimeter module. The presentation of data as a temperature difference plot (ΔT) against the temperature (T) leaves this technique indistinguishable from DTA but the name DSC is retained here

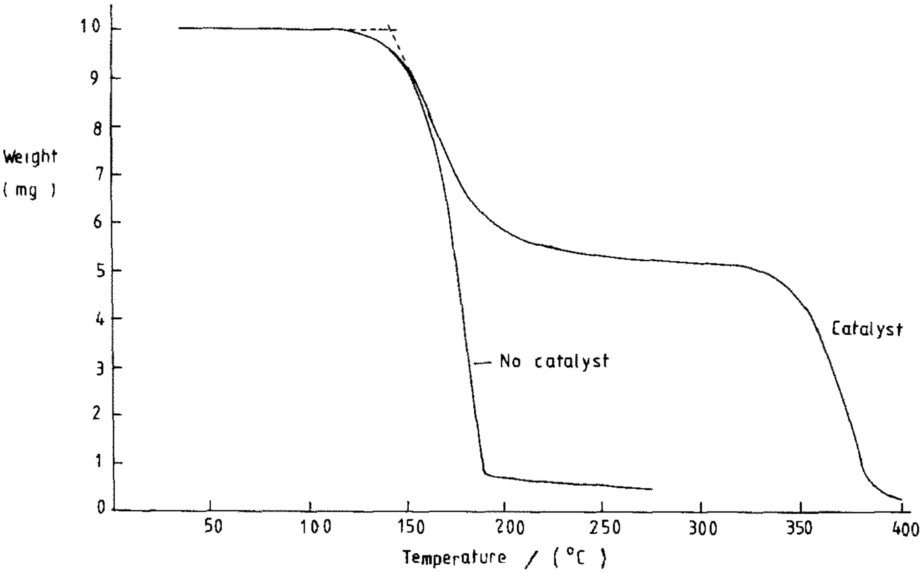


Fig. 1. Determination of T_0 values from TG curves without catalyst and with zinc acetate catalyst (10 mmol Zn/mol BHET), both under vacuum.

because it is commercially so designated. The peak maximum of the reaction peak is determined as shown in Fig. 2. The heating rate used in both TG and DSC experiments was 10°C min^{-1}.

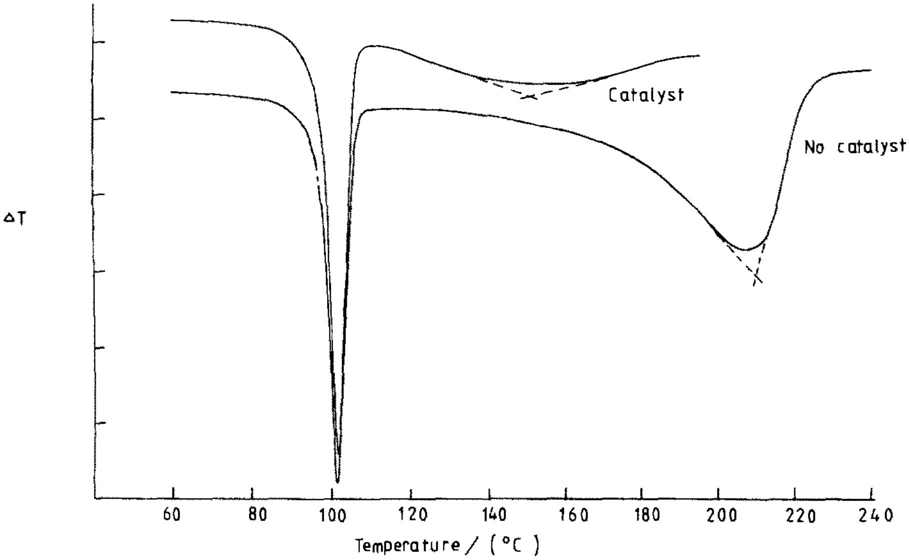
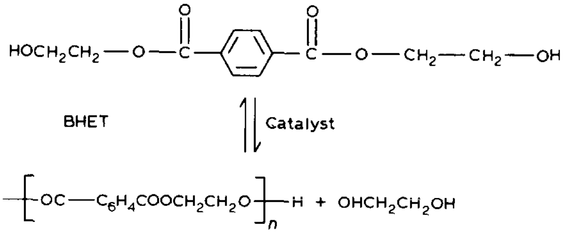


Fig. 2. Determination of $T_{\max}$ values from DSC curves without catalyst and with zinc acetate catalyst (10 mmol Zn/mol BHET) both under vacuum.

RESULTS AND DISCUSSION

Poly(ethyleneterephthalate) is produced industrially by the polycondensation of BHET in the presence of a catalyst. The basic reaction which leads to the formation of PET is:



Ethylene glycol (EG) is formed during this polycondensation and the TG method is based on the mass loss due to the evolution of EG. The temperature at which this mass loss begins is designated T_0 (the onset temperature of the polycondensation reaction). The DSC method of catalytic activity determination is based on the heat changes which occur when the polycondensation is in progress. T_{max} is the temperature at which the DSC peak reaches a maximum.

Figure 2 shows the DSC plots obtained in the absence of catalyst. There is a sharp peak at ca. 105 °C corresponding to the melting of BHET. This peak does not correspond exactly with the melting point of the pure monomer because DSC is a dynamic measurement and the position of the peak depends to some extent on the heating rate. It is necessary, therefore, only to compare DSC curves obtained at the same heating rate. In the absence of catalyst a peak occurs at ca. 211 °C which corresponds to polycondensation of BHET under vacuum (7 mm Hg). Figure 2 also shows data obtained in the presence of zinc acetate catalyst. The polycondensation peak has shifted to a lower temperature (ca. 150 °C at 10 mmol Zn/mol BHET) but has become shallower than the peak observed in the absence of catalyst. The procedure adopted to determine T_{max} is illustrated in the figure.

The possibility that TG data might provide an alternative method to DSC in order to determine the temperature at which polycondensation of BHET occurs was examined. The elimination of ethylene glycol (EG) from the system during polycondensation accounts for the mass loss recorded. The BHET was thoroughly dried prior to use, therefore any mass loss of the sample must be due to either the evaporation of the sample or due to the elimination of EG formed during the polycondensation. Figure 1 shows the TG trace for BHET in the absence of any catalyst; clearly the process occurring is the evaporation of the monomer under vacuum, and the sample has completely evaporated by ca. 200 °C. Hence, the peak observed with DSC at ca. 211 °C is simply that due to evaporation of the monomer. Figure 1 also shows the TG trace obtained in the presence of zinc acetate (10 mmol

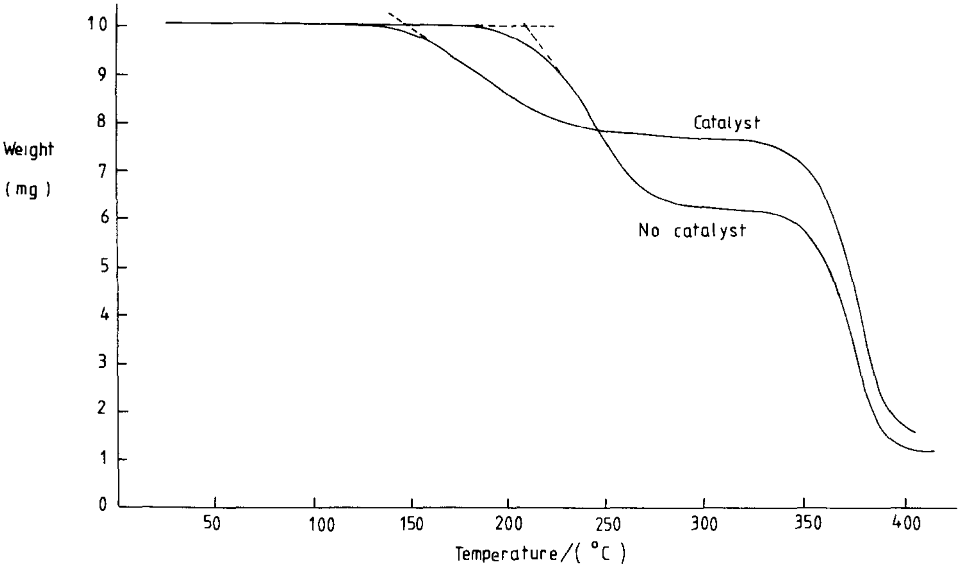


Fig. 3. TG curves of BHET in nitrogen above and in the presence of zinc acetate catalyst (10 mmol Zn/mol BHET).

Zn/mol BHET) also under vacuum. Polycondensation of BHET has occurred in the region 150–200°C but the mass loss (ca. 45%) is more than can be accounted for from the elimination of EG above (24.4%); hence about 31% of BHET has evaporated. Thus there are two competing processes, namely polycondensation and evaporation of the monomer. The shallow peak in the DSC trace in the presence of catalysts corresponds to these simultaneous processes (Fig. 2).

The phenomenon of evaporation of BHET under vacuum is further supported by DSC experiments in which BHET was polymerized in the presence and in the absence of zinc acetate catalyst, the polymerized BHET was cooled and the run was repeated. The polymer melting peak at ca. 264°C was observed only in the case of catalysed polymerization. Thus no or negligible polymerization occurred in the absence of catalysts and the only process taking place was evaporation of BHET.

The TG and DSC experiments were repeated at atmospheric pressure of nitrogen and air. Figure 3 shows the TG data obtained in the absence and in the presence of catalyst, at 1 atm of nitrogen; under these conditions polycondensation is the main process even in the absence of catalyst. TG experiments in air were similar. It is apparent that TG data at atmospheric pressure under nitrogen (or air) represents a convenient method for following the polycondensation of BHET. The DSC data at an atmospheric pressure of nitrogen are shown in Fig. 4. The peaks correspond to the process observed with the TG experiments (Fig. 3). These peaks are some-

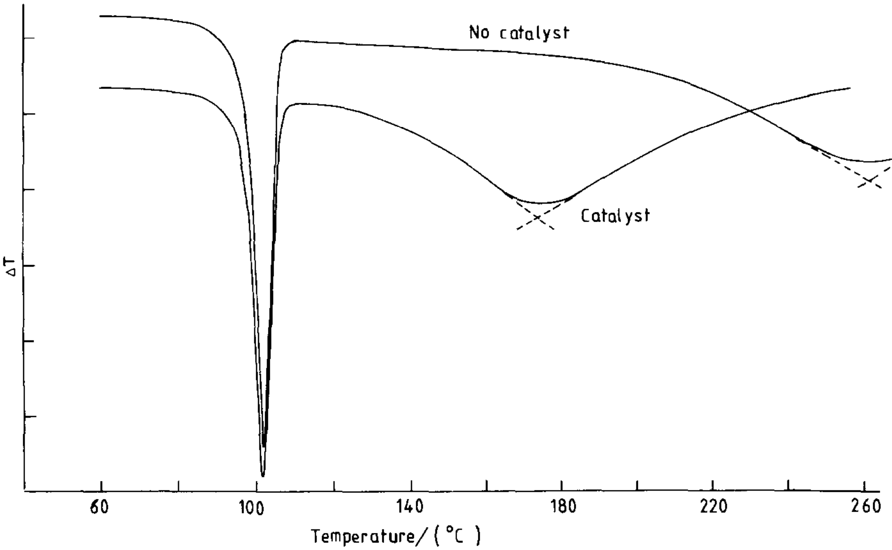


Fig. 4. DSC curves of BHET in air above and in the presence of zinc acetate catalyst (10 mmol Zn/mol BHET).

what sharper than those obtained under vacuum and it was easier to determine the position of T_{max}. At atmospheric pressure, under air and in the absence of catalyst, a peak (for which T_{max} was recorded) was observed at ca. 260 °C. In the presence of zinc acetate this was shifted to a lower value of T_{max}. Hence it it possible to determine the effect of various catalysts on T_{max} values from DSC traces at atmospheric pressures.

The effect of various catalysts and their concentrations on the T_{max} and T_0 values of the polycondensation were recorded at atmospheric pressure. Data were obtained with the following catalysts at a catalyst level of 5 mmol/mol BHET; zinc acetate, antimony trioxide, germanium oxide (although this was added as germanium glycolate), dibutyl tin oxide and potassium titanium oxalate (Table 1). The effect of these mixtures is also recorded in Table 1. The more effective catalysts cause the reaction to occur at lower temperatures. Hence lower values of T_{max} and T_0 from DSC and TG, respectively, correspond to greater activities of the catalysts investigated. It can also be seen from Table 1 that TG and DSC gave the same order of catalytic activity, but that the T_{max} values are higher than the T_0 values. These results show that the most active polycondensation catalyst was zinc acetate ($T_{max} = 176$ °C and $T_0 = 151$ °C) and the least activity was shown by germanium glycolate ($T_{max} = 250$ °C and $T_0 = 205$ °C). The mixtures of catalysts exhibited activities which were intermediate of the catalyst used in the mixture. The results illustrated here show the effect of concentrations of the various catalysts on T_{max} and T_0 values of the BHET polycondensation reaction. The effect of the concentration of zinc acetate catalyst on the T_{max} (DSC)

TABLE 1

A comparison of the T_{max} and T_0 values for various catalytic systems at atmospheric pressure using catalyst concentration of 5×10^{-3} mol/mol BHET

Catalyst	T_{max} (°C) DSC	T_0 (°C) TG
Zn acetate	176	151
SnO(But)$_2$	186	160
Sb_2O_3	228	200
Ge glycolate	250	205
Pot. titanium oxalate	204	185
Sb_2O_3/Zn acetate	182	175
SnO(But)$_2$/Zn acetate	174	155
Sb_2O_3/Ge glycolate	234	204
No catalyst	260	225

and T_0 (TG) values at atmospheric pressure is shown in Fig. 5. The relative effect of the various catalysts can be judged by inspection of Fig. 6. It can be seen that these values are lowered as the catalyst concentration was increased especially at the lower values (up to 5 mmol/mol BHET). The dependence of T_{max} and T_0 values on the chemical nature of the catalyst was, however, much greater than the dependence on possible concentration variation as shown in Fig. 6. The fact that T_{max} is invariably lower in vacuum than in air is shown in Fig. 7. The same is true for the values of T_0

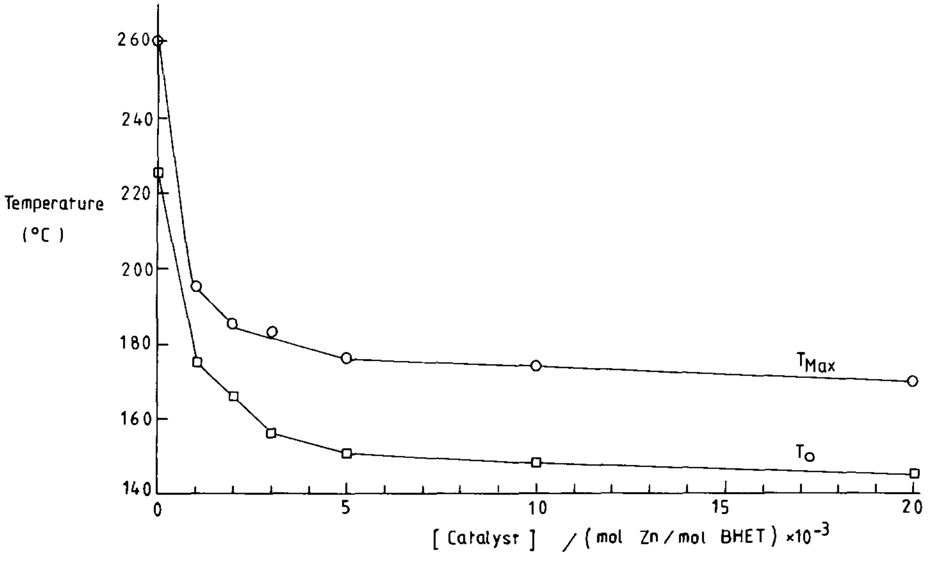


Fig. 5. Effect of concentration of zinc acetate catalyst on T_{max} (DSC) and T_0 (TG) values at atmospheric pressure.

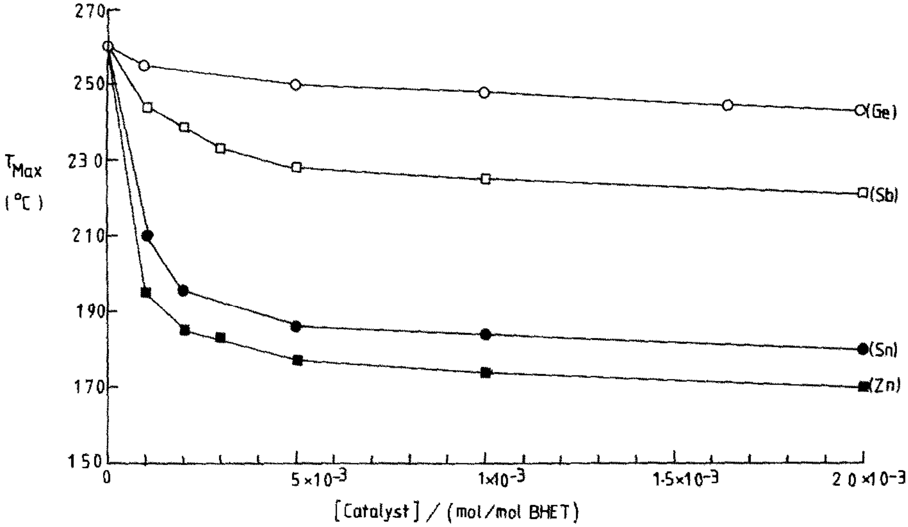


Fig. 6. The effect of concentrations of various catalysts on T_{max} values of BHET polycondensation reaction.

shown in Fig. 8. The fact that T_{max} values are usually higher than corresponding T_0 values is to be expected since T_{max} represents a peak maximum while T_0 corresponds to the initiation of the reaction.

The results shown here confirm Wolf et al.'s [1] studies and show that both DSC and TG can be used to correlate catalyst activity in the polycondensation of BHET. It is recommended that more reliable data are

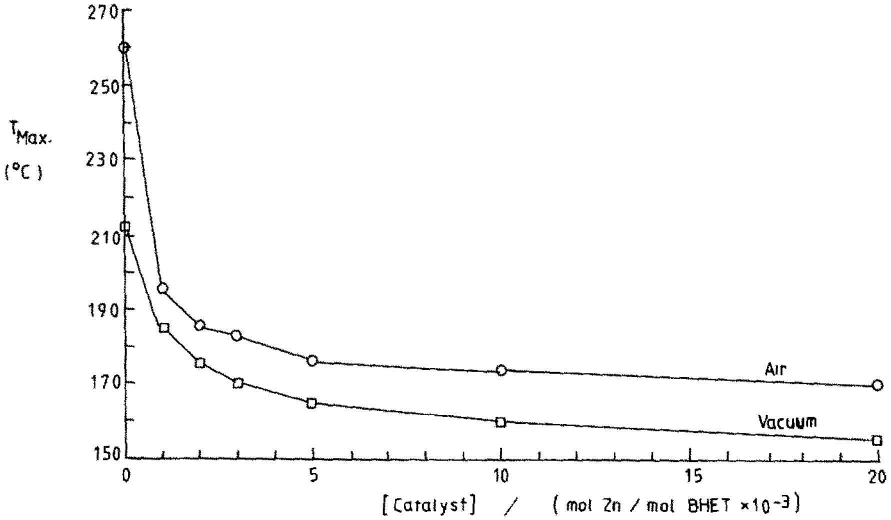


Fig. 7. Comparison of T_{max} values obtained under 1 atm of air and in vacuum.

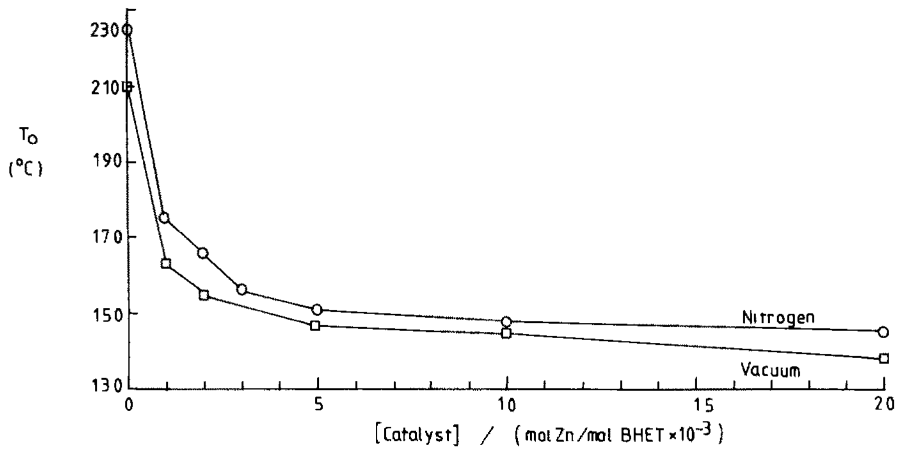


Fig. 8. Comparison of T_0 values obtained under 1 atm of nitrogen and in vacuum.

obtained for comparison purposes when the thermal analysis experiments are carried out at 1 atm of nitrogen or air.

The advantages of DSC and TG techniques over the conventional methods of catalytic activity determination are:

(i) the results obtained by these techniques show better reproducibility,
(ii) the experimental time is much shorter,
(iii) the amount of sample required for evaluation is small, and
(iv) the mixing of catalysts and BHET in definite combinations is much simpler to set up and easier to analyse.

Finally, the order of catalytic activity obtained by both techniques is:
ZnAC > $SnO(But)_2$ > Sb_2O_3, KTiOx > Gegly
where Ac ≡ acetate, But ≡ Butyrate, gly ≡ glycolate, Ox ≡ oxalate).

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