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Optimization of simultaneous thermal analysis for fast screening of polycondensation catalysts

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Abstract

Dynamic simultaneous thermal analysis was optimized to screen activity of different catalysts for polycondensation of bis-hydroxy ethylene terephthalate (BHET) to polyethylene terephthalate. Reactions were performed by heating BHET to 300 °C at a linear heating rate in 50 μl thermal analysis crucibles under inert gas purging. A sensitive and reproducible screening method was obtained after overcoming of critical problems such as monomer evaporation, catalytic activity of crucible material, and optimization of gas purging, monomer amount in the crucible and heating rate. Under the applied conditions mass transport limitations were absent and the reaction was controlled solely by chemistry. The temperature at which maximum reaction rate occurs was used as an index of catalytic activity. It was obtained from maximum differential scanning calorimetry signal together with the maximum derivative of thermogravimetry signal. Temperature at which the reaction starts was also applied as an activity index. It was obtained from the onset of mass loss. The value of these three indices was smaller for more active catalysts.

The optimized method was applied to study the activity of a new polycondensation heterogeneous catalyst based on hydrotalcite. This new catalyst was shown to be much more active than the conventional antimony catalyst under the applied conditions.

Keywords: Simultaneous thermal analysis; Poly(ethylene terephthalate); Catalyst screening; Hydrotalcite

1. Introduction

Poly(ethylene terephthalate) (PET) is an important polymer as reflected in its annual demand (37 million tons was the global demand for 2004) [1]. It is used as a commodity as well as engineering product for diverse applications. Its main end products are fibers, packaging articles, and films. PET has one of the fastest growing markets and will continue this trend in the future boosted by world economic growth and continuous development of new application fields. PET is nowadays synthesized mainly by esterification of purified terephthalic acid (PTA) with ethylene glycol (EG) followed by polycondensation of the esterification products, bis-hydroxy ethylene terephthalate (BHET) and its oligomers. Polycondensation rate is controlled by the removal of the by-product EG. The polycondensation stage occurs in a special type of reactor, which generates a large specific surface area. Antimony (Sb) in different forms, mainly oxide and acetate, is utilized to catalyze the polycondensation step in most of PET plants [2]. However, the presence of Sb as heavy metal in food packaging is a subject of increasing scrutiny. This, together with the search for a more active catalyst, is

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Abbreviations: BHET, bis(hydroxyl ethylene terephthalate); DSC, differential scanning calorimetry; DTG, first derivative of thermogravimetry; EG, ethylene glycol; HT, hydrotalcite catalyst; M_n, number average molecular weight (g/mol); M_w, weight average molecular weight (g/mol); PET, poly(ethylene terephthalate); Sb, antimony; STA, simultaneous thermal analysis; TG, thermogravimetry; TGA, thermogravimetric analysis; T_{max}, temperature at which maximum signal occurs (°C); T_o, onset temperature at which mass loss begins (°C)

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behind the ongoing research in many companies to replace Sb.

In 1978, Wolf et al. [3] applied dynamic differential thermal analysis to screen catalysts for polycondensation of BHET to PET. Bhatty et al. [4] introduced dynamic thermogravimetric analysis (TGA) as a catalyst screening aid in 1986. They used the temperature at which initial mass loss occurs (onset temperature T_0) as an activity index. Zimmerer et al. [5] studied the effect of crucible material on the polycondensation of pure BHET. They found that aluminium has a strong catalytic effect, which makes it non-favourable as a polymerization container material. On the other hand, these authors found that alumina has a negligible activity. Moreover, their experiments showed severe BHET evaporation, which was countered by developing a mathematical model that accounts for its effect of on thermal data evaluation.

The aim of this work was to optimize fast screening of polycondensation catalysts by simultaneous gravimetric and calorimetric thermal analysis (TG/DSC–STA). Application of STA for this aim would give a better panorama of the ongoing physical (monomer evaporation, crystallization, melting, etc.) and chemical (polycondensation) processes. The optimized method was used to study different recipes of a new heterogeneous catalyst based on hydrotalcite. To judge the new catalyst, its efficiency was compared to that of the conventional Sb compounds.

2. Experimental

2.1. Chemicals

BHET (>93%) was purchased from TCI, EG (>99%) from Merck, antimony triacetate from Atofina, hydrotalcite (HT) catalyst from Sasol GmbH. All the applied chemicals were used without further purification.

2.2. Preparation of different polycondensation recipes

Due to technical limitations it was not possible to weigh an amount of catalyst corresponding to 200 ppm in 10 mg of BHET (2×10^{-3} mg of catalyst). For this reason a larger amount of HT–BHET mixture was prepared by mixing of the desired amount of HT and 1 g of BHET at 40 °C as slurry in 25 ml EG for 3 h. After this homogenization process, EG was evaporated at 40 °C under high vacuum overnight. In order to prepare Sb–BHET mixtures, antimony triacetate was completely dissolved in EG by heating it at 60 °C for 1 h and then for another hour at 97 °C. Given amounts of this solution were mixed with BHET at 40 °C for 3 h before drying under high vacuum overnight.

2.3. Isothermal polycondensation

All isothermal runs were done on a STA 220 from Seiko because of its excellent applicability under isothermal conditions. The STA oven was evacuated and refilled with nitrogen at 1 atm pressure before each run to prevent product oxidation.

Pure BHET was heated at 20 K/min to 120 °C where they were held at constant temperature for 60 min before heating them to 280 °C at the same scanning rate where they were held for 240 min. Uncovered crucibles made of aluminium, platinum and alumina were used as polycondensation reactors. The diameter of these crucibles was 4 mm. Nitrogen was applied as purging gas at 50 ml/min. Catalyst was not added in these experiments. These runs were repeated under the same conditions except for 30 min at 280 °C instead of 240 min and another time for 240 min at 200 °C instead of 280 °C. Different amounts of pure BHET were also polymerized in uncovered aluminium crucibles isothermally at 208 °C.

2.4. Dynamic polycondensation

STA 409 PG from Netzsch was applied to perform all dynamic runs as this instrument is very efficient for this type of runs. Various Sb–BHET mixtures and HT–BHET mixtures were condensed by heating to 300 °C at 10 K/min under 50 ml/min nitrogen purging. All these runs were done in aluminium crucibles of 6 mm diameter covered with centrally holed lids. The STA oven was evacuated and refilled with nitrogen at 1 atm before each run. Polycondensation of 200 ppm Sb–BHET and 350 ppm HT–BHET mixtures were performed by changing the following parameters:

(1) monomer amount,
(2) nitrogen purging rate,
(3) lid/without lid, and
(4) heating rate.

2.5. Molecular weight determination

Molecular weight of resulting polymers was measured by gel permeation chromatography (GPC) on an Agilent 1100 system.

3. Results and discussion

The reaction scheme of BHET polycondensation is shown in Fig. 1. Since EG is removed as it is formed, the reaction is considered irreversible. Condensation of 1 mol of BHET produces 1 mol of EG. For complete conversion of free ester

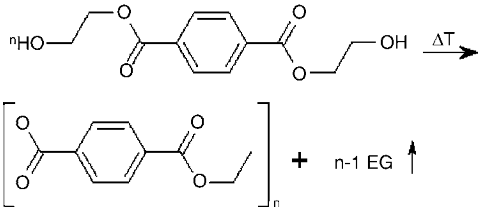

Fig. 1. Reaction scheme of BHET polycondensation to PET.

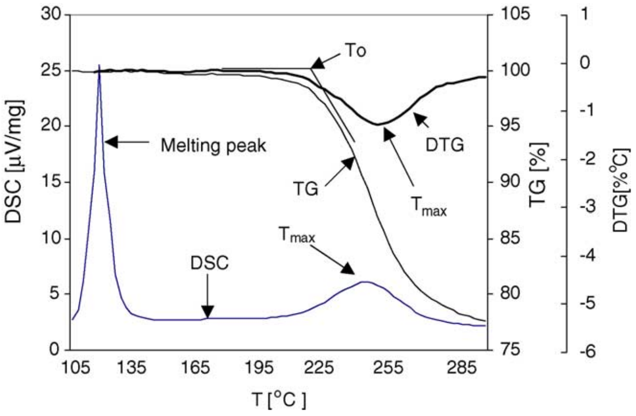

Fig. 2. Thermograms of catalyst–BHET mixture heated at 10 K/min showing the three activity ordering indices: T_{max} of DSC, T_{max} of DTG and T_o of TG.

groups into bound ester groups, 24.4% mass loss as EG by-products is calculated as shown in Eq. (1):

$$\frac{\text{total mass loss}}{\text{original mass}} = \frac{\text{molar mass of EG}}{\text{molar mass of BHET}} = \frac{62\,\text{g/mol}}{254\,\text{g/mol}} = 0.244 \qquad (1)$$

3.1. Screening principle

Thermograms obtained from dynamic polycondensation of a BHET-catalyst mixture are shown in Fig. 2. Two endothermic peaks were obtained by plotting heat flow difference between sample cell and an empty reference cell versus temperature. The first peak at about 114 °C was due to BHET melting. The second peak was due to BHET polycondensation into higher oligomers. Indeed this peak represents the heat of evaporation of EG evolved during polycondensation since BHET polycondensation is almost athermic. A Z-shape curve is obtained by plotting mass loss versus temperature. The Z-shape nature is caused by thermal acceleration and reactant consumption retardation of the polycondensation rate. Mass loss starts at a certain temperature indicating polycondensation onset (T_o). Faster polycondensation ejects detectable amounts of EG at temperatures lower than those in the case of slower reactions. For this reason T_o occurs earlier in faster reactions and therefore can be applied to screen different catalysts according to their activity in polycondensation. A curve with one peak is obtained by plotting the first derivative of mass loss with respect to temperature (DTG) versus temperature. This curve represents mass loss rate and therefore the polycondensation rate. If reactants are consumed earlier, maximum rate will occur also earlier and consequently T_{max} of DSC and DTG will have smaller values. Therefore, these two indices can also be applied as activity ordering parameters in catalyst screening.

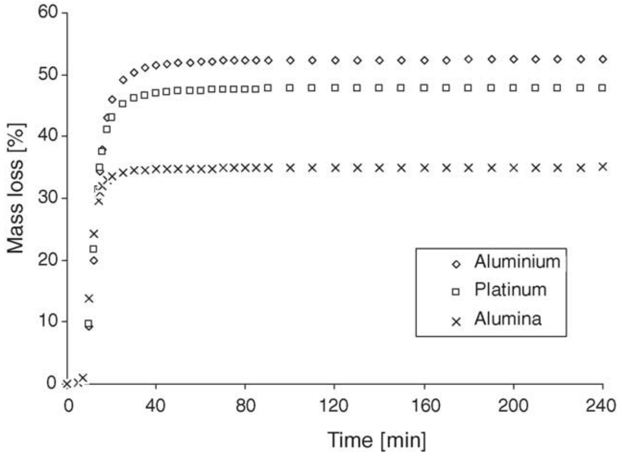

Fig. 3. Mass loss vs. time of BHET polycondensation in aluminium, platinum and alumina pans at 280 °C for 240 min.

3.2. Merits and drawbacks of polycondensation in micro-reactors

The micro-scale of the reactors applied in this work has merits and disadvantages. One important advantage is the very fast reaction rate compared to laboratory scale- or larger reactors. Another virtue is the investigation of polycondensation solely without complexation from side reactions and mass transport limitations. Nevertheless, a main draw back of polycondensation in the micro-reactor is the effect of the reactor material on the reaction. It cannot be neglected as in large reactors since the specific contact area is much greater. This makes it inevitable to use micro-reactors made of relatively inert material if reliable data are to be obtained.

3.3. Catalytic activity of crucible material

Alumina has been reported as a polycondensation catalyst [6]. On the other hand, Zimmerer et al. [5] found alumina to show little activity in catalyzing polycondensation of BHET while aluminium has a very strong activity. They concluded their results from the molecular weight of polymer produced in aluminium, platinum and alumina crucibles. Molecular weight was highest in case of aluminium and lowest for alumina. They deduced also from the ratio of weight and number average molecular weight (M_w and M_n) that aluminium catalyzes also degradation of the formed polymer.

In order to investigate this contradiction between references [5] and [6], Zimmerer experiments were repeated. The 8.9 mg of pure BHET were condensed in aluminium, platinum and alumina pans without covers for 240 min at 280 °C. The resulting TG thermograms are shown in Fig. 3. In all applied crucible materials total mass loss was higher than 24.4%. Total mass loss was highest for aluminium (53%). In platinum, mass loss was slightly lower than that in aluminium (48%) while in alumina it was much lower (35%). Total mass loss values above 24.4% are due to monomer evaporation as condensed monomer has been seen inside the STA oven.

Table 1
Number and weight average molecular weights of PET produced in different pans at 280 °C for 240 min

Sample	M_n (g/mol)	M_w (g/mol)
Platinum at 280 °C for 240 min	36000	137000
Aluminium at 280 °C for 240 min	43000	151000
Alumina at 280 °C for 240 min	30000	105000

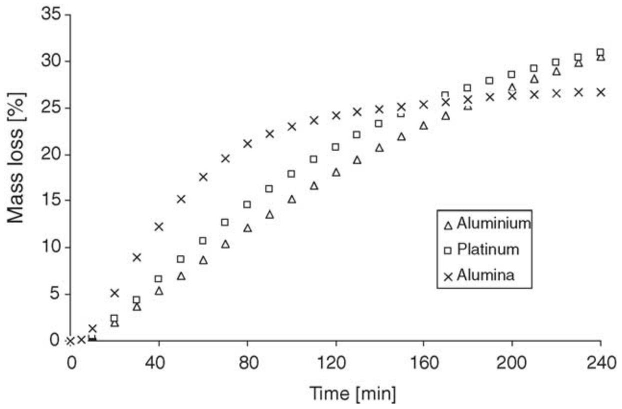

Fig. 4. Mass loss vs. time of BHET polycondensation in aluminium, platinum and alumina pans at 200 °C.

Table 2
Number and weight average molecular weights of PET produced in different pans at 200 °C for 240 min

Sample	M_n (g/mol)	M_w (g/mol)
Platinum at 200 °C for 240 min	400	3500
Aluminium at 200 °C for 240 min	300	1900
Alumina at 200 °C for 240 min	1100	5400

Table 3
Number and weight average molecular weights of PET produced in different pans at 280 °C for 30 min

Sample	M_n (g/mol)	M_w (g/mol)
Platinum at 280 °C for 30 min	14000	32000
Aluminium at 280 °C for 30 min	9000	21000
Alumina at 280 °C for 30 min	20000	74000

BHET is present in the case of slower polycondensation over a period longer than that in the case of fast reaction. This leads to longer evaporation period and subsequently to higher total mass loss. In summary, polycondensation was fastest in alumina and slowest in aluminium. To verify this result, molecular weight of produced polymers was measured and found to agree with that obtained by Zimmerer (Table 1) where aluminium had the highest molecular weight followed by platinum, and alumina. To interpret the contradictory results of molecular weight and total mass loss, additional experiments were done. Pure BHET was condensed in aluminium, platinum and alumina crucibles without covers at 280 °C for just 30 min and at 200 °C for 240 min. The aim of these additional experiments was to study the effect of polymer degradation on the obtained molecular weight. Degradation reaction of bound ester groups is evident at high temperature ($T > 275$ °C) and is believed to become the dominant reaction after a certain degree of conversion of BHET (long thermal treatment at high temperature). Total mass loss order at 200 °C was the same as in the case of 280 °C (Fig. 4). However, the molecular weight order of the obtained polymers was opposite to that at 280 °C: PET produced in aluminium has the lowest molecular weight and in alumina the highest one (Table 2). This new molecular weight order was also obtained after 30 min of polycondensation at 280 °C (Table 3). These results showed that alumina boosts quick formation of high molecular weight polymer, and then boosts degradation of the formed bound ester groups in the rest of the experiment leading to a decrease in molecular weight. Molecular weight order of the polymers obtained at 280 °C for 30 min was similar to that at 200 °C because thermal degradation was not yet severe.

Among the material tested aluminium is the most adequate pan to be used in screening experiments. It is relatively inert and has the smallest interfere with activity of the screened catalysts.

3.4. Monomer evaporation

In this work polycondensation for screening purpose was performed under dynamic conditions. It would be possible to condense BHET isothermally and to classify activities of different catalysts from total mass loss. Total mass loss at isothermal conditions is higher for catalysts with lower activity as shown earlier. However, hindering of monomer evaporation is necessary for quantitative analysis of catalyst activity and reaction kinetics [7]. Also, the dynamic mode of polycondensation has two main benefits. On one hand, it sustains the reaction only for a short period of time at high temperatures, where thermal degradation of the formed ester linkages is a serious problem. On the other hand, it reduces monomer evaporation by starting the reaction at lower temperatures. When high temperatures are reached most of the monomer is already reacted to higher non-volatile oligomers (under applied conditions). Moreover, if isothermal runs are done at low temperature, polycondensation is too slow and at the same time monomer evaporation is not overcome. To demonstrate this fact, different amounts of pure BHET (1, 3, 5 and 10 mg) were heated isothermally at 208 °C in uncovered aluminium pan. The resulting thermograms are plotted in Fig. 5. Mass loss rate and total mass loss increased with decreasing amount of BHET in crucible, and was highest for the smallest applied amount. Mass loss during condensation of 1 mg of BHET was about 60%. This indicates that main mass loss was due to monomer evaporation and not due to EG evolution over the course of polycondensation. This conclusion agrees with the dependence of measured mass loss rate on specific surface area of BHET in the crucible (ratio of surface exposed to purge gas to whole volume), which increases with decreasing amount of monomer. To overcome this severe monomer evaporation, polycondensation was done at

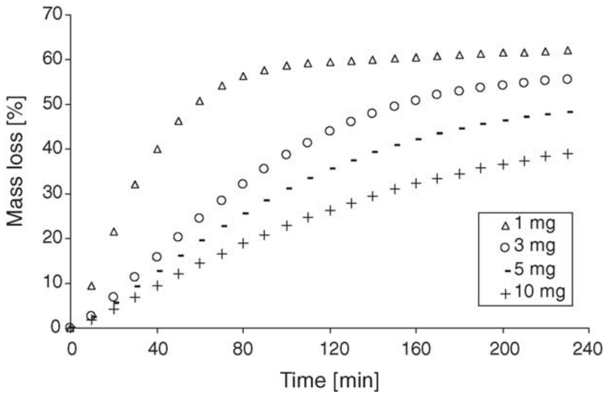

Fig. 5. Mass loss during condensation of different amounts of BHET in open aluminium crucibles isothermally at 208 °C.

dynamic conditions and the crucibles were covered by lids with a central hole. In our experiments, Sb showed lower activity than HT. If monomer evaporation still occurs after lid introduction, its effect should be largest in the case of the smallest applied Sb concentration (200 ppm). The 10 mg of 200 ppm Sb–BHET mixture was heated from room temperature to 300 °C at 10 K/min in aluminium crucible one time covered with holed lid and another time uncovered. Nitrogen purging rate was 50 ml/min. Total mass loss at final temperature of 300 °C was 17.73 and 26.12% in covered and uncovered aluminium crucibles, respectively. To check if the lid suppresses completely monomer evaporation, and if it does not affect the rate of EG removal (which otherwise affects the reaction rate) additional experiments were done. Monomer amount in the crucible was varied in a range around 10 mg, which was applied as standard starting material amount (5, 10 and 20 mg). To see if the lid affects the rate of EG removal the gas purging rate was changed between 30 and 80 ml/min. Higher purging rate should lead to faster removal of EG if the lid is hindering EG. If EG hindering occurs, its effect is strongest in case of highest reaction rate, i.e. highest catalyst concentration of the most active catalyst (in our case HT). For this reason, the purging rate was changed while heating 10 mg of 350 ppm HT–BHET mixture (highest polycondensation rate observed in our experiments). Monomer evaporation was hindered completely after introduction of the holed lid since different starting amounts of BHET result in the same total mass loss (Table 4). Further evidence of monomer evaporation absence is provided by the independence of total mass loss on purging rate (Table 5).

Table 4
Effect of sample weight on T_{max} and total mass loss during condensation of 200 ppm Sb–BHET mixture at 10 K/min under 50 ml/min nitrogen purging in covered pans

Sample mass (mg)	T_{max} of DTG (°C)	Total mass loss (%)
5	285.7	17.82
10	284.5	17.73
20	286.1	17.91

Table 5
Effect of nitrogen purging rate on T_{max} and total mass loss during condensation of 200 ppm Sb–BHET mixture at 10 K/min in covered pans

Purging rate (ml/min)	T_{max} of DTG (°C)	Total mass loss (%)
30	285.4	17.62
40	286.4	17.74
50	284.5	17.73
60	285.7	17.43
80	284.2	17.81

On the other hand, volatilization of EG was not hindered by the lid even in the case of highest rate of EG production (350 ppm HT). This is shown by the independence of T_{max} (maximum reaction rate) as well as total mass loss on purging rate (Table 6). Higher purging rate did not lead to faster removal of EG, which is reflected in the constancy of T_{max} and total mass loss. Therefore, the introduction of the holed lid yielded complete suppression of the monomer evaporation in catalyst presence with no impact on the reaction rate. Interpretation of this lies in the conversion of BHET to higher oligomers before reaching a temperature at which evaporation takes place. These oligomers have much lower vapor pressure than that of BHET.

3.5. Optimal heating rate

In order to study the optimal heating rate for screening, 10 mg of different Sb–BHET as well as HT–BHET mixtures were heated in aluminium crucibles covered with centrally holed lids at 1, 2, 3, 4, 5, 6, 10 and 20 K/min under 50 ml/min nitrogen purging. In the case of small heating rates, solidification of the melt was observed during heating due to fast increase in molecular weight especially when high concentrations of catalyst were applied. This behaviour resulted in a strong retardation of mass loss (diffusion of EG through solid reaction mass), which shifts T_{max} to higher value. When high heating rate was applied, maximum reaction rate did not appear at moderate temperature, especially when low catalyst concentrations were used. As a result, T_{max} did not emerge below 280 °C, above which chain degradation reaction cannot be neglected any more. At 10 K/min no solidification has occurred even for the fastest studied polycondensation (350 ppm HT). At the same time T_{max} of studied samples appeared below 280 °C even with the slowest applied run (200 ppm Sb).

Table 6
Effect of nitrogen purging rate on T_{max} and total mass loss during polycondensation of 350 ppm HT–BHET mixture at 10 K/min in covered pans

Purging rate (ml/min)	T_{max} of DTG (°C)	Total mass loss (%)
30	233.1	21.83
40	232.8	21.72
50	234.2	21.66
60	233.8	22.16
80	232.2	21.72

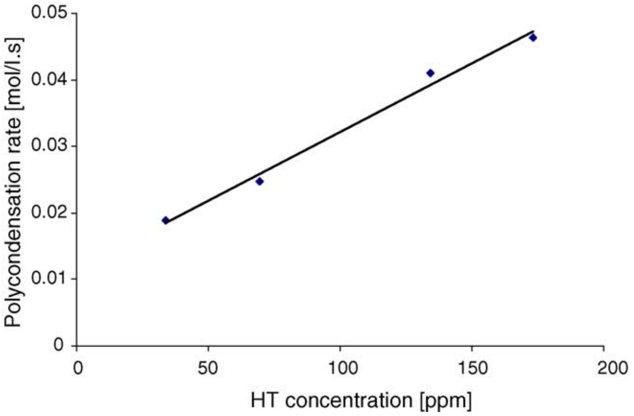

Fig. 6. Dependence of initial polycondensation rate on catalyst concentration during heating at 10 K/min in aluminium crucibles.

3.6. Absence of mass transport limitations

On industrial scale, it is known that polycondensation of PET is limited by mass transport limitations. The first important issue to be fulfilled in catalyst screening is to run the experiments under conditions at which the rate-determining step is chemistry and not mass transport. In our experiments, polycondensation rate increased linearly with catalyst concentration under applied dynamic conditions (Fig. 6). This indicates that the reaction was controlled by chemistry. Furthermore, mass transport limitations of EG inside the melt were absent as changing the starting amounts of BHET did not alter the reaction rate, and subsequently T_{max} and total mass loss (Table 7). As mentioned before, limitation on the gas side of melt–gas interface was also excluded, as different gas purging rate did not affect the polycondensation rate (Table 6).

3.7. Characterization of screening indices

As mentioned before, three signals can be used to screen polycondensation catalysts: maximum DSC peak, maximum DTG peak and TG onset. The DTG peak was easier to recognize than the DSC polycondensation peak due to the higher sensitivity of the thermobalance compared to the DSC head. The DSC signal was relatively weak and became undetectable when oligomers were used instead of BHET as starting material. For example, in the case of pentamer the amount of evolved EG is only one-fifth that evolved in the case of the monomer BHET. In this case T_{max} of DSC was no longer distinguishable from the base line due to the small changes in the system as most of the ester end groups have already reacted to form the oligomers itself. Also, in the case of oligomers as starting material, T_{max} of DSC was superimposed with physical changes such as melting and crystallization of the oligomers.

Table 7
Effect of sample weight on T_{max} and total mass loss during condensation of 350 ppm Sb–BHET mixture at 10 K/min under 50 ml/min nitrogen purging in covered pans

Sample mass (mg)	T_{max} of DSC (°C)	Total mass loss (%)
5	234.5	22.13
10	233.9	21.66
20	234.1	21.92

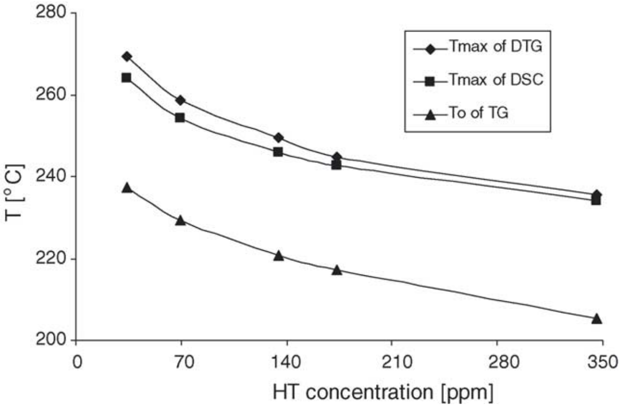

Fig. 7. Different activity ordering indices (T_{max} of DSC and DTG, T_o of TG) in screening of BHET polycondensation with different HT concentration at 10 K/min.

Table 8
Effect of catalyst concentration on difference between T_{max} of DTG and T_{max} of DSC in Sb-catalyzed polycondensation of BHET

Sample mass (mg)	Sb concentration (ppm)	T_{max} of DSC (°C)	T_{max} of DTG (°C)
10	200	280.7	284.5
10	2000	261	262
10	20000	231	229.8

T_o of TG, T_{max} of DSC and T_{max} of DTG showed the same trend (Fig. 7). Measured at same heating rate, their value was dependent on catalyst concentration. Lower catalyst concentration yielded higher values of the three indices.

A delay was found between thermogravimetric and calorimetric results (T_{max} of DSC occurs before T_{max} of DTG) and had a maximum value of about 4° at the applied condition. This delay occurred as EG vapour spent some time to reach melt–gas interface. Smaller melt thickness (shorter path) and higher catalyst concentration (higher concentration gradient) yielded delay of less than one degree (Tables 8 and 9).

The reproducibility of the three aforementioned screening parameters was tested by repeating the polycondensation five times. Standard deviation for T_{max} of DTG and DSC was 0.5% and was 1.5% for T_o of TG.

Table 9
Effect of catalyst monomer amount on difference between T_{max} of DTG and T_{max} of DSC in Sb-catalyzed polycondensation of BHET

Sample mass (mg)	Sb concentration (ppm)	T_{max} of DSC (°C)	T_{max} of DTG (°C)
5	2000	261.1	261.3
10	2000	261	262
20	2000	261.3	263.7

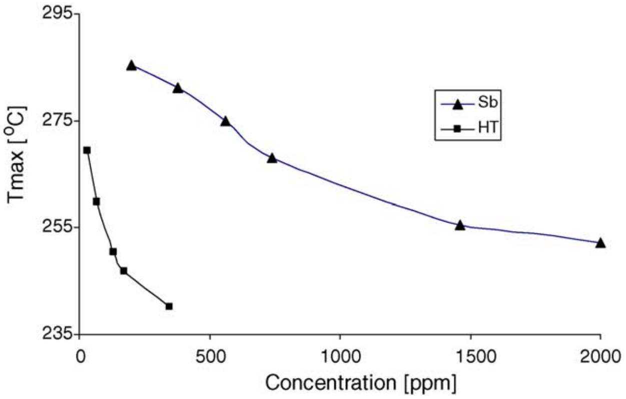

Fig. 8. Activity of Sb and HT in polycondensation of BHET as a function of concentration presented as T_{max} of DTG in dynamic polycondensation at 10 K/min.

3.8. Catalyst screening

Solving of the aforementioned critical problems (monomer evaporation, catalytic activity, etc.) yielded a sensitive and reproducible method for qualitative fast screening of polycondensation catalysts. Moreover, the optimized STA method enables precise quantitative analysis of the polycondensation kinetics in a solely chemistry-controlled regime [7]. Optimal screening is performed in aluminium crucibles covered with a holed lid. A nitrogen purging rate of 50 ml/min is sufficient to carry away EG as it formed whatever is the reaction rate. Heating rate of 10 K/min is satisfactory since reaction takes place exclusively in the melt phase and T_{max} occurs below degradation onset.

The optimized method was applied to screen HT as BHET polycondensation catalyst at different concentrations ranging from 35 to 350 ppm. To demonstrate the strong activity of HT compared to that of conventional Sb catalyst even at much smaller concentrations different Sb–BHET mixtures were screened. The screened Sb range was from 200 to 2000 ppm. Fig. 8 represents T_{max} values obtained from polycondensation of different HT– and Sb–BHET mixtures at 10 K/min up to 300 °C. It is obvious that HT is much more active than Sb even at much smaller catalyst concentration. HT is a cheap environmentally friendly catalyst compared to the heavy-metal Sb. This method indicates that HT is strong candidate to substitute Sb as a polycondensation catalyst.

4. Conclusion

Dynamic STA was utilized for the first time to study catalyzed synthesis of PET from BHET. Reduction of monomer evaporation and application of crucible material with negligible catalytic activity resulted in a reliable and efficient tool for catalyst fast screening in milligram scale. Three parameters can be used to order the activity of different catalysts: T_{max} of DTG, T_{max} of DSC, and T_o of TG. These parameters test the practical efficiency of polycondensation catalyst in boosting chain growth. They are independent of initial mass and gas purging rate but rely strongly on catalyst nature, catalyst concentration and heating rate. Molecular weight measurements of produced polymer showed that these parameters are smaller for more active catalysts. They are reproducible with less than 1.5% standard deviation. T_{max} of DTG is more easily detected than that of DSC especially when oligomers are used as starting material instead of BHET due to overlapping of reaction signal with heating induced physical processes.

The optimized method was applied to study the activity of a new heterogeneous catalyst based on hydrotalcite in comparison to the conventional homogenous antimony catalyst. HT is much more active than Sb even at much lesser concentration. Moreover, HT as environmentally friendly and cheap material may substitute Sb as polyester synthesis catalyst in the near future.

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