Polymerization Technology – Laboratory Course

Differential Scanning Calorimetry. Polyethylene Terephthalate synthesis. Catalyst screening

Subject
Fast screening of polycondensation catalyst.
Determination of the kinetic data of catalyzed polycondensation in polyethylene terephthalate synthesis

Theory
Differential scanning calorimetry (DSC) belongs to the family of thermal analysis methods. In general thermal analysis is the determination of substance properties in dependence on temperature. Thermodynamic data (heat capacity, phase transition, enthalpy) and kinetic data can be determined by methods of thermal analysis. The greatest advantage of thermal analysis is the easy handling and the output of valuable information from small samples of measured substance. Other common thermal analysis methods are thermogravimetric analysis and differential thermal analysis.

DSC measures the energy needed to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to the same temperature program. There are two types of DSC systems in common use.

1. Power compensation DSC
In this system the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are kept identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

2. Heat flux DSC
In heat flux DSC, the sample and reference are connected by a low resistance heat flow path (a metal disc) symmetrically. The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference.

Principle of data acquisition in a differential scanning calorimetry
When a change of heat capacity, phase transition or reaction occurs, the equilibrium between sample and reference is disturbed. The sample temperature is higher (exothermic event) or lower (endothermic event) than the reference. This temperature difference is detected by temperature
controlling system and the differential heat flow between sample and reference is calculated by following equation.

\[
\Delta Q = -K \Delta T
\]  

(1)

\(\Delta Q \,[\text{J s}^{-1}]\) is differential heat flow between sample and reference and the constant \(K \,[\text{J K}^{-1} \text{s}^{-1}]\) has to be determined by calibration.

**Figure 1. Scheme of heat flux DSC instrument.**

**Polyethylene terephthalate synthesis**  
**Introduction**

Polyethylene terephthalate (PET) is a polymer formed by polycondensation of bis-hydroxy ethylene terephthalate (BHET) produced via esterification of ethylene glycol and terephthalic acid. PET is a major polymer which is extensively used in the form of fibers, films and as moulding material in soft drink bottles production.

In this study, PET is produced by the melt polycondensation of BHET in a crucible of DSC (micro-reactor with melt volume 9 µl). Polycondensation is a reversible reaction. In order to push the polycondensation reaction forward the condensate by-product (EG) should be removed as it formed (Scheme 1).

**Scheme 1. Reaction scheme of BHET polycondensation to PET.**
**Screening principle**

Dynamic runs at a heating rate of 10 K/min up to 300 °C are done under 50 ml/min nitrogen purging. In polycondensation of BHET presence of some trace of oxygen in the reaction medium leads to oxidation degradation and other undesired side reactions, on the other hand the by-product of reaction should be removed from reaction medium as it formed; therefore the purging with an inert gas like nitrogen by passing through the DSC system and over the sample is important and necessary.

The obtained thermogram from dynamic HT catalyzed BHET polycondensation is shown in figure 2. Two endothermic peaks are obtained during polycondensation of BHET/catalyst mixture at a constant heating rate. The first peak at about 110 °C is due to BHET melting. The second endothermic peak, in absence of side reactions and monomer evaporation, represents the evaporation of EG produced during polycondensation since BHET polycondensation is almost athermic. This peak represents the rate of EG evaporation and when the evaporation is fast and there is no mass transport limitation, it represents the rate of polycondensation as well. Bell shape of the reaction peak is due to the fact that rate of polycondensation is a function of temperature and concentration of functional groups and it increases by increasing the temperature and decreases by decrease in functional groups concentration. At lower temperature the effect of temperature is dominant while at high temperature concentration effect is dominant. At a certain temperature these two effects compensate each other and reaction has the maximum rate. The temperature at which the maximum of the reaction rate occurs ($T_{\text{max}}$) is used as activity index. If the reactants are consumed earlier, reaction rate is faster and $T_{\text{max}}$ will have the smaller value and this means that applied catalyst is more active. One should consider that it is a relative activity index for catalyst screening and depends on several parameters such as heating rate, catalyst concentration and sample weight.

![DSC Thermogram of catalyzed BHET polycondensation at 10 K/min. (Sample weight: 10 mg).](image)

*Figure 2. DSC Thermogram of catalyzed BHET polycondensation at 10 K/min. (Sample weight: 10 mg).*
Critical problems in screening of polycondensation catalyst

In spite of the important merits of application of DSC in fast screening of polycondensation catalyst such as easy handling, online data acquisition, very fast reaction rate (the reaction is finished in minutes compared to hours in larger scale reactors) due to the large surface to volume ratio of the crucibles which enables rapid removal of the condensate by-product (EG), there were several critical problems which should be solved and optimized.

1. Catalytic effect of crucible material

The large specific surface can be a main drawback if the reactor material has catalytic activity on the investigated reaction. The effect of the reactor material can not be neglected as in large reactors since the specific contact area is much greater. Therefore a micro-reactor made of relatively inert material should be applied. It was found out that aluminium has the lowest catalytic activity and at the same time, excellent thermal conductivity.

2. Monomer evaporation

Monomer evaporation during heating process leads to higher mass loss than expected from EG removal, to avoid this event, crucible with lid having a hole in centre is used and polycondensation is run at dynamic mode which 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.

3. Mass transport limitations

In general rate of BHET polycondensation is limited by mass transport. In the DSC micro-reactor high specific surface area and efficient removal of by-product ensure the absence of mass transport limitation of EG on the melt-gas interface since the variation of purging flow rate did not affect reaction rate. Furthermore, mass transport limitation is absent within the melt since variation of the amount of BHET did not alter the reaction rate.

4. Purging rate

Purging flow rate affects the temperature control, monomer evaporation and efficient EG removal. Consequently, it should be optimized. The optimized purging rate of nitrogen was found out to be 50 ml min\(^{-1}\).

5. Heating rate

Heating rate affects the catalyst screening procedure. At small heating rate the melt solidifies during heating due to fast increase in molecular weight of formed product especially when high catalyst concentrations are applied. This behaviour results in a strong retardation of mass loss (diffusion of EG through a solid reaction mass), which shifts \(T_{\text{max}}\) to higher value. On the other hand, if high heating rate is applied, maximum reaction rate does not occur at moderate temperature, especially when low catalyst concentrations are used. Thus, \(T_{\text{max}}\) does not emerge below 280 °C, above which chain degradation reaction cannot be neglected anymore. Heating rate of 10 K min\(^{-1}\) was found out to be the optimized one.
6. Complexities in quantitative evaluation of polycondensation kinetics in PET synthesis by DSC

Quantitative investigation of BHET polycondensation to PET is not straightforward in DSC since measured signal is affected by several processes. The heat capacities of reactants are functions of temperature. The reaction melt does not form a uniform static film but it moves away from the center of the reactor and accumulates at the periphery and forms a O-ring structure. Moreover, the condensate EG does not leave the melt exclusively by diffusion, and bubbling is the main removal route. Due to intensity of bubbling at the periphery (higher concentration of nucleation agent which are cervices of reactor material), the melt moves outwards in the direction of EG concentration gradient. In most DSC instruments, the temperature sensors are located in the middle of the crucible holder. Since the heat flow signal is derived from the temperature difference between sample and reference temperature sensors, the signal will be smaller if the reaction takes place away from the sample sensor. All these serious problems lead to data misinterpretation in DSC application for quantitative studies.

In order to use DSC for kinetic study of BHET polycondensation, several simplification assumptions are applied.

**Kinetics of PET synthesis**

BHET polycondensation can be treated as a second order reaction between hydroxyl end groups. The reaction rate is described by following equation.

\[
R = -\frac{1}{2} \frac{d[OH]}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) [Cat][OH]^2
\]  

(2)

where \([OH]\) is concentration of hydroxyl end groups \([\text{mol l}^{-1}]\), \(E_a\) is activation energy of reaction \([\text{kJ mol}^{-1}]\) and \(k_0\) is pre-exponential factor of rate constant \([\text{l}^2 \text{ mol}^{-2} \text{s}^{-1}]\), \([Cat]\) is concentration of catalyst \([\text{mol l}^{-1}]\) and \(t\) is time \([\text{s}]\). Integration of this equation leads to following equation for decay of hydroxyl end groups concentration.

\[
\frac{1}{[OH]} - \frac{1}{[OH]_0} = k_0 \exp\left(-\frac{E_a}{RT}\right) [Cat]t
\]  

(3)

The concentration of hydroxyl end groups at time \(t\) during course of reaction is obtained by

\[
[OH]_t = \frac{n_{t,OH}}{V_t}
\]  

(4)

\(n_{t,OH}\) [mol] is mole number of hydroxyl end groups after reaction time \(t\), \(V_t\) [l] is total volume of reaction mixture which assume to be constant at the reaction condition.

The amount of hydroxyl end groups after reaction time \(t\) can be calculated from initial amount of hydroxyl end group and converted one in the form of EG by following equation:

\[
n_{t,OH} = n_{o,OH} - 2n_{t,EG}
\]  

(5)

In each polycondensation step, two hydroxyl end groups are consumed and one EG is produced. Initial mole number of hydroxyl end groups in the reaction medium can be obtained as
The amount of EG produced during polycondensation in DSC can be calculated from the EG evaporation enthalpy in course of polycondensation, $\Delta H(t)$ [J], and the molar vaporization of EG, $\Delta H_{EG}$ [J mol$^{-1}$], as following,

$$n_{EG} = \frac{\Delta H(t)}{\Delta H_{EG}} = \int_{t_0}^{t} Q \, dt$$  

(7)

Molar evaporation enthalpy of EG is also function of temperature, but here for simplification the average value of 48 kJ mol$^{-1}$ can be used.

Decay of hydroxyl end groups concentration can be described by following equation.

$$\frac{d[OH]}{dT} = \frac{d[OH]}{dT} = \beta \frac{d[OH]}{dT}$$  

(8)

If in equation 2, the decay of concentration of hydroxyl end groups is substituted by equation 8, following equation is achieved.

$$\frac{d[OH]}{dT} = -\frac{2}{\beta} k_0 \exp\left(- \frac{E_a}{RT}\right)[Cat] [OH]^2$$  

(9)

At $T_{max}$:

$$\frac{d[OH]}{dT} = \frac{d^2[OH]}{dT^2} = 0$$  

(10)

Therefore:

$$-2 \frac{[Cat]k_0}{\beta} \exp\left(- \frac{E_a}{RT_{max}}\right) \left\{ \frac{E_a}{RT_{max}} [OH]_{max}^2 + 2 [OH]_{max} \frac{d[OH]_{max}}{dT} \right\} = 0$$  

(11)

which leads to

$$\frac{E_a}{RT_{max}^2} [OH]_{max}^2 + 2 [OH]_{max} \frac{d[OH]_{max}}{dT} = 0$$  

(12)

Thus the activation energy can be calculated by following equation,

$$E_a = -2RT_{max}^2 [OH]_{T_{max}}^{-1} \frac{d[OH]}{dT} = -2RT_{max}^2 \left( \frac{d[OH]_{max}}{dT} \right)_{T_{max}} = -2RT_{max}^2 \left( \frac{dX}{dT} \right)_{T_{max}}$$  

(13)
Since:
\[
\left( \frac{dX}{dT} \right)_{\text{max}} = \frac{(\dot{Q})_{\text{max}}}{\beta} \int_{t_{\text{onset}}}^{t_{\text{end}}} \dot{Q} \, dt - \int_{t_{\text{onset}}}^{t_{\text{end}}} \dot{Q} \, dt
\]

Then the equation 13 can be rewritten as following:
\[
E_a = 2RT_{\text{max}} \left( \frac{(\dot{Q})_{\text{max}}}{\beta} \int_{t_{\text{onset}}}^{t_{\text{end}}} \dot{Q} \, dt - \int_{t_{\text{onset}}}^{t_{\text{end}}} \dot{Q} \, dt \right)
\]

Calculation of degree of polymerization and crystallinity

Figure 3 shows the correlation of melting point and degree of polymerization for BHET polycondensation obtained by Yamada in 1988. The melting point of polycondensation product can be obtained from DSC thermogram. Consequently the degree of polymerization can be determined from Figure 3.

According to Carothers’ equation the correlation of conversion and degree of polycondensation is obtained as following,
\[
P_a = \frac{1}{1 - X}
\]

Crystallinity of the product of polycondensation of BHET in DSC can be determined by melting enthalpy of product obtained from DSC thermogram. Therefore the amount of crystalline polymer [g] is calculated,
\[ m = \frac{\Delta H}{\Delta H_m} = \frac{\int_0^t Q_m \, dt}{\Delta H_m} \quad (17) \]

where \( \Delta H_m \) [J g\(^{-1}\)] is specific melting enthalpy of PET. Thus crystallinity of the product is obtained by following equation.

\[ \text{Crystallinity} = \frac{m}{m_{\text{sample}}} \times 100 \quad (18) \]

**Experimental**

10 mg of two different BHET mixtures with two different catalysts: antimony (Sb) and hydrotalcite (HT) are weighted in aluminum crucibles. The crucibles are located in the DSC oven. The following heating program is applied:

1. Heating from 50°C to 300°C at 10 K/min
2. Cooling from 300°C to 80°C at 10 K/min
3. Heating from 80°C to 300°C at 10 K/min
4. Cooling from 300°C to 50°C at 40 K/min

Purging rate is 50 ml/min.
For kinetics and activity study the first heating run is used but for crystallization study the second run is used.

**Analysis**

The data obtained by the DSC program must be exported as an ASCII files. The following tasks should be performed:

1. Comparison of the activity of two catalyst from the value of \( T_{\text{max}} \)
2. Calculate activation energy of catalyzed polycondensation BHET by HT and Sb.
3. Determine the degree of polymerization and end conversion of each mixture.
4. Determine the crystallinity of the product of polycondensation of two different samples.