

Catalytic and Mechanistic Studies of Polyethylene Terephthalate Synthesis

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“Imagination is more important than knowledge”

Albert Einstein

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ABSTRACT OF DISSERTATION

“Catalytic and Mechanistic Studies of Polyethylene Terephthalate Synthesis”

By

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Polyethylene terephthalate synthesis by polycondensation of its monomer bis-hydroxy ethylene terephthalate was investigated. Two catalysts were studied; a homogenous one based on antimony and a heterogeneous one based on hydrotalcite. Two methods were applied to monitor the reaction progress; thermogravimetry and calorimetry. The reaction was performed in bulk under non-isothermal conditions in the melt phase. 10 mg of monomer/catalyst mixtures were heated at a constant heating rate in the range of 100-300 °C. The reaction condensate ethylene glycol was removed efficiently by inert gas purging.

The kinetic parameters of the reaction were determined by fitting of the experimental data with different kinetic models using the software package “Thermokinetics” of Netzsch. Two fitting parameters were applied; activation energy and pre-exponential factor. Polycondensation catalyzed by both catalysts as well as the uncatalyzed reaction are second order with respect to concentration of functional groups. The activation energies of hydrotalcite- and antimony catalyzed polycondensation are 93 ± 5 and 75 ± 5 kJ mol⁻¹ respectively. Hydrotalcite is much more active than antimony in catalyzing the polycondensation at low conversion. Hydrotalcite shows full catalytic activity from the beginning of the reaction while the activity of antimony increases with consumption of functional groups and becomes more active than hydrotalcite at high conversions. This is due to interaction of functional groups with antimony hindering formation of the transition state. A low concentration of antimony enables the reaction to occur solely via the catalyzed reaction path. Relatively high hydrotalcite concentration is needed to exclude the uncatalyzed reaction path. Hydrotalcite activity depends on the ratio of magnesium to aluminum cations in its composition and highest activity occurs at a molar ratio of two. The hydroxide groups of hydrotalcite and the anions in its interlayer are necessary for its catalytic activity. Hydrotalcite activity can be improved by increasing the distance between its layers or decreasing the size of these layers.

Antimony catalyzes the chain prolongation reaction by ligand exchange mechanism within its coordination sphere. Hydrotalcite supports the coupling of two ester chains through a carbonate-analogous structure of the active species. It activates the reactants, rendering the attacking hydroxyl group more nucleophilic in an alkoxide form and the ester carbonyl group more electrophilic. At the same time hydrotalcite fixes the reactant together in a favorable geometry.

ZUSAMMENFASSUNG DER DISSERTATION

“Katalytische und Mechanistische Studien der Polyethylenterephthalat-Synthese”

von

Faissal-Ali El-Toufaily

In dieser Arbeit wurde die Synthese von Polyethylenterephthalat ausgehend von Bis-hydroxyethylenterephthalat untersucht. Es wurden zwei Katalysatoren untersucht, der homogene Katalysator auf Antimon Basis und ein heterogener Katalysator basierend auf Hydrotalcit. Zwei Methoden wurden benutzt, um dem Reaktionsablauf zu verfolgen; die Thermogravimetrie und die Kalorimetrie. Die Reaktion wurde im Masse unter nicht-isothermen Bedingungen in der Schmelze durchgeführt. 10 mg Monomer/Katalysator Mischungen wurden bei einer konstanten Heizrate im Bereich von 100-300 °C erhitzt. Das Kondensat Ethylenglycol wurde effizient durch ein Inertgasstrom aus der Reaktionsmasse entfernt.

Die kinetischen Parametern der Reaktion wurden durch Anpassung an experimentelle Daten mit unterschiedlichen kinetischen Modellen unter Verwendung des Software-Packets „Thermokinetics“ der Firma Netzsch bestimmt. Als kinetische Parameter wurden die Aktivierungsenergie und der Stossfaktor der Reaktion angepasst. Sowohl die Polykondensation, in Gegenwart von Katalysatoren, als auch die unkatalysierte Polykondensation sind Reaktionen zweiter Ordnung bezüglich der Konzentration der funktionellen Gruppen. Die Aktivierungsenergien der Hydrotalcit und Antimon katalysierten Polykondensation sind $93 \pm 5 \text{ kJ mol}^{-1}$ bzw $75 \pm 5 \text{ kJ mol}^{-1}$. Hydrotalcit ist viel aktiver als Antimon in der Katalyse der Polykondensation bei niedrigem Umsatz. Hydrotalcit zeigt eine maximale katalytische Aktivität von Beginn der Reaktion an, während die Aktivität von Antimon mit dem Verbrauch der funktionellen Gruppen zunimmt. Bei hohem Umsatz ist Antimon aktiver als Hydrotalcit. Der Grund dafür sind die Wechselwirkungen zwischen Katalysator und den funktionellen Gruppen, welche die Bildung des Übergangszustandes der Reaktion unterdrücken. Eine niedrige Konzentration von Antimon genügt um die Reaktion ausschließlich katalytisch ablaufen zulassen. Relativ hohe Konzentrationen von Hydrotalcit werden hingegen benötigt um den unkatalysierten Weg auszuschließen. Die Aktivität von Hydrotalcit ist abhängig vom Verhältnis der

Magnesium- und Aluminiumkationen, wobei die höchste Aktivität bei einem Molverhältnis von zwei auftritt. Auch die Hydroxidgruppen und die Anionen zwischen den Hydrotalcitschichten sind für die katalytische Aktivität verantwortlich. Außerdem konnte die Aktivität von Hydrotalcit durch eine Erhöhung des Abstands der Schichten und die Verminderung der Schichtgröße verbessert werden.

Antimon katalysiert die Kettenverlängerungsreaktion durch einen Liganden-Austausch Mechanismus innerhalb seiner Koordinationssphäre. Hydrotalcit dagegen katalysiert die Kopplung von zwei endständige Estergruppen über eine karbonatähnliche Struktur des Übergangszustandes der Reaktion. Dies geschieht dadurch, dass die Nucleophilie der Hydroxylgruppen durch die Umwandlung in Alkoxidgruppen gesteigert wird. Gleichzeitig wird die Elektrophilie der Carbonylgruppen erhöht.

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Abbreviations

AA	Acetaldehyde
ATR/FTIR	Attenuated total reflection/Fourier transform infrared spectrometer
BHET	Bis-hydroxy ethylene terephthalate
DEG	Diethylene glycol
DMF	Dimethyl formamide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
DTG	Derivative of thermogravimetry with respect to temperature
EG	Ethylene glycol
EGMB	Ethylene glycol monobenzoate
ET	Ethylene segment
GC	Gas chromatography
GPC	Gel permeation chromatography
HE	Hydroxy ethylene segment
HPLC	High pressure liquid chromatography
HT	Hydrotalcite
ICTAC	International Confederation for Thermal Analysis and Calorimetry
MS	Mass spectroscopy
PBT	Poly butylene terephthalate
PDT	Poly decamethylene terephthalate
PET	Polyethylene terephthalate
PHT	Poly hexamethylene terephthalate
PSD	Position sensitive detector
PVC	Polyvinyl chloride
Sb	Antimony
SEM	Scanning electron microscopy
SSP	Solid state polycondensation
STA	Simultaneous thermal analysis
TA	Thermal analysis
TE	Terephthalate segment
TEM	Transmission electron microscopy

TG

Thermogravimetry

Symbols

a	Exponent of Mark-Houwink equation	[-]
b	Heating rate	[K s ⁻¹]
$[C]$	Catalyst concentration	[mol l ⁻¹]
$C_{p,MR}$	Heat capacity of the reference measuring system	[J K ⁻¹]
$C_{p,MS}$	Heat capacity of the sample measuring system	[J K ⁻¹]
C_p^l	Specific molar heat capacity of liquid polymeric segment	[J mol ⁻¹ K ⁻¹]
$C_{p,R}$	Heat capacity of the reference	[J K ⁻¹]
$C_{p,s}$	Heat capacity of the sample	[J K ⁻¹]
C_p^s	Specific molar heat capacity of solid polymeric segment	[J mol ⁻¹ K ⁻¹]
$?c_p$	Change in specific molar heat capacity due to the reaction	[J mol ⁻¹ K ⁻¹]
$?G^\ddagger$	Standard molar free energy of activation	[J mol ⁻¹]
$?H^\ddagger$	Molar enthalpy of activation	[J mol ⁻¹]
$?H_R$	Molar reaction enthalpy	[J mol ⁻¹]
$?H_{R,298}$	Molar reaction enthalpy at 298 K	[J mol ⁻¹]
$?H_{R,T}$	Molar reaction enthalpy at temperature T	[J mol ⁻¹]
$?S^\ddagger$	Molar entropy of activation.	[J mol ⁻¹ K ⁻¹]
$?T_{correction}$	Temperature correction	[K]
E	Molar expansivity of polymeric segment	[l mol ⁻¹ K ⁻¹]
$E_{catalyzed}$	Activation energy of catalyzed reaction	[J mol ⁻¹]
$E_{uncatalyzed}$	Activation energy of the uncatalyzed reaction	[J mol ⁻¹]
$[h]$	Intrinsic viscosity	[dl g ⁻¹]
h	Planck constant	[J s]
K_{MH}	Constant of Mark-Houwink equation	[-]
$K^\ddagger$	Equilibrium constant between transition state and reactants.	[l mol ⁻¹]
$k_{catalyzed}$	Rate constant for catalyzed polycondensation reaction	[l ^m mol ^{-m} s ⁻¹]

$k_{o,catalyzed}$	Pre-exponential factor of the Arrhenius equation for catalyzed reaction	$[l^m \text{ mol}^{-m} \text{ s}^{-1}]$
$k_{o,uncatalyzed}$	Pre-exponential factor of the Arrhenius equation for uncatalyzed reaction	$[l^{n-1} \text{ mol}^{1-n} \text{ s}^{-1}]$
$k_{uncatalyzed}$	Rate constant for uncatalyzed reaction	$[l^{n-1} \text{ mol}^{1-n} \text{ s}^{-1}]$
m	Reaction order of catalyzed reaction	$[-]$
M_{BHET}	Molar mass of bis-hydroxy ethylene terephthalate	$[\text{g mol}^{-1}]$
M_{EG}	Molar mass of ethylene glycol.	$[\text{g mol}^{-1}]$
M_n	Number average molecular weight	$[\text{g mol}^{-1}]$
$m_{o,BHET}$	Initial mass of bis-hydroxy ethylene terephthalate	$[\text{g}]$
M_w	Weight average molecular weight	$[\text{g mol}^{-1}]$
M_v	Viscosity average molecular weight	$[\text{g mol}^{-1}]$
n	Reaction order, or Exponent of equation for vaporization enthalpy	$[-]$ $[-]$
N	Avogadro number	$[\text{mol}^{-1}]$
n_{EG}^{DSC}	Amount of ethylene glycol obtained by differential scanning calorimetry	$[\text{mol}]$
n_{EG}^{TG}	Amount of ethylene glycol obtained by thermogravimetry	$[\text{mol}]$
$n_{t,EG}$	Amount of produced ethylene glycol at time t	$[\text{mol}]$
$n_{t,ET}$	Amount of ethylene segments at time t	$[\text{mol}]$
$n_{t,HE}$	Amount of hydroxy ethylene segments at time t	$[\text{mol}]$
$n_{t,TE}$	Amount of terephthalate segments at time t	$[\text{mol}]$
$[OH]$	Concentration of hydroxyl end groups	$[\text{mol l}^{-1}]$
P_n	Degree of polycondensation	$[-]$
P_c	Critical pressure	$[\text{bar}]$
Q_C	Heat amount due to the heat capacity of the melt	$[\text{J}]$
Q_{chem}	Heat amount due to the reaction enthalpy	$[\text{J}]$
$\dot{Q}_{chem}$	Heat flow due to the chemical reaction	$[\text{J s}^{-1}]$
Q_{DSC}	Heat measured by differential scanning calorimetry	$[\text{J}]$

$\dot{Q}_R$	Heat flow to reference	[J s ⁻¹]
$\dot{Q}_S$	Heat flow to sample	[J s ⁻¹]
$Q_{vap,EG}$	Heat amount due to vaporization of ethylene glycol	[J]
R	Universal gas constant	[J mol ⁻¹ K ⁻¹]
R_{chem}	Reaction rate	[mol l ⁻¹ s ⁻¹]
t	Time	[s]
T	Temperature	[K]
T_b	Boiling temperature	[K]
T_c	Critical temperature	[K]
T_{max}	Temperature at maximum reaction rate	[K]
T_o	Polycondensation onset temperature	[K]
V	Reaction volume	[l]
V_m^{298}	Molar volume of polymeric segment at 298 K	[l mol ⁻¹]
V_t	Volume of the melt at time t	[l]
V_{vdW}	Molar Van der Waals volume of polymeric segment	[l mol ⁻¹]
X	Conversion	[-]

Chapter 1: General Introduction

1. Historical and economical perspective

Polymers have changed dramatically many aspects of human life since the launch of their commercial mass production in the beginning of the last century. 235 million tons of synthetic polymers were consumed worldwide in 2003 by important economic sectors such as electro- and electronic industry, packaging industry, building and construction, and automobile industry among others [1]. One of the widely applied polymers is polyethylene terephthalate (PET). Its IUPAC name is poly (oxyethyleneoxyterphthaloyl) [2]. From annual production viewpoint, PET is in the second rank among synthetic polymers equally with polypropylene. This is due to its excellent balance of properties such as impact strength, resistance to creep under pressure, low permeability to carbon dioxide, high melting point, thermal and hydrolytic stability and high clarity.

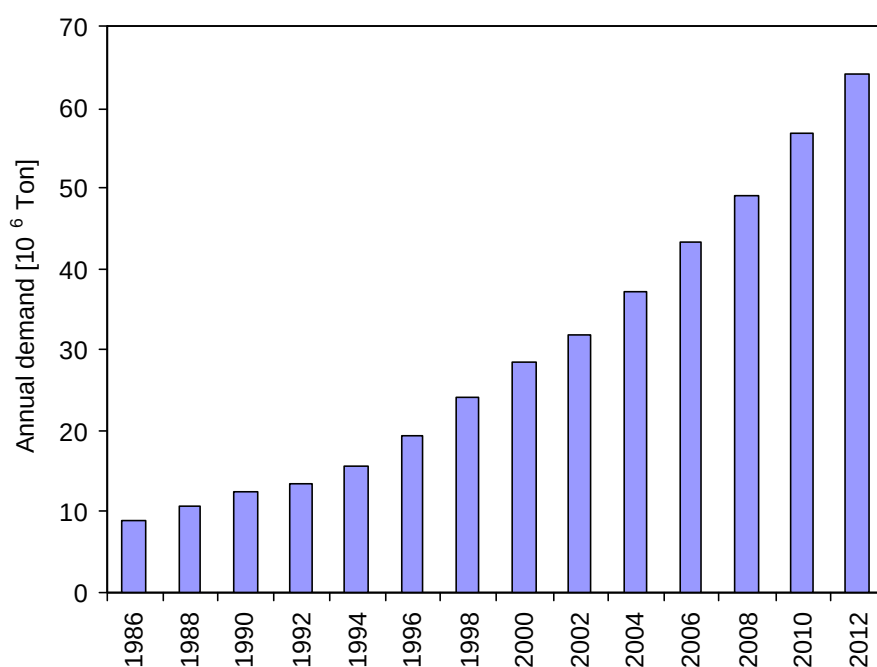


Figure 1.1. The Global annual demand of PET from 1986 to 2004 and the expected one until 2012.

The first step towards PET synthesis was induced in 1928 [3,4]. In an attempt to produce textile fibers, Carothers and coworkers started research activities that led to the synthesis of linear aliphatic polyesters. Carothers stopped investigation of these polymeric

compounds, as they could not be used for the preparation of synthetic fibers due to their low melting points and poor hydrolytic resistance. In 1941, J. R. Whinfield and J. T. Dickson identified PET as an excellent fibre-forming polymer whilst looking for a replacement for silk at British Calico Printers (later ICI) [5]. Because of its good properties and appropriate price, the production of PET fibers grew stronger than any other synthetic textile fiber. Bottles were introduced in 1973 as a new PET application field [6]. Bottling sector has grown very fast and is nowadays the main growth field of the PET market. The driving factor is the continued replacement of glass, polyethylene and aluminium with PET as packaging material for carbonated soft drinks, water, beer and milk among others. Another driving factor is the breakthrough in technology, which enabled large production capacities and thus lowered production costs making PET more competitive. 37 millions ton of PET were consumed worldwide in 2004 (figure 1.1). Two thirds of this amount was used in textile industry and a quarter was transformed into bottles. The rest was applied in production of films and other special items. The expected growth rate in the coming 10 years lies between 8 and 10 %.

2. Objectives

Technically useful PET cannot be produced without application of an efficient catalyst since the uncatalyzed reaction is too slow and many side reactions occur if the reaction mixture is heated at high temperature for a long time. Antimony (Sb) compounds are the catalysts of choice in most PET plants since its invention [5]. The main advantage of Sb is its high selectivity. However, as a heavy metal, Sb application is permitted only within precisely established boundaries [7]. There were many attempts to replace Sb with other catalysts but none of them has succeeded. Despite the importance of catalysis to PET manufacture, the mechanism of the catalyzed polycondensation reaction is poorly understood. Yet a better understanding of how the metal complex interacts with the growing PET chain is important to facilitate further developments in catalyst design.

The goal of this project was to understand the mechanism of Sb catalyzed synthesis of PET and the reasons behind its high selectivity. Another task was the development of a reliable technique for fast screening of polycondensation catalysts. A third objective was the clarification of the fundamental aspects, and the kinetics of a new polycondensation catalyst based on hydrotalcite (HT) as well as the optimization of its catalytic activity by various modifications.

3. Definitions

According to Roempp and Hopp [8,9], the general term used to express conversion of monomers into polymers is polyreaction. Polyreactions can be classified from mechanism point of view as either step-growth or chain-growth polyreactions. Random and sequential polyreactions have been proposed instead [10,11] since these terms have more statistical significance concerning the chemistry involved. Polyreaction is subdivided into three main categories: Polymerization, polycondensation and polyaddition.

Polymerization is a chain-growth polyreaction that does not involve by-products production. Polyethylene, polypropylene, polystyrene and polyvinyl chloride are examples of polymers produced by polymerization. Polycondensation is a step-growth polyreaction that occurs under separation of small molecules by-product. PET and polyamide are formed by polycondensation. Polyaddition is a step-growth polyreaction that does not involve formation of by-products. Polyurethane is an example of a polymer formed by this reaction.

Polymers can be classified into two categories from viewpoint of their thermal behaviour: thermosetting and thermoplastics. Thermosetting polymers do not melt upon heating and degrade at a certain temperature if they are further heated. Thermoplastic polymers are characterized by glass transition and melting temperature.

In view of the previous classification, PET is a thermoplastic polymer, which is produced by step-growth polycondensation polyreaction under evolution of condensates such as water, methanol or ethylene glycol (EG).

4. Industrial production of polyethylene terephthalate

PET is produced industrially by polycondensation of EG with purified terephthalic acid (PTA). The process consists of two steps. PTA is first esterified with EG to form a prepolymer consisting of the monomer bis-hydroxy ethylene terephthalate (BHET) and short-chain oligomers. In the second step, the prepolymer is condensed into PET in the melt phase. This step includes transesterification of hydroxy ethylene terephthalate end groups, and to a smaller extent, esterification of the rest carboxyl groups with hydroxy ethylene terephthalate end groups or EG. The condensate by-products, EG and water, are removed from the melt by high vacuum. PET with higher molecular weight for bottles or technical

yarns, is typically produced by further polycondensation in an additional solid state polycondensation (SSP) under vacuum or an inert gas atmosphere [12].

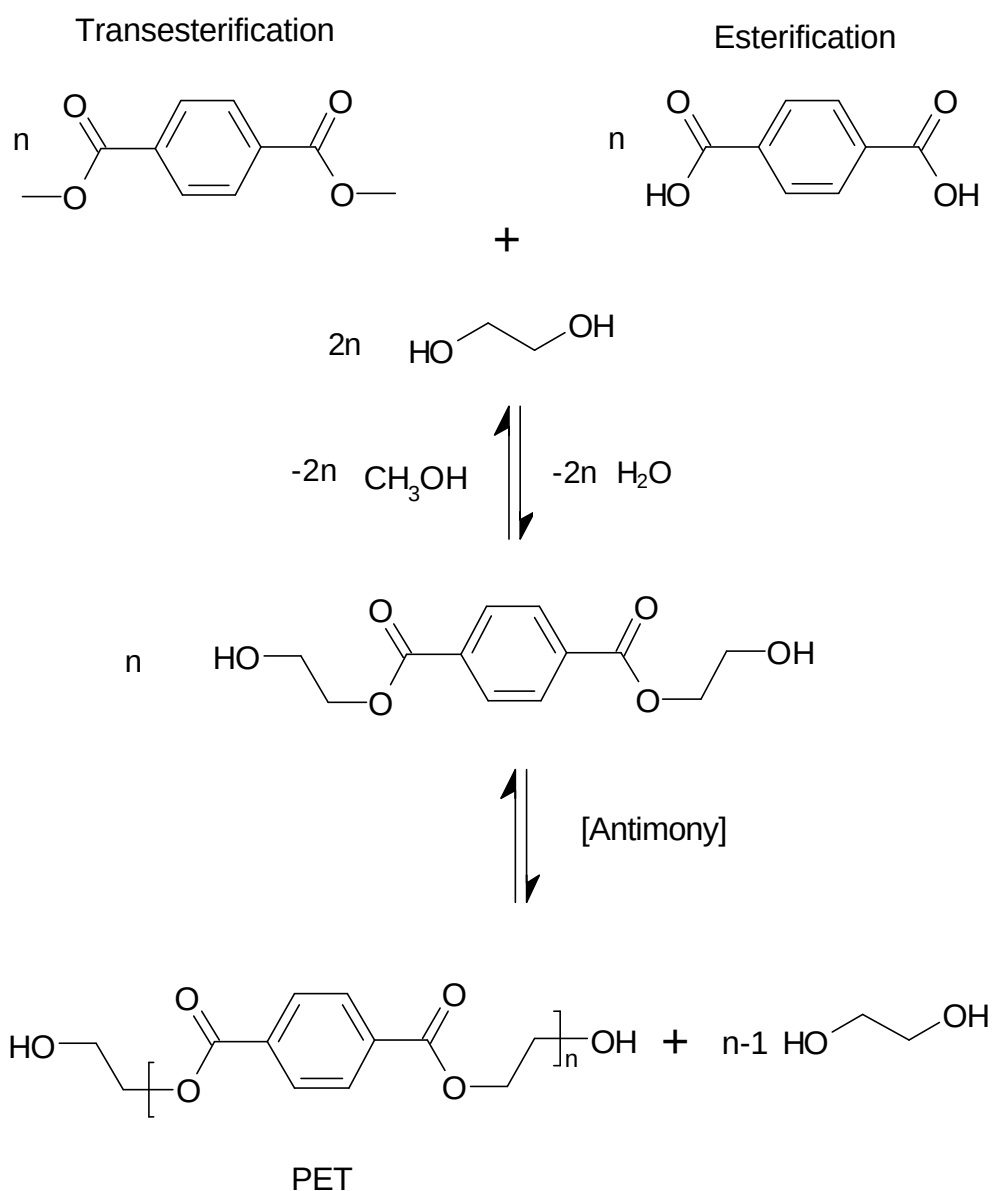
The prepolymer can also be produced by transesterification of dimethyl terephthalate (DMT) with EG, releasing methanol as condensate. In its beginnings, PET production processes were based on DMT as feedstock due to the unacceptable purity of terephthalic acid. However, PTA was produced for the first time in the late 1960s on an industrial scale by recrystallization. This breakthrough resulted in a shift of many processes to PTA as feedstock. Nowadays, more than 70 % of the global PET production is based on PTA. PTA route has the following advantages over the one based on DMT:

- The reaction is faster
- Lower transport and storage costs due to the smaller molecular weight of PTA compared to DMT
- Production of water instead of methanol as condensate by-product, which reduces treatment costs
- No need for transesterification catalyst as the esterification reaction is self-catalyzed
- Lower amounts of polycondensation catalyst are needed
- Higher molecular weight polymer can be achieved
- The quality of the polymer produced by the two processes is comparable

On the other hand, the main problem of the direct esterification route is the low solubility of PTA in EG. To overcome this issue, the temperature of the reaction is raised, and at the same time, the pressure is increased to prevent EG evaporation. Another difficulty is the tendency of PTA to agglomerate when heated in a suspension of EG rendering the homogenization and heat exchange more difficult. However, PTA solubility can be enhanced by addition of molten esterification product or precondensate in the esterification reactor. Physical properties of PTA, DMT and EG are summarized in table 1.1. Limit purity of EG and PTA for PET production are summarized in table 1.2 & 1.3.

PET is produced nowadays principally in two main grades: fibre- and bottle-grade. These standard grades differ mainly in average molecular weight as well as in production recipes such as the amount and type of comonomers, colorants, and stabilizers. Fibre-grade PET contains 0.03-0.4 wt % of titanium dioxide (TiO₂) as a delustering agent. This grade has a number-average molecular weight (M_n) of 15000-20000 g mol⁻¹, which refers to an intrinsic viscosity ($[\eta]$) of 0.55-0.67 dl g⁻¹. Fibre-grade PET for technical yarns such as tyre cord has

high M_n ($[\eta]$ above 0.95 dl g⁻¹). M_n of bottle-grade PET ranges from 24000 to 36000 g mol⁻¹ ($[\eta]$ of 0.75-1.00 dl g⁻¹). Other PET grades are manufactured for packaging films and video tapes with $[\eta]$ of approximately 0.64 dl g⁻¹ [12]. The relation between molecular weight (viscosity average, M_h) and $[\eta]$ is determined by Mark-Houwink equation (equation 1.1). Table 1.4 summarizes the Mark-Houwink constants for PET in different solvents.



Scheme 1.1. PET synthesis route from PTA or DMT as feedstock.

Table 1.1. Physical properties of PTA, DMT and EG [2].

Property	PTA	DMT	EG
<i>Melting point [°C]</i>	-	140.65	- 13
<i>Boiling point [°C]</i>	-	284	197.6
<i>Sublimation point [°C]</i>	404	-	-
<i>Evaporation enthalpy [kJ mol⁻¹]</i>	-	57.3	52.24
<i>Sublimation enthalpy [kJ mol⁻¹]</i>	142	-	-
<i>Burning enthalpy at 25 °C [kJ mol⁻¹]</i>	-3198	-4685	-1184

Table 1.2. Limit purity values of PET grade PTA [2].

Property	Value
<i>Acid value [mg KOH/g]</i>	675
<i>Maximum ash content [ppm]</i>	10
<i>Maximum Fe content [ppm]</i>	1
<i>Maximum Ca-, Ti-, Ni-, Mg-, Mo Content [ppm]</i>	2
<i>Maximum Al-, Na-, K Content [ppm]</i>	25
<i>Maximum water content [%]</i>	0.5
<i>Maximum colour in 5 % dimethyl formamide [APHA]</i>	10

Table 1.3. Limit purity values of PET grade EG [2].

Property	Value
<i>Density at 20 °C [g l⁻¹]</i>	1115.1 – 1115.6
<i>Boiling point [°C]</i>	196 – 200
<i>Melting point [°C]</i>	-13 – -11
<i>Maximum acid content as acetic acid [%]</i>	0.005
<i>Maximum Fe Content [ppm]</i>	0.07
<i>Maximum diethylene glycol content [%]</i>	0.08
<i>Maximum water content [%]</i>	0.08
<i>Maximum ash rest [g/100 ml]</i>	0.005
<i>Maximum acetaldehyde content [ppm]</i>	30
<i>Maximum colour after 24 h heating at 170 °C [Haze number]</i>	10
<i>UV transparency by 220 nm [%]</i>	70
<i>UV transparency by 275 nm [%]</i>	90
<i>UV transparency by 350 nm [%]</i>	95
<i>Maximum Chlorinated derivatives [ppm]</i>	0

Incorporation of comonomers in PET helps to modify its properties. These are either dicarboxylic acids such as isophthalic acid and/or diols such as diethylene glycol (DEG) and cyclohexane dimethanol. PET may also include various additives, such as antioxidant, ultraviolet light stabilizers, extrusion aids, dyes or pigments, and mold release agents. A chain branching agent may also be present during the polycondensation reaction to increase the molecular weight of the final PET resin. The chain branching agent may be present at

any stage during the preparation of the polymer. Among the chain branching agents that may be used are pentaerythritol, dimethylol propionic acid, trimesic acid, and the like [13,14].

$$\log [h] = \log K_{MH} + a \log M_h \quad 1.1$$

Table 1.4. Mark-Houwink constants of PET in various solvents [15].

<i>Solvent</i>	<i>T</i> [°C]	<i>K_{MH}</i>	<i>a</i>	<i>Method</i>
Tetrachloro ethane/Phenol 1:1	20	0.0755	0.685	End group determination
Tetrachloro ethane/Phenol 2:3	25	0.0468	0.68	Light scattering
2-Chlorophenol	25	0.030	0.74	End group determination
1,2-dichlorobenzene/phenol 1:1	25	0.0469	0.68	Light scattering

5. Chemistry

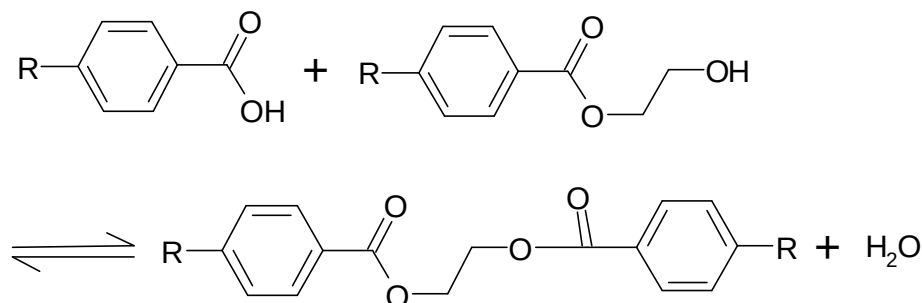
Beside the two main reactions of PET, esterification of carboxyl end groups with hydroxyl end groups and transesterification of hydroxyl end groups with each other, several other reactions take place. These are ester interchange between two ester groups, reaction of carboxyl end groups with bound ester groups known as acidolysis and many side reactions that occur simultaneously with the main reactions. The main side reaction is the thermal scission of PET chains, which results in formation of carboxyl end groups and acetaldehyde, and leads to discoloration of the polymer. Another side reaction is the formation of ether bonds instead of ester ones during reaction of two hydroxyl end groups.

5.1. Esterification

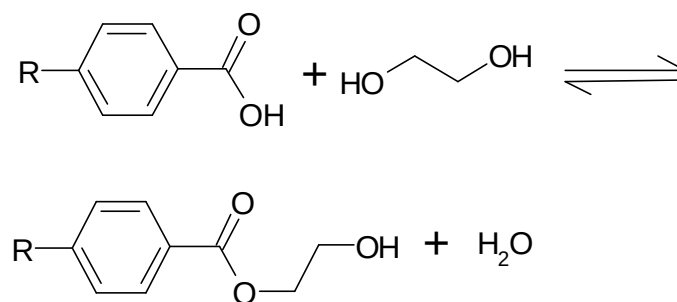
Esterification reaction occurs from the beginning to the end of PET synthesis (scheme 1.2 and 1.3). It is an equilibrium reaction and removal of the condensed water is necessary to minimize the hydrolysis of the formed ester groups. Esterification/hydrolysis has an equilibrium constant of about one and proceeds via an AC₂ mechanism [16, 17]. Although esterification is catalyzed by carboxyl end groups and can be conducted without additional catalyst [18], a catalyst is often used to reduce esterification time, to minimize the DEG content of the final PET product and to improve its colour [19].

Esterification is generally accepted as a third order reaction (2 with respect to acid and 1 with respect to alcohol) [16]. Thus, the acid behaves both as a reactant and a catalyst. The rate constant of esterification was found to increase with the pK_a of the carboxylic acid

[17]. Thermodynamic data, as well as the dependency of the equilibrium constants on temperature, indicate that the esterification reactions are moderately endothermic.



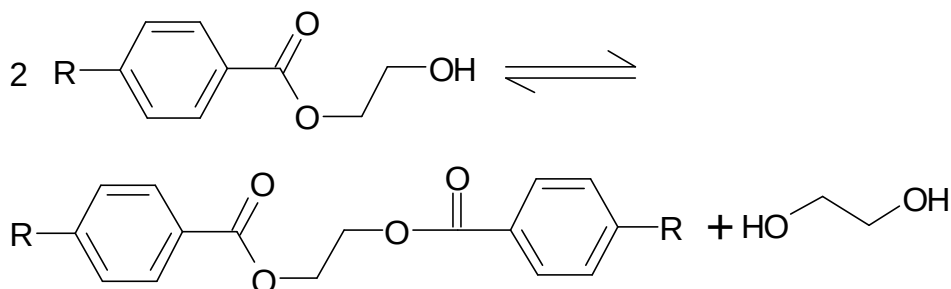
Scheme 1.2. Chain prolongation via esterification.



Scheme 1.3. Esterification of acid end groups with EG.

5.2. Transesterification

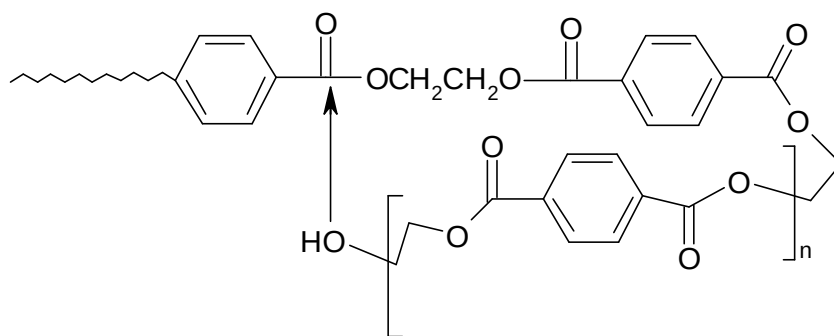
Transesterification, which is termed also polycondensation, is the main growth reaction of PET chains (scheme 1.4). It is the dominant reaction in the second and subsequent stages of PET production, but also occurs to a significant extent in the esterification reactor. The melt polycondensation process involves a gas phase and a homogeneous liquid phase, while the SSP involves a gas phase and two solid phases (crystalline and amorphous). The industrial polycondensation process is accelerated by metal catalysts, mainly Sb compounds. [20–26]. It is accepted that the polycondensation equilibrium constant is close to 0.5, being independent of temperature and degree of polycondensation, and that the normal Flory-Schulz distribution does hold in the PET system. The overall reaction order of polycondensation is 3, being 2 for hydroxyl end groups, and one for catalyst [27]. The reaction rate of polycondensation is generally limited by the rate of EG removal from the reaction mixture. A comprehensive description of the polycondensation process must therefore consider chemical kinetics as well as mass transfer.



Scheme 1.4. Chain prolongation via transesterification of two hydroxyl end groups.

5.3. Oligomers formation

PET contains about 2–3 % of short chain oligomers as a result of a dynamic equilibrium [28], which causes problems during polymer processing. These oligomers can occur as linear or cyclic molecules. Among these oligomers, the cyclic trimer has been postulated to be uniquely stable [29,30]. This could be due to either a mechanism favouring the formation of trimer (kinetic control), or due to the higher stability of trimer compared to other oligomers (thermodynamic control), thus decreasing its rate of further reaction. Back-biting mechanism (cyclo-depolymerization) has been proposed as a probable mechanism for cyclic oligomer formation (scheme 1.5).



Scheme 1.5. Formation of cyclic oligomers via back-biting of hydroxyl end groups.

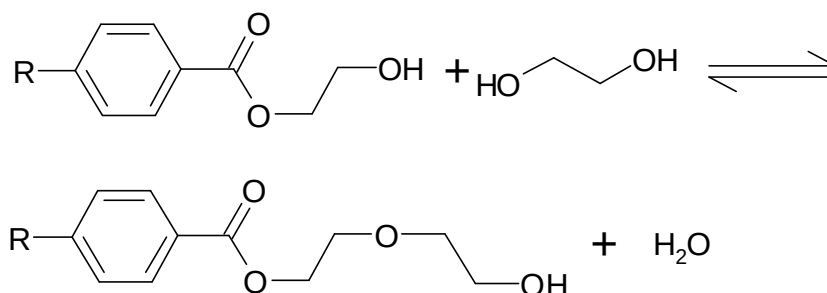
5.4. Etherification

Etherification of EG and/or hydroxyl end groups into DEG is a critical side reaction in PET synthesis (scheme 1.6 and 1.7). Most of the DEG is generated during the initial stages of the synthesis where the acid concentration is still high [31,32]. Another etherification product of EG is dioxane. Dioxane has a high vapour pressure and it is removed from the process as column top product. DEG is less volatile and, as a diol, it can be incorporated into the PET chain as comonomer. In some fibre grades, a DEG content of up to 1.5-2.5 %

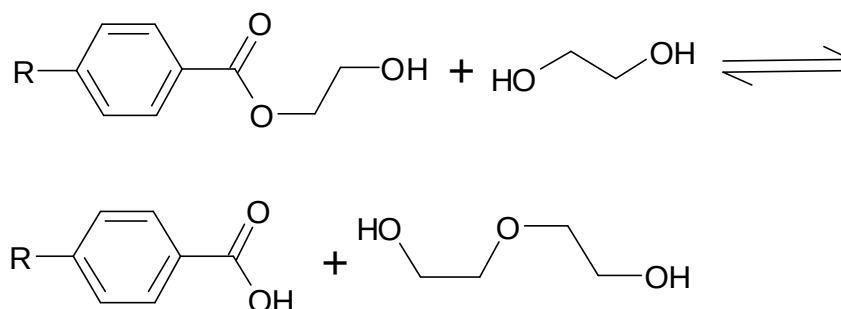
is specified to improve the dye ability. Nevertheless, DEG contents should be as low as possible in other PET grades, because DEG reduces the melting point and the thermal stability of the polymer. DEG formation is slightly exothermic with a reaction enthalpy of approximately -7.1 kJ mol^{-1} .

5.5. Thermal degradation

Thermal degradation of PET is an inevitable problem that occurs at the high temperatures of synthesis and processing. The activation energies of degradation reactions are higher than those of the chain growth reactions, and thus they become more evident with increasing temperature. Degradation reactions reduce the quality of PET by generation of carboxyl end groups and acetaldehyde (AA), and by discolouring it. Thermal and hydrolytic stability of PET decrease with increasing carboxyl end groups content. In standard PET grades this content should not exceed 25 mmol kg^{-1} . AA can diffuse into the food inside PET packaging and affect its flavour.



Scheme 1.6. Formation of bound DEG.

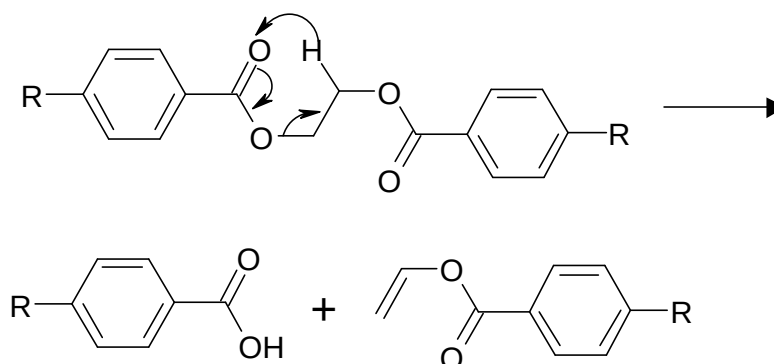


Scheme 1.7. Formation of free DEG.

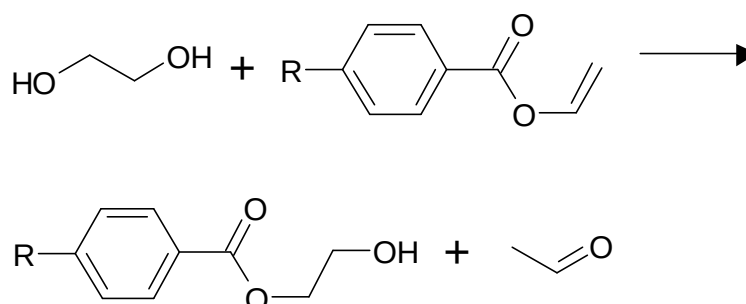
The main degradation reaction is the scission of the ester bonds to yield vinyl end groups and acids via a cyclic transition state (scheme 1.8). The vinyl end group generates

AA upon transesterification and for this reason they are often called ‘potential AA’ (scheme 1.9 & 1.10). Another source of AA is the thermal scission of hydroxyl end groups (scheme 1.11).

Thermal degradation of PET is strongly catalyzed by metal catalysts probably through a Lewis acid mechanism [33-35]. The most active catalysts are zinc, cobalt, cadmium and nickel cations. In oxygen presence, thermo-oxidative degradation takes place, which is much faster than thermal degradation in an inert atmosphere. Oxidative degradation can be minimized by careful operation under an inert gas atmosphere. Thermal degradation can be avoided only by reducing the reaction temperature, which also reduces the polycondensation rate. However, it can be reduced by addition of phosphorus based stabilizers such as phosphoric acid and its esters [36].



Scheme 1.8. Thermal degradation of the ester bonds via cis-scission and formation of vinyl end groups.

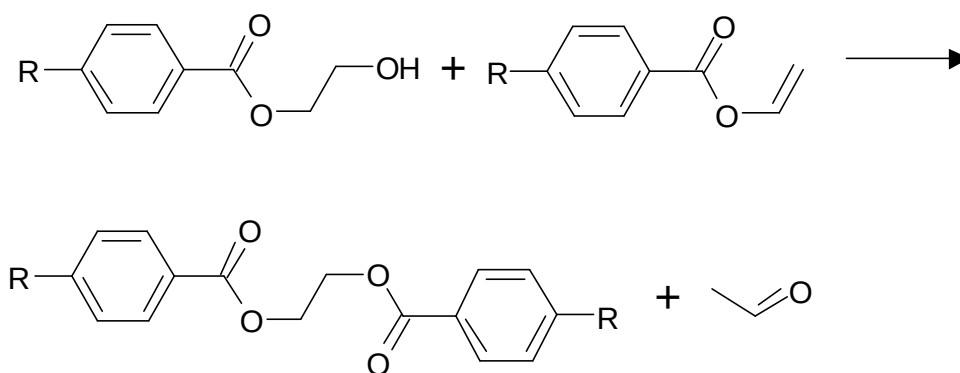


Scheme 1.9. Regeneration of hydroxyl end group and formation of AA.

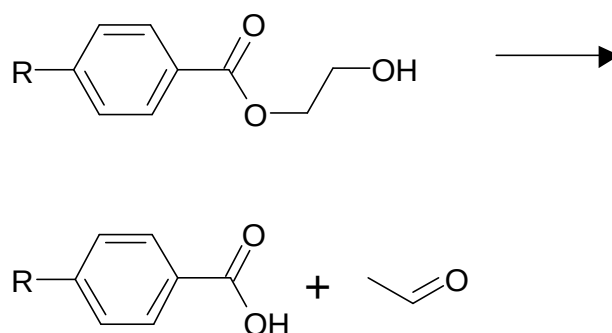
5.6. Colour formation

Colour is an important quality parameter especially for bottle grade PET. Yellow PET is regarded as a low-quality product. The colour is usually measured by a standardized system like the CIELAB. The colour value is obtained by combination of the three parameters L, a

and b. The parameter L characterizes the brightness of the sample between black (0) and white (100), a is the colour coordinate between green (-100) and red (+100) while b is the colour coordinate between blue (-100) and yellow (+100). High-quality PET grades have high L values and low a and b values between -1 and +1. Yellowing of the polymer is caused by thermal as well as by oxidative degradation and is a severe problem in PET synthesis, especially in the production of bottle grades. Formation mechanisms and the nature of chromophores in PET are still not fully understood. Postulated chromophores are polyenaldehydes from the aldol condensation of AA [37] and polyenes from polyvinyl esters [38], as well as quinones [39].



Scheme 1.10. Chain rebuild by reaction of vinyl end group with hydroxyl end group and generation of AA.



Scheme 1.11. Thermal degradation of hydroxyl end groups and formation of AA.

6. Catalysts for polyethylene terephthalate synthesis

Three different compounds of Sb are applied as catalysts for the polycondensation reaction, but the most widely used one is antimony trioxide (Sb_2O_3). The advantage of this compound is its low price compared to the other two compounds, antimony triacetate and

antimony glycoxide. However, the major drawback of this compound is its slow solubility in the reaction mixture. Antimony triacetate comprises 30 % of the applied Sb while the application of antimony glycoxide is limited to certain niche products due to its high prices.

Germanium is mainly used nowadays for Japanese markets where Sb application is prohibited. It is applied together with stabilizers based on phosphorus due to its tendency to support oxidative degradation. The applied compound is germanium dioxide. The main drawback of germanium compounds is their high prices.

Titanium alkoxides are very efficient catalysts for PET synthesis but their application is hindered by the low quality of the produced polymer. Titanium compounds are mostly used with combination of blue toner like cobalt compounds to mask the yellow colour of the produced polymer. To reduce side reactions, phosphorus based stabilizers are used. Another disadvantage of titanium compounds is their precipitation by hydrolysis. Chelate compounds like citric acid or tartaric acid or 2-hydroxy-ketones are added as precipitation stabilizers. Another approach to prevent precipitation is the impregnation of titanium in finely dispersed charcoal or silica. Catalyst particle size must be maintained below 500 nm to yield a clear polymer.

Aluminum compounds were patented by ICI as catalyst in the 1950s. However, severe side reactions limited its widespread.

DuPont patented zeolites as polycondensation catalyst. Zeolites are micro-porous crystalline solids with well-defined structures that have been used as finely distributed additives for polyester. Generally they contain silicon, aluminum and oxygen in their framework and cations, water and/or other molecules within their pores. Zeolites with 1.5-2.5 wt % water content are applied. However, it has been found that aluminum cations dissolved in the polycondensation reaction mass to be the main catalytic active component. Colour and thermal stability are improved by addition of small amount of cobalt as a blue toner and phosphorus compounds as stabilizers.

Beside titanium and aluminium compounds several elements and their combinations like samarium, tin, iron, molybdenum and tungsten, magnesium/potassium/phosphorus and zirconium/silicon/cobalt have been patented as polycondensation catalysts.

7. Polyethylene terephthalate production process

PET is produced batch wise on a small scale as well as continuously in large plants. Batch mode is applied nowadays for specialities and niche products with capacities from 20

to 60 ton per day. Depending on process conditions, applied technology and desired PET grade, six to ten batches per day are usually manufactured, each between 1.5 and 9.0 ton. Batch plants are often designed as multi-purpose plants in which different polyesters are produced.

The huge demand for PET is behind the development of continuously operated large-scale plants. The capacity of continuous PET plants has grown since the late 1960s from 20 ton per day to presently 1500 ton per day in a single line, with the aim still to higher capacities. To increase M_n of PET beyond 20000 g mol⁻¹ for bottle applications with minimum generation of AA and yellowing, further polycondensation is performed in the solid state at relatively low reaction temperature (220-235 °C compared to 275-295 °C for melt polycondensation). The chemistry of SSP is the same as that for melt-phase polycondensation. Mass-transport limitation and a very low transesterification rate cause the necessary residence time to increase from 1-3 h in the melt phase to 8-24 h in the solid state. Since the activation energies of the polycondensation and esterification reactions are lower than that of the side reactions, polycondensation in the solid state is not significantly affected by side reactions.

Polycondensation plants are made up of four main process units:

- Paste preparation unit
- Reaction unit
- Vacuum generation unit
- Distillation unit

A slurry of EG and PTA are mixed in a jacketed stirred tank vessel equipped with a stirrer for viscous fluids (e.g. Intermig) to prepare a paste with molar ratio of EG to PTA between 1.05 and 1.15.

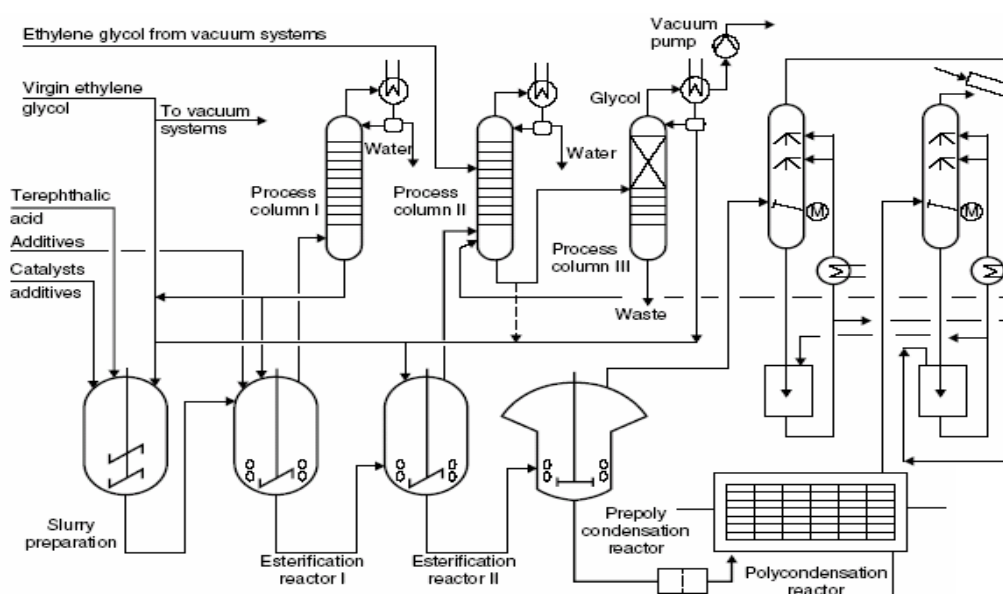
The melt-phase reaction is performed mainly in five continuous reactors in series: two esterification reactors, two pre-polycondensation reactors, and one high-viscosity reactor, which is also called finisher (scheme 1.12). However, the trend is nowadays to reduce the number of reactors in the process as this saves in terms of investment to throughput ratio and maintenance cost. In addition, the compactness of the design allows savings in civil works and steel structures. Several plant engineering companies have claimed new technologies with reduced number of reactors (Zimmer AG: 3 reactors [40], Uhde-Inventa-Fischer: 2 Reactors [41], Aquafil: 1 reactor [42]). In the 2 reactors process of Uhde-

Inventa-Fischer the esterification and the prepolycondensation are done in a special tower reactor (ESPREE[®]) (scheme 1.13, figure 1.2). This design does not contain mechanical agitators and stirring is autogeneous. It is characterized by a high ratio of surface to volume.

Esterification reactors are often stirred-tank reactors. The melt viscosity at the end of esterification is still moderate (0.02 to 0.8 Pa s) and no special stirrer design is required. The stirrer is fixed at the bottom of the reactor by means of an internal bearing housing. In the esterification step, the main task is to ensure sufficient heat for the water evaporation. For this reason, additional heating coils providing a larger heat-transfer area are installed in addition to the heating jackets. In some designs, a combination of recirculation pump and an external heat exchanger are needed to provide sufficient heat transfer. Water is removed via a process column. The bottom product of the column, mainly EG is brought back into the esterification reactor. The top product consists of water with small traces of EG. Usually a reverse-osmosis unit is connected to the distillate flow line to efficiently separate residual EG from the water. The esterification temperature is in the range of 235-285 °C while the pressure is from 1–4 bar. The final prepolymer is transported by gravity, pumps or nitrogen pressure through a filter unit with 10-60 µm mesh size into polycondensation reactor. Additives are usually introduced into the esterification reactor or before the prepolycondensation reactor.

In the polycondensation step, a large specific surface area is required as EG removal is the rate determining step of the polycondensation reaction. Pre-polycondensation reactors are stirred tank reactors with unusual ratio of diameter/height to provide a large gas-liquid interface. From the pre-polycondensation stage, the melt is pumped by gear pumps through a filter system into the Polycondensation reactor (finisher). Finishers consist of horizontal vessels supplied by a series of horizontal stirrers (scheme 1.14). The most applied stirrers are perforated rotating discs and shaftless cages (figure 1.3). Stirrer design is optimized to provide a plug flow of the melt with little back mixing in order to keep the residence time distribution narrow and to achieve higher average polycondensation rate. The final product is discharged from the finisher by pumping through a second filter system before quenching with cold water and granulation. Most of the generated vapour is condensed in spray condensers that are equipped with circulation pumps and an EG cooler. The rest vapour is sucked from the gas phase with a vapour jet located down-stream behind the spray condenser to generate the necessary vacuum for the reaction zone.

Polycondensation temperature ranges between 270 and 295 °C. At 280 °C, the melt enters the polycondensation reactor with a viscosity of about 0.8 Pa s and leaves it with a viscosity of about 400 Pa s. The final degree of polycondensation can be controlled by adjusting vacuum, reaction temperature and average residence time. The actual viscosity is continuously measured by a viscometer at the outlet of the finisher. Finishers are self-cleaning reactors and very little maintenance stops are needed. A scraper is added to the horizontal stirrer to reduce the gap between the stirrer and the wall, thus preventing the polymer from sticking to the reactor wall. The cage-type stirrer is shaftless, which improves the product quality due to the avoidance of polymer sticking to a shaft and thus staying in the reactor for elongated times. Long residence times lead to thermal degradation of the polymer and cause black spots in the transparent final products. Finishers are usually heated solely by friction during stirring of the highly viscous melt. The temperature of reactor wall is lower than that of the melt, which leads to improved product quality by avoiding an overheating of the polymer in contact with reactor wall.



Scheme 1.12. A flow sheet of the continuous 4-reactors process of Zimmer [12,43].

The so-called double-drive disc-type finisher permits the simultaneous operation at two different stirrer speeds. A higher stirrer speed is used for the first reactor part with lower melt viscosity, while a lower stirrer speed is used for the second reactor part with higher melt viscosity. This reactor type can thus be used for the production of high-viscosity PET in only one polycondensation stage. Process vapours are purified in the distillation unit,

which commonly consists of two or three columns and is designed for continuous operation. The purified EG is condensed at the top of the last vacuum rectification column and recycled back to the process. Gaseous AA and other non-condensables are burned to generate energy for the process. High-boiling residues from the bottom of the last column are also burned.

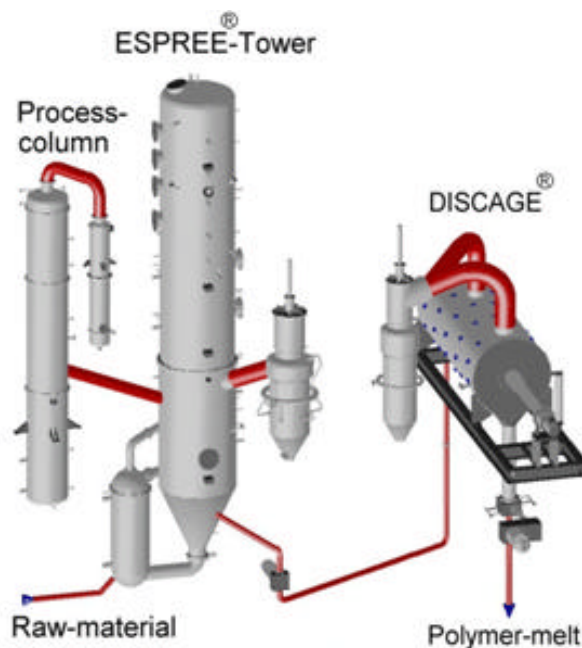
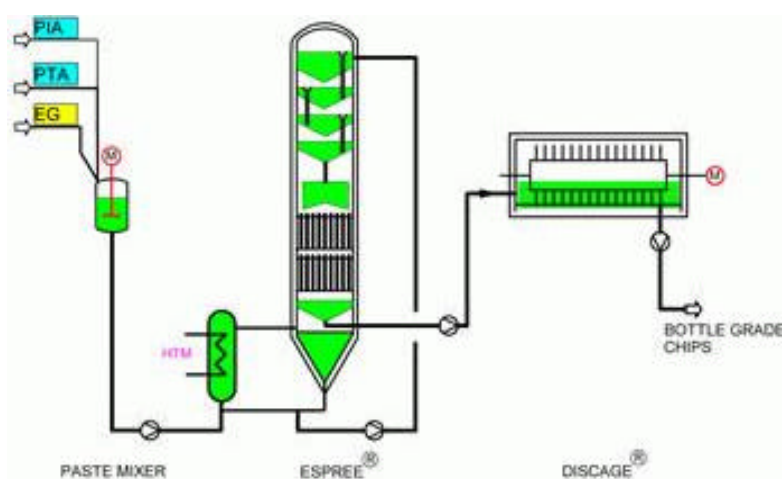
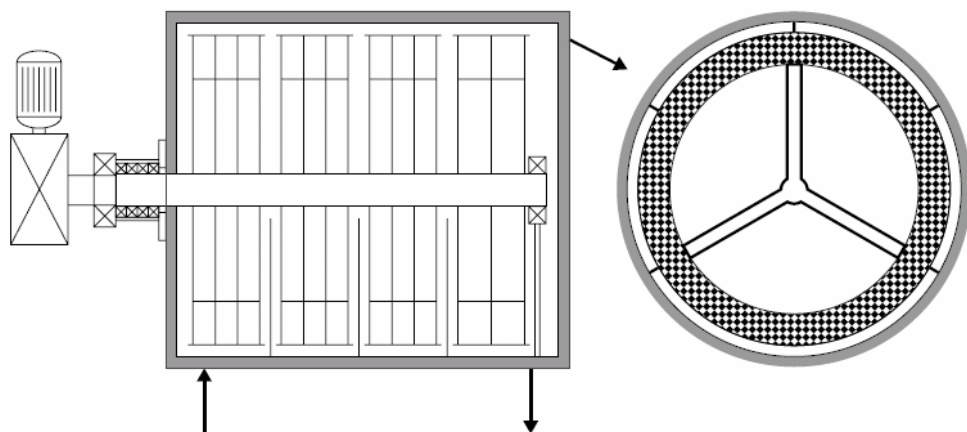


Figure 1.2. The 2-reactors continuous process consisting of an ESPREE tower reactor for esterification and prepolycondensation, and a DISCAGE finisher for polycondensation [41].



Scheme 1.13. The 2-reactors continuous process consisting of an ESPREE tower reactor for esterification and prepolycondensation, and a DISCAGE finisher for polycondensation [41].



Scheme 1.14. A side view of a rotating disc reactor (left), and a cross-section of one perforated disc (right) [12,43].

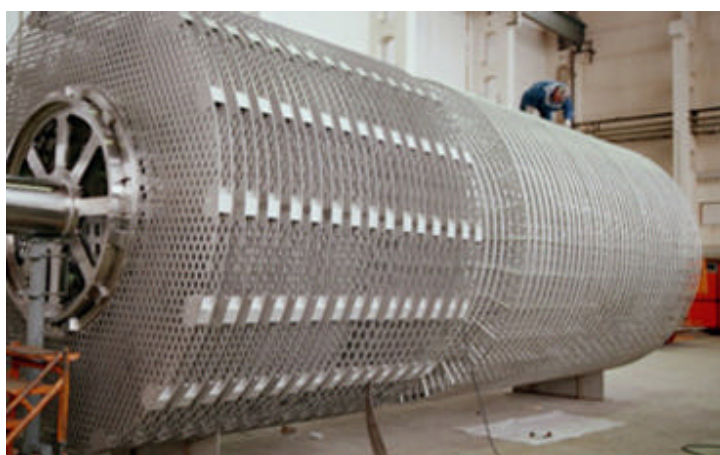


Figure 1.3. The stirrer of the DISCAGE finisher for Fischer polycondensation process [41].

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Chapter 2: Optimization of Simultaneous Thermal Analysis for Fast Screening of Polycondensation Catalysts

Abstract

Dynamic simultaneous thermogravimetric and calorimetric thermal analysis was optimized to screen the activity of different catalysts in polycondensation of bis-hydroxy ethylene terephthalate to polyethylene terephthalate. Reaction was performed by heating mixtures of bis-hydroxy ethylene terephthalate with a catalyst at a constant heating rate to 300 °C 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 is used as an index of catalytic activity. It is obtained from maximum differential scanning calorimetry signal together with the maximum derivative of thermogravimetry signal. Temperature at which the reaction starts is also applied as an activity index. It is determined from the onset of mass loss. The value of these three indices are smaller for more active catalysts.

1. Introduction

Polycondensation of BHET to PET in a thermal analysis oven on a micro-liter scale has several advantages over that in lab-scale and larger reactors [1-4]. The important merits include easy handling, online data acquisition and very fast reaction rate (the reaction is finished in minutes compared to hours in larger scale reactors). The large surface to volume ratio of the crucibles, which are used as micro-reactors, enables rapid removal of the condensate by-product EG, which is the rate determining step due to the reversibility of the polycondensation reaction. However, the large specific surface causes also major problems that can lead easily to data misinterpretation. Catalytic activity of container material and monomer evaporation among others are critical points that should be overcome if reliable results to be obtained.

The aim of this chapter was to optimize simultaneous gravimetric and calorimetric thermal analysis (STA) for fast screening of polycondensation catalysts. Application of STA for this aim would give a better panorama of the ongoing physical (monomer evaporation, crystallization, melting, etc.) and chemical processes (polycondensation).

2. Principle of thermal analysis

International Confederation for Thermal Analysis and Calorimetry (ICTAC) has defined thermal analysis (TA) as "a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature program" [5]. TA includes also isothermal studies, in which material properties are measured as a function of time at a certain temperature. This definition covers a wide range of methods but the main ones and their measured properties are: Thermogravimetry (TG) (mass change), differential scanning calorimetry (DSC) (heat change), differential thermal analysis (temperature), evolved gas analysis (evolved gases), thermodilatometry (physical dimensions), thermomechanical analysis (mechanical properties), thermooptometry (optical properties), thermoelectrometry (electrical properties) and thermomagnetometry (magnetic properties).

2.1. Differential scanning calorimetry

In a DSC, the sample and a reference are placed inside crucibles symmetrically in an oven. In the state of thermal equilibrium, oven, sample and reference have the same temperature. When a change of heat capacity, phase transition or reaction occurs, the

equilibrium is disturbed. The sample temperature is higher (exothermic event) or lower (endothermic event) than that of the reference. This temperature difference (ΔT) is detected and the heat flow is calculated from it (equation 2.1).

$$\Delta \dot{Q} = -K \Delta T \quad [\text{J s}^{-1}] \quad 2.1$$

The constant K has to be determined by calibration. The difference between the heat flowing to the sample and that flowing to the reference is given by equation 2.2:

$$\Delta \dot{Q} = (\dot{Q}_S - \dot{Q}_R) + (C_{p,MS} - C_{p,MR})b \quad 2.2$$

Where $\dot{Q}_R$ is the heat flow to the reference [J s^{-1}], $C_{p,MS}$ is the heat capacity of the sample measuring system [J K^{-1}], $C_{p,MR}$ is the heat capacity of the reference measuring system [J K^{-1}] and b is the heating rate [K s^{-1}].

As can be seen from equation 2.2, not only the heat capacities of the sample and the reference themselves are important, but also the small difference between the heat capacities of their measuring system (sample holder, etc.). This contribution becomes more evident with increasing heating rate but it can be corrected and neglected by subtracting the measurement curve from a zero line (run with two empty crucibles). The heat flow to the sample is given by equation 2.3:

$$\dot{Q}_S = C_{p,s} \frac{dT_s}{dt} + \dot{Q}_{chem} \quad 2.3$$

Where $C_{p,s}$ is the heat capacity of the sample [J K^{-1}], $\dot{Q}_{chem}$ is the heat flow due to the chemical reaction and is given by equation 2.4:

$$\dot{Q}_{chem} = R_{chem} V (-\Delta H_R) \quad 2.4$$

Where R_{chem} is reaction rate [$\text{mol l}^{-1} \text{s}^{-1}$], V is reaction volume [l] and ΔH_R is molar reaction enthalpy [J mol^{-1}].

The heat flow to the inert reference is given by equation 2.5:

$$\dot{Q}_R = C_{p,R} \frac{dT_R}{dt} = C_{p,R} b \quad 2.5$$

Where $C_{p,R}$ is the heat capacity of the reference [J K⁻¹].

Therefore, the differential heat flow is given by equation 2.6:

$$\Delta \dot{Q} = (\dot{Q}_S - \dot{Q}_R) = C_{p,s} \frac{dT_s}{dt} + \dot{Q}_{chem} - C_{p,R} b \quad 2.6$$

2.2. Thermogravimetry

TG is the measurement of mass variations under a controlled temperature program. The plot of mass change as a function of temperature under non isothermal conditions, or as a function of time in isothermal experiments is called a thermogravimetric measurement. Any process occurring with mass change is amenable to investigation by TG such as adsorption or absorption, desorption, dehydration or desolvation, sublimation, vaporization, decomposition, solid-solid reactions and solid-gas reactions. From quantitative results viewpoint, TG is in the first rank among other TA methods as the signal is measured directly by high precision microbalances.

The main components of any TG system are a good precision microbalance and a programmable furnace. Other components are sample temperature sensor, furnace temperature sensor, balance controller, gas purging or vacuum controller, furnace temperature programmer and computer. Specification of components and design varies according to the producer and the required feature in application such as sensitivity, mode of operation and accessible temperature range.

The microbalance weighs material with great sensitivity and precision in the micro gram range. Weighing principle is the null point where a sensor detects deviation of the balance beam from its null position. Null position is usually restored by optical or electronical methods. Null point mechanism ensures that the sample position in the furnace will not change. Most commercial microbalances operate at atmospheric pressure. Vacuum and high-pressure studies normally require specialized equipment, either commercial or home-made, as do experiments with corrosive gases. Robust furnaces are available to withstand corrosive atmospheres, that may exist during certain reactions, as well as temperatures ranging from subambient (e.g., -125 °C) or room temperature up to as high as 1650 °C. A furnace is usually programmable at a wide scope of heating and cooling rates as well as at isothermal conditions. Most applications involve heating rates of 1-50 K min⁻¹, but system with higher and lower heating rates are well established.

The maximal sample weight is dependent on the type of the applied microbalance and is in the range from 1 mg to 3 g. Small sample mass has the advantage that the errors due to temperature gradients throughout the sample are minimized. Big sample mass has advantage that errors due to sample heterogeneity (particle size and size distribution) are smaller.

The use of different furnace gas atmosphere is important as certain type of reactions may be boosted, postponed or suppressed by surrounding the sample with suitable gas conditions. In this way, oxidation reactions may be prohibited by running in an inert gas or promoted by measuring in air or oxygen. This may be achieved by passing the selected gas through the TG system and over the sample under test. The use of flowing gas above the sample is also important to clear the gas produced during reaction or decomposition from the source of the process. Gas purging enables thermogravimetric measurements to be done under different atmospheres: air, oxygen, inert gas and reactive atmosphere. In addition, runs made with increased partial pressure of the same gas being given off by specific types of decomposition reaction, delay such reactions until the increased partial pressure of the sample surrounding gas can be overcome. As a result the decomposition temperature of such reactions is increased and moves up the temperature scale to occur with increased reaction speeds. This results in a steeper weight loss curves and greater DTG (first derivative of TG) peak heights and therefore, in a higher resolution.

In TG experiments many factors can affect the result and/or lead to errors, both sample- and instrument related, and some of which are interactive [6,7]. The main factors are heating rate and sample mass, whose increase tends to increase the temperature at which the investigated process occurs, and to decrease the resolution between successive mass losses. Sample particle size, the way in which it is packed, crucible shape, and gas flow rate also affect the progress of a thermal reaction. Careful attention to consistency in experimental details normally results in good reproducibility. On the other hand, studying the effect of deliberate alterations in such factors as heating rate can provide valuable insights into the nature of observed reactions. Some important error sources such as the buoyant effect of the crucibles, temperature measurement, and calibration must be considered for quantitative measurements to be done.

Sample containers are in most cases cylindrical pans of diameter between 3 and 8 mm and height between 2 and 10 mm. Compatibility between pan material and the investigated

substance must be carefully considered. Pans made of aluminum, platinum, alumina, and silica are common. Temperature sensation is achieved by a thermocouple located near the sample container.

Because of inevitable thermal gradients within the instrument, a measured temperature can never be taken as an accurate reflection of the real sample temperature and reproducible location of the thermocouple is necessary.

2.3. Simultaneous thermal analysis

Running of different thermal analysis measurements simultaneously, i.e. on the same sample at the same time, eliminates the uncertainty inherent in the comparison of results obtained using two different individual thermal analysis units. This is particularly valuable in the case of complex decomposition reactions.

TG is a technique that, although limited in scope to those reactions taking place with a change in weight, gives results that are intrinsically quantitative. Thus once the balance has been calibrated, and the buoyancy effects have been subtracted from the base line, the measured weight losses will faithfully reflect the reaction extent.

DSC is considerably more versatile technique and can detect any reaction that takes place with a change in energy. However, careful calibration using heat capacity measurements and/or materials with known heats of transition is necessary to obtain quantitative results from DSC measurements. The results obtained from DSC are dependent on the experimental conditions and since both the nature of the atmosphere and the crucible type and material affect the results directly, calibration must be carried out under the same conditions as the measurements are to be made. The instrument baseline will reflect changes in the heat capacity of the sample and will also be influenced by changes in the disposition of the sample in the crucible due to melting, bubbling or sintering. These factors can sometimes lead to complications in the interpretation of the results, particularly at high temperatures.

The two techniques are therefore complementary in nature and the TG curve can often be used to aid in the interpretation of DSC data. A stable baseline will be given when a reaction is not taking place and this baseline will not be altered by variations in the programmed heating rate or by physical changes in the sample such as melting or sintering or by changes in specific heat capacity. Although in many cases results obtained from

different TG and DSC instruments can be compared, there are a number of factors, which make it advantageous to carry out the measurements simultaneously. These include differences in the sample heating rates due to different thermal lags in individual instruments, differences in self-heating/cooling of the sample due to different thermal environments and uncertainties in the sample temperature in the TG measurements. More importantly, although the same gas flow rate may be used in TG and DSC experiments, it is unlikely to have the same purging effect on the sample in different types of equipment, which may lead to significant differences in the experimental results. For complex reactions where there are several overlapping stages, it may be difficult to match the energy changes and weight losses when the reactions are carried out separately. This is particularly true when decomposition takes place from a bubbling melt, where there may in any case be small variations from experiment to experiment.

One of the problems in carrying out TG experiments is the uncertainty in measuring the sample temperature since the thermocouple is not in direct contact with the sample crucible. TG data obtained using simultaneous equipment does not suffer from this problem since the sample temperature is measured directly. Also, since the DSC signal is measured simultaneously, the temperature signal of the instrument can be calibrated using the melting points of reference materials. The need for calibration using magnetic transitions or the drop-weight method using fusible links is therefore avoided.

The normal method of constructing a TG/DSC apparatus is to incorporate a DSC head into a thermobalance. The main problem to be overcome in the construction of TG/DSC equipment is to obtain the thermocouple output from the DSC head without affecting the action of the balance. This is normally carried out by using fine wires or ribbons, made of the same material as the thermocouples, to make the connection from the head to the measuring circuit.

3. Experimental

3.1. Apparatus

Catalyst screening was done on a simultaneous thermal analyzer (STA 409 PG from Netzsch). This system enables simultaneous run of differential calorimetric and thermogravimetric measurements. It features a platinum-platinum-10 % rhodium heat-flux DSC plate-type head, mounted to the top of a vertical beam electronic microbalance. The platinum-rhodium wound furnace, specifically designed for DSC studies, gives an

operating range from ambient temperature to 1650 °C. The oven is electrically heated and cooled by liquid nitrogen. The inner room of the oven can be flushed with purge gas (nitrogen in this study), which enables removal of volatile by-products away from the reaction medium. The purge gas flows from the bottom of the oven to its top. The whole system is controlled by a computer, which records the sample mass and temperature and performs all the necessary calculations to obtain the DSC signal. Figure 2.1 shows a scheme of the applied instrument.

3.2. Calibration

The measuring components of the thermal analyzer should be calibrated to obtain reliable measurements: Temperature measuring device and calorimetric head. Calibration serves to correct errors in the measured signal. Calibration should be done under the same conditions at which the sample will be measured. The reasons behind the error in temperature measurement are the long time drift of the electronic amplifier and the aging process of the thermoelement. Temperature calibration eliminates the deviations assuming they are constant. For this reason a series of measurements on calibration materials with exactly known transition temperature (for example melting point) and transition enthalpy (for example melting enthalpy) should be done. Thermoelement- and calorimetric head calibration can be done in one step since the two signals originates from temperature measurement.

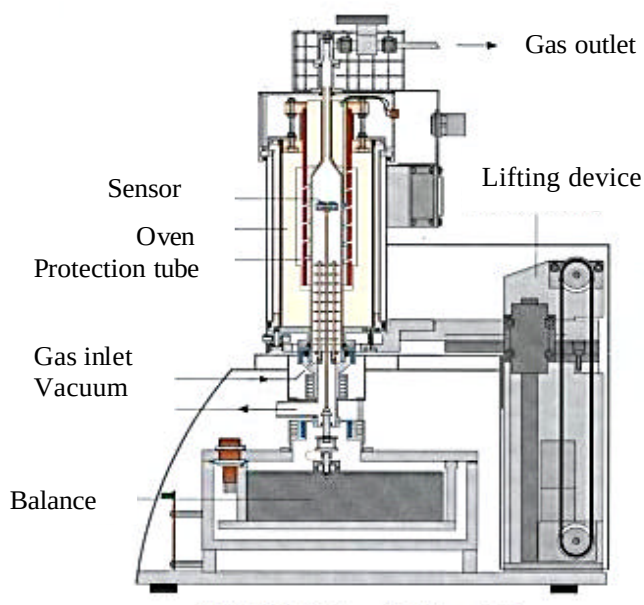


Figure 2.1. Scheme of the applied thermal analyzer STA 409 PG [8].

The calibration should be performed with different materials whose transition occurs at temperatures that cover the whole measuring range since the deviation is temperature dependent. The useful temperature range for running BHET polycondensation reaction is from about 100 °C to 300 °C because at temperature below 100 °C no considerable reaction occurs and at temperature higher than 300 °C side reactions are severe. Table 2.1 summarizes the properties of the four materials that were used as a calibration set.

Table 2.1. The physical properties of the standards used as references for STA calibration.

Material	Formula	Melting point [°C]	Melting enthalpy [J g ⁻¹]	Purity [%]
Biphenyl	C ₆ H ₅ C ₆ H ₅	69.2	120.4	99.0
Rubidium nitrate	RbNO ₃	164.2	26.6	99.99
Potassium perchlorate	KClO ₄	300.8	104.9	99.9
Silver sulfate	Ag ₂ SO ₄	426.4	51.7	99.999

For each calibration material three melting and crystallization runs were done (figure 2.2). The first melting peak was not considered as heat transfer to the sample is still not optimal before its melting and its uniform distribution in the crucible. The second and third peaks are averaged to get the experimental values of the melting onset and the melting enthalpy.

Temperature correction, $\Delta T_{correction}$, is a nonlinear function of the experimental temperature, T_{exp} , and has the following form:

$$\Delta T_{correction} = A + B T_{exp} + C T_{exp}^2 \quad [K] \quad 2.7$$

The value of the 3 parameters A , B and C depends on the time between the calibration experiments and they are usually larger if the time between two calibration experiments is longer. For reliable calorimetric measurements, it is not enough to measure the difference of the heat flow between the sample crucible and an empty reference crucible of the same type, shape and weight. In addition, a zero line was done and was subtracted from each measurement.

The DSC signal of the STA 409 PG is given in $\mu V s^{-1}$ and it should be converted into W by multiplying the measured signal by sensitivity which is obtained by calibration:

$$Sensitivity = \frac{\text{expected heat flow [J]}}{\text{measured DSC signal [mV]}} \quad [J \mu V^{-1}] \quad 2.8$$

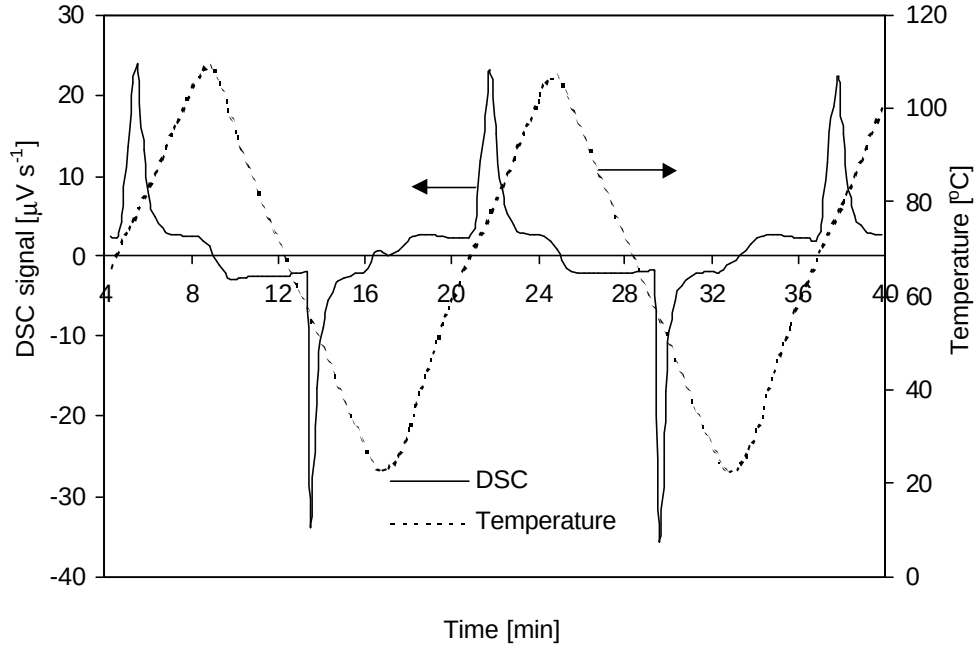


Figure 2.2. Melting-crystallization thermogram of biphenyl at 10 K min⁻¹. Sample mass is 10 mg.

4. Screening principle

Thermograms obtained from dynamic polycondensation of a BHET/catalyst mixture are shown in figure 2.3. Two endothermic peaks are obtained by plotting heat flow difference between sample cell and an empty reference cell versus temperature. The first peak, which occurs at about 114 °C, is due to BHET melting. The second peak was due to BHET polycondensation into higher oligomers. Indeed this peak represents the heat of vaporization 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 (equation 2.9).

$$Polycondensation\ rate = k_o \exp^{-\frac{E}{R.T}} [OH]^n \quad 2.9$$

Where k_o is the pre-exponential factor of Arrhenius equation [$\text{l}^{n-1} \text{mol}^{1-n} \text{s}^{-1}$], E is the activation energy [J mol^{-1}], R is universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], T is the reaction temperature [K], $[OH]$ is concentration of hydroxyl end groups [mol l^{-1}] and n is reaction order.

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 hence it 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. If EG removal is efficient and there is no mass transfer limitations inside the reaction melt or on the melt-gas interface DTG curve represents the polycondensation rate. If reactants are consumed earlier, maximum rate will occur also earlier and consequently the temperature to reach maximum rate ($T_{\max}$) of DSC and DTG will have smaller values. Therefore, these two indices can also be applied as activity ordering parameters in catalyst screening. The total mass loss achieved after a certain reaction time can also be used as a screening index if mass loss is exclusively due to EG removal and monomer evaporation is negligible.

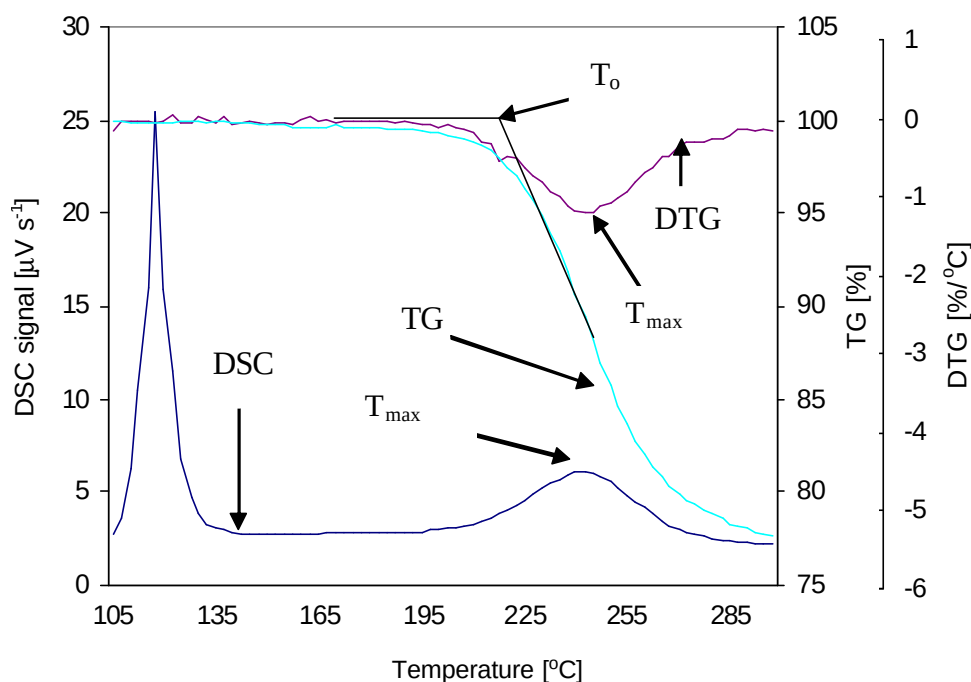


Figure 2.3. Thermograms of catalyst/BHET mixture heated at 10 K min^{-1} showing the three activity ordering indices: $T_{\max}$ of DSC and DTG and T_o of TG. Sample mass is 10 mg.

5. Optimization of simultaneous thermal analysis

5.1. Sample preparation

Due to technical limitations it was not possible to weigh the appropriate amount of catalyst directly in the crucible; for example about 10^{-2} mg of catalyst in case of 2000 ppm catalyst concentration in 10 mg of BHET (ppm is mol catalyst per 10^6 mol BHET). For this reason a larger amount of catalyst mixture in BHET was prepared.

Solvent effect was studied by preparation of mixtures containing 2250 ppm of antimony triacetate in BHET by mixing 2.65 mg of antimony triacetate with 1 g of BHET at 40 °C for 3 h in 10 ml of the following solvents: Water, methanol, acetone and EG. At this temperature, monomer solubility is higher than that at room temperature. However, higher temperature cannot be applied as the monomer may polymerize into higher product.

After this homogenization process, the solvents were evaporated at 40 °C. Three runs of each of the samples were done by heating 10 mg samples at 10 K min^{-1} from room temperature to 300 °C. The $T_{\max}$ of DSC was chosen as activity index. The results are summarized in table 2.2.

Table 2.2. The effect of Sb/BHET mixture preparation in different solvents on the reproducibility of the value of $T_{\max}$ of DSC.

Solvent	EG	Methanol	Acetone	Water
BHET solubility	-	-	+	-
$T_{\max}$ of 1st Run [°C]	262.6	267.0	266.5	268.6
$T_{\max}$ of 2nd Run [°C]	257.8	263.0	267.1	263.2
$T_{\max}$ of 3rd Run [°C]	260.9	265.7	266.2	269.2
Average $T_{\max}$ [°C]	260.4	265.5	266.6	267.0
Standard deviation [%]	0.9	0.8	0.5	1.4

+ completely soluble, - not completely soluble

Antimony triacetate is not the active form of Sb in the polycondensation reaction, which is believed to be antimony glycolate. For this reason, antimony triacetate was completely dissolved in EG by boiling at 197 °C for various periods of time (1-3 h). A given amount of this solution was mixed with BHET at 40 °C for 3 h to yield a 2250 ppm mixture. EG was then evaporated at 40 °C under high vacuum (0.01 mbar) overnight. The $T_{\max}$ of Sb decreased upon glycolysis, which indicates higher activity but it was the same after 1 and 3 h of glycolysis, which indicates that glycolysis was complete after 1 h (table 2.3). Different

forms of Sb have been reported to have the same activity in the polycondensation of BHET. However, in lab-scale and larger reactors the reaction needs between 1 and 5 h to be accomplished depending on the reactor type, and the temperature range is between 275 and 295 °C. In screening experiments, the polycondensation time is from 10 to 20 min depending on heating rate, and at the same time, T_{max} appears in most of the cases below 275 °C depending on catalyst activity and concentration. Therefore, activation time is important and cannot be neglected (short reaction time, low activation temperature). On the other hand, the time required for activation of Sb in large reactors is negligible in comparison to the polycondensation time and at the same time the activation temperature is high. In this case, probably the time of heating the reactants to reaction temperature is enough for activation (several minutes).

Sb acts as a homogeneous catalyst, i.e. it is soluble in the reaction medium. The reproducibility of the method was checked also for heterogeneous catalysts like HT. To this end, 5 mg of HT (MA1 from Bystricko) were mixed with 3 g of BHET in acetone at 40 °C for 15 min before acetone was evaporated in a rotation evaporator at the same temperature and partial vacuum. The results were highly reproducible (table 2.3).

Table 2.3. Effect of glycolysis time on the value of T_{max} of DSC of Sb.

Glycolysis time [h]	1	3
T_{max} of 1st Run [°C]	243.6	246.1
T_{max} of 2nd Run [°C]	245.3	244.1
T_{max} of 3rd Run [°C]	242.2	245.6
Average T_{max} [°C]	243.7	245.3
Standard deviation [°C]	0.6	0.5

Table 2.4. Effect of preparation in acetone on the reproducibility of the T_{max} value of DSC of HT.

T_{max} of 1st Run [°C]	252.0
T_{max} of 2nd Run [°C]	253.0
T_{max} of 3rd Run [°C]	251.1
T_{max} of 4th Run [°C]	251.6
T_{max} of 5th Run [°C]	252.4
Average T_{max} [°C]	252.0
Standard deviation [%]	0.3

Therefore, the preparation of the catalyst mixture for thermal analysis affects the T_{max} values and the reproducibility of these values. Sb should be activated in EG before its study

by STA. On the other hand, preparation of HT in acetone yields reproducible results. Moreover, in comparison to EG, acetone can be removed easily after preparation (minutes compared to hours).

5.2. Catalytic activity of crucible material and monomer evaporation

BHET polycondensation can be considered as an irreversible reaction if EG is removed efficiently as it is formed (high specific surface area, low viscosity, efficient nitrogen purging). Condensation of one mol of BHET produces one mol of EG. For complete conversion of free ester groups into bound ester groups, 24.4 % mass loss as EG by-products is calculated by equation 2.10:

$$\frac{\text{Total mass loss}}{\text{Original mass}} = \frac{\text{Molar mass of EG}}{\text{Molar mass of BHET}} = \frac{62 \text{ g mol}^{-1}}{254 \text{ g mol}^{-1}} = 0.244 \quad 2.10$$

Crucibles made of different material were tested for their catalytic activity on the polycondensation reaction. The commercially available crucibles are made of aluminum, alumina, graphite, platinum, glass, quartz and glass. In addition crucibles made of teflon were prepared in house and tested.

Alumina has been reported as a polycondensation catalyst [9]. On the other hand, Zimmerer et al [3] 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 in case of alumina. They deduced also from the ratio of weight and number average molecular weight (M_w and M_n) that aluminium catalyzes also the degradation of the formed polymer.

In order to investigate the contradiction between reference [3] and [9], Zimmerer experiments were repeated. 8.9 mg of pure BHET were condensed in aluminium, platinum and alumina pans without covers for 240 min at 280 °C without addition of any catalyst. The diameter of these crucibles was 4 mm. The STA oven was evacuated and refilled with nitrogen at one atmosphere pressure before each run to prevent product oxidation. The oven was heated at 20 K min⁻¹ to 120 °C where it was held at constant temperature for 60 min before heating them to 280 °C at the same heating rate where it was held for 240 min. Nitrogen was applied as purging gas at 50 ml min⁻¹. The resulting TG thermograms are shown in figure 2.4. In all applied crucible materials the 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 it was much lower in alumina (35 %).

Total mass loss values above 24.4 % are due to monomer evaporation as condensed monomer has been seen inside the STA oven. BHET exists 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 by gel permeation chromatography (GPC 1100 of Agilent). The order of molecular weight was found to agree with that obtained by Zimmerer (table 2.5), 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 and is believed to become the dominant reaction after a certain degree of conversion of BHET (long thermal treatment at high temperature). The order of total mass loss after BHET polycondensation at 200 °C was the same as in the case of 280 °C (figure 2.5). 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 2.6). The same molecular weight order was also obtained after 30 min of polycondensation at 280 °C (table 2.7). These results showed that alumina boosts quick formation of high molecular weight polymer, and at the same time boosts degradation of the formed bound ester groups, which becomes the dominant reaction after a certain reaction time, leading to a decrease in the 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.

Figure 2.6 shows the total mass loss after polycondensation of 3 mg of pure BHET at 200 °C in open crucibles made of aluminum, glass, quartz and alumina. The highest mass loss was observed in case of aluminum and it was lowest in alumina. Mass loss in glass and quartz was in between. As discussed above, this means that aluminum has lowest activity followed by glass, quartz and alumina. Also, the results in quartz were not reproducible, probably due to the fact that quartz crucibles were hand-made. Furthermore, steel and

copper have showed strong catalytic activity on polycondensation [10] while teflon and graphite showed thermal lag due to their low thermal conductivity (BHET melting onset at 10 K min^{-1} was 101.5, 105.1 and 106.0 °C in aluminum, graphite and teflon respectively).

Table 2.5. Number and weight average molecular weights of PET produced in different pans at 280 °C for 240 min.

<i>Sample</i>	<i>M_n</i> [kg mol ⁻¹]	<i>M_w</i> [kg mol ⁻¹]
<i>Platinum at 280 °C for 240 min</i>	36	137
<i>Aluminium at 280 °C for 240 min</i>	43	151
<i>Alumina at 280 °C for 240 min</i>	30	105

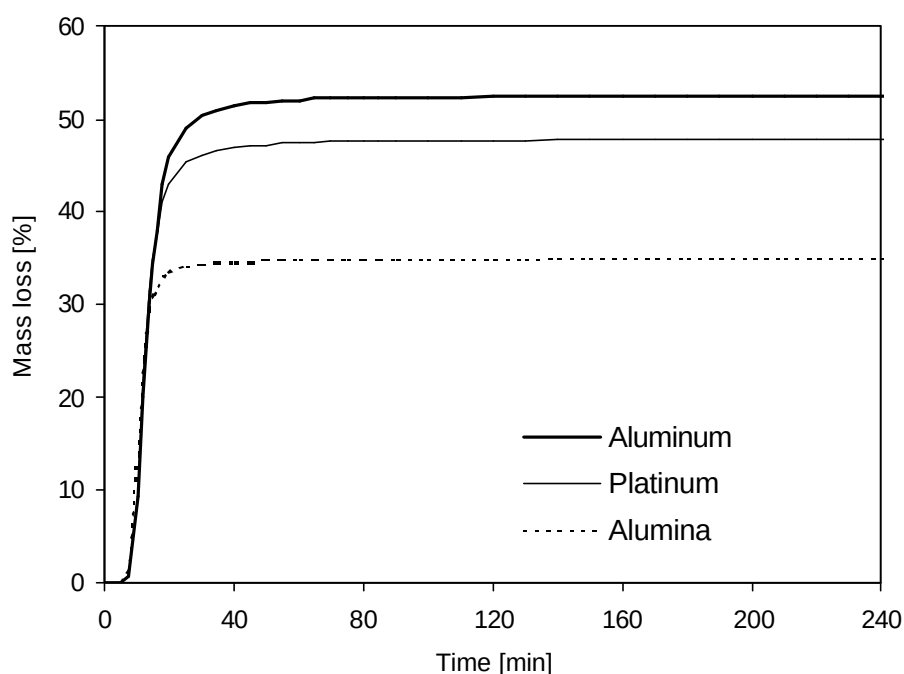


Figure 2.4. Mass loss versus polycondensation time of BHET in aluminium, platinum and ceramic pans at 280 °C for 240 min. Sample mass is 8.9 mg.

Table 2.6. Number and weight average molecular weights of PET produced in different pans at 200 °C for 240 min.

<i>Sample</i>	<i>M_n</i> [kg mol ⁻¹]	<i>M_w</i> [kg mol ⁻¹]
<i>Platinum at 200 °C for 240 min</i>	0.4	3.5
<i>Aluminium at 200 °C for 240 min</i>	0.3	1.9
<i>Alumina at 200 °C for 240 min</i>	1.1	5.4

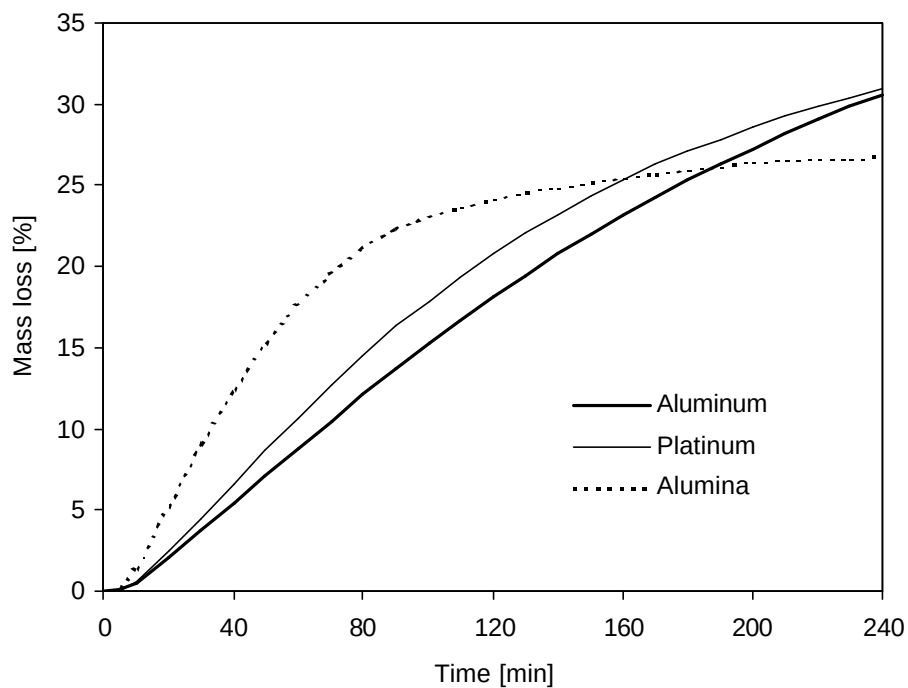


Figure 2.5. Mass loss versus time of BHET polycondensation in aluminium, platinum and ceramic pans at 200 °C. Sample mass is 8.9 mg.

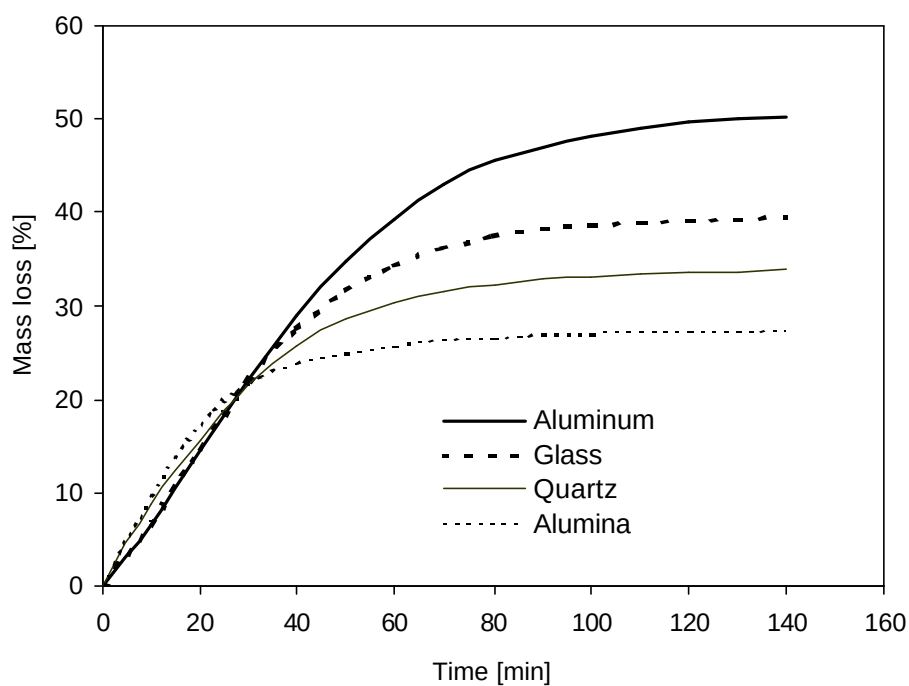


Figure 2.6. Mass loss curve of BHET polycondensation at 200 °C in crucibles made of aluminium, glass, quartz and alumina. Sample mass is 3 mg.

Table 2.7. Number and weight average molecular weights of PET produced in different pans at 280 °C for 30 min.

<i>Sample</i>	<i>M_n</i> [kg mol ⁻¹]	<i>M_w</i> [kg mol ⁻¹]
<i>Platinum at 280 °C for 30 min</i>	14	32
<i>Aluminium at 280 °C for 30 min</i>	9	21
<i>Alumina at 280 °C for 30 min</i>	20	74

Therefore, crucibles made of aluminum were used through this project as it showed the best properties among the studied material. It has the lowest catalytic activity and at the same time, excellent thermal conductivity.

Polycondensation under isothermal conditions is complicated by monomer evaporation as shown above. Running at low temperature does not overcome this problem and at the same time results in a very slow polycondensation rate. To demonstrate this fact, different amounts of pure BHET (3, 9 and 18 mg) were heated isothermally at 180 °C in uncovered aluminium pan. The resulting thermograms are plotted in figure 2.7. 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 3 mg of BHET was about 33 %. This indicates that mass loss was not only due to EG evolution over the course of polycondensation and that monomer evaporation still takes place. 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. At higher temperature (200 and 210 °C) monomer evaporation was more severe while at lower one (150 °C) the mass loss rate was too slow (figure 2.8).

To hinder monomer evaporation, catalyst screening was performed under dynamic conditions and the crucibles were covered by lids with a central hole. Dynamic polycondensation has two main benefits. On one 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). On the other hand, it sustains the reaction only for a short period of time at high temperatures, and thereby prevents thermal degradation of the formed ester linkages. Also, the role of the lid is to prevent monomer loss by overshooting over the crucible wall, and to

reduce the purging effect over the melt and thus making nitrogen carry the more volatile component exclusively.

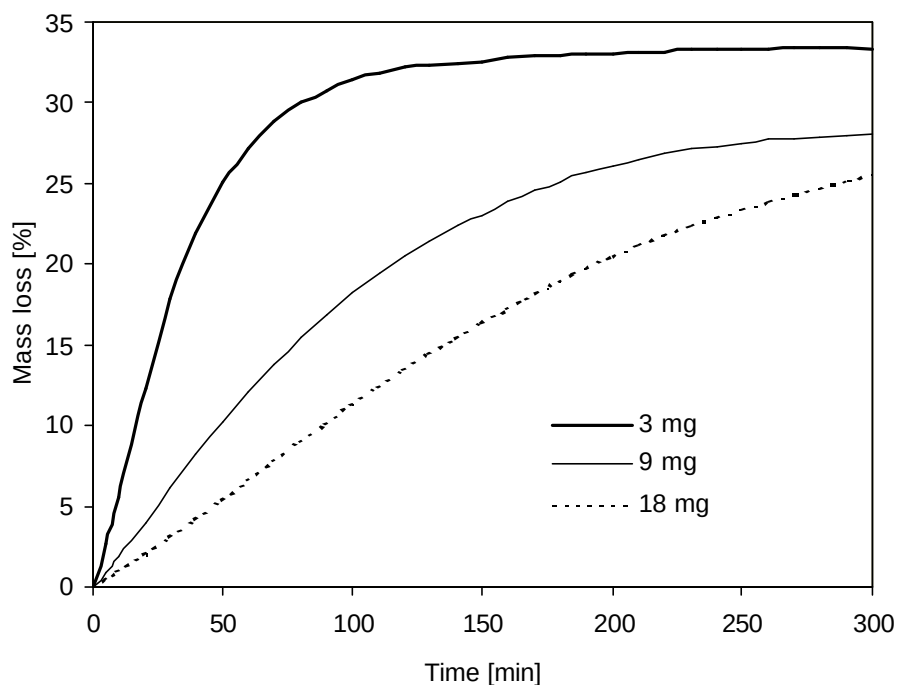


Figure 2.7. Mass loss during condensation of different amounts of BHET in open aluminium crucibles isothermally at 180 °C.

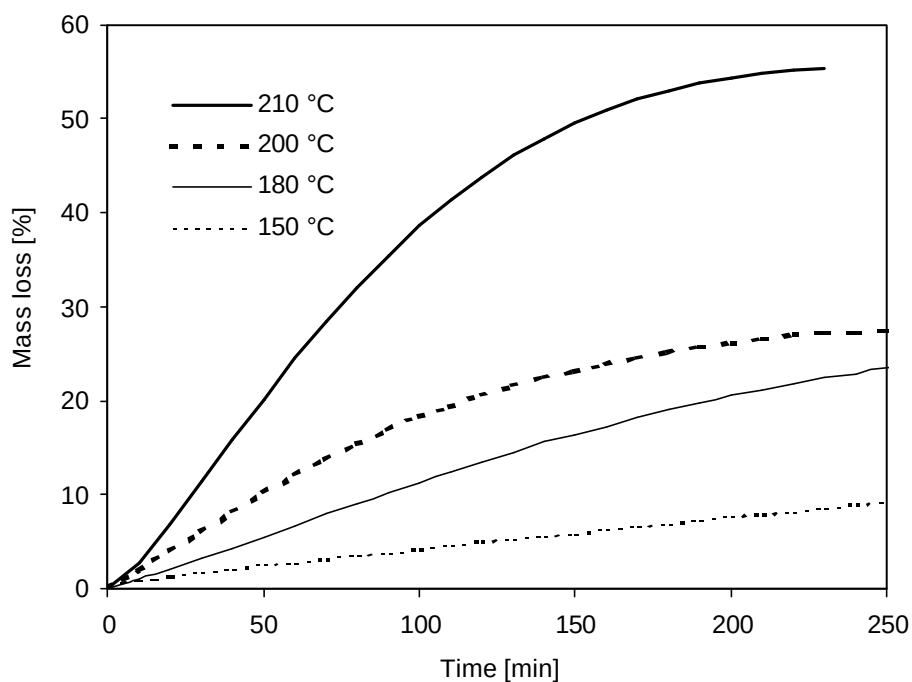


Figure 2.8. Mass loss during condensation of 9 mg of BHET in open aluminium crucibles isothermally at different temperatures.

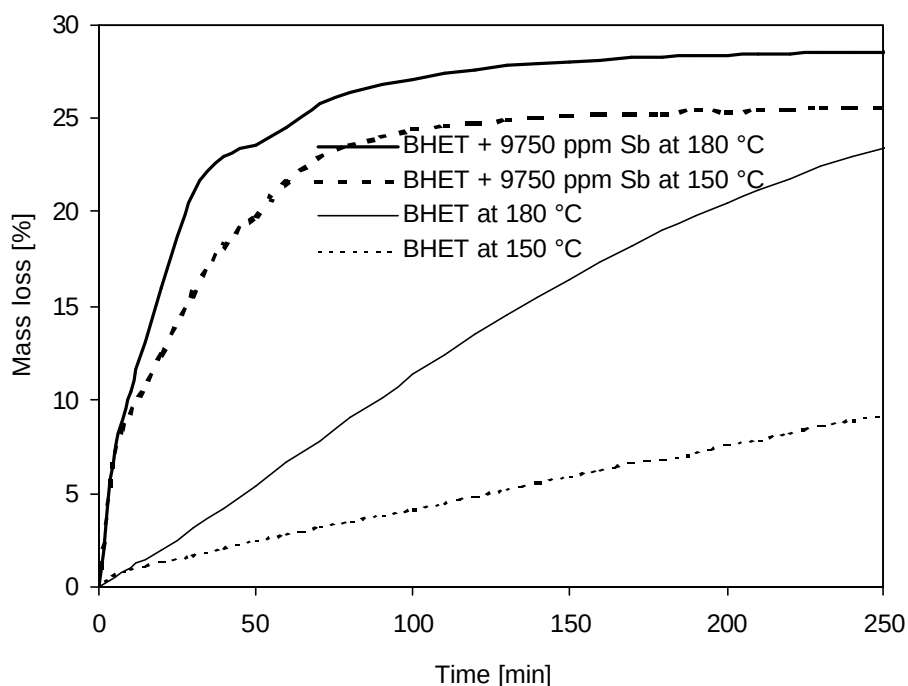


Figure 2.9. Mass loss during isothermal condensation of 9 mg of BHET with and without antimony as catalyst in open aluminium crucibles at 150 and 180 °C.

To check whether the lid suppresses completely monomer evaporation, and whether it does not affect the rate of EG removal (which otherwise affects the reaction rate), a 2000 ppm Sb/BHET mixture was polycondensed at different conditions. Monomer amount in the crucible was varied between 10 and 20 mg while the nitrogen purging rate was changed between 30 and 80 ml min⁻¹. Monomer evaporation was hindered completely after introduction of the holed lid since different starting amounts of BHET resulted in the same total mass loss (table 2.8). Further evidence of monomer evaporation absence is provided by the independence of total mass loss on the gas purging rate.

Higher purging rate should lead to faster removal of EG if the lid is hindering EG. EG volatilization was not hindered by the lid as $T_{\max}$ as well as total mass loss was not dependent on gas purging rate. Therefore, the introduction of the holed lid yielded complete suppression of the monomer evaporation in catalyst presence with no impact on the reaction rate.

Table 2.8. Effect of nitrogen purging rate and sample mass on $T_{\max}$ and total mass loss during polycondensation of 2000 ppm BHET/Sb mixture at 10 K min^{-1} in covered pans.

Purging rate [ml min ⁻¹]	Sample mass [mg]	$T_{\max}$ of DSC [°C]	Total mass loss [%]
40	10	251.2	24.04
60	10	250.4	24.32
80	10	250.6	24.32
30	20	250.0	23.88
50	20	250.7	23.34

5.3. 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^{-1} under 50 ml min^{-1} nitrogen purging. Small heating rate has the advantage that the thermal lag between sample and oven is minimized. Also, higher conversion is achieved as the reaction occurs for longer time in the same temperature range (figure 2.10).

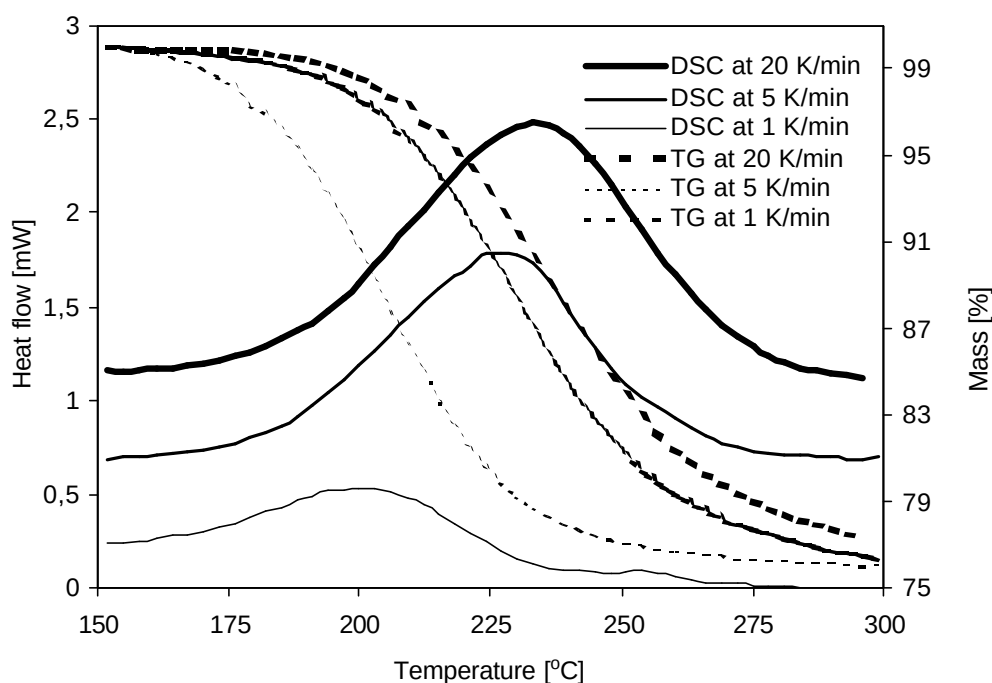


Figure 2.10. Thermograms of polycondensation of 442 ppm HT/BHET mixture at 1, 5 and 20 K min^{-1} . Sample mass is 10 mg.

However, in the case of small heating rates the melt solidifies during heating due to fast increase in molecular weight especially when high catalyst concentrations are applied (figure 2.11). This behaviour results in a strong retardation of mass loss (diffusion of EG through a solid reaction mass), which shifts $T_{\max}$ 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 (figure 2.12). Thus, $T_{\max}$ does not emerge below 280 °C, above which chain degradation reaction cannot be neglected any more. At 10 K min⁻¹ no solidification occurs if reasonable catalyst concentration is applied. At the same time, $T_{\max}$ of the studied samples appeared at relatively low temperatures and therefore thermally initiated side reactions can be neglected.

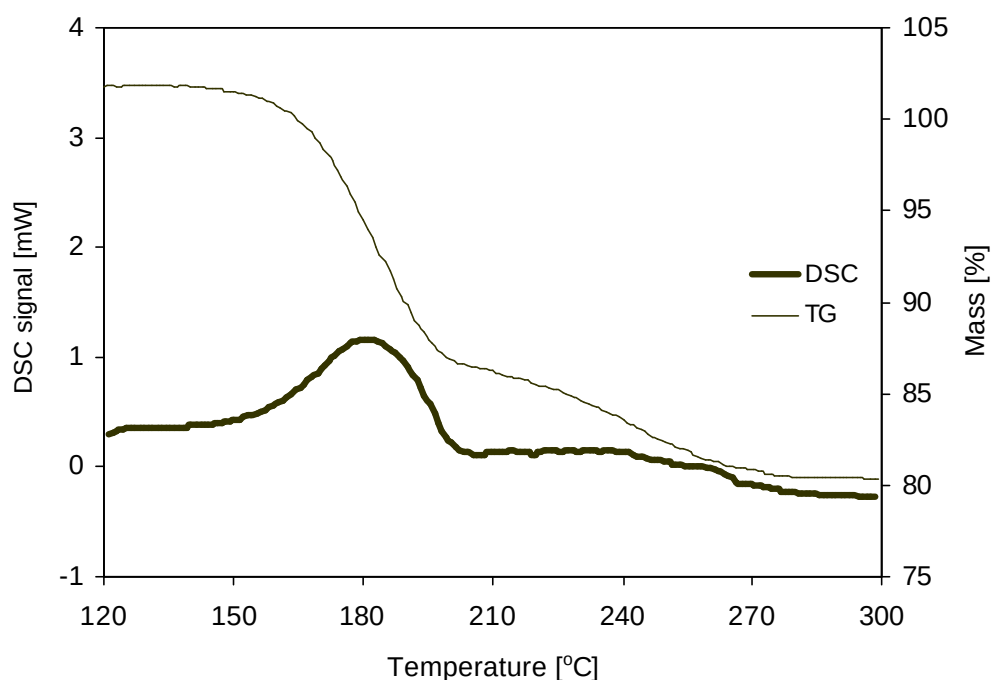


Figure 2.11. Thermograms of polycondensation of 883 ppm HT/BHET mixture at 2 K min⁻¹. Sample mass is 10 mg.

5.4. Absence of 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 STA experiments, polycondensation rate increased linearly with catalyst concentration under applied dynamic conditions (figure 2.13). 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 2.8). Also, limitation on the gas side of melt-gas interface was excluded, as different gas purging rate did not affect the polycondensation rate (table 2.8).

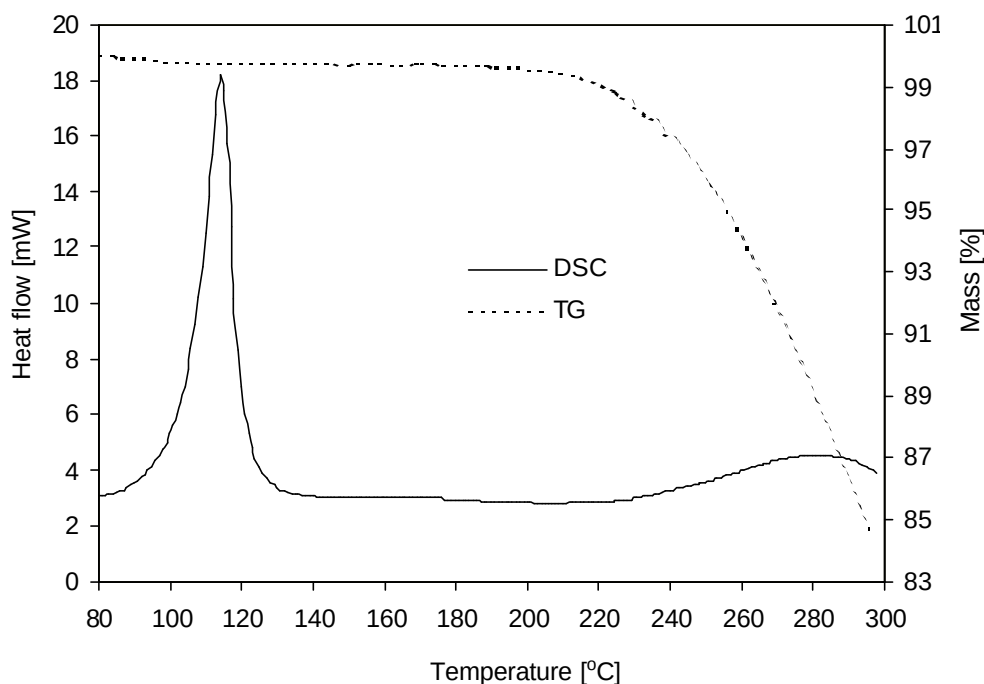


Figure 2.12. Thermograms of polycondensation of 200 ppm Sb/BHET mixture at 10 K min⁻¹. Sample mass is 10 mg.

5.5. Characterization of screening indices

$T_{\max}$ of DTG was easier to recognize than that of DSC due to the higher sensitivity of the thermobalance compared to that of the DSC head especially when oligomers were used instead of BHET as starting material. In the case of pentamer as starting material the DSC signal was relatively weak probably due to the fact that the amount of evolved EG is only one-fifth that evolved in the case of the monomer. In this case, $T_{\max}$ of DSC was no longer distinguishable due to the small changes in the system as most of the ester end groups have already reacted. Also, $T_{\max}$ of DSC was superimposed with physical changes such as melting and crystallization of the oligomers. In this case, total mass loss can also be used as activity index since the vapour pressure of the reactants is too low and oligomer evaporation is negligible.

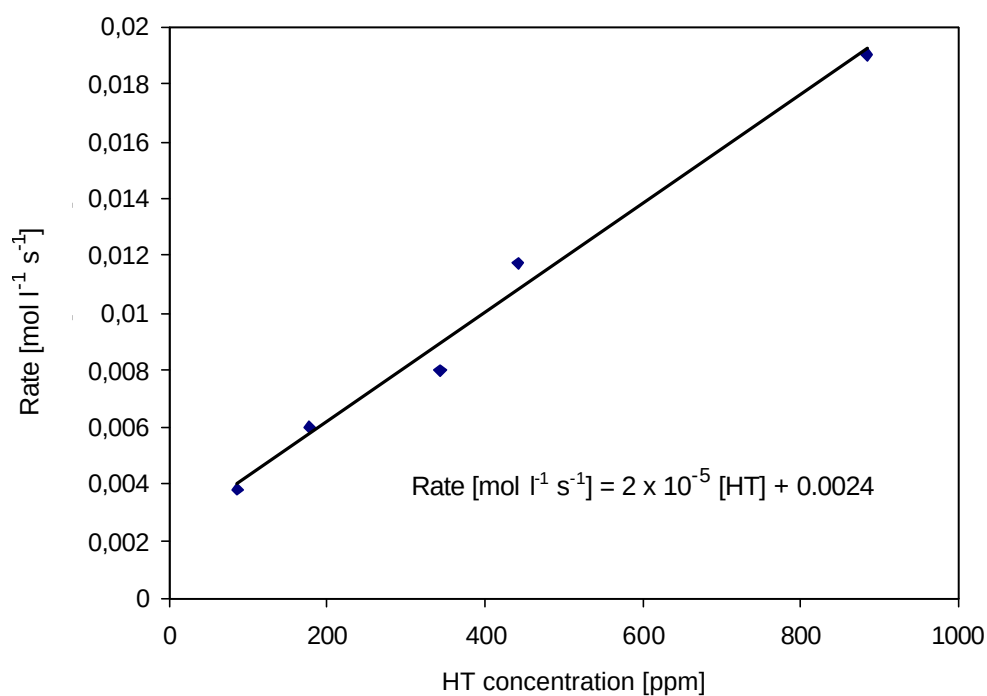


Figure 2.13. Dependence of initial polycondensation rate on catalyst concentration during dynamic polycondensation of BHET.

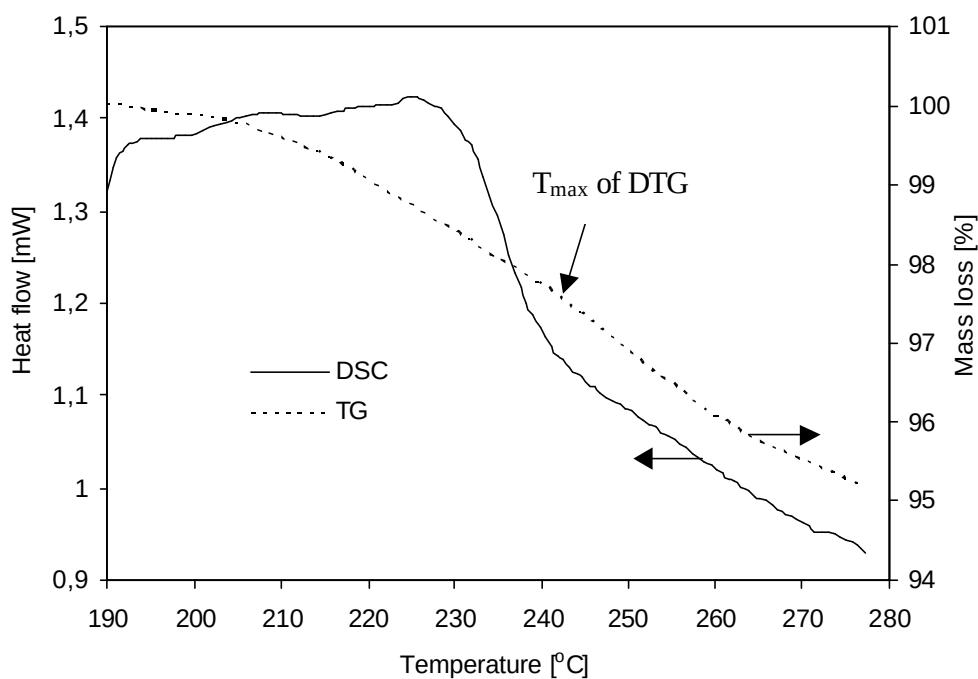


Figure 2.14. Thermograms of condensation of oligomer with average degree of polycondensation of 5 at 3 K min⁻¹. T_{max} of DSC was overlaid by melting and crystallizations signals while T_{max} of DTG was still detectable.

T_o of TG, T_{max} of DSC and T_{max} of DTG showed the same trend (figure 2.15). Measured at same heating rate, their value was dependent on catalyst concentration. Lower catalyst concentration yielded higher values of the three indices. Also their value decreased with decreasing heating rate. Table 2.10 contains the molecular weight of polymers obtained during heating up BHET at 10 K min^{-1} in presence of different Sb concentrations. These values were measured by GPC. It is clear that molecular weight is higher, i.e. reaction rate is higher, for lower values of T_{max} . Table 2.11 shows the melting onset of oligomers produced by condensation of BHET at 10 K min^{-1} to $300\text{ }^{\circ}\text{C}$ in presence of different HT concentrations. Melting onset was used instead of molecular weight because HT as a heterogeneous catalyst (solid particles) may damage the GPC column. Melting point is higher for polymer with larger molecular weight. This indicates that as expected, the more active the catalyst or the higher its concentration is, the lower is the value of the screening indices.

The reproducibility of the three aforementioned screening parameters was tested by repeating the polycondensation 5 times. Standard deviation was 0.3 % for T_{max} of DSC, 1.5 % for T_{max} of DTG and 1.5 % for T_o of TG.

A delay was found between thermogravimetric and calorimetric results (T_{max} of DSC occurs before T_{max} of DTG) whose value was dependent on heating rate. It increased with increasing heating rate and therefore, it probably results from thermal lag between the melt and the oven (table 2.9).

Table 2.9. Effect of heating rate on the difference between T_{max} of DSC and that of DTG during BHET polycondensation catalyzed by 883 ppm HT.

Heating rate [K min ⁻¹]	T_{max} of DTG [^o C]	T_{max} of DSC [^o C]	Difference [^o C]
1	204.4	205.1	0.7
10	230.0	226.0	4.0
20	237.6	232.9	4.7

To establish a relation between screening indices and a parameter that better represents the activity of the studied catalysts, T_{max} was compared to the end conversion of reactants into product (table 2.12). To this end, T_{max} of DSC of HT catalyzed BHET polycondensation at 10 K min^{-1} was plotted against conversion achieved up to $260\text{ }^{\circ}\text{C}$ that was obtained from TG. Figure 2.16 shows a linear relation between conversion and T_{max} of

polycondensation. The fitting line was used as empirical relation between T_{max} and conversion up to 260 °C. Activity was defined in the following equation:

$$Activity = \frac{Conversion[-] \text{ monomer mass [kg]}}{Catalyst \text{ mass [g] reaction time[h]}} \quad 2.11$$

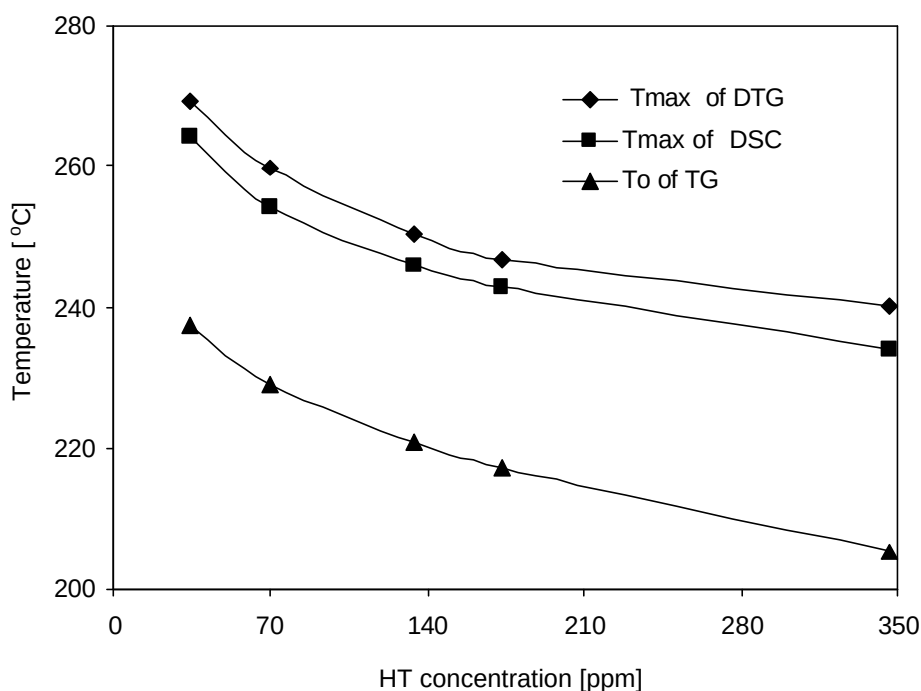


Figure 2.15. Different activity ordering indices (T_{max} of DSC, T_{max} of DTG and T_o of TG) of BHET polycondensation catalyzed with different HT concentrations at 10 K min⁻¹.

Table 2.10. Effect of variation of Sb concentration on T_{max} and average molecular weights of PET obtained from catalyzed polycondensation of BHET.

Sb Concentration [ppm]	T_{max} [°C]	M_n [kg mol ⁻¹]	M_w [kg mol ⁻¹]
720	270.6	4.4	14.4
760	266.5	4.5	14.8
780	264.7	4.6	15.1
900	261.6	4.7	15.3

The conversion was substituted by T_{max} using the fitting equation (figure 2.16) and equation 2.11 was rewritten as:

$$Activity = \frac{(-1.168 T_{max} + 340.72)[-] \text{ monomer mass [g]}}{100 \times Catalyst \text{ mass [g] reaction time[h]}} \text{ [g product g cat}^{-1} \text{ h}^{-1}] \quad 2.12$$

Table 2.11. Effect of variation of HT concentration on $T_{\max}$ of HT catalyzed polycondensation of BHET and on melting point of the produced oligomers.

HT concentration [ppm]	$T_{\max}$ of DSC [°C]	T_m [°C]
83	260	218
145	253	222
285	248	226
442	244	231
883	233	233

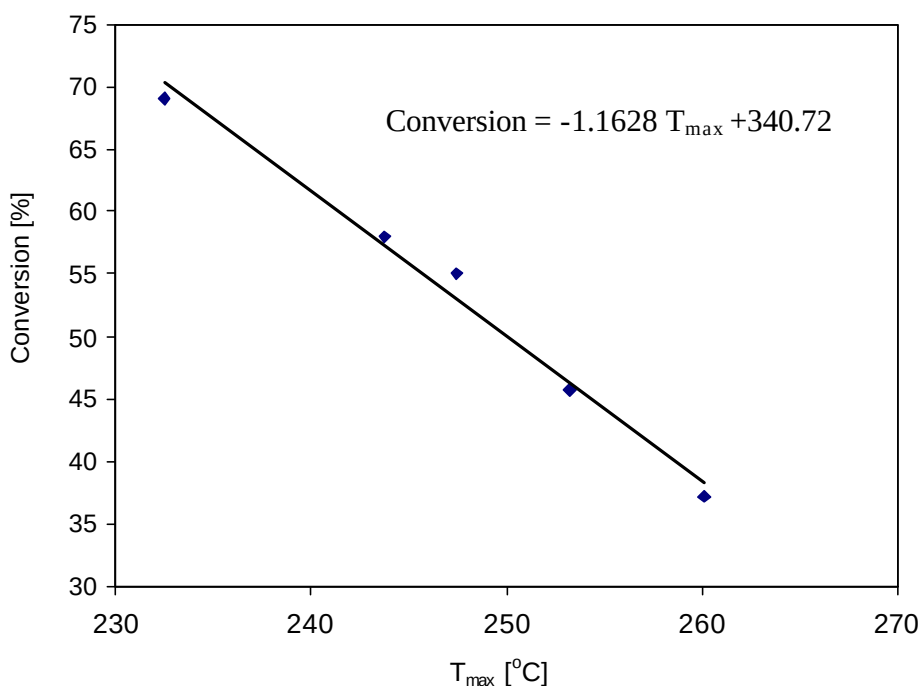


Figure 2.16. Plot of conversion up to 260 °C versus $T_{\max}$ during polycondensation of BHET at 10 K min⁻¹ in presence of different HT concentrations. Sample mass is 10 mg.

Table 2.12. The relation between $T_{\max}$ and conversion of hydroxyl end groups at 260 °C during BHET polycondensation at 10 K min⁻¹ in presence of HT catalyst.

Hydrotalcite concentration [ppm]	$T_{\max}$ [°C]	Conversion [%]
83	260	37
145	253	46
285	248	55
442	244	58
883	233	69

5.6. Determination of activation energy

Rate of BHET polycondensation is considered by the following equation:

$$-\frac{d[OH]}{dt} = 2k_{o,catalyzed} e^{-\frac{E_{catalyzed}}{RT}} [OH]^m [C] + k_{o,uncatalyzed} e^{-\frac{E_{uncatalyzed}}{RT}} [OH]^n \quad 2.13$$

Where t is time [s], $[C]$ is catalyst concentration [mol l^{-1}], $k_{o,catalyzed}$ is the pre-exponential factor of the Arrhenius equation for catalyzed reaction [$\text{l}^m \text{mol}^{-m} \text{s}^{-1}$], $k_{o,uncatalyzed}$ is the pre-exponential factor of the Arrhenius equation for uncatalyzed reaction [$\text{l}^{n-1} \text{mol}^{1-n} \text{s}^{-1}$], m is reaction order of catalyzed reaction, n is reaction order of uncatalyzed reaction, $E_{catalyzed}$ is activation energy of catalyzed reaction [J mol^{-1}], $E_{uncatalyzed}$ is the activation energy of the uncatalyzed reaction [J mol^{-1}].

In the presence of an efficient catalyst in high concentration at low temperature ($T < 250^\circ \text{C}$) conversion by uncatalyzed path can be neglected and equation 2.13 can be simplified into equation 2.14:

$$-\frac{d[OH]}{dt} = 2k_{o,catalyzed} \exp^{-\frac{E_{catalyzed}}{RT}} [OH]^m [C] \quad 2.14$$

$$\text{Since } \frac{d[OH]}{dt} = \frac{d[OH]}{dT} \frac{dT}{dt} = \beta \frac{d[OH]}{dT} \quad 2.15$$

$$\Rightarrow \frac{d[OH]}{dT} = -\frac{2}{b} k_{o,catalyzed} e^{-\frac{E_{catalyzed}}{RT}} [OH]^m [C] \quad 2.16$$

$$\text{At maximum reaction rate: } \frac{d \frac{d[OH]}{dT}}{dT} = \frac{d^2[OH]}{dT^2} = 0 \quad 2.17$$

$$\Rightarrow \frac{d \left(-\frac{2}{b} k_{o,catalyzed} \exp^{-\frac{E_{catalyzed}}{RT}} [OH]^m [C] \right)}{dT} = 0 \quad 2.18$$

$$\Rightarrow -\frac{2}{b} [C] k_{o,catalyzed} \exp^{-\frac{E_{catalyzed}}{RT_{max}}} \left\{ \frac{E_{catalyzed}}{R T_{max}^2} [OH]_{max}^m + m [OH]_{max}^{m-1} \frac{d[OH]_{max}}{dT} \right\} = 0 \quad 2.19$$

$$\Rightarrow \frac{E_{catalyzed}}{R T_{max}^2} [OH]_{max}^m + m [OH]_{max}^{m-1} \frac{d[OH]_{max}}{dT} = 0 \quad 2.20$$

$$\Rightarrow \frac{E_{catalyzed}}{R T_{max}^2} = -m [OH]_{max}^{-1} \frac{d[OH]_{max}}{dT} \quad 2.21$$

$$\Rightarrow E_{catalyzed} = -R T_{max}^2 m [OH]_{max}^{-1} \frac{d[OH]_{max}}{dT} \quad 2.22$$

For second order reaction:

$$E_1 = -2 R T_{max}^2 [OH]_{max}^{-1} \frac{d[OH]_{max}}{dT} \quad 2.23$$

To check the reliability of this equation, it was applied to the polycondensation of BHET at 5 K min⁻¹ in presence of 442 ppm of HT as a catalyst. The T_{max} of DTG was 227.1 °C and the concentration of hydroxyl end groups at this temperature was 6.2 mol l⁻¹ while the reaction rate was 0.145 mol l⁻¹ K⁻¹. As it will be shown later, HT catalyzed polycondensation of BHET is a second order reaction and therefore m is 2. By substitution of these values in equation 2.22 the activation energy of this reaction was calculated to be 99 kJ mol⁻¹. This value is in the range of that determined by detailed kinetic study of this reaction (93 kJ mol⁻¹).

6. Conclusion

Dynamic STA was utilized to study the catalyzed synthesis of PET from its monomer BHET. This method is a reliable and efficient tool for fast screening of polycondensation catalyst in milligram scale. However, there are several critical points that should be carefully optimized to avoid data misinterpretation. Monomer evaporation should be hindered by application of a lid with holes and tuning of gas purging rate. Also, crucible made of relatively inert material should be used and the screening should be done in absence of mass transfer limitations. Heating rate should be carefully chosen and the catalyst should be introduced in its active form.

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 and rely strongly on catalyst nature, catalyst concentration and heating rate. 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 when oligomers are used as starting material instead of BHET due to overlapping of reaction signal with heating-induced physical processes.

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Chapter 3: Complications in Quantitative Evaluation of Polyethylene Terephthalate Synthesis by Differential Scanning Calorimetry

Abstract

The application of differential scanning calorimetry for the kinetic investigation of polyethylene terephthalate was studied. The reaction extent obtained by differential scanning calorimetry was less than that obtained by thermogravimetry and molecular weight measurements. The reason behind these discrepancies was the movement of the reaction melt within the crucible of DSC during polycondensation. Video microscopy showed that reaction melt does not form a uniform static film but it moves away from the center of the crucible and accumulates at the periphery. Moreover, the condensate ethylene glycol does not leave the melt exclusively by diffusion, but bubbling is the main removal route. As bubbling was more intensive at the periphery, the melt moves radially outwards in the direction of ethylene glycol concentration gradient.

1. Introduction

In the previous chapter, the qualitative fast screening of polycondensation catalysts by STA was described. In this chapter, the application of DSC as a tool for quantitative investigation of the kinetics of BHET polycondensation was studied. In a literature survey, no paper was found on the investigation of the kinetics of PET synthesis by DSC although this method was used to study certain polycondensation reactions (Phenol with formaldehyde, bisphenol with diglycol ether and sodium sulfide with dichloro benzene).

2. Experimental

Polycondensation was performed inside cylindrical crucibles made of the following material: Aluminium, platinum, copper, nickel, steel, glass, ceramic and graphite. The diameter of the aluminium crucibles was varied between 4 and 40 mm. For kinetic investigations, crucibles with diameter of 7 mm were placed in the oven of the STA 409 PG, where polycondensation was performed under different heating rates. For video microscopy of the PET melt during polycondensation, the crucibles were placed in an electrically heated autoclave having a glass view window in its cover. The setup used is shown in figure 3.1. The reaction by-product EG was carried away by vacuum or nitrogen purging.

3. Results and discussion

Possible sources of differential heat flow during BHET polycondensation are the enthalpy of the polycondensation reaction, vaporization enthalpy of EG, enthalpy of side reactions, heat capacity of the melt and its change with variations of composition and temperature, and vaporization enthalpy of BHET and its oligomers.

The most probable side reaction at the applied conditions is the thermal degradation of hydroxyl end groups and formation of acetaldehyde and carboxylic acid end groups (scheme 1.11). However, this reaction is neglected at the applied conditions as the reaction starts at low temperature and when it reaches high temperature most of the end groups have been already reacted. At the same time, the activation energy of thermal degradation is higher than that of the polycondensation. STA coupled to IR has shown that the main volatiles of the reaction are EG while other components are negligible (figure 3.2). No relevant carbonyl bands have been observed in the 1650-1750 cm^{-1} region. Also, monomer

evaporation was efficiently hindered by covering the pans with a centrally holed lid, without affecting the condensate removal [1].



Figure 3.1. Setup for video microscopy: Autoclave with top glass window in which different cylindrical reactors are placed and observed online by video microscopy.

The difference in the heat of formation between products and reactants at room temperature showed that the polycondensation reaction is slightly exothermic and produces 2.32 kJ per mole of formed ester bonds at 298 K. Reaction enthalpy (DH_R) changes with temperature according to the following equation:

$$DH_R(T) = DH_{R,298} + \int_{298}^T DC_p dT \quad [\text{J mol}^{-1}] \quad 3.1$$

Where $DH_{R,298}$ is the reaction enthalpy at 298 K [J mol^{-1}], $DH_{R,T}$ is the reaction enthalpy at temperature T [J mol^{-1}] and DC_p is the change in the heat capacity due to the reaction [J K^{-1}].

According to Van Krevelen [2] the heat capacity of polymeric species can be calculated by the summation of the specific heat capacities of its segments. Table 3.1 summarizes the heat capacities of segments building up PET at room temperature. By comparison of the

heat capacities of the products and reactants in each polycondensation step, DC_p is calculated to be zero. Therefore, the polycondensation enthalpy remains constant during the reaction.

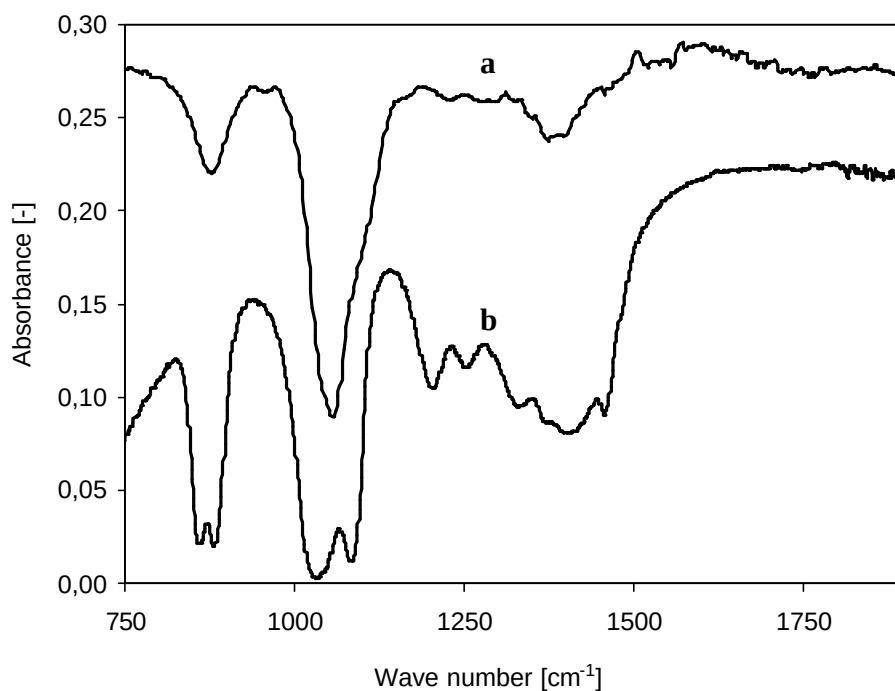
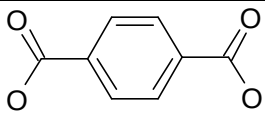
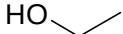
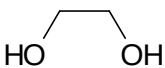


Figure 3.2. IR spectra of the evolved gas from BHET polycondensation at 280 °C (a) and EG (b).

Table 3.1. Structure, name and specific heat capacity of the segments building up PET in liquid and solid state.

<i>Segment</i>	<i>Name</i>	C_P^l [J mol ⁻¹ K ⁻¹]	C_P^s [J mol ⁻¹ K ⁻¹]
	Bound terephthalic acid	243.2	170.8
	Bound hydroxy ethylene	105.6	67.7
	Bound ethylene	60.8	50.7
	Ethylene glycol	150.4	84.7

EG is set free during polycondensation and is removed away from the reaction mass. Therefore, the overall heat capacity of the melt will decrease as the reaction proceeds. A net loss of 33 % is calculated to occur after complete polycondensation of one mol of BHET.

The increase in specific heat capacity of the liquid polymeric segments, C_p^l , with temperature is given by the following equation [2]:

$$c_p^l(T) = c_p^l \{ 0.64 + 0.0012 T \} \quad [\text{J mol}^{-1} \text{K}^{-1}] \quad 3.2$$

Heat capacity of liquid BHET is higher than that of solid one. The specific heat capacities of liquid and solid BHET at room temperature are 454.3 and 306.2 J K⁻¹ mol⁻¹ respectively. This means that the differential heat flow will increase after fusion of BHET by almost 50 %.

The vaporization enthalpy of EG at boiling point (DH_{vb}) can be calculated [3,4] from its boiling temperature (T_b), critical temperature (T_c) and critical pressure (P_c) by the following relation:

$$DH_{vb} = R T_b \frac{3.978 \frac{T_b}{T_c} - 3.958 - 1.555 \ln P_c}{1.07 - \frac{T_b}{T_c}} \quad [\text{J mol}^{-1}] \quad 3.3$$

$DH_{vb} = 53000 \text{ J mol}^{-1}$ as P_c , T_c and T_b are 65,157 bar, 645 K and 470.6 K respectively [5].

Thek and Stiel [6] proposed an equation to account for variation of vaporization enthalpy with temperature:

$$DH_{v2} = DH_{v1} \left(\frac{1 - \frac{T_2}{T_c}}{1 - \frac{T_1}{T_c}} \right)^n \quad 3.4$$

Viswanath and Kuloor [3, 7] proposed the following equation for calculation of the exponent n :

$$n = \left[0.002646 \frac{DH_{vb}}{R T_b} + 0.8794 \right]^{10} \quad 3.5$$

By substitution of DH_{vb} and T_b in equation 3.5, n is calculated to be 0.4123. Figure 3.4 represents a plot of the calculated DH_v and the experimental one against temperature. DH_v decreases strongly with temperature and becomes zero at the critical temperature (372 °C). Due to the deviation of the experimental values of DH_v from the theoretical ones at temperature above 150 °C, the experimental values were used to calculate heat flow.

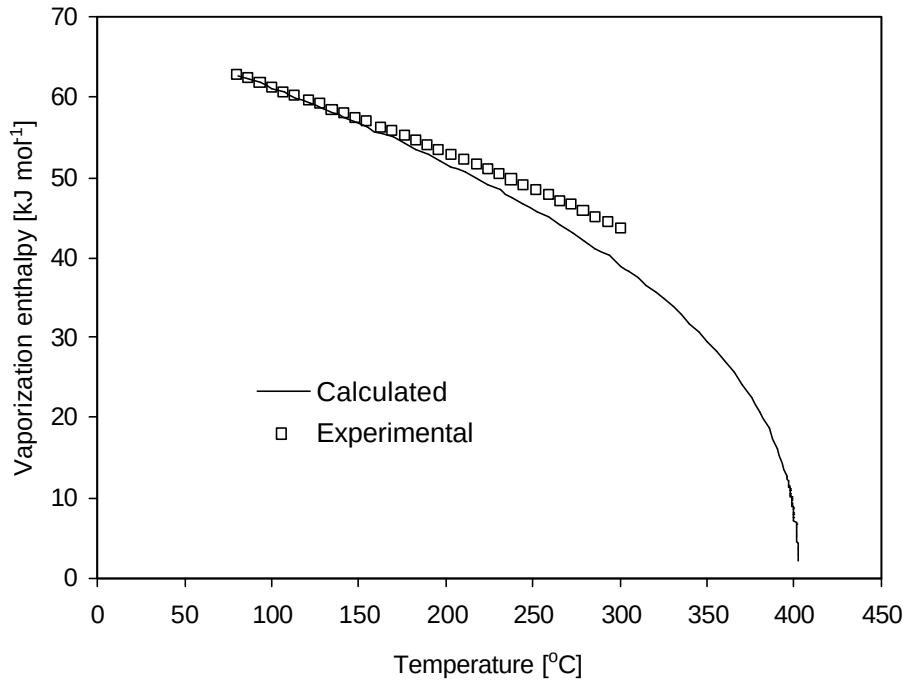


Figure 3.4. The change of EG vaporization enthalpy with temperature.

The heat capacity of the melt as a function of temperature, $C_p(T)$, is given by:

$$C_p(T) = C_{p,\rho}(T) - n_{EG}^{DSC}(T) c_{p,EG}(T) \quad [\text{J K}^{-1}] \quad 3.6$$

Where $n_{EG}^{DSC}(T)$ is the amount of EG produced up to a certain temperature T .

The amount of heat that flows to the crucible due to the heat capacity of the melt is given by:

$$Q_C = \int C_p(T) dT = \int C_{p,\rho}(T) dT - n_{EG}^{DSC}(T) \int c_{p,EG}(T) dT \quad [\text{J}] \quad 3.7$$

The amount of heat that flows to the crucible due to the reaction enthalpy is given by:

$$Q_{chem} = n_{EG}^{DSC}(T) DH_R \quad 3.8$$

The amount of heat that flows to the crucible due to vaporization of EG, $Q_{vap,EG}$, is given by:

$$Q_{vap,EG}(T) = n_{EG}^{DSC}(T) DH_v(T) \quad 3.9$$

Measured heat, Q_{DSC} , is given by:

$$Q_{DSC}(T) = Q_{vap,EG}(T) + Q_{chem}(T) + Q_C(T) \quad 3.10$$

By substitution of equations 3.7, 3.8 and 3.9 in equation 3.10:

$$Q_{DSC}(T) = n_{EG}^{DSC}(T) DH_v(T) + n_{EG}^{DSC}(T) DH_R + \int C_{p,o}(T) dT - n_{EG}^{DSC}(T) \int c_{p,EG}(T) dT \quad 3.11$$

Equation 3.11 can be rewritten as:

$$Q_{DSC}(T) - \int C_{p,o}(T) dT = n_{EG}^{DSC}(T) \left\{ DH_v(T) + DH_R - \int c_{p,EG}(T) dT \right\} \quad 3.12$$

Therefore, $n_{EG}^{DSC}(T)$ is given by:

$$n_{EG}^{DSC}(T) = \frac{Q_{DSC}(T) - \int C_{p,o}(T) dT}{DH_v(T) + DH_R - \int c_{p,EG}(T) dT} \quad [\text{mol}] \quad 3.13$$

To check the reliability of the amount of EG produced up to a certain temperature obtained by DSC, it was compared to that of measured by TG, n_{EG}^{TG} . The measurement of the number of moles of produced EG from TG data is straight forward and is given by:

$$n_{EG}^{TG}(T) = \frac{\text{mass loss [g]}}{62 \text{ g mol}^{-1}} \quad [\text{mol}] \quad 3.14$$

Figure 3.5 shows the total expected heat flow of polycondensation of BHET in presence of 442 ppm HT as a catalyst at 5 K min^{-1} and the calculated components of this heat flow (heat flow due to melt heat capacity, reaction enthalpy and EG vaporization). The results were calculated from TG data.

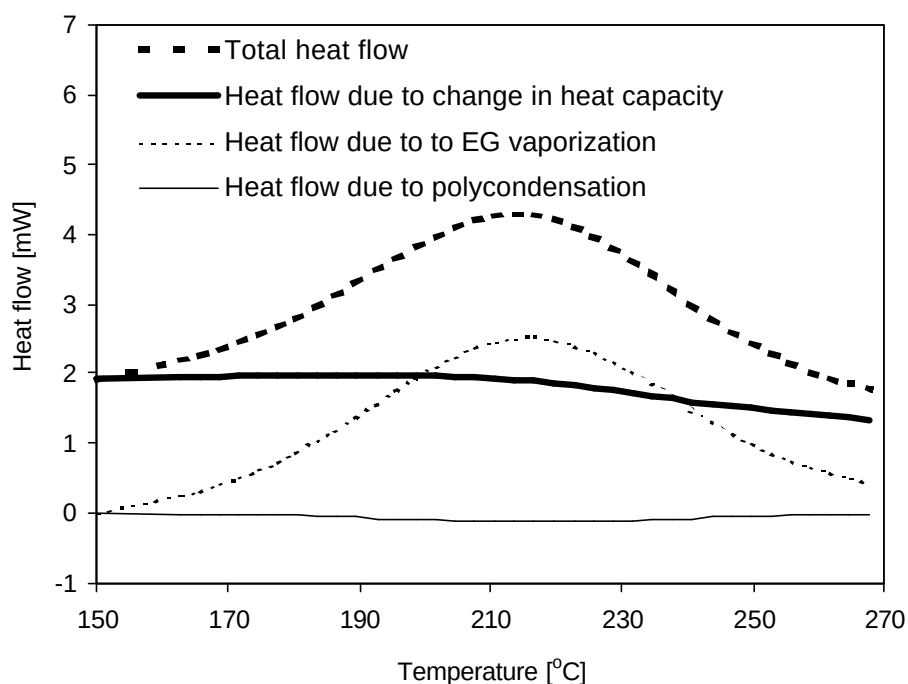


Figure 3.5. Differential heat flow of BHET polycondensation at 5 K min^{-1} catalyzed with 442 ppm of HT. The different contributions of this heat flow and their summation were calculated from TG data. Sample mass is 10 mg.

The degree of polycondensation, P , is calculated by Carother's equation:

$$P = \frac{1}{1 - X} \quad 3.15$$

Where the conversion, X , is calculated by the following equation:

$$X = \frac{n_{EG}(T)}{\text{Total } n_{EG}} = \frac{n_{EG}(T)}{n_{BHET}} = \frac{254 \text{ g mol}^{-1} n_{EG}(T)}{m_{o,BHET}} \quad 3.16$$

Figure 3.7 shows the conversion as a function of temperature obtained from DSC and TG.

M_n is calculated from P by the following equation:

$$M_n = 192P + 62 \quad [\text{g mol}^{-1}] \quad 3.17$$

M_n measured by GPC was found to agree very well with that calculated from TG data, while it was far from that of DSC (Table 3.2). Table 3.3 shows the conversion of hydroxyl end groups that is calculated from DSC data that corresponds to 80 % conversion calculated from TG data, for polycondensation at different heating rate and different catalyst concentrations. The conversion obtained by DSC was lower than that obtained by TG, and

was not the same under different conditions. The uncertainty does not lie in the DSC system, as the melting enthalpy of BHET was reproducible and close to the expected value of 33 kJ mol⁻¹.

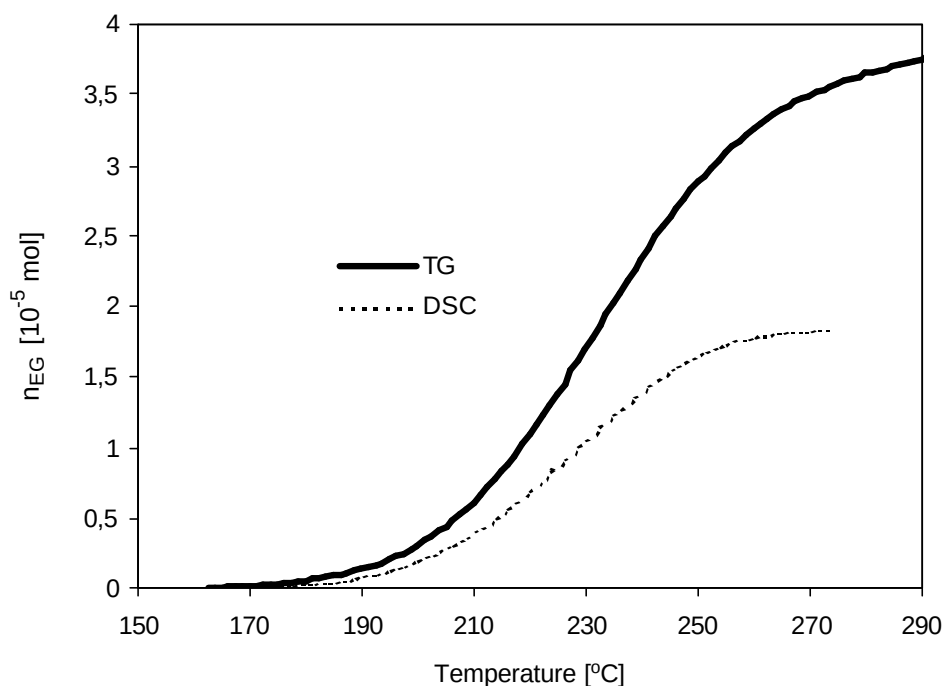


Figure 3.6. The amount of produced EG as a function of temperature measured by TG and calculated from DSC during polycondensation of BHET at 5 K min⁻¹ in presence of 442 ppm HT as catalyst. Sample mass is 10 mg.

PET accumulation at the periphery was independent of the wetting effect of the reactor material as material with high- (copper and steel) and low wetting ability (nickel) toward PET yielded the same behaviour. PET accumulated at the periphery of reactors made of graphite, ceramic, steel, platinum, copper, aluminium, nickel, glass and quartz (figure 3.9). Melt displacement was also independent of reactor size as changing reactor diameter (between 4 and 400 mm) and height (between 2 and 20 mm) showed no effect on it (figure 3.10). It was also independent of temperature as it occurred at different temperatures (120-300 °C), although at higher temperatures displacement was faster. In case of higher reaction rate (higher catalyst concentration) the melt was more close to the periphery (figure 3.11). An explanation of the melt movement may be the faster evaporation of EG at the periphery due to higher concentration of nucleation agents (cervices in reactor material), which

generates an EG concentration gradient. Due to this gradient, EG dissolved in PET migrates from the centre outwards to the periphery carrying the PET with it (figure 3.12).

To interpret the uncertainty of DSC polycondensation data, video microscopy was used to monitor online PET synthesis from BHET. EG was found to bubble through the melt, and was very intensive at the periphery (figure 3.8). The melt was seen to move from the centre of the reaction crucible to the periphery accompanied by continuous bubbling. At the end, the polymer was present only at the periphery in form of an O-ring while the crucible centre was not covered at all with polymer (figure 3.9-3.11).

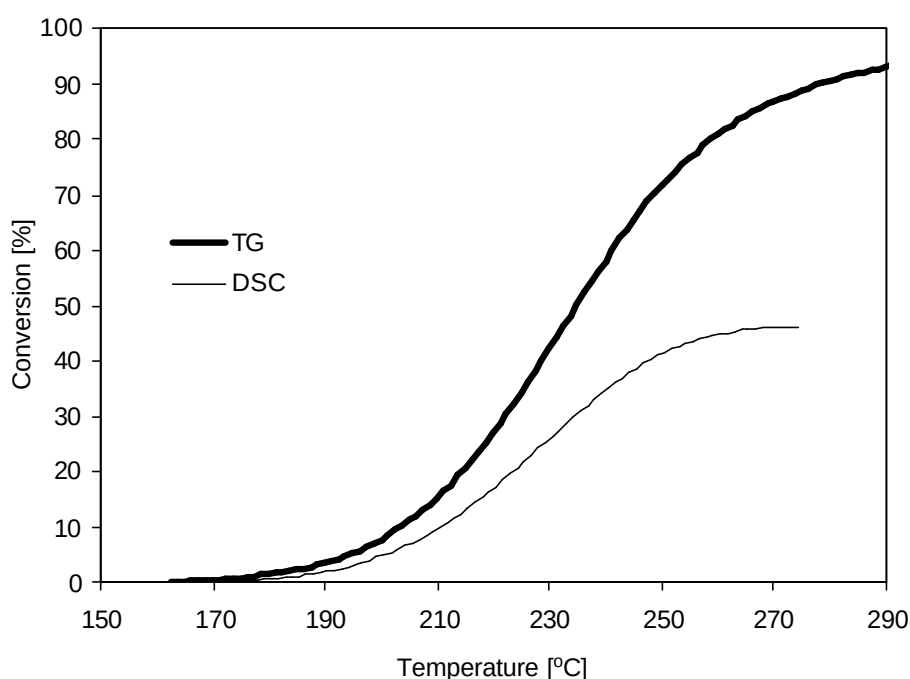


Figure 3.7. The conversion of hydroxyl end groups as a function of temperature measured by TG and calculated from DSC during polycondensation of BHET at 5 K min⁻¹ in presence of 442 ppm HT as catalyst. Sample mass is 10 mg.

Table 3.2. Molecular weight of the polycondensation product measured by GPC and calculated from TG and DSC.

Method	GPC	TG	DSC
$M_n [g mol^{-1}]$	2200	2000	800

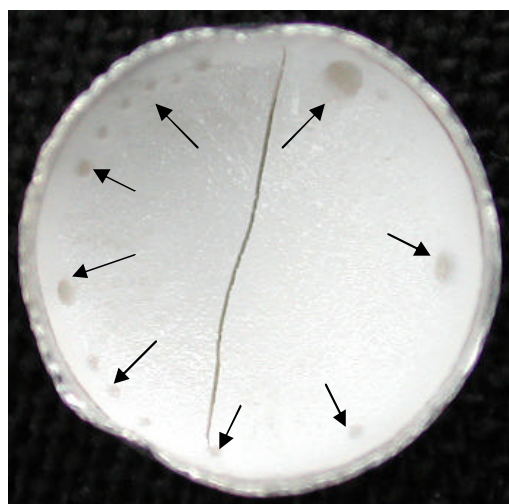


Figure 3.8. Bubbles of EG in quenched PET at the periphery of aluminium crucible.

Table 3.3. The melting enthalpy of BHET measured at different conditions and the reactant conversion calculated from DSC data at 80 % conversion obtained by TG.

<i>Catalyst concentration</i> [ppm]	<i>Heating rate</i> [K min ⁻¹]	<i>Melting Enthalpy</i> [kJ mol ⁻¹]	<i>Conversion</i> [%]
442	10	32.5	45
442	8	34.3	42
442	5	33.3	46
883	10	32.7	51

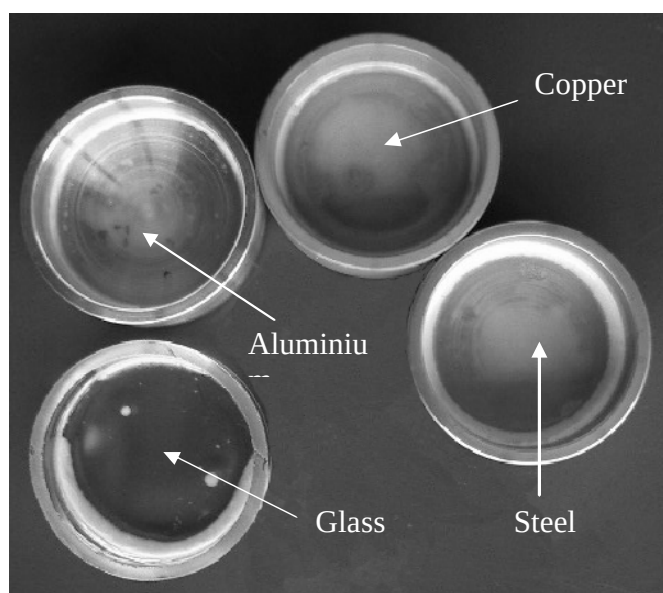


Figure 3.9. Accumulation of PET melt during polycondensation at periphery of crucibles made of different materials with 25 mm diameter and 8 mm height.



Figure 3.10. Accumulation of PET melt during polycondensation at periphery of crucibles made aluminium with diameter of 20, 25, 30 and 35 mm and height of 20 mm.

In most DSC instruments, the temperature sensors (thermocouples or resistances) 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. Moreover, bubble formation and displacement of reactants leads to drastic uncertainties in DSC measurement [8-10].

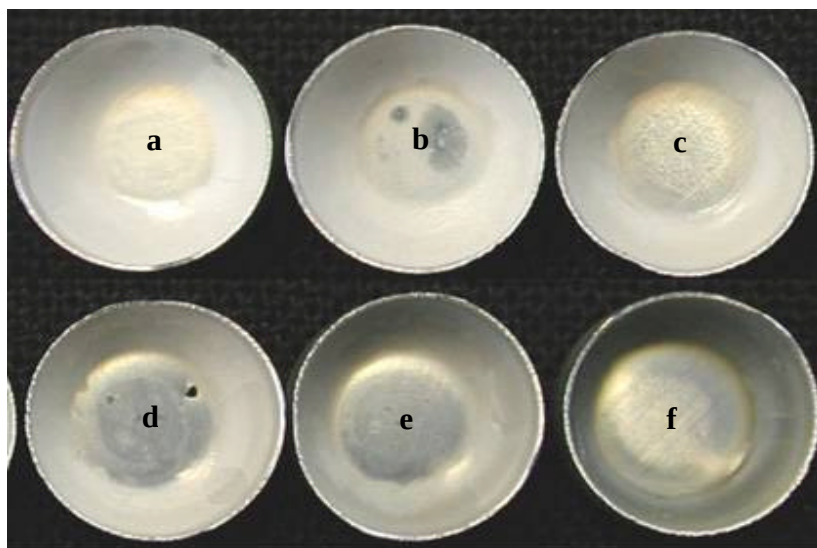


Figure 3.11. The effect of reaction rate on melt displacement: faster reaction (higher catalyst concentration) leads to stronger displacement. 200 ppm Sb (a), 1000 ppm Sb (b), 2000 ppm Sb (c), 5000 ppm b (d), 10000 ppm Sb (e), 20000 ppm Sb (f).

4. Conclusion

Investigation of polycondensation in PET synthesis by DSC is not a straightforward task. The measured signal is a complex one as it originates from a sum of different physical and chemical processes. Moreover, reactant displacement and formation of condensate bubbles during reaction are a serious uncertainty source. Another complication comes from the change of heat transport properties of the sample due to drastic changes in the sample geometry. Therefore, DSC is not a recommended tool to evaluate quantitatively polycondensation kinetics as it is complicated by serious problems leading to data misinterpretation.

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Chapter 4: Studies on Hydrotalcite Catalyzed Synthesis of Polyethylene Terephthalate in Melt

Abstract

Hydrotalcite catalyzed synthesis of polyethylene terephthalate was studied to clarify the effect of hydrotalcite properties on its catalytic activity. Hydrotalcite was modified by various treatments to tune its activity as a polycondensation catalyst. Hydrotalcite activity was found to decrease upon calcination. However, rehydration of the calcinated hydrotalcite resulted in higher catalytic activity than that of the untreated catalyst. Hydrotalcite activity is dependent on the ratio of magnesium to aluminum cations in its composition, and highest activity occurs at a molar ratio of two. Replacement of the carbonate anions of hydrotalcite by more nucleophilic ones like hydroxide and alkoxide groups resulted in a faster polycondensation reaction. Hydrotalcite has two assembly orders; primary lamination of sheets into plates and secondary agglomeration of plates into particles. Hydrotalcite with larger sheet size showed lower activity. On the other hand, milling of hydrotalcite particles did not affect its activity as it probably enters the reaction on a plate level, which is not affected by milling. Polycondensation resulted in expansion of the hydrotalcite sheets under the effect of formed polymer. Reuse of hydrotalcite after polycondensation followed by depolycondensation resulted in a large activity enhancement.

1. Introduction

Hydrotalcite, a white powdery mineral similar to talc, was discovered in Snarum, Sweden in 1842. It is a hydroxy carbonate of magnesium and aluminum and occurs in nature in laminated and/or fibrous masses. The exact formula, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, was first published by Manasse in 1915 [1]. In 1942 Feitknecht proposed a structure composed of consecutive layers of brucite ($\text{Mg}(\text{OH})_2$) and gibbsite ($\text{Al}(\text{OH})_3$) [2]. Feitknecht called these material “doppelschichtstrukturen” from which the present synonym of HT originates, layered double hydroxides. Feitknecht’s proposal was rebutted by Almann at the end of the 1960’s [3]. He showed that both cations are localized within the same layer with water and carbonate between these layers. The HT structure is similar to that of brucite, where magnesium cations are octahedrally coordinated to six hydroxide ions, giving rise to edge-shared layers of octahedra. In HT, Al^{3+} substitutes part of the Mg^{2+} resulting in a net positive charge in the hydroxide layers. Anions situated in the space between the brucite-like layers counter-balance this positive charge (figure 4.1). A big family of HT-like compounds can be obtained by substituting Mg^{2+} by other divalent and trivalent cations having ionic radii that do not deviate much from that of Mg^{2+} (0.65 Å) [4]. HT-like compounds was synthesized from various combinations of Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mg^{2+} and Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Ga^{3+} . Compounds containing V^{4+} and Li^+ have also been reported [5,6]. The $\text{M}^{2+}/\text{M}^{3+}$ ratio can be varied, although within a limited range. In case of Mg/Al-HT, the lowest ratio without formation of pure $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$ zone is 2:1. Below this ratio Al^{3+} is present in neighboring octahedral, which leads to formation of $\text{Al}(\text{OH})_3$ [7]. Above 3:1 ratio, the high concentration of Mg^{2+} octahedra acts as nuclei for the formation of brucite [4]. Smaller differences in ionic radii between the M^{2+} and M^{3+} facilitates higher $\text{M}^{2+}/\text{M}^{3+}$ ratio. $\text{Mg}^{2+}/\text{Ga}^{3+}$ HT-like compounds was synthesized with a $\text{Mg}^{2+}/\text{Ga}^{3+}$ ratio as high as 7.7 [8]. Beside tuning of the type and ratio of cations, much wider spectra of HT-like compounds can be obtained by changing the nature of the interlayer anions.

The anionic clays based on HT-like compounds have found many practical applications. HT has been used as such or (mainly) after calcination. The most interesting properties of the oxides obtained by calcination are the following:

- High specific surface area.
- Basic properties.

- Formation of homogeneous mixtures of oxides with very small crystal size, stable to thermal treatments, which by reduction form small and thermally stable metal crystallites.

1.1. Preparation of hydrotalcite-like compounds

The most applied synthesis route for HT-like compounds is the co-precipitation. For the preparation of HT-like compounds under low super-saturation conditions low concentrations of metal-nitrates or chlorides are used. Precipitation is done by increasing the pH from 7 to 10. Generally, the synthesis temperature is between 50-70 °C [9]. This usually results in more crystalline material than when preparation takes place via high super-saturation (fast addition, pH >10 [10]) since in the latter case the rate of nucleation is higher than the rate of crystal growth [4]. It is also possible to prepare HT-like compounds by hydrothermal treatment of a $\text{Al}_2\text{O}_3/\text{MgO}$ mixture with variation of the Mg/Al ratio and the temperature [11]. A typical and key feature of many HT-like compounds is the ability to restore the layered structure from the calcinated product via exposure to water. This “memory effect” is used to replace interlayer carbonate for other ions, by exposure of the calcinated HT to a solution containing the desired anion, *e.g.*, organic anions [12] and poly oxometalates [13]. In the absence of CO_3^{2-} and other anions, this exposure to water results in the reconstruction of the layered structure with OH^- ions in the interlayer [14].

1.2. Application of hydrotalcite-like compounds

HT-like compounds have manifold applications. Bromide- or phosphate- interlayered HT-like compounds are used as flame-retardant additives in plastics [15,16]. Another major application of HT is in pharmaceuticals as anti-acid and drug carriers [17,18]. Furthermore, HT like compounds can be used as heat stabilizers in polyvinyl chloride (PVC). The stabilization activity originates from the capacity of HT to react with HCl during PVC degradation thus preventing the autocatalysis of this reaction [19,20]. HT-like compounds are used successfully as anion exchangers in many occasions. As a catalyst, HT found applications in the following fields:

- Basic catalysis (polymerization of alkene oxides, aldol condensation).
- Reforming of hydrocarbons (naphtha and CH_4) with water.
- Hydrogenation reactions (production of CH_4 , CH_3OH , higher alcohols, paraffins and olefins from syngas, hydrogenation of nitrobenzene).

- Oxidation reactions.

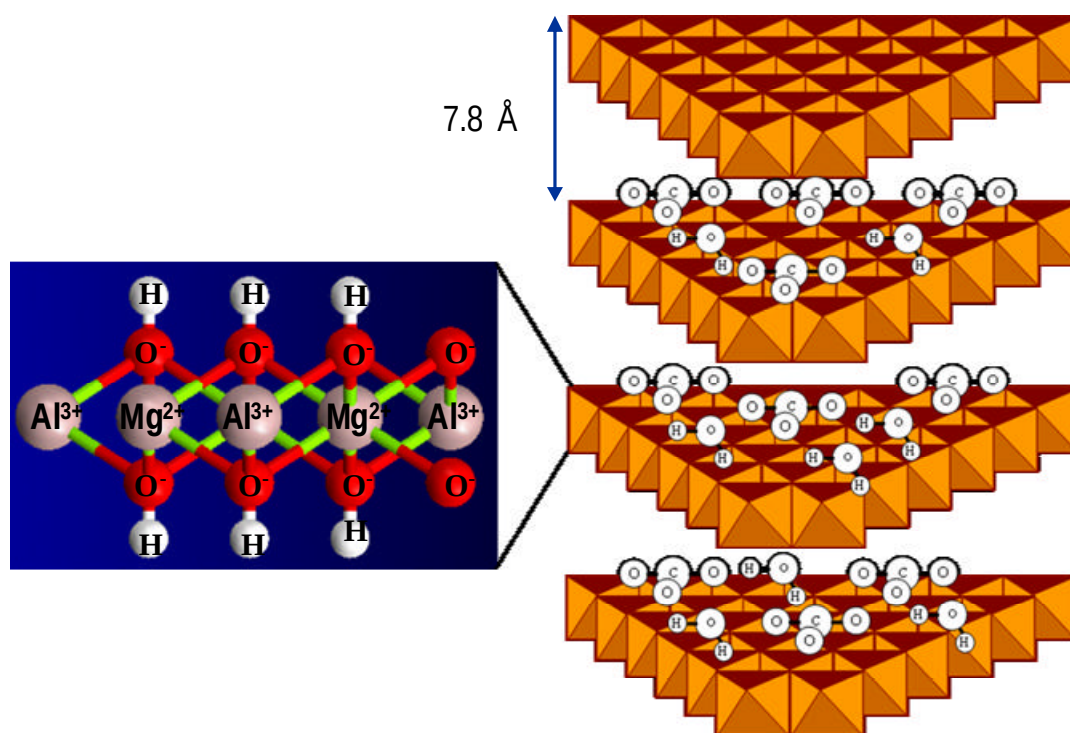


Figure 4.1. The layered structure of HT and the layered double hydroxide structure of its sheets.

1.3. Hydrotalcite as a catalyst for polyethylene terephthalate synthesis

Recently, the researchers at the Dow Chemical Company have patented HT-like compounds as safer, cheaper and more efficient catalysts for PET production [21,22]. It is a hazardless material and can be applied in contact with food without any restrictions. In order to optimize the catalytic activity of HT as a polycondensation catalyst, the effect of the ratio of aluminum to magnesium in its composition, the effect of hydroxide groups content, the effect of the type of counter balancing anions, the effect of the size of layers and the effect of interlayer distance on HT catalytic activity were studied.

2. Experimental

2.1. Calcination and rehydration procedures

About 5 mg of HT (HYBOT MA1 from Bystricko) were placed in aluminum crucibles and then introduced into a DSC oven (DSC 7 from Perkin Elmer), where they were calcinated at different temperatures for various periods of time. The calcination atmosphere

was air or nitrogen. The calcinated HT was mixed in acetone with the appropriate amount of BHET to yield an 830 ppm catalyst mixture before acetone was removed. In rehydration experiments, the calcinated HT was directly dropped into a 100 ml round bottom flask containing 50 ml of distilled water and stirred for 15 min before the appropriate amount of BHET in acetone solution was added. This mixture was stirred for another 15 min before water and acetone were evaporated at 40 °C and 400 mbar.

2.2. Hydrothermal aging

3 g of HT (HYBOT MA1 from Bystricko) were weighed into a 200 ml teflon lined steel autoclave that can withstand pressure up to 15 bar. 100 ml of distilled deionized water was added to HT before the autoclave was closed and placed in an oven whose temperature was set to 150 °C. Aging time was changed between 2 and 170 h.

2.3. Catalyst separation from polymer after polycondensation

5 g of 10^4 ppm HT/BHET (HT is Pural 61 from Sasol) mixture were polymerized for 30 min at 280 °C and 0.1 mbar in a 25 ml teflon lined cylindrical glass vessel without external stirring. After cooling to room temperature, the polymer was dissolved in hexafluoro isopropanol. The polymer solution was added to tetrachloro ethane to form a binary phase mixture (tetrachloro ethane is the lower phase). This mixture was centrifuged for 5 min at a rotation speed of 1000 rpm. The polymer solution phase and most of the tetrachloro ethane phase were removed by a syringe. The rest material was dried at 40 °C under high vacuum.

2.4. Reuse of hydrotalcite after polycondensation

10 g of 10^4 ppm HT/BHET (HT is HYBOT MA1 from Bystricko) mixture were polymerized for 10 min at 240 °C in a teflon lined 25 ml cylindrical glass vessel without external stirring at 0.1 mbar. The produced polymer was depolymerized by stirring in a 250 ml of EG for 24 h at 198 °C. The concentration of HT in the resulting monomer was reduced to 830 ppm by addition of the appropriate amount of BHET before EG was evaporated at 50 °C under high vacuum.

2.5. Catalyst screening

The activity of the following catalysts: HT with different ratio of magnesium to aluminum (Pural 70, 61, 30 and 10 from Sasol) and HT calcinated at different temperatures

(HYBOT MA1 from Bystricko), rehydrated HT (HYBOT MA1 from Bystricko) after calcination, brucite, aluminum acetate, magnesium acetate and a mixture containing 61 mol % magnesium acetate and 39 mol % aluminum acetate, was investigated by the STA 409 PG.

2.6. Material characterization

Scanning electron microscopy was done on a high resolution microscope of the type S-4000 from Hitachi. Transmission electron microscopy was done on a microscope of the type JSEM 200 B from Jeol. The specific surface area (BET measurements) of different HT catalysts was measured on a Gemini III 2375 surface area analyzer from Micrometrics. X-ray measurements were done on a Siemens D5000 powder diffractometer (CuK alpha radiation with Ge monochromator, Bragg-Brentano geometry, flat sample on Si sample holder, position sensitive detector (PSD)).

3. Results and Discussion

3.1. Hydrotalcite structure

Scanning- and transmission electron microscopy showed that HT has two orders of assembly; primary strong assembly of hexagonal layers into plates (the distance between two layers is 0.78 nm) and secondary assembly of plates into particles (figure 4.2-4.4). The shape of the plates is often hexagonal due to the structure of the crystal nucleation agent (a hexagon of hydroxide groups). TEM showed that the plates have a wide size distribution.

HT is not completely stable at the reaction condition (high temperature) and some of its cations are released. To check whether HT is acting as a homogeneous catalyst, its activity was compared to that of magnesium cations, aluminum cations and a mixture of these cations resembling HT composition. The activity is represented as the intrinsic viscosity of the final product after polycondensation of 200 g BHET at 280 °C for 90 min under high vacuum, which reflects the achieved conversion (table 4.1). HT was more active than magnesium cations, aluminium cations or the mixture of both. Also, the selectivity of HT was higher as reflected in the colour of the produced polymer. The polymer colour was white when HT was applied as a catalyst while it was yellow to brown in case of catalysis by HT components (table 4.1). Therefore, HT is assumed to act as a heterogeneous catalyst.

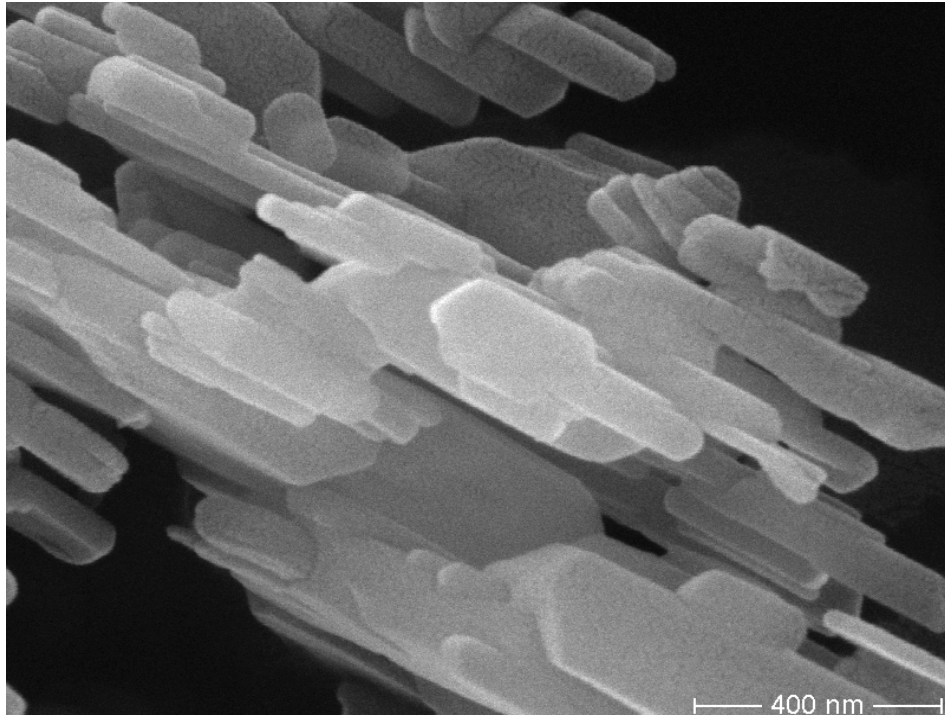


Figure 4.2. High resolution SEM micrograph of a HT particle representing a side view.

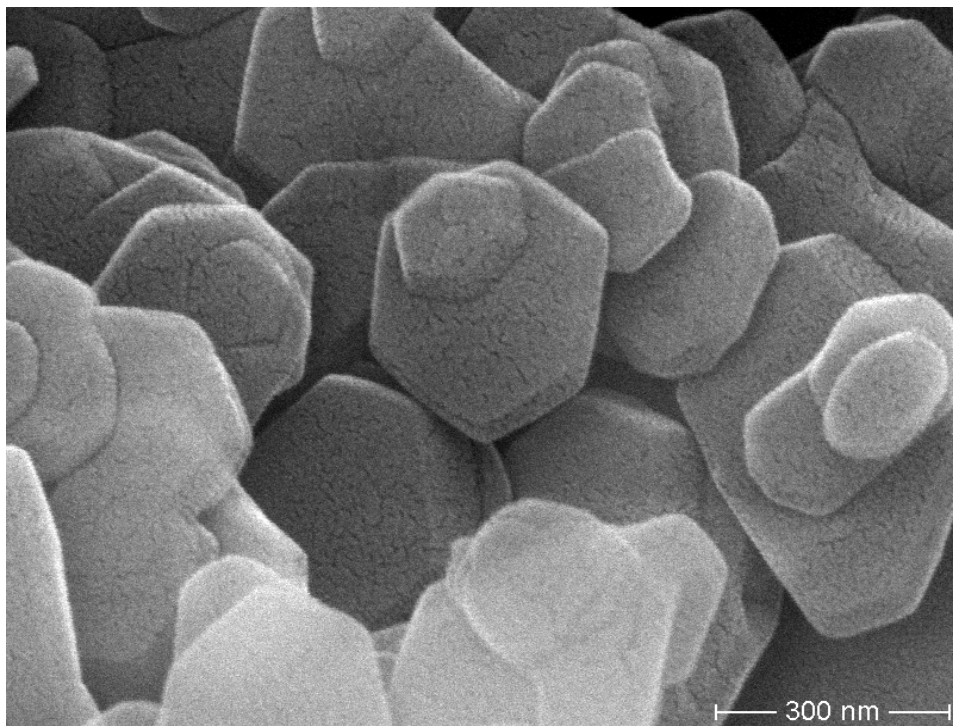


Figure 4.3. High resolution SEM micrograph of a HT particle representing a top view.

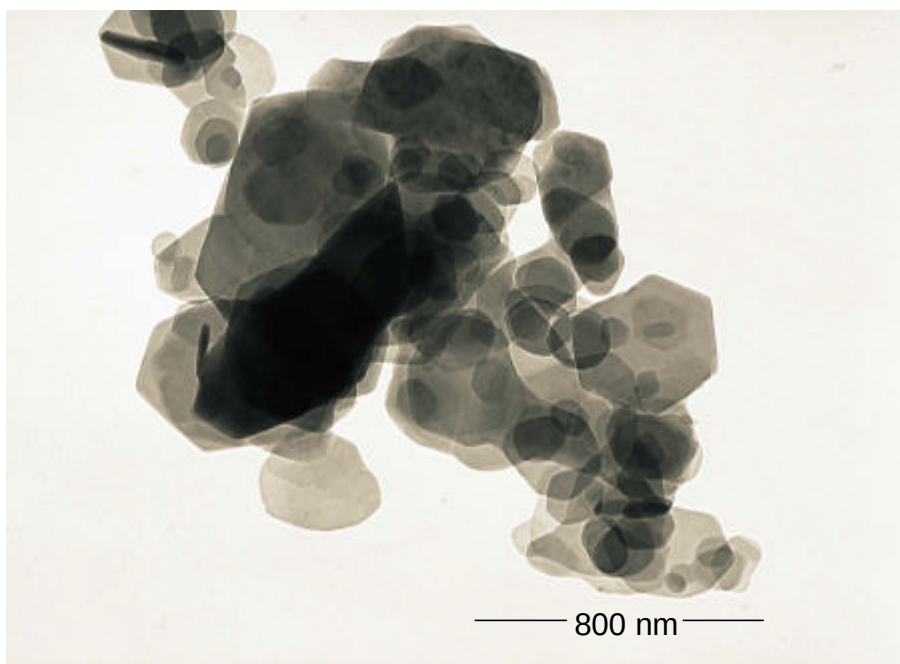


Figure 4.4. TEM micrograph of a HT particle.

Table 4.1. Final intrinsic viscosity of the product of BHET polycondensation at 280 °C for 90 min catalyzed by HT, magnesium acetate, aluminum acetate and a mixture of aluminum and magnesium acetate.

<i>Catalyst</i>	<i>[η] at 25 °C [dl g⁻¹]</i>	<i>Polymer colour</i>
Al(Ac) ₃	0.198 ± 0.002	brown
Mg(Ac) ₂	0.485 ± 0.003	yellow
33 mol % Al(Ac) ₃ + 67 mol % Mg(Ac) ₂	0.492 ± 0.003	brown
HT	0.639 ± 0.005	white

3.2. Effect of hydrotalcite composition on its catalytic activity

The effect of the ratio of divalent to trivalent metal of HT on its catalytic activity was investigated. Table 4.2 shows the activity of HT as a function of its molar ratio of magnesium cations to aluminum ones. The catalytic activity of HT increases with increasing magnesium cations content and reaches a maximum at 67 mol % of magnesium cations before it goes down again to a very low activity at 100 mol % of magnesium cations (brucite). The activity has no direct correlation with specific surface area, as the catalysts with very high specific surface area do not show the highest activity. Several studies [4,7,8] showed that HT has the highest positive charge and consequently the maximum number of

counter balancing anions when the ratio of magnesium cations to aluminum ones in its composition is 2:1.

Therefore, the counter balancing anions of HT are important for its catalytic activity.

Table 4.2. Activity and specific surface area of HT with different ratio of aluminum cations to magnesium ones.

$Mg^{2+}/(Al^{3+} + Mg^{2+})$ [-]	Activity [g product g cat ⁻¹ h ⁻¹]	BET surface [m ² g ⁻¹]
0.1	400 ± 20	335 ± 17
0.3	1520 ± 80	224 ± 11
0.67	1720 ± 80	88 ± 5
0.7	1180 ± 60	262 ± 13
1	490 ± 20	44 ± 2

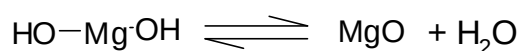
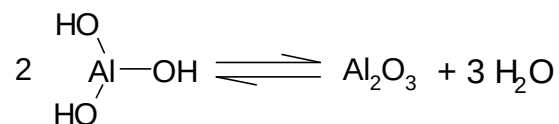
3.3. Effect of hydroxide groups content of hydrotalcite on its catalytic activity

Calcination of HT results in its dehydroxylation and decarboxylation [4,6,9]. HT was calcinated to study the effect of hydroxide content on its catalytic activity in BHET polycondensation. Figure 4.5 shows the mass loss during HT calcination. Longer calcination time as well as higher calcination temperature leads to stronger dehydroxylation and decarboxylation. Table 4.3 shows the activity of HT after calcination at different temperatures for 1 and 16 h. The activity of HT decreases with increasing calcination time and temperature. Moreover, the specific surface area of HT strongly increases upon calcination (table 4.3). It increases with increasing calcination time and temperature. This increase is due to formation of cracks and crevices in the HT stacks that preserve their overall morphology after calcination. Also, calcination of HT boosts its basicity and acidity. Basicity increases due to the formation of magnesium oxide (MgO) while formation of alumina (Al₂O₃) is responsible for enhanced acidity (scheme 4.1) [6, 9-13]. This indicates that HT does not act as a base and/or an acid.

Hence, HT activity depends on the presence of hydroxide and/or carbonate groups and unlike other heterogeneous catalysts; it is not related to its specific surface area.

HT dehydroxylation by calcination is a reversible process and the original double hydroxide structure is restored upon contact with water [6]. Calcinated HT resumes its activity in catalyzing BHET polycondensation after rehydration and the activity is slightly higher than that of the original HT (table 4.4). Also, the activity increased with increasing

calcination temperature and time. Rehydration was done in pure water in absence of carbonate or other anions. In this case water reacts with the peroxide anions and hydroxide anions are formed in the gallery between the layers as counterbalancing anion.



Scheme 4.1. Formation of alumina and magnesium oxide upon HT calcination.

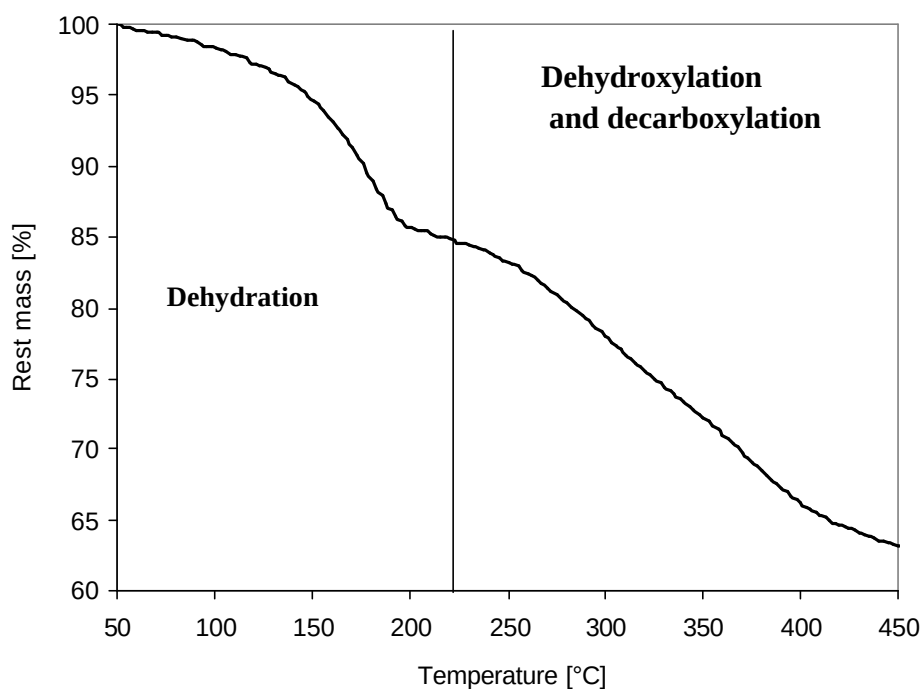


Figure 4.5. TG thermogram of HT at a heating rate of 5 K min⁻¹. Sample mass is 10 mg.

Table 4.3. The activity and specific surface area of HT after calcination for different periods of time at different temperature.

<i>Calcination Temperature</i> [°C]	<i>Time</i> [h]	<i>Activity</i> [g product g cat ⁻¹ h ⁻¹]	<i>BET surface</i> [m ² g ⁻¹]
250	1	1210 ± 60	101 ± 6
250	16	1100 ± 50	105 ± 6
450	1	1160 ± 60	143 ± 9
450	16	870 ± 40	378 ± 23
Original HT	-	1720 ± 80	88 ± 5

Therefore, the hydroxide groups of HT are necessary for its activity. Figure 4.6 shows a scanning electron micrograph of the rehydrated HT. HT plates are randomly oriented in all directions and not parallel to each other as in the original one. Hence, higher activity after rehydration may be due to better distribution of the catalyst in the reaction mixture or due to replacement of the carbonate groups by hydroxide groups.

Table 4.4. The activity of HT after calcination at different temperatures for different periods of time followed by rehydration.

<i>Calcination temperature</i> [°C]	<i>Time</i> [h]	<i>Activity</i> [g product g cat ⁻¹ h ⁻¹]
250	1	1790 ± 90
250	16	1830 ± 90
450	1	1980 ± 100
450	16	2100 ± 110
Original HT	-	1720 ± 80

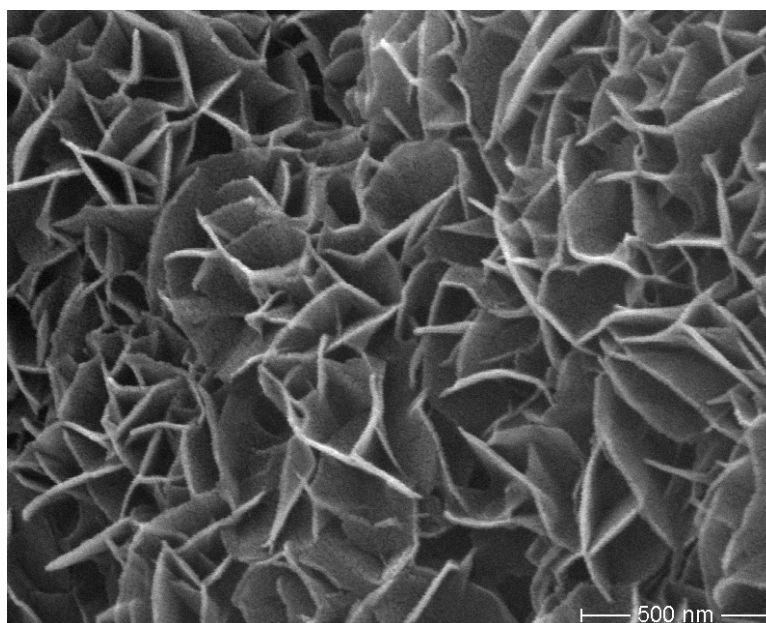


Figure 4.6. High resolution SEM micrograph of calcinated HT after rehydration. The hexagonal stacks of HT are randomly distributed in all directions.

3.4. Effect of the type of counter-balancing anions on hydrotalcite activity

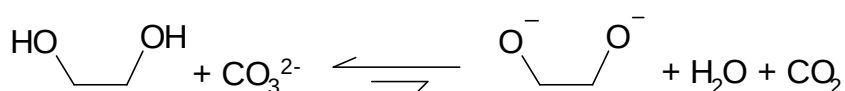
The carbonate anions of HT were exchanged with glycoxide anions to study the effect of the type of counter-balancing anions on HT activity. The exchange reaction was done by

heating of HT in EG at 198 °C (scheme 4.2) [9]. Glycolysis was done for different periods of time to investigate the effect of partial glycolysis. Glycolized HT shows higher activity than that of original or rehydrated HT. The activity increases with the extent of glycolysis (heating time) and reaches a maximum value after 20 h (table 4.5). So, 20 h of heating is needed for complete replacement of the carbonate anions with glycoxide ones at 198 °C.

Therefore, the nature of the anions between the layers plays a role in the activity of HT since the activity decreases by changing the interlayer anion from glycoxide into carbonate. Also, the activity of rehydrated HT was higher than that of the original one while it was lower than that of the glycolized HT. In this case the activity increases with increasing nucleophilicity of the inter layer anions (glycoxide > hydroxide > carbonate). Probably the reaction mechanism involves reaction of the interlayer anions with BHET and formation of new anions (alkoxide).

Table 4.5. Effect of glycolysis duration at 198 °C on the catalytic activity of HT.

<i>Glycolysis duration</i>	<i>Activity</i>
<i>[h]</i>	<i>[g product g cat⁻¹ h⁻¹]</i>
2	1820 ± 90
10	1970 ± 90
15	2060 ± 100
20	2200 ± 110
26	2200 ± 110
Original HT	1720 ± 80



Scheme 4.2. Carbonate groups replacement by glycoxide ones as counter balancing anion.

3.5. Effect of hydrotalcite particle size on its catalytic activity

Figure 4.7 shows the particle size distribution of HT before and after manual milling by a pistil and a mortar. The distribution was established by counting 1500 particles from a high resolution SEM micrograph. The activity of HT did not change after milling and surprisingly; the surface area became smaller (decreased from 88 m² g⁻¹ to 47 m² g⁻¹). Electron microscopy showed that the milled HT is more packed than the original one.

To explain this result, HT was stirred for 2 min in butanol in ultrasonic bath and then it was spread over a silica chip, which was pre-etched with oxygen plasma [14]. After evaporation of butanol, part of the HT was distributed over the silica as single stacks (figure 4.8). This means that the stacks of HT are not strongly assembled together and its stirring in butanol or other organic polar solvents results in its separation. If HT is added to a solution of the monomer and stirred for a period of time before evaporation of the solvent, the monomer will set between the stacks preventing their re-assembly and thus resulting in a better distribution of HT in the monomer (figure 4.9).

Therefore, HT enters the reaction probably on a plate level and the particles disintegrate after mixing with BHET in a solvent. Milling may have reduced the size of HT particles but not the size of the plate themselves.

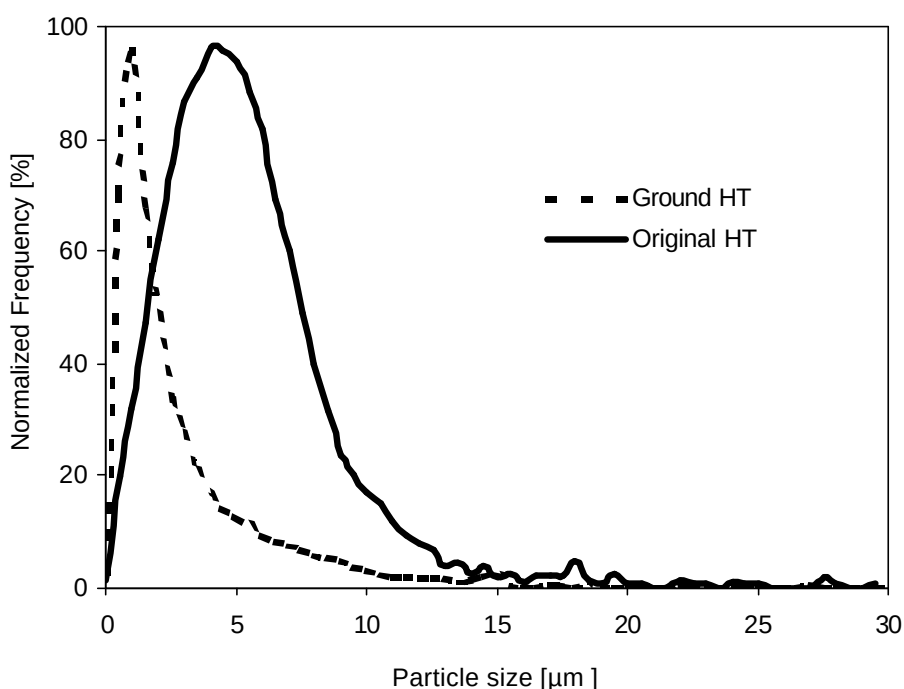


Figure 4.7. Particle size distribution of HT before and after milling by a pistil and mortar.

3.6. Effect of hydrotalcite plate size on its activity

Hydrothermal treatment of HT results in transformation of the small crystallites into larger and well organized ones. Figure 4.10 shows HT before and after hydrothermal treatment. The plates became much bigger and were more ordered. Figure 4.11 shows the x-ray diffraction patterns of HT before and after hydrothermal aging. The diffraction of the 003 basal planes that gives the distance between the layers became sharper and that of the

012 basal plane became smaller which indicates higher crystallinity and order. This fact is supported by the increase in the ratio of the intensities of the diffraction from the 006 basal plane to that of the 003 one. The activity of HT decreased with aging and reached almost a constant value after 96 h of aging (table 4.6).

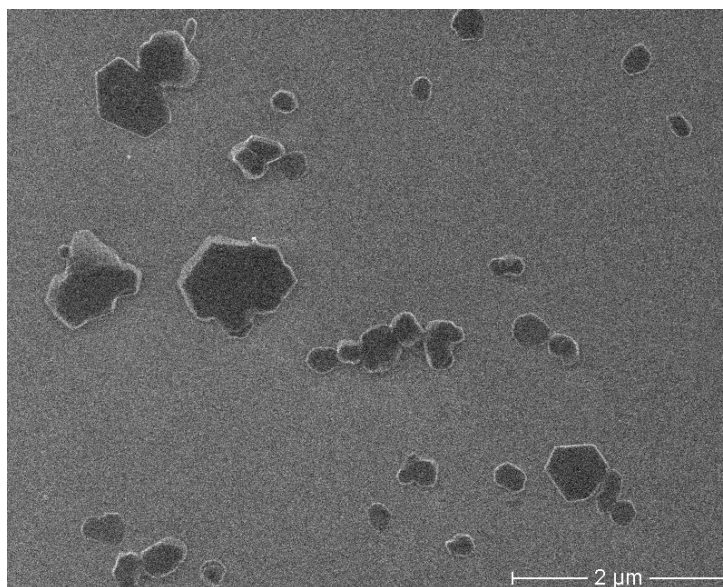


Figure 4.8. High resolution SEM micrograph of HT spread as a slurry over a plasma-etched silica chip followed by solvent evaporation.

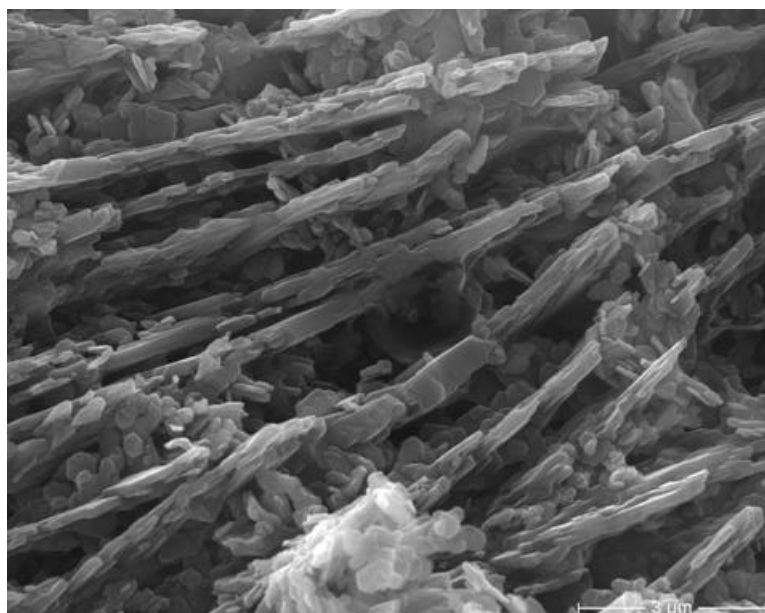


Figure 4.9. SEM micrograph of a mixture of BHET and HT with 1:1 weight ratio.

HT composition and interlayer distance was not changed by aging. Therefore, the activity decreased upon aging probably due to increased segregation of the catalyst in the reaction mass (same catalyst amount and larger catalyst particles).

Table 4.6. Effect of hydrothermal aging time at 150 °C on the catalytic activity of HT.

<i>Hydrothermal aging time</i> <i>[h]</i>	<i>Activity</i> <i>[g product g cat⁻¹ h⁻¹]</i>
6	1500 ± 70
16	1450 ± 70
24	1350 ± 60
96	1180 ± 60
170	1150 ± 60
Original HT	1720 ± 80

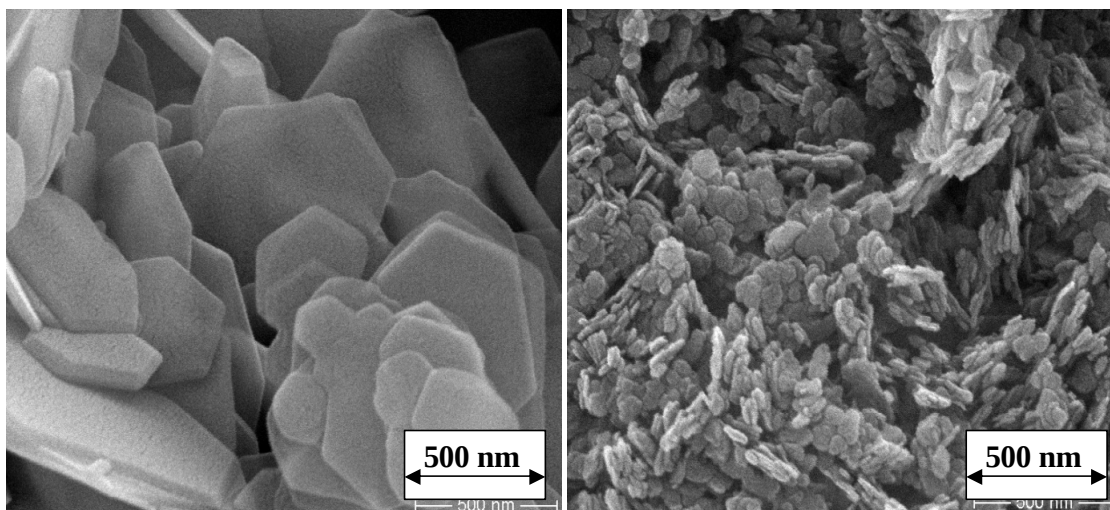


Figure 4.10. High resolution SEM micrograph of HT before (right) and after hydrothermal aging for 7 days at 150 °C (left).

3.7. Effect of hydrotalcite interlayer distance on its catalytic activity

The interlayer distance between two HT layers can be increased by replacement of carbonates by more bulky anions. The interlayer distance of HT was increased from 0.29 nm to 2.2 nm by replacement of the carbonate by dodecyl sulfate. The activity of HT increased from 1720 g product g cat⁻¹ h⁻¹ to 2230 g product g cat⁻¹ h⁻¹ upon intercalation of dodecyl sulfate.

Figure 4.12 shows HT after polycondensation for 30 min at 280 °C and separation of the excess polymer by extraction and centrifugation. The layers of HT were expanded from

each other after polymerization and surrounded by polymer as was shown by insitu energy dispersive x-ray. A possible explanation for this behaviour is the intercalation of the monomer between the layers. As the reaction starts, the monomer flows from the reaction medium into the active centres in the layers and the polymer pressure probably pushes the layers away from each other.

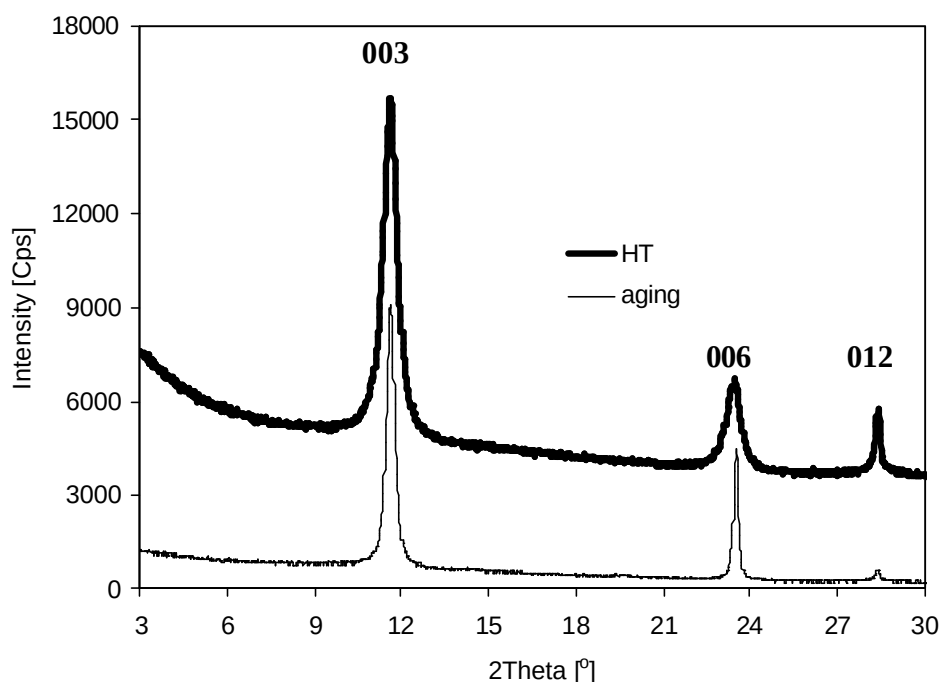


Figure 4.11. X-ray diffraction pattern of HT before and after hydrothermal aging for 7 days at 150 °C.

Reused HT after depolymerization showed a very high activity in BHET polycondensation (3360 g product g cat⁻¹ h⁻¹ compared with 1720 g product g cat⁻¹ h⁻¹ for original HT).

Therefore, better distribution of the catalyst in the reaction mixture (higher degree of homogenisation) results in improved reaction rate at the same catalyst concentration. The high activity of reused HT after polycondensation is probably due to separation of a fraction of the layers from each other (exfoliation).

4. Conclusion

Although free hydroxide groups do not show considerable activity as a BHET polycondensation catalyst, hydroxide groups of HT are necessary for its catalytic activity.

This means that the stereo-specific position and not only the nature of these groups are important. Probably, the hydroxide groups of HT fix the reactants in a close proximity with a favourable geometry. Also, HT activity is proportional to the number and the nucleophilicity of its interlayer anions. Probably, the chain ends of reactants are activated in the form of alkoxide species by reaction with the interlayer anions and removal of a proton from the hydroxyl end groups. The rate of proton removal depends on the nucleophilicity of the interlayer anions. Therefore, polycondensation of BHET with HT as a catalyst probably occurs by reaction of an alkoxide end group with ester end group fixed close to it.

HT particles probably disintegrate into stacks at the beginning of the reaction, as milling of HT samples does not improve its catalytic activity. However, better distribution of HT in the reactants leads to higher activity. This can be achieved by application of HT with a small sheets size in the exfoliated form. The sheet size can be controlled by synthesis while exfoliation can be achieved by pre-treatment of HT.

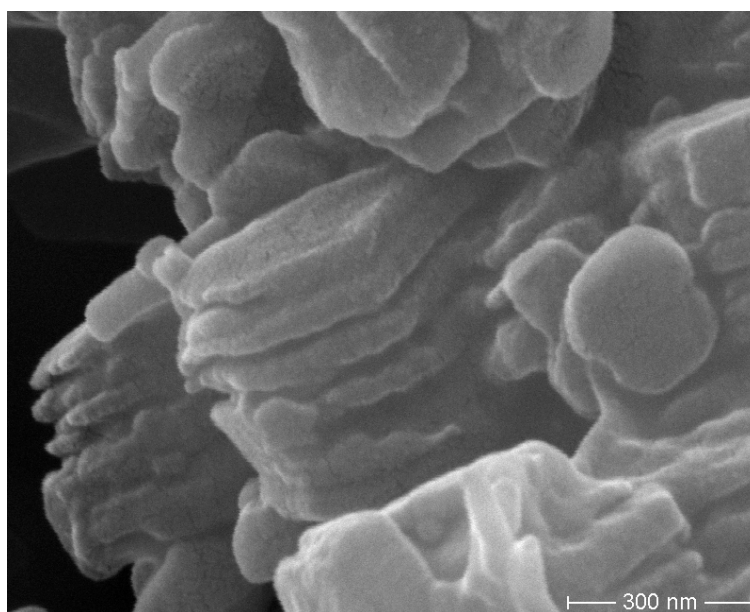


Figure 4.12. High resolution SEM micrograph of HT after polycondensation. The layers were surrounded by polymer and were expanded from each other.

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Chapter 5: Kinetics and Mechanistic Investigation of Hydrotalcite Catalyzed Synthesis of Polyethylene Terephthalate in Melt.

Abstract

Hydrotalcite catalyzed polycondensation of bis-hydroxy ethylene terephthalate was studied by thermogravimetry to elucidate the kinetics. The reaction was found to follow a second order kinetics with respect to hydroxyl end groups. The overall activation energy of the polycondensation was found to decrease with increasing catalyst concentration before it levels out to the value of $93 \pm 5 \text{ kJ mol}^{-1}$ at high catalyst concentration. This is due to the uncatalyzed reaction that takes place parallel to the catalyzed one. The activation energy of the uncatalyzed path was found to be $156 \pm 5 \text{ kJ mol}^{-1}$. IR spectroscopy and x-ray diffraction showed that the monomer intercalates between the layers of hydrotalcite at the beginning of the reaction enabling the complexation of oxygen containing functional groups with the hydroxide groups of the catalyst. Based on these findings a polycondensation mechanism is proposed. One end group of the monomer is activated in the form of alkoxide that counter balances the positive charge of the hydrotalcite layer. This alkoxide group attacks an ester carbonyl group fixed close to it generating a new ester bond and a glycoxide species. The role of hydrotalcite is to activate the reactants, rendering the attacking hydroxyl group more nucleophilic and the ester carbonyl group more electrophilic, and at the same time fixing the reactant together in a favorable geometry.

1. Introduction

TG was used to investigate the kinetics of HT catalyzed BHET polycondensation under dynamic temperature conditions. Infrared spectroscopy and x-ray diffraction were used to investigate the interaction between the functional groups of BHET with HT.

2. Experimental

A mixture containing 33.3 weight % HT in BHET (HT is pural 61 from Sasol) was prepared by dissolving 20 g of BHET in acetone at 40 °C before 10 g of HT were added to this solution. After 15 min of mixing, acetone was evaporated in a rotary evaporator at 400 mbar. The mixture was then introduced into a 100 ml 3 necks-round bottom flask connected to a condenser. The flask was flushed well with nitrogen before immersing it in a salt bath whose temperature was set at 280 °C. The flask was then taken out of the salt bath and cooled down to room temperature under continuous nitrogen purging. The product was collected and pre-cooled in liquid nitrogen before it was ground in an ultracentrifugation mill from Retsch.

HT/BHET mixtures with different concentrations were prepared by mixing the appropriate amount of HT (HT is pural 61 from Sasol) with BHET in EG at 60 °C for 1 h followed by evaporation of EG under high vacuum overnight. Polycondensation runs for kinetic investigations were done in the STA 409 PG.

IR spectroscopic investigations were done on an attenuated total reflection/Fourier transform spectrometer (ATR/FTIR Spectrum One of Mettler Toledo). X-ray measurements were done on a Siemens D5000 powder diffractometer.

3. Results and Discussion

3.1. Calculation of hydroxyl end groups concentration

Oligomerization of pure BHET enables investigation of the polycondensation reaction over a wide conversion range without complications from competing reactions like esterification if acid end groups are present. In addition, the properties of the melt does not change a lot in a wide conversion range as the viscosity changes strongly only at very high conversion. For example, 75 % conversion of the functional groups is needed to build up a tetramer. At the same time, the viscosity and related properties does not change much from monomer to tetramer.

Polycondensation inside an STA oven enables online data acquisition of the reaction progress [1,2]. When the polycondensation reaction starts, EG is set free as condensate by-product and is carried away from the reaction medium by inert gas purging. This leads to mass loss that is recorded as a function of time and temperature. The number of moles of produced EG as a function of time, $n_{t,EG}$, is calculated by the following equation:

$$n_{t,EG} = \frac{\text{mass loss}}{M_{EG}} \quad [\text{mol}] \quad 5.1$$

Where M_{EG} is the molar mass of EG.

The initial number of hydroxyl end groups, $n_{o,OH}$, is given by:

$$n_{o,OH} = 2n_{o,BHET} = \frac{2m_{o,BHET}}{M_{BHET}} \quad [\text{mol}] \quad 5.2$$

Where $n_{o,BHET}$ is the initial number of moles of BHET, $m_{o,BHET}$ is the initial mass of BHET and M_{BHET} is the molar mass of BHET.

In each condensation step two hydroxyl end groups are consumed and one EG is produced. The number of moles of hydroxyl end groups remaining after a reaction time t , $n_{t,OH}$, can be calculated from the amount of produced EG by the following equation:

$$n_{t,OH} = n_{o,OH} - 2n_{t,EG} = \frac{2m_{o,BHET}}{M_{BHET}} - \frac{2\text{mass loss}}{M_{EG}} \quad [\text{mol}] \quad 5.3$$

For kinetic studies it is required to convert the number of moles of hydroxyl end groups into concentration via dividing it by the melt volume, V_t :

$$[OH]_t = \frac{n_{t,OH}}{V_t} \quad [\text{mol l}^{-1}] \quad 5.4$$

The kinetic data published in literature use the concentration of hydroxyl end groups in the form of molality (number of moles divided by the mass of the melt) and not as molarity (number of moles divided by the volume of the melt) due to the continuous change of volume with reaction progress [3]. Under isothermal conditions, the volume decreases with conversion due to material loss as condensate and continuous increase of melt density. Under dynamic conditions, melt volume changes during polycondensation due to the following facts:

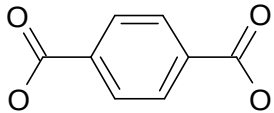
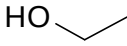
- 1) Loss of material as condensate by-product.
- 2) Continuous variation of the density with conversion and formation of a distribution of higher oligomers that have different molar volumes.
- 3) Thermal expansion of the melt with increasing temperature.

According to Van Krevelen [4], polymers can be considered to be made of segments. By this approach, volume variations can be accounted for by summation of the molar volumes of the segments building the different oligomers. PET can be considered to be made of the following three segments; hydroxy ethylene (*HE*), terephthalate (*TE*) and ethylene (*ET*). The molar volume of these segments can be calculated by approximation from their Van der Waals volumes by the following relation:

$$V_m^{298} = 1.6 V_{vdW} \quad [l \text{ mol}^{-1}] \quad 5.5$$

Where V_m^{298} is the molar volume of this segment at 298 K and V_{vdW} is its Van der Waals volume. The molar volumes and other physical properties of these segments are shown in Table 5.1.

Table 5.1. Different segments of PET and their physical properties.

Segment	Symbol	V^{298} [l mol ⁻¹]	E [l mol ⁻¹ K ⁻¹]	Density at 298 K [g ml ⁻¹]
	T	0.1115	6.97 x 10 ⁻⁵	1.472
	HE	0.0455	2.84 x 10 ⁻⁵	0.991
	E	0.0327	2.04 x 10 ⁻⁵	0.858

The overall distribution of the segments making the melt at any conversion is given by the following equation:

$$(2 - 2X) HE + 1 TE + \frac{X}{2} ET \quad 5.6$$

Where X is the conversion and is given by:

$$X = 1 - \frac{n_{t,OH}}{n_{o,OH}} \quad 5.7$$

Different segments have different expansivities but the molar thermal expansion of the different segments can be described by the following equation [4]:

$$E = 1.3 \times 10^{-3} V_{vdW} \quad [l \text{ mol}^{-1} \text{ K}^{-1}] \quad 5.8$$

The molar volume of the segments at any temperature T, V_m^T , can be calculated by:

$$V_m^T = V_m^{298} + E(T - 298) \quad [l \text{ mol}^{-1}] \quad 5.9$$

The volume of the melt at any time, V_t , is given by:

$$V_t = n_{t,HE} V_{m,HE} + n_{t,ET} V_{m,ET} + n_{t,TE} V_{m,TE} \quad [l] \quad 5.10$$

Where $n_{t,HE}$ is the number of moles of HE segments at time t, and it is given by:

$$n_{t,HE} = n_{o,OH} - 2n_{t,EG} = \frac{2m_{o,BHET}}{M_{BHET}} - 2n_{t,EG} \quad [\text{mol}] \quad 5.11$$

$n_{t,ET}$ is the number of moles of ethylene segments at time t, and it is given by:

$$n_{t,ET} = n_{t,EG} \quad [\text{mol}] \quad 5.12$$

$n_{t,TE}$ is the number of moles of terephthalate segments and it is constant over time and equal to:

$$n_{t,TE} = n_{o,BHET} = \frac{m_{o,BHET}}{M_{BHET}} \quad [\text{mol}] \quad 5.13$$

Figure 5.1 shows a plot of the molar and the molal concentration of hydroxyl end groups as a function of temperature during polycondensation of BHET in presence of 883 ppm HT at 5 K min^{-1} . There is a difference between the two values, where the molal concentration was $7.878 \text{ mol kg}^{-1}$ at the beginning of the reaction while the molar concentration of hydroxyl end groups was 9.243 mol l^{-1} .

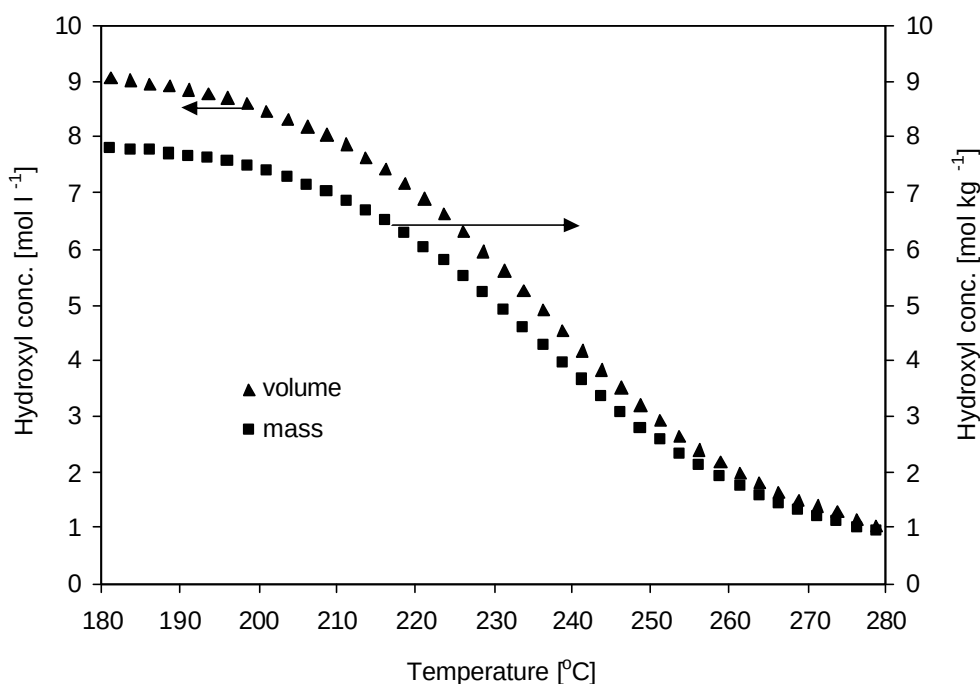


Figure 5.1. Evolution of concentration of hydroxyl end groups (molarity and molality) during polycondensation of BHET at 5 K min⁻¹ in presence of 883 ppm of HT.

3.2. Kinetics

Due to the wide variety of the chemical species present in the reacting melt (oligomers with different chain lengths), the polycondensation is considered as a reaction between hydroxyl end groups. This assumption is reasonable since the consumptions of hydroxyl end groups, and consequently the production of EG, occurs only when two hydroxyl end groups react together. According to Flory, functional groups have equal reactivity if they are separated by more than three carbons. It was assumed that all the hydroxyl end groups have the same reactivity since they have the same chemical vicinity (ethylene terephthalate) regardless of the chain length of the parent oligomers. The polycondensation is considered as an irreversible one since the EG removal is efficient and mass transfer limitations in the melt as well as on the melt-gas interface are absent under the applied conditions (chapter 2).

The reaction order of HT catalyzed polycondensation was determined by the method of integration. Since the polycondensation was done under dynamic conditions, the relation between concentration of hydroxyl end group, time and temperature was studied instead of the relation between the concentration of hydroxyl end groups and time. Plots of the first

term of the equations 5.14-17 versus $\frac{1}{T}$ were done and linearity was obtained in case of equation 5.16 (figure 5.2 and 5.3). Hence, the HT catalyzed polycondensation of BHET is a second order one with respect to the concentration of hydroxyl end groups.

$$\text{Zero order kinetics: } \ln \left\{ \frac{[OH]_o - [OH]}{[HT] t} \right\} = \ln k_o - \frac{E}{R T} \quad 5.14$$

$$\text{First order kinetics: } \ln \left\{ \frac{\ln \frac{[OH]_o}{[OH]}}{[HT] t} \right\} = \ln k_o - \frac{E}{R T} \quad 5.15$$

$$\text{Second order kinetics: } \ln \left\{ \frac{\frac{1}{[OH]} - \frac{1}{[OH]_o}}{[HT] t} \right\} = \ln k_o - \frac{E}{R T} \quad 5.16$$

$$\text{Third order kinetics: } \ln \left\{ \frac{\frac{1}{[OH]^2} - \frac{1}{[OH]_o^2}}{2[HT] t} \right\} = \ln k_o - \frac{E}{R T} \quad 5.17$$

For detailed kinetic investigations, the software package “Thermokinetics” from Netzsch was used to fit the experimental conversion-temperature curves with second order kinetics. Two fitting parameters are used; activation energy and pre-exponential factor. The fitting quality determines whether the assumed kinetic model is adequate and whether the calculated kinetic parameters are valid. The multivariate nonlinear regression is the core of this software. It applies a combination of embedded algorithms to solve a system of differential equations relevant to the assumed kinetic model. Fitting is done by the iterative search for the parameter values that minimize the sum of squared differences of the measured reaction rate, $R_{measured}$, and the calculated reaction rate, $R_{calculated}$, for all data points. That is, it searches for the parameter values that makes the sum of $(R_{measured} - R_{calculated})^2$ minimum.

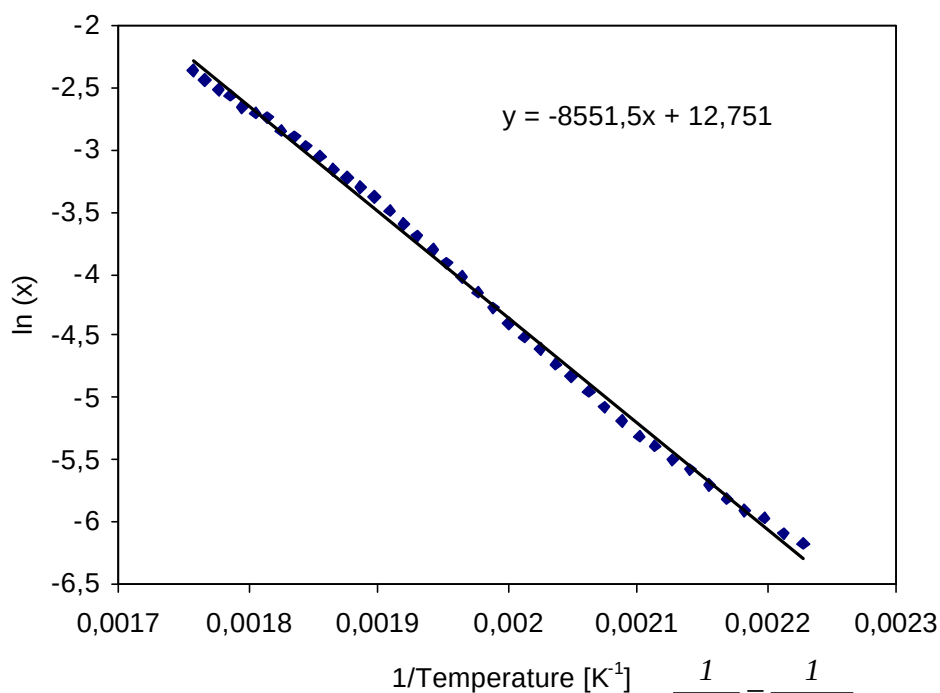


Figure 5.2. Fitting of the first term of equation 5.16 (x is $\frac{1}{[HT] t} - \frac{1}{[OH]_o}$) versus $1/T$ for BHET polycondensation catalyzed with 883 ppm of HT at 5 K min^{-1} .

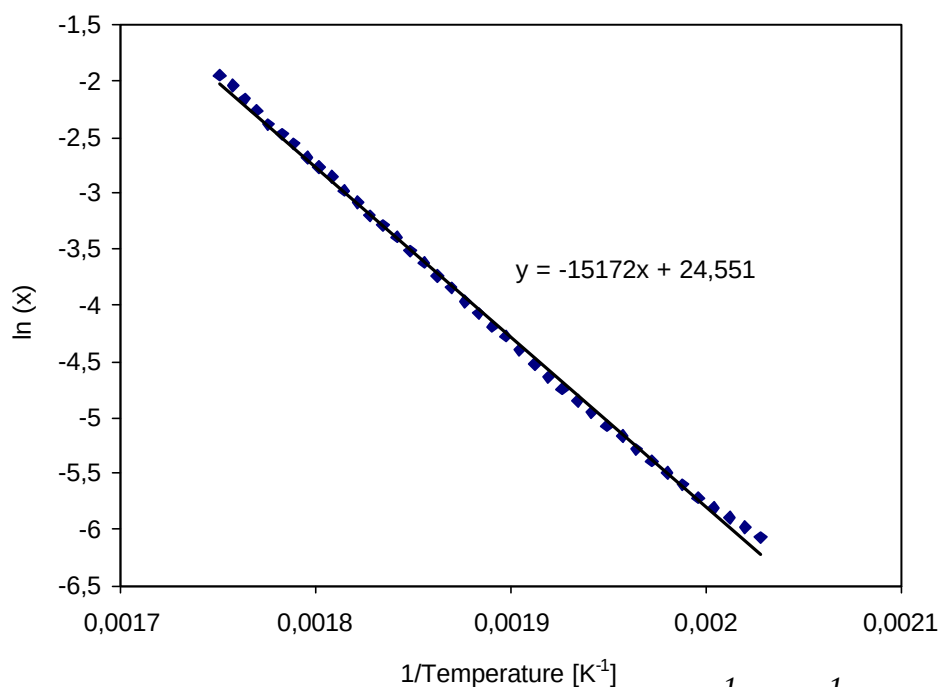


Figure 5.3. Fitting of the first term of equation 5.16 (x is $\frac{1}{[HT] t} - \frac{1}{[OH]_o}$) versus $1/T$ for BHET polycondensation catalyzed with 86 ppm of HT at 5 K min^{-1} .

Figure 5.4 & 5.5 shows the evolution of the molal and molar concentration hydroxyl end groups in polycondensation of BHET at three different heating rates (5, 8 and 10 K min⁻¹) in presence of 442 ppm HT as a catalyst and their fitting with a second order reaction. The activation energy was 135 kJ mol⁻¹ and 126 kJ mol⁻¹ in case of molal and molar concentration respectively. There is a significant difference between the two values. The activity of reacting species is proportional to their collisions number i.e. to their number in a certain space. Therefore the use of molar concentration yields more accurate results and for this reason it will be applied in the rest of this work.

Figure 5.6 shows the reaction progress during BHET polycondensation at 5 K min⁻¹ in presence of different HT concentrations, and fitting of the experimental data with a second order kinetics. Figure 5.7 is a plot of the activation energy of the polycondensation reaction as a function of HT concentration. Activation energy drops strongly with increasing HT concentration before it levels out to the value of 88 ± 5 kJ mol⁻¹. In the range of low HT concentration, the activation energy drops linearly with catalyst content (figure 5.8). The activation energy of the uncatalyzed reaction was determined by extrapolation to be 153 ± 5 kJ mol⁻¹ from molal concentration calculation and 146 kJ mol⁻¹ from molar concentration calculation.

The rate of polycondensation can be considered by the following equation:

$$Rate = -\frac{1}{2} \frac{d[OH]}{dt} = k_{catalyzed} [HT] [OH]^m + k_{uncatalyzed} [OH]^n \quad 5.18$$

Where $[HT]$ is HT concentration [mol l⁻¹], $k_{catalyzed}$ is rate constant for catalyzed polycondensation reaction [l^m mol^{-m} s⁻¹] and $k_{uncatalyzed}$ is rate constant for uncatalyzed reaction [lⁿ⁻¹ mol¹⁻ⁿ s⁻¹].

The uncatalyzed BHET polycondensation is a second order reaction [5]. By fitting, the overall reaction order of the HT catalyzed polycondensation was found to be a second order reaction. Also, at high HT concentration, where uncatalyzed reaction is negligible, the reaction was shown to fit well with a second order one.

Therefore, the reaction rate can be written in the following form:

$$-\frac{d[OH]}{dt} = 2(k_{uncatalyzed} + k_{catalyzed} [HT])[OH]^2 \quad 5.19$$

By writing the rate constant in its Arrhenius form the following equation is obtained:

$$-\frac{d[OH]}{dt} = 2(k_{o,uncatalyzed} \exp^{\frac{-E_{uncatalyzed}}{RT}} + k_{o,catalyzed} \exp^{\frac{-E_{catalyzed}}{RT}} [HT]) [OH]^2 \quad 5.20$$

Where $k_{o,uncatalyzed}$ is the pre-exponential factor for the uncatalyzed reaction path [$l \text{ mol}^{-1} \text{ s}^{-1}$], $k_{o,catalyzed}$ is pre-exponential factor for catalyzed reaction [$l^2 \text{ mol}^{-2} \text{ s}^{-1}$], $E_{uncatalyzed}$ is activation energy of uncatalyzed reaction [J mol^{-1}], $E_{catalyzed}$ is activation energy of catalyzed reaction [J mol^{-1}], R is universal gas constant [$\text{J mol}^{-1} \text{ K}^{-1}$] and T is temperature [K].

By fitting of the polycondensation reaction with equation 5.20 and applying the activation energy values of $146 \pm 5 \text{ kJ mol}^{-1}$ and $88 \pm 5 \text{ kJ mol}^{-1}$ for uncatalyzed and catalyzed reaction respectively, the following values of the pre-exponential factors were found: $2.97 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ for uncatalyzed polycondensation and $1.03 \times 10^8 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ for catalyzed one. And therefore,

$$-\frac{d[OH]}{dt} = 2(2.97 \times 10^{11} \exp^{\frac{-146000}{RT}} + 1.03 \times 10^8 \exp^{\frac{-88000}{RT}} [HT]) [OH]^2 \quad 5.21$$

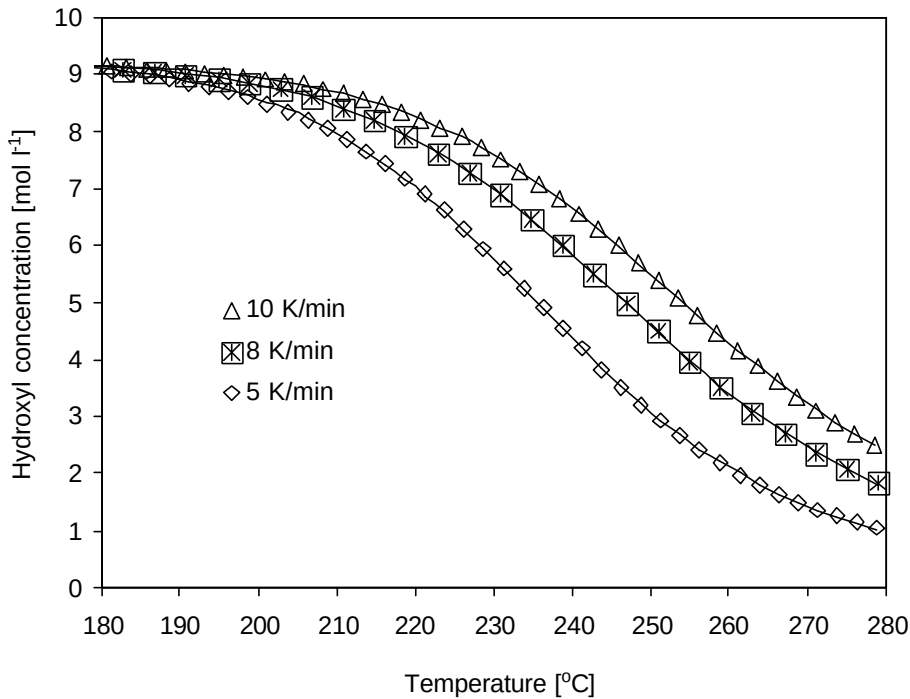


Figure 5.4. Decay of molar concentration of hydroxyl end groups during polycondensation of BHET at different heating rates in presence of 442 ppm of HT. Solid line is fitting with a second order kinetics.

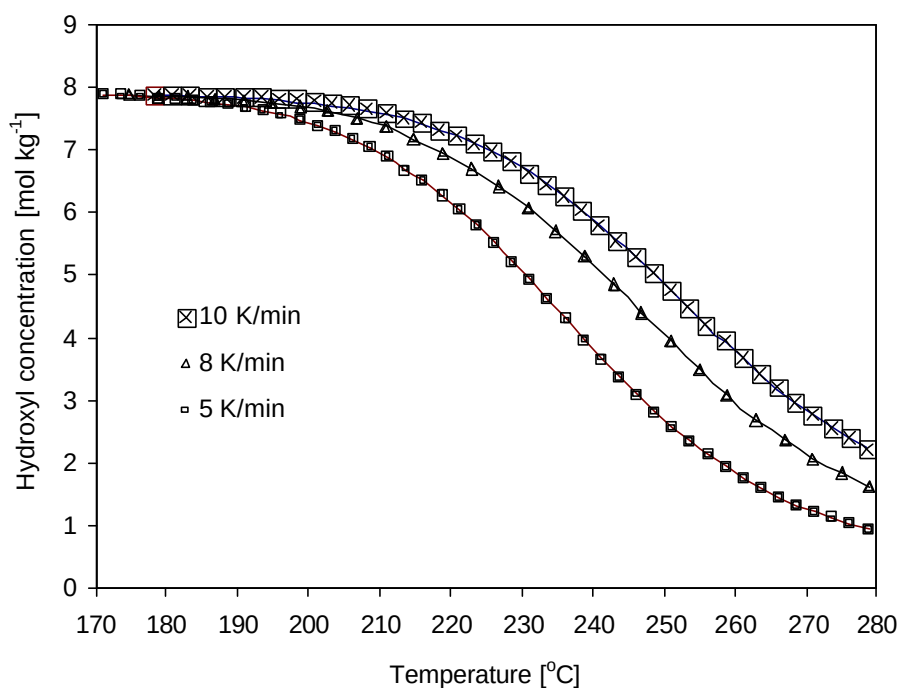


Figure 5.5. Decay of molal concentration of hydroxyl end groups during polycondensation of BHET at different heating rates in presence of 442 ppm of HT. Solid line is fitting with a second order kinetics.

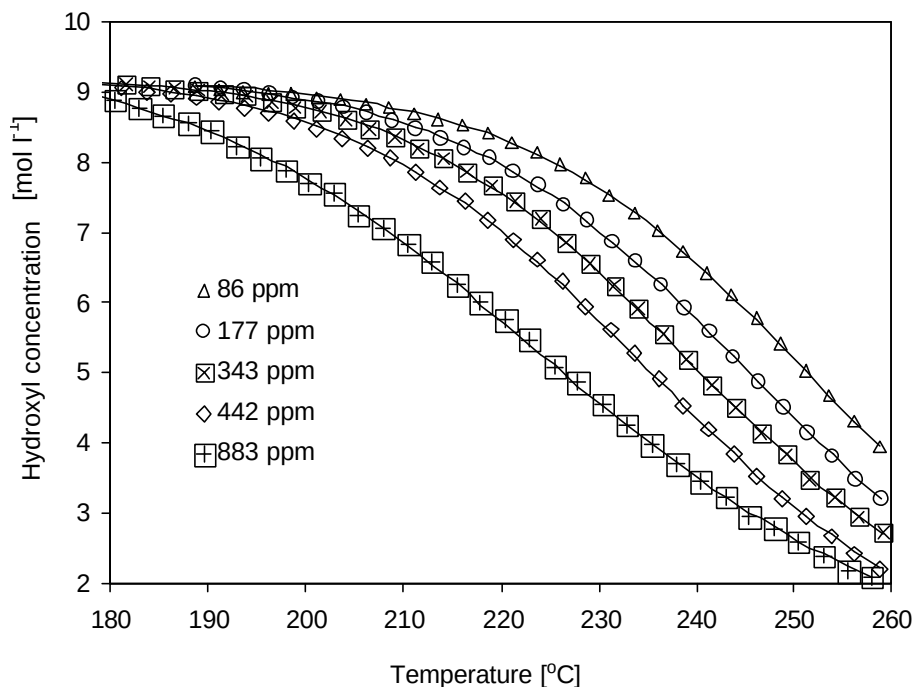


Figure 5.6. Conversion of hydroxyl end groups as a function of temperature during polycondensation of BHET at 5 K min⁻¹ in presence of different HT concentrations. Solid line is fitting with a second order kinetics.

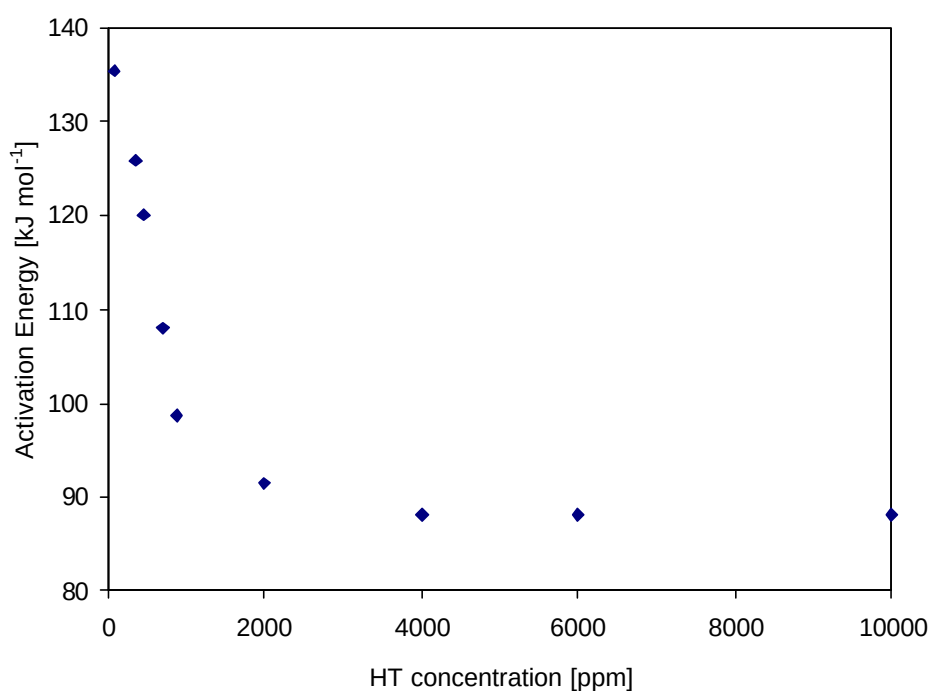


Figure 5.7. Plot of overall activation energy of BHET polycondensation as a function of HT concentration.

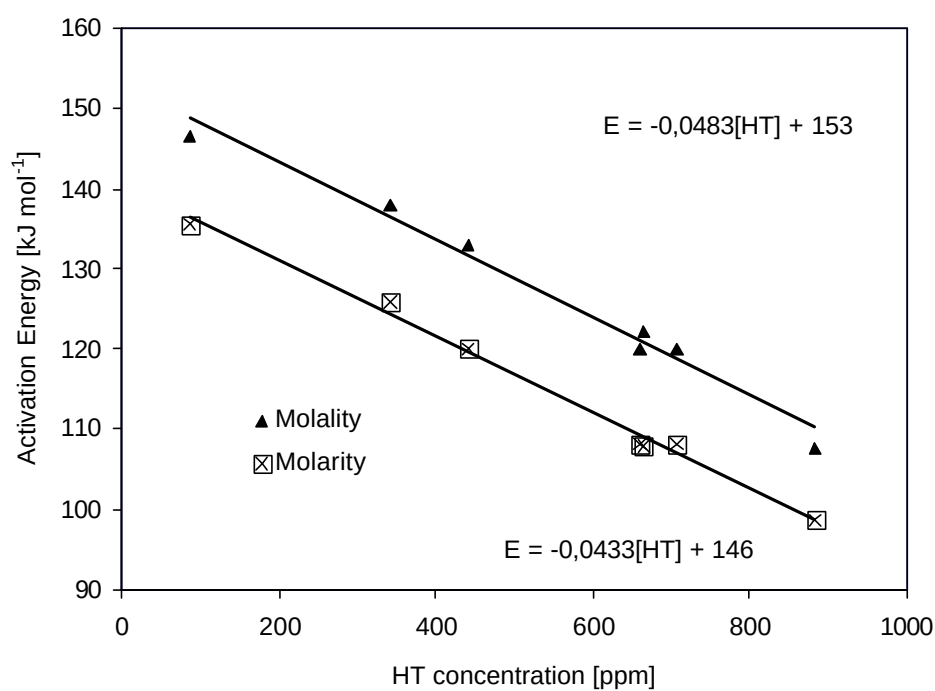


Figure 5.8. Plot of overall activation energy of BHET polycondensation as a function of HT concentration in the range of low concentration.

The activation energy for BHET polycondensation catalyzed by 2000 ppm HT was found by fitting to be 95 kJ mol⁻¹. However for higher HT concentrations the melt solidified during the reaction due to the increase of the average molecular weight of the melt and subsequently the melting point faster than that of the reaction temperature (figure 5.9). Increasing of heating rate from 5 to 20 K min⁻¹ did not prevent the solidification of the melt (figure 5.10). For this reason, the fitting of the polycondensation runs with HT concentration over 2000 ppm was done only for a small experimental range (265 to 280 °C). Therefore, the fitting was not so reliable.

To this end, equation 5.18 was rewritten in the following form:

$$-\frac{d[OH]}{dt} = k_{uncatalyzed} + k_{catalyzed} [HT] \quad 5.22$$

By plotting the first term of equation 5.22 against $[HT]$ the intercept will be $k_{uncatalyzed}$ and the slope will be $k_{catalyzed}$. Figure 5.11 shows the fitting at different temperatures and table 5.2 summarizes the results (values of $k_{uncatalyzed}$ and $k_{catalyzed}$).

Table 5.2. The values of $k_{uncatalyzed}$ and $k_{catalyzed}$ for HT catalyzed polycondensation at different temperatures obtained by linear fitting of equation 5.3.

Temperature [°C]	$k_{catalyzed}$ [l ² mol ⁻² s ⁻¹]	$k_{uncatalyzed}$ [l mol ⁻¹ s ⁻¹]
215	0.02677	0.0000244
225	0.04962	0.0000550
235	0.08816	0.0001114
245	0.13998	0.0002271
255	0.19572	0.0004483
265	0.20971	0.0009000

By plotting $\ln(k)$ versus $\frac{1}{T}$ the slope will be $-\frac{E}{R}$ and the intercept will be $\ln(k_o)$. Figure 5.12 and 5.13 shows that $E_{uncatalyzed} = 156 \pm 5$ kJ mol⁻¹, $k_{o,uncatalyzed} = 6.58 \times 10^{11}$ l mol⁻¹ s⁻¹, $E_{catalyzed} = 93 \pm 5$ kJ mol⁻¹ and $k_{o,catalyzed} = 3.04 \times 10^8$ l² mol⁻² s⁻¹.

According to the transition state theory of reaction kinetics (Eyring) the rate constant of a given reaction, k can be written in the following form:

$$k = \frac{R T K^\ddagger}{N h} \quad 5.23$$

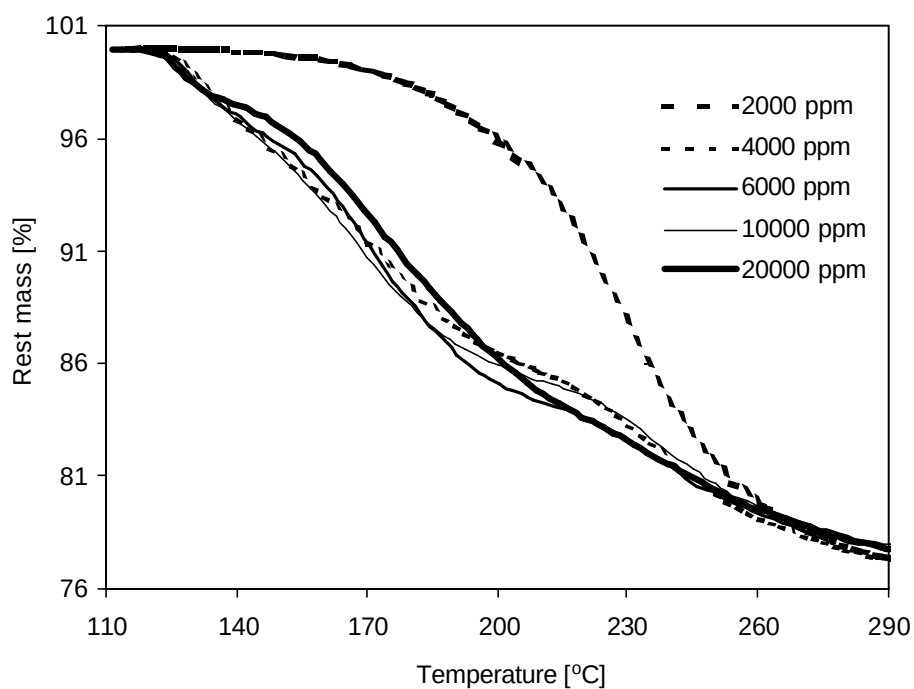


Figure 5.9. TG thermograms of BHET polycondensation at 5 K min⁻¹ in presence of high concentration of HT. The kinks in the thermograms are due to solidification and remelting of reaction mixture.

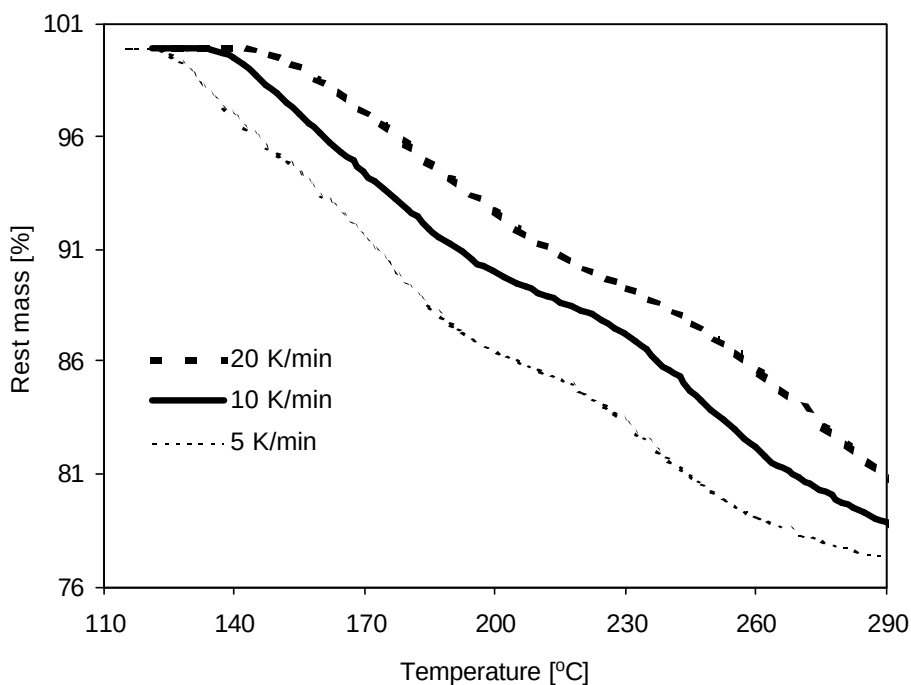


Figure 5.10. TG thermograms of BHET polycondensation at 5, 10 and 20 K min⁻¹ in presence of 4000 ppm of HT. The kinks in the thermograms are due to solidification and remelting of reaction mixture.

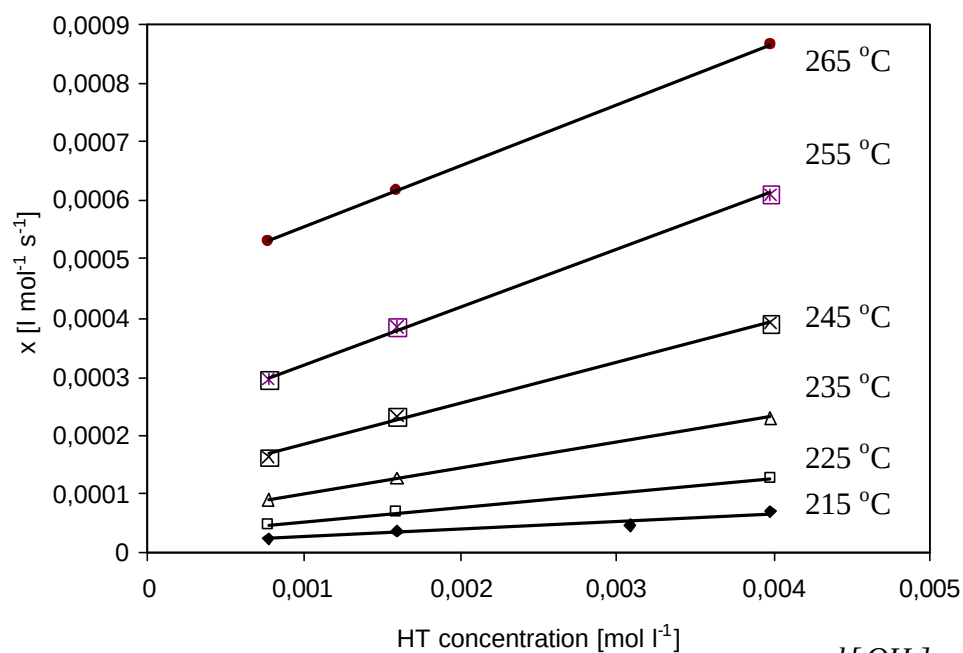


Figure 5.11. Plot of the first term of equation 5.22 (x is $-\frac{d[OH]}{2[OH]^2 dt}$) versus HT concentration at different temperatures.

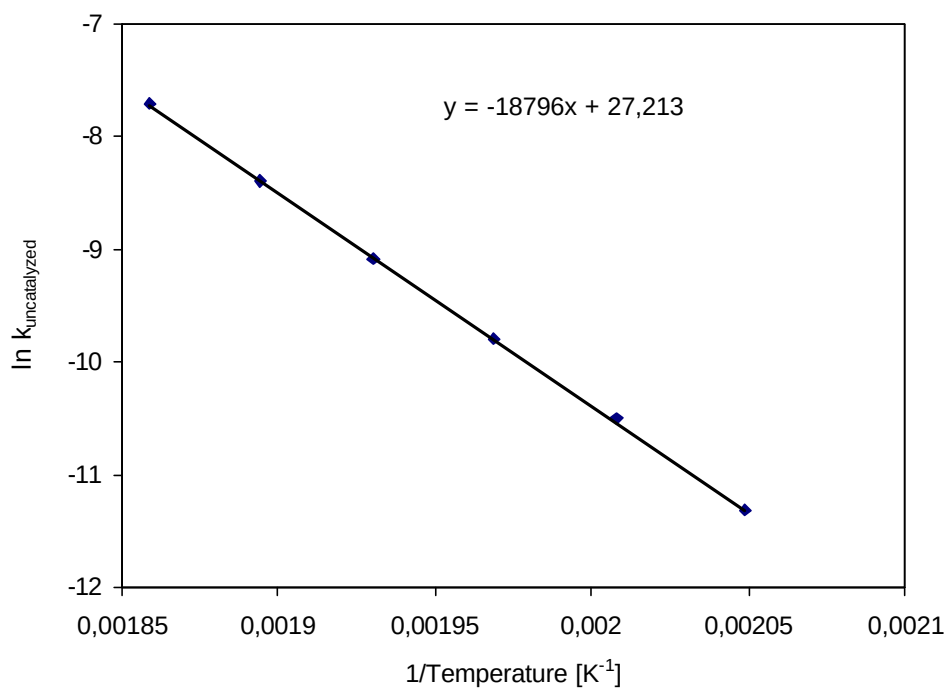


Figure 5.12. Plot of $\ln k_{uncatalyzed}$ versus $1/T$. $k_{uncatalyzed}$ in $[l mol^{-1} s^{-1}]$.

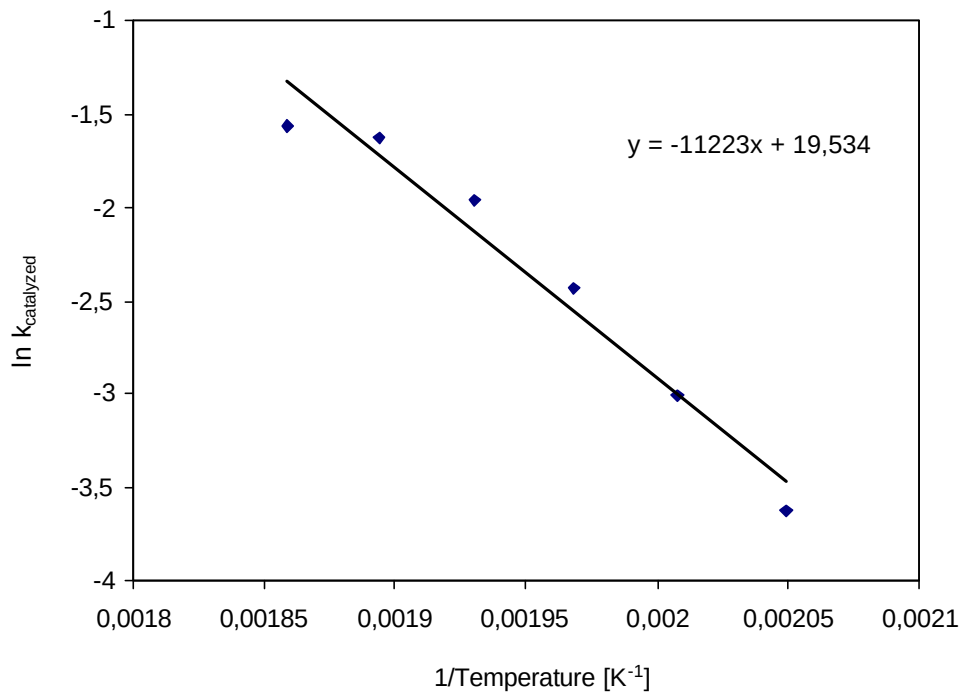


Figure 5.13. Plot of $\ln k_{\text{catalyzed}}$ versus $1/T$. $k_{\text{catalyzed}}$ in $[\text{l}^2 \text{mol}^{-2} \text{s}^{-1}]$

Where N is Avogadro number, h is Planck constant and $K^\ddagger$ is the equilibrium constant between transition state and reactants.

From thermodynamics:

$$DG^\ddagger = -R T \ln K^\ddagger = DH^\ddagger - T DS^\ddagger \quad 5.24$$

Where $\Delta G^\ddagger$ is the standard molar free energy of activation, $\Delta H^\ddagger$ is the molar enthalpy of activation and $\Delta S^\ddagger$ is the molar entropy of activation. From equation 5.24 the following relation is obtained:

$$\ln K^\ddagger = -\frac{DH^\ddagger - T DS^\ddagger}{R T} \quad 5.25$$

Which leads to:

$$K^\ddagger = \exp\left(\frac{-DH^\ddagger}{R T}\right) \exp\left(\frac{DS^\ddagger}{R}\right) \quad 5.26$$

By substitution of 5.26 in 5.23 the following equation for k is obtained:

$$k = \frac{R T}{N h} \exp\left(\frac{-DH^\ddagger}{R T}\right) \exp\left(\frac{DS^\ddagger}{R}\right) \quad 5.27$$

Equation 5.27 can be rewritten as:

$$\frac{k}{T} = \frac{R}{N h} \exp\left(\frac{-DH^\ddagger}{R T}\right) \exp\left(\frac{DS^\ddagger}{R}\right) \quad 5.28$$

Which gives:

$$\ln \frac{k}{T} = \ln \frac{R}{N h} + \frac{DS^\ddagger}{R} - \frac{DH^\ddagger}{R T} \quad 5.29$$

By plotting $\ln \frac{k}{T}$ versus $\frac{1}{T}$ the slope will be $-\frac{DH^\ddagger}{R}$ while the intercept will be $\ln \frac{R}{N h} + \frac{DS^\ddagger}{R}$.

Therefore,

$$DS^\ddagger = R \left(\text{intercept} - \ln \frac{R}{N h} \right) \quad 5.30$$

Figure 5.13 shows the plot $\ln \frac{k_{\text{catalyzed}}}{T}$ versus $\frac{1}{T}$. From the slope and the intercept, the following activation parameters are obtained for HT catalyzed polycondensation of BHET:

$$DS^\ddagger = -102 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } DH^\ddagger = 88 \text{ kJ mol}^{-1}.$$

At polycondensation temperature of 285 °C $\frac{DS^\ddagger}{R}$ is -12.2 and $-\frac{DH^\ddagger}{R T}$ is -19.2, which

indicates that the probability of transition state formation is not as important as that of the overcoming of the energy barrier. The relatively low activation entropy indicates also catalysis at surface, which supports the conclusion that HT is acting as a heterogeneous catalyst.

3.3. Interaction of hydroxyl- and ester group with hydrotalcite

The IR absorption spectra of BHET, HT, a 50/50 wt % mixture of both and the product of the polycondensation this mixture for 1 min at 280 °C are represented in figure 5.14. HT has absorption bands in the range 1300-1450 cm⁻¹ that correspond to carbonate. BHET has several absorption bands in the range 1067-1262 cm⁻¹ due to its C–O vibration, a doublet at

1710-1717 cm^{-1} due to carbonyl stretching and various bands between 1365-1497 cm^{-1} that corresponds to benzene. After heating the BHET/HT mixture for 1 min at 280 $^{\circ}\text{C}$, the absorption spectrum changed strongly where the shape and position of the C–O and the carbonyl vibration bands were strongly shifted. A new broad band appeared in the range 1475-1650 cm^{-1} and was interpreted as due to strongly restricted carbonyl stretching. Probably, this is caused by strong hydrogen bonding to HT. The carbonate bands disappeared upon polycondensation and most likely alkoxides replaced them as counter balancing anions.

IR spectroscopy clearly indicated that all the oxygen-containing functionalities of BHET and its oligomers strongly interact with HT. The carbonates removal is a fast reaction and occurs at the beginning of the polycondensation.

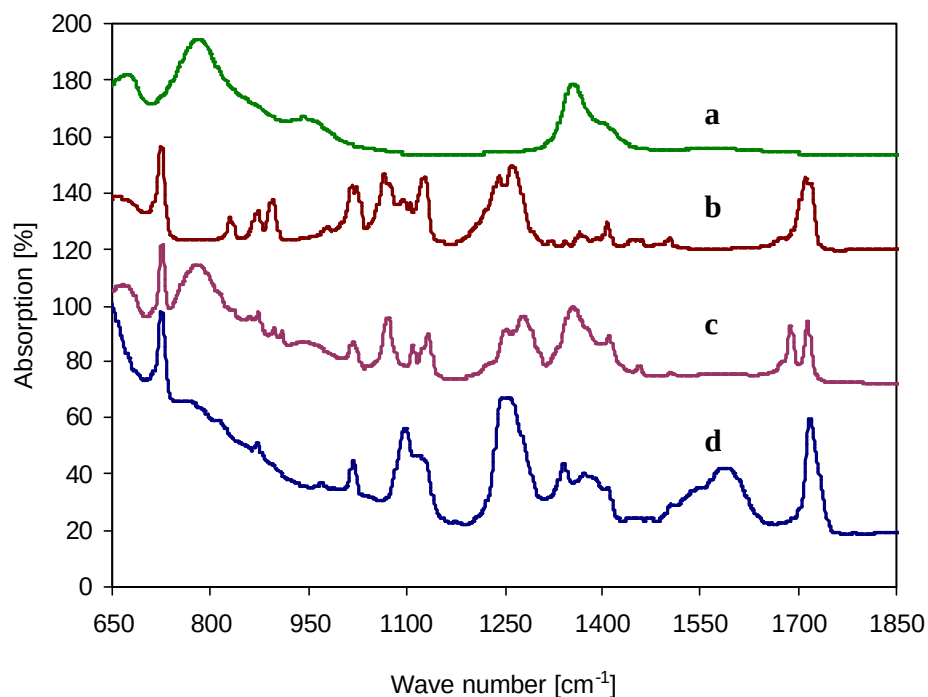


Figure 5.14. IR spectra of HT (a), BHET (b), a 50/50 wt % mixture of both (c) and the product of polycondensation of this mixture for 1 min at 280 $^{\circ}\text{C}$ (d).

3.4. X-Ray diffraction

Figure 5.15 shows the x-ray diffraction patterns of HT and that of the milled product of polycondensation of 1: 2 weight ratio of BHET/HT at 280 $^{\circ}\text{C}$ for 5 and 60 min. In HT, the 003 diffraction peak that gives the distance between the layers, occurs at an angle that corresponds to a distance of 0.76 nm. After polycondensation of 2:1 weight ratio of

BHET/HT at 280 °C for 5 min, the 003 diffraction peak appeared at a distance of 1.41 nm. The same results were obtained after polycondensation for 60 min.

The increase in the distance between the HT layers is probably due to intercalation of BHET. If the thickness of HT layer is considered (0.48 nm) [5] then the intercalated molecule has a size of 0.93 nm. This value is very close to that of terephthalate [6]. Hence, this means that BHET is intercalated not in extended form but in the form shown in scheme 5.1. This form ensures that all the polar groups are in close vicinity to the hydroxyl groups of the layers, and at the same time, ensures that the hydrophobic benzene ring is away from the layers. This interpretation is supported by the strong shift in the carbonyl IR absorption band after polycondensation with HT.

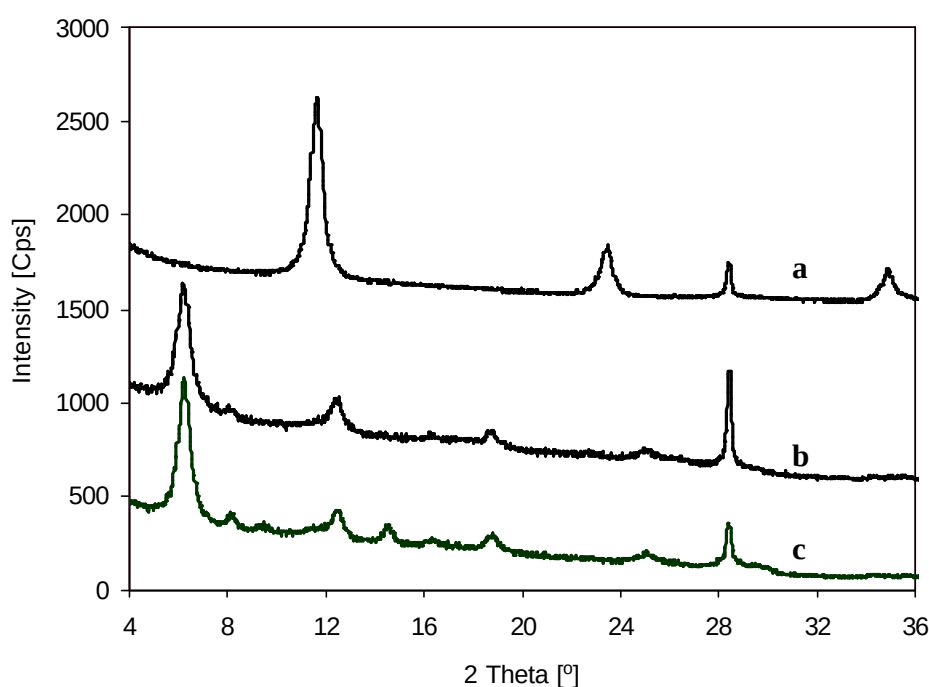


Figure 5.15. X-ray diffraction patterns of HT (a) and the milled product of polycondensation of 1: 2 weight ratio of HT/BHET at 280 °C for 5 (b) and 60 min (c).

3.5. Mechanism of hydrotalcite catalyzed polycondensation

In the previous chapter, it was shown that the hydroxide groups of HT are necessary for its catalytic activity. The catalytic activity was also dependent on the nucleophilicity of the interlayer anions. As was shown by IR and x-ray, the carbonate anions do not exist during polycondensation as they most probably react at the beginning of the reaction with alcoholic groups present in the reaction medium and leads to the formation of alkoxides.

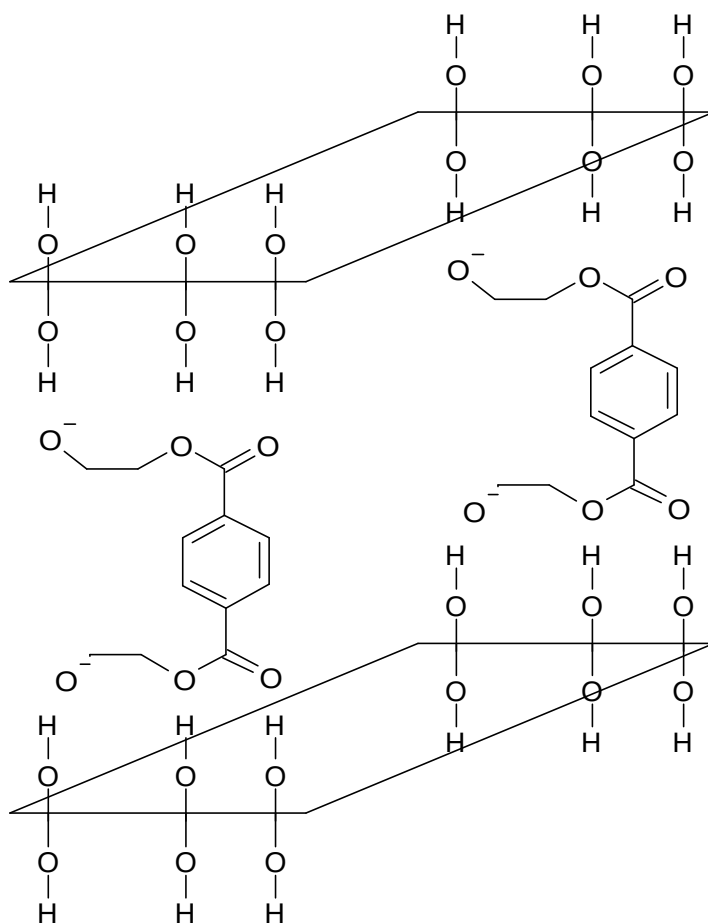
Based on these investigations and kinetic studies, a mechanism for HT catalyzed BHET polycondensation was proposed consisting of the following steps:

Step 1: Activation of HT through the reaction of its carbonates anions with the hydroxyl end groups of the reactants forming alkoxides groups and releasing carbon dioxide and water (scheme 5.2). This is a very fast process as 1 min of polycondensation at 280 °C was enough to remove all the carbonates anions.

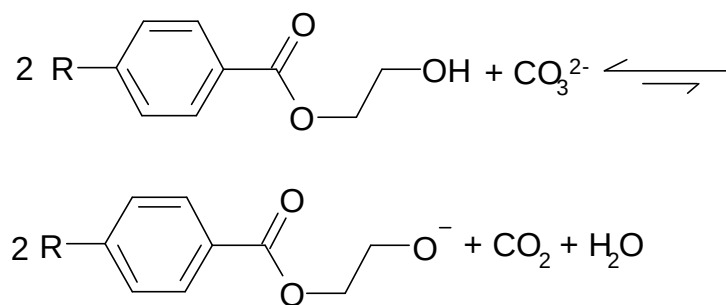
Step 2: Complexation of an ester group through its oxygen functionalities to two hydroxide groups adjacent to the alkoxide group by hydrogen bonding forming carbonate like intermediate (scheme 5.3).

Step 3: The alkoxide group reacts with the ester group beside it forming a new ester bond and a glycoxide species (scheme 5.4).

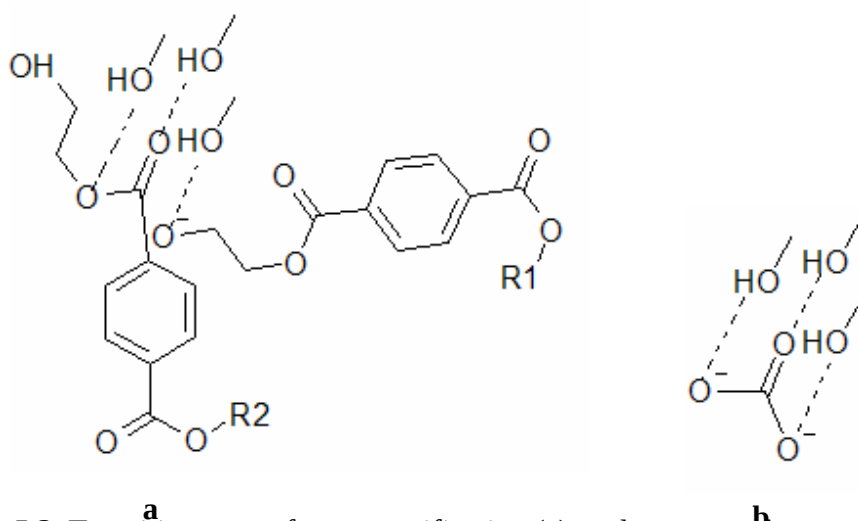
Step 4: Proton exchange between a new hydroxyl end group and the glycoxide group regenerating the active species and releasing EG (scheme 5.5).



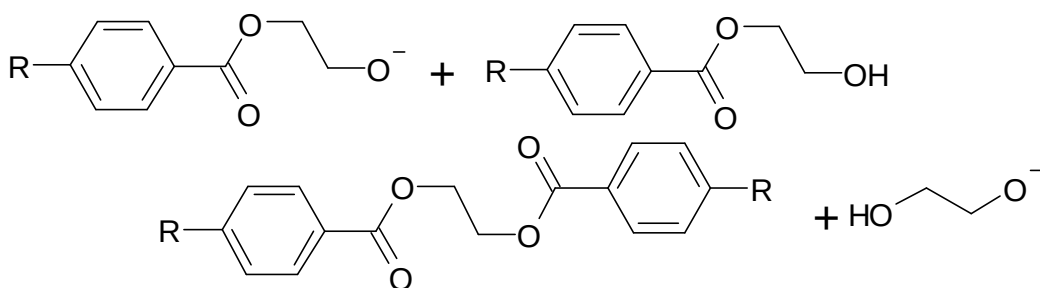
Scheme 5.1. Intercalation of BHET in the gallery of HT layers in a twisted alkoxide form.



Scheme 5.2. Catalyst activation and generation of active terminal groups in the form of alkoxide group.

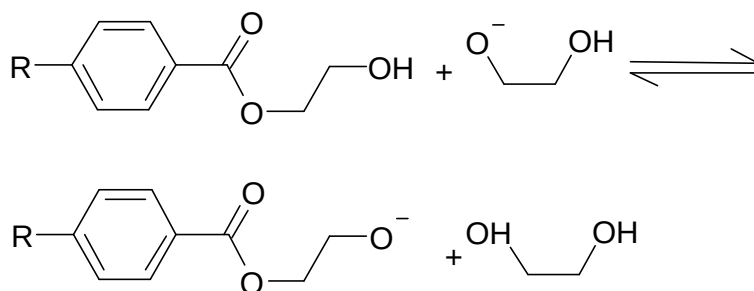


Scheme 5.3. Transition state of transesterification (a) analogous to carbonate fixed in the interlayer gallery by hydrogen bonds (b).



Scheme 5.4. Chain prolongation via reaction of an alkoxide group with terminal ester and generation of a glycoxide group.

The second order overall kinetics in hydroxyl end groups limits rate determining step to step 3: chain prolongation through the break of the ester group. This is expected since the other steps (steps 2 and 4) are very fast: Complexation of an ester group to HT by hydrogen bonding and proton transfer between alcohol and alkoxide group.



Scheme 5.5. Regeneration of active alkoxides groups by a proton transfer to a glycolate group.

4. Conclusion

The hydroxides groups of HT probably acts as a template for the transition state of the transesterification reaction, which has carbonate analogous structure. Three adjacent hydroxides groups fix the ester group of a chain and the alkoxide end group of another chain in a close proximity. The alkoxide group attacks the ester group generating a new ester bond and a glycolate anion. Kinetic studies indicated that this step is rate determining one.

The principle of equal reactivity is valid for PET synthesis starting from the monomer and the reaction can be modelled as a reaction between hydroxyl end groups. The overall activation energy of polycondensation decreases with catalyst concentration, which indicates that the uncatalyzed reaction path takes place up to relatively high catalyst concentration. In case of homogenous catalyst like antimony, much lower catalyst concentration is needed for the reaction to occur solely via catalyzed path. This is due to the better distribution of the catalytic sites in the reaction melt.

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Chapter 6: Mechanistic Investigation of Antimony Catalyzed Polyethylene Terephthalate Synthesis in Melt

Abstract

Chemical aspects of polyethylene terephthalate synthesis via antimony catalyzed polycondensation of hydroxyl end groups were studied on model molecules as well as on chemical species present during industrial process. These studies include spectroscopic investigation, electroconductometry and thermal analysis. It was found that antimony does not interact with carbonyl oxygen of ester groups but with their alcoholic oxygen. Moreover, activity of antimony was observed to increase with consumption of hydroxyl end groups. Kinetic studies showed that the main barrier for polycondensation activation is of entropic nature. Antimony was shown to stabilize hydroxyl end groups against thermal degradation. Based on this work a polycondensation mechanism was proposed in which activation occurs on one hand by formation of a chelate ligand on antimony composed of the hydroxyl end group and the alcoholic oxygen of the ester end group. On the other hand, attacking hydroxyl end group is complexed to the same antimony rendering it more nucleophilic, and at the same time bringing the reactant together in a favorable geometry. Increase of antimony activity with hydroxyl end groups consumption may be due to competition of these groups with the ester alcoholic oxygens on complexation with antimony, which hinders chelate structure formation.

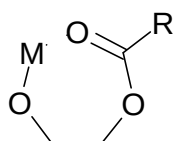
1. Introduction

Despite the importance of catalysis to PET manufacture, its mechanism is poorly understood. This is not due to a lack in experimental investigations since more than 150 articles have been published on this subject since 1950 [1]. The reason lies in the nature of this reaction (reversibility and parallel reactions) and in the production conditions (high temperature causing many side reactions, changing pressure from 5 bar into 0.3 mbar, high viscosity, changing catalyst concentration by precipitation, deactivation or volatilization). One more reason is the complexity of the spectra of the reaction medium, which is composed of different species (different oligomers and functional groups). These complications are behind the big differences, and in many cases, the contradiction in the published kinetic data.

Several attempts were done to clarify the polycondensation mechanism. All the published papers agree that polycondensation proceeds by nucleophilic attack of hydroxyl oxygen of one end group on the carbonyl carbon of another end. Different mechanisms have been proposed for activation of this reaction, which can be classified into two categories: The catalyst activates the attacking hydroxyl oxygen by forming metal alkoxides or activates the carbonyl carbon by complexation with carbonyl- or ester oxygen. Zimmermann [2] proposed a 7-member ring transition state formed by chelating of the metal with the hydroxyl end group and the carbonyl-oxygen of the same chain end (scheme 6.1). This ring is similar to that formed by intramolecular hydrogen bonding. According to this mechanism, polycondensation then proceeds by attack of hydroxyl end group of a second chain on the activated carbonyl-carbon. He explained the low activity of Sb at polycondensation beginning as to be caused by hindering of this chelate formation due to high concentration of hydroxyl end groups that compete with the carbonyl oxygen.

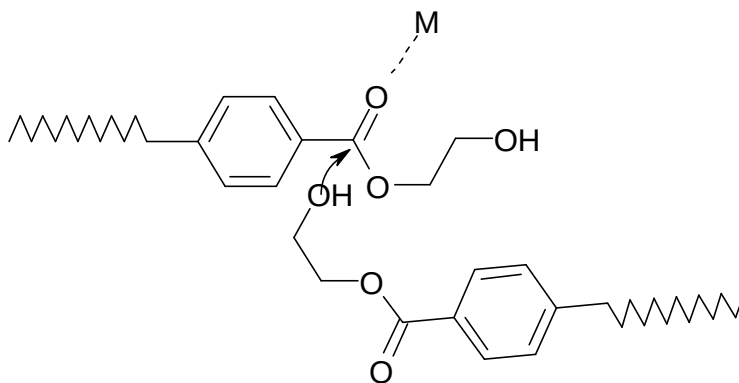
According to Tomita, Wolf, Pilati and Chung [3-9] activation takes place by simple complexation between metal catalyst and carbonyl oxygen (scheme 6.2). Tomita organized activity of different metal catalysts in a bell-shape curve based on stability of a complex formed between different metals and the carbonyl group of the dibenzoyl methane. Highest activity is observed when the stability of this complex is optimum (top of the bell). Kamatani et al [10] proposed an octahedral complex analogous to that proposed by Zimmermann. They proposed that the primary step in this mechanism involves coordination of the metal ion to the ester carbonyl group, which lowers the electron density on the carbonyl carbon atom and facilitates nucleophilic attack of an activated second

chain end group on it. Maerov [11] proposed a mechanism for Sb catalyzed polycondensation that does not involve metal-carbonyl coordination (scheme 6.3). A penta-coordinate metal centre is formed from the metal and the two glycol oxygens of one chain end coordinated to it. Rearrangement within the coordination sphere then results in the formation of new ester linkage, which couples the two growing polymer chains, and a new metal glycolate species. This mechanism was supported by Parshall and Ittel [12] and Santacesaria [13], and for titanium catalyst by Weingart [14].



Scheme 6.1. 7-member ring chelate structure of activated complex for chain growth in polycondensation reaction proposed by Zimmermann [2].

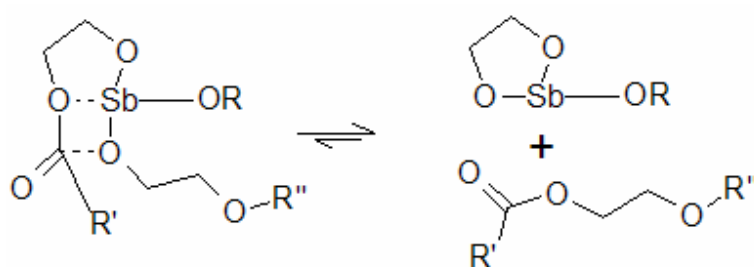
Rafler et al proposed activation by formation of a linear complex involving a metal and three different chains [15]. In a later paper [16] he proposed activation of carbonyl with a proton from alkoxo acids formed by excess reaction of hydroxyl end groups with metal (scheme 6.4).



Scheme 6.2. Structure of activated complex for Lewis acid mechanism of chain growth in polycondensation reaction.

Otton et al [17,18] proposed different mechanisms for different metals. In case of alkali metals they proposed activation of attacking nucleophile by metal via glycoxide formation. Divalent Lewis acid catalysts like zinc, manganese and cobalt form complex with carbonyl oxygen. For Sb and titanium they proposed a mechanism based on alkoxide ligand exchange.

IR spectroscopy was used intensively in investigation of polycondensation mechanism on model molecules. Application of model molecules enables the overcome of the challenges of medium viscosity and complexity of polymer spectra. Antimony trichloride, which is a strong Lewis acid, caused strong bathochromic shifts in IR carbonyl absorption band of benzoate ($15\text{ cm}^{-1} < \nu < 130\text{ cm}^{-1}$) in benzoate-antimony trichloride mixture [7]. Reason of these shifts was interpreted as due to partial complexation between Sb and ester carbonyl oxygen. Pilati [9] observed by IR measurements adduct formation between different metal catalysts and carbonyl of benzoic acid but could not see this adduct between the same metals and model molecules representing functional groups of polybutylene terephthalate (PBT). More adequate model system for spectroscopic investigation was used by Rafler [15,16]. He measured IR spectra of equimolar ethylene glycol monobenzoate (EGMB) and metal alkoxide mixtures with and without methyl tetrachloride as a solvent. No shifts in the carbonyl band were observed even by changing reagents concentrations. Otton et al investigated mixtures of butyl benzoate and titanium butoxide. They concluded from the small bathochromic shift of 4 cm^{-1} in the carbonyl band upon catalyst addition to be due to complexation of the metal with ester alcoholic oxygen and not with ester carbonyl oxygen. Kelly [19] recently used IR spectroscopy for investigation of PET polycondensation with model molecules. Different metal alkoxides were reacted in a 1:1 mixture at room temperature in a solvent with EGMB and no significant shifts in carbonyl absorption band were observed in all isolated Sb compounds compared to that of EGMB.



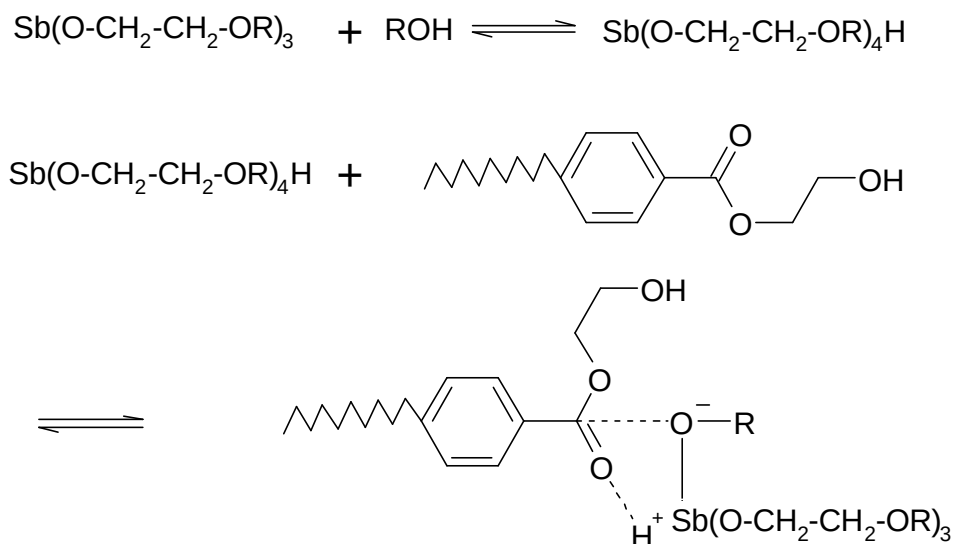
Scheme 6.3. Maerov mechanism for Sb catalyzed polycondensation [11].

2. Experimental

2.1. Preparation of antimony glycolate

Antimony glycolate $[\text{Sb}(\text{EG})_2]$ was prepared by the boiling of antimony triacetate in EG for 5 h under nitrogen atmosphere. To a 100 ml reaction flask equipped with magnetic stirrer and reflux condenser 2 g of antimony triacetate and 80 g of EG were added. After

that the reaction mixture was cooled down to 70 °C and EG was removed under high vacuum.



Scheme 6.4. Mechanism for Sb catalyzed polycondensation proposed by Rafler.

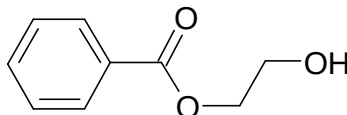
2.2. Preparation of ethylene glycol monobenzoate

EGMB (scheme 6.5) was prepared from chlorohydrin and sodium benzoate. In a 2 l 3-neck flask, 0.69 mol of sodium benzoate, 0.69 mol of chlorohydrin and 1.5 l of dimethyl formamide (DMF) were placed. This mixture was stirred at a rotation speed of 380 rpm for 5 h at 145 °C. The reaction mixture was then filtered under vacuum to get rid of produced sodium chloride. Distillation of DMF at 15 mbar and 40 °C yielded a product with 98.4 mol % monoester, 1 mol % benzoic acid and 0.3 mol % DMF as obtained by analysis in gas chromatography coupled to mass spectrometer (GC-MS). The product was then extracted with 500 ml diethyl ether together with 100 ml of 0.5 mol % sodium hydroxide solution. The extraction was done twice with diethyl ether and the organic layer was back-washed twice with 100 ml of 5 mol % NaHCO₃ solution and twice with 100 ml of distilled water. The washed organic layer was dried on sodium sulphate. The ether was removed in a rotary evaporator where the distillation was performed under reduced pressure. GC-MS analysis showed that the content of DMF and benzoic acid in the pure product was negligible.

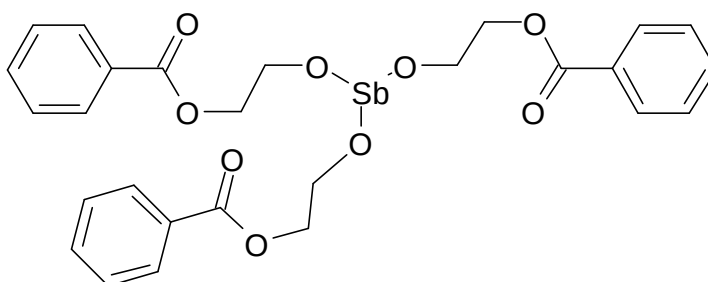
2.3. Preparation of antimony glycooxide monobenzoate complex $[Sb(EGMB)_3]$

1:3 mole ratio of antimony triacetate and EGMB were stirred for 3 days in cyclopentanone at 40 °C under dry nitrogen atmosphere. The product $[\text{Sb}(\text{EGMB})_3]$ was

obtained after cooling and filtering through a Buchner funnel followed by drying in a high vacuum oven overnight at room temperature (scheme 6.6).



Scheme 6.5. Ethylene glycol monobenzoate (EGMB).



Scheme 6.6. Antimony glycoxide monobenzoate complex $[Sb(EGMB)_3]$.

2.4. Preparation of oligomers

BHET was condensed under vacuum at 220 °C for 3 h in a 250 ml round bottom flask connected to an adapter equipped with a thermometer, a condenser and a stirrer. The product was stirred in boiling water 3 times to remove completely residual monomer. Dimer and trimer were separated by recrystallization in di-chloro ethane and tetra-chloro ethane respectively. Hydroxyl end group concentration in dimer and trimer fractions were determined by high pressure liquid chromatography (HPLC). Different oligomers with average degree of polycondensation between 5 and 7 were synthesized from different ratio of PTA to EG in a 2 l reactor from Juchheim at 270 °C and 3 bar. Hydroxyl end group concentration in oligomers was determined from viscometric measurements and titration with potassium hydroxide (KOH).

2.5. Sample characterization

IR investigations were done on attenuated total reflection/Fourier transform (ATR/FTIR) spectrometers (Spectrum One spectrometer from Perkin Elmer and ReactIR 1000 spectrometer from Mettler Toledo). Electroconductivity of Sb solutions in EG was measured by LF 538 conductometer from WTW.

2.6. Headspace analysis

500 mg of BHET/Sb mixtures containing from 200 ppm to 10000 ppm Sb were weighed into 22 ml glass vials. These vials were sealed by means of a teflon septum and a steel cap. After conditioning the vials for 240 min at 150°C, 500 µl of the headspace were injected into a GC-MS (HP GC 6890/HP MSD 5873) where separation and detection took place.

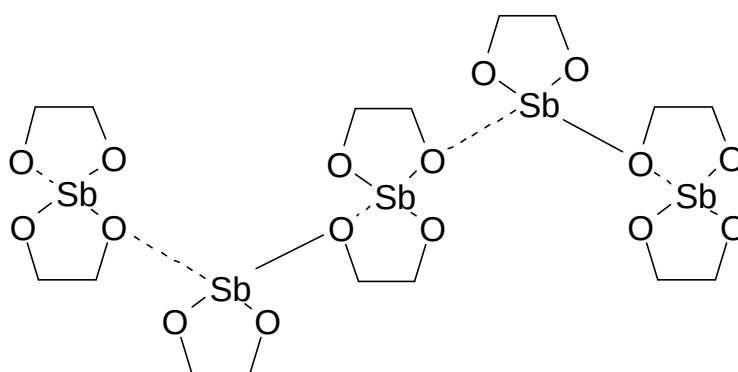
3. Results and Discussion

3.1. Hydroxyl- and ester group complexation with antimony catalyst

The IR absorption spectra of EG, Sb_2O_3 and that of $\text{Sb}(\text{EG})_2$ are presented in figure 6.1 and 6.2. Sb_2O_3 has two bands at 578 and 672 cm^{-1} that correspond to Sb—O vibration. EG has a doublet at 858 and 879 cm^{-1} and another one at 1030 and 1083 cm^{-1} that corresponds to C—O vibration. The C—H vibration of EG has a doublet at 2867 and 2925 cm^{-1} while the O—H vibration occurs as a wide band at 3290 cm^{-1} . The shape and the position of all the absorption bands of EG were strongly affected by the presence of Sb. In $\text{Sb}(\text{EG})_2$, the C—O absorption bands occurred as a strong peak at 883 cm^{-1} with two shoulders at 896 and 909 cm^{-1} , and a triplet at 1021, 1031 and 1047 cm^{-1} . The multiple bands at 588 and 707 cm^{-1} are due to Sb—O stretching and Sb—O—C wagging respectively. The bands between 707 and 725 cm^{-1} in the spectrum of $\text{Sb}(\text{EG})_2$ are not present in the spectra of EG or Sb_2O_3 . These values, which are larger than that of Sb—O absorption bands, perhaps correspond to absorption bands of partial bond formed from interaction between Sb and O that does not belong to the complexation sphere of this Sb. This explanation is supported by X-ray structure elucidation of di-antimony tri-glycoxide done by Parkin et al [20] (scheme 6.7). They found that the length of complete bond (Sb—O) to be 2.046 Å while the length of partial bond (Sb.....O) is 2.474 Å. This means that IR absorption band of Sb.....O should be at about 700 cm^{-1} compared to that of Sb—O at 578 cm^{-1} . This indicates that EG forms a 5-member chelate ring with Sb. This proposal is supported by the shift of the C—H band due to the strain and movement restriction.

The spectra of Sb_2O_3 , EGMB and $\text{Sb}(\text{EGMB})_3$ are shown in figure 6.3-6. The terminal C—O stretching band of EGMB appeared as a doublet at 1094 and 1117 cm^{-1} and that of the ester C—O stretching occurred as a singlet peak at 1267 cm^{-1} . The C=O absorption band occurred as a doublet at 1700 and 1714 cm^{-1} which corresponds to hydrogen bonded and free vibration respectively. The C—H bands occurred around 2950 cm^{-1} while that of the O—H occurred as a very broad band around 3400 cm^{-1} .

The O—H stretching band of EGMB disappeared when reacted with Sb, which means that an alkoxide species was formed. Also, the C—H bands were strongly affected by the presence of Sb. The absorption band of terminal C—O of Sb(EGMB)₃ was clearly different than that of EGMB ensuring strong interaction with Sb. It appeared as a doublet at 1096 and 1107 cm⁻¹. The ester C—O stretching band was broadened and shifted to smaller wave number, which indicates complexation between Sb and the ester alcoholic oxygen. The C=O absorption band position was unchanged upon complexation with Sb and appeared as strong band at 1715 cm⁻¹ and a small shoulder at 1676 cm⁻¹. O—C=O bending of EGMB has a strong absorption band at 707 cm⁻¹. In Sb(EGMB)₃, this band was overlaid by that of Sb—O.



Scheme 6.7. Structure of [Sb₂(-O-CH₂-CH₂O-)₃] determined by x-ray studies [20].

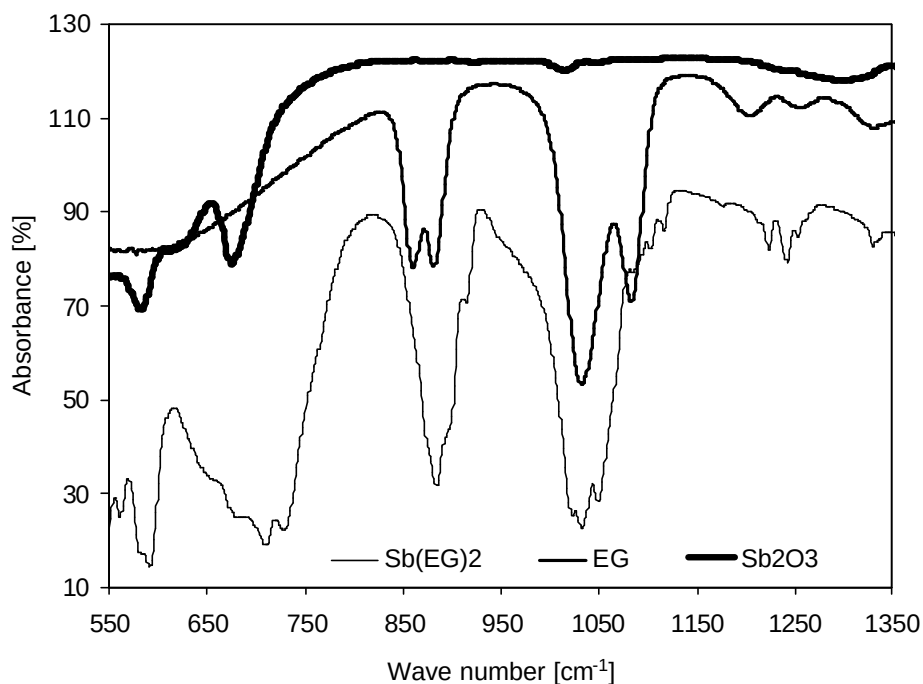


Figure 6.1. IR spectra of Sb₂O₃, EG and Sb(EG)₂ between 550 and 1350 cm⁻¹.

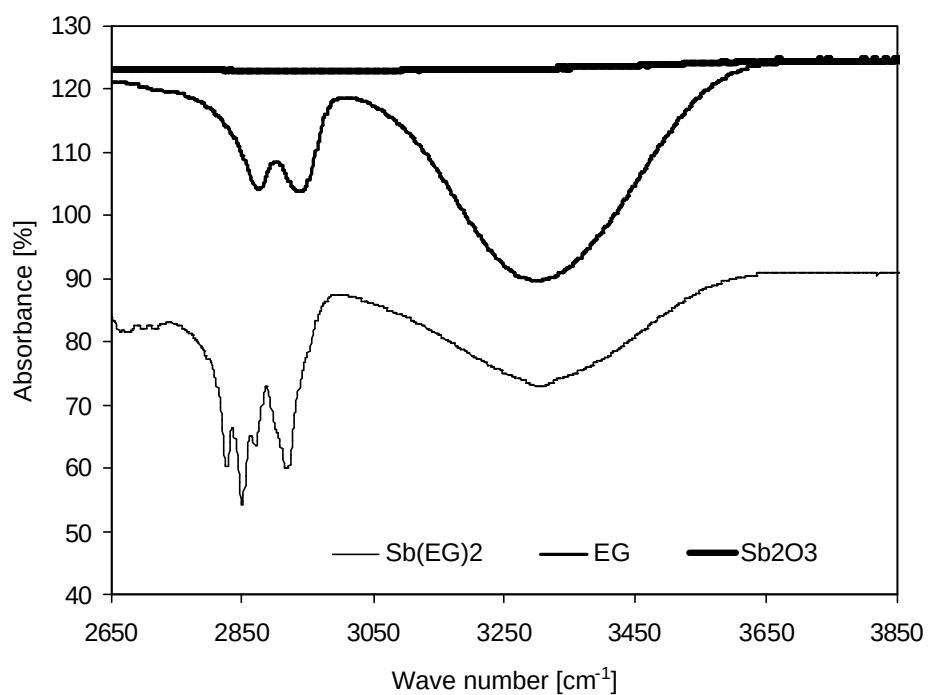


Figure 6.2. IR spectra of Sb_2O_3 , EG and $\text{Sb}(\text{EG})_2$ between 2650 and 3850 cm^{-1} .

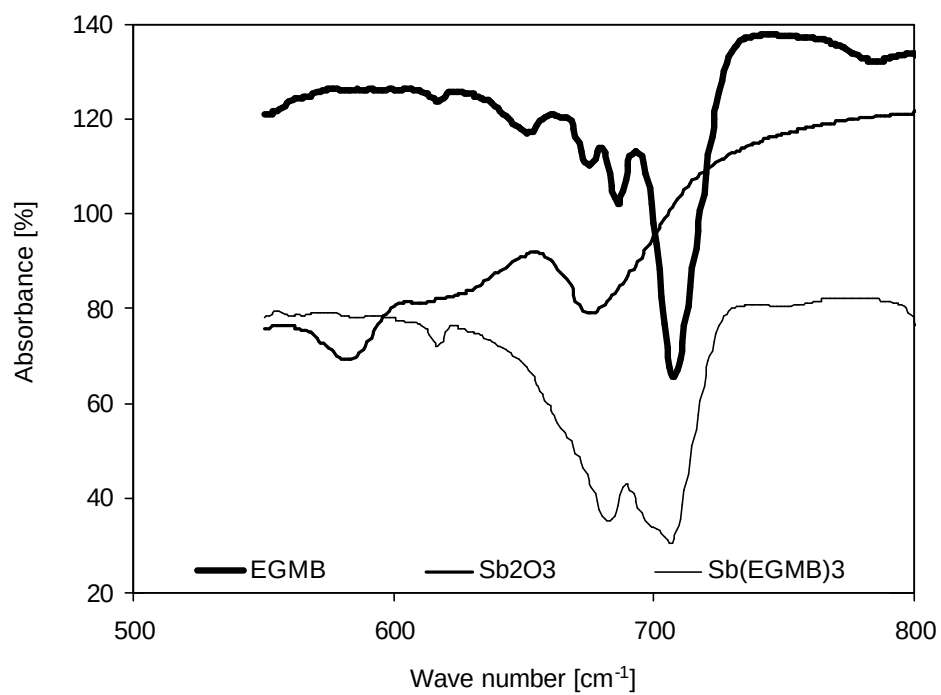


Figure 6.3. IR spectra of Sb_2O_3 , EGMB and $\text{Sb}(\text{EGMB})_3$ between 500 and 800 cm^{-1} .

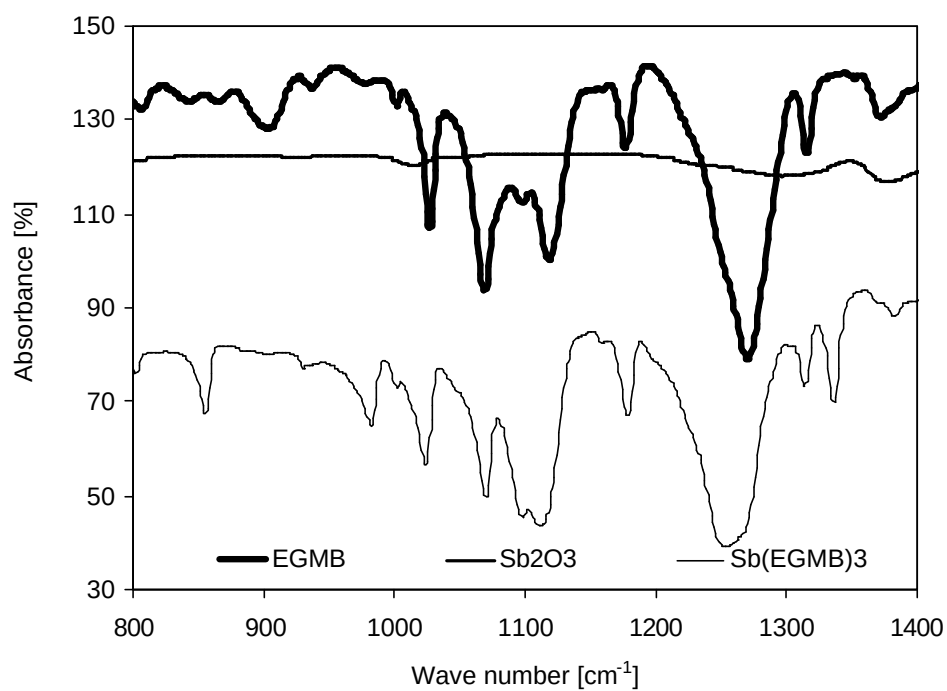


Figure 6.4. IR spectra of Sb_2O_3 , EGMB and $\text{Sb}(\text{EGMB})_3$ between 800 and 1400 cm^{-1} .

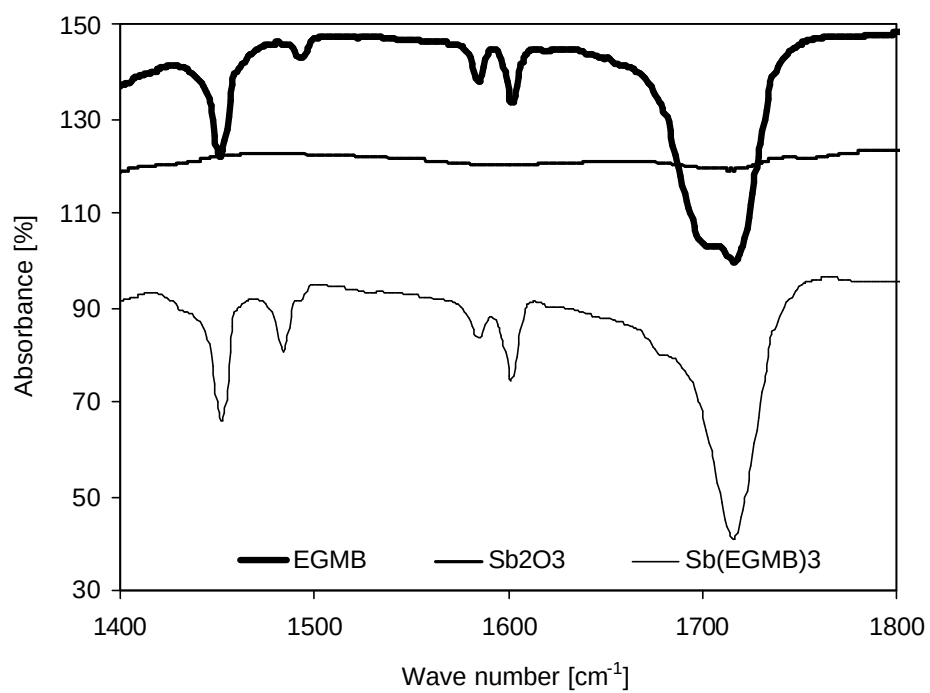


Figure 6.5. IR spectra of Sb_2O_3 , EGMB and $\text{Sb}(\text{EGMB})_3$ between 1400 and 1800 cm^{-1} .

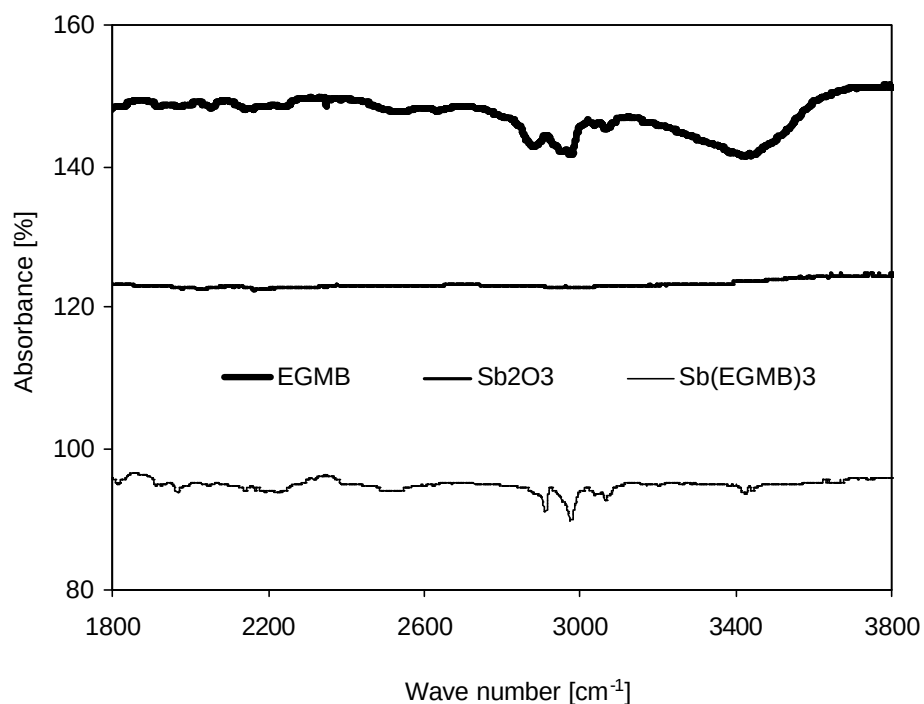


Figure 6.6. IR spectra of Sb_2O_3 , EGMB and $\text{Sb}(\text{EGMB})_3$ between 1800 and 3800 cm^{-1} .

IR spectroscopy shows that Sb interacts with ester alcoholic oxygen. Any signs of Sb-carbonyl interactions were not observed. Also, it was shown that $\text{Sb}(\text{EG})_2$ and $\text{Sb}(\text{EGMB})_3$ form five member chelate rings consisting of Sb and $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$.

3.2. Solvation of antimony complexes by hydroxyl end groups

Figure 6.7 shows the O-H stretching IR absorption band of different BHET/Sb mixtures with Sb concentration of 0, 1000 and 4000 ppm. For pure BHET only one band was observed at 3440 cm^{-1} , which corresponds to hydrogen bonded hydroxyl group. After addition of 1000 ppm of Sb a new band appeared at 3520 cm^{-1} while the intensity of the old band decreased. This new band is due to stretching of hydroxyl group not bonded by hydrogen bond to carbonyl oxygen. By increasing Sb content to 4000 ppm the new band became very strong while the old band appeared as a small shoulder. So, hydroxyl end groups available for hydrogen bonding decreased with increasing Sb concentration and only 4000 ppm of Sb was sufficient to prevent most of hydroxyl groups from making hydrogen bonds to carbonyls.

This means that Sb complex is probably solvated in a cage consisting of a big amount of hydroxyl end groups, as above estimated, making these hydroxyl groups non-available for

hydrogen bonding with carbonyl groups. Hydrogen bonding between hydroxyl end groups and carbonyl oxygen is intramolecular as dilution of the 1000 ppm BHET/Sb mixture in chloroform yielded the same intensity ratio of bonded and non-bonded hydroxyl adsorption bands.

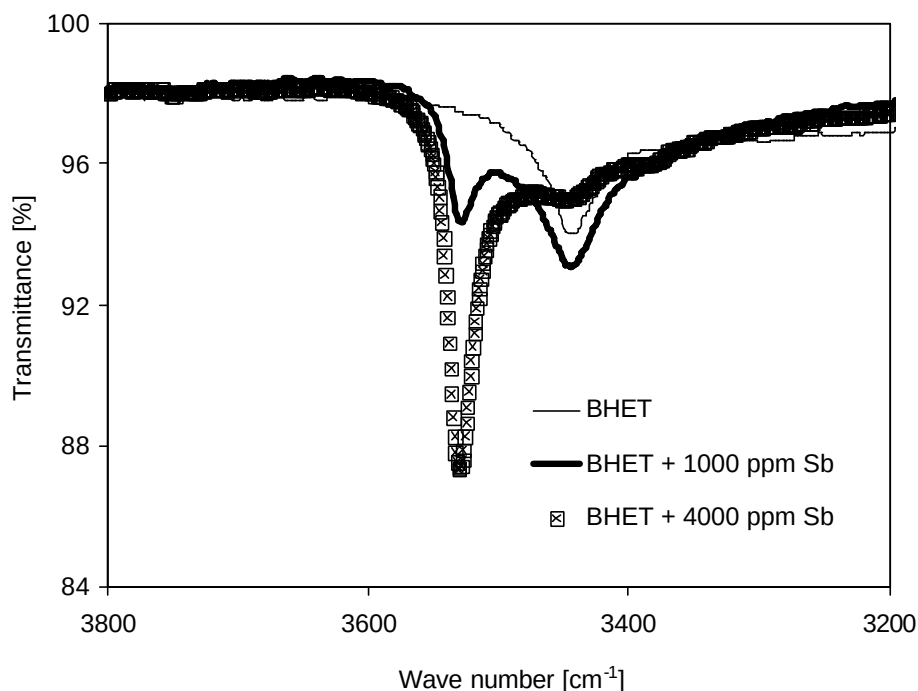


Figure 6.7. IR spectra of BHET and its mixtures with 1000 ppm and 4000 ppm Sb.

Another fact supporting this hypothesis comes from headspace analysis of different BHET/Sb mixtures, which were condensed isothermally at 150 °C for 4 h. EG is generated as condensate during polycondensation of BHET. However, side reactions are also present such as AA generation by a back-biting mechanism in which the hydroxyl end group interacts with the carbonyl next to it [21]. Figure 6.8 shows the content of EG and AA in the headspace. AA concentration decreases with increasing Sb concentration and reaches undetectable level at 4940 ppm Sb. At the same time, EG content increased due to higher conversion. This means that 4940 ppm of Sb was probably sufficient to prevent hydroxyl interaction with carbonyl at 150 °C.

3.3. Catalytic activity of hydrotalcite and antimony in polycondensation of BHET

Sb catalyzed polycondensation of BHET is slower than that catalyzed by HT. Activation energies of both reactions were determined and found to be $75 \pm 5 \text{ kJ mol}^{-1}$ for Sb catalyzed

polycondensation and $93 \pm 5 \text{ kJ mol}^{-1}$ for that catalyzed by HT. To interpret this result (Sb has lower activity and activation energy at the same time), reactants were changed from BHET with hydroxyl end groups concentration of 7.78 mol kg^{-1} to dimer and trimer fractions having hydroxyl end groups concentrations of 4.72 mol kg^{-1} and 2.52 mol kg^{-1} respectively. Relative activity of Sb to HT enhanced strongly with decreasing hydroxyl end groups concentration (figure 6.9). Another proof for enhancement of the rate of Sb catalyzed polycondensation with increasing consumption of hydroxyl end groups comes from the isothermal polycondensation at 280°C of oligomers with five and seven average degree of polycondensation, which corresponds to hydroxyl end groups concentration of 1.49 and 1.05 mol kg^{-1} respectively (Table 6.1). The activity of each catalyst is represented as the total mass loss in the form of evaporated EG after 30 min of polycondensation. At this condition Sb was more active than HT.

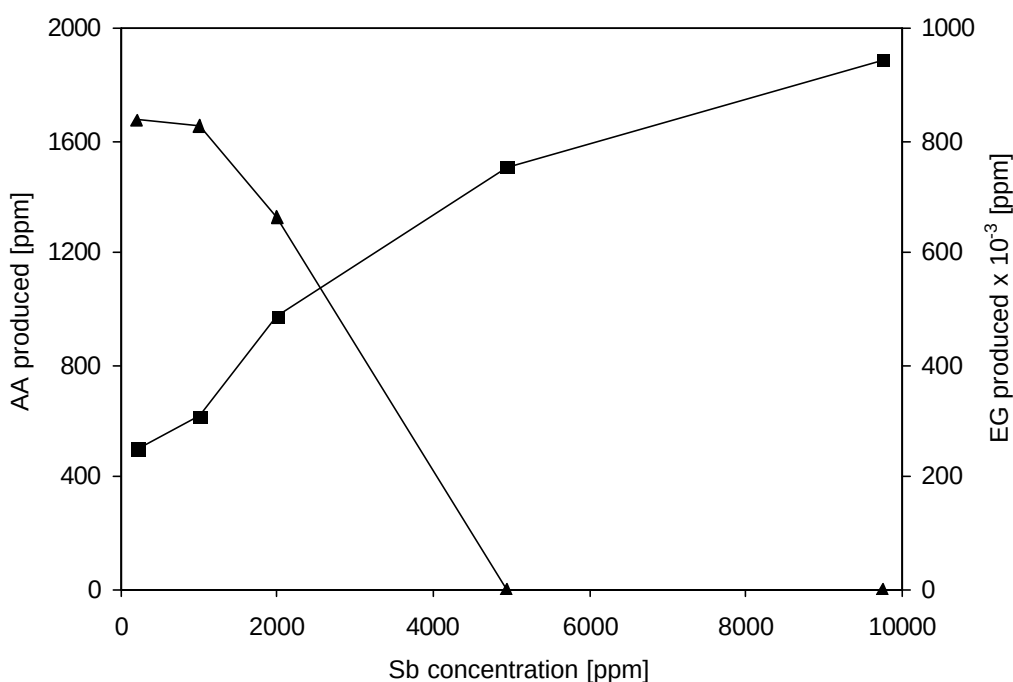


Figure 6.8. AA and EG concentration in headspace of different mixtures of BHET/Sb after polycondensation for 4 h at 150°C .

3.4. Activation Enthalpy and Entropy

The following activation parameters are obtained for Sb catalyzed polycondensation of BHET:

$$DS^\ddagger = -188 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } DH^\ddagger = 70 \text{ kJ mol}^{-1}.$$

At polycondensation temperature of 285 °C $-\frac{DS^\ddagger}{R}$ is 22.56 and $\frac{DH^\ddagger}{RT}$ is 15.03 which indicates that the probability of transition state formation is small and plays the major role in determining the reaction rate.

Table 6.1. Relative activity of Sb to HT in polycondensation of two different oligomers with different hydroxyl end group concentrations ([OH]) at 280 °C for 30 min represented by total mass loss percent as EG condensates.

Average degree of polycondensation	Mass loss/350 ppm HT [%]	Mass loss/350 ppm Sb [%]	[OH] [mol kg⁻¹]
5	3.4	4.6	1.49
7	2.4	3.5	1.05

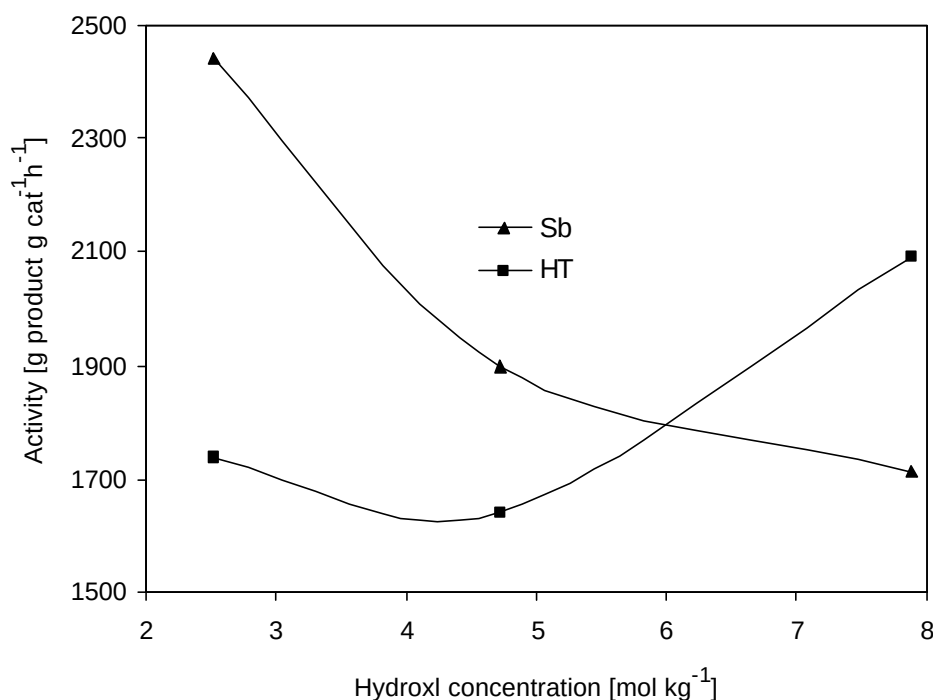


Figure 6.9. Relative activity of Sb and HT at different hydroxyl end groups concentration.

3.5. Electroconductivity of antimony solutions in ethylene glycol

Solutions of Sb in EG with concentration between 920 ppm and 2150 ppm were prepared. Electrical conductivity was measured at temperature between 20 °C and 80 °C and was found to increase with increasing temperature (figure 6.10), but decreased with increasing concentration. If Sb is forming ionic species such as alkoxo acids, the

conductivity should increase with increasing catalyst concentration, which excludes the hypothesis of mechanisms based on these intermediates. The decrease in conductivity with increasing concentration of Sb may be interpreted as aggregates formation between catalyst molecules [20].

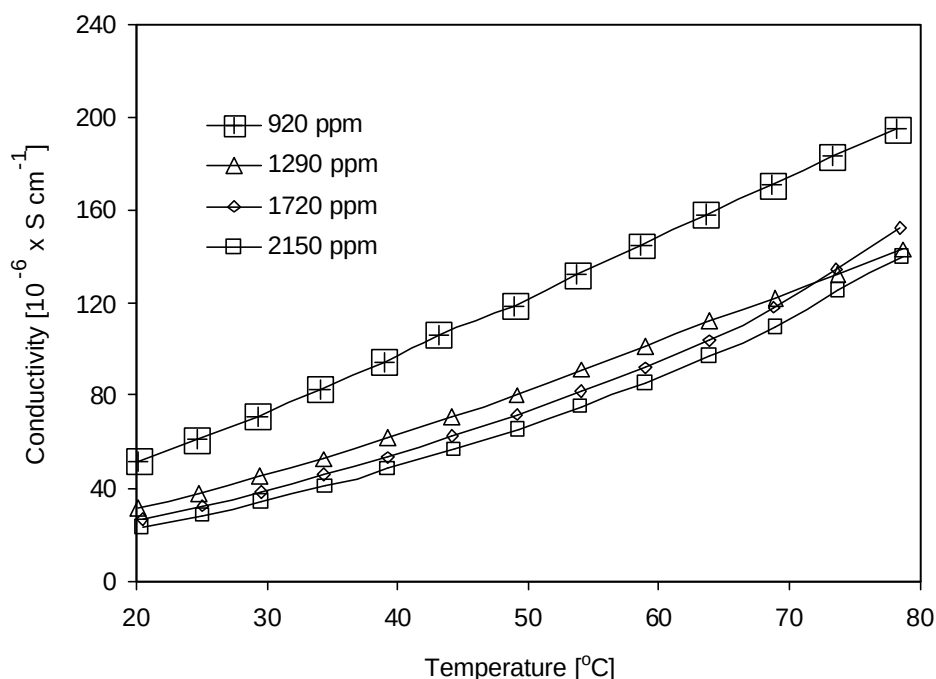


Figure 6.10. Electroconductivity as a function of temperature for solutions of Sb in EG with different concentrations.

3.6. Mechanism of antimony catalyzed polycondensation

Thermal degradation of PET occurs by acid catalyzed chain scission mechanism [21]. Zimmermann found that this mechanism is catalyzed via metal-carbonyl interaction. Since the carbonyl group acts as a Lewis base, the strength of this interaction depends on the Lewis acidity of the metal. One of the most important features of Sb is its low activity in thermal degradation. This is due to its free electron lone pair, which reduces its Lewis acidity (Sb^{III} is amphoteric while Sb^{V} is clearly acidic [23]) and therefore, its interaction with carbonyl oxygen. Supported by IR studies, studies on para-substituents by Santacesaria [13] and other published results [14,15,18], any complexation of Sb to ester carbonyl oxygen is excluded. On the other hand, the alcoholic oxygen of ester groups can form coordinative bond with Sb as was shown by IR studies of this paper where a molar ratio of hydroxyl end groups to Sb of 3:1 was used. In practice much lower concentration of

Sb is applied (about 8000:1 ratio of hydroxyl end groups to Sb at the beginning of polycondensation, and decreases with conversion), so formation of this bond is hindered by competition of other donor ligands such as the oxygen of the hydroxyl end groups. Hydroxyl oxygen being more nucleophilic than ester alcoholic oxygen, as the later is connected to electrophilic carbonyl group, reacts preferentially with the weak electrophilic Sb. However, ester alcoholic oxygen-Sb bond formation is aided by being part of a chelate system, as chelate structure dramatically increases complex stability [22]. Also, formation of this bond becomes favourable as the concentration of hydroxyl end groups decays. This fact is reflected in increasing activity of Sb with increasing conversion of hydroxyl end groups. Therefore, activation of ester groups is done by complexation of its alcoholic oxygen to Sb.

The electron lone pair of Sb also interferes in the stereochemistry of its complexes as it pushes the ligands together [23]. Six-coordinate Sb^{III} is pentagonal bipyramidal instead of being octahedral with lone pair in an axial position, and four-coordinate Sb^{III} complexes are trigonal bipyramidal instead of being tetrahedral or square planar, with a stereochemically active lone pair. The angles between ligands in four-coordinate Sb^{III} complexes are not equal and one of them is only about 70° [20]. So, this electron lone pair boosts bringing up the reacting functionalities together in a favourable configuration in the transition state.

The second question to be answered is whether this activated ester group reacts with a free hydroxyl end group or with bound a hydroxyl end group within the same Sb coordination sphere. A free hydroxyl end group is capable of attacking activated ester groups as diphenyl antimony glycolate showed activity in catalyzing polycondensation [11]. In this compound only one alkoxide can be attached to the Sb since the two phenyl ligands are stable. However, Sb with one phenyl ligand and without any phenyl ligands (two and three free ligands respectively) has higher activities because the activated ester group can be attacked intramolecularly by adjacent alkoxide which is much active than hydroxyl end group.

Kinetic investigation of Sb catalyzed polycondensation showed that the main barrier for activation is of entropic nature. Also, the activation entropy for polycondensation decreases in the order PET, poly(hexamethylene terephthalate) (PHT) and poly(decamethylene terephthalate) (PDT) [24]. Activation entropies were found to be -196.9 , -184 and $-176.9 \text{ J mol}^{-1} \text{ K}^{-1}$ for PET, PHT and PDT respectively. The value of the three activation entropies are most likely to be for that of ordering two molecules together. Also, the

activation entropy decreases with the size of the ring formed from Sb and alkyl diol (ethylene-, hexamethylene- and decamethylene glycol). The chelate ring is composed of 5 members in case of PET, 9 members in case of PHT and 13 members in case PDT. It is known that ring stability decreases with increasing size up from 7-member ring. This means that rate limiting step involves breaking of a chelate ring which is easier for 13- and 9-member rings than that of 5-member ring. Breaking of the chelate ring by exchanging to hydroxyl end group occurs after the glycolate ligand ($-\text{CH}_2-\text{CH}_2-\text{OH}$) has been already exchanged. Therefore, the polycondensation step in the most probable reaction path requires presence of more than one hydroxyl end group as ligands on Sb. Although polycondensation can be intermolecular between free chain and another chain coordinated to Sb, it is much slower than intramolecular one. Intramolecular polycondensation is favourable due to better spatial configuration (alkoxide in next vicinity to carbonyl) and due to activation of the attacking chain in the form of alkoxide.

As a result of IR spectroscopic investigation, thermal analysis, kinetic studies and a wide literature survey the following mechanism for Sb catalyzed polycondensation is proposed consisting of the following steps:

Step 1: Reaction of applied Sb compound with EG and formation of $\text{Sb}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O})(-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH})$ which is the pre-catalyst.

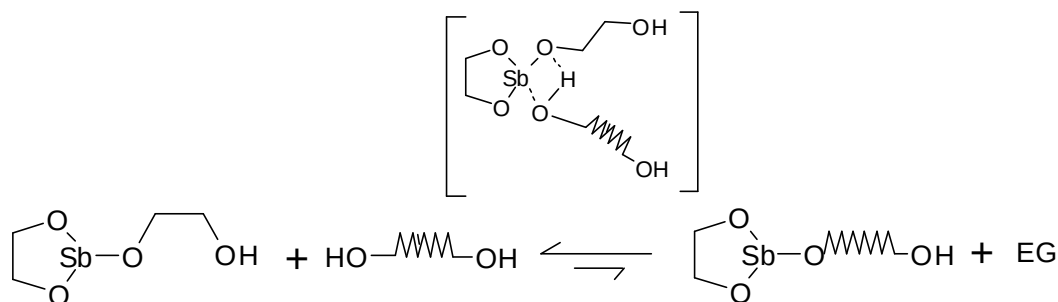
Step 2: Exchange of hydroxyl end group of one chain with the monodentate glycolate ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$) on $\text{Sb}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O})(-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH})$ to form chain-Sb complex having one chain end and a bidentate glycoxide $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ as ligands (scheme 6.8). This compound is the active species.

Step 3: Exchange of one chain end with one of the two coordination sites of the bidentate glycoxide ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) by breaking the chelate structure to form chain-Sb complex having two chain ends and the monodentate glycolate ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$) as ligands. The equilibrium in this step lies far to the side of reactants (scheme 6.9).

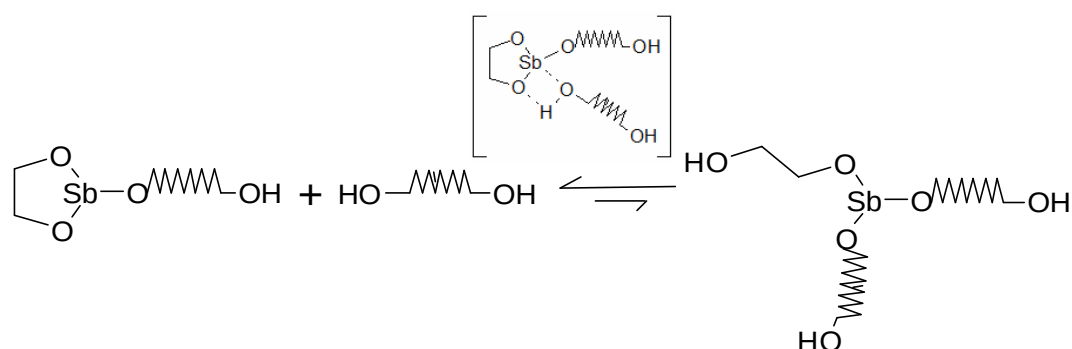
Step 4: Intramolecular rearrangement within chain-Sb complex coordination sphere coupling the two coordinated chains. The driving force for step 4 is the re-establishment of the chelate ligand ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) on the Sb complex (scheme 6.10).

The generally observed second order overall kinetics in the concentration of hydroxyl end groups and first order in Sb concentration limits rate determining step to two elementary steps: Chelate breaking step (step 3) and chain prolongation step (step 4). Probability of transition state formation in step 3 is low as it involves chelate breaking in

addition to the spatial freedom restriction of two reactant molecules upon coming together. On the other hand, step 4 involves formation of a chelate structure. Moreover, in this step movement restriction is intramolecular one which means it is not as severe as in case of step 3. So, it is expected that the activation entropy of this step is positive or just slightly negative. This means that rate determining step of this mechanism is most probably chelate breaking step.

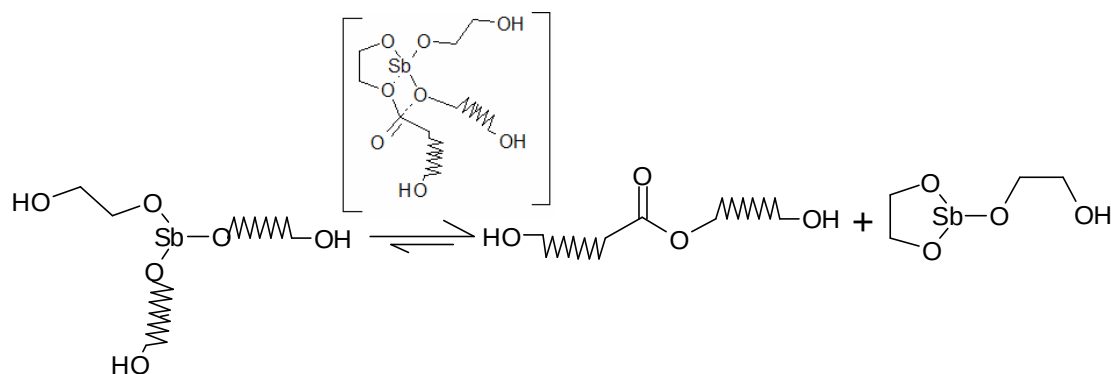


Scheme 6.8. Proposed mechanism for activation of a chain end by coordination to Sb in the form of alkoxide and release of an EG molecule.



Scheme 6.9. Proposed mechanism for activation of a second chain end by coordination to Sb in the form of alkoxide and breakage of the chelate ligand (-O-CH₂-CH₂-O-).

Sb does not show full activity in the initial phase of polycondensation due to hindering of Sb-chain end ester chelating by hydroxyl end groups competition, regardless if these end groups are functionalities on EG, BHET or its oligomeric species. As chain prolongation is hindered, the hydroxyl end group of the monodentate glycolate ligand will kick one of the two chains out and re-establish the chelate structure.



Scheme 6.10. Proposed mechanism for coupling of two chain ends by intramolecular rearrangement within Sb coordination sphere and generation of Sb glycolate.

4. Conclusion

A mechanism for the Sb catalyzed polycondensation in the synthesis of PET is proposed. Sb activates polycondensation of two chain ends by forming a five member chelate ring with one of them, thereby bringing its carbonyl close to the second chain's alkoxide end. Intramolecular rearrangement within Sb coordination sphere links these two chains and generates a chelate Sb glycoxide species. The polycondensation rate determining step was concluded to be the coordination of a second hydroxyl chain end to Sb by breaking the Sb glycoxide chelate. Low activity of Sb at high concentration of hydroxyl end groups was explained on the basis of hindering Sb-chain chelate building due to competition with free hydroxyl end groups. The lone electron pair on Sb^{III} plays a major role in its usefulness as PET polycondensation catalyst. It reduces its Lewis acidity and therefore its activity in chain thermal scission. Also, this electron pair pushes together the ligands coordinated to Sb, and thus bringing them in close proximity to react. Moreover, Sb stabilizes the hydroxyl end groups, in which it is solvated, against degradation by back biting mechanism.

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Appendix

Table 1.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
96.6	58.7	100.7
98.6	59.7	100.6
100.5	60.7	100.7
104.2	61.7	100.7
110.0	62.7	100.6
115.8	63.7	100.7
121.8	64.7	100.7
127.4	65.7	100.7
132.1	66.7	100.6
136.8	67.7	100.6
141.8	68.7	100.6
146.8	69.7	100.6
151.9	70.7	100.6
156.9	71.7	100.6
161.9	72.7	100.6
166.9	73.7	100.5
171.9	74.7	100.4
176.9	75.7	100.4
181.9	76.7	100.4
186.9	77.7	100.3
191.9	78.7	100.1
196.9	79.7	100.0
201.9	80.7	99.8
206.9	81.7	99.6
211.9	82.7	99.2
216.9	83.7	98.6
221.9	84.7	97.7
226.9	85.7	96.7
231.9	86.7	95.2
236.9	87.7	93.6
241.9	88.7	91.7
246.9	89.7	89.7
251.9	90.7	87.6
257.0	91.7	85.6
262.0	92.7	83.8
267.0	93.7	82.2
272.0	94.7	80.9
277.0	95.7	79.8
282.0	96.7	79.0

Table 1: TG data of polycondensation of 86 ppm HT/BHET mixture at 5 K/min. Sample mass is 9.98 mg.

Table 2.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
97.0	59.0	100.7
99.0	60.0	100.6
101.0	61.0	100.6
105.1	62.0	100.6
111.1	63.0	100.6
116.8	64.0	100.6
123.0	65.0	100.6
128.3	66.0	100.6
133.0	67.0	100.5
137.7	68.0	100.5
142.7	69.0	100.5
147.8	70.0	100.5
152.8	71.0	100.5
157.8	72.0	100.4
162.8	73.0	100.4
167.8	74.0	100.3
172.8	75.0	100.3
177.8	76.0	100.2
182.8	77.0	100.1
187.8	78.0	100.0
192.8	79.0	99.8
197.8	80.0	99.6
202.8	81.0	99.2
207.8	82.0	98.7
212.8	83.0	98.0
217.8	84.0	97.0
222.8	85.0	95.8
227.8	86.0	94.3
232.9	87.0	92.5
237.9	88.0	90.6
242.9	89.0	88.6
247.9	90.0	86.6
252.9	91.0	84.7
257.9	92.0	83.1
262.9	93.0	81.7
267.9	94.0	80.5
272.9	95.0	79.6
277.9	96.0	78.9
282.9	97.0	78.4

Table 2: TG data of polycondensation of 177 ppm HT/BHET mixture at 5 K/min. Sample mass is 10.06 mg.

Table 3.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
95.9	58.4	100.9
97.9	59.4	100.9
99.7	60.4	100.9
102.5	61.4	100.9
107.7	62.4	100.9
113.7	63.4	100.9
119.4	64.4	101.0
125.4	65.4	101.0
130.4	66.4	100.9
135.0	67.4	100.9
139.9	68.4	100.8
144.9	69.4	100.8
150.0	70.4	100.9
155.0	71.4	100.8
160.0	72.4	100.8
165.0	73.4	100.8
170.0	74.4	100.7
175.0	75.4	100.6
180.0	76.4	100.5
185.0	77.4	100.4
190.0	78.4	100.2
195.0	79.4	99.9
200.0	80.4	99.5
205.0	81.4	98.9
210.0	82.4	98.0
215.0	83.4	97.0
220.0	84.4	95.8
225.0	85.4	94.1
230.0	86.4	92.2
235.0	87.4	90.2
240.1	88.4	88.2
245.1	89.4	86.2
250.1	90.4	84.6
255.1	91.4	83.0
260.1	92.4	81.9
265.1	93.4	80.8
270.1	94.4	80.0
275.1	95.4	79.5
280.1	96.4	78.9
285.1	97.4	78.6

Table 3: TG data of polycondensation of 343 ppm HT/BHET mixture at 5 K/min. Sample mass is 9.99 mg.

Table 4.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
96.3	58.6	102.0
98.3	59.6	102.0
100.2	60.6	102.0
103.5	61.6	102.0
109.0	62.6	101.9
115.0	63.6	102.0
120.8	64.6	102.0
126.6	65.6	102.0
131.4	66.6	101.8
136.1	67.6	101.8
141.0	68.6	101.8
146.1	69.6	101.8
151.1	70.6	101.8
156.2	71.6	101.7
161.1	72.6	101.7
166.1	73.6	101.7
171.1	74.6	101.6
176.1	75.6	101.5
181.1	76.6	101.3
186.1	77.6	101.1
191.1	78.6	100.8
196.1	79.6	100.3
201.1	80.6	99.7
206.2	81.6	98.8
211.1	82.6	97.7
216.1	83.6	96.3
221.1	84.6	94.6
226.2	85.6	92.8
231.2	86.6	90.8
236.2	87.6	88.8
241.2	88.6	86.9
246.2	89.6	85.2
251.2	90.6	83.8
256.2	91.6	82.5
261.2	92.6	81.5
266.2	93.6	80.8
271.2	94.6	80.2
276.2	95.6	79.7
281.2	96.6	79.3
286.2	97.6	79.0

Table 4: TG data of polycondensation of 442 ppm HT/BHET mixture at 5 K/min. Sample mass is 10.10 mg.

Table 5.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
65.0	43.3	99.3
67.6	44.3	99.3
70.0	45.3	99.3
72.0	46.3	99.3
73.8	47.3	99.3
75.6	48.3	99.3
77.5	49.3	99.3
79.6	50.3	99.3
81.6	51.3	99.3
83.7	52.3	99.3
85.7	53.3	99.2
87.7	54.3	99.2
89.7	55.3	99.2
91.7	56.3	99.2
93.7	57.3	99.2
95.7	58.3	99.2
97.7	59.3	99.2
99.5	60.3	99.2
102.9	61.3	99.1
111.3	62.3	99.2
121.2	63.3	99.2
131.4	64.3	99.1
139.9	65.3	99.1
147.6	66.3	99.0
155.4	67.3	98.9
163.5	68.3	98.9
171.6	69.3	98.8
179.6	70.3	98.7
187.6	71.3	98.6
195.6	72.3	98.2
203.6	73.3	97.7
211.7	74.3	96.6
219.7	75.3	95.0
227.7	76.3	92.9
235.7	77.3	90.3
243.7	78.3	87.5
251.8	79.3	84.7
259.8	80.3	82.2
267.9	81.3	80.2
275.8	82.3	78.9
283.8	83.3	77.8

Table 5: TG data of polycondensation of 442 ppm HT/BHET mixture at 8 K/min. Sample mass is 10.34 mg.

Table 6.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
95.2	47.3	99.1
97.7	47.8	99.1
99.9	48.3	99.0
102.8	48.8	99.1
106.8	49.3	99.1
111.9	49.8	99.0
117.5	50.3	99.0
123.2	50.8	99.1
129.4	51.3	99.1
135.4	51.8	99.1
140.8	52.3	99.1
145.8	52.8	99.0
150.7	53.3	99.0
155.5	53.8	99.0
160.5	54.3	99.0
165.5	54.8	99.0
170.5	55.3	99.0
175.6	55.8	99.0
180.7	56.3	99.0
185.7	56.8	98.9
190.7	57.3	98.8
195.7	57.8	98.8
200.7	58.3	98.6
205.7	58.8	98.4
210.8	59.3	97.9
215.8	59.8	97.2
220.8	60.3	96.4
225.8	60.8	95.4
230.8	61.3	94.2
235.8	61.8	92.7
240.9	62.3	91.1
245.9	62.8	89.4
250.9	63.3	87.7
256.0	63.8	85.9
261.0	64.3	84.3
266.1	64.8	82.9
271.1	65.3	81.7
276.0	65.8	80.6
281.0	66.3	79.7
286.0	66.8	79.1
291.0	67.3	78.5

Table 6: TG data of polycondensation of 442 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.23 mg.

Table 7.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
97.2	59.1	102.1
99.2	60.1	102.0
101.3	61.1	102.1
105.7	62.1	102.1
111.8	63.1	102.1
117.4	64.1	102.1
123.6	65.1	102.1
128.9	66.1	102.1
133.5	67.1	102.0
138.3	68.1	102.0
143.3	69.1	102.0
148.3	70.1	102.0
153.4	71.1	102.0
158.4	72.1	101.9
163.4	73.1	101.7
168.3	74.1	101.5
173.3	75.1	101.2
178.4	76.1	100.8
183.4	77.1	100.2
188.3	78.1	99.4
193.3	79.1	98.4
198.3	80.1	97.3
203.4	81.1	96.4
208.4	82.1	94.8
213.4	83.1	93.3
218.4	84.1	91.7
223.4	85.1	90.0
228.4	86.1	88.3
233.4	87.1	86.7
238.4	88.1	85.4
243.4	89.1	84.2
248.4	90.1	83.2
253.4	91.1	82.2
258.5	92.1	81.7
263.5	93.1	81.0
268.5	94.1	80.5
273.5	95.1	80.2
278.4	96.1	79.8
283.5	97.1	79.5

Table 7: TG data of polycondensation of 883 ppm HT/BHET mixture at 5 K/min. Sample mass is 9.97 mg.

Table 8.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
95.4	47.4	96.0
97.9	47.9	96.0
100.1	48.4	96.0
103.1	48.9	96.0
107.2	49.4	96.0
112.4	49.9	96.0
117.9	50.4	96.0
123.7	50.9	96.1
130.0	51.4	96.1
135.9	51.9	96.1
141.2	52.4	96.0
146.2	52.9	96.0
151.1	53.4	96.0
156.0	53.9	96.0
161.0	54.4	96.0
165.9	54.9	96.0
171.0	55.4	96.0
176.0	55.9	96.0
181.1	56.4	95.9
186.1	56.9	95.9
191.2	57.4	95.9
196.2	57.9	95.9
201.2	58.4	95.8
206.2	58.9	95.8
211.2	59.4	95.6
216.2	59.9	95.4
221.2	60.4	95.1
226.2	60.9	94.6
231.3	61.4	94.0
236.3	61.9	93.1
241.3	62.4	92.2
246.3	62.9	90.9
251.3	63.4	89.5
256.4	63.9	87.9
261.4	64.4	86.2
266.4	64.9	84.4
271.4	65.4	82.6
276.5	65.9	80.9
281.5	66.4	79.4

Table 8: TG data of polycondensation of 86 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.03 mg.

Table 9.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
95.0	47.3	97.1
97.5	47.8	97.1
99.7	48.3	97.1
102.5	48.8	97.1
106.5	49.3	97.1
111.5	49.8	97.1
117.0	50.3	97.1
122.7	50.8	97.2
129.0	51.3	97.2
135.0	51.8	97.2
140.4	52.3	97.1
145.4	52.8	97.1
150.3	53.3	97.1
155.2	53.8	97.1
160.1	54.3	97.1
165.1	54.8	97.1
170.2	55.3	97.1
175.2	55.8	97.1
180.3	56.3	97.1
185.3	56.8	97.1
190.3	57.3	97.2
195.4	57.8	97.1
200.4	58.3	97.0
205.4	58.8	96.9
210.4	59.3	96.8
215.4	59.8	96.5
220.4	60.3	96.0
225.4	60.8	95.4
230.4	61.3	94.6
235.4	61.8	93.5
240.5	62.3	92.3
245.5	62.8	90.8
250.5	63.3	89.2
255.6	63.8	87.5
260.6	64.3	85.8
265.6	64.8	84.0
270.7	65.3	82.4
275.7	65.8	80.9
280.7	66.3	79.6
285.7	66.8	78.5

Table 9: TG data of polycondensation of 177 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.01 mg.

Table 10.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
95.4	47.4	97.4
97.9	47.9	97.4
100.1	48.4	97.4
103.1	48.9	97.4
107.2	49.4	97.4
112.4	49.9	97.4
118.0	50.4	97.4
123.7	50.9	97.4
130.0	51.4	97.5
135.9	51.9	97.5
141.2	52.4	97.4
146.2	52.9	97.4
151.1	53.4	97.4
155.9	53.9	97.4
160.9	54.4	97.4
165.9	54.9	97.4
171.0	55.4	97.4
176.0	55.9	97.4
181.1	56.4	97.4
186.1	56.9	97.4
191.2	57.4	97.3
196.2	57.9	97.2
201.2	58.4	97.1
206.2	58.9	96.9
211.2	59.4	96.5
216.2	59.9	96.0
221.2	60.4	95.2
226.2	60.9	94.3
231.2	61.4	93.2
236.3	61.9	91.9
241.3	62.4	90.4
246.3	62.9	88.7
251.3	63.4	87.0
256.4	63.9	85.2
261.4	64.4	83.4
266.5	64.9	81.9
271.5	65.4	80.5
276.5	65.9	79.3
281.5	66.4	78.3
286.5	66.9	77.6

Table 10: TG data of polycondensation of 343 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.07 mg.

Table 11.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
94.6	47.2	96.8
97.1	47.7	96.8
99.3	48.2	96.9
102.0	48.7	96.8
105.7	49.2	96.8
110.6	49.7	96.8
116.0	50.2	96.8
121.6	50.7	96.9
127.9	51.2	96.9
134.0	51.7	96.9
139.5	52.2	96.9
144.6	52.7	96.8
149.5	53.2	96.9
154.4	53.7	96.8
159.3	54.2	96.8
164.3	54.7	96.8
169.3	55.2	96.7
174.4	55.7	96.7
179.4	56.2	96.6
184.5	56.7	96.4
189.5	57.2	96.1
194.5	57.7	95.6
199.5	58.2	95.2
204.5	58.7	94.5
209.6	59.2	93.5
214.6	59.7	92.5
219.6	60.2	91.3
224.6	60.7	89.9
229.6	61.2	88.5
234.6	61.7	87.0
239.6	62.2	85.4
244.7	62.7	83.7
249.7	63.2	82.4
254.7	63.7	81.1
259.8	64.2	79.9
264.8	64.7	78.8
269.8	65.2	78.1
274.8	65.7	77.3
279.8	66.2	76.8
284.8	66.7	76.1

Table 11: TG data of polycondensation of 883 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.03 mg.

Table 12.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
91.8	44.0	97.9
97.0	45.0	97.8
102.2	46.0	97.9
107.2	47.0	97.9
112.0	48.0	97.8
116.6	49.0	97.9
122.3	50.0	97.9
127.6	51.0	97.8
132.4	52.0	97.8
137.2	53.0	97.8
142.2	54.0	97.7
147.2	55.0	97.6
152.2	56.0	97.5
157.2	57.0	97.4
162.2	58.0	97.2
167.2	59.0	97.0
172.2	60.0	96.8
177.2	61.0	96.5
182.2	62.0	96.1
187.2	63.0	95.6
192.2	64.0	95.0
197.2	65.0	94.3
202.2	66.0	93.4
207.2	67.0	92.5
212.2	68.0	91.5
217.2	69.0	90.1
222.2	70.0	88.4
227.2	71.0	86.6
232.2	72.0	84.7
237.2	73.0	82.9
242.3	74.0	81.4
247.3	75.0	80.1
252.2	76.0	79.0
257.3	77.0	78.2
262.3	78.0	77.5
267.3	79.0	76.8
272.3	80.0	76.4
277.3	81.0	76.0
282.3	82.0	75.6
287.3	83.0	75.4

Table 12: TG data of polycondensation of 2000 ppm HT/BHET mixture at 5 K/min. Sample mass is 10.24 mg.

Table 13.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
91.0	43.8	97.6
96.1	44.8	97.5
101.3	45.8	97.5
106.3	46.8	97.5
111.1	47.8	97.4
115.7	48.8	97.4
121.2	49.8	97.4
126.6	50.8	97.0
131.5	51.8	96.0
136.3	52.8	95.0
141.2	53.8	94.1
146.2	54.8	93.2
151.2	55.8	92.4
156.2	56.8	91.6
161.2	57.8	90.7
166.2	58.8	89.7
171.2	59.8	88.7
176.2	60.8	87.6
181.2	61.8	86.6
186.2	62.8	85.7
191.2	63.8	84.9
196.2	64.8	84.3
201.2	65.8	83.8
206.3	66.8	83.4
211.3	67.8	83.0
216.2	68.8	82.6
221.2	69.8	82.0
226.3	70.8	81.3
231.2	71.8	80.5
236.3	72.8	79.7
241.3	73.8	78.9
246.3	74.8	78.2
251.3	75.8	77.5
256.3	76.8	77.0
261.3	77.8	76.5
266.3	78.8	76.1
271.3	79.8	75.7
276.3	80.8	75.4
281.3	81.8	75.1
286.3	82.8	74.9

Table 14.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
90.5	43.7	99.4
95.7	44.7	99.4
100.8	45.7	99.3
105.8	46.7	99.4
110.6	47.7	99.3
115.1	48.7	99.4
120.7	49.7	99.3
126.1	50.7	98.8
131.0	51.7	97.8
135.8	52.7	96.9
140.8	53.7	96.3
145.8	54.7	95.6
150.8	55.7	95.0
155.8	56.7	94.2
160.8	57.7	93.2
165.8	58.7	92.0
170.7	59.7	90.6
175.7	60.7	89.1
180.7	61.7	87.9
185.7	62.7	86.8
190.8	63.7	85.8
195.7	64.7	85.0
200.7	65.7	84.4
205.8	66.7	84.0
210.8	67.7	83.6
215.8	68.7	83.3
220.8	69.7	82.9
225.8	70.7	82.5
230.7	71.7	81.9
235.8	72.7	81.3
240.8	73.7	80.7
245.8	74.7	80.0
250.8	75.7	79.5
255.8	76.7	79.1
260.8	77.7	78.7
265.8	78.7	78.3
270.8	79.7	78.0
275.8	80.7	77.7
280.8	81.7	77.5
285.8	82.7	77.2

Table 13: TG data of polycondensation of 4000 ppm HT/BHET mixture at 5 K/min. Sample mass is 10.23 mg.

Table 14: TG data of polycondensation of 6000 ppm HT/BHET mixture at 5 K/min. Sample mass is 10.18 mg.

Table 15.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Mass</i> [%]
90.4	43.7	96.0
95.5	44.7	95.9
100.7	45.7	95.9
105.7	46.7	95.9
110.5	47.7	95.8
115.2	48.7	95.8
120.9	49.7	95.8
126.1	50.7	95.2
130.9	51.7	94.2
135.8	52.7	93.3
140.7	53.7	92.6
145.8	54.7	91.7
150.8	55.7	90.9
155.8	56.7	89.9
160.8	57.7	88.8
165.8	58.7	87.7
170.8	59.7	86.4
175.8	60.7	85.3
180.8	61.7	84.3
185.7	62.7	83.4
190.7	63.7	82.7
195.8	64.7	82.1
200.8	65.7	81.7
205.8	66.7	81.4
210.8	67.7	81.1
215.8	68.7	80.8
220.8	69.7	80.3
225.7	70.7	79.8
230.7	71.7	79.2
235.8	72.7	78.4
240.8	73.7	77.7
245.8	74.7	77.1
250.8	75.7	76.4
255.8	76.7	75.9
260.8	77.7	75.4
265.8	78.7	75.0
270.8	79.7	74.7
275.8	80.7	74.4
280.8	81.7	74.1
285.8	82.7	73.9

Table 16.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Heat flow</i> [mW]
94.6	47.2	1.3
97.1	47.7	1.3
99.3	48.2	1.4
102.0	48.7	1.6
105.7	49.2	2.5
110.6	49.7	6.3
116.2	50.2	17.8
121.7	50.7	18.6
127.9	51.2	6.7
134.0	51.7	4.2
139.5	52.2	3.4
144.6	52.7	3.1
149.5	53.2	2.9
154.4	53.7	2.9
159.3	54.2	2.9
164.3	54.7	3.0
169.3	55.2	3.0
174.4	55.7	3.0
179.4	56.2	3.0
184.5	56.7	3.0
189.5	57.2	3.0
194.5	57.7	3.1
199.5	58.2	3.2
204.5	58.7	3.3
209.6	59.2	3.5
214.6	59.7	3.7
219.6	60.2	4.0
224.6	60.7	4.2
229.6	61.2	4.6
234.6	61.7	4.8
239.6	62.2	4.9
244.7	62.7	4.9
249.7	63.2	4.8
254.8	63.7	4.6
259.8	64.2	4.4
264.8	64.7	4.0
269.9	65.2	3.6
274.9	65.7	3.3
279.8	66.2	3.0
284.8	66.7	2.7

Table 15: TG data of polycondensation of 10000 ppm HT/BHET mixture at 5 K/min. Sample mass is 9.99 mg.

Table 16: DSC data of polycondensation of 442 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.23 mg.

Table 17.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Heat flow</i> [mW]
65.9	43.7	0.6
68.5	44.7	0.5
70.7	45.7	0.5
72.6	46.7	0.4
74.4	47.7	0.4
76.3	48.7	0.4
78.2	49.7	0.4
80.3	50.7	0.5
82.3	51.7	0.5
84.4	52.7	0.5
86.4	53.7	0.5
88.4	54.7	0.4
90.4	55.7	0.5
92.3	56.7	0.5
94.3	57.7	0.5
96.3	58.7	0.5
98.3	59.7	0.5
100.2	60.7	0.5
105.2	61.7	1.9
114.7	62.7	15.0
124.7	63.7	6.7
134.4	64.7	2.6
142.5	65.7	2.1
150.1	66.7	2.0
158.1	67.7	2.1
166.2	68.7	2.1
174.3	69.7	2.1
182.3	70.7	2.1
190.3	71.7	2.2
198.3	72.7	2.4
206.3	73.7	2.6
214.3	74.7	3.0
222.3	75.7	3.3
230.4	76.7	3.6
238.4	77.7	3.7
246.4	78.7	3.6
254.5	79.7	3.2
262.5	80.7	2.7
270.5	81.7	2.2
278.5	82.7	1.8

Table 18.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Heat flow</i> [mW]
95.4	58.2	0.4
97.4	59.2	0.4
99.3	60.2	0.4
101.6	61.2	0.6
106.3	62.2	1.9
112.4	63.2	8.8
118.0	64.2	11.3
124.1	65.2	1.9
129.3	66.2	1.3
133.9	67.2	1.2
138.7	68.2	1.2
143.7	69.2	1.3
148.8	70.2	1.3
153.9	71.2	1.2
158.9	72.2	1.2
163.8	73.2	1.2
168.8	74.2	1.2
173.8	75.2	1.3
178.8	76.2	1.3
183.8	77.2	1.3
188.8	78.2	1.4
193.8	79.2	1.5
198.8	80.2	1.6
203.8	81.2	1.8
208.8	82.2	1.9
213.8	83.2	2.1
218.8	84.2	2.2
223.8	85.2	2.3
228.9	86.2	2.3
233.9	87.2	2.3
238.9	88.2	2.2
243.9	89.2	2.0
248.9	90.2	1.7
253.9	91.2	1.5
258.9	92.2	1.3
263.9	93.2	1.1
268.9	94.2	1.0
273.9	95.2	0.9
278.9	96.2	0.8
283.9	97.2	0.7

Table 17: DSC data of polycondensation of 442 ppm HT/BHET mixture at 8 K/min. Sample mass is 10.34 mg.

Table 18: DSC data of polycondensation of 442 ppm HT/BHET mixture at 5 K/min. Sample mass is 10.1 mg.

Table 19.

<i>Temperature</i> [°C]	<i>Time</i> [min]	<i>Heat flow</i> [mW]
95.4	47.4	1.0
97.9	47.9	1.1
100.1	48.4	1.1
103.1	48.9	1.5
107.2	49.4	2.9
112.4	49.9	9.2
117.8	50.4	22.6
123.6	50.9	10.6
130.0	51.4	4.8
135.9	51.9	3.4
141.2	52.4	2.9
146.2	52.9	2.6
151.1	53.4	2.5
156.0	53.9	2.5
161.0	54.4	2.5
166.0	54.9	2.6
171.0	55.4	2.6
176.1	55.9	2.7
181.1	56.4	2.7
186.1	56.9	2.8
191.2	57.4	3.0
196.2	57.9	3.1
201.2	58.4	3.3
206.2	58.9	3.5
211.2	59.4	3.7
216.2	59.9	3.8
221.2	60.4	4.0
226.3	60.9	4.0
231.2	61.4	4.1
236.2	61.9	4.0
241.3	62.4	3.9
246.3	62.9	3.6
251.4	63.4	3.3
256.4	63.9	3.0
261.4	64.4	2.7
266.5	64.9	2.4
271.5	65.4	2.1
276.5	65.9	1.9
281.5	66.4	1.7
286.5	66.9	1.6

Table 19: DSC data of polycondensation of 883 ppm HT/BHET mixture at 10 K/min. Sample mass is 10.03 mg.

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Veröffentlichungen

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