CHEMICAL RECYCLING OF POLY(ETHYLENE TEREPHTHALATE) AND INVESTIGATION OF CONDITIONS FOR EFFECTIVE RESYNTHESIS

by

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ABSTRACT

CHEMICAL RECYCLING OF POLY(ETHYLENE TEREPHTHALATE) AND INVESTIGATION OF CONDITIONS FOR EFFECTIVE RESYNTHESIS

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Keywords: Bis(2-hydroxyethyl) terephthalate, chemical recycling, poly(ethylene terephthalate), repolymerization, solid state polymerization

The increase in plastic production leads to formation of more and more plastic waste, which causes the destruction of the natural environment system. Poly(ethylene terephthalate) (PET) has become one of the most investigated polymers because of its high consumption as bottles, textile products etc. The high consumption of PET-based products means huge quantities of PET waste, which causes significant environmental pollution. Therefore, recycling of PET waste is an important issue to be addressed.

The main objective of the thesis was the production of high-quality PET from PET waste. Accordingly, the PET materials were chemically recycled in the first part of the study. Different types of PET materials; transparent PET beverage bottles, coloured PET beverage bottles, PET yarns without finish and PET yarns with finish were depolymerized by glycolysis method. ($Zn(OAc)_2$), 1,3-Dimethylurea/$Zn(OAc)_2$ deep eutectic solvent

(1,3-DMU/$Zn(OAc)_2$ DES) and Butyl-3-methylimidazolium bromine ([Bmim]Br) were used as catalysts in depolymerization reactions. The obtained Bis(2-hydroxyethyl) terephthalate (BHET) was characterized with regards to its chemical structure and thermal properties and compared to commercially available BHET. Additionally, the yields of different applied glycolysis processes were evaluated. It was found that the type of the input PET material does not cause any significant difference in the properties of the BHET obtained. Moreover, it was found that using the different catalyst systems did not lead to significant difference in the quality of BHETs. When BHET yield was considered, $Zn(OAc)_2$ was the most efficient catalyst. On the other hand, 1,3-DMU/$Zn(OAc)_2$ DES resulted in the shortest reaction time to reach complete glycolysis.

In the second part of the thesis, experiments were conducted to resynthesize PET from recycled BHET and increase its molecular weight by solid state polymerization (SSP). The effects of different reaction conditions were investigated for an optimum synthesis reaction. The influence of the reaction time of the repolymerization and the applied vacuum amount and time on the chemical structure, physical and thermal properties of the PET product was investigated. Moreover, EG in various concentrations and phosphoric acid were added to the repolymerization reactions and their effects on the synthesized PET's properties were evaluated. The catalyst concentrations were changed to determine the best catalyst concentration that leads to the formation of PET with the desired properties. Finally, a polymerization reaction was carried out with untreated BHET to evaluate the differences in the properties of PET obtained from recycled BHET compared to PET synthesized from untreated BHET. It was found that the use of different catalyst concentrations and the application of different vacuum times significantly affected the properties of PET polymer obtained. During the solid-state polymerization that was performed to increase the molecular weight of the polymer, different reaction conditions such as different reaction times and reaction temperatures were applied to the synthesized PET products. Besides, the effect of BHET particle size on the PET properties was investigated. The obtained recycled PET was characterized with regards to its chemical structure as well as its physical and thermal properties. It was found that the application of SSP resulted in an increase in the intrinsic viscosity (IV) of the PET products.

ÖZET

POLİETİLEN TEREFTALATIN KİMYASAL GERİ DÖNÜŞÜMÜ VE YENİDEN SENTEZİ İÇİN ETKİLİ KOŞULLARIN İNCELENMESİ

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Anahtar Kelimeler: Polietilen tereftalat, Bis(2-hidroksietil) tereftalat, kimyasal geri dönüşüm, repolimerizasyon, katı hal polimerizasyonu

Plastik üretiminin artması, giderek daha fazla plastik atık oluşumuna yol açmakta, bu da doğal çevrenin tahrip olmasına neden olmaktadır. Polietilen tereftalat (PET), yüksek tüketimi nedeniyle en çok araştırılan polimerlerden biri haline gelmiştir. PET ürünlerinin yüksek tüketimi, büyük miktarda PET atığı yol açar, bu durum önemli ölçüde çevre kirliliğine neden olur. Buna göre, PET atıklarının geri dönüşümü ele alınması gereken önemli bir konu haline gelmiştir.

Bu durum göz önünde bulundurulduğunda, tezin temel amacı PET atıkları kullanılarak yüksek kaliteli PET üretimiydi. Çalışmanın ilk basamağında PET malzemeleri olarak kimyasal geri dönüşüm yöntemiyle kullanılarak geri dönüştürüldü. Farklı PET malzemeleri türleri; şeffaf PET içecek şişeleri, renkli PET içecek şişeleri, apresiz PET iplikler ve apreli PET iplikler, çinko asetat ($Zn(OAc)_2$) kullanılarak glikoliz yöntemiyle depolimerize edildi. Çalışmanın birinci amacının için ikinci basamağında, PET ipliklerin farklı katalizörler kullanılarak depolimerizasyonu araştırıldı. Katalizör olarak, ($Zn(OAc)_2$), 1,3-Dimetilüre/$Zn(OAc)_2$ derin ötektik çözücü (1,3-DMU/$Zn(OAc)_2$ DES) ve Butil-3-metilimidazolyum bromin ([Bmim]Br) kullanıldı. Elde edilen Bis(2-

hidroksietil) tereftalat (BHET), kimyasal yapısı ve termal özellikleri açısından analiz edildi ve ticari olarak temin edilebilen BHET ile karşılaştırıldı. Ayrıca uygulanan farklı glikoliz işlemlerinin verimleri de değerlendirildi. Kullanılan PET malzemesi çeşidinin, elde edilen BHET'in özelliklerinde önemli bir farklılığa neden olmadığı tespit edildi. Ayrıca farklı katalizör sistemlerinin kullanılmasının BHET'lerde kalite açısından önemli bir farklılığa yol açmadığı tespit edildi. BHET verimi dikkate alındığında $Zn(OAc)_2$ en etkili katalizör olmuştur. Diğer taraftan 1,3-DMU/$Zn(OAc)_2$ DES kullanılması glikoliz reaksiyonunun en kısa sürede tamamlanmasını sağlamıştır.

Çalışmanın ikinci amacı geri dönüştürülmüş BHET’den PET elde edilmesiydi. Bu amaç için, repolimerizasyon reaksiyonları gerçekleştirildi. Sentez koşullarını optimize etmek amaçlı farklı reaksiyon koşulları altında çeşitli repolimerizasyon reaksiyonları gerçekleştirildi. Repolimerizasyonun reaksiyon süresinin ve uygulanan vakum süresinin PET ürününün özellikleri üzerindeki etkisi araştırıldı. Ayrıca repolimerizasyon reaksiyonlarına fosforik asit ve çeşitli konsantrasyonlarda etilen glikol eklenerek oluşan PET üzerindeki etkileri değerlendirildi. Eklenen katalizör konsantrasyonları değiştirilerek istenen özelliklere sahip PET oluşumuna yol açan en optimum katalizör konsantrasyonu araştırıldı. Son olarak, geri dönüştürülmüş BHET kullanımının, elde edilen PET üzerindeki etkisini görmek amacıyla işlenmemiş BHET kullanılarak bir polimerizasyon reaksiyonu gerçekleştirildi. Farklı katalizör konsantrasyonlarının kullanılması ve farklı vakum sürelerinin uygulanmasının PET özelliklerinde en büyük değişikliklere yol açtığı tespit edildi. Üçüncü amaç için, sentezlenen PET ürünlerine reaksiyon süresi, reaksiyon sıcaklığı ve parçacık boyutu gibi açılardan farklı reaksiyon koşullarında katı hal polimerizasyon işlemleri uygulandı. Elde edilen geri dönüştürülmüş PET, kimyasal yapısının yanı sıra fiziksel ve termal özelliklerine göre de analiz edildi. SSP uygulamasının PET ürünlerinin IV değerinde artışa yol açtığı tespit edildi.

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Dedicated to my beloved family

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ABBREVIATIONS

BHET: Bis(2-hydroxyethyl) terephthalate
CEG: Carboxyl end group
DEG: Diethylene glycol
DMT: Dimethyl terephthalate
DSC: Differential scanning calorimetry
EG: Ethylene glycol
FTIR: Fourier-transform infrared spectroscopy
GPC: Gel permeation chromatography
M_n: Number average molecular weight
M_w: Weight average molecular weight
NMR: Nuclear magnetic resonance
PET: Poly(ethylene terephthalate)
SSP: Solid state polymerization
TGA: Thermal gravimetric analysis
T_m: Melting temperature
TPA: Terephthalic acid
TTIP: Titanium tetraisopropoxide

CHAPTER 1

1. INTRODUCTION

1.1. PET and Its Properties

PET is a thermoplastic polymer that is commercially popular due to its various favorable properties such as light weight and high tensile strength (Mandal and Dey, 2019). PET is formed by a repeating unit consisting of an aromatic ring and a short aliphatic chain (Figure 1.1). These aromatic and aliphatic groups are linked by ester bonds and this structure gives PET good properties. The combination of aromatic and aliphatic groups makes the polymer a relatively stiff macromolecule compared to other aliphatic polymers. Moreover, PET has moderately high thermal stability because the polymer chains do not exhibit segmental mobility (Venkatachalam et al., 2012). Therefore, PET demonstrates excellent mechanical and thermal properties. Also, its properties such as light weight, good chemical resistance and optical transparency make it a commonly used polymer in different industries (Mandal and Dey, 2019).

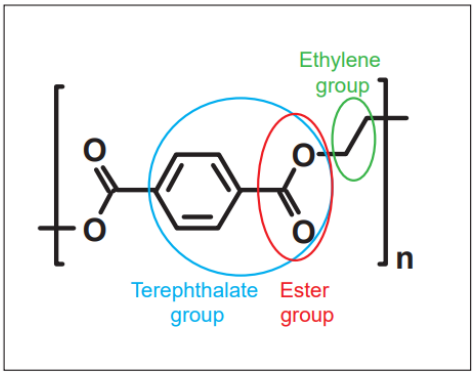


Figure 1.1. Structure of PET.

Since the chemical and geometric structures of PET can have higher regularities, it belongs to the class of crystallizable polymers. Therefore, PET can either be semi-crystalline or amorphous. The degree of crystallinity of PET has a great influence on its properties; for example, PET with a higher degree of crystallinity has a higher glass transition temperature. In addition, highly crystalline PET exhibits some improved mechanical properties, such as higher modulus and tensile strength compared to amorphous ones (Demirel et al., 2011). Besides crystallinity, molecular weight is another important factor that determines the various properties of PET. Therefore, the area of application of PET is determined by the molecular weight of it. For example, PET, which has a very low molecular weight has insufficient mechanical properties, so it is not very suitable for commercial applications. The molecular weight of PET also has a considerable influence on its degradation and thus on its effects to the environment (Farah et al., 2015). The general properties of PET can be found in the Table 1.1.

Table 1.1. General properties of PET (Awaja and Pavel, 2005).

Property	**Value**
Molecular weight (of repeating unit)	192 g/mol
Weight-average M_w	30000-80000 g/mol
Density	1.41 g/cm^3
Melting temperature	255-265^{0}C
Glass transition temperature	69-115^{0}C
Tensile strength (Young's modulus)	1700 Mpa
Breaking strength	50 Mpa

1.2. Usage of PET and Importance of PET Recycling

Plastics are materials that have worldwide usage in various applications (i.e., food, construction, textile industry, etc.) due to their durability, low cost and weight advantages (Hopewell et al., 2009). Plastic production is increasing annually which indicates that the demand for plastics is increasing. If the current growth rate continues in this way, it is predicted that plastic production will double in the next 20 years (Lebreton, and Andrady, 2019). Every year, more than 350 million tons of plastic are produced worldwide, and only about 16% of plastic waste is recycled (Soong et al., 2022). So, the advantages aside, plastics also pose risks to the environment due to their worldwide high-volume consumption and inappropriate disposal (Hopewell et al., 2009).

Among all plastics, PET is the one of the most commonly produced polymers and it is frequently used in bottles, textile fibres, films, and other moulded products. It is mainly used in the textile and packaging industry, so that the most of the PET is used for fiber and bottle production (Jankauskaitė et al., 2008). PET is especially appropriate for the production of beverage bottles because of its low weight, high strength, optical transparency, and low CO_2 permeability (Falkenstein et al., 2020). In the beverage industry (e.g. water, carbonated soft drinks and coffee), 67% of bottle demand is met by PET bottles (Benyathiar et al., 2022). Every year, approximately 56 million tons of PET are produced worldwide, most of them for disposable materials such as bottles (Soong et al., 2022). The huge amounts of PET products mean huge amounts of PET waste, data demonstrate that PET accounts for 12% of the world's total volume of solid waste. Although PET is a very useful product for various applications, its waste causes significant environmental pollution. Therefore, recycling of PET waste is an important issue to be addressed (Suhaimi et al., 2022).

1.3. Methods of PET Recycling

The driving forces for PET recycling are its high consumption rates and slow degradation in environment (Jankauskaitė et al., 2008). The most preferred method for PET recycling is based on mechanical recycling, which includes, contaminant removal by different processes (e.g., washing, drying or melting) then grinding of the material and finally pelletizing (Ragaert et al., 2017). Mechanical recycling has some drawbacks such as it causes the degradation of the PET properties, which leads to formation of low-quality products. Moreover, the complex form of the waste stream prevents the mechanical recycling of contaminated PET waste. These drawbacks are not encountered when the chemical recycling process is used (Raheem et al., 2019). Chemical recycling stands as an ideal way to recover PET monomers in pure state. PET can fully be converted to its monomers by chemical recycling methods such as methanolysis, glycolysis, hydrolysis aminolysis, and ammonolysis reactions (Ragaert et al., 2017). In these reactions, the use of a catalyst contributes to the process by lowering the required reaction temperature, reducing energy requirements, preventing undesirable side reactions, and providing inexpensive and rapid routes to recovery (Singh and Tandon, 2014; Khoonkari et al., 2015).

In methanolysis, PET is treated with methanol at high pressure and high temperatures, and a catalyst can also be used. Dimethyl terephthalate (DMT) and ethylene glycol (EG) are formed when the process is complete. Methanolysis is a beneficial process because methanol and EG can be easily recovered and reused after the recycling process is complete. However, it is a very costly method, especially due to the preference for novel PET production processes that use terephthalic acid (TPA) instead of DMT as a starting material as the conversion of DMT to TPA significantly increases the cost of methanolysis (Al-Sabagh et al., 2016). Hydrolysis is divided into three types, namely acid, alkaline and neutral hydrolysis. As a result of hydrolysis EG and TPA monomers are formed. The alkaline hydrolysis of PET is usually carried out in the presence of aqueous solutions of sodium hydroxide, potassium hydroxide or ammonia solution, while the acid hydrolysis of PET is performed in the presence of concentrated sulfuric acid. Furthermore, alkaline hydrolysis requires high temperatures and high pressure, whereas acid hydrolysis does not. Neutral hydrolysis of PET is performed with water or steam under high temperatures and pressure (Carta et al., 2003; Spychaj, 2002). Although the hydrolysis products TPA and EG can be directly to re-synthesize PET, this method is not preferred mostly in some industries due to the extreme process conditions (high temperature, pressure and long reaction time) and the high cost of TPA purification (Raheem et al., 2019). In aminolysis, the reaction is generally performed using primary amine aqueous solutions (i.e., methylamine, ethylamine, etc.) and after completion of the reaction bis(2-hydroxyethyl) terephthalamide is synthesized. Potassium sulphate and sodium acetate are commonly used catalysts in aminolysis (Al-Sabagh et al., 2016). Aminolysis of PET has not yet been used on a commercial scale, probably because an amine, which is often toxic or expensive, is required for the process (Thiounn and Smith, 2020). In ammonolysis, PET reacts with ammonia in an EG environment to form terephthaldiamide. The reaction is carried out under pressure and at high temperatures (Raheem et al., 2019). Currently, ammonolysis is not a widely used method for the chemical recycling of PET, as the product terephthalamide is not an economically important chemical in its natural state and is therefore preferred as a starting material for the production of value-added products (Gupta and Bhandari, 2019). In glycolysis, PET is degraded by the use of excess glycols (i.e. EG, diethylene glycol (DEG), propylene glycol, etc.) at high temperatures in the presence of esterification catalysts. As a result of the reaction, bis(2-hydroxyethyl) terephthalate (BHET) is produced (Khoonkari et al., 2015). Glycolysis has been widely used on a commercial scale thanks to its advantageous sides in terms of PET chemical recycling (Park and Kim, 2014).

1.3.1. Glycolysis of PET

Glycolysis is a frequently studied and used method for the chemical recycling of PET thanks to its advantages such as simplicity, flexibility and cheapness (Park and Kim, 2014).

Glycolysis reaction can be explained in two steps. In the first step, the free electron pair on the EG attacks the carbonyl carbon of the ester group of the polymer. In the second step, the hydroxyl ethyl group of the EG links with the carbonyl carbon of PET resulting in cleavage of the long polymer chain into short oligomers with following formation of BHET. Briefly, the process can be explained as the cleavage of ester linkages and replacement by hydroxyl ends (Sheel and Pant, 2019). The reaction mechanism of glycolysis of PET is shown in Figure 1.2.

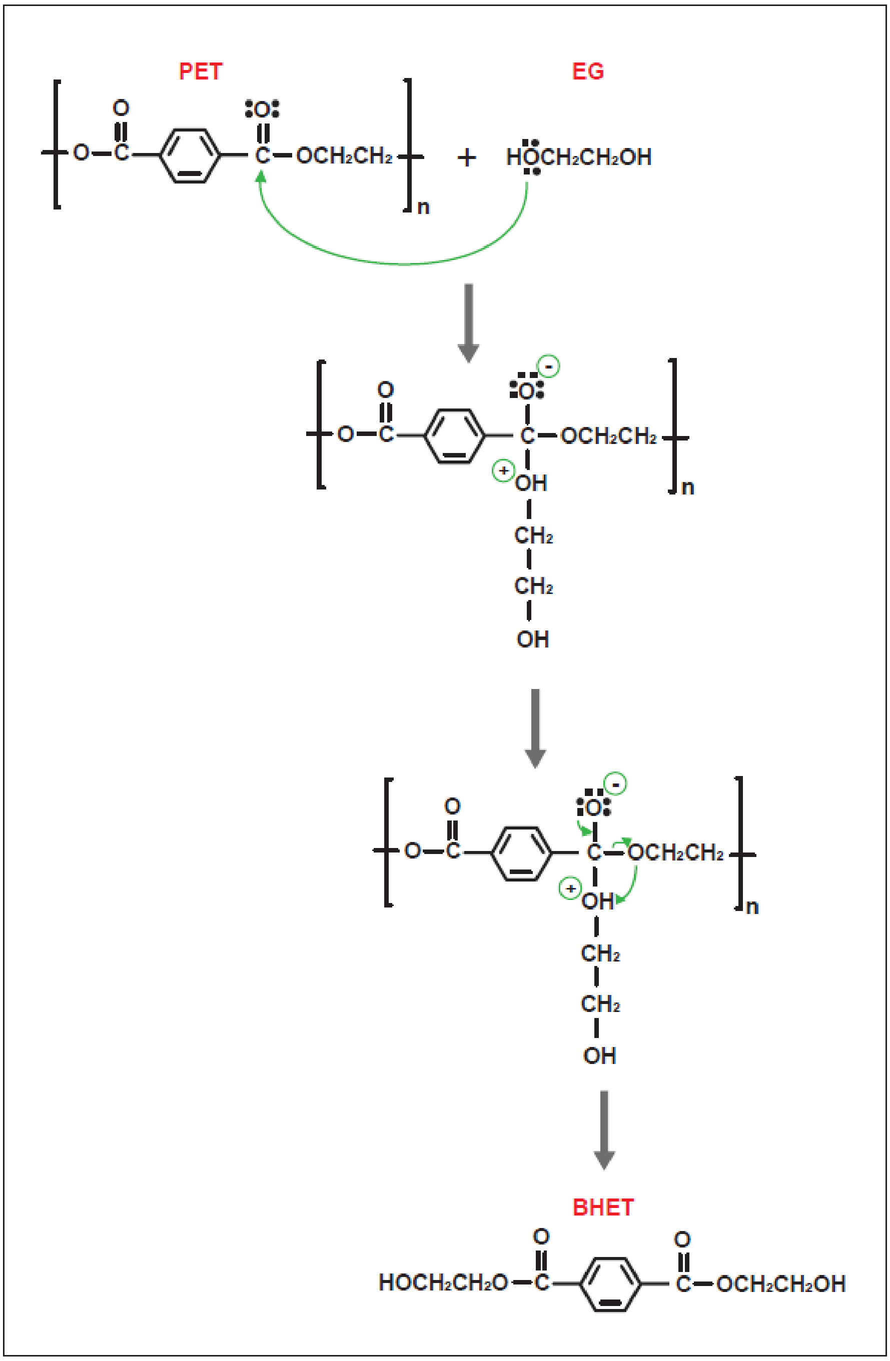


Figure 1.2. Glycolysis mechanism of PET.

Glycolysis is a beneficial process because of the various potential implementations of the products formed, and the main product BHET can be used in the production of PET (Thiounn and Smith, 2020). In the presence of a catalyst, the depolymerization reaction of glycolysis is completed in less time with the highest efficiency and quality, compared to other chemical recycling methods. The catalysts used in the glycolysis process are mainly metal acetates such as manganese, zinc, lead and cobalt. Among the metal acetates, it is observed that zinc acetate demonstrates best performance (Khoonkari et al., 2015).

In addition to metal acetates, ionic liquids (ILs) can also be used as catalysts for the PET glycolysis reaction. The main benefit of using IL as catalyst is its easy removal from the final products and repetitive utilization (Sheel and Pant, 2019). Wang et al. (2009) were the first to report the PET glycolysis process catalyzed by ILs. They found that 1-butyl-3-methylimidazolium bromine [Bmim]Br, a kind of neutral ionic liquid that has a good catalytic effect and a reasonable price, achieved 100% conversion of PET (Wang et al., 2009). After this discovery, various metallic IL catalysts such as [Bmim][$ZnCl_3$] have been developed which have shown satisfactory performance. Due to the poor durability of metallic catalysts and their harmful impacts on the environment, metal-free ILs have been developed, such as [Bmim]OH. However, the metal-free ILs still need to be improved as most of them, which have better catalytic performance, require a complex and expensive synthesis process (Xin et al., 2021).

Furthermore, apart from the traditional PET glycolysis reaction, novel glycolysis method, solvent-assisted glycolysis, have been developed. Recently, a new environmentally friendly type of catalyst has been explored called Deep Eutectic Solvent (DES), a novel solvent that can be used in solvent-assisted glycolysis. Thanks to DESs, glycolysis can take place in a short time under mild conditions and these solvents can be prepared easily (Sheel and Pant, 2019). They are also considered alternatives to ILs as they are less toxic and more biodegradable than ILs. DESs are synthesized by combining urea and metal salts in various molar ratios (Wang et al., 2015). Liu et al. (2018) synthesized DESs using various urea derivatives and metal salts and found that the amino group of the urea derivatives enhanced the PET glycolysis process. Steric hindrance and basicity of the amino group were the key factors affecting the catalytic performance. They stated that 1,3-dimethylurea/$Zn(OAc)_2$ (1,3-DMU/$Zn(OAc)_2$)DES was the most efficient catalyst for the PET glycolysis process among urea-metal salt combinations, and the yield of BHET reached 82% in 20 minutes (Liu et al., 2018).

Several conditions such as glycolysis time, glycolysis temperature, and catalyst concentration affect the glycolysis reaction of PET. The major effects on the glycolysis conversion of PET are in the following ascending order: glycolysis time < glycolysis temperature < catalyst concentration (Nikles and Farahat, 2005). An improvement in glycolysis time, glycolysis temperature or catalyst concentration leads to an increase in reaction yield, but after a certain threshold the trend is stable and no remarkable change occurs (Khoonkari et al., 2015). Table 1.2 demonstrates the various investigated catalysts and reaction conditions used in the glycolysis of PET.

Table 1.2. Studies that have investigated different types of catalysts and reaction conditions for the glycolysis of PET.

Catalyst	**EG/PET Ratio (weight)**	**Temperature (^{o} C)**	**Time**	**Pressure**	**Result**	**Reference**
Zn $(Ac)_2$	3	196	1 h	atmospheric pressure	80% BHET yield	Hu et al., 2019
1,3-DMU/Zn $(OAc)_2$	4	190	20 min	atmospheric pressure	82% BHET yield	Liu et al., 2018
[Bmim]Cl	4	180	8 h	atmospheric pressure	70.1% BHET yield	Wang et al., 2009
[Bmim]OH	10	190	2 h	atmospheric pressure	71.2% BHET yield	Yue et al., 2011
Choline acetate	4	180	4 h	atmospheric pressure	85.2% BHET yield	Liu et al., 2020
MnO_2/HGO	18.5	200	10 min	atmospheric pressure	100% BHET yield	Jin et al., 2020
γFe_2O_3	3.7	300	1 h	1.1 Mpa	> 90% BHET yield	Bartolome et al., 2014
$ZnMn_2O_4$	5.6	260	1 h	5 atm	92.2% BHET yield	Imran et al., 2013
Na_{12} $[WZn_3(H_2O)_2(ZnW_9O_{34})_2$	4	190	40 min	atmospheric pressure	84.5% BHET yield	Fang et al., 2018
$SiW_{11}Zn$	4	185	30 min	atmospheric pressure	84% BHET yield	Geng et al., 2015
Fe_3O_4-boosted MWCNT	10	190	2 h	atmospheric pressure	100% BHET yield	Al-Sabagh et al., 2016
Perkalite F100	5.6	240	1 h	atmospheric pressure	80% BHET yield	Guo et al., 2018

1.4. PET Synthesis

PET is synthesized by step-growth polymerization, whereby the synthesis process takes place in two steps: (I) esterification/transesterification and (II) polycondensation. As a result of the first step, prepolymers are produced that contain BHET and short-chain oligomers. BHET can be produced in two routes: The first route is the esterification of TPA, the second route is the transesterification of DMT (Scheirs and Long, 2003). In the first route, TPA reacts with EG and while reaction proceeds water is formed as a by-product. The reactant mixture should be used as a slurry, as TPA is poorly soluble in EG (Pang et al., 2006). In general, the molar ratio EG/TPA is 1:1.5. In this route, the reaction is performed at temperatures between 240–265˚C and at pressures around 0.4 Mpa. Antimony acetate, antimony trioxide, germanium dioxide or titanium is commonly used as a catalyst to accelerate the reaction (Deopura et al., 2008). In the second route, DMT reacts with EG, and methanol is formed as a by-product during the reaction. The molar ratio EG/TPA is 1:2.1–2 (Pang et al., 2006). The reaction is carried out at temperatures between 150-210°C at atmospheric pressure and in an inert atmosphere. Catalysts such as zinc and manganese acetates are commonly used in the reaction (Barber, 2017). The reactions of TPA and DMT routes are shown in Figure 1.3A and B, respectively. In the past, the DMT route was preferred because high-purity TPA was not available. However, today, pure PET is available and the TPA route is increasingly used for the production of PET. This is because the TPA route offers several advantages compared to the DMT route. For example, using the TPA route results in a higher yield and molecular weight of the product in a shorter time. Also, since only a small amount of catalyst is used, the synthesized product is much purer. The energy saving in the TPA route is higher because, less EG is used, which means that less EG needs to be distilled (Deopura et al., 2008).

Once BHET is synthesized, the second step, polycondensation, can be carried out and EG is formed as a by-product of the polycondensation process. In this step, the synthesized BHET is gradually heated up to 280°C (Pang et al., 2006). The reaction is performed in reduced pressure (< 1 mbar) (Barber, 2017). The common catalysts used in the polycondensation step are antimony and titanium-based catalysts. Although germanium oxide is an active catalyst for the polycondensation of PET, it is not usually used, especially for commercial production, due to its high cost (MacDonald, 2002). The reaction of polycondensation step is shown in Figure 1.3C. There are several studies on the mechanism of polycondensation reactions. Thanks to these studies, it has been established that the reaction proceeds through the nucleophilic attack of the hydroxyl end group on the ester carbonyl group (Figure 1.4). A coordination complex is formed between the metal catalyst and the ester-carbonyl bond of BHET. This complex leads to an increase in the polarity of the bond, which facilitates a nucleophilic attack (Ravindranath and Mashelkar, 1986). Some studies also assume that metal catalysts behave like a Lewis acid in the formation of coordination complexes. According to this assumption, the efficiency of the catalysts can be related to their acidity, i.e. a stronger Lewis acid is a more efficient polycondensation catalyst for the polycondensation of BHET (Chung, 1989).

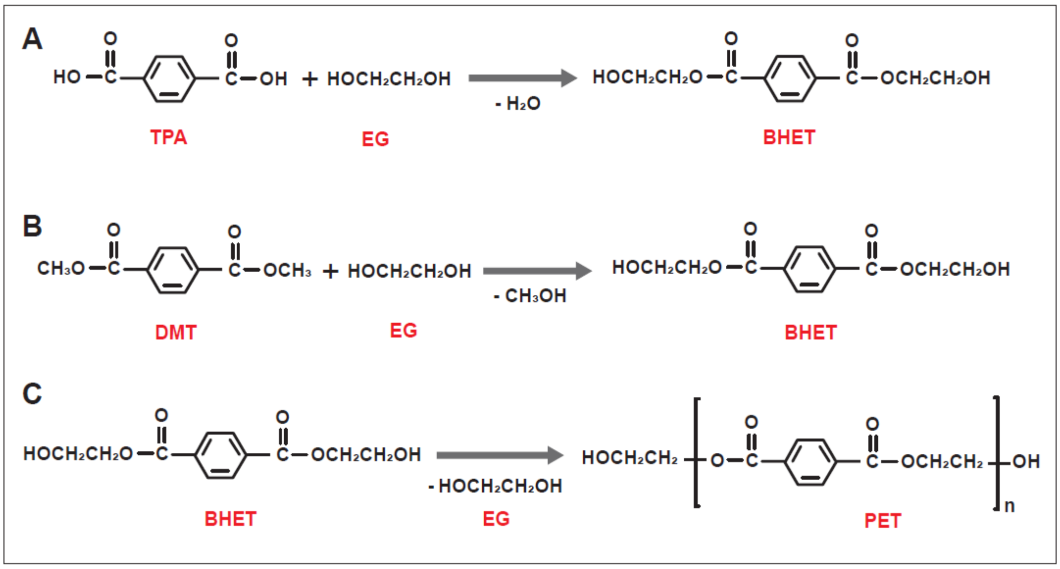


Figure 1.3. PET polymerization mechanism.

1.4.1. PET Synthesis from BHET

BHET, the main product of the glycolysis of PET, is used in various industries, e.g. in the production of resins and foams as well as in the synthesis of PET in one step. So, if the monomer that serves as the starting material for the PET synthesis is BHET, the synthesis process consists only of the polycondensation step of BHET. In general, polycondensation processes are carried out at high temperatures and low pressure. The usual catalysts are antimony and titanium-based catalysts. In addition to these catalysts, distinctive catalyst systems have been developed and used for polycondensation in recent studies. Several studies show that the PET product from the polycondensation of BHET has similar properties to virgin PET (Westover and Long, 2023). Table 1.3 summarizes an overview of the various investigated catalysts and reaction conditions used in the polycondensation of BHET.

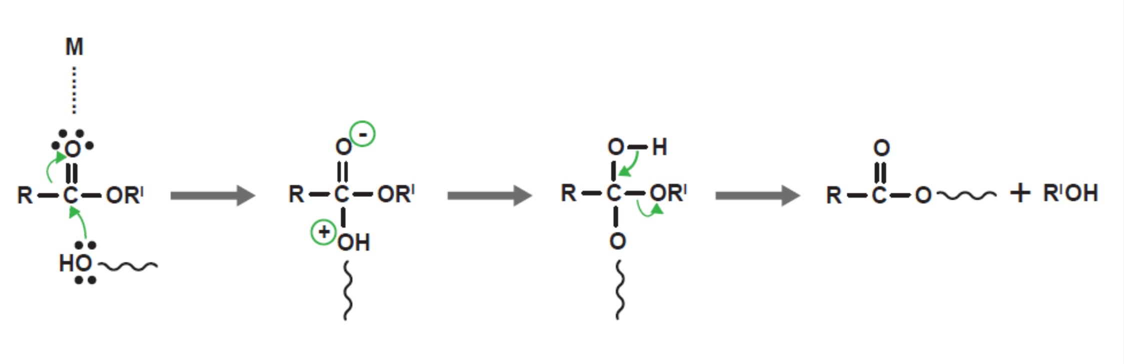


Figure 1.4. Mechanism for formation of PET.

1.4.2. Degradation reactions of PET

Due to the very high temperatures (approx. 280°C) used in the polycondensation step, degradation reactions occur that compete with the polycondensation reactions. There are three primary degradation processes: thermal degradation, oxidative degradation, and hydrolytic degradation. These degradation processes lead to various changes such as a decrease in the molecular weight of the synthesized polymer and the formation of acetaldehyde (Venkatachalam et al., 2012). Thermal degradation occurs during synthesis temperatures above 250℃. During thermal degradation, the ester linkages undergo random scission which leads to PET breakdown (Buxbaum, 1968). The hydrogen of the methylene group which is located at the β position to the carbonyl group may form a six membered transition state. Then scission of the bond takes place, which leads to the formation of a vinyl ester and carboxyl end units.

This is followed by a rearrangement of vinyl ester; acetaldehyde is formed as a result of this process (Venkatachalam et al., 2012). In addition, the formed vinyl chain and the carboxyl chain can undergo several reactions that lead to the formation of new structures. First of all, vinyl terminated unit and carboxyl terminated unit can react with each other which generates an anhydride. Moreover, carboxyl terminated unit and vinyl terminated unit may react with hydroxyl terminated polymer. While regenerated PET and acetaldehyde are formed as a result of the reaction between hydroxyl and vinyl terminated unit, reaction between hydroxyl and carboxyl terminated unit results in the formation of regenerated PET and water. Carboxyl-terminated units and vinyl-terminated units can react with hydroxyl-terminated polymers. Other possibilities are carboxyl end groups (CEGs) reacting with each other or units with vinyl end groups reacting with each other. When carboxyl end units react with each other, an anhydride and water are formed. On the other hand, when vinyl end units react with each other, polyene segments are formed (Van Hoof, 2012). Reactions of thermal degradation are shown in Figure 1.5.

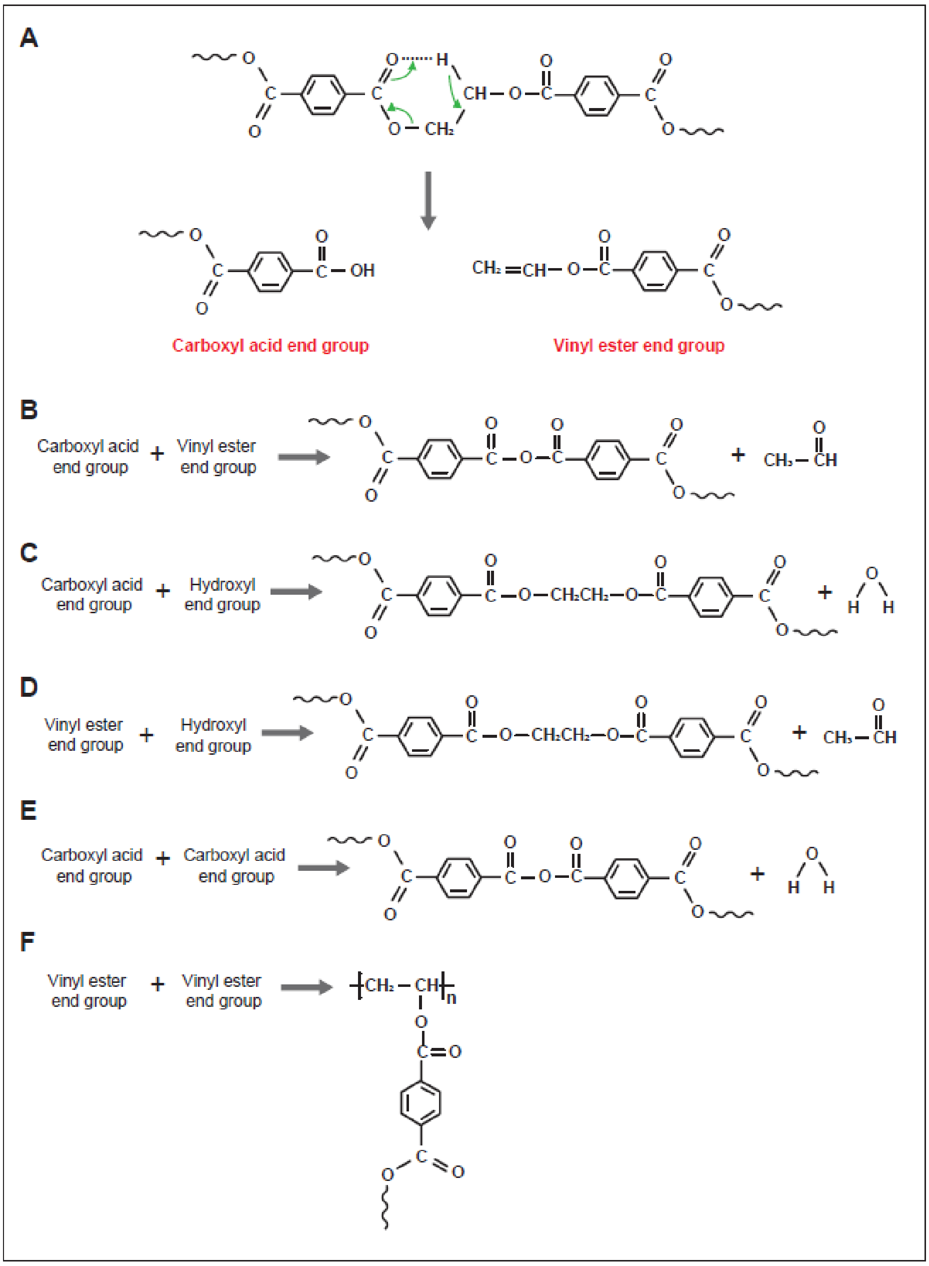


Figure 1.5. Thermal degradation of PET.

Another considerable side reaction that takes place during PET synthesis is the formation of DEG. DEG can be formed by etherification of EG or by the reaction of intermediates formed during thermal degradation before they are rearranged into acetaldehyde. Most of the DEG is formed during the initial stages of polycondensation in the preheating stage and in the low vacuum stages. In contrast, only a small amount of DEG is formed in the final high vacuum stage. As DEG is a less volatile condensation product, it is possible to be incorporated into the PET chain. DEG reduces the melting point and thermal stability of synthesized PET, therefore the DEG contents should be minimized as much as possible (Scheirs and Long, 2003). Reactions of DEG formation are shown in Figure 1.6.

The presence of moisture in the medium leads to hydrolytic degradation, which begins at temperatures around 100°C (Venkatachalam et al., 2012). During hydrolytic degradation, each water molecule breaks the chain from an ester bond, which leads to an increase in the number of short chains. When a long chain is broken, two chains are formed, one of which has a CEG and the other a hydroxyl end group. To reduce the occurrence of hydrolytic degradation, pre-drying to a low moisture level should be carried out before processing (Hosseini, et al, 2006). Reaction of hydrolytic degradation is shown in Figure 1.7.

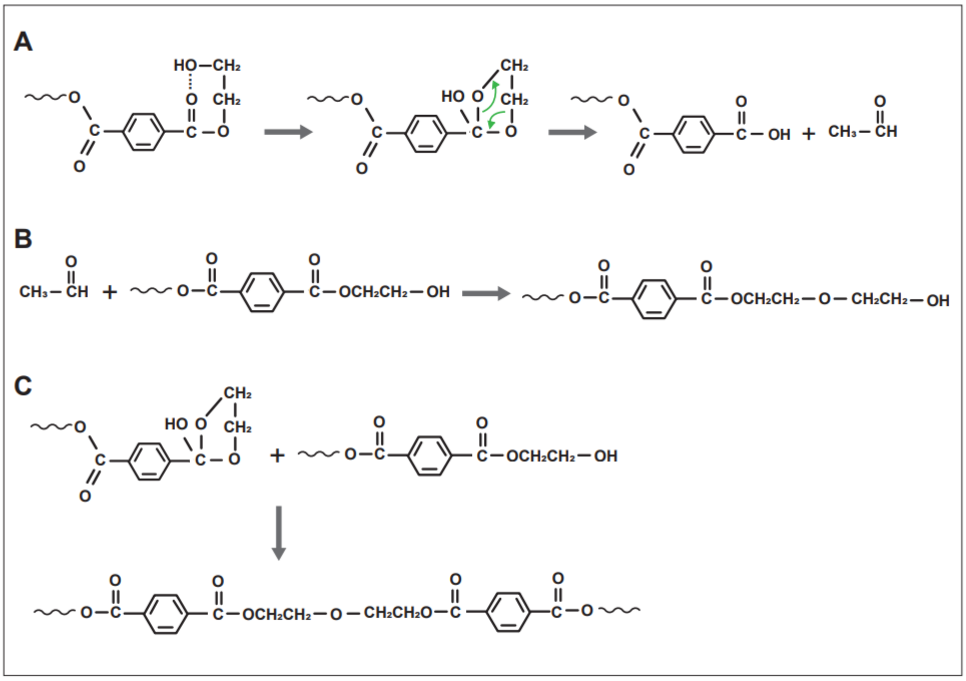


Figure 1.6. Reactions of DEG formation. (A) Intermediate step (B) Hydroxyl terminated intermediates (C) PET having DEG unit in the backbone.

Table 1.3. Studies that have investigated catalysts and reaction conditions for polycondensation for BHET.

Catalyst	**Time and Temperature Procedure**	**Vacuum (mbar)**	**IV (dL/g)**	**References**
Antimony (III) Oxide	4 h at 280°C (with vacuum)	0.047	0.67	Guo et al., 2020
Ethylene glycol antimony	1 h at 240°C 1 h at 240°C (with vacuum) 50 min at 275°C (with vacuum)	0.3	0.581	Wang et al., 2015
Sodium titanium tris(glycolate)	1 h at 240°C 1 h at 240°C (with vacuum) 50 min at 275°C (with vacuum)	0.3	0.675	Wang et al., 2015
Titanium (IV) tetrabutoxide	3 h at 260°C (with vacuum)	1	0.66	Ahmadnian et al., 2008
Antimony (III) Oxide	3 h at 260°C (with vacuum)	1	0.42	Ahmadnian et al., 2008
$(Ti_3(PO_4)_4)$+TPP	2 h at 230°C 260-280°C (with vacuum)	1	0.6	Zhang et al., 2023
TSP-44	1 h 40 minutes at 280°C (with vacuum)	< 0.5	0.7	Yin et al., 2010
Antimony (III) Acetate + 1-(p-nitrobenzyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	4 h at 280°C (with vacuum)	5	25500 g/mol (Mw)	Dou et al., 2012
Antimony (III) Oxide	1 h 10 min at 240°C (with gradually vacuum) 290°C (with vacuum)	0.2	0.64	Kulkarni, 2020
TBD: MSA	1 h at 250-270°C 4 h at 250-270°C (with vacuum)	10	12000 g/mol (Mn)	Jehanno et al., 2018

Thermooxidative degradation stems from the participation of oxygen, which is present in the medium, in the synthesis reactions at high temperatures. This type of degradation process begins with the generation of hydroperoxide at the methylene group in the diester bond and then continues with the scission of the chain (Botelho et al., 2001). DEG units are identified as reactive sites along the PET chain and thermo-oxidative degradation tends to start at the ether link of the DEG unit. When ether links are exposed to thermal oxidation, hydroxyl radicals are formed and as a result of the reaction between these radicals and aromatic groups, di-hydroxyl compounds are formed. In the last step of the oxidation process, quinone structures are formed which are incorporated into the PET backbone. This type of thermo-oxidative route can be a reason for the color formation in PET (Romão et al., 2009). Reactions of thermo-oxidative degradation are shown in Figure 1.8.

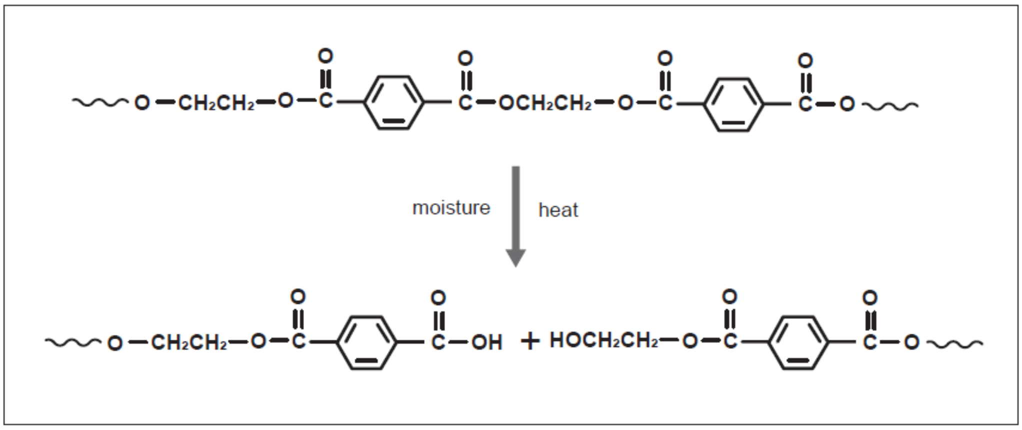


Figure 1.7. Hydrolytic degradation of PET.

1.4.3. Methods for increasing the intrinsic viscosity of PET

Degradation reactions, which take place during synthesis and compete with the polycondensation reactions lead to the cleavage of the polymer chains, resulting in the formation of short polymer chains with a dominant CEG. As a result of these degradation reactions, the number of CEGs increases and the molecular weight of the PET polymer decreases considerably, which leads to a reduction in intrinsic viscosity (IV). Low IV is an undesirable property of PET polymers as it leads to the formation of inferior quality PET-based products that are not suitable for most applications (Dimonie et al., 2012). Various methods have been developed to overcome this problem. Some of the most commonly used methods are the addition of stabilizers towards the end of the synthesis process and the application of a solid-state polymerization process to synthesized recycled PET (Barber, 2017).

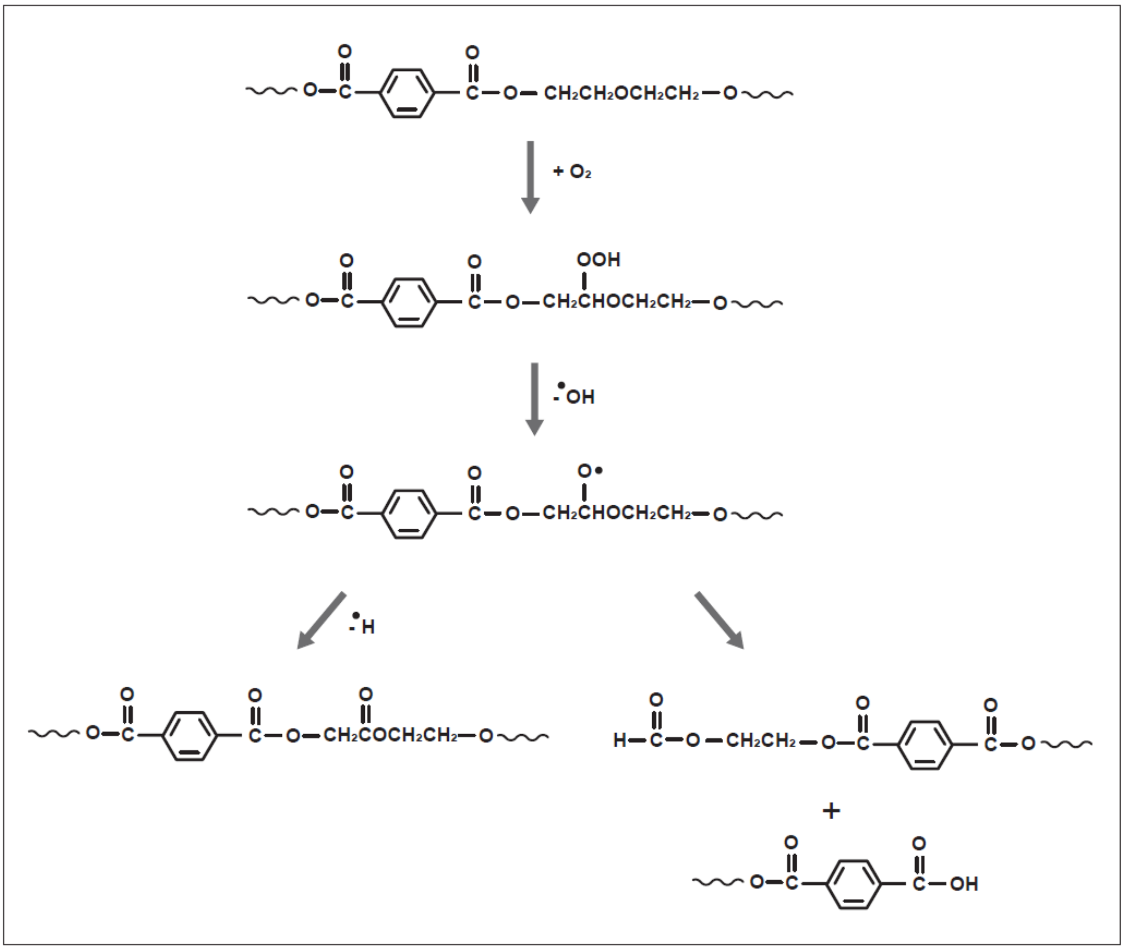


Figure 1.8. Thermooxidative degradation of PET.

1.4.3.1. Stabilizers

Stabilizers improve the thermal stability and reduce degradation and discoloration during the PET polymerization process, which leads to a reduction in product quality. The addition of stabilizers can, for example, contribute to maintain the IV of PET, which helps to prevent the production of inferior products. The stabilizers commonly used in the production of PET are phosphorus-containing chemicals such as phosphoric acid or phosphorous acids (Scheirs and Long, 2003).

Some catalysts are added during the polymerization reaction of PET, and antimony (III) oxide is one of the most commonly used catalysts. After the initiation step was completed, it was observed that the polycondensation rate was faster in the presence of antimony (III) oxide and phosphoric acid than in the presence of antimony (III) oxide alone. A higher polycondensation rate led to an increase in the molecular weight of the PET product, indicating a positive effect of phosphoric acid on increasing the molecular weight and reducing the CEGs. This acceleration was explained by the formation of a catalytic complex structure between antimony (III) oxide and phosphoric acid, which suppressed the formation of side reactions (Kamatani et al., 1980).

Moreover, the residues of some catalysts can be the cause of thermal instabilities. The residues from titanium-based catalysts, another commonly used catalyst in the PET polymerization process, are very active, resulting in a lack of control during the PET polycondensation stage (Fortunato et al., 1994). Therefore, these catalysts can lead to the formation of various undesirable side reactions (e.g. ester interchange reaction) and consequently to the formation of discolored, yellowish colored PET products (Yang et al., 2010). Phosphorus-containing chemicals with acidic OH groups control the activity of titanium-based catalysts and inhibit unwanted ester interchange reactions through the interaction between OH of the phosphorus-containing chemical and the titanium-based catalyst, likely leading to the formation of chelate-titanate species (Fortunato et al., 1994). In this way, the phosphorus-containing chemical can improve the thermal stability and reduce the discoloration of the product when the titanium-based catalyst is used during polymerization (Scheirs and Long, 2003).

1.4.3.2. Solid state polymerization

SSP of PET is performed by heating the PET prepolymer to a temperature above its glass transition temperature (~80°C) but below its melting temperature (~255°C) (Chang et al., 1983). The most suitable SSP temperature for PET can be assumed to be 200-250°C. In this temperature range, the degradation reaction has only an insignificant effect and the end groups also have sufficient mobility to react with each other (Vouyiouka et al., 2005). During the SSP process, by-products (e.g. EG) are formed which are removed with the contribution of an inert gas stream or a vacuum.

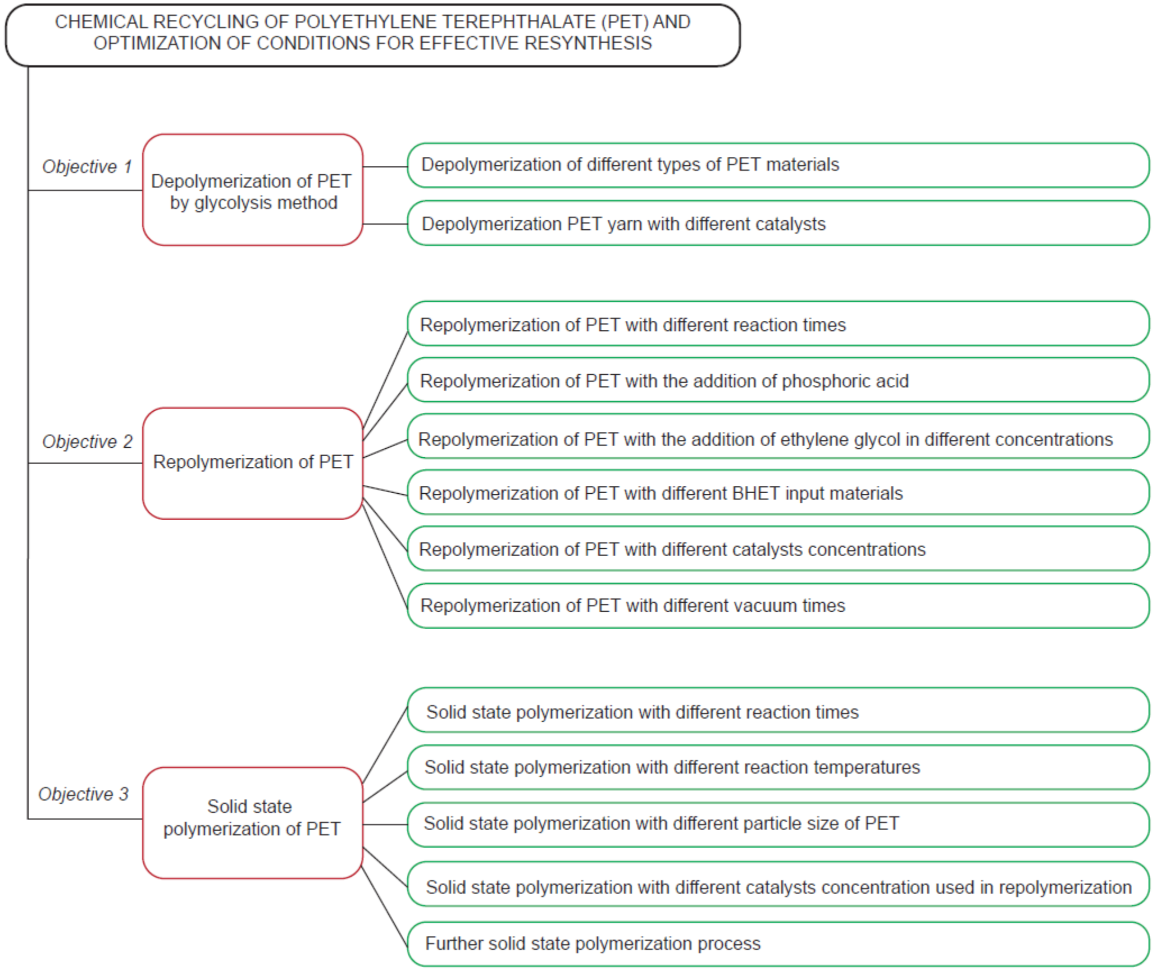
There are several factors that influence the SSP process. Temperature is one of the most significant factors affecting SSP. The overall rates for the SSP of PET increase with increasing temperature indicating that an increase in temperature contributes to produce PET with a higher IV. The PET prepolymer contains inactive functional end groups. These end groups are highly constrained by the crystalline structure; therefore, they do not have adequate mobility during SSP to take place in the reaction at a given temperature. It is possible to activate some of the inactive end groups by increasing the temperature so that inactive end groups that are immobilized at lower temperatures are mobilized and participate in the reaction during SSP. Due to the limited mobility of the chain ends that make up the PET prepolymer, SSP also requires a lot of time, and a longer reaction time leads to PET with a higher IV (Duh, 2001). Another factor is the particle size of PET, and a reduction in particle size leads to an increase in the SSP rate. The reason for this is that with a smaller particle size, the total surface area of the PET particles becomes larger, which facilitates the diffusion of by-products. As a result, the PET particles achieve a higher IV (Wu et al., 1997). In addition, the type and amount of catalyst used in the melt polymerization has an influence on the SSP process. It was found that the antimony catalyst, which is one of the most commonly used catalyst types in PET production by melt polymerization, also has an influence on SSP. The SSP rate increases with increasing antimony concentration and reaches its maximum value at a certain antimony concentration. The reason why an increase in the catalyst concentration leads to an increase in the reaction rate can be explained by the fact that the catalyst reduces the activation energy required for the reaction. Therefore, the use of a higher concentration of antimony catalyst in the melt polycondensation has a positive effect on the SSP of PET prepolymer, resulting in the production of PET polymer with higher IV (Duh, 2002).

CHAPTER 2

2. OBJECTIVES

This study has three main successive objectives. The first objective is to recycle PET waste to obtain pure BHET and investigate the effects of different types of PET feedstock and catalyst systems on the glycolysis of PET to obtain a BHET monomer that has similar properties to commercial BHET. To achieve the first objective, five different PET feedstocks were depolymerized by the glycolysis method using three types of catalysts. The effects of PET feedstocks, catalysts and glycolysis reaction conditions on the yield and properties of the BHET product were analyzed. The second objective is to convert recycled BHET into PET and optimize the synthesis conditions. PET was synthesized from recycled BHET under different reaction conditions. The influence of time and temperature, the addition of phosphoric acid, the addition of different concentrations of EG, the type of BHET input material, the concentration of the catalyst and the vacuum time on the properties of the PET product were investigated. The third objective was to investigate the properties of PET products to which different SSP processes were applied. The fulfillment of these objectives led to the completion of the closed loop, which can be seen as the development of a possible route for the synthesis of recycled PET from PET waste. To achieve these objectives, the workflow given in Figure 2.1 was followed.

Figure 2.1. General workflow of the thesis.



CHAPTER 3

3. MATERIALS AND METHODS

3.1. Materials

Waste transparent PET beverage bottles, waste colored PET mineral water bottles were collected from consumers, PET yarn without finish and two types of PET yarns with finish were provided by KordSA and used as input material for the depolymerization process. $Zn(OAc)_2$, 1,3-DMU/$Zn(OAc)_2$ DES, [Bmim]Br IL as catalyst, EG, isopropanol and commercial BHET monomer (as reference) were purchased from Sigma-Aldrich.

In the repolymerization process, recycled BHET were used as input material, provided from KordSA. Antimony (III) oxide (Sb_2O_3) and Titanium tetraisopropoxide (TTIP) used as catalysts, Phosphoric acid (H_3PO_4) as a stabilizer, 1-butanol and EG were purchased from Sigma-Aldrich. In the SSP reactions, the PET samples obtained from repolymerization reactions of BHET were used as the input material.

3.2. Methods

3.2.1. Depolymerization of PET by glycolysis method

3.2.1.1. Depolymerization of different types of PET materials

The glycolysis method was used to depolymerize different types of PET materials. The required amounts of PET, EG and $Zn(OAc)_2$ were combined in a two-necked flask with reflux condenser, thermometer, stirrer and argon inlet. The mixture was heated to 210°C and mixed at 600 rpm for 1 h. 1000 mL of distilled water was added to an empty flask and the resulting mixture was poured through a stainless-steel filter mesh into the distilled water. Unpolymerized PET (fraction I) was separated from the mixture by filtration. The mixture was then placed on the heater, stirred at 600-800 rpm for 1 h and then filtered using a vacuum filtration system. The filter residue was dried at 50°C for 15 hours (fraction II). The final filtrate containing BHET monomers was stored in a refrigerator at 4°C for 48 h. The BHET crystals were collected through a filter and dried at 50°C for 24 h (fraction III). The scheme of the separation process of the depolymerization products was shown in Figure 3.1. This depolymerization method was applied to different PET materials. The PET materials used were transparent PET, colored PET (green), PET (polyester) yarn without finish and two types of PET yarns with finish (103895-Code208 and 108619-T6900). The BHETs produced from the different PET materials are listed in the Table 3.1.

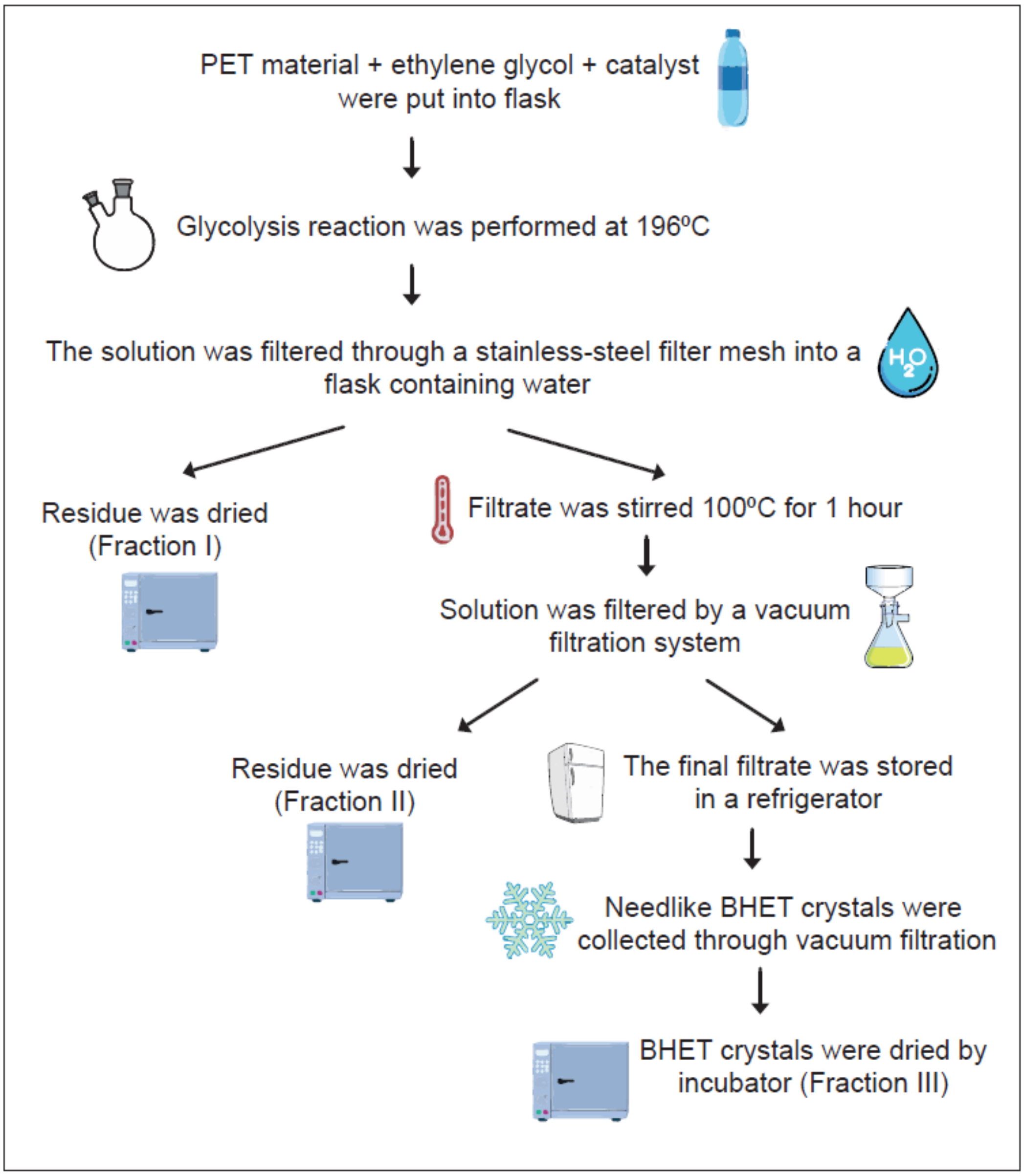


Figure 3.1. General method for the depolymerization of PET.

Table 3.1. List of BHETs prepared using different input materials.

Type of PET Material	Type of Catalyst	Time (min)	Total Pet (g)	Ethylene Glycol (mL)	Catalyst (g)
Transparent PET	$Zn(OAc)_2$	60	37.0025	100	0.2291
PET yarn	$Zn(OAc)_2$	60	36.9942	100	0.2222
103895-Code208	$Zn(OAc)_2$	60	37.0047	100	0.2222
108619-T6900	$Zn(OAc)_2$	60	37.0460	100	0.2223
Colored PET (green)	$Zn(OAc)_2$	60	37.0405	100	0.2222

3.2.1.2. Synthesis of 1,3-DMU/$Zn(OAc)_2$ DES

3.95 g of 1,3-dimethylurea (1,3-DMU) and 2.05 g of $Zn(OAc)_2$ were placed in a single-necked flask equipped with a thermometer and stirrer. The mixture was heated to 120℃ and mixed at 300 rpm for 4 h. The resulting mixture was dried at 50℃ for 15 h.

3.2.1.3. Depolymerization of PET yarn with different catalysts

The glycolysis method was used to depolymerize PET yarn with different catalysts. Three different catalysts were used in depolymerization reactions, and these catalysts are $Zn(OAc)_2$, 1,3-DMU/$Zn(OAc)_2$ DES and [Bmim]Br IL. In the first depolymerization reaction, the required amounts of PET yarn (without finish), EG and $Zn(OAc)_2$ were combined in a two-necked flask with reflux condenser, thermometer, stirrer and argon inlet. The mixture was heated to 210°C and mixed at 600 rpm for 1 h. In the second depolymerization reaction, 1,3-DMU/$Zn(OAc)_2$ DES was used as a catalyst and after combining PET yarn (without finish), EG and 1,3-DMU/$Zn(OAc)_2$ DES in a two-necked flask, the mixture was heated to 210°C and mixed at 600 rpm for 20 min. In the last depolymerization reaction, [Bmim]Br IL was used as a catalyst. The same reaction conditions as for the other depolymerization reactions were applied for 24 h. The same procedure was then applied to the products obtained from all depolymerization reactions. The mixture obtained by the depolymerization reaction was mixed with 1000 mL of distilled water after being passed through a stainless-steel filter. Fraction I was separated from the mixture by filtration. The mixture was heated and stirred for 1 h and then filtered.

Fraction II was dried at 50°C for 15 h. Fraction III was stored in a refrigerator at 4°C for 48 h. The BHET crystals were collected through a filter and dried at 50°C for 24 h. The BHETs produced by using different catalysts are listed in the Table 3.2.

Table 3.2. List of the BHETs prepared using different catalysts.

Type of PET Material	**Type of Catalyst**	**Time (min)**	**Total PET (g)**	**Ethylene Glycol (mL)**	**Catalyst (g)**
PET yarn	$Zn(OAc)_2$	60	36.9942	100	0.2222
PET yarn	1,3-DMU/$Zn(OAc)_2$ DES	20	36.9562	100	1.8509
PET yarn	[Bmim]Br IL	1440	4.9995	18	1.0320

3.2.2. Repolymerization of PET

3.2.2.1. General repolymerization method

Certain amounts of BHET, catalyst, optionally phosphoric acid and EG were combined in a three-necked flask equipped with condenser, thermometer, mechanical stirrer and argon inlet. By placing a one-necked flask at the other end of the condenser in an ice bath, the by-products formed during the reaction were collected. First, the mixture was heated to 190°C and stirred at 100 rpm. The temperature was gradually increased to 275°C while maintaining the target time. After the mixture was heated up to and kept at 275°C for a while, vacuum was applied to the mixture. At the end of the specified time under vacuum at 275°C, polymerization was terminated by simultaneously switching off the vacuum, the heater and the stirrer and the polymer was allowed to cool and solidify in the flask. The solidified polymer is removed by breaking open the flask in which it is contained.

3.2.2.2. Repolymerization of PET with different reaction times

Two different time & temperature conditions were applied to investigate the effect on PET product obtained. In the first synthesis, recycled BHET, Antimony (III) oxide (200 ppm) and TTIP (~ 30 ppm) were added to a 500 mL three-necked flask equipped with a condenser and a magnetic stirrer. The mixture was heated to 190°C and after 1 h the temperature was increased to 220°C. The mixture was kept at this temperature for 2 h and then increased to 275°C. After 20 min, the vacuum was applied for 30 min while the temperature was maintained at 275°C. At the end of 30 min, polymerization was terminated by simultaneously switching off the vacuum, heater and stirrer. This PET synthesis process is referred to as "Polymerization 1". In the second synthesis, the recycled BHET, Antimony (III) oxide and TTIP were added to a flask. As in the first synthesis, the temperature was increased to 190°C for 1 h, then to 220°C for 2 h. The temperature was increased to 245°C and kept at this temperature for 2 h. After that, the temperature was increased to 275°C. After 20 min, the vacuum was applied for 30 min while the temperature was maintained at 275°C. At the end of 30 min, the polymerization was terminated. This PET synthesis process is referred to as "Polymerization 2". The conditions for these syntheses are given in the Table 3.3.

3.2.2.3. Repolymerization of PET with the addition of phosphoric acid

Two different syntheses were carried out, one of which contained a phosphoric acid stabilizer, while the other did not contain phosphoric acid, in order to observe the effect of phosphoric acid on the PET product obtained. The phosphoric acid stabilizer was prepared by dissolving phosphoric acid (0.036 mol) in 1-butanol (15.43 mL) and then mixing with EG (125 mL). The synthesis conditions for the first experiment were Polymerization 1. The same process was used as in Polymerization 1, with the only difference that a phosphoric acid stabilizer (80 ppm) was added shortly before the vacuum was applied. This PET synthesis process is referred to as "Polymerization 3" (Table 3.3).

3.2.2.4. Repolymerization of PET with the addition of EG in different concentrations

Four different syntheses were performed. These syntheses contained different concentrations of EG to determine whether the addition of EG and the concentrations of EG added have an influence on the PET product obtained. In the first synthesis, the same process was used as in Polymerization 2, with the only difference that a phosphoric acid stabilizer (80 ppm) was added shortly before the vacuum was applied. This PET synthesis process is referred to as "Polymerization 4". In the other three syntheses, the same procedure was used as in the first synthesis, with the only difference being that different concentrations of EG was added before the reaction started. In these syntheses, the molar ratios of [BHET]: [EG] were 2:1, 1:1 and 1:2 (Table 3.3).

3.2.2.5. Repolymerization of PET with different BHET input materials

Two different syntheses were carried out using different types of BHETs as the input material. To observe whether recycled BHET has any effect on the PET product, recycled BHET was used in the first synthesis, while BHET from Sigma-Aldrich was used in the other synthesis. The process conditions of Polymerization 1 were used for both syntheses (Table 3.3).

3.2.2.6. Repolymerization of PET with different catalyst concentrations

Different concentrations of catalysts were used to investigate the effects of the concentration of catalysts used on the polymerization process and the properties of the PET obtained. In the general procedure of the synthesis reactions, 200 ppm Antimony (III) oxide and 30 ppm TTIP were used. The synthesis reactions were carried out with increasing concentrations of only one of the catalysts and with increasing concentrations of both catalysts simultaneously. In addition, the synthesis reactions were carried out with increasing concentrations of Antimony (III) oxide without the addition of TTIP (Table 3.3).

3.2.2.7. Repolymerization of PET with different vacuum times

Five different synthesis reactions were performed in which different vacuum times were applied to investigate whether the applied vacuum time has an influence on the PET product obtained. The same procedure was used for these synthesis reactions, with the only difference being that different vacuum times at 275°C were applied at the end of the reaction. The vacuum times were set to 30 min, 1 h, 90 min, 2 h and 3 h (Table 3.3).

Table 3.3. Conditions of polymerization of PET.

	BHET Type	**Catalyst**	**[BHET:EG] Mole Ratio**	**Time and Temperature**	**Vacuum Time**	**Vacuum Pressure**
Polymerization 1	Recycled BHET	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (30 ppm)	-	1 h at 190°C 2 h at 220°C 20 min at 275°C	30 min at 275°C	2 mbar
Polymerization 2	Recycled BHET	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (33 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	25 mbar
Polymerization 3	Recycled BHET	Antimony (III) oxide (200 ppm), titanium tetraisopropoxide (30 ppm) and phosphoric acid (80 ppm)	-	1 h at 190°C 2 h at 220°C 20 min at 275°C	30 min at 275°C	-1 bar*
Polymerization 4	Recycled BHET	Antimony (III) oxide (200 ppm), titanium tetraisopropoxide (30 ppm) and phosphoric acid (80 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	-1 bar*
Polymerization 5	Recycled BHET	Antimony (III) oxide (200 ppm), titanium tetraisopropoxide (30 ppm) and phosphoric acid (80 ppm)	1:1	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	-1 bar*
Polymerization 6	Recycled BHET	Antimony (III) oxide (200 ppm), titanium tetraisopropoxide (30 ppm) and phosphoric acid (80 ppm)	2:1	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 m at 275°C	30 min at 275°C	-1 bar*
Polymerization 7	Recycled BHET	Antimony (III) oxide (200 ppm), titanium tetraisopropoxide (30 ppm) and phosphoric acid (80 ppm)	1:2	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	-1 bar*

Table 3.3. Conditions of polymerization of PET *(continued)*.

	BHET Type	**Catalyst**	**[BHET:EG] Mole Ratio**	**Time and Temperature**	**Vacuum Time**	**Vacuum Pressure**
Polymerization 8	Purchased from Sigma Aldrich	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (30 ppm)	-	1 h at 190°C 2 h at 220°C 20 min at 275°C	30 min at 275°C	12 bar
Polymerization 9	Recycled BHET	Antimony (III) oxide (300 ppm) and titanium tetraisopropoxide (53 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	1 mbar
Polymerization 10	Recycled BHET	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (52 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	7 mbar
Polymerization 11	Recycled BHET	Antimony (III) oxide (300 ppm) and titanium tetraisopropoxide (30 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	9 mbar
Polymerization 12	Recycled BHET	Antimony (III) oxide (400 ppm) and titanium tetraisopropoxide (30 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	36 mbar
Polymerization 13	Recycled BHET	Antimony (III) oxide (300 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	7 mbar

Table 3.3. Conditions of polymerization of PET *(continued)*.

	BHET Type	**Catalyst**	**[BHET:EG] Mole Ratio**	**Time and Temperature**	**Vacuum Time**	**Vacuum Pressure**
Polymerization 14	Recycled BHET	Antimony (III) oxide (400 ppm)	-	1 h at 190°C 2 h at 220°C 2 h at 245°C 20 min at 275°C	30 min at 275°C	15 mbar
Polymerization 15	Recycled BHET	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (32 ppm)	-	1 h at 190°C 2 h at 220°C 20 min at 275°C	1 h at 275°C	7 mbar
Polymerization 16	Recycled BHET	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (30 ppm)	-	1 h at 190°C 2 h at 220°C 20 min at 275°C	1 h 30 minutes at 275°C	7 mbar
Polymerization 17	Recycled BHET	Antimony (III) oxide (200 ppm) and titanium tetraisopropoxide (32 ppm)	-	1 h at 190°C 2 h at 220°C 20 min at 275°C	2 h at 275°C	7 mbar
Polymerization 18	Recycled BHET	Antimony (III) oxide (300 ppm) and titanium tetraisopropoxide (39 ppm)	-	1 h at 190°C 2 h at 220°C	3 h at 275°C	9 mbar

[*] The pressure was measured as -1 bar using an analog manometer in these reactions, where the measurement was not done using a digital manometer.

3.2.2.8. Solid state polymerization of PET

A certain amount of PET obtained from the PET synthesis under the reaction condition Polymerization 2 was pulverized using a mortar and pestle. The pulverized PET was placed in a three-necked flask equipped with a condenser, a thermometer, and an argon inlet. In the first SSP reaction (SSP 1), the PET was heated to 220°C and when the temperature reached 220°C, vacuum was applied. After 6 hours, the SSP was terminated by simultaneously switching off the vacuum and the heating. In the second SSP (SSP 2), the PET was heated to 230°C and then a vacuum was applied for 6 hours. In SSP 3, the same PET product obtained using the reaction conditions of Polymerization 2 was pulverized and then passed through a 90-micron sieve and then the same procedure as for SSP 1 was applied. In another SSP process (SSP 4), the PET obtained from the PET synthesis under the reaction condition Polymerization 9 was placed in a three-necked flask and the same procedure as in "SSP 1" was used. PET samples were taken after 2 hours, 4 hours and 6 hours for all SSP processes. In the last SSP process (SSP 5), the PET obtained from SSP 1 was passed through a 90-micron sieve and then kept under vacuum at 220°C for 6 hours. Samples were taken after 3h and 6h. The conditions for SSP reactions are given in the Table 3.4.

Table 3.4. Conditions of SSP of PET.

	Melt Polymerization Catalyst Concentration		**Temperature (°C)**	**Time (hour)**	**Particle Size (µm)**
	Antimony (III) oxide	Titanium tetraisopropoxide			
SSP 1	200 ppm	33 ppm	220	6	> 90
SSP 2	200 ppm	33 ppm	230	6	>90
SSP 3	200 ppm	36 ppm	220	6	<90
SSP 4	300 ppm	52 ppm	220	6	>90
SSP 5	200 ppm	33 ppm	220	12	<90

3.2.3. Characterization

3.2.3.1. Fourier-transform infrared (FTIR) spectroscopy

The FT-IR analysis of the BHET and PET samples was performed with the Thermo Scientific Nicolet IS50 spectrometer. A minimum of 32 scans with a signal resolution of 4 cm-1 within the 600-4000 cm-1 range were averaged to obtain FT-IR spectra.

3.2.3.2. Differential scanning calorimetry (DSC)

A Mettler Toledo 3+ was used for the DSC analysis of the BHET samples. The samples were heated from 25° to 260°C, then cooled to 25°C, and then reheated to 260°C again. Data was collected at a heating/cooling rate of 10°C/min. The heating rate was set to 10 K/min. Dry nitrogen was used as purge gas at a flow rate of 60 mL/min. 1st heating steps are shown on the thermograms.

The DSC analysis of the PET samples was performed using the TA Instrument. The samples were heated from 25°C to 300°C, then cooled to 25°C and then reheated to 300°C. The heating rate was set to 10°/min and nitrogen was used as purge gas. 2nd heating steps are shown on the thermograms.

3.2.3.3. Thermal gravimetric analysis (TGA)

TGA analysis of BHET samples was performed using the Mettler Toledo TGA DSC 3+ by heating from 25°C to 750°C. The heating rate and N_2 flow rate were set to 10 K/min and 100 mL/min, respectively. The TA Instrument was used for TGA analysis of the PET samples. The analysis was performed between 20°C and 800°C in nitrogen atmosphere and between 800°C and 1000°C in oxygen atmosphere. The heating rate was set to 20°C/min.

3.2.3.4. Nuclear magnetic resonance (NMR)

The NMR spectra of the BHET samples were recorded with the Varian UNITY INOVA digital spectrometer operating at 500 MHz. The chemical structure of the BHETs was analyzed by ^1H NMR in deuterium dimethylsulfoxide solvent (DMSO-d6). The NMR spectra of the PET samples were recorded with the Mercury-VX 400 BB spectrometer operating at 400 MHz. The chemical structure of the PET samples was analyzed by ^{1}H NMR in solvent of deuterated trifluoroacetic acid (TFA-d1).

3.2.3.5. Intrinsic viscosity (IV)

The IV analysis of the PET samples was performed using the IV miniPV-HX Automated Viscometer. The PET sample was dissolved in o-chlorophenol and then placed in an automatic viscometer.

3.2.3.6. Carboxyl end group (CEG)

For the CEG analysis, PET samples were dissolved in o-cresol chloroform at a certain concentration. 0.1 N potassium hydroxide was used as titrant and the resulting solution was added to the automatic titrator. The instrument used for the CEG analysis was Metrohm.

3.2.3.7. Gel permeation chromatography (GPC)

Prior to GPC analysis, approximately 6 mg PET was dissolved in 2 ml 1,1,1,3,3,3 hexafluoroisopropanol. The resulting solution was filtered with a 0.45 mm PTFE filter. The sample was filtered into a 1 ml autosampler vial and the cap of the vial was closed. The vial was then placed in the device for analysis. The instrument used for the GPC analysis was the GPC-Wyatt technology.

CHAPTER 4

4. Depolymerization of PET by Glycolysis Method

4.1. Introduction

PET is a one of the main types of plastics that is produced in large quantities and is very useful for various applications. The high production of PET leads to huge amounts of PET waste, which causes destruction of the natural environment. Therefore, recycling of PET waste is an important task that needs to be considered (Suhaimi et al., 2022). Accordingly, the PET materials were chemically recycled in the first part of the study. For the chemical recycling of PET, the glycolysis method was preferred thanks to its advantages such as simplicity, efficiency and cheapness. Different types of PET materials; transparent PET beverage bottles, coloured PET beverage bottles, PET yarns without finish and PET yarns with finish were depolymerized by glycolysis method using zinc acetate ($Zn(OAc)_2$). In the second step, the depolymerization of PET yarns using different catalysts was investigated. ($Zn(OAc)_2$), 1,3-Dimethylurea/$Zn(OAc)_2$ deep eutectic solvent (1,3-DMU/$Zn(OAc)_2$ DES) and Butyl-3-methylimidazolium bromine ([Bmim]Br) were used as catalysts in depolymerization reactions. The yields of applied glycolysis processes were evaluated. In addition, the obtained BHET was analysed by using FTIR, DSC, TGA and NMR.

4.2. Results and Discussion

4.2.1. Depolymerization of different types of waste PET materials

4.2.1.1 PET conversion rate and BHET yield

As a result of applying the depolymerization process to different types of PET materials, BHETs were obtained. The PET conversion rates and BHET yields were calculated, and the equation used to calculate the BHET yield is presented as an Equation 4.1 in which the BHET yield is equal to the moles of BHET collected divided by the total moles of fed PET units.

$$\mathrm{YBHET} = \frac{n_{BHET}}{n_{units}} \times 100\% \quad \text{...............} \quad \text{Equation 4.1.}$$

The PET conversion rates were higher than 98% regardless of the PET materials used in all glycolysis reactions. This result showed that long polymer chains were successfully cleaved into short oligomers or monomers. The steps after the depolymerization process were the heating, stirring and re-filtering of the oligomers and BHET mixture so that the BHET was purified from the oligomers. After that, the yield of the BHET could be calculated. When evaluating the BHET yields, it was found that the BHET yields were higher than 80% as desired, except for the depolymerization of green PET bottles. The PET conversion rates and BHET yields obtained from the depolymerization of different types of PET materials are presented in Table 4.1.

Table 4. 1. PET conversion rates and BHET yields obtained.

Type of PET Material	**PET Conversion (%)**	**BHET Yield (%)**
Transparent PET	99.82	82.07
PET yarn	99.80	87.88
PET yarn (103895-Code208)	99.95	87.59
PET yarn (108619-T6900)	99.63	85.06
Colored PET (green)	98.15	66.97

When green PET bottles were depolymerized using $Zn(OAc)_2$ as the catalyst, the BHET yield was 66.97%, which was probably due to the fact that the colorants and additives had adverse effects on glycolysis. During the depolymerization of the green PET bottles, it was observed that it took a very long time for the green PET bottle pieces to disintegrate into smaller pieces, and at the end of the reaction, it was observed that the homogeneity of the mixture was lower compared to other depolymerization reactions. This observation suggested that the colorants and additives had a slowing effect on the depolymerization reaction. Another evaluation that supported this inference was that PET conversion was high, but BHET yield was low, which might indicate that there was enough time for oligomers to form but not enough time for the oligomers to cleave into smaller BHET molecules. Another possibility was that the colorants and additives reduced the swelling capacity of PET in EG, which hindered the contact with the catalyst (Yang et al., 2024).

In this case, the short reaction time might not be sufficient to fully swell PET and complete degradation did not occur. In addition, it was observed that the colorants and additives tended to discolor the glycolized products. While the oligomers appear green, the BHET has a yellowish color.

When the BHET yields obtained from the depolymerization reaction of PET yarn with finish were examined, it was found that the BHET yields were as high as those obtained from the depolymerization reaction of PET yarn without finish. This demonstrated that the chemicals contained in the finish did not have a negative influence on the reaction and did not play a chemical role in the process.

4.2.1.2. FTIR analysis

In the FTIR spectra, given in Figure 4.1, all the BHETs displayed the same peaks. The peaks at 1709 cm^{-1} and 1260 cm^{-1}corresponded to the stretching of the C=O bond and the C-O bond, respectively. These were the main bands that approved the generation of the ester bond during the glycolysis of PET (Ghaderian et al., 2015). The absorption peak around 2960 cm^{-1} represented the C-H bond bands in the structure of methyl groups. The absorption peak at 3440 cm^{-1} was assigned to the hydroxyl (OH) groups, indicating that the polymer chain was cleaved and BHET was formed (Silva et al., 2018). When comparing the OH peaks of BHET from the depolymerization reaction of PET bottles and BHET from the depolymerization reaction of PET yarn, it could be seen that the OH peaks of BHET from the depolymerization reaction of PET yarn were broader and slightly shifted to lower frequencies. It is known that hydrogen bonding leads to a broadening and shifting of absorption peaks to lower frequencies. Therefore, the reason for the broadening and shifting of the OH peak, may be the presence of hydrogen bonds (Sahoo et al., 2018). Furthermore, when the absorbance peaks of all the obtained BHETs were compared with the absorbance peaks of commercial BHET, it was observed that the peaks were largely similar, confirming that the depolymerization reaction and BHET synthesis was successful.

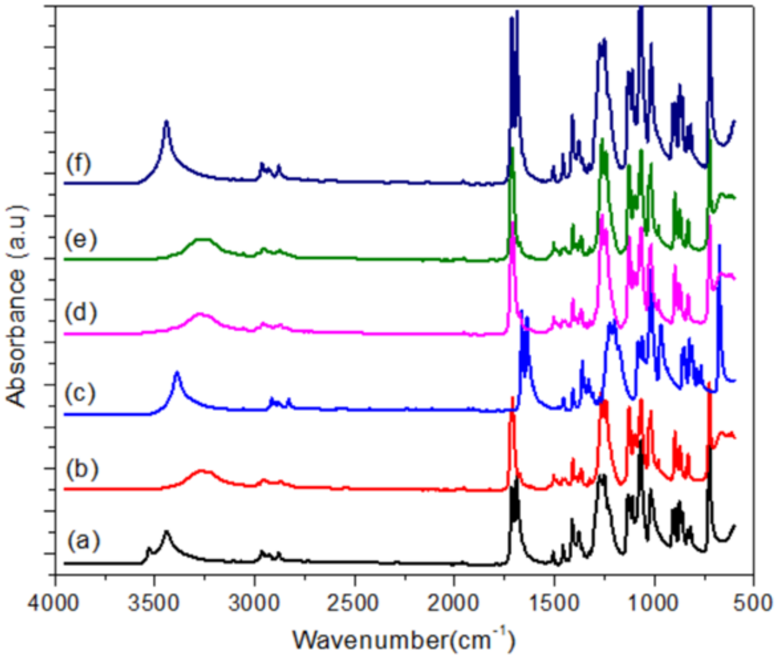


Figure 4.1. FTIR spectra of BHETs obtained from different input materials in comparison with each other and with the commercial BHET: (a)Transparent PET; (b)PET yarn; (c) Colored PET (green); (d) PET yarn (103895-Code208); (e) PET yarn (108619-T6900); (f) Reference.

4.2.1.3. DSC analysis

The DSC thermograms of the samples showed endothermic peaks at about 110 °C and a sharp endothermic peak at about 110°C was also observed in the DSC thermogram of the commercial BHETs, which showed that the obtained BHETs were similar to the commercial BHETs in terms of their melting point (Figure 4.2). However, the melting temperature of the BHETs obtained from polyester yarns (about 116°C) was higher than the melting temperature of the BHETs obtained from PET bottles and also the commercial BHETs. Also, BHETs obtained from PET yarns had a higher enthalpy. This was attributed to the higher degree of crystallinity of PET yarns.

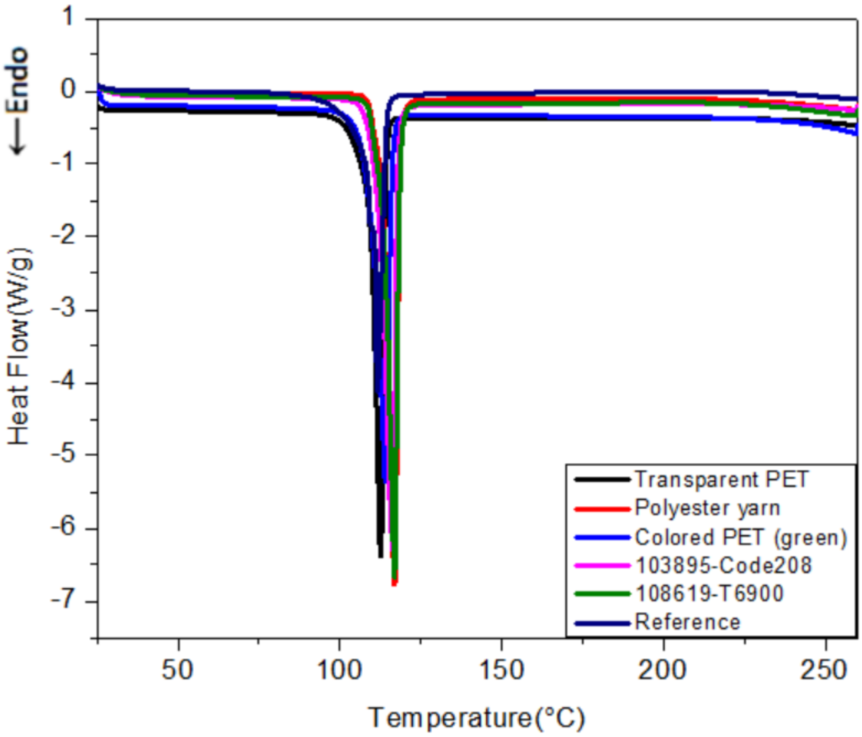


Figure 4.2. DSC thermograms of BHETs obtained from different input materials in comparison with each other and with the commercial BHET.

4.2.1.4. TGA analysis

The decomposition process of all BHETs is divided into two steps. The first step takes place between 25-370°C with an initial temperature of 240°C, with a weight loss of about 25% due to the thermal decomposition of BHET. The second step takes place between 370-750°C with an initial temperature of 400°C and has a weight loss of about 60%, which is caused by the thermal decomposition of PET formed by the repolymerization of BHETs that takes place through the heating process (Al-Sabagh et al., 2014). According to the TGA thermograms (Figure 4.3), all the BHETs obtained displayed this characteristic decomposition behavior. Moreover, the decomposition profile of the commercial BHET was very similar to the decomposition profile of all BHETs obtained which was a desired result. It was found that the residue percentage of BHET obtained from the colored bottle was slightly higher than the residue percentage of BHET obtained from other input materials and commercial BHET. This showed that the trace amount of colorants and additives contained in PET remained as residues when the BHET itself was burned. In addition, the residue percentage of BHET obtained from the PET yarns with finish was found to be similar to the residue percentage of BHET obtained from the PET yarns without finish. This could be an indication that no finish residues remained on the BHET obtained from PET yarns with finish.

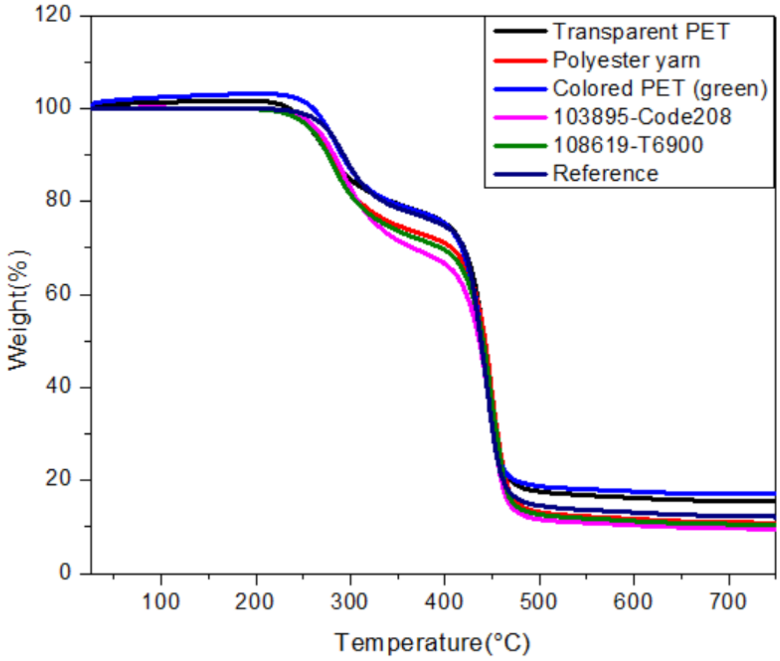


Figure 4.3. TGA thermograms of BHETs obtained from different input materials in comparison with each other and with the commercial BHET.

4.2.1.5. ^{1}H-NMR analysis

The ^{1}H-NMR spectra of the BHETs obtained from different PET waste materials are presented in Figure 4.4. All the BHETs obtained displayed similar signals on the ^{1}H-NMR spectra. The signal at δ=8.1 ppm (s, 4H) was assigned to the four aromatic protons of the benzene ring. The signals at 3.7 ppm (m, 4H) and 4.3 ppm (t, 4H) corresponded to the methylene protons of $CH_2{-}OH$ and $COO{-}CH_2$, respectively. The signal at 4.9 ppm (t, 2H) represented the OH groups located at both ends of the BHET (Figure 4.4). In the ^{1}H-NMR spectra, two signals could be observed in addition to the signals assigned to the protons of BHET. The first at 2.5 represented the protons of DMSO-d6, which was used as a solvent, and the second at 3.3 ppm represents the protons of H_2O (Lima et al., 2017). When these ^{1}H-NMR spectra of BHETs were compared with ^{1}H-NMR spectrum of pure BHETs found in the literature, it could be concluded that the BHETs obtained from glycolysis reactions were in high purity despite the different nature of the input waste PET materials.

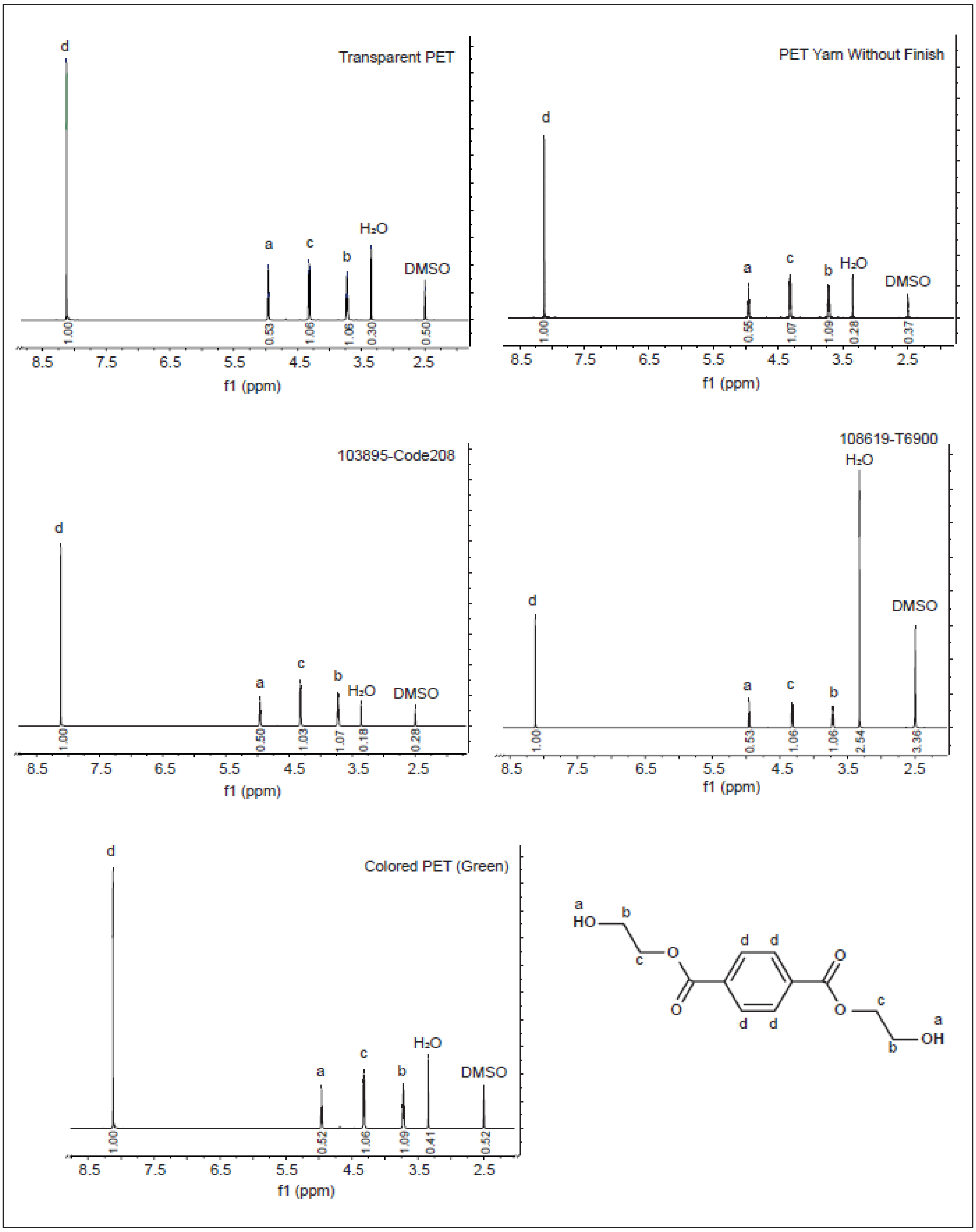


Figure 4.4. Comparison of the ^{1}H NMR spectra of BHETs obtained from the glycolysis with different catalysts.

4.2.2. Depolymerization of PET yarn with different catalysts

4.2.2.1 PET conversion rates and BHET yield

The PET conversion rates were higher than 96% regardless of the catalyst used. When investigating the required reaction times, it was found that when using the 1,3-DMU/$Zn(OAc)_2$ DES catalyst, 20 minutes was sufficient to complete the glycolysis reaction, whereas when using the $Zn(OAc)_2$ catalyst, 60 minutes was required to complete the glycolysis reaction for the same amount of input PET. On the other hand, when [Bmim]Br IL was used as a catalyst, it was observed that a much longer reaction time was required. Thus, when the reaction is evaluated in terms of reaction time efficiency, the best result was obtained with the 1,3-DMU/$Zn(OAc)_2$ DES catalyst. The H-bonds formed thanks to the DES might have allowed the formation of more catalytically active sites. Briefly, various hydrogen and oxygen atoms present in urea, EG and PET structures could form hydrogen bonds with each other and lead to an increase in the number of catalytically active sites. The coordination bonds formed between Zn^{2+} and the oxygen of the hydroxyl group in EG is known to lengthen the O-H bond of the hydroxyl group in EG, leading to an increase in the electronegativity of the oxygen atoms, which facilitates the loss of the hydrogen atoms. This can cause the easier attack of oxygen on the carbon of the ester group of PET, leading to an increased rate of the glycolysis reaction (Wang et al., 2015). Thus, if the reaction time of glycolysis is a critical parameter, 1,3-DMU/$Zn(OAc)_2$ may be preferred as a catalyst.

As for the BHET yield, it was sufficiently high when $Zn(OAc)_2$ and 1,3-DMU/$Zn(OAc)_2$ were used as catalysts. The BHET yield was higher when $Zn(OAc)_2$ was used compared to 1,3-DMU/$Zn(OAc)_2$, indicating that the addition of $Zn(OAc)_2$ dissolved in a solvent in liquid form led to a slight decrease in BHET yield compared to addition in pure solid form. When [Bmim]Br IL was used as the catalyst for recycling PET yarn, the BHET yield was 18.72% (Table 4.2). When compared to other types of catalysts, this BHET yield was considered as too low. The main advantage of using IL as a catalyst is that it can be easily removed from the final products, resulting in the formation of high purity BHET. It is also known that metallic catalysts have some harmful effects on the environment, so metal-free ILs may be preferred as catalysts when focusing more on environmental issues (Khoonkari et al., 2015). However, the low yield and long reaction time make [Bmim]Br IL a less recommendable catalyst compared to other catalysts.

Table 4.2. PET conversion rates and BHET yields obtained.

Type of Catalyst	**PET Conversion (%)**	**Yield (%)**
$Zn(OAc)_2$	99.80	87.88
1,3-DMU/$Zn(OAc)_2$ DES	99.34	78.59
[Bmim]Br IL	96.75	18.72

4.2.2.2. FTIR analysis

The FTIR spectra of the BHETs obtained by using different catalysts are presented in Figure 4.5. All the BHETs obtained and commercial BHET displayed the same peaks in the FTIR spectra. In section 4.2.1.2. the absorption peaks representing the chemical structure were explained. Thanks to the agreement of the absorption peaks of the BHETs obtained by us with the commercial BHET and the definition of the absorption peaks of BHET in the literature, it could be claimed that the obtained BHETs were almost pure regardless of the catalyst used. When comparing the OH peaks of BHET obtained with $Zn(OAc)_2$ with other BHETs, it could be seen that the OH peak of BHET obtained with $Zn(OAc)_2$ was broader and slightly shifted to lower frequencies. In the literature, this is associated with the presence of hydrogen bonding (Sahoo et al., 2018). However, this was not observed when other catalysts were used, the OH peaks were narrower and at the same frequency as commercial BHET (Figure 4.5).

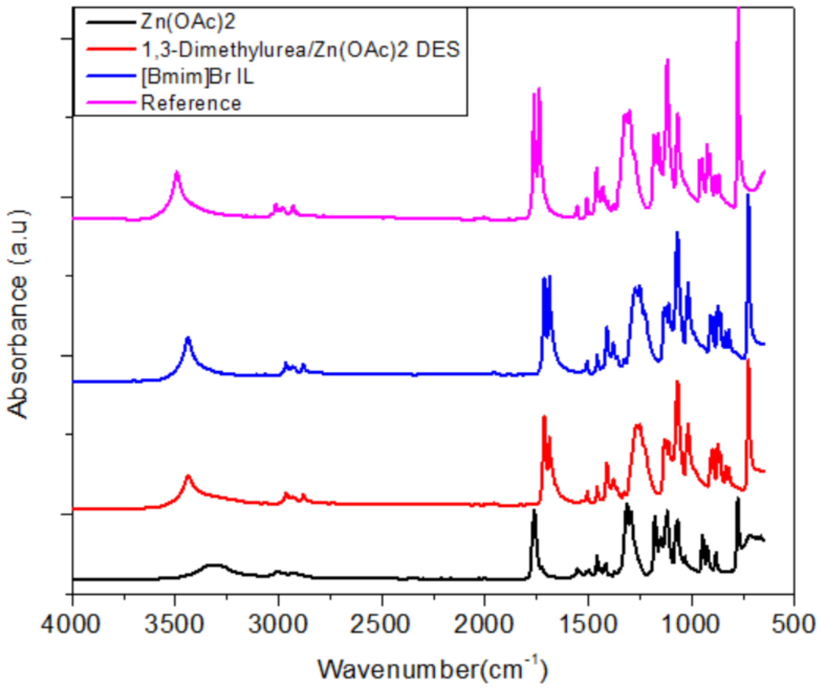


Figure 4.5. FTIR spectra of BHETs obtained from the glycolysis with different catalysts in comparison to commercial BHET.

4.2.2.3. DSC analysis

A sharp endothermic peak around 110°C was observed in the DSC thermogram of the commercial BHET. The DSC thermograms of the obtained BHETs also showed endothermic peaks at around 110°C, which showed that the BHETs obtained were similar to commercial BHET with regards to their melting behaviour and crystal structure (Figure 4.6). On the other hand, it was observed that BHET obtained as a result of the glycolysis reaction with the use of $Zn(OAc)_2$ as a catalyst had higher enthalpy value which meant it required higher amount of heat to melt.

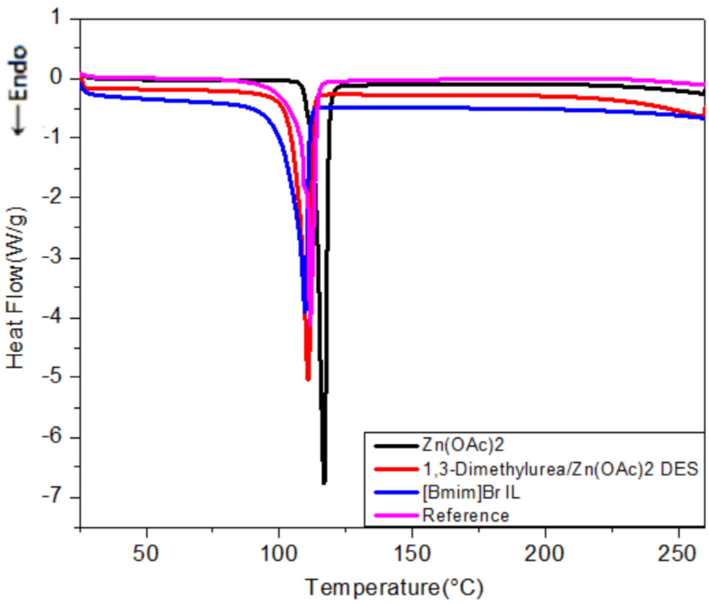


Figure 4.6. DSC thermograms of BHETs obtained from the experiments with different catalysts in comparison to commercial BHET.

4.2.2.4. TGA analysis

As explained in Section 4.2.1.4, TGA thermograms of a BHET are divided into two steps. The first step takes place between 25-370℃ and the second step between 370-750 ℃. When analyzing the decomposition profile of BHETs obtained from glycolysis reactions in which different catalysts were used, these two decomposition steps were clearly visible. Therefore, it could be said that the use of a catalyst had no significant effects on the decomposition profiles of BHET. However, when examining the decomposition profile of BHET obtained by glycolysis using [Bmim]Br IL catalyst, the percentage weight loss in the first step was much higher and the weight loss in the second step was much lower compared to the decomposition profiles of other BHETs (Figure 4.7). This showed that less amount of BHET was converted to PET during the TGA analysis.

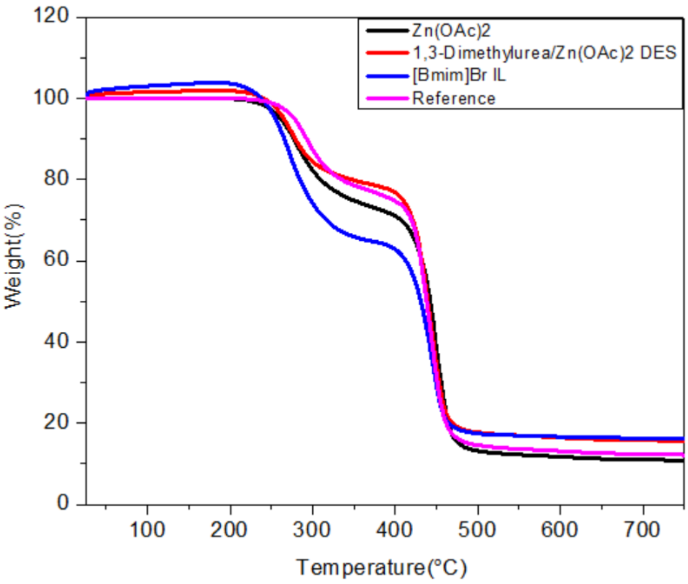


Figure 4.7. TGA thermograms of BHETs obtained from the experiments with different catalysts in comparison to commercial BHET.

CHAPTER 5

5. Repolymerization of PET

5.1. Introduction

Monomers which are obtained from chemical recycling of PET can serve as the starting material for the production of new materials. BHET, the main product of the glycolysis of PET, is also used in various industries, e.g. in the production of resins and foams as well as in the synthesis of PET in one step. When the BHET is used as the starting material for the resynthesis of PET, the synthesis process consists only of the polycondensation step of BHET. In general, polycondensation processes are carried out at high temperatures and low pressure. The usual catalysts are antimony and titanium-based catalysts (Westover and Long, 2023).

In the second part of the study, BHET was converted to PET and SSP was applied to increase the molecular weight of PET polymer. Repolymerization reactions were performed to synthesize PET from recycled BHET. Several repolymerization reactions were carried out under different reaction conditions to investigate the effects of different synthesis conditions. The influences of the reaction time of the repolymerization and the applied vacuum time on the properties of the PET products were investigated. In addition, EG in different concentrations and phosphoric acid were added to the repolymerization reactions and their effects on the PET products obtained were evaluated. The catalyst concentrations added were changed and the best catalyst concentration leading to the formation of PET with the desired properties was investigated. Finally, a polymerization reaction with untreated BHET was carried out to evaluate the difference in the properties of PET compared to PET obtained from recycled BHET. The IV value and the number of CEGs of the obtained recycled PET samples were analysed. Furthermore, the obtained PET samples were analysed by FTIR, DSC, TGA, NMR and GPC.

SSP processes were performed under different reaction conditions varying the reaction time, and reaction temperature. Besides the effect of the particle size was investigated. Moreover, SSP reactions were performed with PET samples obtained from repolymerization reactions in the presence of different catalyst concentrations to analyse the effect of catalyst concentration on the SSP process. IV values and number of CEGs of the obtained PET samples were analysed. Moreover, the obtained PET samples were analysed using DSC.

The results with regards to IV, CEG, melting temperature, thermal decomposition temperature of the polymers obtained from repolymerization reactions are presented in Table 5.1.

5.2. Results and Discussion

5.2.1. Repolymerization of PET

5.2.1.1. Effect of the repolymerization reaction time

In contrast to the Polymerization 1, in which the temperature was kept at 220°C for 2 hours and then directly increased to 275°C in the Polymerization 2 after the BHET was kept at 220°C it was kept at 245°C for 2 hours and then the temperature was increased to 275°C, which means that Polymerization 2 has a longer reaction time at low temperature. It was found that the reaction time at low temperature values led to a slight increase in the IV value and a decrease in the number of CEGs (Figure 5.1). Theoretically, the polymerization of PET is a second order reaction with respect to BHET alone and accordingly, the degree of polymerization is directly proportional to the time and the number of moles of BHET. Therefore, an increase in time likely led to an increase in the degree of polymerization, resulting in a higher molecular weight of the PET product (Lin and Baliga, 1986).

Table 5.1. Summary of the results of all repolymerization reactions using BHET.

	IV (dL/g)	**CEG (mmol/kg)**	**% Crystallinity**	**Melting temperature (°C)**	**Decomposition temperature (°C)**
Polymerization 1	0.116	40.3	54.70	233.65	447.87
Polymerization 2	0.140	13.4	58.35	241.49	450.09
Polymerization 3	0.148	20.4	58.24	243.44	446.43
Polymerization 4	0.135	69.7	56.80	238.48	449.81
Polymerization 5	0.117	22.3	56.07	236.61	449.90
Polymerization 6	0.137	14.6	56.55	239.09	448.14
Polymerization 7	0.132	17.1	56.57	235.48	447.39
Polymerization 8	0.130	27.9	55.34	238.58	445.22
Polymerization 9	0.145	16.0	58.33	243.33	452.40
Polymerization 10	0.227	27.6	57.83	244.98	450.20
Polymerization 11	0.499	14.5	59.79	247.30	449.25
Polymerization 12	0.188	14.1	57.85	243.94	450.00
Polymerization 13	0.301	15.8	60.30	245.78	452.31
Polymerization 14	0.324	25.9	58.72	242.31	454.90
Polymerization 15	0.200	22.7	59.47	245.22	450.23
Polymerization 16	0.312	10.9	61.03	253.74	450.65
Polymerization 17	0.244	43.9	59.27	248.45	450.44
Polymerization 18	insoluble	insoluble	59.69	249.92	450.45

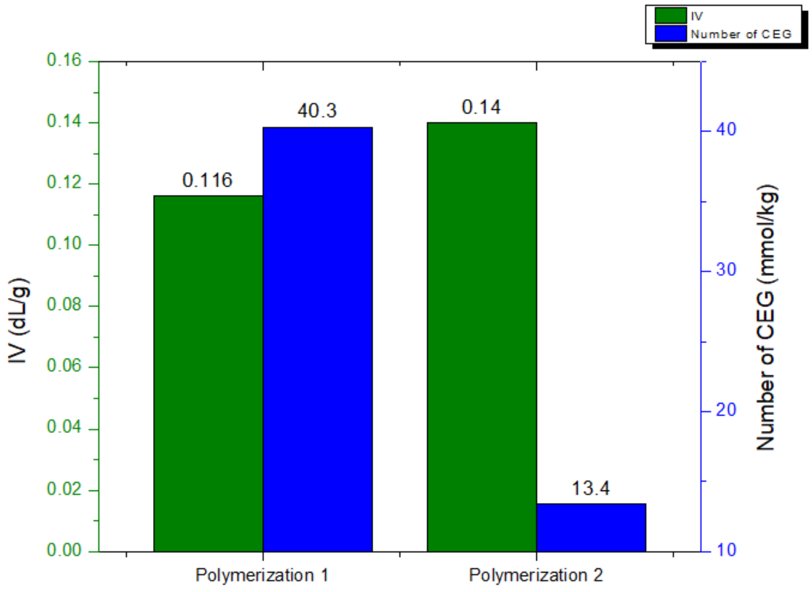


Figure 5.1. Comparison of the IV values and the number of CEG of PET obtained from Polymerization 1 and Polymerization 2.

Since the increase in molecular weight is known to be directly proportional to the increase in IV, our results are consistent with existing theory and literature. A higher IV means longer polymer chains, which are subject to less cleavage and less formation of CEGs (Venkatachalam et al., 2012). Therefore, it is logical that the resulting polymer with higher IV also has a lower number of CEGs. When the results are examined in terms of temperature, 245°C can be accepted as a low temperature for the PET synthesis process. In short, the degradation reactions result in the breaking of the polymer chains, leading to the formation of short polymer chains with a dominant CEG, resulting in a low IV (Dimonie et al.,2012). Therefore, 245°C is not sufficient for degradation reactions to take place, which means that this temperature set for the reaction before vacuum may not lead to a reduction in IV.

5.2.1.1.1. DSC analysis

The PET obtained from Polymerization 1 and Polymerization 2 were analyzed using DSC. The DSC thermograms of the 2nd heating cycle of these PETs are shown in Figure 5.2. They both had distinct peaks for melting temperature (T_m), and while the T_m of Polymerization 1 was 233.65°C, the T_m of Polymerization 2 was 241.49°C. It could be clearly seen that increasing the polymerization reaction time at relatively low temperatures caused the curve of the DSC thermogram to shift towards higher temperatures and become narrower. Since the molecular weight of PET obtained from Polymerization 2 was higher, the crystallinity of its macromolecular chains was greater, which contributed to the formation of a more perfect crystal structure. This resulted in the melting peaks to shift towards higher temperature and become much narrower (Chen et al., 2007). The area under the peak of the PET obtained by Polymerization 2 (57.5 J/g) was larger than the area under the peak of the PET obtained by Polymerization 1 (51.4 J/g). In other words, more energy was needed to melt the PET obtained by Polymerization 2, which could be due to its higher crystallinity.

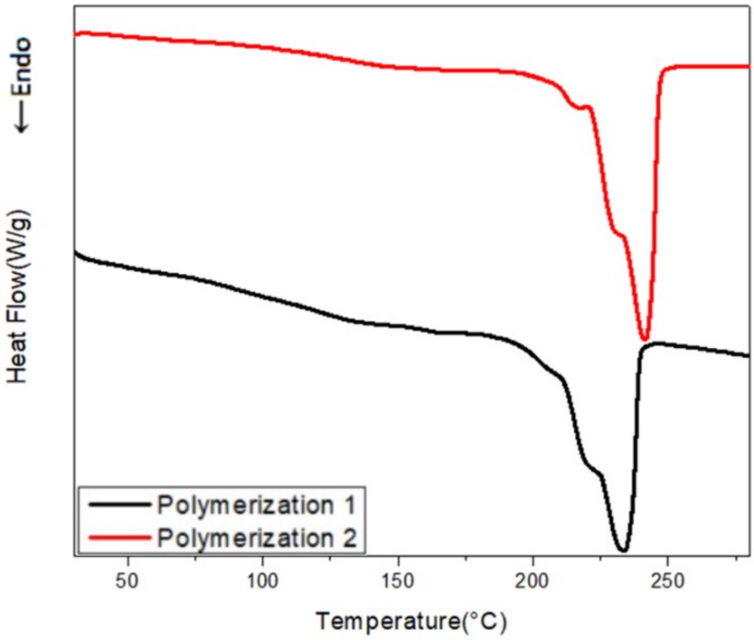


Figure 5.2. Comparison of the DSC thermograms of PET obtained from Polymerization 1 and Polymerization 2.

5.2.1.2. Effect of the addition of phosphoric acid

A phosphoric acid stabilizer was added shortly before the vacuum was applied in order to analyze its effect on the polymerization reaction (Polymerization 3). It is known that phosphoric acid is one of the most commonly used stabilizers for PET polycondensation, which improves thermal stability and reduces the degradation of the PET polymerization process. The addition of stabilizers can help to maintain the IV of PET and suppress the number of CEGs (Scheirs and Long, 2003). It was found that the addition of phosphoric acid resulted in a minor increase in the IV value and a decrease in the number of CEGs (Figure 5.3).

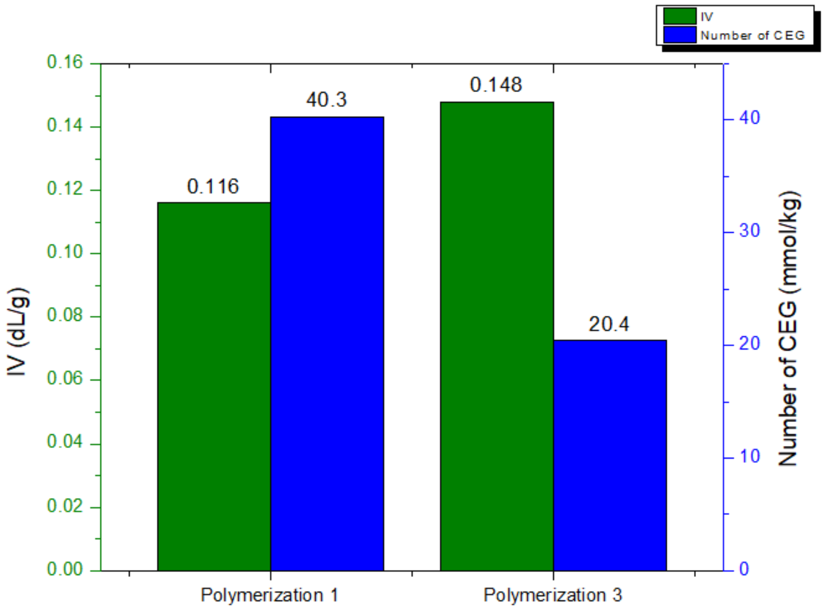


Figure 5.3. Comparison of the IV values and the number of CEG of PET obtained from Polymerization 1 and Polymerization 3.

The phosphoric acid stabilizer forms a complex structure with the antimony (III) oxide catalyst, and this structure accelerates the polycondensation rate, resulting in an increase in molecular weight and a decrease in the number of CEGs (Figure 5.4A). (Kamatani et al., 1980). Furthermore, the phosphoric acid stabilizer forms a complex structure with the titanium-based catalysts, the residues of which can be the cause of various undesirable side reactions and thermal instabilities (Fortunato et al., 1994). Both antimony (III) oxide and titanium tetraisopropoxide catalysts were used in our polymerization reactions. It was therefore possible for complex structures to form between the phosphoric acid and the catalysts, which could lead to an acceleration of the polycondensation rate and the suppression of undesirable side reactions resulting in an increase in the IV value and a decrease in the number of CEGs (Figure 5.4B). However, the IV increase was not too high, which could be explained by the fact that although the complex structures formed could have limited PET pyrolysis and undesired reactions, they could also have limited the effect of the titanium catalyst on chain growth, resulting in a reduction in molecular weight.

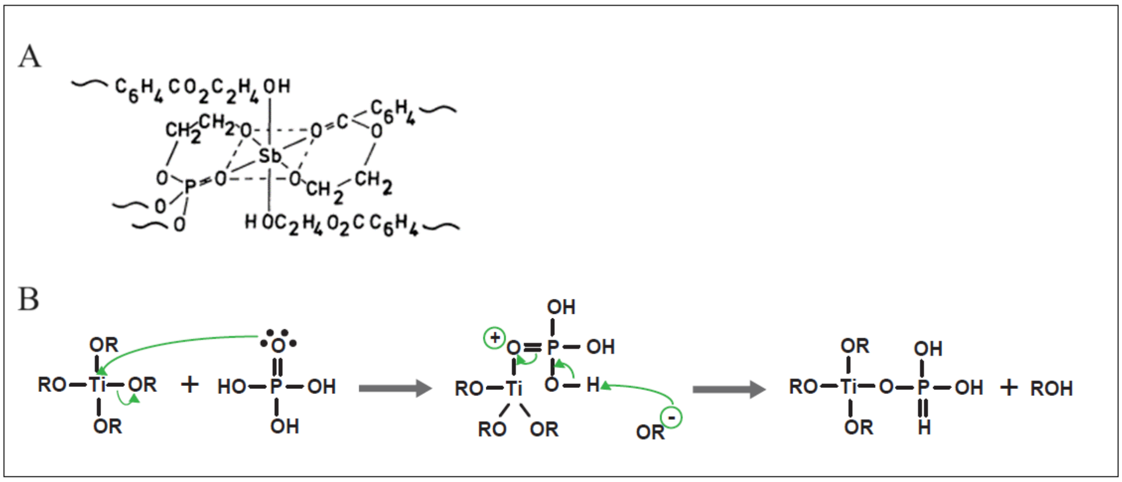


Figure 5.4. (A) Complex structure consisting of phosphoric acid and antimony (III) oxide catalyst (Kamatani et al., 1980). (B) Complex structure consisting of phosphoric acid and titanium-based catalyst.

5.2.1.2.1. DSC analysis

The DSC thermograms of PET obtained from Polymerization 1 and Polymerization 3 were analyzed and compared with each other (Figure 5.5). As a result of the phosphoric acid addition the melting peak shifted towards higher temperatures and became narrower. The addition of phosphoric acid contributed to higher T_m values, indicating that the addition of the stabilizer could have suppressed the formation of ether structures in the PET chains, which meant that the ratio of the aliphatic part to the aromatic part in the PET chain decreased. This led to the lower flexibility of the PET molecular chains, lower mobility and enhanced crystal integrity (Patkar and Jabarin, 1993). The area under the peak of the PET obtained by Polymerization 3 (56.8 J/g) was larger than the area under the peak of the PET obtained by Polymerization 1 (51.4 J/g). It can therefore be claimed that the addition of phosphoric acid led to an increase in crystallinity.

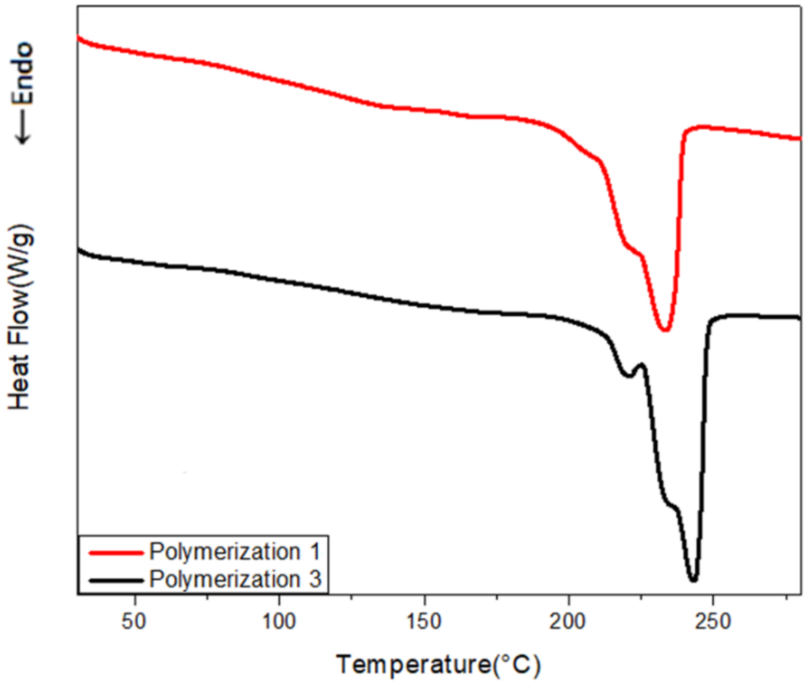


Figure 5.5. Comparison of the DSC thermograms of PET obtained from Polymerization 1 and Polymerization 3.

5.2.1.3. Effect of the addition of EG in different concentrations

Three syntheses contained different concentrations of EG to determine whether the addition of EG and the concentration of EG added had an effect on the PET product obtained. The same procedure was used in the synthesis reactions and the molar ratios of [BHET]:[EG] were 2:1, 1:1 and 1:2. As a control, the synthesis was also carried out without the addition of EG using the same procedure. It was predicted that the addition of EG to the synthesis process could lead to an increase in the molecular weight of the resulting PET. Recycled BHET was used as the starting material for PET polymerization.

The addition of EG means the presence of free EG in the mixture, so that the added catalysts can be easily dissolved at the beginning of the reaction and uniformly mixed into the low-viscosity mixture (Duh, 2002). Additionally, since the input material used is recycled BHET, it may not be 100% pure BHET and may contain structures that have two CEGs or one CEG instead of two hydroxyl end groups. These structures, which have a CEG, can react with EG and form an hydroxyl end group, whereby water is removed. As a result of this reaction, BHET can be formed, which can contribute to a polycondensation reaction and convert into PET (Figure 5.6) (Deopura et al., 2008).

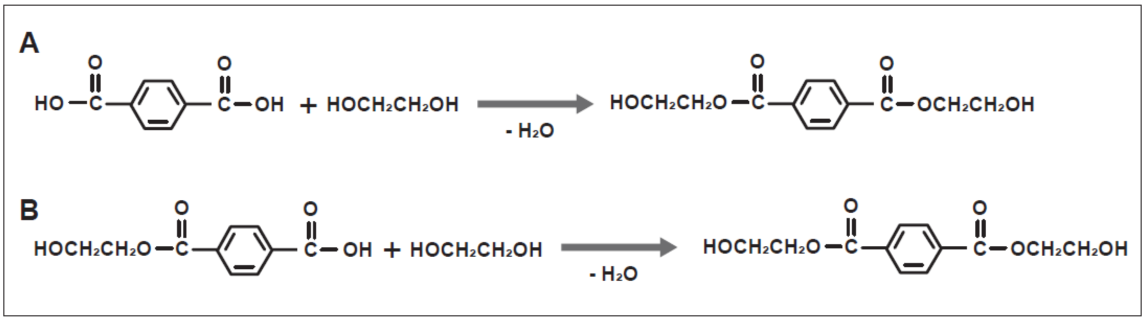


Figure 5.6. Mechanism of BHET formation (A) BHET formation by reaction of a structure with two CEGs with EG. (B) BHET formation by reaction of a structure with one CEG with EG.

It was found that the addition of EG did not lead to a significant increase in the IV value and a decrease in the number of CEGs (Figure 5.7). Only the number of CEGs of PET obtained with polymerization 4 was higher. This might be due to the fact that the reaction had to be interrupted for a while and then resumed due to the unexpected experimental conditions. This may also indicate that EG did not react with structural groups that had two CEGs or one CEG, which could be considered as evidence that recycled BHET contained a very small number of different structures of BHET. It can also be mentioned that the dissolution and uniform mixing of the catalysts in EG at the beginning of the reaction did not have a great influence on the PET obtained.

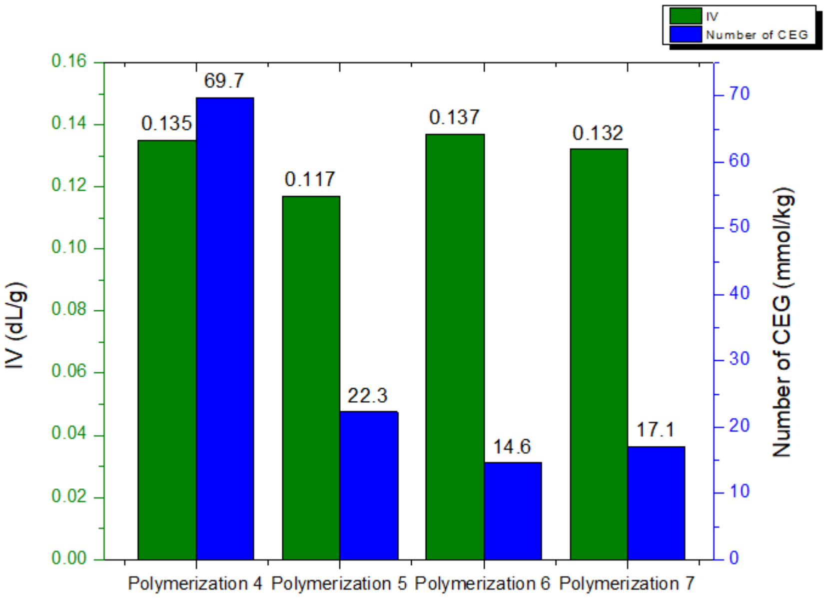


Figure 5.7.Comparison of the IV values and the number of CEG of PET obtained from polymerization reactions containing different concentrations of EG.

5.2.1.3.1. DSC analysis

The DSC thermograms of PET obtained by polymerization reactions with the addition of different concentrations of EG supported the conclusion that EG had no considerable influence on the PET obtained, as it was found that the addition of EG has no significant effect on the melting curves of PET obtained (Figure 5.8).

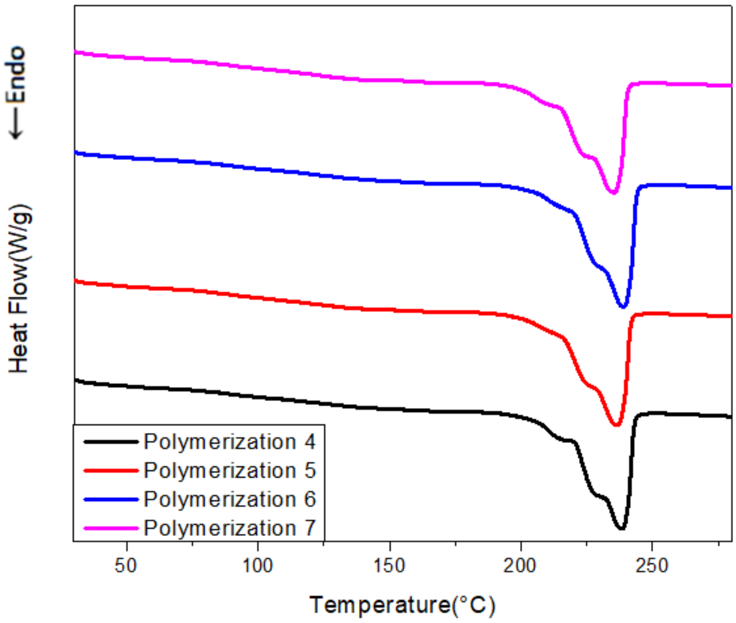


Figure 5.8. Comparison of the DSC thermograms of PET obtained from polymerization reactions containing different concentrations of EG.

5.2.1.4. Effect of the type of BHET input material

Two different syntheses were performed with two types of BHETs as input material. To observe whether recycled BHET had any effect on the PET product, recycled BHET and BHET from Sigma-Aldrich were used in different syntheses under the same conditions. The results showed that PET obtained from recycled BHET had a slightly lower IV value and a higher number of CEGs (Figure 5.9). The reason for this small difference in terms of IV value and number of CEGs may be due to the presence of impurities of any kind in the recycled BHET, as well as relatively low degrees of polymerizations in both samples.

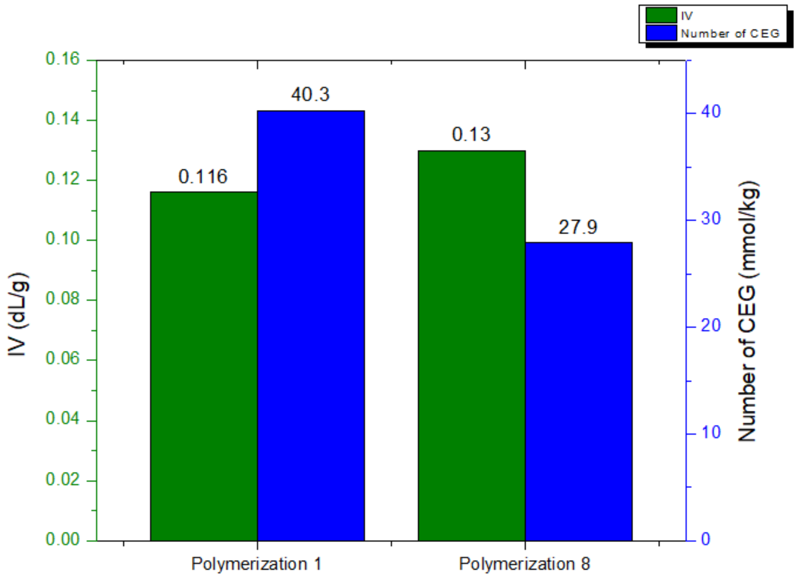


Figure 5.9. Comparison of the IV values and the number of CEG of PET obtained from Polymerization 1 and Polymerization 8.

The literature indicates that the purification step for BHET is very crucial, and all impurities should be removed before the polymerization process, as the impurities in recycled BHET tend to bind to the polymer chain. Recycled BHET may also contain some inorganic impurities, which are responsible for color changes and the promotion of oxidative degradation. Besides that, even a small amount of moisture can lead to hydrolysis of the ester links during polymerization, which shows how important it is to remove impurities before the polymerization process. Therefore, the presence of impurities can affect the physical properties of the final product, such as reducing the IV value, which has a negative impact on the processability of the products and their resistance to long-term degradation (Koo et al., 2013). On the other hand, although the IV value of PET obtained from recycled BHETs was lower, the difference was too small, indicating that the recycled BHETs were largely free of impurities.

5.2.1.4.1. DSC analysis

When the DSC thermograms of PET obtained from different input materials were analyzed, it was observed that the PET obtained from recycled BHET had a slightly lower T_m than the PET obtained from the BHET purchased from Sigma Aldrich (Figure 5.10). This reduction in T_m could be due to the chemical heterogeneity of PET resynthesized from recycled BHET, which likely contained some impurities (Kumar and Sainath, 1987). The areas under the T_m peaks of PET products, which were obtained from different input materials, were very close to each other. From this it could be concluded that impurities, which were assumed to be present in traces, did not have a major influence on crystallinity.

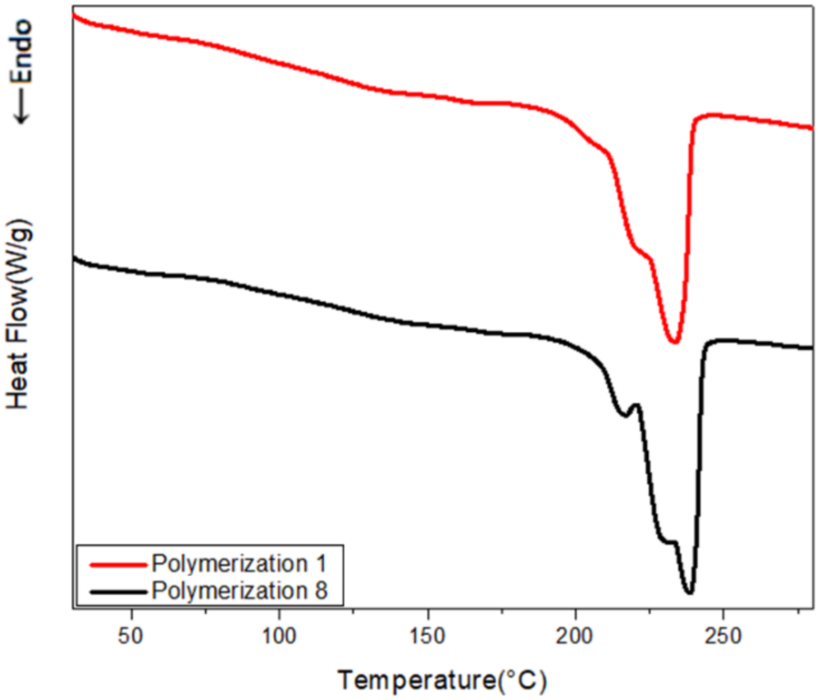


Figure 5.10. Comparison of the DSC thermograms of PET obtained from Polymerization 1 and Polymerization 8.

5.2.1.5 Effect of catalyst concentration

Several PET synthesis reactions were carried out with different catalyst concentrations to determine whether the concentration of catalyst had an influence on the PET product obtained. The same process conditions were used, the only difference was the concentration of Antimony (III) oxide and TTIP added to the reaction flask together with BHET at the beginning of the reaction process. In the general procedure of the synthesis reactions, 200 ppm Antimony (III) oxide and 30 ppm TTIP were used.

Initially, the concentrations of both Antimony (III) oxide and TTIP were increased. While the concentration of Antimony (III) oxide was increased to 300 ppm, TTIP was increased to about 50 ppm. It was found that increasing the concentration of both catalysts did not result in a significant change in the IV value and the number of CEGs. This showed that although a higher concentration of catalysts was used in the reaction, while their ratio to each other was similar, PET with a similar IV value and a similar number of CEGs was obtained.

In a further step, the reactions were carried out with the concentration of one catalyst remaining the same, while the concentration of the other catalyst was increased. In the first reaction, 200 ppm Antimony (III) oxide and 52 ppm TTIP were used. Increasing the concentration of TTIP led to a slight increase in both the IV value and the number of CEGs. This may due to higher concentration of TTIP enhanced the degradation reaction which resulted the cleavage of the long polymer chains. In the second reaction, only the concentration of Antimony (III) oxide was increased to 300 ppm, while the concentration of TTIP remained the same at 30 ppm. While the increase in the concentration of Antimony (III) oxide had no major effect on the CEG, a significant IV increase was observed (Figure 5.11).

Considering these results, it could be argued that an increased concentration of Antimony (III) oxide or TTIP led to the formation of PET with a higher IV value. This could be explained by the fact that a higher concentration of catalyst enhanced the propagation reaction, resulting in PET with a higher molecular weight (Shah et al., 1984). However, it was also found that the increase in TTIP concentration did not lead to as great increase in the IV value of the PET formed as the increase in Antimony(III) oxide led to. It was reported that polycondensation catalysts could accelerate both the propagation and degradation reactions. When the effect of these two catalysts on the propagation reaction and the possible degradation reaction was investigated, both catalysts were efficient in improving the propagation reaction and led to the formation of PET with the desired properties. On the other hand, a catalyst that accelerated the degradation reaction could inhibit the further increase in the molecular weight of PET. The studies indicated that a titanium-based catalyst significantly accelerated both the propagation reaction and degradation reactions, while an antimony-based catalyst slightly accelerated the degradation reactions (Tomita, 1976). This could be the reason why Antimony (III) oxide led to a higher increase in the IV value of PET. When the number of CEGs of the PET samples obtained was compared, it was also found that an increase in the concentration of TTIP led to the formation of PET, which had a higher number of CEGs.

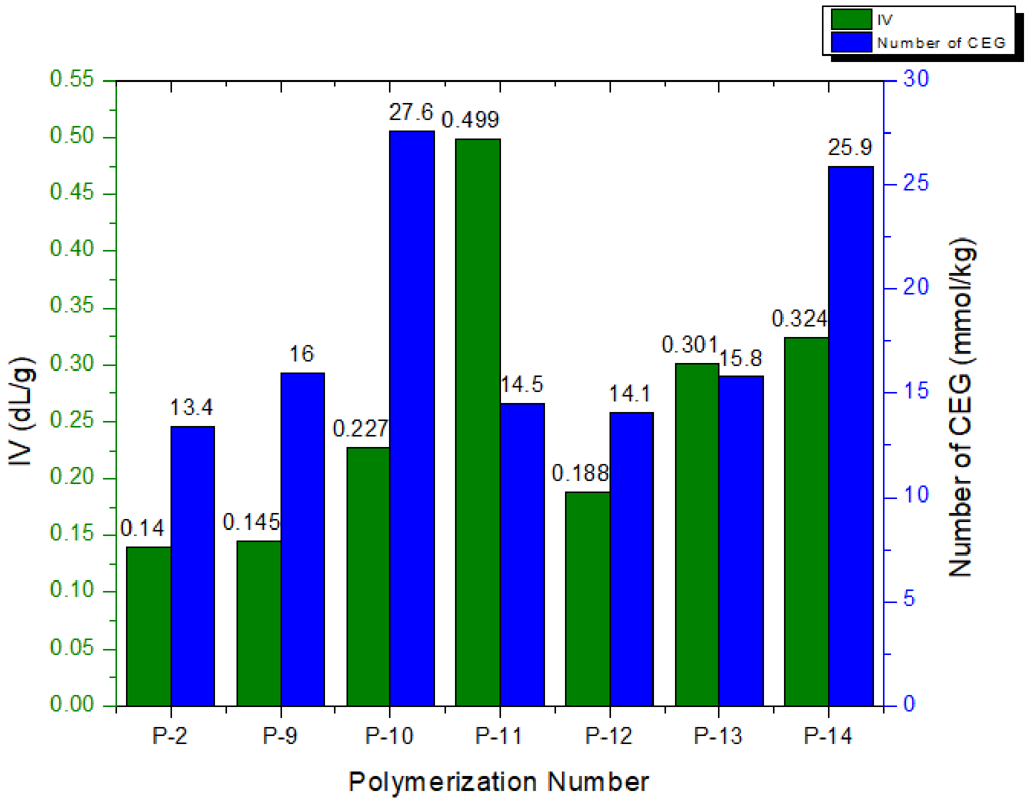


Figure 5.11. Comparison of the IV values and the number of CEG of PET obtained from polymerization reactions containing different concentrations of catalysts.

Based on these results, synthesis reactions were carried out in which the concentration of Antimony (III) oxide was further increased. In one of the synthesis reactions, 400 ppm Antimony (III) oxide and 30 ppm TTIP were used. When the IV value of PET obtained as a result of this reaction was compared with the IV value of PET obtained as a result of Polymerization 11, it was observed that a further increase in the concentration of Antimony (III) oxide led to a decrease in the IV value of PET. This could be related to the formation of degradation reactions. However, considering the results of other synthesis reactions, it could be claimed that this decrease in IV value was due to another reason. One possible reason could be the vacuum value reached in each reaction. In this specific synthesis reaction, the pressure could only be reduced to 36 mbar, which was higher compared to the reduced pressures of the other reactions and could have prevented the removal of EG.

Since increasing the concentration of only Antimony (III) oxide led to a significant increase in the IV of the PET obtained, but increasing the amount of both catalysts had no effects on the IV of the PET obtained, the polymerization reactions were carried out with a higher concentration of Antimony (III) oxide and without the addition of TTIP. Therefore, two reactions were carried out without the presence of TTIP under the same conditions, with the only difference that 300 ppm Antimony (III) oxide was used in the first reaction and 400 ppm Antimony (III) oxide in the second reaction. Although PET samples with a significantly high IV value were obtained compared to the IV values of PET samples obtained as a result of previous polymerization reactions, it was found to be lower compared to the IV value of the PET sample obtained as a result of Polymerization 11 (Figure 5.11).

This suggested that TTIP is a highly effective catalyst that contributed to the propagation of the polymerization reaction, leading to the formation of PET with higher IV, but the use of a higher concentration of TTIP may result the degradation reactions that lead to the cleavage of the long polymer chains. Another possible interpretation of this result could be that the catalysts inhibited each other's activity when added in a certain ratio to each other. Therefore, changing this ratio could have contributed to the propagation of the polymerization reaction.

5.2.1.5.1. DSC analysis

Analysis of the DSC thermograms of PET samples obtained from different polymerization reactions containing different concentrations of catalyst showed that the PET obtained from Polymerization 11 had a higher T_m point (Figure 5.12AB). This can be considered a predictable result, considering that the PET obtained from polymerization 11 had the highest IV value (0.499 dL/g). However, the T_m points of the PET samples obtained was too close to each other, indicating that the change of catalyst used for the polymerization process did not have a great influence on the thermal properties of the PET product.

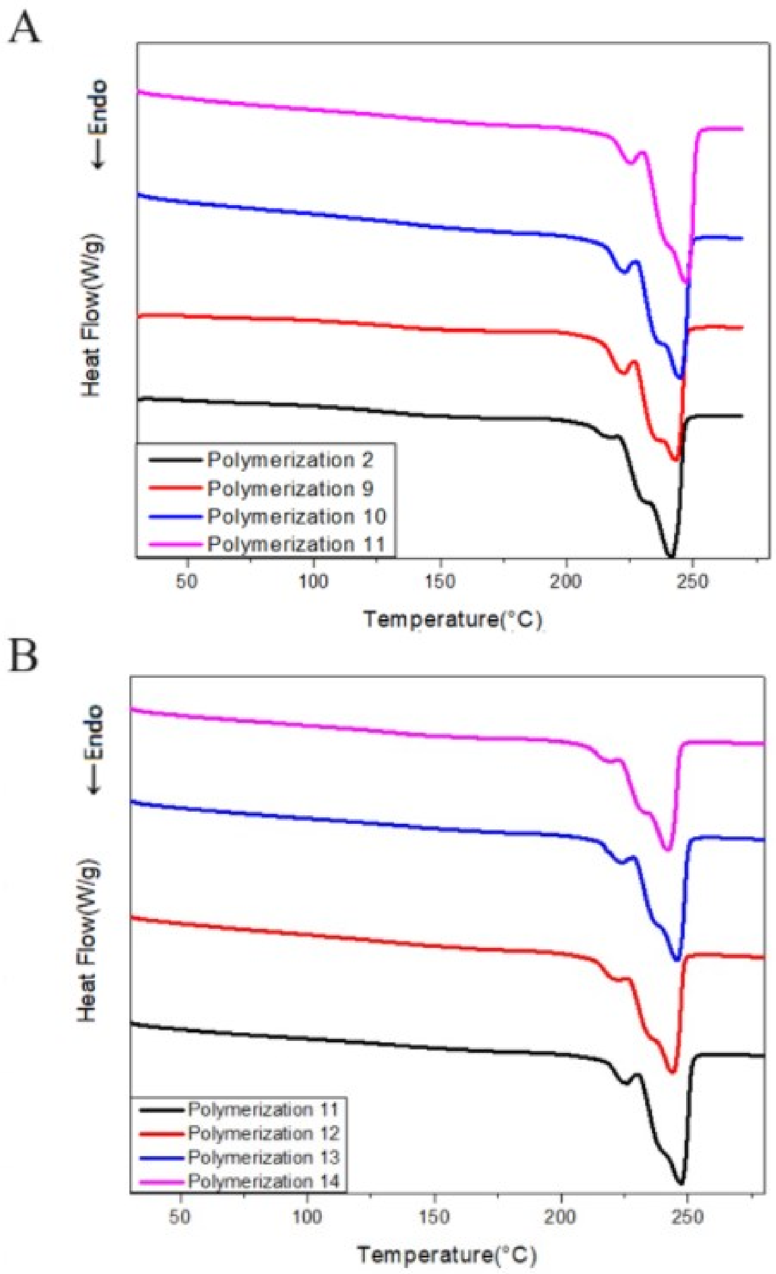


Figure 5.12. Comparison of the DSC thermograms (A) Comparison of the DSC thermograms of PET obtained from polymerization reactions (2, 9, 10 and 11) containing different concentrations of catalysts. (B) Comparison of the DSC thermograms of PET obtained from polymerization reactions.

5.2.1.6. Effect of the applied vacuum time

Five different PET synthesis reactions with different vacuum times were carried out to determine whether the vacuum time had an influence on the PET product obtained. The same process conditions were used, the only difference being the vacuum times, which were applied at 275°C. The vacuum times were set to 30 min, 1 h, 90 min, 2 h, and 3 h. It was found that the PET with the highest IV value and the lowest number of CEGs was obtained with a vacuum application of 90 min. When analyzing vacuum times of up to 90 min, it could be clearly observed that an increase in vacuum time led to a dramatic increase in the IV value and a decrease in the number of CEGs (Figure 5.13). During the polymerization, the polymer molecules grow, which is accompanied by a considerable increase in the viscosity of the polymer melt. The increase in the viscosity of the polymer melt leads to the formation of a strong diffusion resistance, which makes the removal of EG (or other side reaction products, if present) more difficult. Therefore, at the end of the reaction, a low pressure must be applied to complete the polymerization. Moreover, a greatly reduced pressure helps to ensure that the condensation products can be easily removed, which favors the polymerization reaction (Kumar and Sainath, 1987).

Although low pressures have a positive effect on the polymerization reactions, we could not reach such a low pressure with our experimental setup in all syntheses. In general, the polymerization reactions were performed under vacuum at a pressure of about <25 mbar. Therefore, the vacuum time was increased in the expectation that a similar effect would occur when very low pressures (around 1 mbar) were reached. The results were consistent with the expectations. Increasing the vacuum time up to 90 min led to an increase in the IV value and a decrease in the number of CEGs, which showed that the polymerization reaction continued to occur with continuous removal of EG.

On the other hand, the IV value decreased and the number of CEGs tended to increase when the vacuum was applied for longer than 90 min at 275°C. This was likely due to the PET being exposed to very high temperatures over a long period of time. When PET was exposed to temperatures of around 280°C at the end of the polycondensation process, degradation reactions set in. Therefore, it is possible to claim that the degradation rate of PET during polycondensation strongly depends on the reaction temperature (Zimmerman and Kim, 1980). At high temperatures, there are two important degradation reactions that can lead to the formation of CEG, which can be accompanied by a decrease in IV. In the first case, a random chain scission occurs between thermally weak bonds (C-O) on ester linkages which can be accelerated by various transesterification catalysts. After the formation of a six-membered transition state, chain scission results in two shorter polymer chains, one of which contains a vinyl ester end unit and the other a carboxyl end unit. In the second case, degradation occurs via the hydroxyl end group and suggests that degradation probably occurs via a five-membered orthoester-like intermediate and produces acetaldehyde as a by-product after the formation of the ethylene oxide intermediate. The consumption of hydroxyl end groups and the accumulation of structures with acid and vinyl end groups determines the thermal and hydrolytic stability of PET and is also an important indicator for the beginning of the decrease in molecular weight (Ravindranath and Mashelkar, 1986).

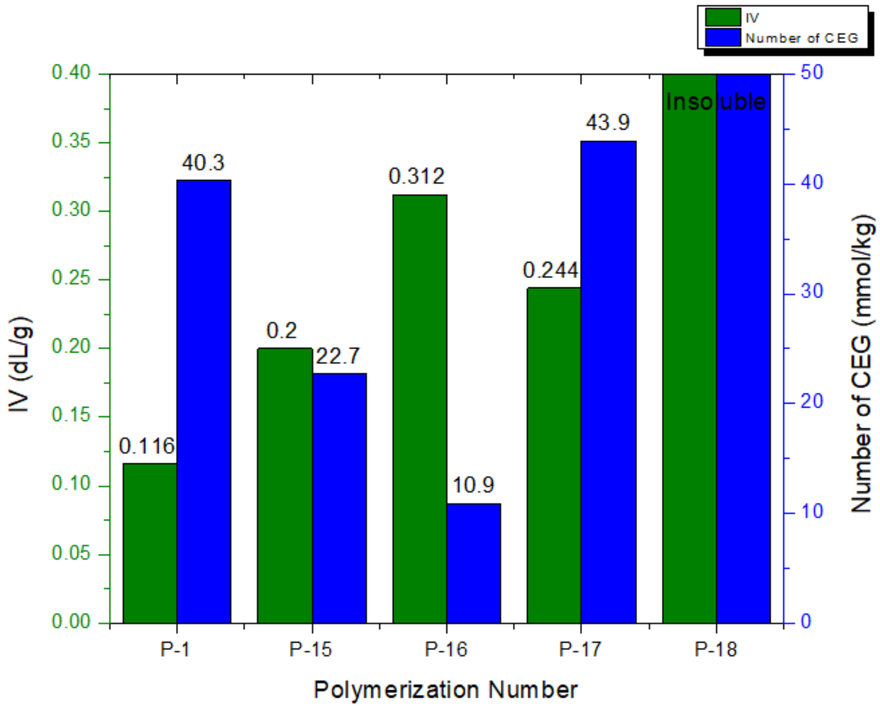


Figure 5.13. Comparison of the IV values and the CEG number of PET from polymerization reactions in which different vacuum times were used.

It was also observed that the polymer turned yellowish when the vacuum was applied at 275°C for longer than 90 min, which could indicate that the degradation reactions became dominant. It is also known that during the PET melting process, thermo-oxidative degradation, which takes place at high temperatures (approx. 280°C) in the presence of oxygen (even with very low oxygen content), is primarily responsible for the discoloration of the PET obtained. These thermo-oxidative reactions, which initially begin on the polymer surface, lead to changes in the surface chemistry that result in color formation. Moreover, the structures formed as a result of chain scission by thermal degradation reactions can take place in further reactions and the structures resulting from these reactions can be the reason for the color change on PET. Therefore, it was logical to claim that there was a positive correlation between the percentage of CEGs and the yellowness of PET. It is also known that the degree of yellowing is related to the heating time, i.e. a longer reaction time leads to the formation of more yellowish PET (Ciolacu et al., 2006).

5.2.1.6.1. DSC analysis

When the DSC thermograms of the PET obtained were compared, it could be seen that the PET had the highest T_m when the vacuum was applied for 90 min (Figure 5.14). Thus, a vacuum lasting up to 90 min, during which EG was continuously removed, resulted in a shift of the melting curve to higher temperatures. In longer vacuum durations the degradation reaction dominated, and the melting curve shifted slightly back to lower temperatures.

It was observed that the melting curves showed broad peaks at a vacuum time of less than 90 min due to the formation of the smaller peak forming at lower temperatures. When the vacuum time reached 90 min, the small peak in the thermogram was observed to disappear. The area under the peak of the PET obtained was smallest when the vacuum was applied for 90 min. It can therefore be stated that the PET with the highest molecular weight led to a decrease in crystallinity. This can be explained by the fact that the increase in chain length inhibits chain packing, which results in a decrease in the degree of crystallinity (Spinacé and De Paoli, 2001).

The occurrence of multiple melting peaks in the DSC thermogram is explained by two reasons in the literature. The first reason is that the polymer contains a variety of crystallization forms. The second reason is that the originally irregularly arranged chain segment rearranges itself after endothermy in the melting process and melts again near the melting point (Zhao et al., 2020). The occurrence of multiple melting peaks could be attributed to the first reason. Short polymer chains might have led a variety of crystallization forms, which consequently resulted in lower IV. The occurrence of multiple melting peaks could also be attributed to the second reason, as a double peak was observed when the IV was lower. It is known that the ease of rearrangement of fine structures of semi-crystalline polymers depends on the molecular weight and that the rearrangement is much easier when heating the folded chain crystals in low molecular weight polymer than in higher molecular weight polymer. While the low-temperature peak could be assigned to crystals that grew mainly during isothermal crystallization, the high-temperature peak could be assigned to the originally regularly arranged chain segment crystals (Kamide and Yamaguchi., 1972).

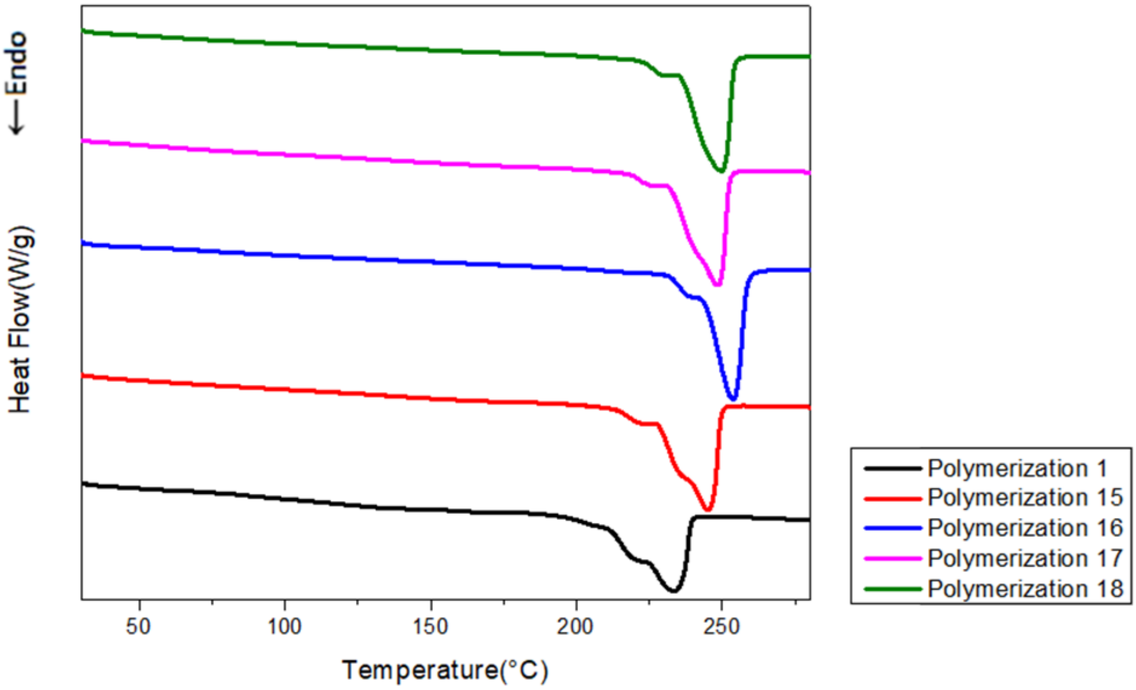


Figure 5.14. Comparison of the DSC thermogram of PET from polymerization reactions in which different vacuum times were used.

5.2.1.7. Comparative analysis of PET

5.2.1.7.1. FTIR analysis

Polymerization 1 and Polymerization 2 were analyzed with FTIR. The same peaks could be seen in the FTIR spectra of PET obtained from both polymerizations. In the FTIR spectra of both PET, an absorption peak at 1712 cm^{-1} was observed, corresponding to the stretching of the C=O bond (ester carbonyl group). Two peaks that formed around 1250 cm^{-1} and 1110 cm^{-1} were attributed to the C–O stretching of the ester (terephthalate group). Moreover, the peaks at 1505 cm^{-1} as well as 872 cm^{-1}, 722 cm^{-1} represented the benzene ring. There was also a low intensity peak at 3430 cm^{-1} which corresponded to the –OH stretching. The presence of this peak indicated that BHET/oligomers were still present in the PET polymers, although they were highly reduced (Edge et al., 1996). The peak around 2970 cm^{-1} was attributed to the C-H bond decreases compared to the BHET spectra, showing that EG containing a C-H bond was eliminated and longer polymer chains were formed (Chinchillas et al., 2019). Furthermore, when analyzing the FTIR spectra of other PET samples obtained from different polymerization reactions, it was found that the addition of phosphoric acid or EG, the use of different input materials and also the use of catalysts at different concentrations had no effect on the FTIR spectra. In all of the FTIR spectra, the peak at 3430 cm^{-1}, which corresponds to –OH stretching, significantly disappeared, which was the main expectation. When analyzing the effects of vacuum duration on the FTIR spectra, it was found that when the vacuum duration was longer than 1 h, the peak at 3430 cm^{-1} largely disappeared compared to a shorter vacuum duration, suggesting that more EG was removed when the vacuum duration was longer than 1 h (Figure 5.15).

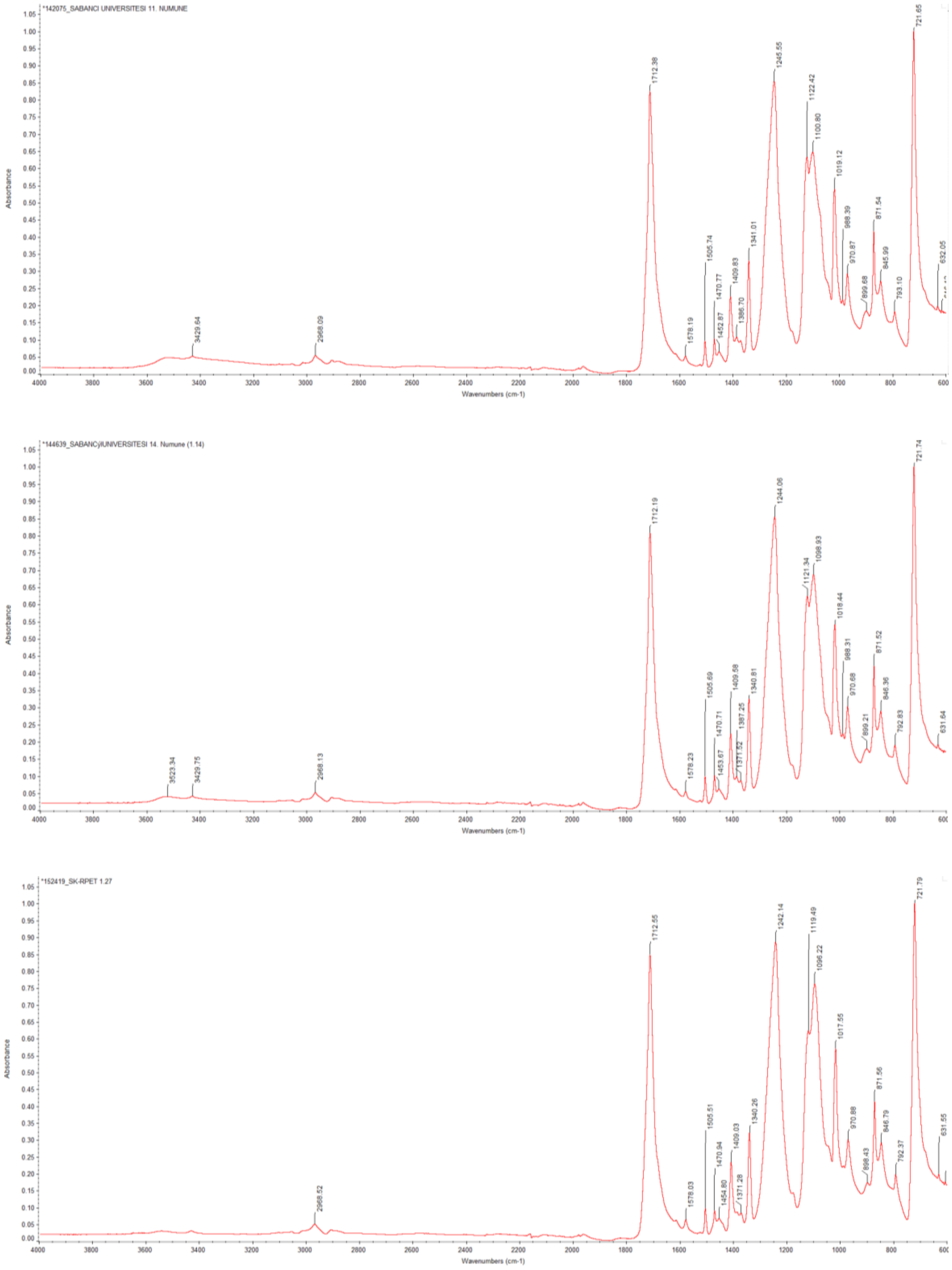


Figure 5.15. FTIR spectra of PET samples obtained from Polymerization 1, Polymerization 2 and 16, respectively.

5.2.1.7.2. TGA analysis

The PET samples obtained from different PET polymerization reactions were analyzed by TGA (Figure 5.16). According to the TGA thermograms, the decomposition profile of all PET contained a step in which weight loss was the greatest. It was observed that the temperature of maximum weight loss rate (T_{max}) was between 445-455°C, in parallel with literature. This weight loss, which started at about 400°C and reached a maximum at about 448°C, was due to the decomposition of PET. When comparing the T_{max} of the PET samples obtained, it was found that the T_{max} values of some PET samples were slightly higher than others, which could be explained by their higher thermal stability. PET samples with a higher T_{max} had a higher thermal stability (Hu et al., 2020). Moreover, it is reported that PET forms a considerable amount of carbonaceous residues in a nitrogen atmosphere (Alshammari et al., 2019). While the first tests were performed under nitrogen purge, the TGA analysis was continued in an oxygen atmosphere up to 800°C. This allowed the resulting carbonaceous structures to react with oxygen, resulting in further weight loss. In most of the TGA thermograms of the PET samples, a weight loss was observed at around 805°C, indicating the degradation of the carbonaceous structures. The presence of the final residue might therefore be related to inorganic structures such as catalysts or other impurities.

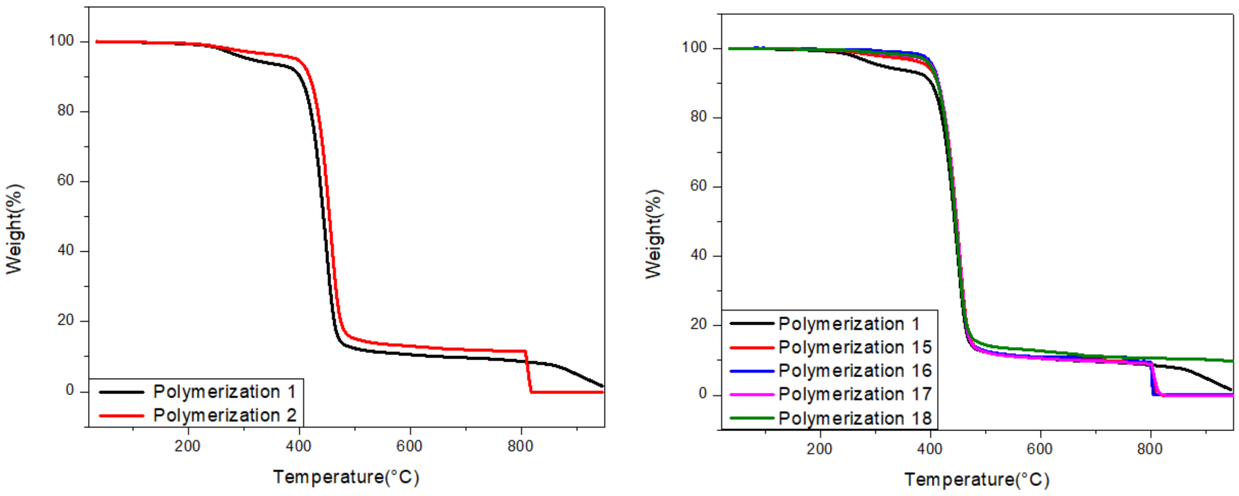


Figure 5.16. TGA thermograms of PET obtained from polymerization reactions in which different reaction times (left) and vacuum times (right) were used.

5.2.1.7.3. NMR analysis

In addition to the GPC method which is commonly used method to analyze the number average molecular weight (M_n), M_n of PET samples can also be compared with each other by NMR analysis. In order to use the NMR method to calculate the Mn of PET samples, assumptions had to be made. The first assumption was that there were two EG groups at both ends of the PET polymer chain. The second assumption was that the PET polymer chain contained no DEG units.

When these assumptions were taken into account, the protons labelled 'a' and 'b' represented the protons on the aromatic ring and the protons on the EG group in the repeating units, respectively. On the other hand, 'c' and 'd' represented end group protons close to ester and hydroxyl groups respectively (Figure 5.17). Since the aromatic ring contains 4 hydrogen atoms, the integral value of 'a' was divided to 4, and the EG groups in the end group (represented by 'c' and 'd') contain 8 hydrogen atoms, therefore the total integral of 'c' and 'd' was divided to 8.

A proton corresponding to the values was then found and the M_n of the PET sample could be determined. For example, the integral of 'a' for Polymerization 1 was 39.42 and was then divided by 4, giving 9.855. The integral of 'c' + 'd' for polymerization 1 was 15.16 and this number was divided by 8 and the answer was 1.895. Then 9.855 was multiplied by 2 as we expected 2 EG groups at the end of the PET chain. The number found was divided by 1.895 and the number found was multiplied by 192 as the molecular weight of the repeating unit of PET is 192 g/mol. In the last step, 254 was added to the calculated number, since the molecular weight of the end groups is 254 g/mol. Thanks to these calculations, the M_n for Polymerization 1 was found to be 2251 g/mol. The same calculation method was used to find M_n of other PET samples obtained from other polymerization reactions (Table 5.2).

When the M_n of the PET samples calculated from the NMR results were compared with the IV values of the samples, the approach was found consistent. It can be seen that the PET sample with the lowest molecular weight also had the lowest IV value. The same result was valid for the PET sample with the highest IV value.

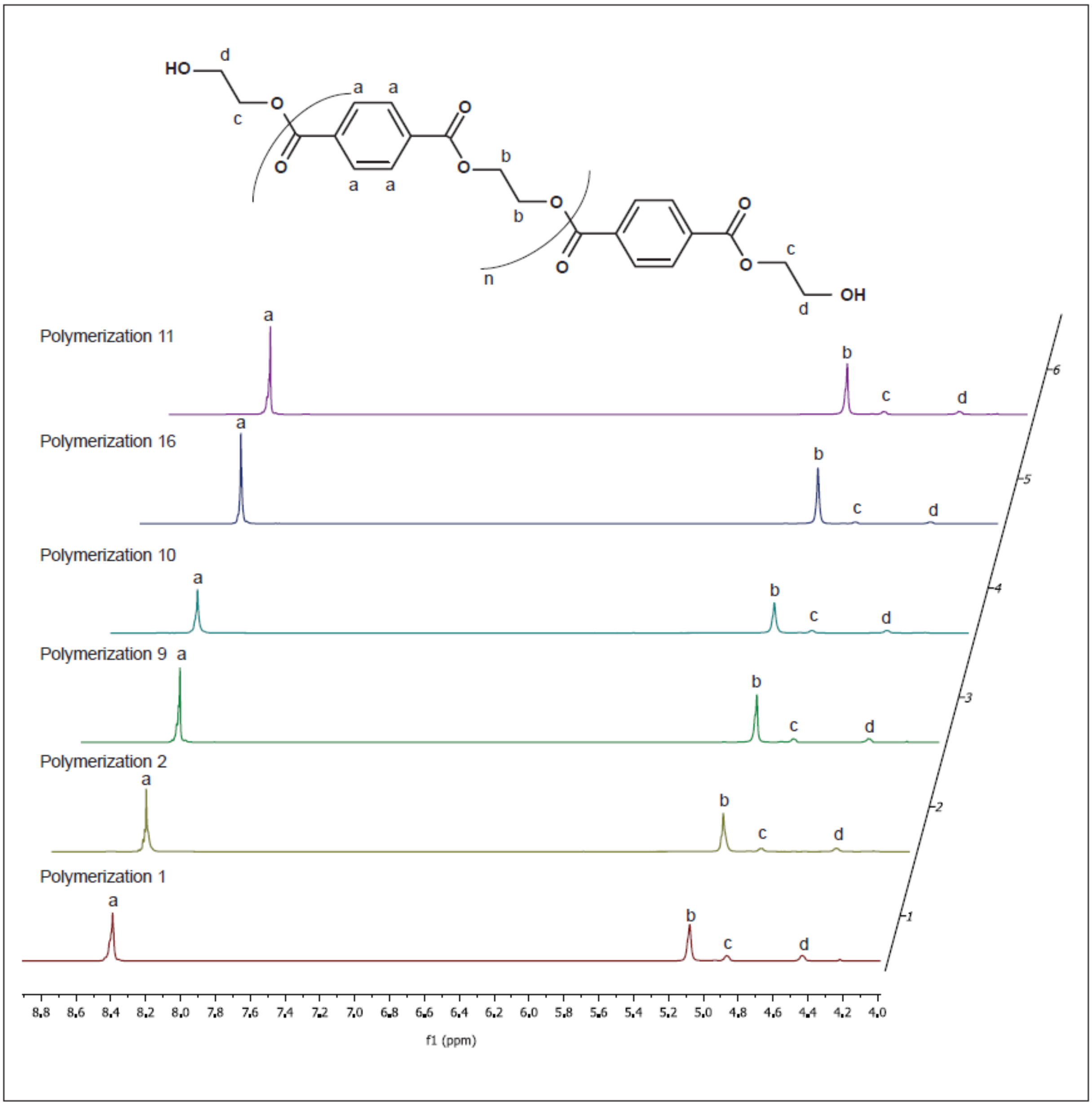


Figure 5.17. Comparison of the NMR spectra of PET samples obtained from the polymerization with different conditions.

Table 5.2. Integrals of the NMR peaks of PET samples and their Mn found with the developed method.

	IV	**8.4 ppm**	**5.1 ppm**	**4.8 ppm**	**4.4 ppm**	**Aromatic Ring in Repeating unit**	**EG in Repeating unit**	**EG in End Groups**	**M_n (g/mol)**
Polymerization 1	0.116	39.42	32.7	7.87	7.29	9.855	8.175	1.895	2251.003
Polymerization 2	0.14	41.35	36.2	6.59	5.84	10.3375	9.05	1.55375	2808.851
Polymerization 9	0.145	41.05	36.24	6.19	5.37	10.2625	9.06	1.445	2981.197
Polymerization 10	0.227	42.7	38.2	5.47	5.03	10.675	9.55	1.3125	3377.2
Polymerization 16	0.312	40.97	38.03	4.72	4.54	10.2425	9.5075	1.1575	3651.944
Polymerization 11	0.499	42.17	38.61	4.87	4.33	10.5425	9.6525	1.15	3774.278

5.2.2. Solid state polymerization

5.2.2.1. Effect of the reaction time

In SSP 1, the PET was heated to 220°C and when the temperature reached 220°C, a vacuum was applied for up to 6 h. Samples of PET were taken after 2 h, 4 h and 6 h to observe how IV and CEG change over time (Figure 5.18). It was observed that the IV increased parallel to time and the number of CEGs changed inversely proportional to time. The increase in IV in 0-2 h was much higher than in 2-6 h. The reason for this might have been the SSP reaction taking place near the pellet surface in the initial stages, during which the diffusion of by-products was possibly very fast and therefore not hindered by crystallinity. In the initial stages, the chemical reaction progresses rapidly and leads to a drastic increase in IV. Over time, the end-group concentrations at the pellet surface are depleted and the SSP reactions take place at greater depths within the pellet, providing greater resistance to the diffusion of by-products due to the higher crystallinity. This resistance has an adverse effect on the reaction rate, which delays the increase in IV. For this reason, SSP also requires a lot of time, and a longer reaction time results in PET with a higher IV (Kim et al., 2003). During the SSP process, the number of CEGs continues to decrease, which shows that the esterification reaction takes place throughout the process (Wu et al., 1997).

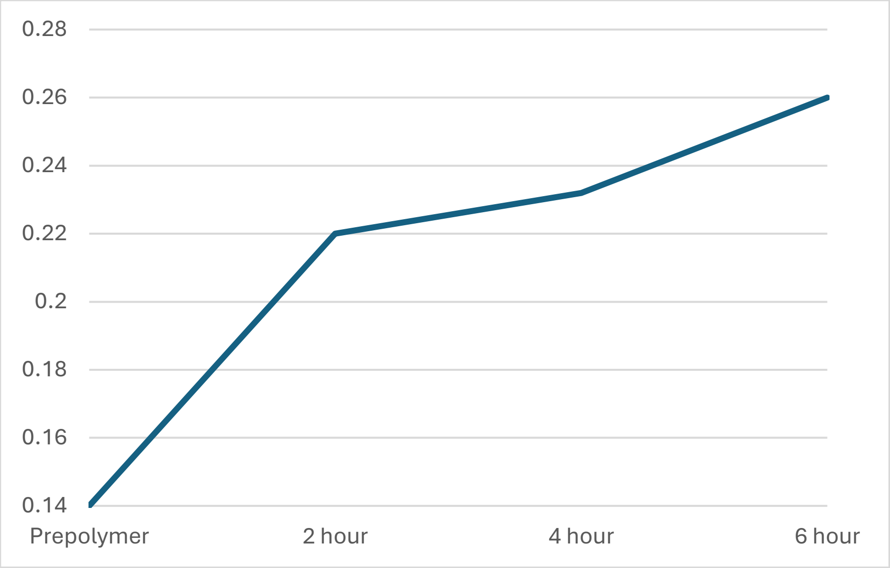


Figure 5.18. Comparison of the IV values of PET samples were taken after 2 hours, 4 hours and 6 hours.

5.2.2.1.1. DSC analysis

Moreover, PET samples were taken after 2 h, 4 h and 6 h and analyzed using DSC. The DSC thermograms of the 2nd heating cycle of these PETs in comparison to each other are shown in Figure 5.19. The T_m of the PET sample obtained shifted towards higher temperatures with the progress of the SSP reaction. It is known that an increase in molecular weight leads to an increase in melting temperature.

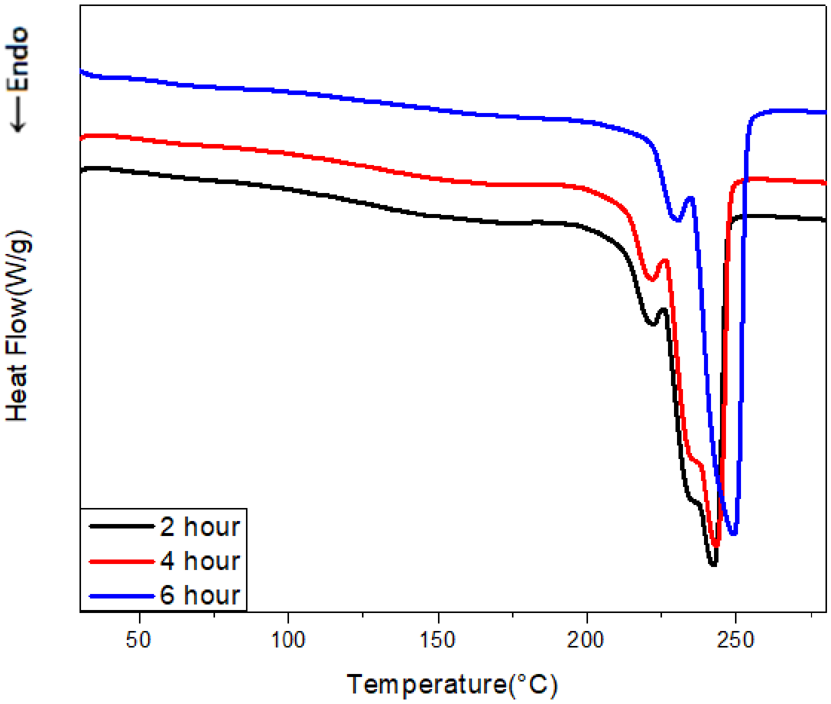


Figure 5.19. Comparison of the DSC thermograms of PET samples taken after 2 hours, 4 hours and 6 hours.

5.2.2.2. Effect of the reaction temperature

While in the SSP 1, the PET was kept at 220°C, in SSP 2, the PET was kept at 230°C to analyze the effect of temperature on SSP process. In both cases, SSP led to an increase in the IV value and to a decrease in the number of CEGs on the PET obtained after the polymerization process, as predicted, since SSP allows the removal of the EGs remaining in the PET obtained by polymerization. The duration of the SSP was set at 6 h and the PET samples were taken at a specific time interval. For each hour in which samples were taken, the IV value of the samples from SSP 2 was higher and the number of CEGs lower than in the samples from SSP 1 (Figure 5.20). It is likely that the PET prepolymer contained inactive functional end groups that were highly constrained by the crystalline structure and didn't have sufficient mobility during SSP at lower temperatures. Some of the inactive end groups might have been activated by increasing the temperature so that inactive end groups that were immobile at lower temperatures were mobilized and participated in the reaction during SSP. Therefore, an increase in temperature led to higher overall rates for the SSP, suggesting that an increase in temperature helped produce PET with a higher IV (Duh, 2001). Furthermore, the decrease in the number of CEGs was more dramatic at higher temperatures. The change in the number of CEGs was parallel to the rate of the esterification reaction, which increased with the increase in temperature. Briefly, a higher SSP temperature accelerated the reaction rates in the esterification reaction and thus led to a greater decrease in the number of CEGs (Wu et al., 1997).

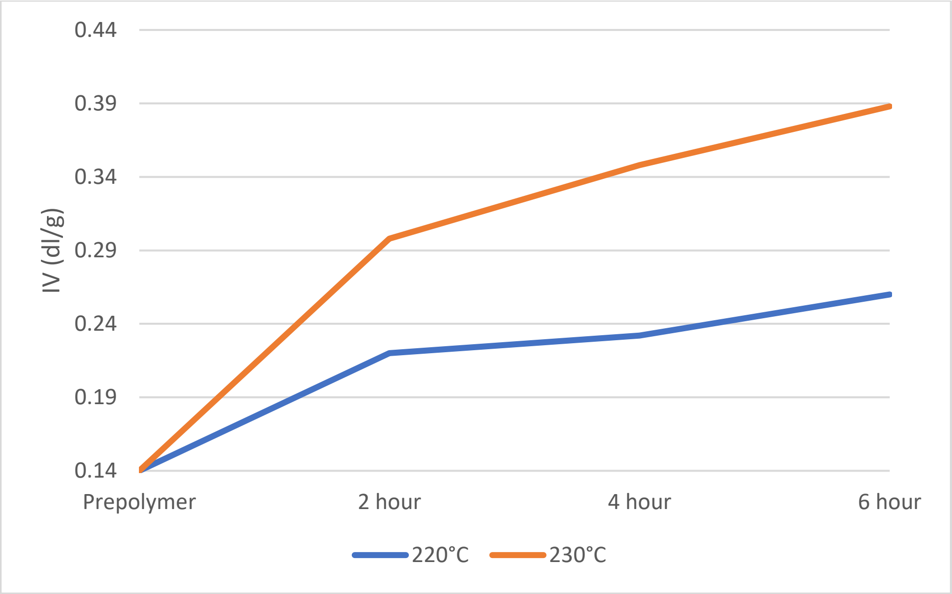


Figure 5.20. Comparison of the IV values of PET samples obtained with SSP at different reaction temperatures.

5.2.2.2.1. DSC analysis

The DSC thermograms of the PET samples obtained at reaction temperatures of 220°C and 230°C are presented in Figure 5.21. Higher reaction temperature in the SSP process led to a shift of T_m to a higher temperature.

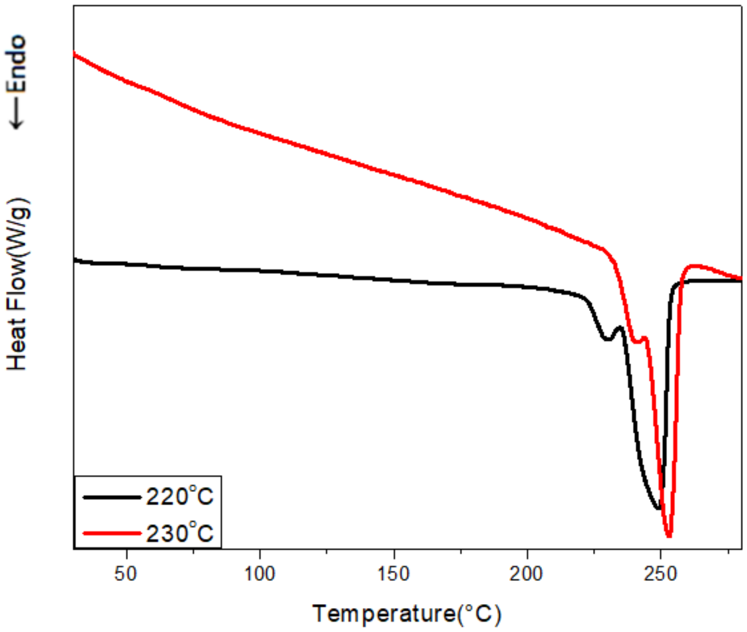


Figure 5.21. Comparison of the DSC thermograms of PET samples obtained with SSP at different reaction temperatures.

5.2.2.3. Effect of the PET particle size in SSP

While the SSP process is applied directly to PET in SSP 1, PET was pulverized and then passed through a 90-micron sieve before application of SSP in SSP 3. Since the PET samples of SSP 3, which were taken after 4 h and 6 h, were insoluble, the IV values could not be determined. Therefore, the IV value of the PET samples of SSP 3 taken after only 2 h could be compared with the PET samples of SSP 1 taken after 2 h (Figure 5.22). The analyses showed that a reduction in particle size led to an increase in IV value which could be associated with an increase in total surface area of the PET particles. The use of smaller particles, which had a larger total surface area, facilitated the diffusion of by-products (Wu et al., 1997). It is concluded that the use of smaller particles could be an efficient method to obtain PET samples with a higher IV. When the number of CEGs of SSP 4, which were taken after 4 h, were compared with the number of CEGs of SSP 1, which were taken after 4 h, it was observed that the decrease in the number of CEGs up to 4 h was higher in SSP 3, which was related to the faster reaction rate.

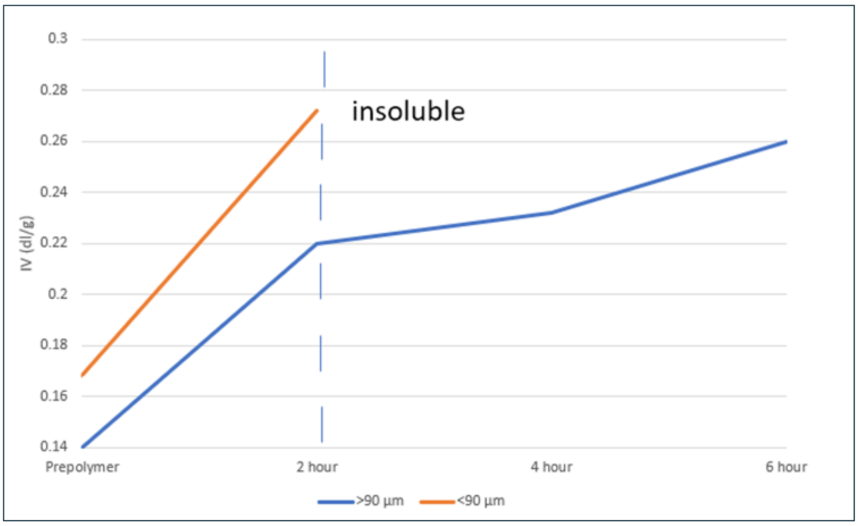


Figure 5.22. Comparison of the IV values of PET samples obtained from PET (prepolymer) with different particle sizes.

5.2.2.3.1. DSC analysis

When melting curves of PET samples obtained at the end of 6 h from SSP 1 and SSP 3 examined, it was observed that applying SSP to smaller particles led to a shift of T_m to a higher temperature (Figure 5.23). Although the IV value of the SSP 3 sample that was taken after 6 h could not be measured, the shift of T_m to higher temperatures showed that the IV value of SSP4 was likely higher than the IV value of SSP1, taken after 6 h.

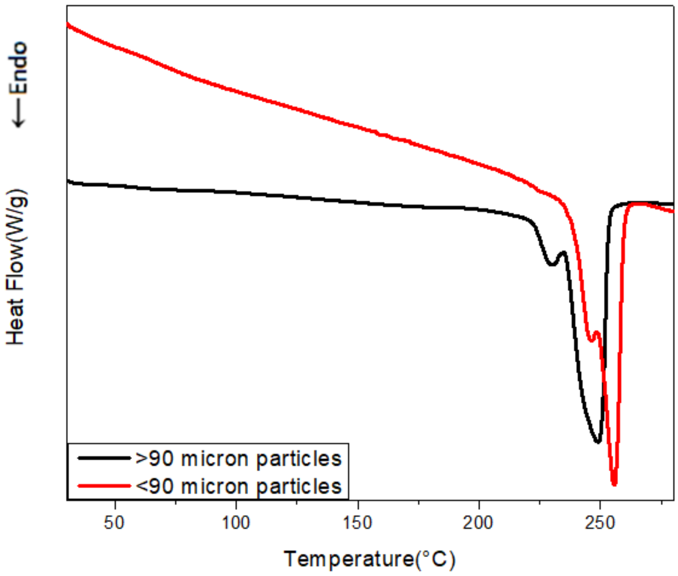


Figure 5.23. Comparison of the DSC thermograms of PET obtained from the solid state polymerization of PET (prepolymer) with different particle sizes.

5.2.2.4. Effect of the catalyst concentration used in repolymerization

In SSP 1 the PET obtained from the PET synthesis under the reaction condition Polymerization 2 was used, and in SSP 4 the PET obtained from the PET synthesis under the reaction condition Polymerization 9 was used. Higher amounts of catalysts were used in Polymerization 9 than in Polymerization 2. Therefore, the influence of the amount of catalyst used in the melt polymerization on the SSP process was analyzed by comparing these SSP processes. It was found that the SSP rate increased with increasing catalyst concentration. The reason why increasing the catalyst concentration led to an increase in the reaction rate can be explained by the fact that the catalyst reduced the activation energy required for the reaction. Therefore, using a higher concentration of antimony catalyst in the melt polycondensation had a beneficial influence on the SSP of PET prepolymer, resulting in the production of PET polymer with higher IV (Duh, 2002). For both samples, the degree of decrease in the number of CEGs was similar, however the reaction rate was higher for SSP4 (Figure 5.24). This demonstrated that the amount of antimony used in the melt polycondensation led to a reduction in the activation energy of the ester exchange reactions of SSP and had no significant influence on the activation energy of the esterification reactions of SSP. This is the reason why the amount of antimony used in melt polycondensation had a positive effect on the production of PET polymers with higher IV but did not have a major impact on the number of CEGs of PET (Kokkalas et al., 1995).

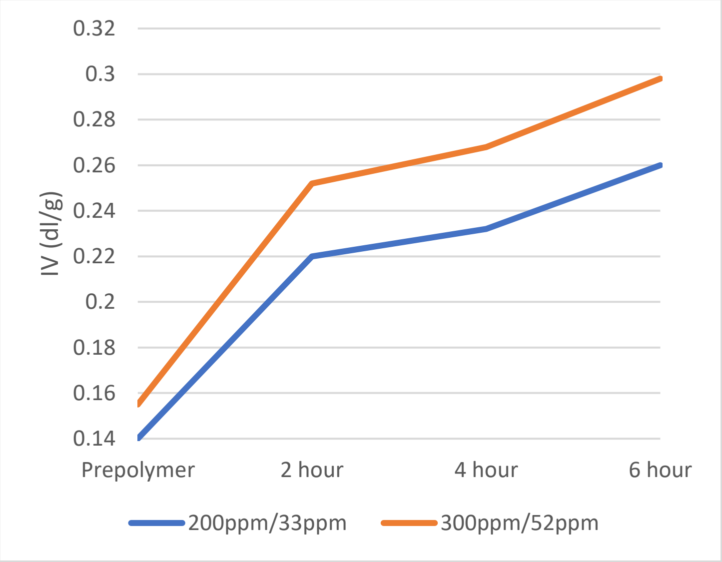


Figure 5.24. Effect of the catalyst concentration used in the repolymerization on the IV values of the PET (SSP 1 and SSP 4).

5.2.2.4.1. DSC analysis

The analysis of the DSC thermograms of these PET samples showed that although the use of higher amounts of catalyst during the melt polymerization positively influenced the SSP process, it had no significant influence on the thermal properties of the final PET product (Figure 5.25).

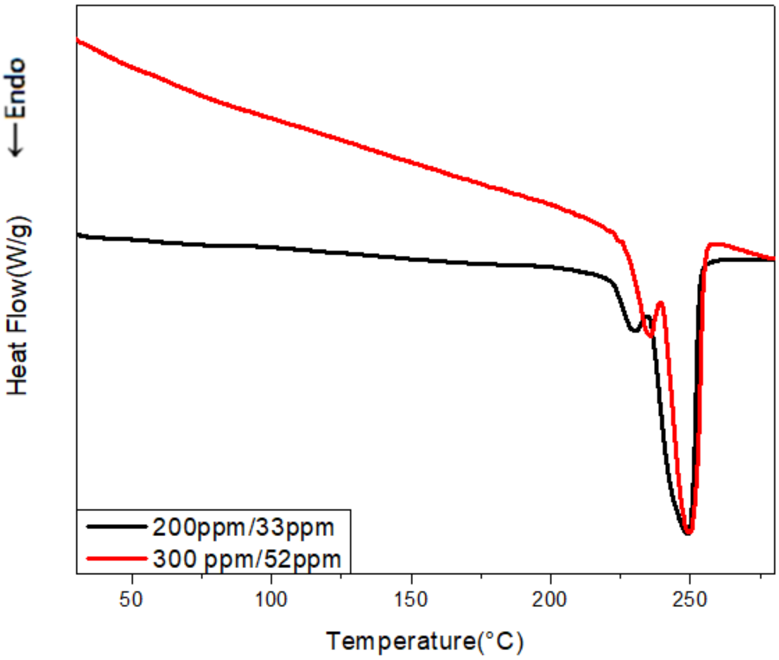


Figure 5.25. Comparison of the DSC thermograms of PET obtained from SSP in which PET (prepolymer) was obtained from polymerization reactions containing different catalyst concentrations.

5.2.2.5. Effect of the application of further SSP

The SSP 1 was passed through a 90-micron sieve and then kept under vacuum at 220°C for 6 hours (SSP 5). It was observed that the IV value SSP 5 continued to increase (Figure 5.26). This could be an indication that a longer reaction time was associated with higher IV. In addition, the rate of increase of the IV value was greater in the first stages of SSP 5 than in the last stages of SSP 1. This is because PET was passed through a 90 micron sieve prior to the application of SSP 5 and the smaller particle size means that the surface area of the PET particles becomes larger, which facilitates the diffusion of by-products. Therefore, the SSP reaction in SSP 5 (especially in the initial phase) takes place close to the surface of the particles, which means that the diffusion of the by-products is very fast and therefore not hindered by crystallinity (Kim et al., 2003). As expected, “the number of CEGs continues to decrease, which is why the esterification reaction takes place in SSP 5 (Wu et al., 1997).

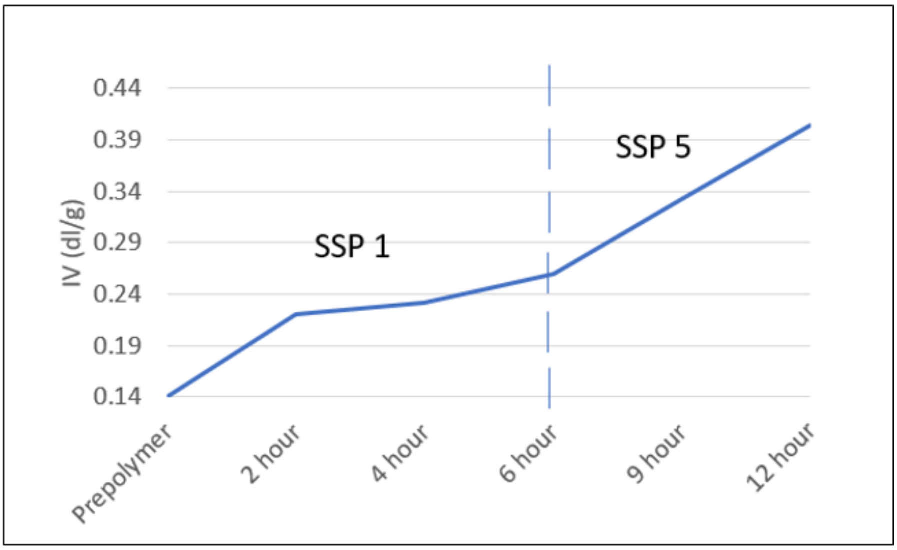


Figure 5.26. Effect of the application of further SSP on the IV values of PET samples (SSP 1 and SSP 5).

5.2.2.5.1. DSC analysis

DSC thermograms of SSP1 and SSP5 are presented in Figure 5.27. The T_m of SSP 5 was higher than the T_m of SSP 1. The higher Tm of SSP 5 showed that the polymerization reactions continued to take place as the reaction time was prolonged up to 12 hours.

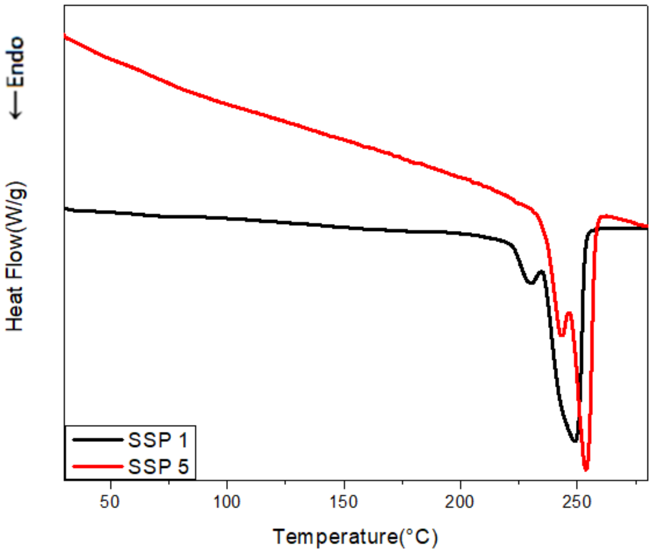


Figure 5.27. Comparison of the DSC thermograms of PET samples obtained from SSP 1 and SSP 5.

CHAPTER 6

6. CONCLUSIONS

6.1. Depolymerization of PET by Glycolysis Method

The aim of the first part of the study was to obtain pure BHET crystals by using different input materials and catalysts. In order to fulfil this aim, PET glycolysis reactions were performed, and, in these reactions, five types of input materials and three types of catalyst were used. Yield of BHET crystals for each glycolysis reaction were determined and characterization methods were employed to utilize the quality of BHET.

Regardless of the input material, the BHETs obtained displayed similar properties. There was no significant difference in quality in the BHETs obtained, they were in high purity and had similar properties with commercial BHET. Therefore, it was shown that the input material used, which contained various additives, did not cause any significant difference in the properties of the BHET obtained and that a PET material containing additives could be broken down into its pure monomers by the glycolysis method without additional processing.

Moreover, it was found that although using the different catalyst systems did not lead to significant difference in quality in the BHETs, they affected glycolysis process and BHET yield. When BHET yield was considered, $Zn(OAc)_2$ was the most efficient catalyst. On the other hand, 1,3-DMU/$Zn(OAc)_2$ DES led the glycolysis reaction to complete in shortest time which made 1,3-DMU/$Zn(OAc)_2$ DES the most recommendable catalyst in terms of reaction time.

6.2. Repolymerization of PET

There are several factors that have a great influence on the PET polymerization process, and optimizing the conditions for the PET polymerization process leads to the formation of PET with a higher IV value and a lower number of CEGs.

The longer reaction time at relatively low temperatures resulted in a slight increase in the IV value and a decrease in the number of CEGs. This showed that a longer period of time allowed the polymerization reaction to propagate at temperatures where no degradation reactions took place. The addition of phosphoric acid, one of the most commonly used stabilizers, to the polymerization reaction had a positive effect on the properties of the PET product. Thanks to its ability to improve thermal stability and suppress the formation of degradation reactions during the polymerization process, it could help maintain the IV and prevent the increase in the number of CEGs of PET. On the other hand, the addition of EG did not have any considerable influences on the properties of the PET formed, which was due to the fact that BHET was highly pure and did not contain a significant number of different structures. The use of 300 ppm antimony (III) oxide and 30 ppm titanium tetraisopropoxide in PET polymerization reactions as catalysts led to the best results in terms of catalyst amount. The use of this amount of catalyst accelerated the reaction rate of polymerization, but did not significantly enhance the degradation reaction, which was the desired outcome. As a result of applying vacuum for 90 min at 275°C, the PET with the highest IV value and the lowest number of CEGs was obtained when comparing the PET samples to which different vacuum times were applied during polymerization. Therefore, 90 min can be accepted best duration for applying vacuum, which provided continuous removal of EG without domination of degradation reactions under the polymerization reaction conditions and setup used in this study.

6.2.1. Solid State polymerization of PET

The effects of reaction time, reaction temperature, particle size and the amount of catalyst used in the melt polymerization on the SSP process, and the properties of the PET product were analyzed. In order to analyze the influence of reaction time, PET samples were taken at certain time intervals, and it was observed that the IV value of the PET sample increased with increasing reaction time. This showed that the polymerization reaction propagated slowly which continued to occur at determined reaction time. Furthermore, carrying out the SSP reaction at higher temperatures led to the formation of PET with higher IV. This can be explained by the ability of higher temperatures to activate inactive end groups and involve them in the reaction. Therefore, increasing the temperature leads to higher overall rates for the SSP. During the SSP process, the use of smaller particles had a positive influence on the SSP reaction. This was most likely due to the diffusion of the by-products readily from the PET particles and removal from the reaction system. The use of smaller PET particles meant the use of particles with a larger particle surface area, which facilitated the diffusion of by-products. It was shown that the use of a higher amount of catalyst in melt polymerization also had an influence on the SSP process. In the SSP process, the catalysts were also active, which accelerated the reaction rate. In conclusion, SSP was observed to be very effective in improving the properties of the PET, especially IV value. The creation of more suitable conditions may lead to further improvement in PET molecular weight and properties.

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PRESENTATIONS

Kori S., Atılal E., Ekinci D., Kızıldağ N., Ugur G., Dizman B., Unal S. Recycling and Re-Synthesis of Poly(ethylene terephthalate). The IX. Polymer Science and Technology Congress with International Participation, September 2024 (Accepted for Oral Presentation).

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SCHOLARSHIPS

Sakıp Sabancı 25% Encouragement Scholarship ………………………..2019 – 2020

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