# INVESTIGATION OF POLYETHYLENE TEREPHTHALATE SYNTHESIS VIA SOLUTION POLYMERIZATION TECHNIQUE

by

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INVESTIGATION OF POLYETHYLENE TEREPHTHALATE SYNTHESIS VIA SOLUTION POLYMERIZATION TECHNIQUE

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*Dedicated to my family*

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# ABSTRACT


## INVESTIGATION OF POLYETHYLENE TEREPHTHALATE SYNTHESIS VIA SOLUTION POLYMERIZATION TECHNIQUE

Poly (ethylene terephthalate) (PET) is a thermoplastic polyester commonly used in the industry owing to its good mechanical strength, thermal stability, high solvent resistance and low-cost production. According to application area, various molecular weight PET is produced mostly at high temperature at melt phase under vacuum. Although melt polymerization is feasible and widely used, there are disadvantages of the system such as degradation of PET due to the long reaction time at high temperature and formation of side products such as diethylene glycol. To avoid such degradations, melt polymerization is used to obtain PET's that are considered medium molecular weights then solid state polymerization is employed to produce higher molecular weight PET's. However, SSP requires very long reaction times (12-24 h) which makes it very inconvenient and expensive. Therefore, in the present work, an alternative pathway that could potentially replace the SSP process was investigated. The main goal was to synthesize PET-anhydrides, in other words, polyester anhydrides, that may act as chain extenders when reacted with –OH terminated medium molecular weight PET's. During such effort, syntheses of polyacid anhydrides, then PET polyesters, then finally PET polyester anhydrides were investigated. These reactions were all carried out by solution polymerization techniques which is not a reported technique for the synthesis of PET. The scope and the limitation of such a process for the synthesis, and its effect on the final polymer properties are discussed. The results from templatize chain coupling reactions of PET using the polyanhydrides and polyester anhydrides is presented.

# ÖZET

## POLİETİLEN TEREFTALAT SENTEZİNİN SOLÜSYON POLİMERİZASYON YÖNTEMİ İLE İNCELENMESİ

Endüstride yaygın olarak kullanılan polietilen tereftalat (PET) yüksek ısı, mekanik ve çözücü dayanıklılığına ve düşük maliyetli üretime sahiptir. Kullanım alanına göre farklı moleküler ağırlığına sahip PET, eriyik polimerleşme yöntemi ile yüksek sıcaklık altında vakum uygulanarak sentezlenir. Eriyik polimerleşme metodu yaygın olarak kullanılmasına rağmen sentez süresinin uzun olması ve yüksek sıcaklık kullanılması degredasyona ve dietilen glikol gibi yan ürün oluşumuna sebep olur. Bu sorunlarla karşılaşmamak için orta moleküler ağırlığa sahip PET, eriyik polimerleşme ile sentezlendikten sonra moleküler ağırlığı, katı hal polimerleşme yöntemi ile arttırılabilir. Ancak; katı hal polimerleşmesi uzun sürdüğü için (12-24 saat) hem zahmetli hem de ekonomik olarak uygun değildir. Bu nedenle, bu çalışmada katı hal polimerleşmesi yerine kullanılabilecek yöntem araştırılmıştır. Bu çalışmanın esas amacı PET-anhidrit sentezlemek ve bu sentezlenen PET-anhidritleri orta ağırlıktaki PET zincirlerini bağlamak için kullanmaktır. Bu amaç için sırasıyla poliasit anhidrit, PET ve PET-anhidrit sentezleri incelenmiştir. Bütün sentezler solüsyon polimerleşme tekniği ile yapılmıştır. Solüsyon polimerleşme yöntemi PET sentezi için kullanılan bir yöntem olmadığı için bu tekniğin kısıtlamaları ve polimer üzerindeki etkileri ele alınmıştır. Ayrıca, polianhidrit ve PET-anhidrit örneklerinin zincir uzatma reaksiyonları ve PET'in moleküler ağırlığı üzerindeki etkileri araştırılmıştır.

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# LIST OF ACRONYMS/ABBREVIATIONS

| | |
|---|---|
| BOZ | 2,2'-bis (2-oxazoline) |
| $CDCl_3$ | Deuterated Chloroform |
| COOH | Carboxylic Acid |
| DCM | Dichloromethane |
| DEG | Diethylene Glycol |
| DMT | Dimethyl Terephthalate |
| DSC | Differential Scanning Calorimetry |
| EG | Ethylene Glycol |
| EtOH | Ethanol |
| FTIR | Fourier Transform Infrared Spectroscopy |
| GPC | Gel Permeation Chromatography |
| HFIP | 1,1,1,3,3,3-Hexafluoro-2-propanol |
| IPC | Isophthaloyl Chloride |
| IV | Intrinsic Viscosity |
| $M_n$ | Number Average Molecular Weight |
| $M_w$ | Weight Average Molecular Weight |
| $NaHCO_3$ | Sodium Hydrogen Carbonate |
| NMR | Nuclear Magnetic Resonance Spectroscopy |
| NX3P | 2-4-6-tris(dimethylaminomethyl) phenol |

| | |
|---|---|
| OH | Hydroxyl |
| PDI | Polydispersity Index |
| PLA | Poly (lactic acid) |
| PMDA | Pyromellitic Dianhydride |
| PEA | Polyester Anhydride |
| PET | Poly (ethylene terephthalate) |
| RT | Room Temperature |
| SSP | Solid State Polymerization |
| $T_c$ | Crystallization Temperature |
| TEA | Triethylamine |
| TFA | Trifluoroacetic Acid |
| $T_g$ | Glass Transition Temperature |
| THF | Tetrahydrofuran |
| $T_m$ | Melting Temperature |
| TIP | Titanium (IV) Isopropoxide |
| TPA | Terephthalic Acid |
| TPC | Terephthaloyl Chloride |

# 1. INTRODUCTION

## 1.1. Polyethylene Terephthalate

Polyethylene terephthalate, hereafter called PET, is a widely appreciated engineering thermoplastic polymer owing to its good physical and mechanical properties [1]. Its strength, toughness and low production cost make it widely used in different industrial areas such as automobile, electrics and textile. Moreover, PET demonstrates resistance to chemicals, heat as well as atmospheric and biological agents; therefore it is also commonly preferred for food packaging and bottle containers [2]–[4].

PET is a semi-crystalline polyester and its superior properties are coming from crystallinity [5]. As seen in Figure 1.1, its repeating unit is consisting of an aromatic ring and a short aliphatic chain which are bound with an ester linkage. Electron movements in aromatic rings lead to close proximity with each other which is called π-π stacking and two carbon distance between aromatic rings on the polymer chain is not able to provide flexibility. Therefore, π-π stacking and limited mobility increase the crystallinity [6].

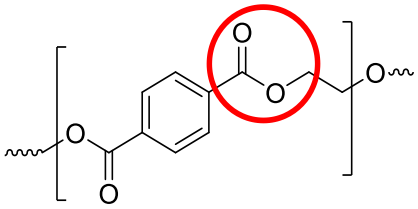



Figure 1.1. PET Repeating Unit.

Two scientists J. Rex Whinfield and J. T. Dickson at the Calico Printers Association Laboratories invented PET in 1941. Afterwards, Imperial Chemical Industries (ICI) in the Britain and DuPont in the USA purchased the production rights and then PET was sold under the brand names of Terylene in England and of Dacron in the USA [7], [8]. Besides, PET fiber was manufactured as Tervira and Diolen in Germany [9].

Table 1.1. Physical and chemical properties of PET [10].

| **Property** | **Value** |
|---|---|
| Molecular weight of repeating unit | 192 g/mol |
| Weight-average $M_w$ | 30000-80000 g/mol |
| Density | 1.41 g/cm$^3$ |
| Glass transition temperature ($T_g$) | 69-115$^0$C |
| Melting temperature | 255-265$^0$C |
| Breaking strength | 50 MPa |
| Tensile strength (Young's modulus) | 1700 MPa |
| Yield strain | 4 % |
| Impact strength | 90 J/m |
| Water absorption (after 24 h) | 0.5 % |

General properties of PET are seen in Table 1.1. These distinguished properties like high melting point make it handy for different industrial applications [5].

## 1.2. PET in Industry

Synthetic organic polymers have become a part of everyday life since the early 20$^{th}$ century and their role has been increasing. As seen in Figure 1.2, plastic production has been accelerating for each types [11].

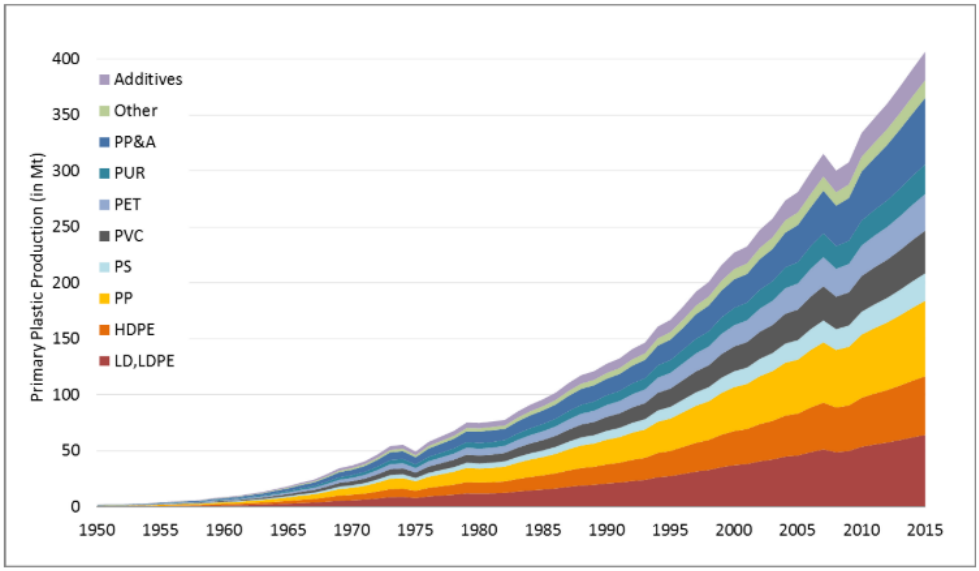



Figure 1.2. Global Primary Plastic Production (in million metric tons) [11].

After discovery of PET, different studies were conducted, and PET film was made at late 1950s. Afterwards, video, photographic and X-ray film had been produced. The development of blow-moulded PET reached at early 1970s [12].

Most of the global production of PET consists of water and carbonated soft drink bottles as depicted in Figure 1.3. In general, PET is strong, stable and durable. Therefore, the demand for PET is high. In 2017, PET resin production capacity was 30.3 million tons worldwide [13]. PET is chosen for bottles because of its glass-like transparency, lightweight as well as resistance to break. Besides, another reason for the frequent usage of PET is sufficient gas barrier ability which improves the shelf life of carbonated drink by delaying internal $CO_2$ escape [12], [14].

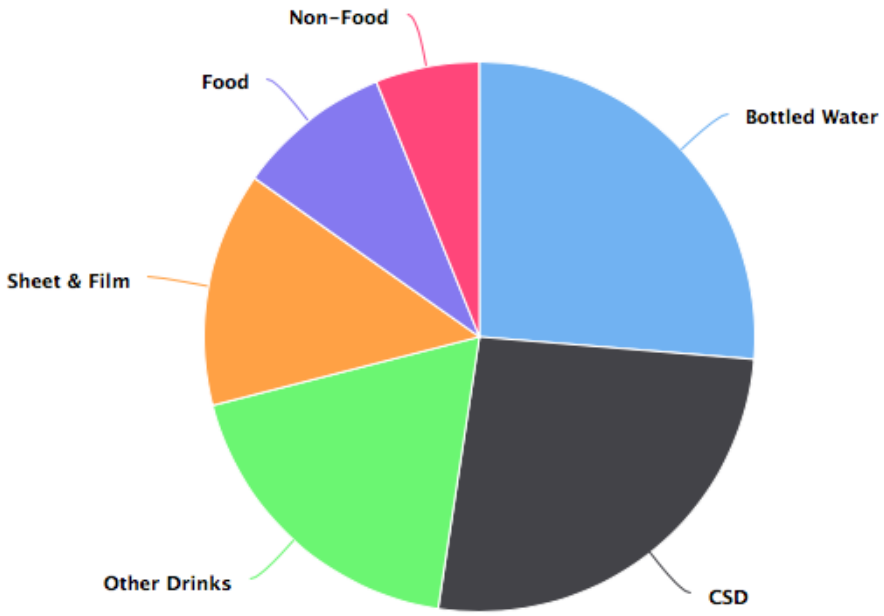



Figure 1.3. Global PET Consumption by End-Segment (2016) [13].

PET is a thermoplastic polymer; therefore, it can be modified according to application area and the requirements of the final product. Molecular weight and crystallinity degree are the two main parameters to be changed. As seen in Table 1.2, PET with different IV values are used depending on the application [10].

Table 1.2. Intrinsic Viscosity of PET products.

| **Application Area** | **IV (dl/g)** |
|---|---|
| Recording tape | 0.60 |
| Fibres | 0.65 |
| Carbonated drink bottles | 0.73-0.8 |
| Industrial tyre cord | 0.85 |

Orientation of polymer chains can be arranged by mechanical stretching or thermal crystallization. If polymer chains are forced to align in one direction, fibres are obtained. In order to generate films and sheets, polymer chains are arranged in two directions [14]. PET fibres are preferred for clothing because they act as moisture barrier and provide creep resistance [13]. Although high molecular weight PET with adequate crystallinity offers good mechanical properties such as stiffness and toughness, it should also gain sufficient flexibility to resist bursting and breaking under pressure [12].

In addition, PET has good electrical properties so it can be used as insulating materials because it demonstrates high dielectric strength, resistance to moisture and it is thermally stable [15]. Therefore, PET resins with various properties can be synthesized depending on the industrial applications.

## 1.3. PET Synthesis

### 1.3.1. Melt Polymerization

PET is obtained by step-growth polymerization [16]. At first, PET was synthesized by the reaction between terephthalic acid (TPA) or its derivatives (such as esters and dihalides) and ethylene glycol [17]. Nowadays, two routes are commonly preferred for PET manufacturing; terephthalic acid pathways and dimethyl terephthalate (DMT) pathway [18].

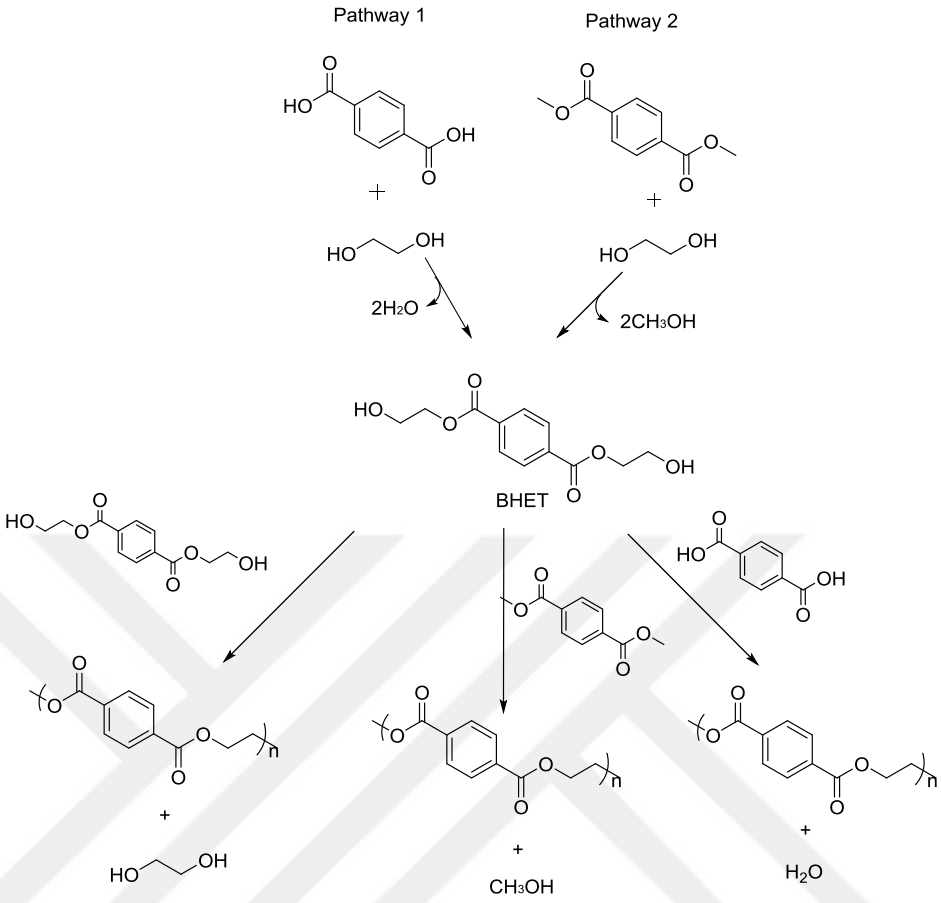



Figure 1.4. PET Synthesis Route.

As seen in Figure 1.4, PET formation is a two steps reaction for both TPA and DMT methods. The first step is called esterification for TPA and transesterification for DMT or precondensation generally in which ethylene glycol reacts with acidic monomers to form bis (hydroxyethyl terephthalate) (BHET) as well as short chain oligomers in the presence of a catalyst. Water and methanol are distilled off for TPA and DMT pathways, respectively. Reactions undergo at a temperature range of $240^0$C-$265^0$C that is higher than the melting point of the target polymer [16], [18]–[20]. Compared to DMT, TPA provides higher esterification rate and less catalyst. Antimony, germanium and titanium containing catalyst are usually used for TPA while zinc, lead and mercury type catalysts are used for DMT. Although methanol is more volatile than water, methanol is highly flammable which require special handling, therefore, TPA pathway is considered to be more feasible. On the other hand, TPA is hard to melt and to dissolve in a suitable solvent. Therefore, efficient mixing is important for high quality products [18].

The second step is polycondensation reaction at higher temperature and reduced pressure to gain increased molecular weight polyesters from BHET and oligomers, which is catalyzed by transesterification catalysts such as antimony and titanium [17], [20]. Polycondensation takes place in two ways. In first case, the reaction proceeds between carboxyl end group and hydroxyl end group and then water is eliminated. In another situation, hydroxyethyl end group reacts with ester end group and ethylene glycol is eliminated. The latter case predominates in later stages. Intrinsic viscosity of the final product obtained is usually in between 0.5-0.7 dl/g [18].

This synthetic method produces polyesters with a number-average molecular weight around 30,000 g/mol. As reaction time increases, molten phase viscosity is also increased so that even mixing thus heating becomes problem. In addition to stirring difficulties, some side ester interchange reactions and degradations, which will be explained later, occur which compete with the desired polycondensation reactions [19]. In order to eliminate such side reactions and obtain higher molecular weight products, solid state polymerization is then carried following the melt process.

### 1.3.2. Solid State Polymerization

PET has been used in many application areas depending on its IV and molecular weight. For instance, PET having IV of 0.5-0.7 dl/g can be used as filament fibers and films. However, beverage bottle and tire cord filament industries require PET having IV value greater than 0.7 dl/g [21]. Consequently, solid state polymerization is performed on the amorphous resins in order to raise the molecular weight. However, this requires extended reaction times owing to the low reaction rate. When compared to melt polymerization, temperature is lower in SSP so that side reactions and thermal degradation become less significant. For the solid prepolymer, the SSP temperature is arranged such that it is higher than the $T_g$ of the amorphous phase but lower than the $T_m$. Reaction temperature is high enough to activate end groups to react each other, however, it should be 10-40$^0$C below the $T_m$ in order to prevent any agglomeration and sintering. [22], [23].

In addition to the reaction temperature, reaction time, initial prepolymer IV (or $M_n$), crystallinity, catalysts as well as vacuum and gas transport affect the efficiency of SSP [21]–[25].

For PET synthesis, SSP temperature can be in the range of 200-250$^0$C. Temperature should be arranged carefully in order to provide enough flexibility to the end groups and diffusion but not so high to initiate side reactions and sticking [22].

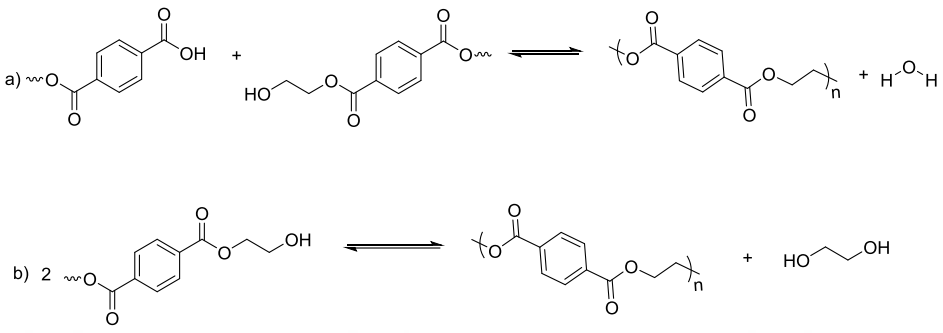



Figure 1.5. SSP Pathways [21].

SSP is mostly based on the reaction between the end groups of the polymer chains, as depicted in Figure 1.5. Similar to the melt phase, it can be either between -COOH and -OH end groups or two hydroxyethyl end groups, as explained in previous part where water and EG are by-products, respectively. Moreover, reaction progress is followed by depletion of the end groups [22], [26]. As reaction proceeds, by-products can be removed by vacuum or inert gas stream, therefore, forward reaction dominates. When vacuum is applied, residual unreacted TPA, BHET, monohydroxyethyl terephthalate and cyclic oligomers are removed as sublimates. It was observed that the reaction was faster when vacuum was applied rather than the nitrogen sweep [26]. On the other hand, inert gas usage has some advantages such as inhibiting the polymer oxidation [22].

SSP relies on the availability and mobility of the end groups at the amorphous phase, therefore, initial end group concentration and crystallinity play an important role [21], [24]. When high molecular weight polymer chains which have low end group concentration are used at the beginning, higher molecular weight ($M_n$) product may be obtained at the end of SSP because even if two polymer chains are reacted, increase in $M_n$ will be high. However, the coincide of end groups gets harder [22]. Furthermore, the ratio of [COOH]/[OH] is also important because esterification and transesterification reactions are competitive. The predominant route is determined by the diffusion rates of the by-products [23]. For instance, diffusion rate of water is higher than of EG at 230$^0$C [22].

Additionally, degree of crystallinity has an effect on end-group mobility and by-product diffusion which influences SSP production. Furthermore, distribution and size of crystallites also affect the movement of the prepolymer [21], [25].

## 1.4. Degradation

PET is known to be strong and durable as well as resistant to environmental conditions [27]. However, manufacturing conditions, which are explained in previous part, are harsh so that degradation reactions are inevitable. As reactions time increases in the melt-phase to generate a polymer with higher molecular weight and intrinsic viscosity, the possibility of competition between degradation reactions and polycondensation reactions is raised. The three main degradation pathways are thermal degradation, oxidative degradation and hydrolytic degradation [28].

Thermal degradation takes place when the temperature is between 250-300$^0$C in the absence of oxygen. Ester linkages in PET makes it vulnerable; therefore, chain scission occurs randomly at these points [15].

Thermal degradation starts with scission of the ester linkage either in the chain or at the chain ends. In each case, molecular weight of the polymer decreases and the number of carboxy end group (CEG) increases [28].

As seen in Figure 1.6, the hydrogen of the methylene group at β-position to carbonyl group is able to form six-membered cyclic intermediate which is broken to form carboxy terminated and vinyl ester terminated units [29]. After β scission, the produced vinyl ester further reacts to generate acetaldehyde which is toxic and regulated for food-contact products [14]. Besides, carboxy terminated unit may react with hydroxyl terminated polymer and water is produced as a side product [29]. In other words, polymer chains first break and then combine again which leads to CEG dominant polymer mixture and side products.

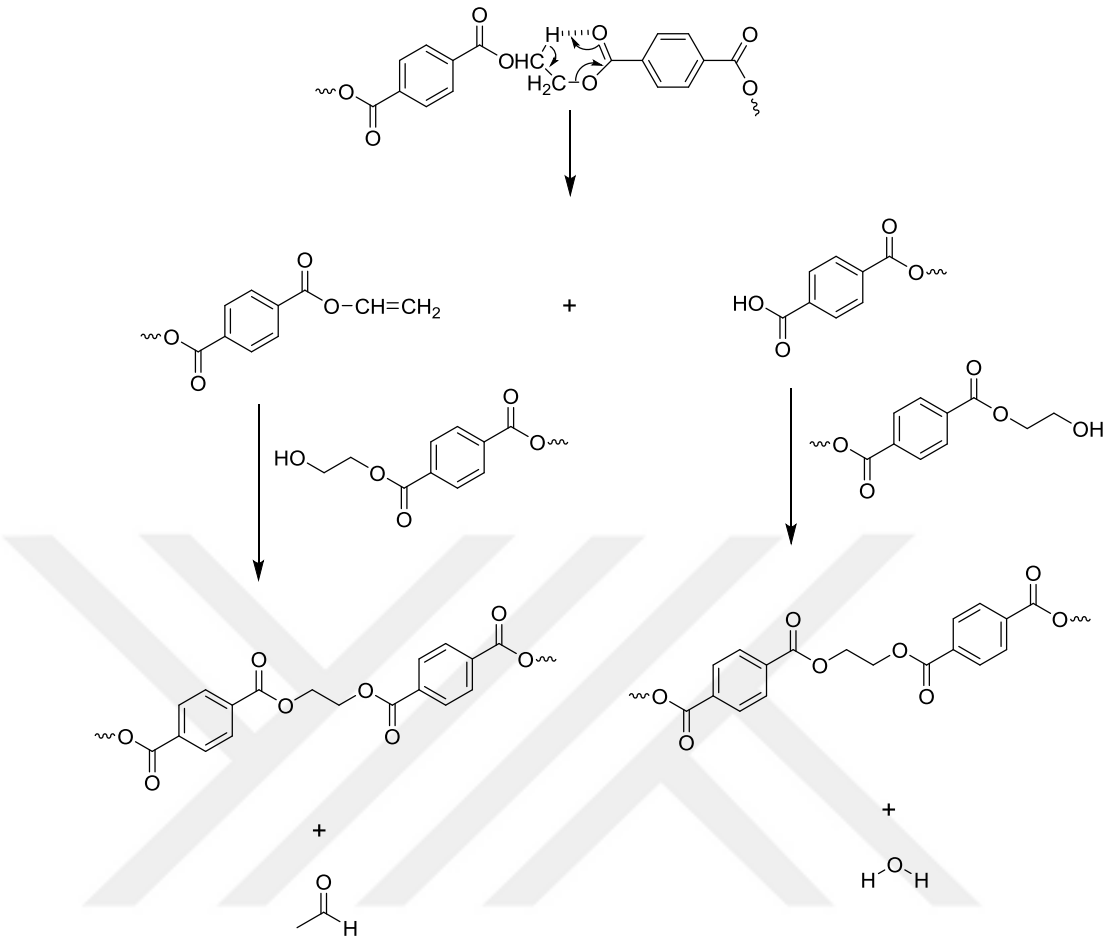


Figure 1.6. Thermal Degradation of PET [29].

Additionally, the produced vinyl ester and carboxylic acid can react with each other to form anhydride bond. The further possible reactions are seen in Figure 1.7 [30].

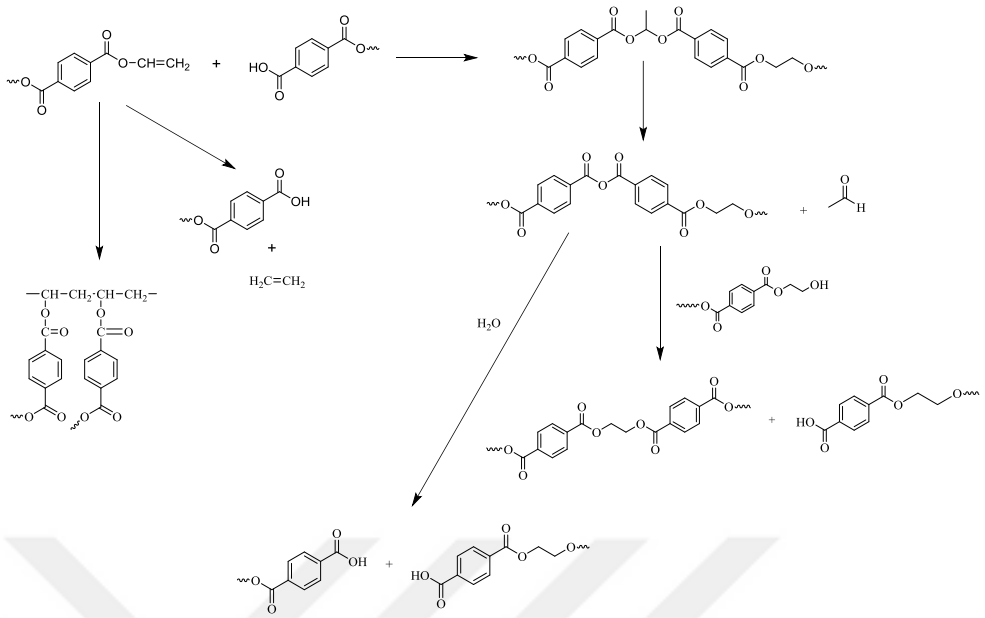


Figure 1.7. Reaction Network of Thermal Degradation [30].

As seen in the Figure 1.8, the hydroxyl end group can attack to ester carbonyl so that cyclic and shorter polymer chains occur [29].

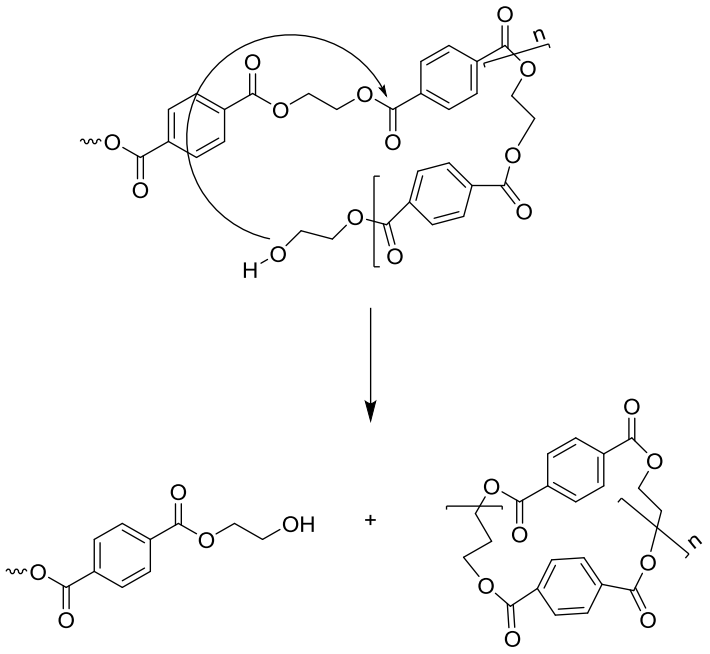


Figure 1.8. Cyclization [29].

Moreover, hydroxyl end group can interact with adjacent carbonyl rather than attacking different carbonyl to provide cyclization. In this case, CEG chain and acetaldehyde are produced. As seen in the Figure 1.9, if the intermediate is faced to ethylene glycol or hydroxyl terminated another chain, diethyl glycol (DEG) terminated and DEG bounded polymers will be generated respectively [28].

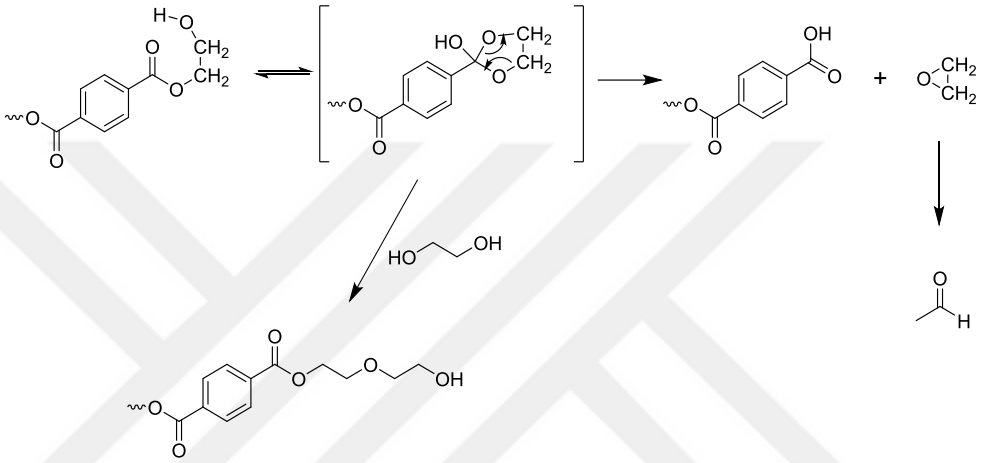


Figure 1.9. DEG Formation [28].

When DEG end group is formed, it is not able to stay like this. Under high temperature, it will degrade further. As depicted in Figure 1.10, dioxane and CEG chains are produced [31].

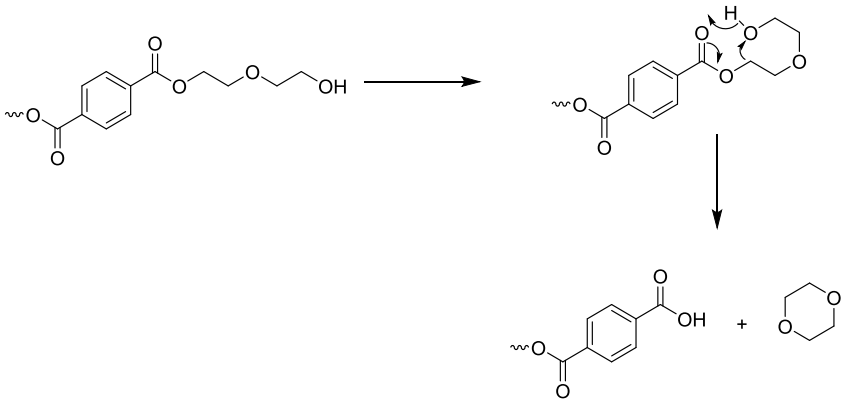


Figure 1.10. Dioxane Formation [31].

In addition to heat, when moisture is present in the medium, hydrolytic degradation takes place and smaller chains are formed as depicted in Figure 1.11 [32], [33].

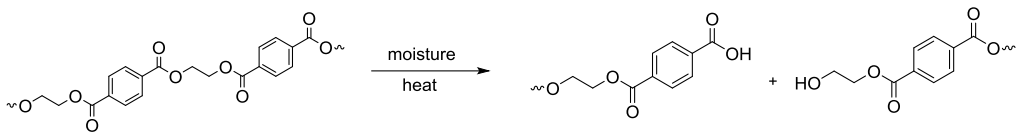



Figure 1.11.Hydrolytic Degradation of PET [32].

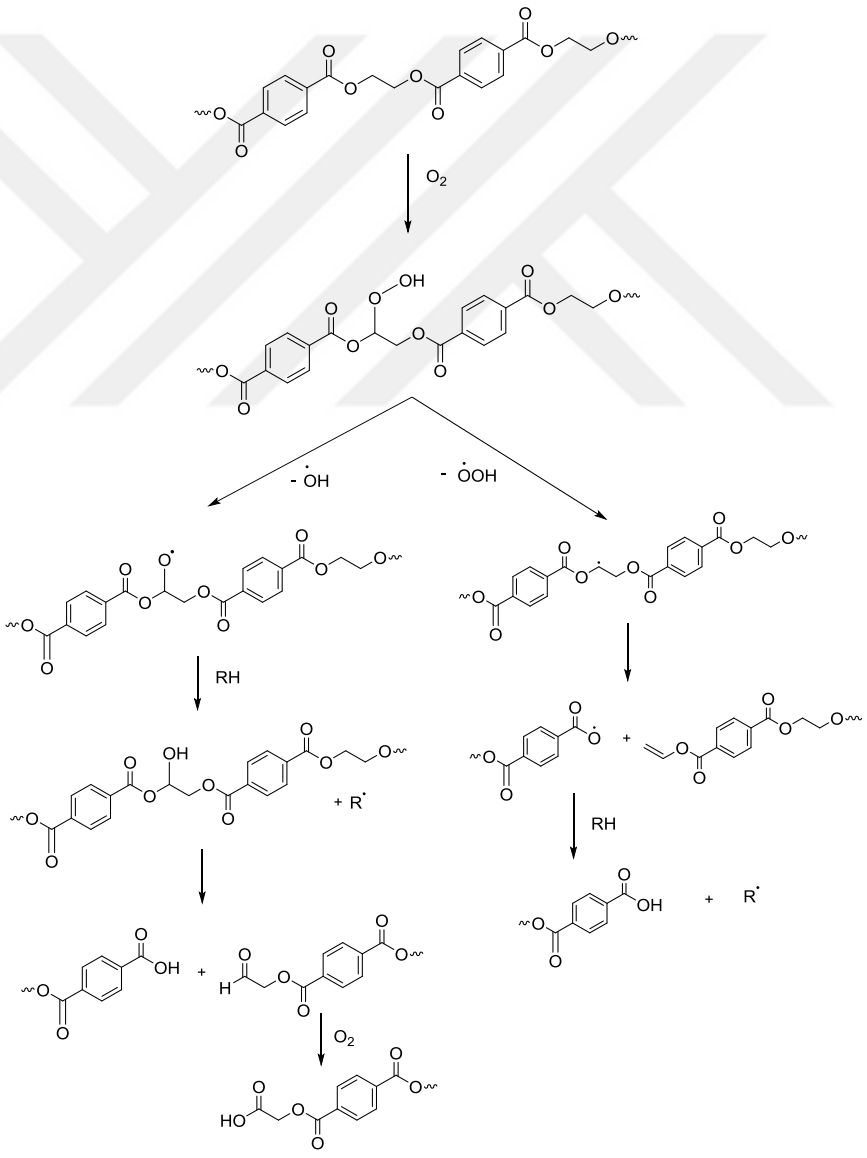



Figure 1.12. Thermooxidative degradation of PET [15].

The third process is thermooxidative degradation. In this case, oxygen is present in the hot molten state. As seen in Figure 1.12, CEG content increases as molecular weight decreases. The rate of degradation is directly proportional to oxygen content [15].

## 1.5. Chain Extension

Like SSP, chain extension is an alternative post-polymerization method. Although SSP enables to produce high-molecular-weight polyesters, it has very low reaction rate and needs special equipment for large scale production [34]. In order to overcome such problems and reduce the expenses, chain extenders have been used which leads to high-molecular-weight polymers in a shorter time. They are generally added to polymer melt and bring two end groups of host polymer chains together [34]–[37].

Chain extenders are usually multifunctional preferably bifunctional low molecular weight compounds. If a bifunctional chain extender is used, outcome polymer will be linear. On the other hand, branched or cross-linked polymers will be generated if a multifunctional chain extender is chosen [36].

The right choice of a chain extender and a correct concentration usually enable to synthesize PET with desired IV, instead of SSP [36]. There are some parameters to be considered for a proper chain extender. For instance, it should be thermally stable at the processing temperature. Besides, the reaction between end groups and chain extender should be fast and almost irreversible under these conditions. After extension, interference in polymer orientation and side products are not wanted [38].

For PET, various types of chemicals can be used as chain extenders. Cyclic imino esters, di or poly-epoxy compounds, bisoxazolines and tetracarboxylic anhydrides are some examples [34], [36], [38]. PET that possesses higher molecular weight as well as lower carboxyl end group content shows better mechanical and chemical properties. Therefore, chain extenders which react with -COOH end groups are advantageous [34]. 2,2’-bis(2-oxazoline) (BOZ) is an example of bifunctional chain extender that reacts with -COOH end

group of PET. Ring opening reaction proceeds with no side product elimination as a result of increased IV [39].

In the contrary, dianhydrides are tetra-functional chain extenders so that they cause branching and crosslinking. Unlike BOZ, they give reaction with -OH end groups [40]. The most commonly used one is pyromellitic dianhydride (PMDA) [36].

## 1.6. Polyanhydride

Anhydride linkage is beneficial for different types of application areas owing to instability of degradation. As mentioned before, anhydrides can be used as chain extenders. For instance, epoxy resins can be cured with dicarboxylic acid anhydrides [41], [42]. It has been shown that hydroxyl terminated poly(amine-ester) polymer crosslinked with succinic anhydride [43]. Moreover, poly(maleic anhydride-co-vinyl acetate) was found to be a crosslinker for cellulose [44].

Like anhydride itself, polyanhydrides have been used for many purposes since it was first found by Bucher and Slade in 1909. Biomedicine industry pay attention to polyanhydrides owing to their hydrolytic instability and change in degradability rate. When release controlling is the issue, polyanhydrides are the first one that comes to mind. Although ester functional group is hydrolytically degradable, anhydrides have shorter lifetime [45]. They can be used in many bio-related applications. For example, materials such as drugs, proteins as well as DNA fragments can be delivered. Besides, they can be used in vaccines. In addition to acidic or alkaline environment, they undergo degradation under physiological conditions and the rate of degradation can be manipulated by altering the monomer types and ratios. What is more, polyanhydrides demonstrate surface erosion degradation so that bioactive agent inside it is not affected directly from the environmental conditions [46]–[48].

Poly (lactic acid) (PLA) is itself a biocompatible material which takes part in tissue engineering and drug delivery system. PLA extended with succinic anhydride was proved to increase molecular weight significantly [49].

### 1.6.1. Poly(ester-anhydride)

On the other hand, anhydride can be part of polymer backbone. For instance, sebacic and adipic anhydrides were incorporated to L-lactic acid and then produced ester-anhydride co-polymer was able to encapsulate DNA for further delivery process [50]

Poly(ester-anhydride) is an attractive group of polymers because it contains both ester and anhydride linkages. Although both functional groups are hydrolytically degradable, ester bond is more durable than the anhydride bond. Therefore, it is possible to create a carrier of biomaterial by changing ester/anhydride ratio to provide sufficiently controlled release [46], [51], [52]. It has been shown that the ester-anhydride copolymer of polylactic acid (PLA) and polysebacic acid (PSA) underwent melting at temperature 35-80$^0$C depending on the ratio of PLA to PSA [53].

# 2. AIM OF THE STUDY

The aim of the study is to synthesize low molecular weight poly (ethylene terephthalate) by solution polymerization technique in one step. In order to reach this goal, terephthaloyl chloride (TPC) was reacted with ethylene glycol (EG) in the presence of triethylamine (TEA). Limited studies on solution polymerization for PET synthesis were found in the literature. Therefore, possible limitations and scope of this technique was investigated. The main idea was to diminish degradation reactions and eliminate side products that are formed during the conventional melt polymerization techniques that are carried out at high temperatures. In addition, anhydride linkages were targeted to obtain PET based polyester anhydrides. The effect of reaction conditions on the polymerization was investigated. The final products were analyzed by using FTIR, NMR, DSC and GPC measurements. Finally, the effect of anhydrides onto PET systems were investigated under melt mixing conditions.

# 3. EXPERIMENTAL

All chemicals were used as received from the manufacturer (Merck, Sigma-Aldrich, Acros Organics, Synthron). Dry solvents were prepared by using molecular sieves.

## 3.1. Synthesis

### 3.1.1. Polyanhydride Synthesis

1.1.1.1. Synthesis of benzoic anhydride. 1.0 mol of benzoyl chloride was dissolved in dichloromethane (DCM) and then 1.0 mol of triethyl amine (TEA) was added slowly. After mixing 15 minutes, 0.5 mol of water added to the mixture. The reaction was stopped after 30 minutes. The product was obtained after extraction. The anhydride bond was confirmed with FTIR by the presence of 1779 $cm^{-1}$ and 1722 $cm^{-1}$ peaks.

2.1.1.1. Synthesis of poly (isophthalic anhydride). IPC (0.02 mol, 4.06 g) was dissolved in 40 mL DCM. TEA (0.04 mol, 4.05 g) was added slowly and mixed for 15 minutes. Afterwards, distilled water (0.01 mol, 180 μL) was added. The reaction was kept mixing at room temperature for 30 minutes. When the reaction finished, the product was precipitated into a mixture of ethanol and $NaHCO_3$ (aq) (pH was 9) by the ratio of 5:2 (v/v). The anhydride peaks were seen at 1722 $cm^{-1}$ and 1788 $cm^{-1}$.

3.1.1.1. Synthesis of poly (terephthalic anhydride). TPC (0.02 mol, 4.06 g) was dissolved in 40 mL DCM. TEA (0.02 mol, 2.02 g) was added slowly and mixed for 15 minutes. Afterwards, distilled water (0.01 mol, 180 μL) was added. The reaction was kept mixing at room temperature for 30 minutes. When the reaction finished, the product was precipitated into a mixture of ethanol and $NaHCO_3$ (aq) (pH was 9) by the ratio of 5:2 (v/v). The anhydride peaks were observed at 1723 $cm^{-1}$ and 1788 $cm^{-1}$.

TPC (0.01 mol, 2.03 g) was dissolved in 50 mL THF. TEA (0.02 mol, 2.02 g) was added slowly and mixed for 15 minutes. Afterwards, distilled water (0.005 mol, 90 μL) was

added. The reaction was kept mixing at room temperature for 30 minutes. When the reaction finished, the product was precipitated into a mixture of ethanol and $NaHCO_3$(aq) (pH was 9) by the ratio of 5:2 (v/v). The anhydride peaks were seen at 1722 $cm^{-1}$ and 1786 $cm^{-1}$.

### 3.1.2. PET Reactions with Poly (terephthalic anhydride) in Melt

Low IV PET (IV= 0.355 dl/g, $M_n$=5005 g/mol, $M_w$=12690 g/mol, PDI=2.535) with OH/COOH end group ratio 3/1 was used in the experiments which were conducted in melt reaction system. PET powders were kept in the vacuum oven at $105^0$C and 10 mbar before usage. Approximately 15 g PET powder was placed into glass melt reactor and about 0.3 g synthesized poly (terephthalic anhydride) was added. Three different catalysts titanium IV isopropoxide (TIP), 2-4-6-tris(dimethylaminomethyl) phenol (NX3P), zinc acetate, were used where each were added in two different amounts (3% and 1%, mol percent with respect to -OH end group concentration). Before heating, nitrogen gas was swept for 5 minutes. Then, the reactor was immersed into hot silicon oil bath at $280^0$C. The reactor was heated by using ESM-4450 48 x 48 1/16 DIN Universal Input PID Process Controller with Smart I/O Module system. The reaction was assumed to start when the powder was molten. After 30 minutes mixing, 2 minutes vacuum was applied and then the product was collected. These solid products were analyzed by GPC and viscometer.

### 3.1.3. PET synthesis in Solution

PET synthesis was done in an inert system. In order to provide this environment, dry solvents were prepared by using molecular sieves. The molecular sieves were activated at $300^0$C for minimum 16 hours. The solvents were used minimum 2-3 days after preparation. Ethylene glycol stock solution was prepared beforehand by combining 3 mL EG and 57 mL THF over activated molecular sieves. For PET-10 synthesis, TPC (0.01mol, 2.03 g) was mixed firstly under nitrogen gas flow for 5 minutes. Then, it was dissolved in 30 mL dry THF. TEA (0.02mol, 2.02 g) was diluted with 10 mL dry THF in another round bottom flask under $N_2$ and then added to reaction vessel dropwise. After mixing 15 minutes, 10 mL ethylene glycol stock (0.0089mol, 0.55g) was added slowly and mixed at room temperature for 1hour. When the reaction finished, the product was precipitated into a mixture of ethanol and $NaHCO_3$(aq) (pH was 9) by the ratio of 5:2 (v/v). The final product was white powder with 44.3% conversion. In addition to NMR, they were analyzed with GPC and DSC. **$^1$H NMR** (400 MHz, CDCl3) δ 11.29 (d, J = 3.6 Hz, 899H), 8.23 (s, 2H), 8.22 (s, 2H), 8.20 (s,

6H), 8.18 (s, 12H), 8.16 (s, 12H), 8.13 (d, J = 3.6 Hz, 123H), 8.10 (s, 9H), 4.79 (d, J = 5.7 Hz, 138H), 4.60 (s, 8H), 4.47 (d, J = 7.1 Hz, 7H), 4.18 (s, 7H), 3.25 (d, J = 6.6 Hz, 6H), 1.44 (t, J = 7.1 Hz, 11H), 1.36 (t, J = 7.1 Hz, 10H), 1.26 (s, 4H).

Different ratios of the starting materials were tried, and the detailed information is given in Table 3.1.

Table 3.1. Reaction conditions for PET syntheses.

| Samples | Rxn Time | Temperature | TPC (mol) | TEA (mol) | EG (mol) |
|---|---|---|---|---|---|
| **PET-1** | 7.5 h | RT | 1.07 | 2.15 | 1 |
| **PET-2** | 7.5 h | $40^0$C | 1.07 | 2.15 | 1 |
| **PET-3** | 1 h | RT | 1.12 | 2.25 | 1 |
| **PET-4** | 1 h | RT | 1.26 | 2.53 | 1 |
| **PET-5** | 1 h | RT | 1.10 | 2.22 | 1 |
| **PET-6** | 1 h | RT | 0.95 | 1.89 | 1 |
| **PET-7** | 1 h | RT | 0.83 | 1.66 | 1 |
| **PET-8** | 1 h | RT | 0.79 | 1.58 | 1 |
| **PET-9** | 1 h | RT | 0.97 | 1.95 | 2 |
| **PET-10** | 1 h | RT | 1.12 | 2.25 | 1 |
| **PET-11** | 1 h | RT | 1.05 | 2.10 | 1 |
| **PET-12** | 1 h | RT | 1.09 | 2.17 | 1 |

### 3.1.4. PET-Anhydride Synthesis in Solution

Ethylene glycol stock solution was prepared beforehand by combining 3 mL EG and 57 mL THF over activated molecular sieves. TPC (0.01mol, 2.03 g) was mixed firstly under nitrogen gas flow for 5 minutes. Then, it was dissolved in 30 mL dry THF. TEA (0.02 mmol, 2.02 g) was diluted with 10 mL dry THF in another round bottom flask under $N_2$ and then

added to reaction vessel dropwise. After mixing 15 minutes, 10 mL ethylene glycol stock (0.0089mol, 0.55g) and various percent of distilled water were added together slowly and mixed at room temperature for 1hour. The ratios were seen in Table 3.2. Water moles were calculated according to TPC and their mol ratios were given in parentheses. When the reaction finished, the product was precipitated into a mixture of ethanol and $NaHCO_3$(aq) (pH was 9) by the ratio of 5:2 (v/v). The final product was a white powder, which was analyzed by FTIR, NMR, GPC and DSC. For representative, PEA-1 was synthesized with 50% conversion. **$^1$H NMR** (400 MHz, CDCl3) δ 11.47 (s, 15098H), 8.38 (d, J = 3.2 Hz, 63H), 8.33 (s, 74H), 8.31 (d, J = 3.3 Hz, 18H), 8.30 – 8.17 (m, 102H), 8.13 (d, J = 4.2 Hz, 419H), 4.80 (d, J = 5.6 Hz, 430H), 4.61 (d, J = 3.9 Hz, 27H), 4.47 (d, J = 7.1 Hz, 37H), 4.19 (d, J = 4.1 Hz, 23H), 4.08 (s, 2H), 4.05 (s, 1H), 4.03 (d, J = 3.6 Hz, 4H), 3.26 (d, J = 7.1 Hz, 17H), 1.45 (t, J = 7.1 Hz, 52H), 1.36 (s, 29H).

Table 3.2. Mol ratios of PET-anhydride syntheses.

| **Samples** | **TPC (mol)** | **TEA (mol)** | **EG (mol)** | **Water percent*** |
|---|---|---|---|---|
| **PEA-1** | 1.12 | 2.25 | 1 | 25% (0.275) |
| **PEA-2** | 1.12 | 2.25 | 1 | 20% (0.220) |
| **PEA-3** | 1.12 | 2.25 | 1 | 10% (0.110) |
| **PEA-4** | 1.12 | 2.25 | 1 | 5% (0.055) |
| **PEA-5** | 1.12 | 2.25 | 1 | 10% (0.110) |
| **PEA-6** | 1.12 | 2.25 | 1 | 20% (0.220) |
| **PEA-7** | 1.12 | 2.25 | 1 | 25% (0.275) |

### 3.1.5. PET Reactions with PET-Anhydride in Melt

Low IV PET (IV= 0.355 dl/g, $M_n$=5005 g/mol, $M_w$=12690 g/mol, PDI=2.535) with OH/COOH end group ratio 3/1 was used in the experiments which were conducted in melt reaction system. PET powders were kept in the vacuum oven at $105^0$C and 10 mbar before usage. Approximately 15 g PET powder was placed into glass melt reactor and about 0.3 g

synthesized PET-anhydride was added. Three different catalysts titanium IV isopropoxide (TIP), 2-4-6-tris(dimethylaminomethyl) phenol (NX3P), zinc acetate, were used with 3%-mol percent with respect to -OH end group concentration. Before heating, nitrogen gas was swept for 5 minutes. Then, the reactor was immersed into hot silicon oil bath at $280^0$C. The reactor was heated by using ESM-4450 48 x 48 1/16 DIN Universal Input PID Process Controller with Smart I/O Module system. The reaction was assumed to start when the powder was molten. After 30 minutes mixing, 2 minutes vacuum was applied and then the product was collected. These solid products were analyzed by GPC.

## 3.2. Analysis

### 3.2.1. FTIR Analysis

The samples were dried at vacuum cell before FTIR analysis. The sample powder was examined by Thermo Fisher Scientific Nicolet 380 FTIR. 64 scans were applied, and resolution was 2.

### 3.2.2. NMR Analysis

The samples were dissolved in a mixture of deuterated chloroform and trifluoro acetic acid at a ratio of 5/1 and 10/1. Brucker 400 NMR was used. Chemical shifts (ppm) were referenced to residual solvent.

### 3.2.3. Gel Permeation Chromatography (GPC) Analysis

The samples were dissolved in hexafluoroisopropanol (HFIP) and filtered with 0.45 μm filter. Wyatt Gel Permeation Chromatography with Shodex GPC HFIP 803 SEC/805 SEC/LG SEC column was used for GPC analysis. Column temperature was 40°C and flow rate was 0.7 mL/min.

### 3.2.4. Intrinsic Viscosity Analysis

PET samples were dissolved in o-chlorophenol at 0.02 g/mL concentration. Ubbelohde viscometer was used at 25°C for IV measurements.

### 3.2.5. Differential Scanning Calorimetry (DSC) Analysis

The samples were analyzed by DSC with the method in Table 3.3.

Table 3.3. DSC run method.

| Initial T ($^0$C) | Final T $^0$C) | Rate ($^0$C/min) | Hold time (min) |
|---|---|---|---|
| 0 | 300 | 10 | 2 |
| 300 | 0 | 10 | 2 |
| 0 | 300 | 10 | 2 |

# 4. RESULTS AND DISCUSSION

## 4.1. Dicarboxylic Acid Polyanhydrides

This study began first by the synthesis of benzoic acid anhydride to develop a method of detection for the anhydrides formed. As presented in the experimental part, the FTIR peaks showed anhydride characteristic peaks at 1779 $cm^{-1}$ and 1722 $cm^{-1}$ (Figure 4.1.). According to literature, anhydrides have two characteristic carbonyl peaks which are results of symmetric and asymmetric stretching in infrared spectrum [54]. Based on this knowledge, FTIR was used to confirm anhydride bond formation in the products.

Then the syntheses of diacid polyanhydrides were targeted. Due to our interest on PET type of aromatic polyesters, polyanhydrides of *tere*- and *iso*-phthalic acid (TPC, IPC) were chosen. Instead of the diacids, the corresponding diacid chlorides were used for the synthesis of polyanhydrides. Thus, both IPC and TPC were used as monomers and the reactions were carried out in the solution (DCM or THF) where partial hydrolysis of acid chlorides to carboxylic acid then the subsequent reaction of the latter with the nonhydrolyzed diacid chloride was aimed.

The syntheses of polyanhydride were started with IPC as a monomer because of its higher solubility. Isophthaloyl chloride (IPC), triethylamine (TEA) and water were mixed together in a ratio of 1:2:0.5 in DCM. The same reaction procedure was followed for TPC monomer instead of IPC. However, the ratio of TPC to TEA was 1:1. When 2 equivalents of TEA was used, the final product became yellowish although extraction and precipitation were employed, and amine peaks were seen in FTIR. The used TPC had solubility problem so that it might not be involved in the reaction completely. Therefore, used TEA was diminished. The solvent was changed to THF instead of DCM. The solution of TPC in DCM was cloudy; however, it gave clearer solution in THF indicating better solubility.

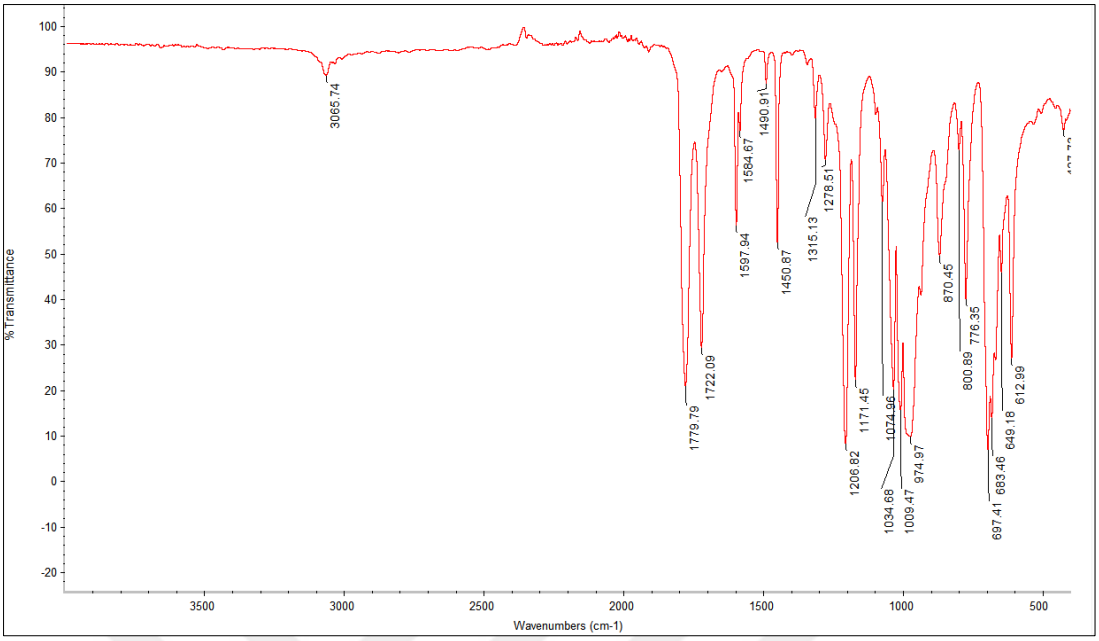



Figure 4.1. FTIR spectrum of benzoic anhydride.

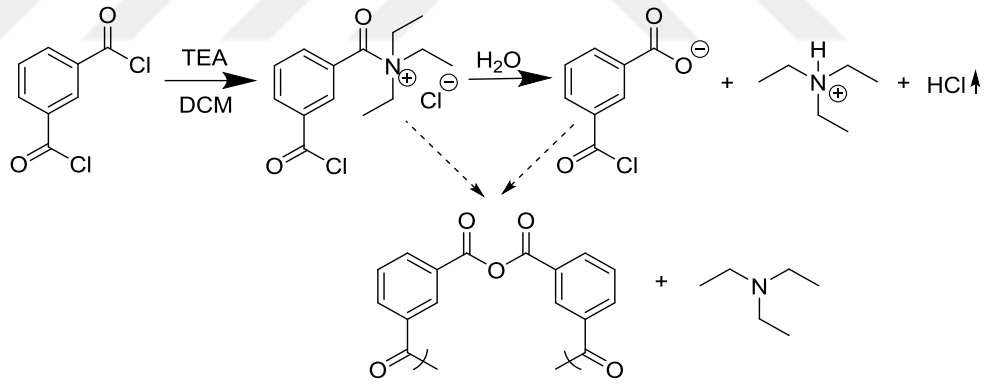



Figure 4.2. The proposed anhydride formation from the partial hydrolysis of IPC and/or its intermediates.

The proposed reaction mechanisms are seen in Figure 4.2 and Figure 4.3. For simplicity, reaction is shown only for one side. When TEA is added, acyl ammonium salt intermediates are formed. Synthesis of poly (terephthalic anhydride) by hydrolysis of terephthaloyl chloride/triethylamine intermediate adduct was studied by Subramanyan *et. al* [55]. They concluded that equimolar amounts of two reactants produced quaternary acyl

ammonium salt and unreacted terephthaloyl chloride. Upon addition of little amount of water, some intermediates are expected to form carboxylates which should in principle then attack the activated acyl ammonium salt to form anhydride bond.

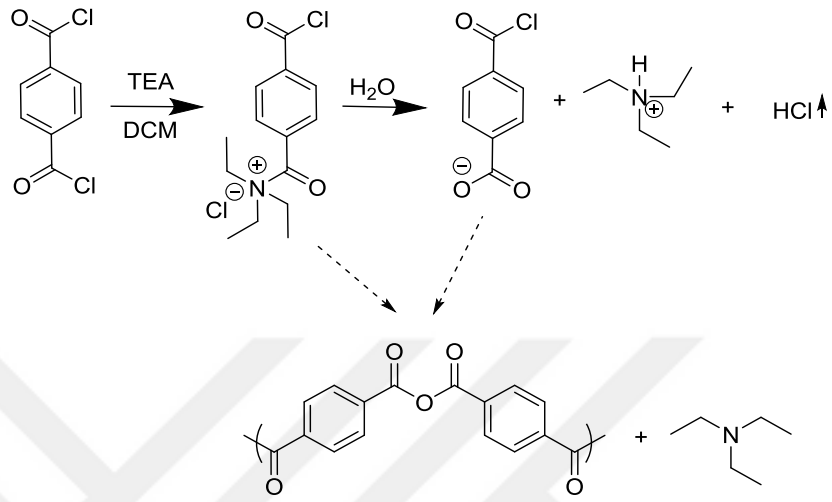



Figure 4.3. The proposed anhydride formation from the partial hydrolysis of TPC and/or its intermediates.

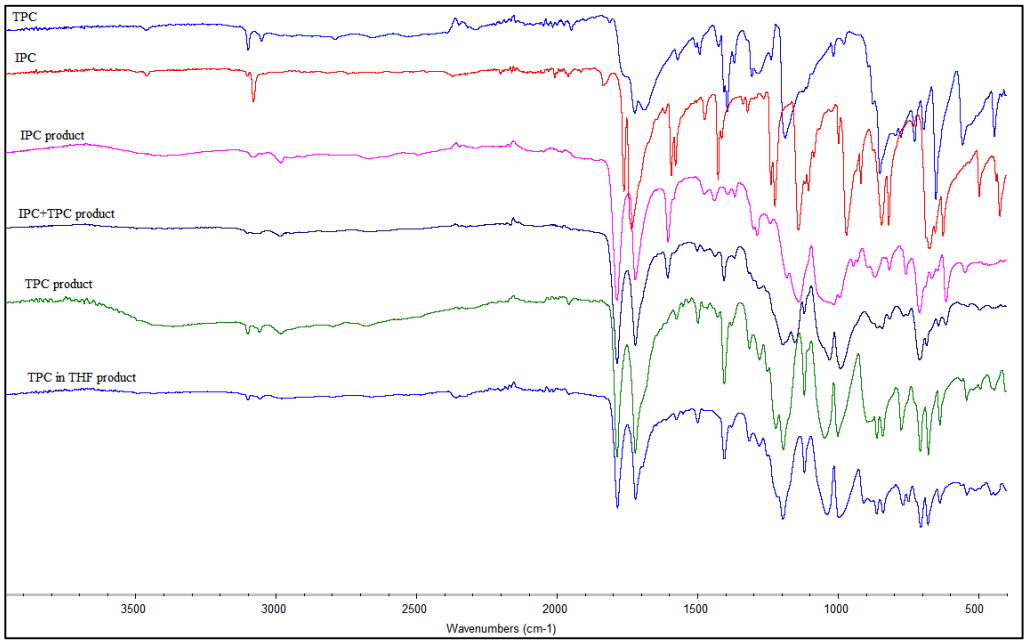



Figure 4.4. FTIR spectrum of polyanhydrides synthesized from diacid chlorides.

Anhydride formation was confirmed by FTIR for all polyanhydride products. As seen in Figure 4.4., peaks had similar patterns for all samples. The main difference was that 1,4 position on aromatic ring (TPC) showed C=C stretching peak at around 1400cm$^{-1}$ while 1,3 position (IPC) demonstrated C=C stretching peak at around 1600 cm$^{-1}$. It was clearly seen that the product synthesized from both IPC and TPC monomers had the two peaks corresponding to the *ortho* and *para* positions of aromatic rings.

The synthesized polyanhydrides were insoluble in common solvents and mixtures. This presented a challenge for the next step where chain extension reactions of hydroxyl- and carboxylic acid-terminated PET were targeted by using the synthesized polyanhydrides in solution. Due to the solubility issue the polyanhydride samples were directly mixed with powdered PET and then melt and stirred together in a melt polymerization set-up in the absence of any solvent. In other words, the polyanhydrides were used as a melt additive for the chain extension studies of the PET oligomers, a process well known by the PET manufacturers.

## 4.2. Chain Extension Studies of PET in Melt

The synthesized poly (terephthalic anhydride)s were reacted with PET in a melt system (Table 4.1.). Firstly, different amounts of poly (terephthalic anhydride) were employed without any catalyst. 0.15 g (1% by weight) of anhydride did not demonstrate significant change in terms of IV and $M_n$ when compared to the reference sample (sample 1, Table 4.1.) which was obtained by only melting and stirring the low IV PET for 30 minutes at 280$^0$C. On the other hand, 0.60 g (4 % by weight) of anhydride was the most destructive; both IV and molecular weights were decreased significantly. When 0.30 g (2% by weight) was used, a decrease was observed but the change was not as much as the one observed with 0.60g. As the polyanhydride amount was increased, the changes also increased.

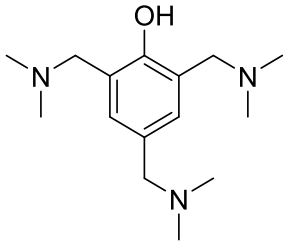



Figure 4.5. NX3P structure.

In the next step, the chain extension reactions were carried out with a catalyst. Since the above experiments showed that a change in molecular weight was obtained at minimum of 0.30 g of polyanhydride with acceptable degradation, this amount of polyanhydride was chosen as a standard concentration for the catalyst studies. Three different catalysts, titanium IV isopropoxide (TIP), 2-4-6-tris (dimethylaminomethyl) phenol (NX3P) (Figure 4.5.), zinc acetate, were used at two different concentrations 3% and 1%-mol percent with respect to -OH end group concentration. The GPC and IV results are given in Table 4.1.

Table 4.1. The result of melt products. *

| **Sample** | **Anhydride (g)** | **Catalyst type** | **Catalyst amount (mol%)** | **IV (dl/g)** | $M_n$ **(g/mol)** | $M_w$ **(g/mol)** | **PDI** |
|---|---|---|---|---|---|---|---|
| **1(blank)** | - | - | - | 0.404 | 5086 | 13260 | 2.608 |
| **2** | 0.15 | - | - | 0.408 | 4632 | 12130 | 2.619 |
| **3** | 0.30 | - | - | 0.340 | 3689 | 9622 | 2.608 |
| **4** | 0.60 | - | - | 0.270 | 2358 | 5671 | 2.405 |
| **5** | - | NX3P | 1 | 0.398 | 4357 | 11260 | 2.584 |
| **6** | - | NX3P | 3 | 0.400 | 4184 | 10920 | 2.610 |
| **7** | 0.30 | NX3P | 1 | 0.324 | 3266 | 8446 | 2.586 |
| **8** | 0.30 | NX3P | 3 | 0.336 | 2776 | 7039 | 2.536 |
| **9** | - | TIP | 1 | 0.406 | 4306 | 11510 | 2.673 |
| **10** | - | TIP | 3 | 0.396 | 4618 | 11710 | 2.535 |

Table 4.1. The result of melt products. * (cont.)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **11** | 0.30 | TIP | 1 | 0.328 | 3496 | 9072 | 2.595 |
| **12** | 0.30 | TIP | 3 | 0.340 | 3162 | 8061 | 2.550 |
| **13** | - | Zinc | 1 | 0.404 | 4899 | 13940 | 2.846 |
| **14** | - | Zinc | 3 | 0.432 | 6714 | 16250 | 2.421 |
| **15** | 0.30 | Zinc | 1 | 0.332 | 3525 | 8990 | 2.550 |
| **16** | 0.30 | Zinc | 3 | 0.340 | 3473 | 9620 | 2.770 |

**Initial PET IV= 0.355 dl/g, $M_n$=5005 g/mol, $M_w$=12690 g/mol, PDI=2.535.*

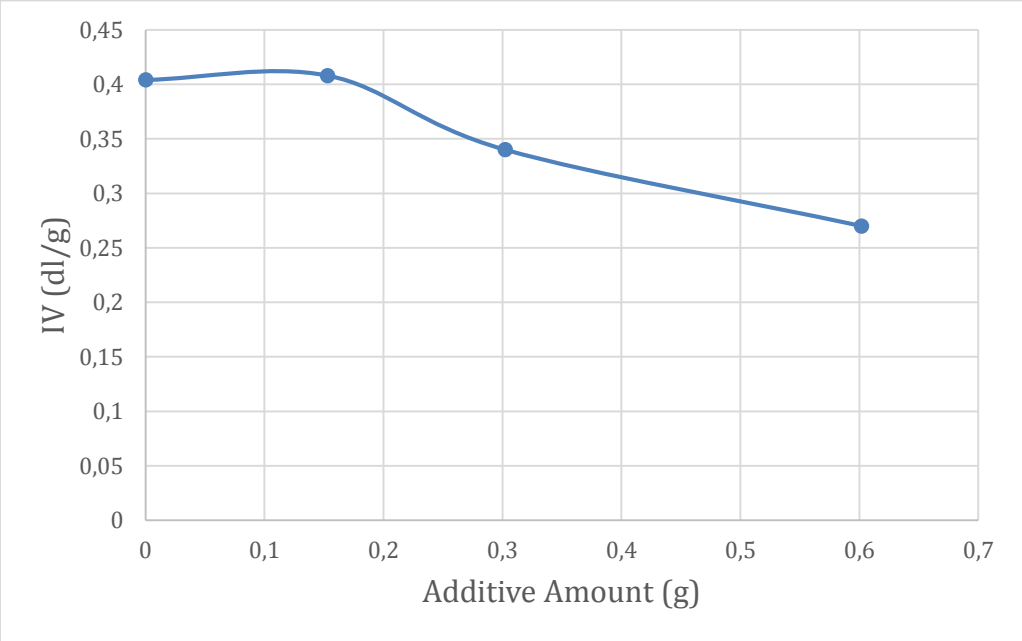



Figure 4.6. The graph of IV change according to additive amount without catalyst.

As seen in Figure 4.6., IV did not change so much when 0.15 g of poly (terephthalic anhydride) was added. After that, IV decreased as the polyanhydride amount increased. The same situation was observed in molecular weight. Figure 4.7 and Figure 4.8. show that molecular weights decreased when the amount of additive was raised. It was obvious that the synthesized poly (terephthalic anhydride) broke the PET chains without catalyst (Table 4.1. entries 2-4). The overall results show that chain scission reactions are the predominant reactions although theoretically some chain extension reactions are possible.

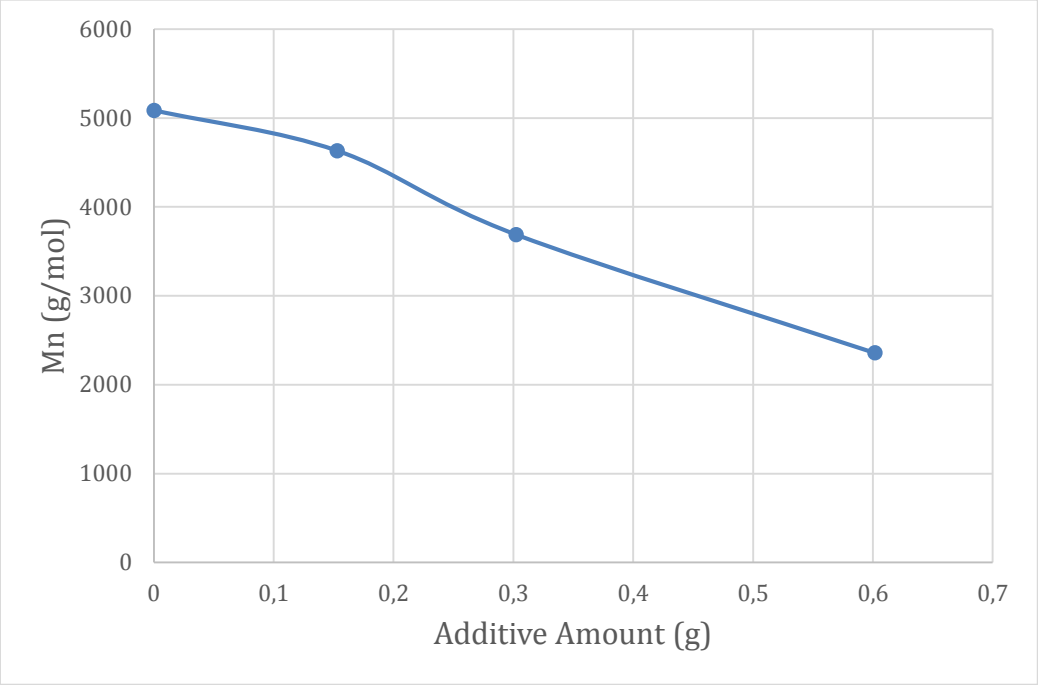



Figure 4.7. The graph of $M_n$ changes according to additive amount without catalyst.

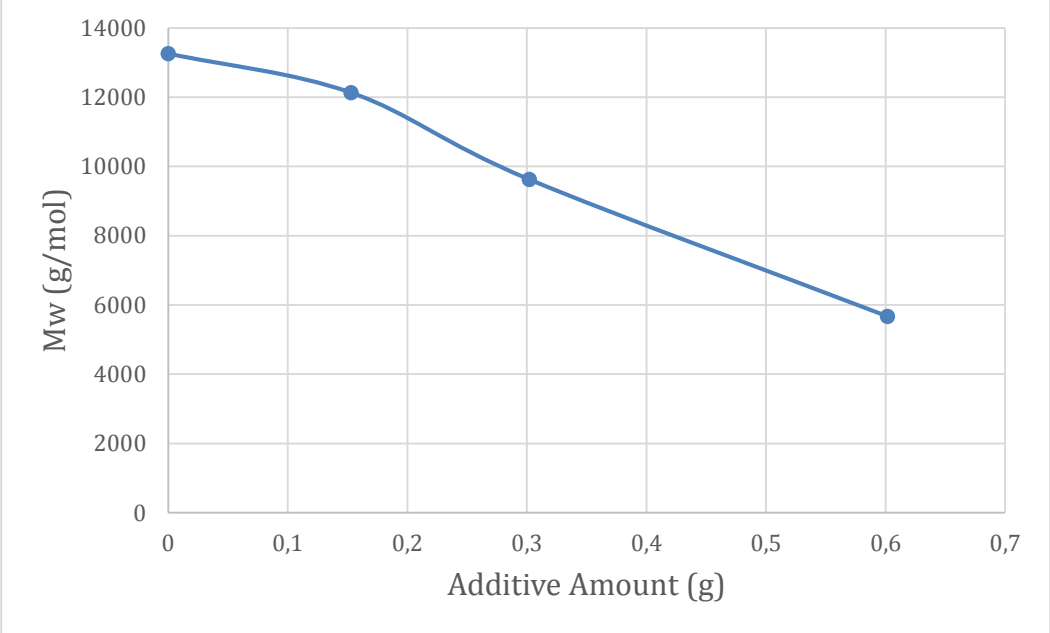



Figure 4.8. The graph of $M_w$ changes according to additive amount without catalyst.

As seen in Figure 4.9., PDI slightly increased and then decrease as the amount of additive increased. This result seemed to show that molecular weight of the polymer chains was getting smaller when larger chains were cut by poly (terephthalic anhydride). When comparing the result of sample 1 and 4, the molecular weight values were nearly decreased

by half. Therefore, it could be said that the polymer distribution was cumulated around the smaller polymer chains.

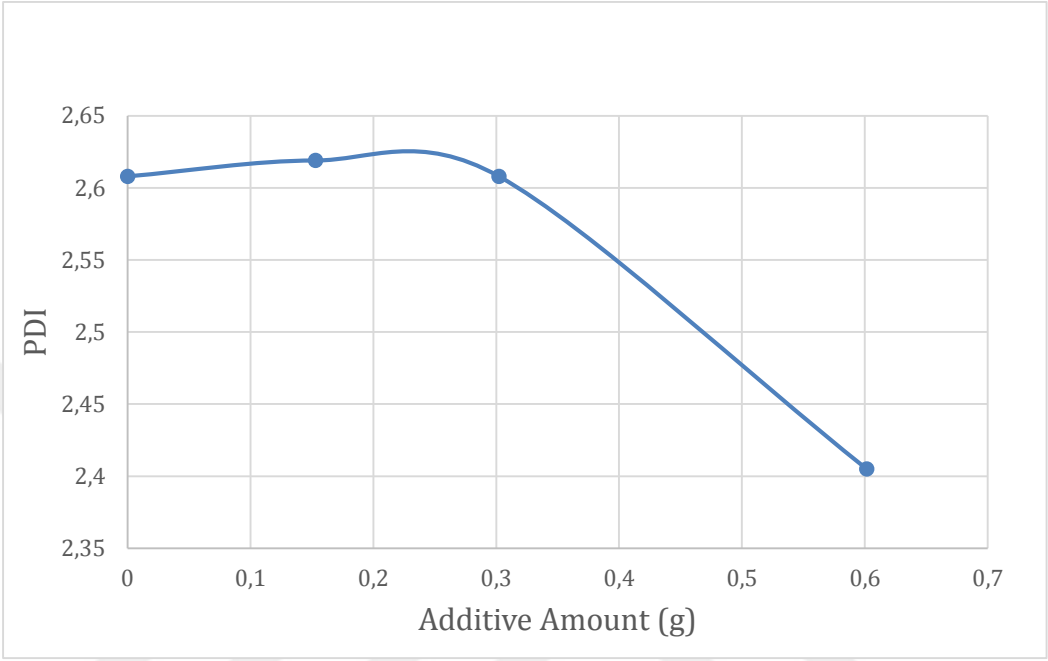



Figure 4.9. The graph of PDI change according to additive amount without catalyst.

Control experiments were conducted for each type of catalyst in the absence of polyanhydride. When 1% (mol percent with respect to -OH concentration) of catalysts were used (Table 4.1. entries 5,9and 13), NX3P and TIP showed decrease in molecular weights where zinc acetate did not cause a significant change. Then, the catalyst amounts were increased (Table 4.1. entries 6, 10 and 14). When compared to the blank (sample 1, Table 4.1.), 3% (mol percent with respect to -OH concentration) of zinc acetate increased both IV and molecular weight. It can be said that; zinc acetate alone catalyses the esterification reaction of PET itself. Similar to results of 1% (mol percent with respect to -OH concentration) catalyst used samples (Table 4.1., entries5,9), NX3P and TIP decreased IV and molecular weights when catalyst amount was increased to 3% (mol percent with respect to -OH concentration) (Table 4.1. entries 6,10). Although they are often chosen as esterification catalyses, they seem to induce degradation as well.

After control experiments, 0.3 g (2% by weight) of anhydride and 1% (mol percent with respect to -OH concentration) of catalyst were used together. In general, all three catalysts demonstrated decrease in both IV and molecular weight compared to the blank (sample 1, Table 4.1.). The control experiments are given in Table 4.2.

Table 4.2. The control samples for 1% (mol percent with respect to -OH concentration) catalyst.

| | **Named** | **Polyanhydride** | **Catalysts** |
|---|---|---|---|
| **Sample 1** | Blank | - | - |
| **Sample 3** | Anhydride Blank | 0.3 g | - |
| **Sample 5** | Catalyst Blank | - | 1% NX3P |
| **Sample 9** | Catalyst Blank | - | 1% TIP |
| **Sample 13** | Catalyst Blank | - | 1% zinc acetate |

When 1% (mol percent with respect to -OH concentration) of catalyst was used with 0.3 g (2% by weight) of anhydride, the results are compared to three types of blanks which are the blank (sample 1, only PET melting and mixing), anhydride blank (sample 3, PET and anhydride reacted), and catalyst blank for each catalyst (PET and 1%-mol percent with respect to -OH concentration of catalyst were processed in the melt system) (Table 4.1 and Table 4.2).

- NX3P (sample 7, Table 4.1.), showed lower IV and molecular weight. It can be said that NX3P and the anhydride degraded PET the most.
- TIP (sample 11, Table 4.1.) showed lower IV. It demonstrated similar molecular weights with the anhydride blank; however, its corresponding catalyst blank (sample 9, Table 4.1.) had higher molecular weights. It could be said that TIP did not accentuate anhydride adverse effects.
- Zinc acetate (sample 15, Table 4.1.) demonstrated similar results. Therefore, it could be possible that zinc acetate had small contribution on polymer degradation.

Then, the experiments were conducted with 3% (mol percent with respect to -OH concentration) of catalyst. The control samples are given in Table 4.3.

Table 4.3. The control samples for 3% (mol percent with respect to -OH concentration) catalyst.

| | **Named** | **Polyanhydride** | **Catalysts** |
|---|---|---|---|
| **Sample 1** | Blank | - | - |
| **Sample 3** | Anhydride Blank | 0.3 g | - |
| **Sample 6** | Catalyst Blank | - | 3% NX3P |
| **Sample 10** | Catalyst Blank | - | 3% TIP |
| **Sample 14** | Catalyst Blank | - | 3% zinc acetate |

When 3% (mol percent with respect to -OH concentration) of catalyst was used with 0.3 g (2% by weight) of anhydride, the comparative results according to three types of blanks which are the blank (sample 1, only PET melting and mixing), anhydride blank (sample 3, PET and anhydride reacted), and catalyst blank for each catalyst (PET and 3% mol percent with respect to -OH concentration of catalyst were processed in the melt system) (Table 4.1 and Table 4.3) are as follow:

- NX3P (sample 8, Table 4.1.) demonstrated significant decrease in terms of IV and molecular weight. The catalyst together with anhydride broke the PET chains.
- TIP (sample 12, Table 4.1.) displayed a decrease in IV and molecular weight.
- Zinc acetate (sample 16, Table 4.1.) had similar results with anhydride blank. On the other hand, its catalyst blank (sample 14, Table 4.1.) showed enhanced results so that IV and molecular weight of commercial PET were increased. It could be said that zinc acetate accelerated anhydride destructive process.

It can be said that 1 % (mol percent with respect to -OH concentration) of catalyst was not so effective. When the catalyst amount was increased to 3% (mol percent with

respect to -OH concentration), the decrease in IV and molecular weight was the dominant observation. The most significant decrease was observed with NX3P.

### 4.2.1. Conclusion on the Chain Extension Studies with Polyanhydrides

As a result, the synthesized polyanhydrides did not act as chain extenders but contrarily they served as catalyst for chain scission. It is well known that PET and polyesters degrade faster when their terminal carboxylic acid content is high. Therefore, any additive with a carboxylic content seems to induce similar degradation. Catalyst addition such Lewis acids (Zn and Ti-catalysts or) and tertiary amines (NX3P) does not alter the outcome, the degradation process takes over any polycondensation reactions if any happens.

## 4.3. PET Synthesis in Solution

Since the diacid polyanhydrides and their use as chain extenders for PET oligomers resulted mostly in carboxylic acid catalyzed chain scission reactions, next ways to reduce the carboxylic acid content with respect to the overall polymer mass were investigated. A possible pathway was described as follow; if low to medium molecular weight PET could be synthesized with some anhydride bonds in the polymer backbone, those anhydrides could then be used as chain extenders for -OH terminated PET (most of the commercial PET's contain 75% of -OH termination), where only oligomeric acid terminated PET would be released as by-product (Figure 4.10.). Some of the latter could even be incorporated into the main backbone through condensation reactions.

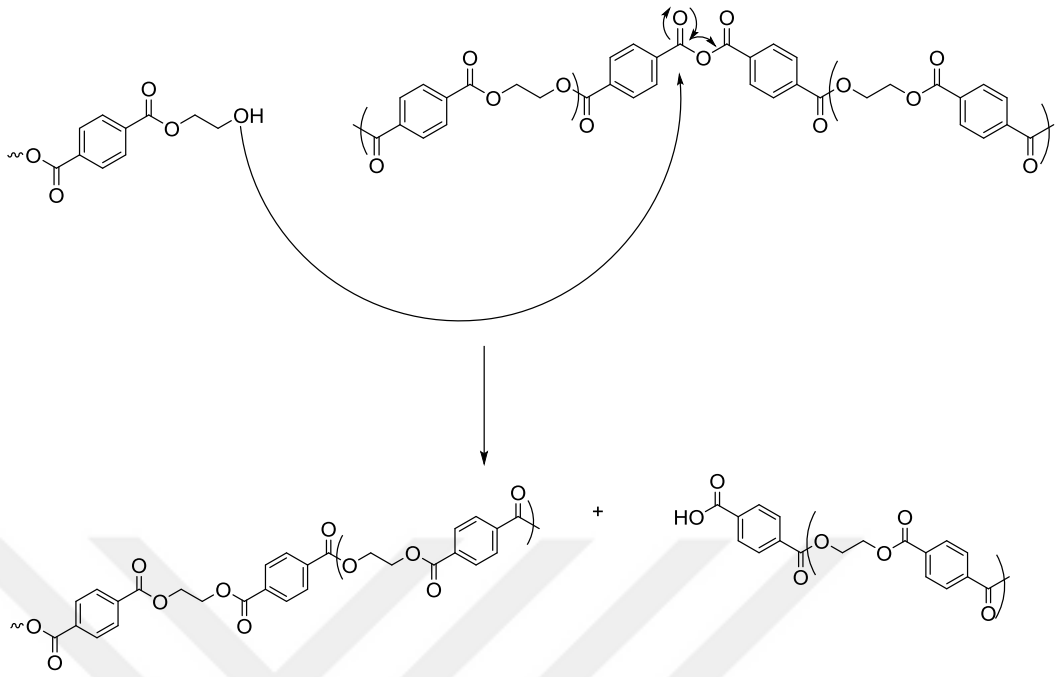


Figure 4.10. PET chain extension with synthesized PET-Anhydride.

Therefore first, we concentrated our efforts on the synthesis of PET. For the syntheses TPC and ethylene glycol were reacted in THF in the presence of TEA as a catalyst and acid scavenger. The polymerizations were conducted at room temperature for one hour.

From the very beginning of our trials it became clear that the PET that were synthesized contained anhydride bonds as evidenced by the peaks in IR. This could be the outcome of a moisture leakage or some hydrolyzed TPC in the commercial bottle. The reactions were repeated with extreme precautions under inert conditions to avoid moisture, and purification of TPC was done with $NaHCO_3$(aq) extraction but these did not change the results. The anhydrides were always present. As will be discussed next, later it was found out that the anhydrides were mostly due the starting material, TPC, that has been hydrolyzed to TPA during the shipping and storage. Nonetheless, initial experiments were carried where several parameters were changed such as time, temperature and the amount of excess monomer.

At the beginning, before the reaction time was set to one-hour, prolonged times and increased temperatures were employed (PET-1 and PET-2) but no significant change in terms of degree of polymerization (DP) was detected. During the syntheses of PET-1 and

PET-2, to follow the polymerizations, 4 mL of sample was collected from the reaction mixture at different time intervals. The products were then analyzed by GPC. The $M_n$ values and the amount of collected products are given in Table.4.4. Both at room temperature and 40 $^0$C, molecular weights did not increase significantly after one hour, they were set around 2500 g/mol (analysis results of 2-, 4- and 5-hours sample of PET-2 (40$^0$C) seem inaccurate and should be discarded. We still showed them, since such data was often observed). As will be discussed later, the solubility of PET has been a main challenge both in the syntheses and analyses of PET. We believe that in the analyses of these samples (PET-2), the solubility was as an issue again and that the data shown and the low molecular weight peaks belong to the GPC eluent, HFIP. The feed ratio of TPC to EG was 1.07 for these reactions. Theoretically, 14 repeating unit was expected; therefore, the polymer' molecular weight should be around 2700 g/mol. At the end of the reactions, when PET-1 and PET-2 compared (only difference was reaction temperature), $M_n$ values were found the be similar; which were 2506 g/mol and 2739 g/mol, respectively. Thus, both reactions seemed to reach the theoretical value. This is unexpected since the molecular weights should be attained at 100% conversion, at lower conversions the $M_n$ value should be inferior. The actual conversions in the experiments were around 50-60%. This may point out to a reaction mixture where the PET oligomers that are forming during the condensation process are more available than the monomeric diacid chloride maybe due to better solubility. Thus, once the polymerization starts, chain growth is faster than the first initial condensation. The observed fixed molecular weight could be due to the precipitation that becomes prominent at a given molecular weight due to the solubility issue. So in terms of solubility, it seems like up to certain molecular weight the oligomers or their acyl ammonium salts are more soluble than the starting TPC (or its acyl ammonium salt) but then, they precipitate as the chain length increase. This assumption needs further prove where additional experiments have to be done to be conclusive.

Table 4.4. The $M_n$ values for PET-1 (left) and PET-2 (right)*.

| Time | $M_n$ (g/mol) (RT) | Products amount (mg) |
|---|---|---|
| 10 min | 155.5 | 105 |
| 30 min | 186.1 | 97 |
| 1 hour | 2576 | 113 |
| 2 hours | 2521 | 109 |
| 3 hours | 2332 | 163 |
| 5 hours | 2408 | 134 |
| 6 hours | 2173 | 102 |
| 7.5hours | 2506 | - |

| Time | $M_n$ (g/mol) (40 $^0$C) | Product amount (mg) |
|---|---|---|
| 1 hour | 2587 | 86 |
| 2 hours | 138.5 | 107 |
| 3 hours | 2396 | 142 |
| 4 hours | 207.5 | 95[a] |
| 5 hours | 192.3 | 142 |
| 6 hours | 2421 | 154 |
| 7.5hours | 2739 | - |

**Reactions were conducted for 7.5 hours.*

*[a] 3.6 mL reaction mixture was collected instead of 4 mL.*

At this point, before we present the results further, we would like to discuss in details the solubility problems that were encountered since one should always remember that the accuracy of the results that will be presented later, mostly depend on how soluble the PET was in a particular solution at the time of isolation, preparation and analyses of the sample. It is fair to say that the analyses were shaded by the low solubility of PET in general.

### 4.3.1. Solubility of the Products

Solubility was the main obstacle in the whole project. PET is already known to have limited solubility; later as will be discussed, the low molecular weight analogues and the presence of anhydride linkages in some PET made it even more difficult to dissolve. Common laboratory solvents such as ethyl acetate, THF, chloroform, DCM and so forth were tried separately as well as in different combinations, clear solutions could not be obtained. It is possible that smaller PET chains are more prone to precipitation than their higher molecular weight counter parts since they can possibly acquire the thermodynamically most stable form (precipitated crystallite) faster. As will be presented in

DSC analyses of the samples, the low molecular weight PET's tend to crystalize very efficiently.

PET is known to be soluble in HFIP; however, the synthesized products had also limited solubility in it. In order to analyze by NMR, they needed to be dissolved. It was found that, these products were soluble in a mixture of HFIP and deuterated chloroform (1:5 v/v). However, HFIP peaks at around 4 ppm were overlapping with the EG repeat unit peaks. Therefore, other solvents and mixtures were sought and trifluoroacetic acid addition was found in the literature [3], [56]. The products were found to dissolve in deuterated chloroform-trifluoroacetic acid mixture in a ratio of 5 to 1 v/v. This was the minimum TFA amount needed to dissolve the products. TFA is a strong acid and its intensity in the NMR spectrum repressed other peaks so that its amount had to be minimized. The products synthesized with new TPC (less hydrolyzed to TPA or anhydride) needed lesser amount of TFA to be solubilized (10 to 1 v/v). In addition to the solvent ratio, we observed that the products were dissolved easier when TFA and $CDCl_3$ were mixed beforehand and then added to the polymers. Otherwise, the products did not dissolve properly when sequential addition of the two was employed.

### 4.3.2. Results of PET Synthesized in Solution

As explained in previous section, products were dissolved in a mixture of deuterated chloroform and TFA (ratio of 5 to 1 v/v for old TPC used products, ratio of 10 to 1 v/v for new TPC used products) for the NMR. Nonetheless, TFA affected the aromatic protons; therefore, interpretation of the peaks around 8 ppm was difficult and often misleading. For commercial PET, a single peak is observed at approximately 8 ppm which corresponds to the symmetrical aromatic protons. In the case of the synthesized PET; however, there were more than one peak most probably due to the oligomeric PET's obtained. Repeat units that were closer to the end groups had different chemical shifts than the ones that were in the mid-sections. In addition, residual anhydride formation was also detected in the PET structures; which made the analysis even more complicated. Therefore, it was difficult to assign each aromatic peak on the $^1$H-NMR spectrum to a given oligomer chain, therefore, additional experiments were done with the solvent system and PET's with and w/o anhydrides.

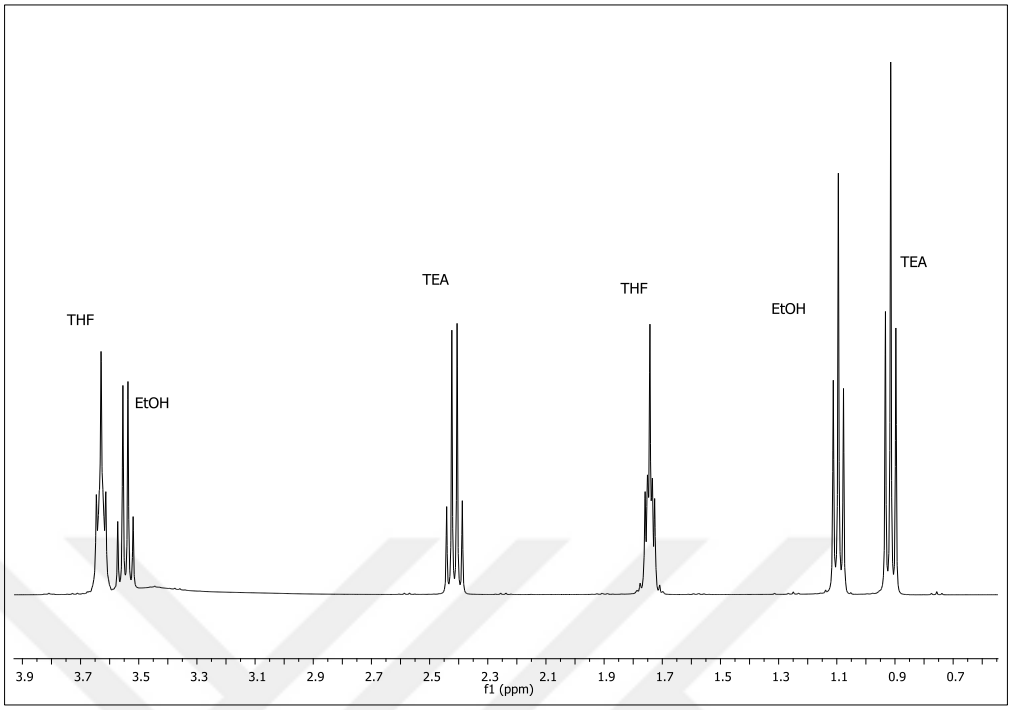



Figure 4.11. $^{1}$H NMR spectrum of the used solvents.

Although the products were kept in a vacuum oven, trace amounts of solvents were still detected. In order to observe the effect of TFA on the solvents, THF (reaction solvent), TEA and EtOH (precipitation solvent) were mixed and then analyzed by NMR (Figure 4.11). After getting the spectrum, 0.05 mL of TFA was added to NMR tube and analyzed again. As seen in Figure 4.12, solvent peaks were shifted to lower field. Besides, a multiplet peak at 4.36 ppm appeared; which was assumed to belong to TFA ethyl ester. The corresponding protons of ester and other solvents were seen in the region between 1.0 ppm and 1.5 ppm and they were controlled with COSY NMR. According to the literature, the esterification reaction of TFA begins immediately when acid and alcohol are mixed [57].

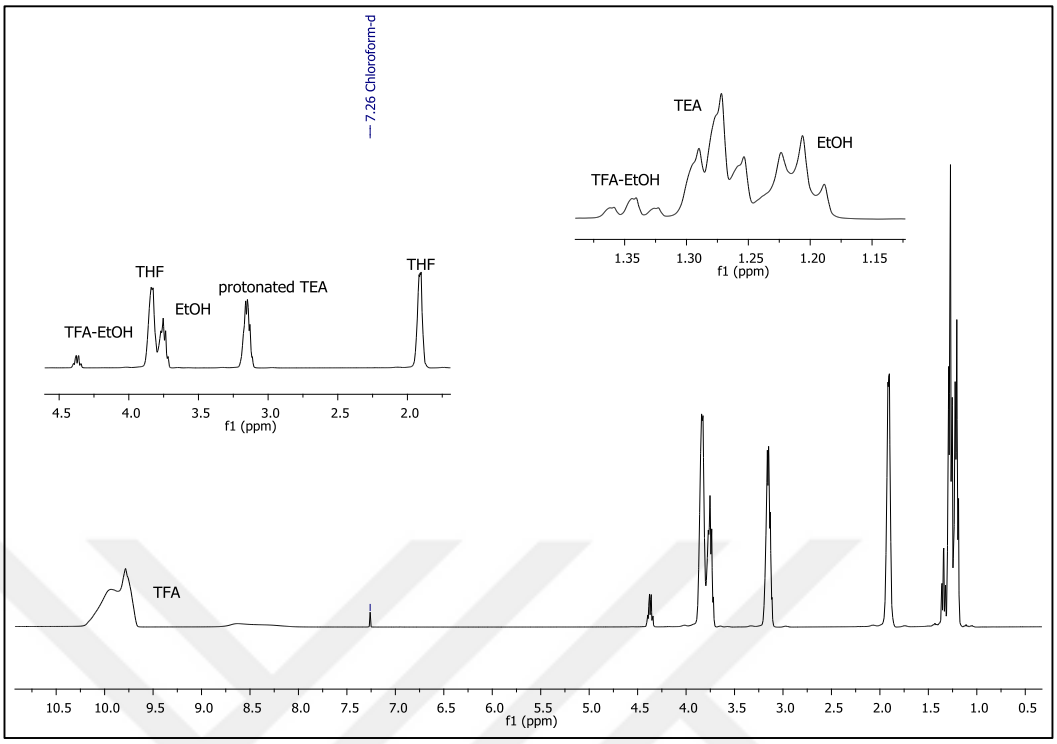



Figure 4.12. $^{1}$H NMR spectrum of the used solvents with TFA.

After defining peaks coming from the residual solvents in $^{1}$H-NMR, the rest of the peaks were assigned to the product. Some of the possible polymer structures are given in Figure 4.13. There were three possibilities with respect to the end groups; 1) two ends could be carboxylic acid, 2) two ends could be alcohol and 3) one end carboxylic acid the other one alcohol. During the PET synthesis residual anhydride bonds were formed as confirmed by FTIR (for instance Figure A.5 for PET-2.).

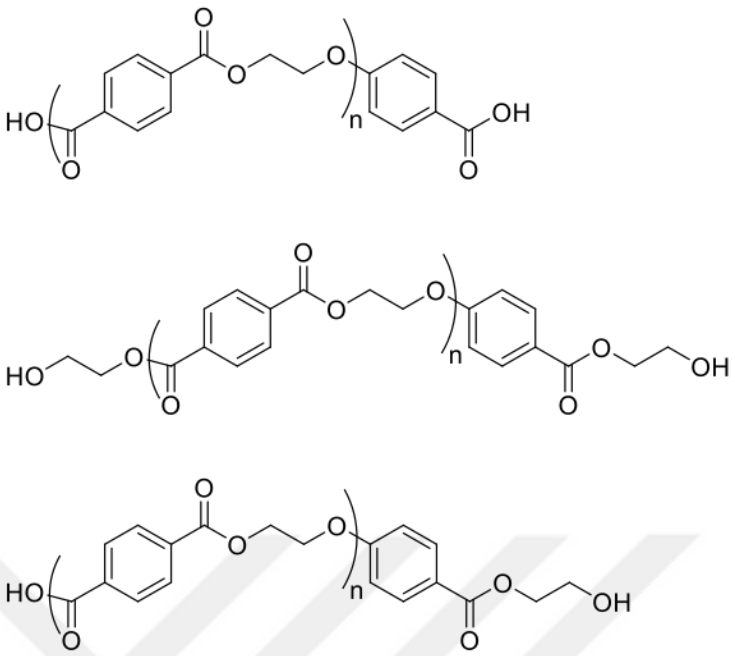


Figure 4.13. The possible PET end group structures.

Representatively, the $^{1}$H-NMR of PET-10 synthesized with excess (1.12 eq) TPC is shown in Figure 4.14. Terminal EG protons are observed around 4.2 ppm and 4.6 ppm. As explained before, TFA ethyl ester peak appeared between two end group methylene protons (written as TFA-EtOH on spectrum). There were some impurities coming from TFA; which were between 0-1.5 ppm. $^{13}$C-NMR spectra of PET-10 is given in Figure 4.15. Only one carbonyl carbon correlated to ester is seen in $^{13}$C-NMR spectra at approximately 167 ppm. Aromatic carbons are around 130 ppm and ethylene carbons of EG are around 60 ppm. Besides, peaks corresponding to TFA are also observed at 115 ppm and 160 ppm.

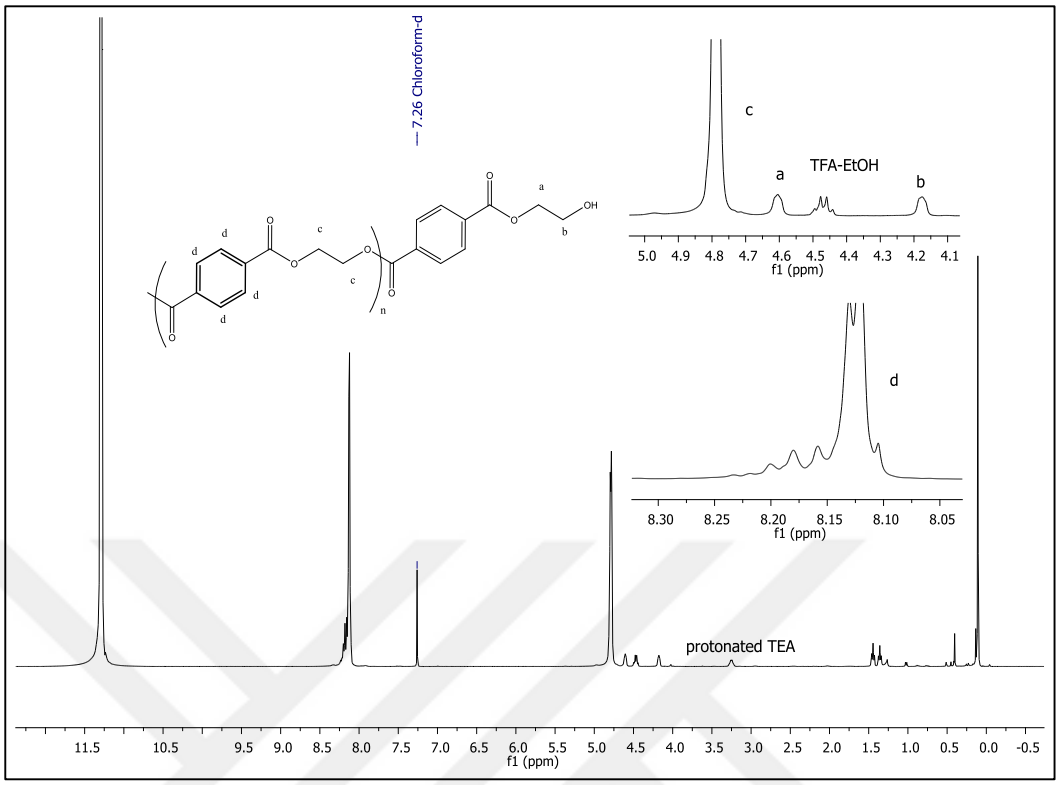



Figure 4.14. $^{1}$H NMR of PET-10.

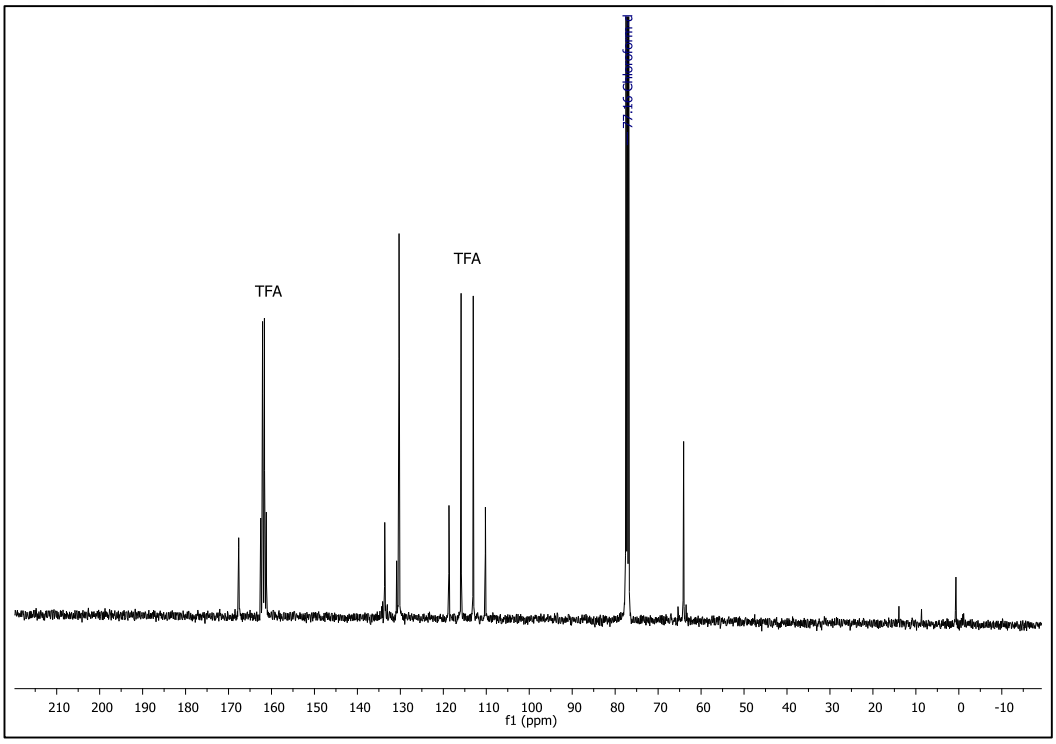



Figure 4.15. $^{13}$C NMR of PET-10.

Degree of polymerization of the products were calculated from both NMR and GPC. For DP calculation from GPC, $M_n$ was divided by the molecular weight of PET repeating unit (192 g/mol). On the other hand, DP calculations from NMR were more challenging and assumptions had to be made. Terminal methylene protons of EG peaks were distinct therefore were used them for molecular weight ($M_n$) and DP calculations. There were two possibilities, the terminal EG could be present at both ends or at only one end. The polymers' degree of polymerization were calculated based on both assumptions (Table 4.5.). The protons referred as 'c' were the EG methylene protons in the repeating units corresponding to 4 protons. The protons 'a' and 'b' were end group protons close to ester ($OCOC\underline{H_2}CH_2OH$) and hydroxyl groups ($OCOCH_2C\underline{H_2}OH$) respectively. The integral values of 'a' and 'b' as expected were the same. According to the first assumption where two ends had EG, the integral of 'a' (or b) was divided by 4. According to the second where assumption only one end-group had EG, the integral was divided by 2. After finding the one proton corresponding values, they were divided, and DP was found. For instance, the integral of 'c' was 1 and that of 'a' was 0.05 for PET-10. Therefore, DP was (1/4) / (0.05/2) = 10.0 for one ended, (1/4) / (0.05/4) = 20.0 for two ended found. Similar calculations were done for the rest of the samples (Table 4.5). It is important to mention that this method based on EG terminated protons is somewhat blind to the -COOH terminated chains. A third hidden assumption is that the -COOH terminated chains would follow a similar trend where a symmetrical molecular weight distribution is assumed similar to -OH terminated chains. This is an assumption that can be proven wrong if properly both end groups can be quantified. However, due to the limited solubility of the products, it was hard to apply methods that could enable the determination of both end groups (-OH and -COOH) in a precise quantitative way. For instance, it was found in the literature that end group determination can be done by $^{31}$P-NMR after phosphor derivations of the hydroxyl- and carboxylic-end groups [58].

As said before, more than one aromatic peak was observed when analyzing the $^1$H-NMR results. During the identification of the peaks, it was assumed that the two protons located at downfield region (8.33 and 8.38 ppm) were related to the anhydride bonds. Few observations lead to make this assumption where $^1$H-NMR results were corroborated with FTIR results. Firstly, PET-1 sample did not demonstrate anhydride carbonyl stretching at FTIR spectrum (Figure A.2.) and it's the most deshielded proton at 8.24 ppm rather than

8.33 and 8.38 ppm (Figure A.3). Secondly, PET-4 had the smallest anhydride peak in FTIR (Figure A.11.) and it had the smallest integral value at 8.38 ppm compared to the other products which were synthesized from old TPC. Finally, PET-10 which was synthesized with new TPC had neither anhydride carbonyl stretching (Figure A.29) nor peaks located higher than 8.24 ppm (Figure 4.14). Therefore, peaks at 8.38 ppm and 8.33 ppm were said to be aromatic protons close to the anhydride bonds (indicated as ‘e’ and ‘f’; respectively).

Table 4.5. NMR integrals and GPC results of PET products*.

| | **c** (EG repeat) | **a** (EG end | **DP** (one end OH) | **DP** (both ends OH) | **d** (aromatic repeat) | **e** (anhydride) | **f** (anhydride) | **TPC/EG** (feed) | **TPA/EG** (observed in NMR) | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ | **DP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PET-1** | 1 | 0.09 | 5.56 | 11.11 | 1.00 | - | - | 1.07 | 1.43 | 1033 | 1040 | 1.007 | 5.4 |
| **PET-2** | 1 | 0.05 | 10.00 | 20.00 | 0.94 | 0.12 | 0.15 | 1.07 | 1.50 | - | - | - | - |
| **PET-3** | 1 | 0.07 | 7.14 | 14.28 | 0.95 | 0.12 | 0.13 | 1.12 | 1.46 | 2340 | 2391 | 1.022 | 12.2 |
| **PET-4** | 1 | 0.05 | 10.00 | 20.00 | 0.94 | 0.05 | 0.08 | 1.26 | 1.26 | 2431 | 2536 | 1.043 | 12.6 |
| **PET-5** | 1 | 0.06 | 8.33 | 16.67 | 0.93 | 0.09 | 0.10 | 1.10 | 1.35 | 2235 | 2297 | 1.028 | 11.6 |
| **PET-6** | 1 | 0.09 | 5.56 | 11.11 | 0.98 | 0.16 | 0.20 | 0.95 | 1.54 | 2488 | 2506 | 1.007 | 12.9 |
| **PET-7** | 1 | 0.09 | 5.56 | 11.11 | 0.98 | 0.13 | 0.18 | 0.83 | 1.49 | 2429 | 2456 | 1.011 | 12.6 |
| **PET-8** | 1 | 0.09 | 5.56 | 11.11 | 1.00 | 0.10 | 0.12 | 0.79 | 1.35 | 2376 | 2411 | 1.015 | 12.4 |
| **PET-9** | 1 | 0.15 | 3.33 | 6.67 | 1.03 | 0.34 | 0.40 | 0.49 | 1.81 | 2497 | 2511 | 1.006 | 12.9 |
| **PET-10** | 1 | 0.05 | 10.00 | 20.00 | 0.99 | - | - | 1.12 | 1.10 | 2197 | 2264 | 1.03 | 11.4 |
| **PET-11** | 1 | 0.08 | 6.25 | 12.50 | 0.96 | 0 | 0.01 | 1.05 | 1.14 | 2189 | 2231 | 1.019 | 11.4 |
| **PET-12** | 1 | 0.05 | 10.00 | 20.00 | 1 | 0 | 0.01 | 1.09 | 1.14 | 2091 | 2135 | 1.021 | 10.9 |

** PET-1 was synthesized at room temperature for 7.5 hours, PET-2 at 40 $^0$C for 7.5 hours. The other reactions were conducted at room temperature for one hour. 50-60% conversions were obtained.*

PET-3, 4, and PET-5 were synthesized with excess TPC so they are assumed to be carboxylic acid terminated. However, peaks corresponding to –OH termination were also present. As seen in Table 4.5., PET-3 and PET-5 were produced with approximately %10 of excess TPC so that they were expected to form polymers that had about 10 repeating units. However, their NMR data showed that PET-3 and PET-5 had DP's around 7 and 8; respectively. We observed that DP measured rarely matched the calculations based on the use of excess EG or TPC. This might be an additional indication that the oligomers that are forming during the condensation process are more available than the monomeric diacid chloride. This may be due the solubility difference of the acyl ammonium intermediates formed during the reaction. TPC is known to react with TEA to form acyl ammonium salts. In the case of monomeric TPC two acyl ammonium salts are formed [55] at *para* position of the aromatic ring making it less soluble and thus less available to start a chain growth. In addition, the conversion of the polymers were around 50-60%; so that significant amount of starting materials was lost. Such low conversion also supports the hypothesis that polymerization progresses on synthesized oligomers in the reaction vessel as some acyl ammonium salt of TPC does not participate. Another factor might be the purity of TPC. A considerable amount of TPA was found to be present in the old commercial TPC which was most probably leading to a stoichiometric imbalance.

The observed ratios of TPC to EG in $^{1}$H-NMR were always higher than the feed ratios; except for PET-4. The increased observed ratios (PET-3, PET5-8) might be explained by the existence of the anhydrides. However, the found anhydride amount did not fully match the increased observed ratio either. For instance, 10% of anhydride was observed for PET-5. Its TPC to EG feed ratio was 1.10 so that the ratio of TPC to EG in the final product should be approximately 1.20; however, 1.35 was observed in $^{1}$H-NMR. One possible explanation could be residual monomeric TPA which might be coming from old-hydrolysed TPC (can also be produced during reaction). Although the final product was precipitated into a mixture of ethanol and water with sodium bicarbonate (to solubilize TPA), residual amount of TPA could be entrapped between the PET chains. Therefore, aromatic protons of unremoved TPA might have increased the observed ratio in $^{1}$H-NMR. To check this, TPA was dissolved in a mixture of chloroform/trifluoroacetic acid (NMR solvent) in a ratio of 10 to 1 v/v and as expected its aromatic peaks were observed at 8.24 ppm. Therefore, residual amount of TPA in the final products was identified by $^{1}$H-NMR. On the other hand, in the

case of PET-4, the feed and the observed ratio of TPC/EG in the $^{1}$H-NMR spectrum were the same (1.26). It was expected to form polymer with 4 repeating units because its TPC was about %25 higher than EG. However, the measurements indicated 10 repeating units if it assumed to have only one alcohol end. The unexpectedly increased DP could be explained by the differences of solubilities of the monomer and the oligomers as discussed before.

In addition to carboxylic ended polymer synthesis attempts, PET-6, 7 and PET-8 were synthesized with EG excess so that they assumed to be alcohol ended. As seen in Table 4.5., although their TPC/EG feed ratios were different (0.95 eq to 0.79 eq), similar DP's were calculated again (11, assumed to be both alcohol ended) from $^{1}$H-NMR analysis. It could be said that increased EG amount did not affect the PET polymerization in terms of molecular weight. Besides, DP's observed from both NMR (11) and GPC (12) matched if they are assumed to be both equally alcohol terminated. In addition, the integral of anhydride protons (e and f, Table 4.5.) of PET-6,7,8 (EG excess) were higher compared to the result of products which were synthesized with excess TPC (PET-3,4,5). It is highly possible that residual amount of water might come from EG. When increased amount of EG was used, the amount of water coming with it also increased, more water produced more anhydrides. To eliminate this EG was then dried over activated molecular sieves.

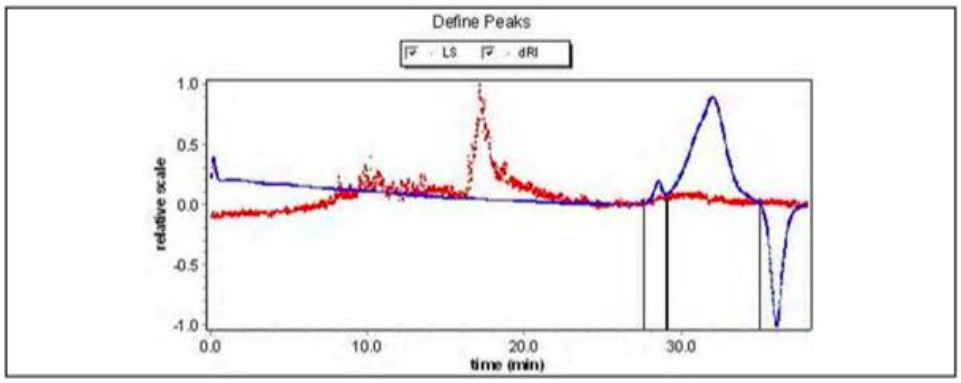



Figure 4.16. GPC spectrum of PET-5.

The GPC measurements were quite challenging due to solubility issues. The analyses were done at Kordsa Global R&D Center, İzmit, where an HFIP based system was used. For representative purpose, PET-5 GPC spectrum is shown in Figure 4.16. The red line

corresponds to the light scattering and blue line to the refractive index detectors. The results of the other PET products are given Table 4.5. All samples had $M_n$ between 2100 g/mol and 2500 g/mol. Polydispersity of the samples were closed to 1 for all. Based on these data, similar molecular weights and narrow PDI's, several assumptions can be made. First, it is possible that GPC samples did not dissolve entirely in HFIP (GPC solvent) and thus only polymers passing through the GPC filter were analyzed. Second, polymers might have precipitated during the synthesis when they reached a certain length due to solubility issues since it is well known that PET is not soluble in THF (polymerization solvent). Third, the observed low PDI can be the outcome of the solubility of the smaller chains getting eliminated during the precipitation into the mixture of ethanol and water with a pH 9. If carboxylic acid end groups of low molecular weight oligomers are also deprotonated such chains may be more soluble in water so that only longer and more –OH terminated chains precipitate and therefore a fractionation is induced in terms of $M_n$ and the type of end group (OH *vs* COOH).

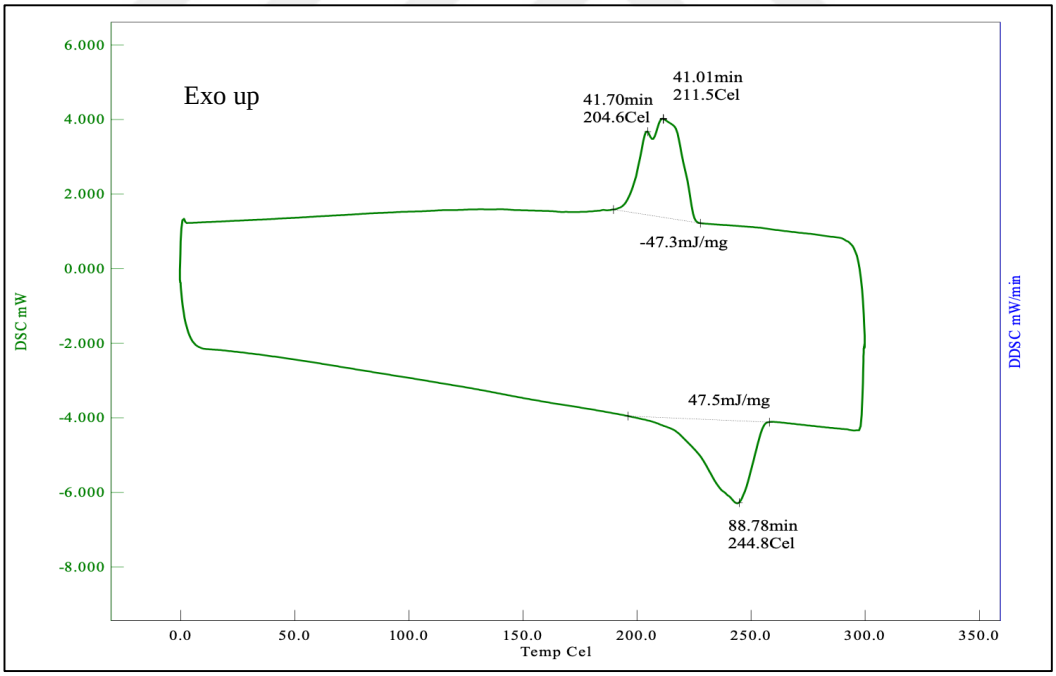



Figure 4.17. DSC thermogram of PET-10.

Next the samples were analyzed by DSC. As an example, DSC thermogram of PET-10 is shown in Figure 4.17. The first heating cycle was cut from the spectrum in order to

simplify the thermogram. Although PET-10 did not show a $T_g$, it had distinct $T_c$ (211.5 $^0$C) and $T_m$ (244.8 $^0$C) peaks and the area under the peaks were the same (47 mJ/mg). In other words, the polymer released certain amount of energy during crystallization and then used the same amount of energy to melt. Therefore, it could be said that the synthesized low molecular weight PET oligomers become fully crystalline which may explain the lack of any $T_g$ peak. The results are given in Table 4.6 and explained by grouping the samples. The other samples' thermogram are given in Appendix.

Table 4.6. DSC results of PET products*.

| | **1st cycle (heating) ($^0$C)** | | | **1st cycle (cooling) ($^0$C)** | | **2nd cycle (heating) ($^0$C)** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ | $T_c$ | $T_m$ | $T_{c1}$ | $T_{c2}$ | $T_g$ | $T_c$ | $T_{m1}$ | $T_{m2}$ |
| **PET-1** | - | 134 | 225 | 204 | - | - | - | 231 | - |
| **PET-2** | - | 147 | 231 | 271 | 158 | 64 | - | 204 | - |
| **PET-3** | - | 168 | 223 | 166 | 156 | - | - | 211 | - |
| **PET-4** | 68 | 167 | 230 | 192 | 162 | - | - | 206 | 228 |
| **PET-5** | - | 161 | 229 | 188 | - | - | - | 224 | - |
| **PET-6** | 54/65 | 166 | 218 | 232 | 137 | 56 | 123 | 197 | - |
| **PET-7** | 61 | 167 | 220 | 236 | 161/135 | - | - | 179 | 207 |
| **PET-8** | 62 | 167 | 231 | 185 | 163 | - | - | 221 | - |
| **PET-9** | 59 | 161 | 212 | 194 | - | 63 | - | 250 | - |
| **PET-10** | 67 | - | 211 | 211 | 205 | - | - | 245 | - |
| **PET-11** | 68 | - | 213 | 217 | 201 | - | - | 242 | - |
| **PET-12** | 65 | - | 213 | 220 | 208 | - | - | 234 | - |

** PET-1 was synthesized at room temperature for 7.5 hours, PET-2 at 40 $^0$C for 7.5 hours. The other reactions were conducted at room temperature for one hour.*

According to the DSC results (Table 4.6), most of the PET samples (PET-4 and PET-7,8,10-12) had $T_g$ at first cycle of heating and then $T_g$ was not detected at the 2nd cycle. It could be said that polymer chains reoriented themselves during the process to form almost fully crystalline structures.

Detailed observations will be given below. For a more general conclusion, the reader may decide to skip this part and read the consecutive paragraph.

For PET-1 and PET-2 (reaction time 7.5 hours, TPC/EG=1.07);

- At 1st cooling, PET-2 (40 $^0$C) showed small $T_c$ at 271 $^0$C; however, $T_c$ peak at 158 $^0$C was more distinct. PET-1 (RT) had higher $T_c$ (204 $^0$C) than PET-2 (158 $^0$C).
- At 2nd heating, only PET-2 (40 $^0$C) showed $T_g$ at 64 $^0$C and its $T_m$ was smaller than PET-1 (RT).

For PET-3,4,5 (acid chloride excess, TPC/EG feed ratios:1.12, 1.26, 1.10; respectively);

- PET-4 had the highest amount of TPC (1.26 eq). Only it demonstrated $T_g$ at first cycle (68 $^0$C).
- At 1st cooling, PET-4 $T_c$ peak was sharp and there was an additional small peak while the other two had a broad $T_c$ peak.
- At 2nd heating, PET-3 had the smallest $T_m$ and PET-4 and PET-5 had similar melting temperature (224 $^0$C and 228 $^0$C).

For PET-6,7,8 (alcohol excess, TPC/EG feed ratios: 0.95, 0.83, 0.79; respectively);

- At 2nd heating, only PET-6 (TPC/EG =0.95) gave $T_g$.
- At 2nd heating, $T_m$ values were increased as TPC to EG ratio decreased, like 1st cycle. However, these values were smaller than the first case.

For PET-10,11,12 (acid chloride excess, new TPC, TPC/EG feed ratio: 1.12, 1.05, 1.09; respectively);

- At 1st heating, $T_g$ was observed for all of them and the $T_g$ values were similar (65 $^0$C-68 $^0$C)

- At 2nd cycle, crystallization temperature and melting temperature were distinct and the areas under the curves were close to each other.
- $T_m$ at 1st heating (about 210 $^0$C) was smaller than that at 2nd heating (about 240 $^0$C).

Polyesters synthesized with the new TPC had higher melting temperature than the others (240 $^0$C vs 220 $^0$C) except for PET-9. Possibly because these polymers had the least number of anhydrides disturbing the symmetrical structure. Therefore, residual anhydrides (observed in old TPC used syntheses) seem to decrease the melting temperature at the given molecular weights (2100g/mol-2500g/mol). All samples, except PET-2,6-9, did not show $T_g$ at 2nd heating so it can be said that their amorphous regions were readily reoriented to give almost fully crystalline structures.

### 4.3.3. Conclusion on the Syntheses of PET in Solution

As a result, changing TPC/EG molar feed ratio did not affect much the molecular weights, most probably due the solubility and impurity problems. The products synthesized with new TPC gave better results because anhydride formation was mostly eliminated. DSC results showed that the presence of anhydrides decreases the melting temperature. One possible explanation is that anhydride bond disturbs the symmetrical structure of PET.

Table 4.7. The overall results of PET products.

| | **DP (NMR) (one end)** | **DP (NMR) (both end)** | **$M_n$ (g/mol)** | **DP (GPC)** | **$T_g$ ($^0$C) (2nd cycle)** | **$T_m$ ($^0$C) (2nd cycle)** |
|---|---|---|---|---|---|---|
| **PET-1** | 5.56 | 11.11 | 1033 | 5.4 | - | 231 |
| **PET-2** | 10.00 | 20.00 | - | - | 64 | 204 |
| **PET-3** | 7.14 | 14.28 | 2340 | 12.2 | - | 210 |
| **PET-4** | 10.00 | 20.00 | 2431 | 12.6 | - | 228 |
| **PET-5** | 8.33 | 16.67 | 2235 | 11.6 | - | 224 |
| **PET-6** | 5.56 | 11.11 | 2488 | 12.9 | 56 | 197 |
| **PET-7** | 5.56 | 11.11 | 2429 | 12.6 | - | 207 |

Table 4.7. The overall results of PET products (cont.)

| | | | | | | |
|---|---|---|---|---|---|---|
| **PET-8** | 5.56 | 11.11 | 2376 | 12.4 | - | 221 |
| **PET-9** | 3.33 | 6.67 | 2497 | 12.9 | 63 | 250 |
| **PET-10** | 10.00 | 20.00 | 2197 | 11.4 | - | 245 |
| **PET-11** | 6.25 | 12.50 | 2189 | 11.4 | - | 242 |
| **PET-12** | 10.00 | 20.00 | 2091 | 10.9 | - | 234 |

## 4.4. PET-Anhydride Synthesis in Solution

In the next step, the syntheses of PET polyester anhydrides were deliberately targeted. Similar to the synthesis of PET in solution, TPC was dissolved in dry THF and then a mixture of EG with different amount of water was added to the reaction vessel. In other words, in order to insert anhydride bonds into the polyester chains, water was added to the diacid chloride to promote controlled and limited hydrolysis to acid which in turn was expected to react with the remaining excess acid chlorides *in situ* to form a dimeric acid chlorides with an anhydride linkage. There are different possible structure (explained later) depending on how and in which order EG and water react with acid ammonium intermediates. The possible anhydride bond formation mechanism is given in Figure 4.18 where EG reacts first with the TPC and then water attacks. Polymerization continues on the end acyl ammonium group.

In FTIR, PET-anhydride samples showed two peaks at 1715 $cm^{-1}$ and 1789 $cm^{-1}$ as expected corresponding to two carbonyl peaks. The peak at 1715 $cm^{-1}$ was corresponding to ester carbonyl stretching and most probably overlapping the anhydride's second peak. It was observed that if the % transmittance of the peak at 1789 $cm^{-1}$ was getting equal to that at 1715 $cm^{-1}$, the product solubility decreased. In other words, increased number of anhydride bond among the polyesters limited the polymer solubility.

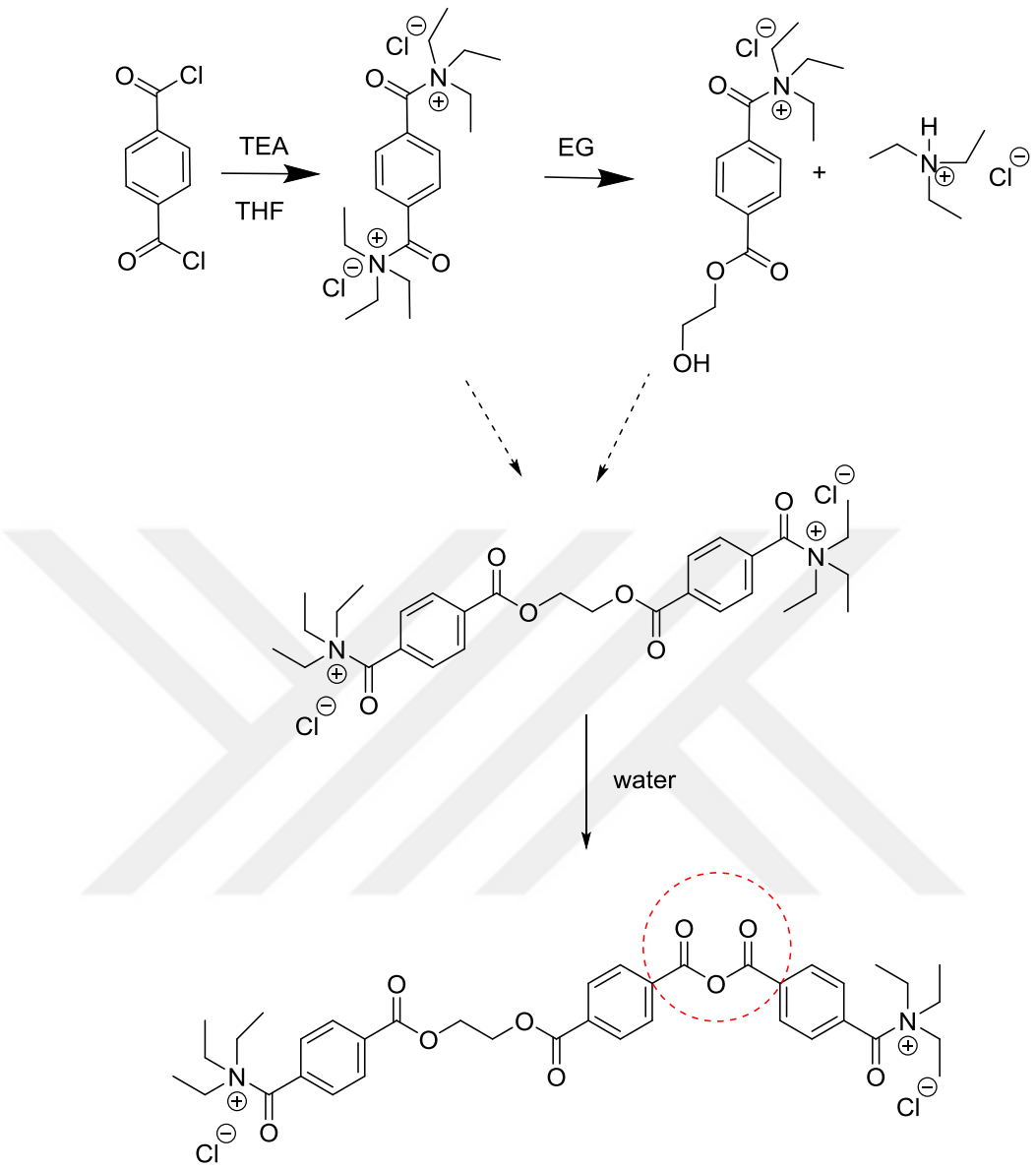



Figure 4.18. The proposed reaction mechanism of anhydride bond formation.

These products were also difficult to dissolve in routine NMR solvents and mixtures compared to PET counterparts. Their solubilities depended on how the polymerization was carried out. For example, the addition order of water and EG altered the solubility significantly. Interestingly, it was found that, anhydride products became more soluble when EG and water were first mixed together prior to the addition onto the diacid chloride, rather than their sequential addition (first water then EG). A plausible explanation might be that the randomness of the anhydrides, in other words the distribution of the anhydride linkages in the polyester is highly affected by how the water and EG is added onto the TPC. Some possible structures are shown in Figure 4.19. It is most likely that anhydrides and even

polyanhydrides (anhydrides of acids only) were forming immediately upon the addition of water in the absence of EG; and then, EG continued to elongate polymer chains once it was added (Figure 4.19-b). Therefore, polyanhydride blocks are most likely responsible for the limited solubility since these blocks being 1,4 substituted and having lower degree of freedom introduced harder segments into the polyester chains. When EG and water were mixed together, however, solubility problem was mostly solved. By doing this, the chance of forming ‘a’ and ‘c’ structures (Figure 4.19), in other words longer segments of polyesters and shorter segments of anhydrides was most probably increased.

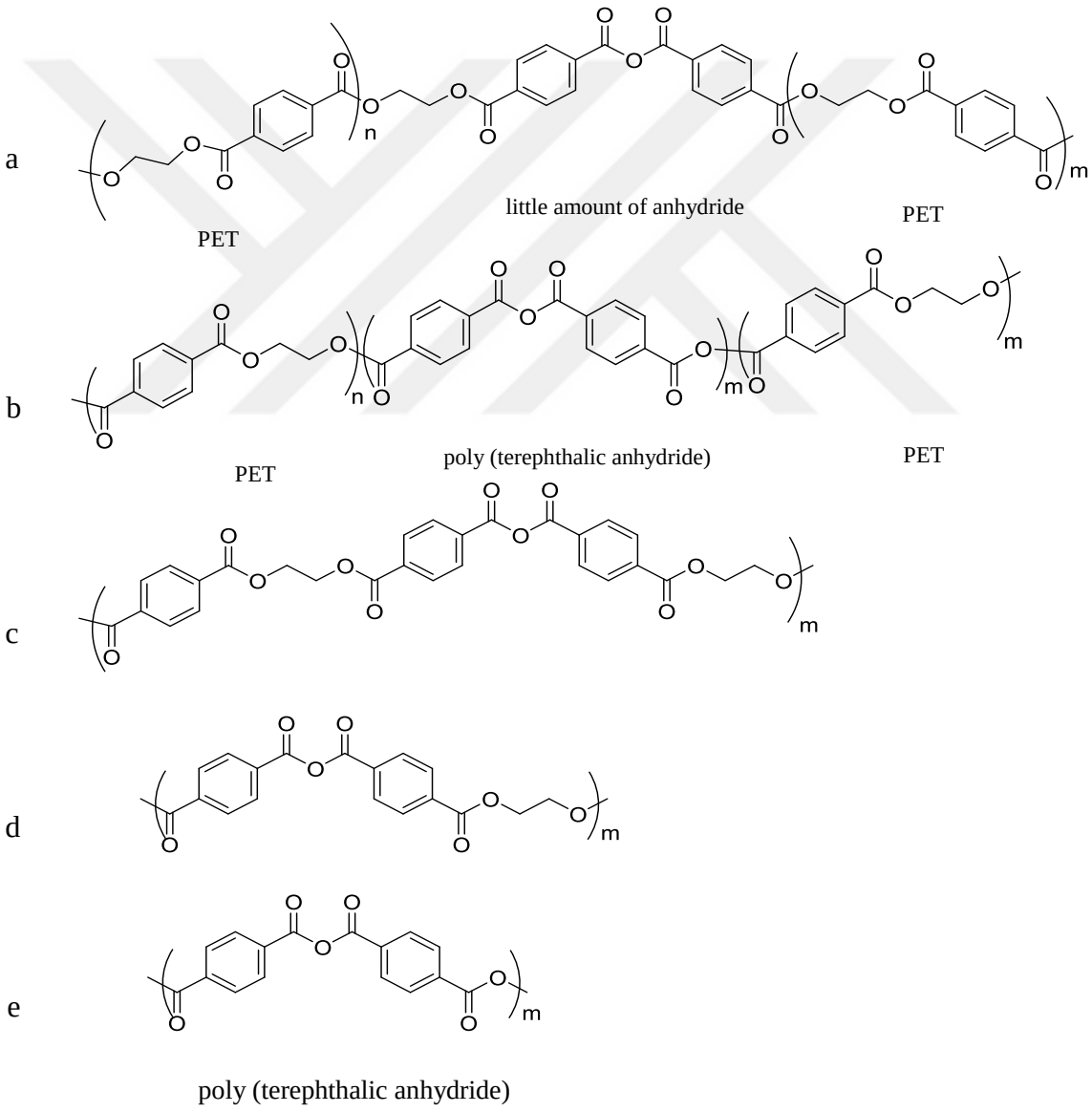



Figure 4.19. The possible anhydride structures.

### 4.4.1. Analysis of PET-Anhydrides Synthesized in Solution

For NMR analysis, the products synthesized with the old and the new TPC were dissolved in chloroform-trifluoroacetic acid mixture in a volume ratio of 5 to 1 and 10 to 1, respectively. Although the samples were first fully soluble in the mixture of deuterated chloroform and TFA, the ones with higher anhydrides precipitated partially in the NMR tube after a while. For that reason, NMR samples were prepared freshly, and analyses were done immediately. In accordance with this, the products synthesized with new TPC (containing almost no hydrolyzed TPC) did not demonstrate precipitation during and after analyses; which also supported the hypothesis that increased amount of anhydride limits the solubility. The $^{1}H$- $^{13}C$-NMR spectra of PEA-1 are given in Figure 4.20 and Figure 4.21. as example of PET-anhydrides.

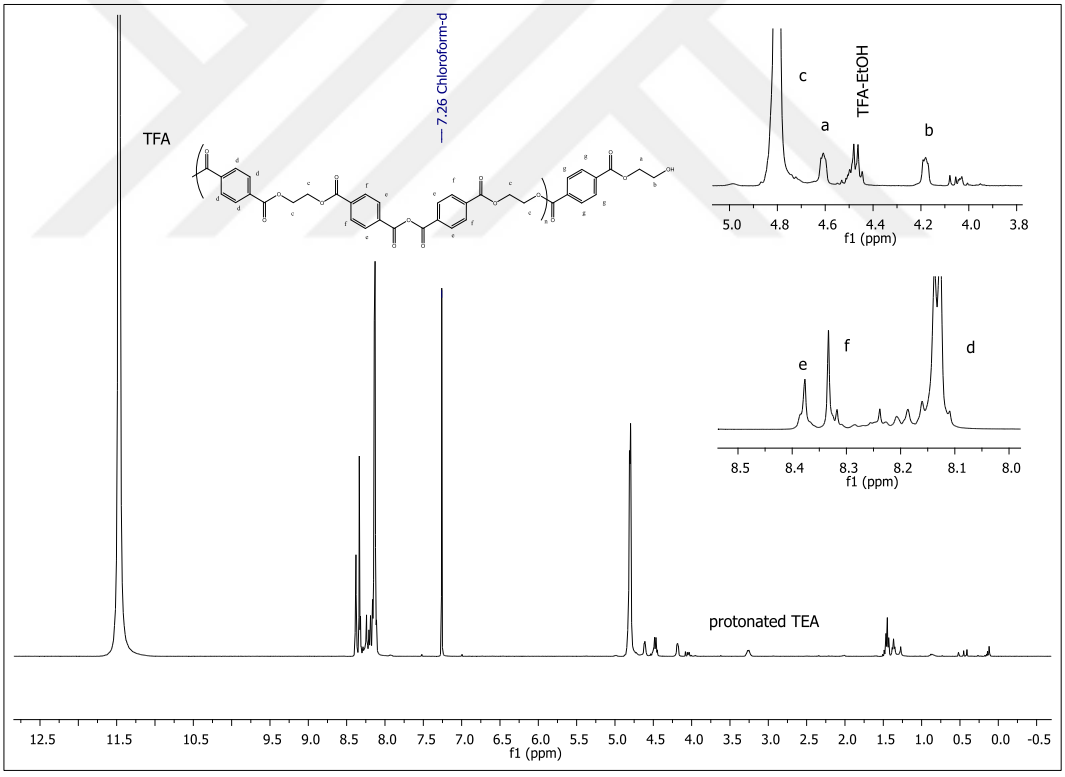



Figure 4.20. $^{1}H$ NMR of PEA-1.

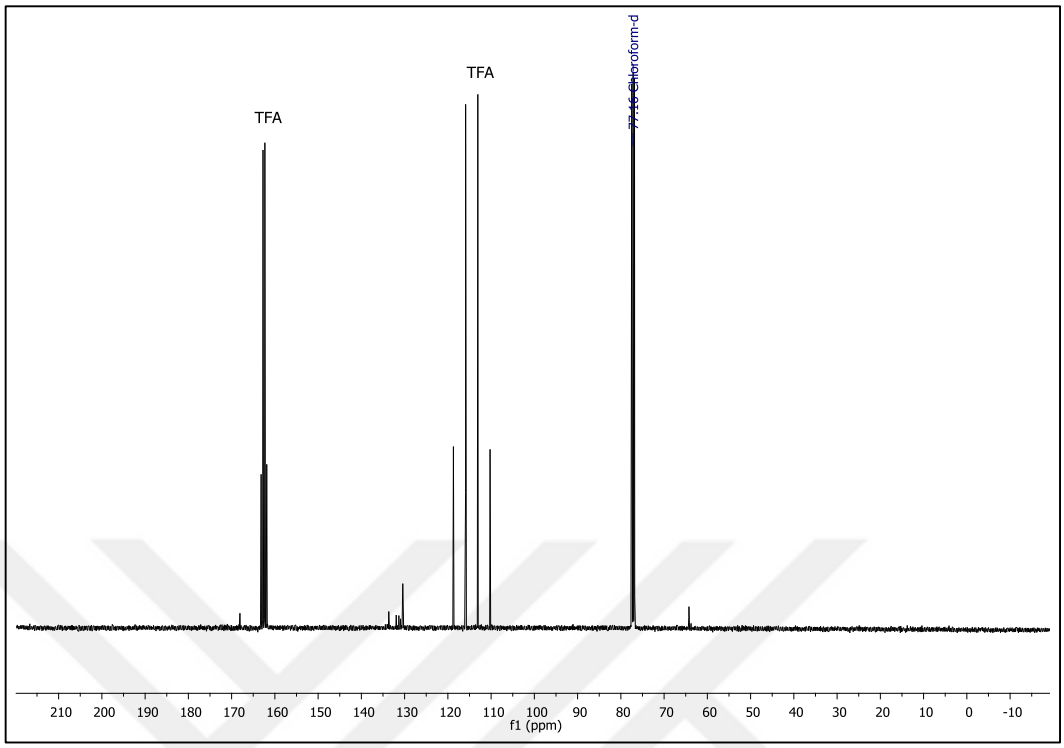



Figure 4.21. $^{13}$C NMR of PEA-1.

$^{13}$C-NMR spectrum of PEA-1 is shown in Figure 4.21. Although the presence of the anhydrides was evident in $^{1}$H-NMR, the extra carbonyl peaks that were expected for the anhydride carbonyl carbons were not detectable in $^{13}$C-NMR. It is well known that $^{13}$C-NMR detection limit is higher than the $^{1}$H-NMR, it is possible that the concentration of the anhydride peaks was not enough to be detectable by $^{13}$C-NMR. Aromatic carbons are observed at 130 ppm where ethylenic carbons appear around 65 ppm. Besides, carbon peaks of TFA are also present at 115 ppm and 160 ppm.

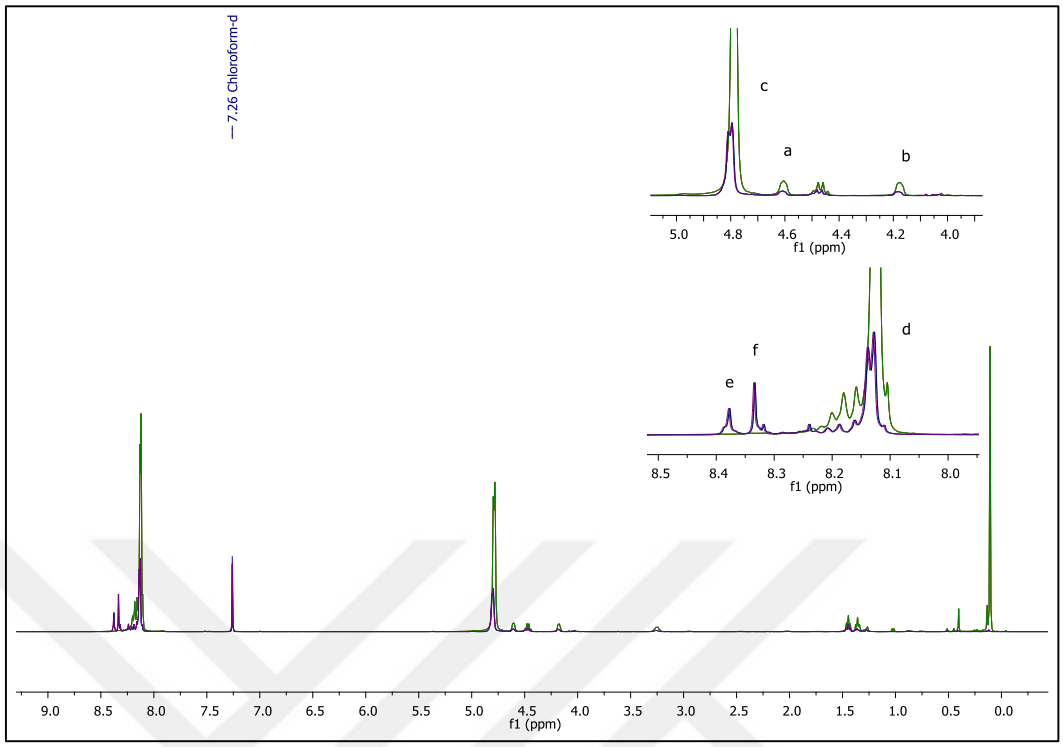



Figure 4.22. Comparison of PET and PET-Anhydride

A comparative analysis was carried out in order to differentiate and assign aromatic anhydride protons. The $^{1}$H-NMR spectra of PET and PET-anhydride were taken and compared. The overlapping spectra are given in Figure 4.22. The purple spectrum belongs to PET-anhydride and green spectrum corresponds to PET sample free of anhydrides. PET-anhydride spectrum is similar to PET spectrum except for the peak at 8.3 ppm. For PET-anhydride samples, the most deshielded protons were located at 8.38 ppm and 8.33 ppm, which were assumed to be the aromatic protons of the anhydrides (e and f). Indeed, as explained in the previous part, PET samples synthesized with old TPC contained higher concentration of unwanted anhydrides and these reflected themselves in the higher integrals values of the peak at 8.30's. In addition, in the standard PET samples that were presented in the previous section (PET 2-9) residual aromatic anhydride protons could be detected by the presence of these peaks, however the PET-anhydride samples had higher number of anhydrides according the integral values (Table 4.8) of these peaks. Therefore, the peaks at around 8.30's were assigned to the anhydride neighboured aromatic protons.

Table 4.8. NMR integrals and GPC results of the PEA products*.

| | **c** (EG repeat) | **a** (EG end group) | **DP (one)** | **DP (both)** | **d** (aromatic repeat) | **e** (anhydride) | **f** (anhydride) | **water percent** | **TPC/EG (feed)** | **TPA/EG (observed in NMR)** | $M_n$ **(g/mol)** | $M_w$ **(g/mol)** | $M_w/M_n$ | **DP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PEA-1** | 1 | 0.06 | 8.33 | 16.67 | 0.97 | 0.15 | 0.17 | 25% | 1.12 | 1.52 | 2401 | 2438 | 1.015 | 12.5 |
| **PEA-2** | 1 | 0.08 | 6.25 | 12.50 | 0.98 | 0.17 | 0.20 | 20% | 1.12 | 1.57 | 2370 | 2416 | 1.019 | 12.3 |
| **PEA-3** | 1 | 0.06 | 8.33 | 16.67 | 0.95 | 0.15 | 0.18 | 10% | 1.12 | 1.54 | 2270 | 2310 | 1.018 | 11.8 |
| **PEA-4** | 1 | 0.07 | 7.14 | 14.29 | 0.97 | 0.16 | 0.22 | 5% | 1.12 | 1.59 | 2431 | 2473 | 1.017 | 12.6 |
| **PEA-5** | 1 | 0.05 | 10.00 | 20.00 | 0.93 | _ | _ | 10% | 1.12 | 1.07 | 2213 | 2277 | 1.029 | 11.5 |
| **PEA-6** | 1 | 0.06 | 8.33 | 16.67 | 0.90 | 0.01 | 0.00 | 20% | 1.12 | 1.14 | 1025 | 1050 | 1.025 | 5.3 |
| **PEA-7** | 1 | 0.06 | 8.33 | 16.67 | 0.85 | 0.05 | 0.06 | 25% | 1.12 | 1.27 | 1076 | 1102 | 1.024 | 5.6 |

**Reaction were conducted at room temperature for one hour. EG and water were mixed prior to addition. Water mol percent with respect to TPC. 50-60% conversions were obtained.*

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As seen in Table 4.8., the integral values of the proton ‘e’ and ‘f’ were almost equal; which was expected because these were on the same aromatic group neighboring the anhydride bond. TFA made it hard to differentiate aromatic protons. There were some small peaks between 8.15 ppm and 8.24 ppm, which were not assigned. In order to identify peaks, the old commercial TPC was analyzed by $^{1}$H-NMR (Figure A.61), one peak at 8.25 ppm (corresponding to symmetric aromatic protons of TPC) was observed distinctly with a small peak located at 8.21 ppm (assumed to aromatic protons of TPA). When 0.05 ml of trifluoroacetic acid (deuterated chloroform and trifluoroacetic acid was the NMR solvent) was added into the same NMR tube (Figure A.62), two small peaks (8.24 ppm and 8.26 ppm) were detected close to the main peak (8.28 ppm for aromatic protons of TPC). Therefore, the observed peaks at 8.24 ppm in $^{1}$H-NMR of the synthesized polymers were assumed to be coming from TPA (as impurity in the commercial bottle or produced in the reaction).

PEA-1 to 4 (synthesized with old TPC, water percent decreased from PEA-1 to PEA-4) results as given in Table 4.8. The calculated ratio of TPA to EG in NMR was much higher than the feed ratio of TPC to EG. The same situation was observed in PET samples synthesized in solution as explained in Section 4.3.2. One reason might be the anhydrides because these products had aromatic anhydride protons in higher amounts. For instance, PEA-1 demonstrated approximately 15% of anhydride (e) and its TPC/EG feed ratio was 1.12. Theoretically, 1.27 was expected to be observed in NMR when aromatic protons are compared to EG protons; however, 1.52 was calculated. Therefore, another source of aromatic protons might be again unreacted TPA. Although the products were precipitated into an ethanol/water mixture with pH 9 (in order to solubilize TPA), some residual amount of TPA might still be present.

In the case of PEA-5,6,7 (synthesized with new TPC, water percent increase from PEA-5 to PEA-7), smaller anhydride aromatic peaks were observed. The feed and observed ratios of TPA to EG were closer. Although they were small, the integrals of anhydride protons (e and f) increased as the added water percent increased. In PEA-7, 25% of water (mol percent with respect to TPC) showed a significant increase where its integral was 0.05 for ‘e’ protons while 20% of water containing product (PEA-6) showed 0.01 value. However, PEA samples synthesized with old TPC demonstrated much higher integral values for anhydride protons (0.15 *vs* 0.05). This was also observed in PET samples as explained in section 4.3.2. where it was speculated that TPC purity was responsible for the anhydride

formation. In addition to TPC purity, EG seems tp contain residual water although it was dried over molecular sieves in THF.

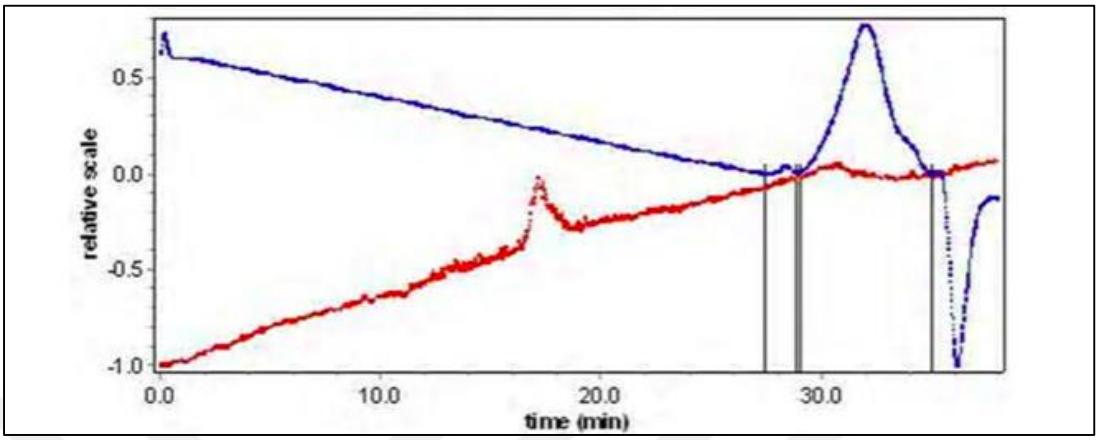



Figure 4.23. GPC spectrum of PEA-1.

In addition to NMR, the samples were analyzed with GPC. In GPC spectrum, two peaks were observed. As seen in Figure 4.23., one peak was small and appeared very close to second broad peak. The values of the smaller peak were taken into account and are showed in Table 4.8. As explained in PET part, GPC results gave similar molecular weight for all of the samples. This could arise from the solubility problem or the polymers had precipitated when they reached a certain molecular weight during the synthesis and a fractionation was induced during the isolation process as explained earlier (page 48).

Lastly, the products were analyzed with DSC. As a representative example, DSC thermogram of PEA-1 is given in Figure 4.24 where the first heating cycle is not shown to simplify the thermogram. $T_g$ is observed at 51 $^0$C for PEA-1. Then, a broad $T_c$ with a maxima at 123 $^0$C is observed followed by a melting endotherm at 199 $^0$C. During the cooling, two $T_c$ are observed at 230 $^0$C and 138 $^0$C. The other thermograms are given in Appendix. The detailed data for all samples is shown in Table 4.9.

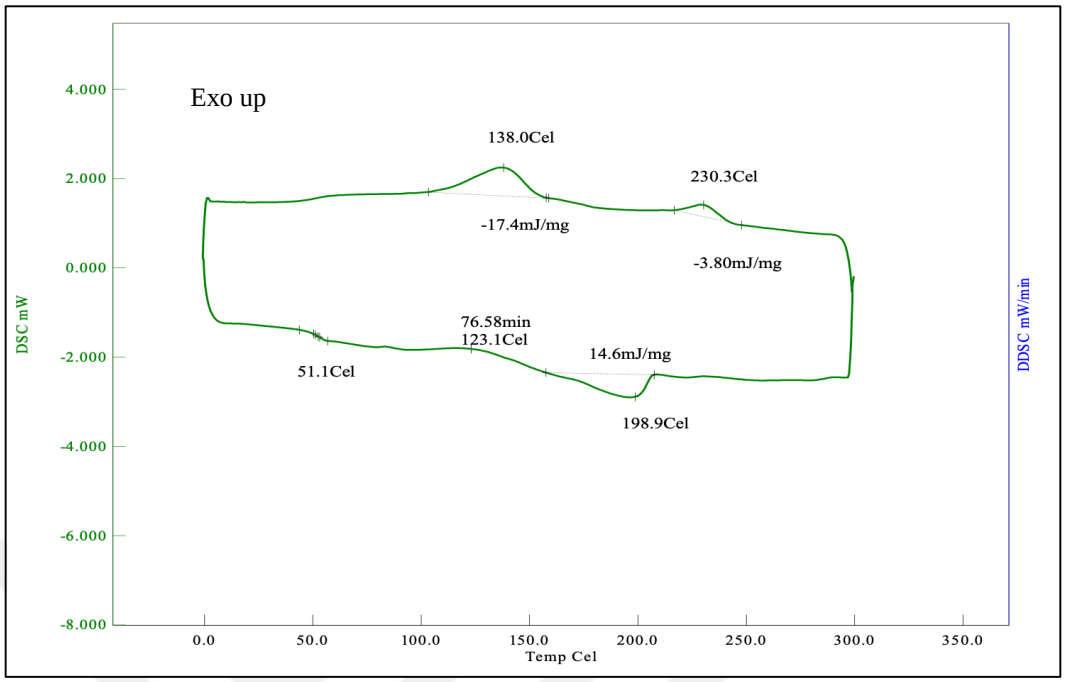



Figure 4.24. DSC Thermogram of PEA-1.

Table 4.9. DSC results of PEA products.

| | **1st cycle (heating) ($^0$C)** | | | **1st cycle (cooling) ($^0$C)** | | **2nd cycle (heating) ($^0$C)** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ | $T_c$ | $T_m$ | $T_{c1}$ | $T_{c2}$ | $T_g$ | $T_c$ | $T_{m1}$ | $T_{m2}$ |
| **PEA-1** | - | 124/170 | 223 | 230 | 138 | 51 | 123 | 199 | - |
| **PEA-2** | - | 131/166 | 222 | 256 | 123/62 | 57 | 126 | 195 | - |
| **PEA-3** | - | 128/165 | 223 | 261 | 140 | 51 | 123 | 196 | - |
| **PEA-4** | - | 134/170 | 215 | 239 | 69 | 52 | 138 | 185 | - |
| **PEA-5** | 67 | - | 217 | 216 | 209 | - | - | 239 | - |
| **PEA-6** | 62 | 163 | 222 | 204 | 196/183 | - | - | 228 | 238 |
| **PEA-7** | 65 | 167 | 215 | 187 | 179/171 | - | - | 217 | - |

For those interested, detailed observations are written below. Afterwards, a general conclusion is given.

For PEA-1,2,3,4 (from PEA-1 to PEA-4, water percent decreased, with old TPC);

- At 1st heating, they had similar melting temperatures (220 $^0$C) except for PEA-4 (215 $^0$C) which had the smallest amount of water (5% -mol percent with respect to TPC). The same situation was observed at 2nd heating melting temperatures.
- At 1st cooling, they had broad peaks corresponding to $T_c$.
- At 2nd heating, $T_g$ was observed. They had similar values (51 $^0$C) except for PEA-2 (57 $^0$C) which had 20% of water (mol percent with respect to TPC).
- At 2nd heating, there existed a $T_c$ peak between $T_g$ and $T_m$. This $T_c$ peak was so distinct for PEA-2 (20% mol percent with respect to TPC) (Figure A.44). It can be said that the polymer chains did not become fully crystalline and there were still amorphous regions. Unlike PEA-2, this $T_c$ was seen as a broad peak indistinctly for PEA-1,3 and 4 (Figure A.41, A.47 and A.50).
- At 2nd heating, the observed $T_m$ (about 195 $^0$C) values were slightly smaller than that at 1st heating (about 220 $^0$C).

For PEA-5,6,7 (from PEA-5 to PEA-7, water percent increased, with new TPC);

- At 1st heating, $T_g$ was observed. While PEA-5 (%10 mol percent with respect to TPC) and PEA-7 (%25 mol percent with respect to TPC) had similar $T_g$ (65 $^0$C) and melting points (215 $^0$C), PEA-6 (%20 mol percent with respect to TPC) showed lower $T_g$ (62 $^0$C) and higher $T_m$ (222 $^0$C).
- At 1st cooling, sharp peaks were observed but they seemed to be combination of more than one peak. For instance, PEA-7 had an exotherm peak with three tips (Figure A.60).
- At 2nd heating, $T_m$ values decreased as water percent was increased (239 $^0$C- 217 $^0$C).

In general, DSC results were compared in order to understand TPC purity effect on polymer properties and an interesting $T_g$ behavior was observed. First four samples (PEA-1-4 with old TPC) demonstrated $T_g$ at 2nd cycle; however, the others (PEA-5-7 with new TPC) showed $T_g$ at 1st cycle. However, thermal history of the products formed during precipitation into the mixture of ethanol and water were erased during first heating; therefore, the comparison of the results of 1st heating and 2nd heating might be misleading. For that reason,

only 2nd heating was considered. At 2nd heating, PET-5,6,7 (having less anhydride) had higher $T_m$ (about 235 $^0$C) than the others (having more anhydride) (about 195 $^0$C). Therefore, anhydride assumed to decrease melting point. Moreover, only melting point was observed and $T_g$ (amorphous region feature) was not detected at 2nd heating for poly(ester-anhydride) synthesized with new TPC so that it can be said that they completely reorganized to form crystalline structure. This postulation was also be supported by the calculated energies from the thermograms. For PEA-7 (Figure A.60), 49 mJ/mg was calculated from both $T_c$ and $T_m$ peaks. Finally, the fact that PEA1-4 samples show $T_g$ at the second heating reinforces the idea that the anhydrides affect the crystallinity. The presence of the anhydrides disturbs the crystallinity and in the higher anhydride containing polymers amorphous regions are present enough to show $T_g$ values.

### 4.4.2. Conclusion on PET-Anhydride Synthesized in Solution

As a result, the addition of a known amount of water increased the anhydride formation but in an uncontrolled way. The direct relationship between water percent and produced anhydride was not evident. The products synthesized with the old, thus partially hydrolyzed TPC contained more anhydride compared to those made with new TPC; as expected. Similar to PET samples, increased amount of anhydride linkages decreased the melting point, thus indicating a loss in the symmetry of polymer chains.

Table 4.10. The overall results of PEA products.

| | **DP (NMR) (one end)** | **DP (NMR) (both end)** | **$M_n$ (g/mol)** | **DP (GPC)** | **$T_g$ ($^0$C) (2nd cycle)** | **$T_m$ ($^0$C) (2nd cycle)** |
|---|---|---|---|---|---|---|
| **PEA-1** | 8.33 | 16.67 | 2401 | 12.5 | 51 | 199 |
| **PEA-2** | 6.25 | 12.50 | 2370 | 12.3 | 57 | 195 |
| **PEA-3** | 8.33 | 16.67 | 2270 | 11.8 | 51 | 196 |
| **PEA-4** | 7.14 | 14.29 | 2431 | 12.6 | 52 | 185 |
| **PEA-5** | 10.00 | 20.00 | 2213 | 11.5 | - | 239 |
| **PEA-6** | 8.33 | 16.67 | 1025 | 5.3 | - | 228/238 |
| **PEA-7** | 8.33 | 16.67 | 1076 | 5.6 | - | 217 |

## 4.5. Chain Extension Studies with PET-Anhydride in Melt

The PET-anhydride synthesized with the new TPC and 20%-mol percent (with respect to TPC) of water were reacted with Low IV PET (IV= 0.355 dl/g, $M_n$=5005 g/mol, $M_w$=12690 g/mol, PDI=2.535, OH/COOH end group ratio was 3/1) in a melt system. The question was that could the PET-anhydride lead to the formation of higher molecular weight PET by reacting with the lower molecular weight -OH terminated PET's and acting as a coupling agent through a mixed anhydride mechanism. The advantage of such a coupling agent was clear. The anhydride used for coupling, PET-anhydrides, would release only PET oligomers upon the coupling reactions (Figure 4.10). So, nothing that can act as an impurity would be released to the PET chains. One should remember that, the coupling agents used by the industry, act most of the time as impurities affecting adversely the crystallinity and the kinetics of crystallization.

For the experiments 2% by weight PET-anhydride as a coupling agent and 3%-mol percent (with respect to -OH end group concentration) of catalyst was used. Three different catalysts, titanium IV isopropoxide (TIP), 2-4-6-tris (dimethylaminomethyl) phenol (NX3P), zinc acetate, were investigated. The reactions were done at $280^0$C in the melt for 30 minutes.

The samples were analyzed by GPC and the results are given in Table. 4.11. Sample 17 was prepared by only mixing commercial PET and synthesized PET-anhydride without any catalyst. When results are compared to the blank (sample 1, Table 4.11.) which was obtained by melting and stirring only low IV PET in the melt system for 30 minutes at $280^0$C, it was found out that the molecular weights decreased and the polydispersities increased. Therefore, it can be said that the synthesized PET-anhydride seemed to degrade commercial PET even in the absence of any catalyst.

Table 4.11. The results of melt products*.

| Sample | PET-Anhydride (g) | Catalyst type | Catalyst amount (mol%) | IV (dl/g) | $M_n$ (g/mol) | $M_w$ (g/mol) | PDI |
|---|---|---|---|---|---|---|---|
| **1(blank)** | - | - | - | 0.404 | 5086 | 13260 | 2.608 |
| **17** | 0.30 | - | - | - | 2113 | 8317 | 3.936 |
| **18** | 0.30 | zinc acetate | 3 | - | 2327 | 8315 | 3.573 |
| **19** | 0.30 | NX3P | 3 | - | 2283 | 8776 | 3.844 |
| **20** | 0.30 | TIP | 3 | - | 2287 | 8549 | 3.739 |

**Initial PET IV= 0.355 dl/g, $M_n$=5005 g/mol, $M_w$=12690 g/mol, PDI=2.535*

In the presence of the catalysts, interestingly, three catalysts decreased the molecular weights almost in similar manners. In all three samples' (18,19 and 20, Table 4.11.) number-average molecular weights were measured approximately 2300 g/mol. In addition, sample 17 which was produced with PET and PET-anhydride had also the same $M_n$. Therefore, it is possible that the destructive effect of PET-anhydride dominates the process. As seen in Table 4.12., when catalysts were used separately without any anhydride, molecular weights were higher (above 4000 g/mol) compared to PET- anhydride used samples ($M_n$ about 2300 g/mol). Thus, the observed decomposition seems to come mainly from the anhydrides. The mechanism was not studied; however, an acid catalyzed chain scission is suspected.

Table 4.12. Catalysts Control Results*.

| | Catalysts | IV (dl/g) | $M_n$ (g/mol) | $M_w$ (g/mol) | PDI |
|---|---|---|---|---|---|
| **Sample 6** | 3% NX3P | 0.400 | 4184 | 10920 | 2.610 |
| **Sample 10** | 3% TIP | 0.396 | 4618 | 11710 | 2.535 |
| **Sample 14** | 3% zinc acetate | 0.432 | 6714 | 16250 | 2.421 |

**Initial PET IV= 0.355 dl/g, $M_n$=5005 g/mol, $M_w$=12690 g/mol, PDI=2.535*

### 4.5.1. Conclusion on the Chain Extension Studies with PET-Anhydride

As a result, PET-anhydride did not act as chain extenders. Contrarily, they behaved like a catalyst for chain scission as well as repressed the other used catalysts (zinc acetate, TIP and NX3P). Therefore, chain scission reactions are most probably catalysed by the acids formed from anhydrides.

# 5. CONCLUSIONS

In this study, firstly, polyanhydrides of terephthalic acid were synthesized and their chain extender abilities were examined. The polyanhydrides did not meet the expectations and degraded PET instead of coupling. Then PET oligomers and PET-anhydrides were synthesized in solution polymerization. When the PET-anhydrides were added to commercial PET as a melt coupling agent, degradation rather that molecular weight increase was observed. It is possible that acids produced from anhydrides catalyzes the chain scission reactions.

During the study, it was found that the syntheses of PET polymers by a solution process is rather difficult, first, due to solubility issues. The route from diacid chlorides, secondly, requires high purity acid chlorides, otherwise high concentrations of anhydrides are formed.

In the synthesis of PET-anhydrides, it was found that the presence and the distribution of anhydrides change the solubility and crystallization behavior of the polyester anhydrides. A more random distribution leads to higher solubility. A higher amount of anhydride leads to lower melting point.

In conclusion, the synthesis of any oligomeric PET type of polymer by a solution process, seems rather challenging. One may try to optimize the conditions for such a system, however, in these cases the purification and analyses of the products present extra difficulties that one must be ready to face.

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# APPENDIX A: SPECTROSCOPY DATA

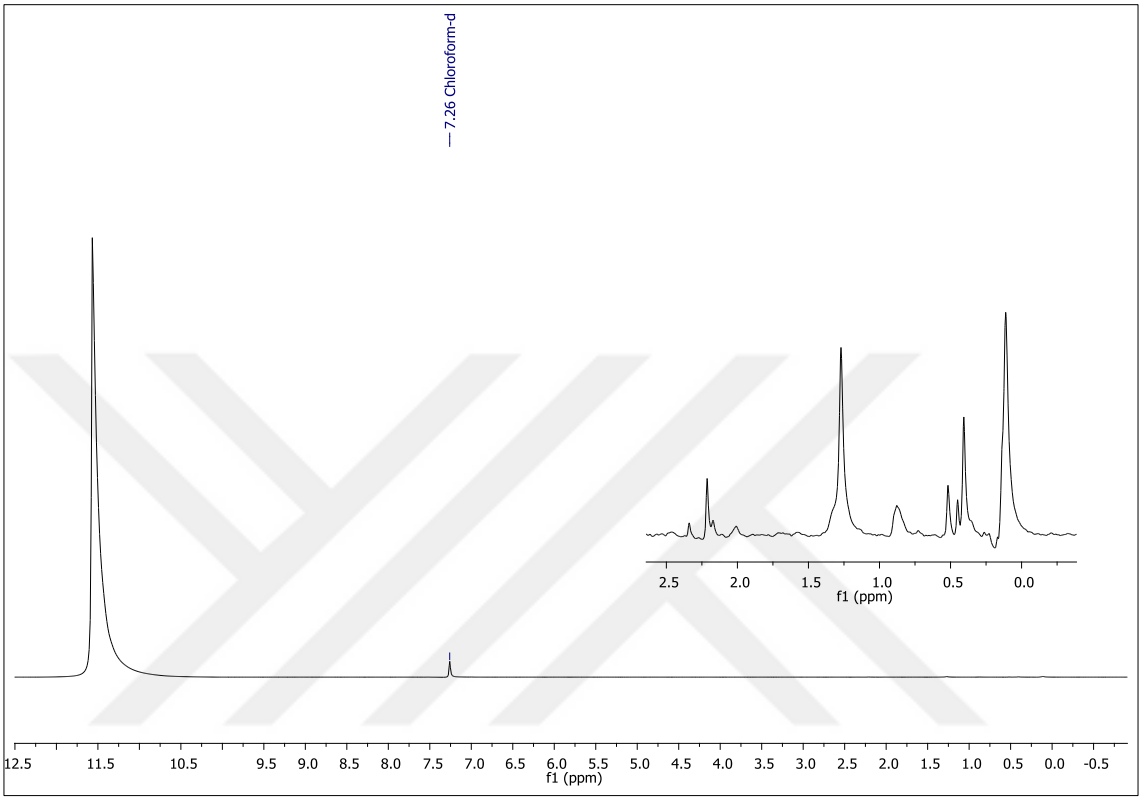



Figure A.1. $^{1}H$ NMR of the used TFA.

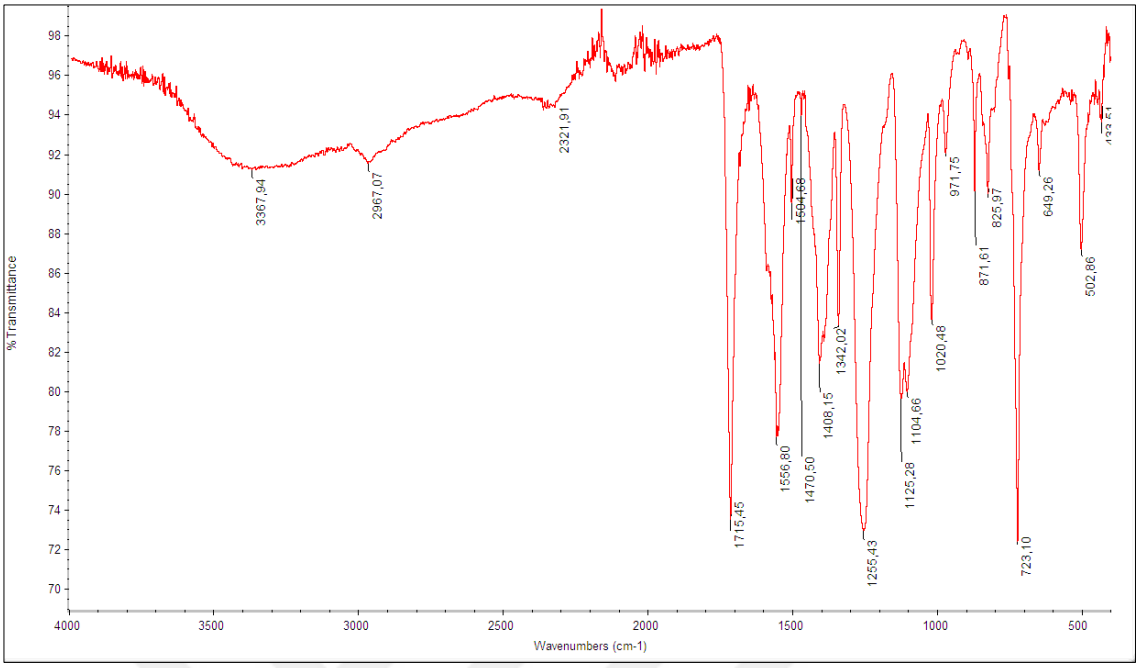



Figure A.2. FTIR Spectrum of PET-1.

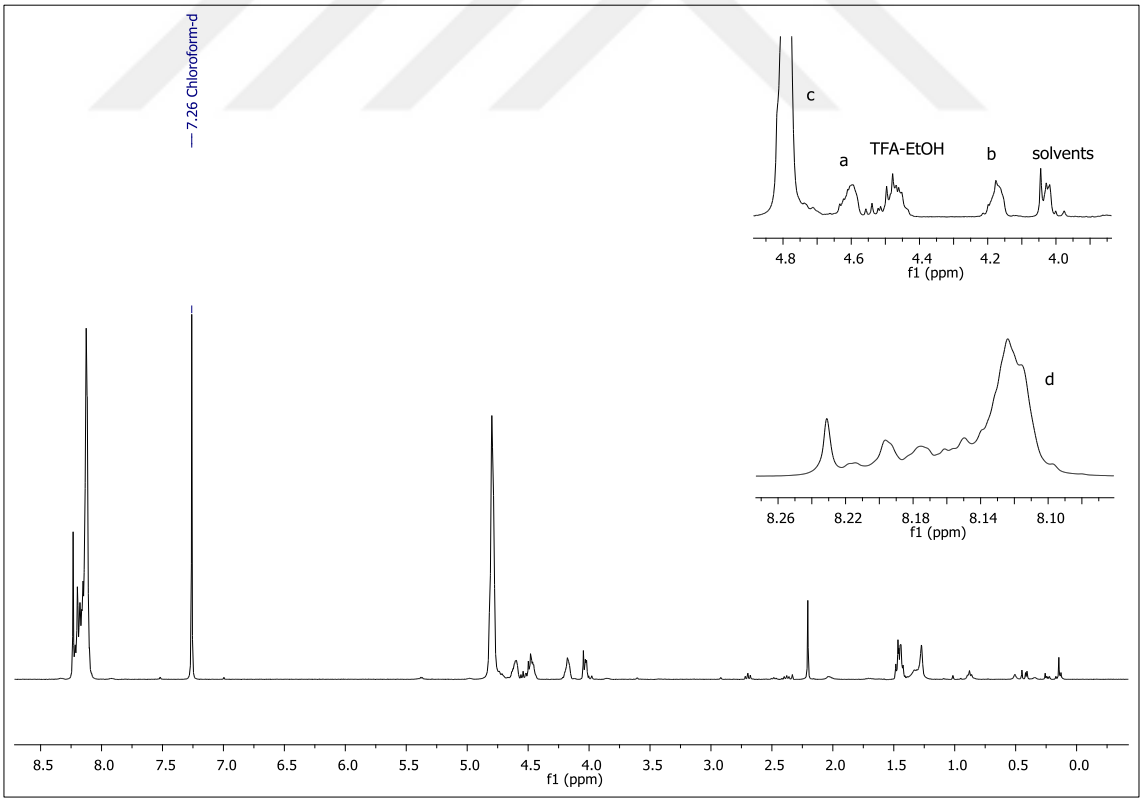



Figure A.3. $^{1}$H NMR of PET-1.

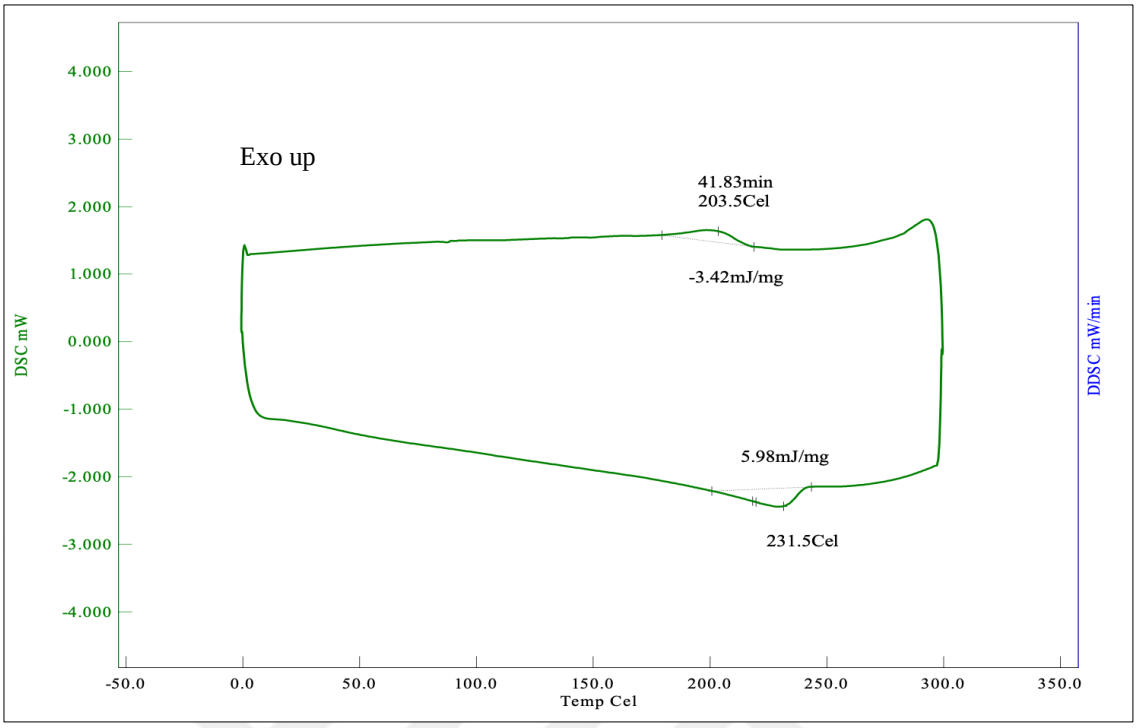



Figure A.4. DSC Analysis of PET-1.

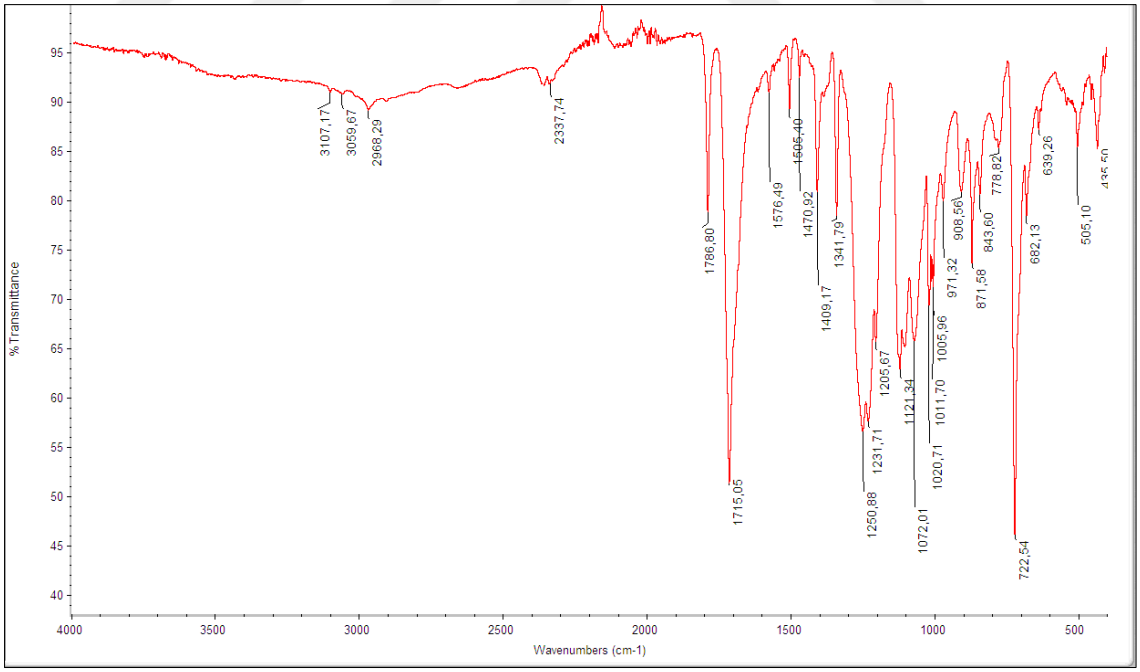



Figure A.5. FTIR Spectrum of PET-2.

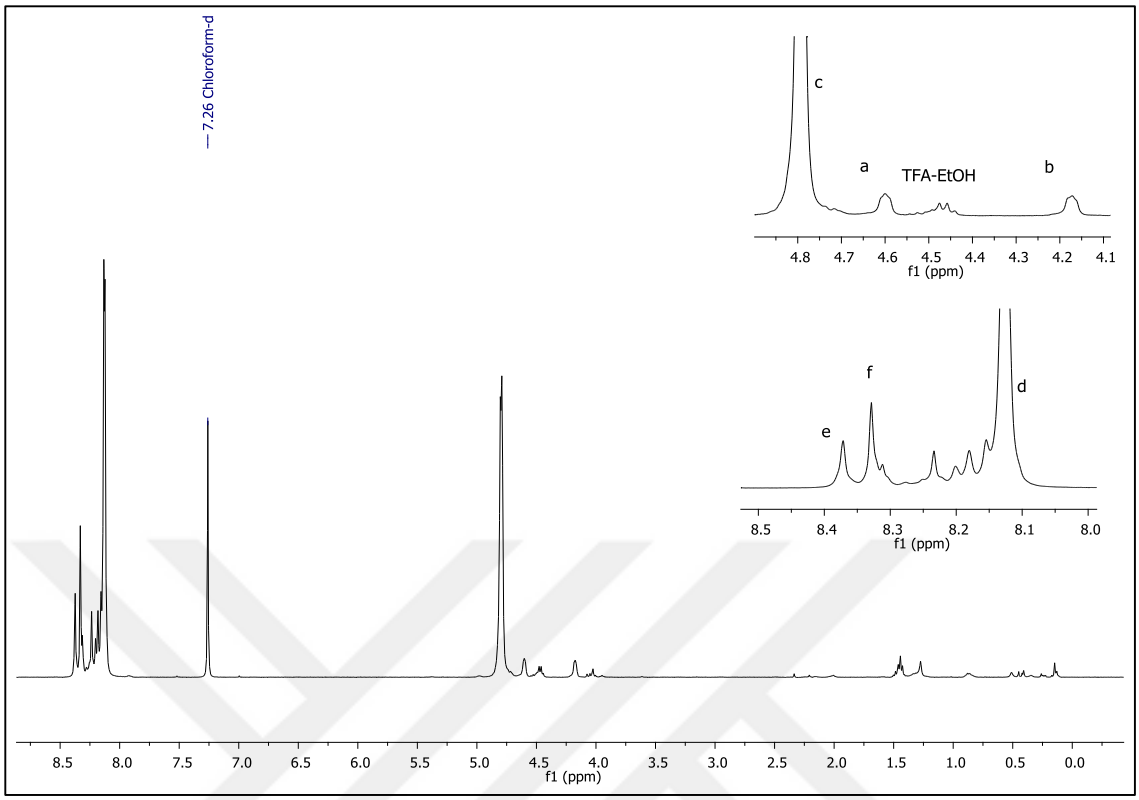



Figure A.6. $^{1}$H NMR of PET-2.

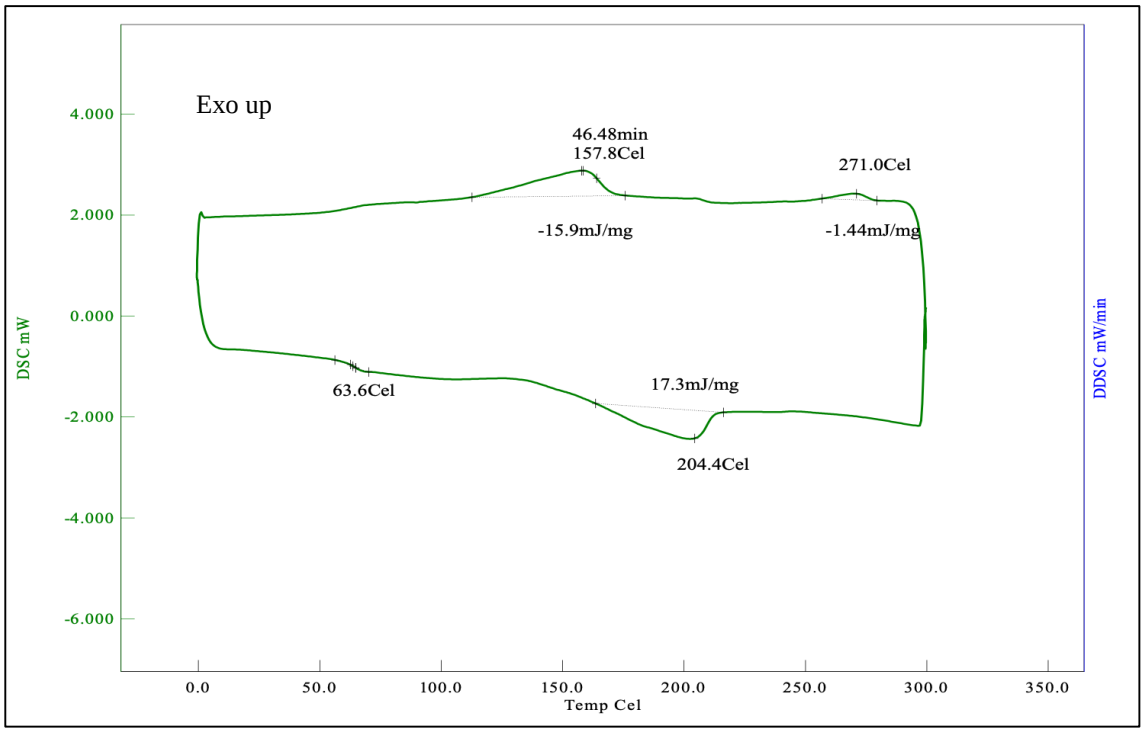



Figure A.7. DSC Analysis of PET-2.

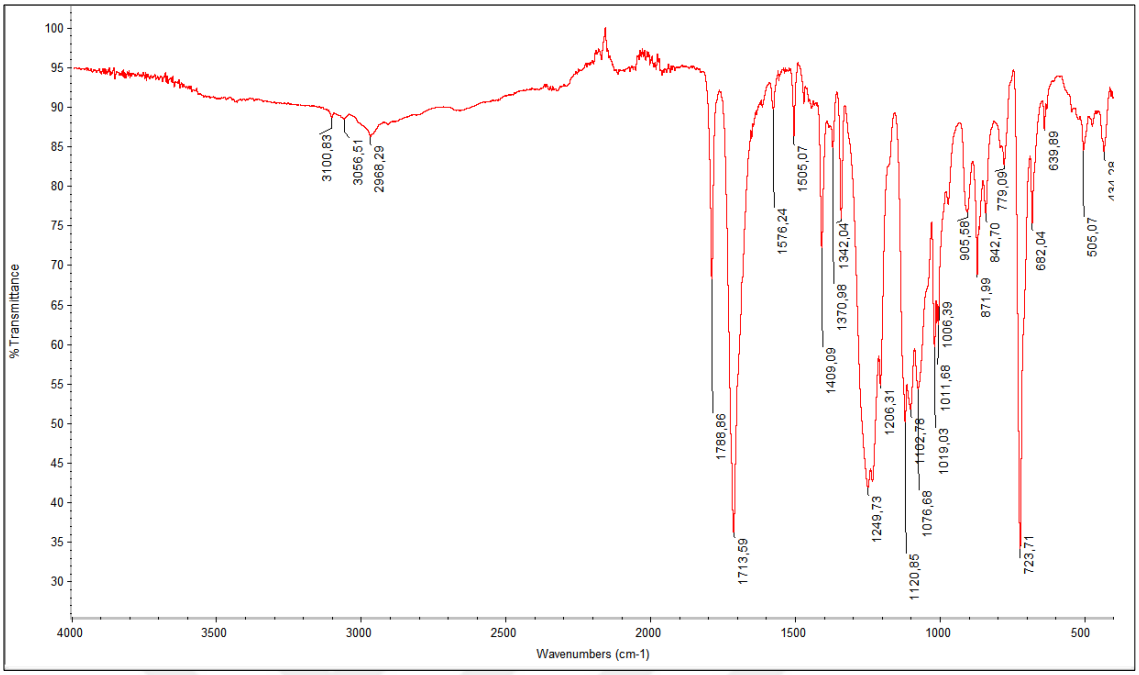



Figure A.8. FTIR Spectrum of PET-3.

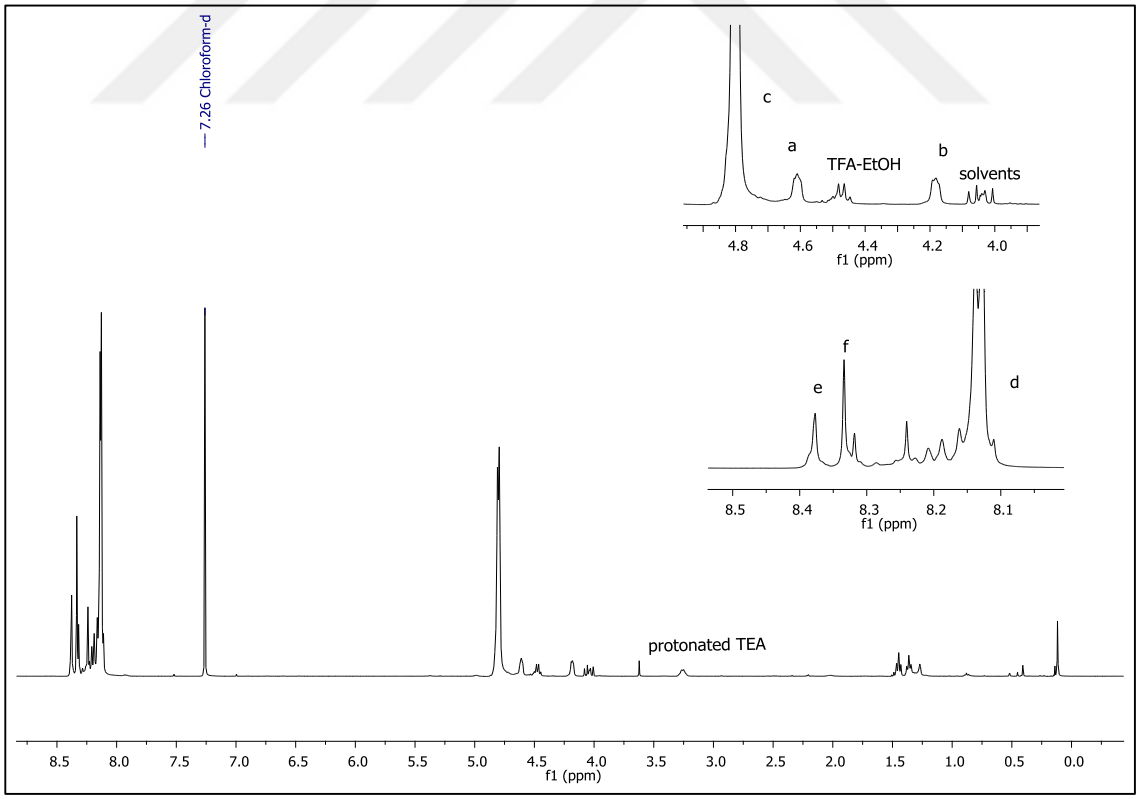



Figure A.9. $^{1}$H NMR of PET-3.

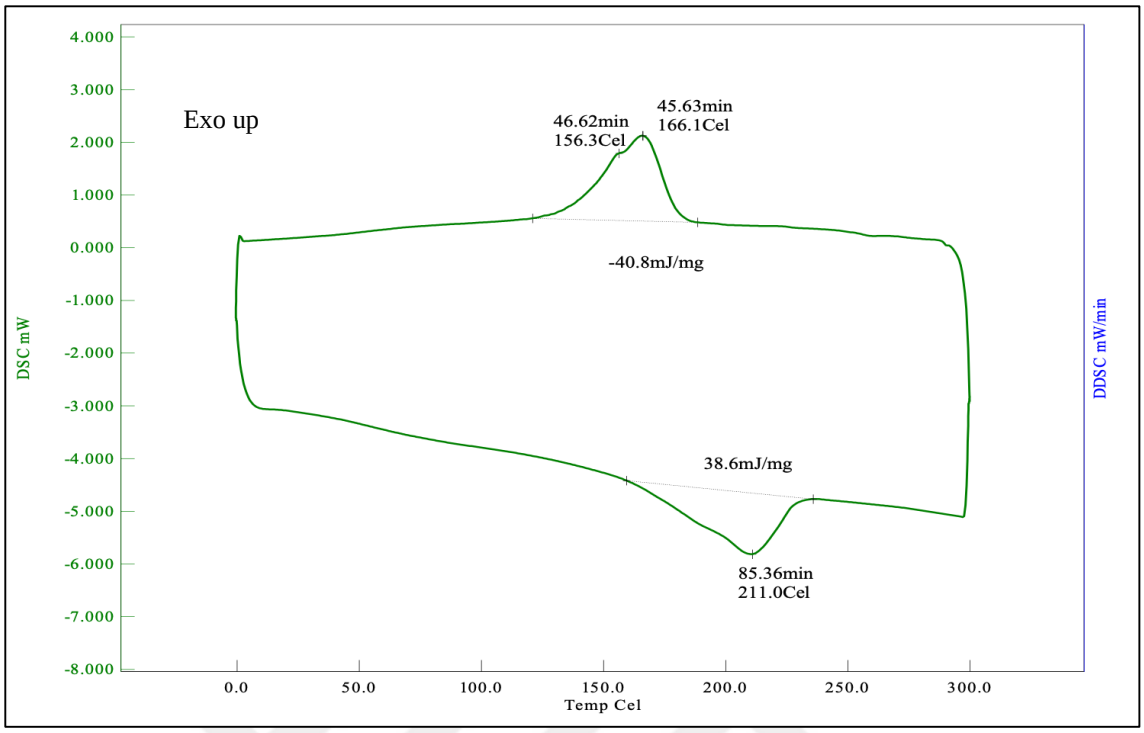



Figure A.10. DSC Analysis of PET-3.

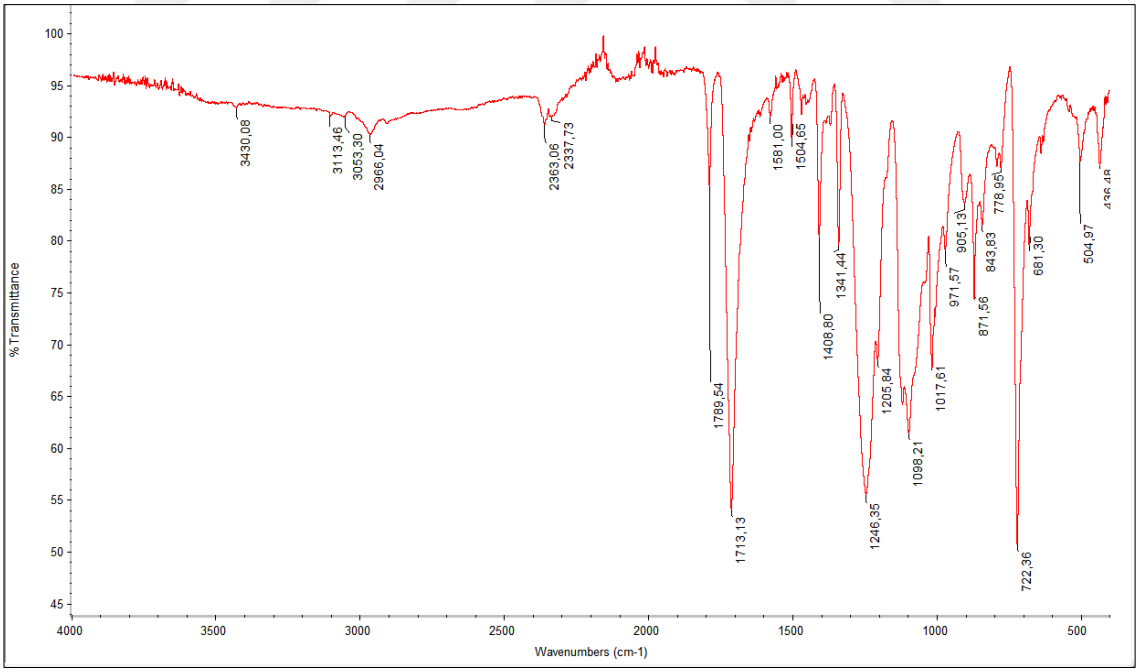



Figure A.11. FTIR Spectrum of PET-4.

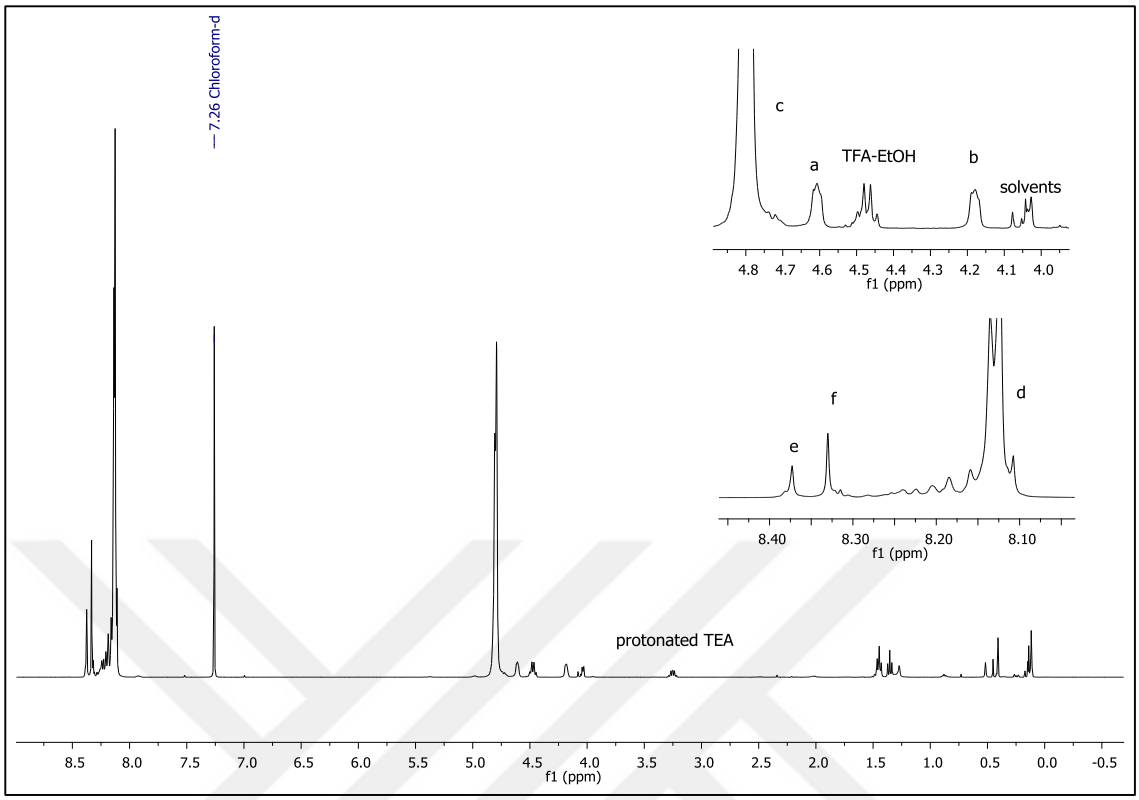



Figure A.12. $^{1}$H NMR of PET-4.

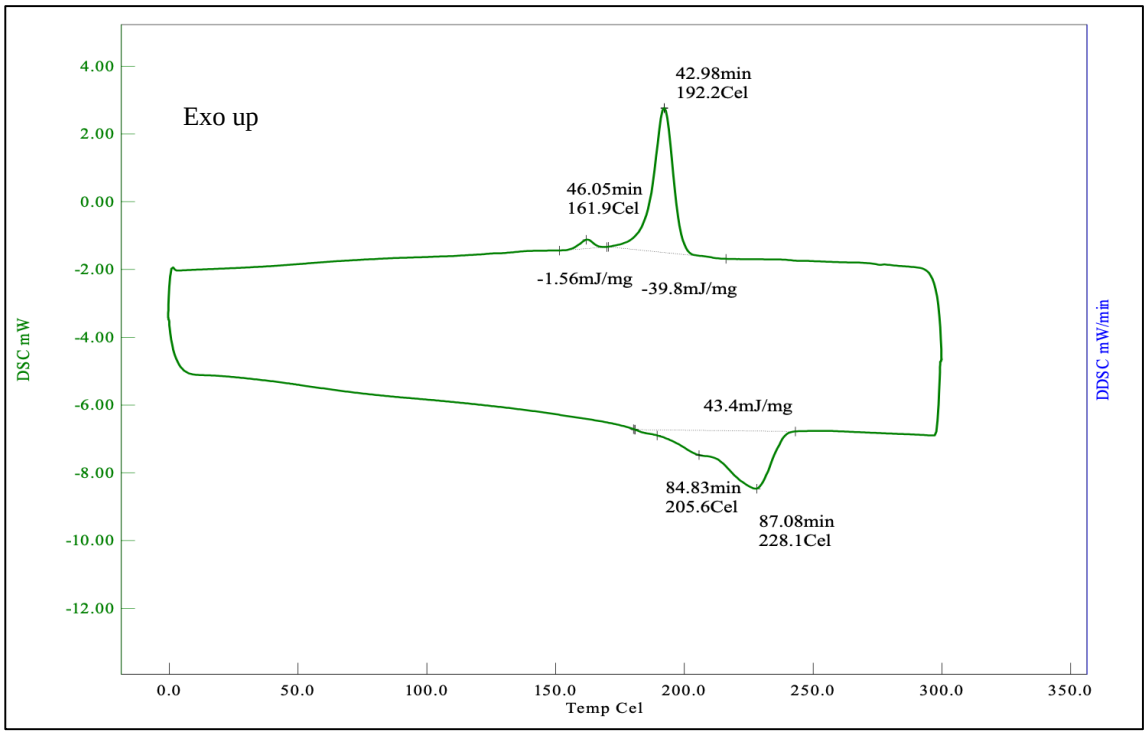



Figure A.13. DSC Analysis of PET-4.

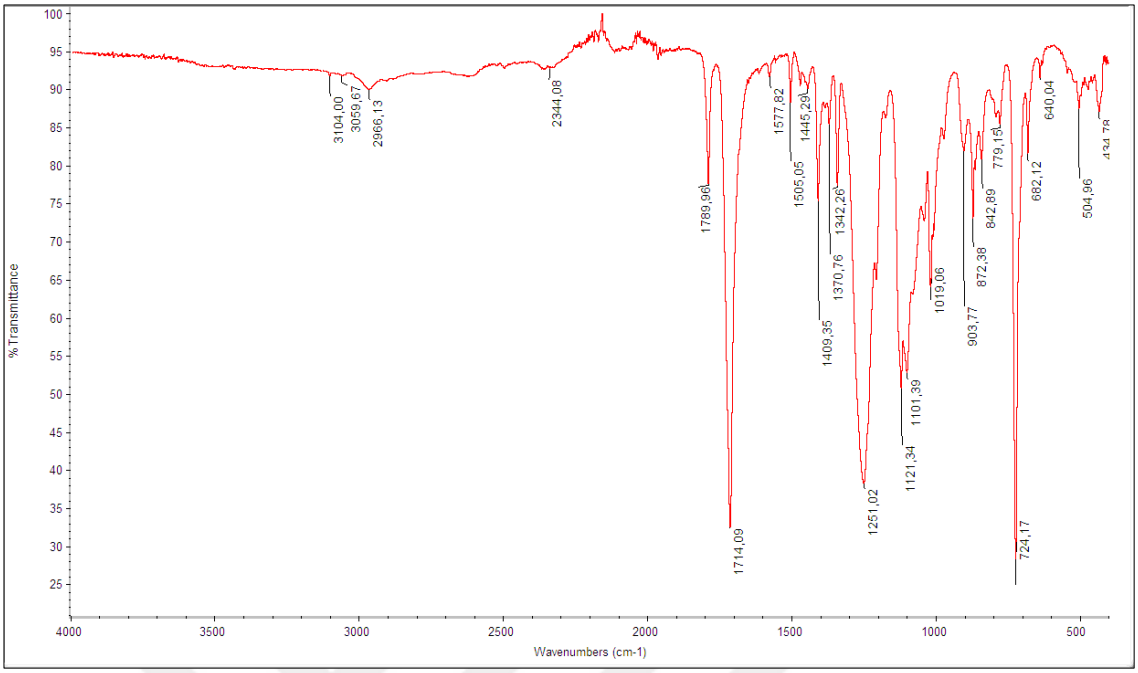



Figure A.14. FTIR Spectrum of PET-5.

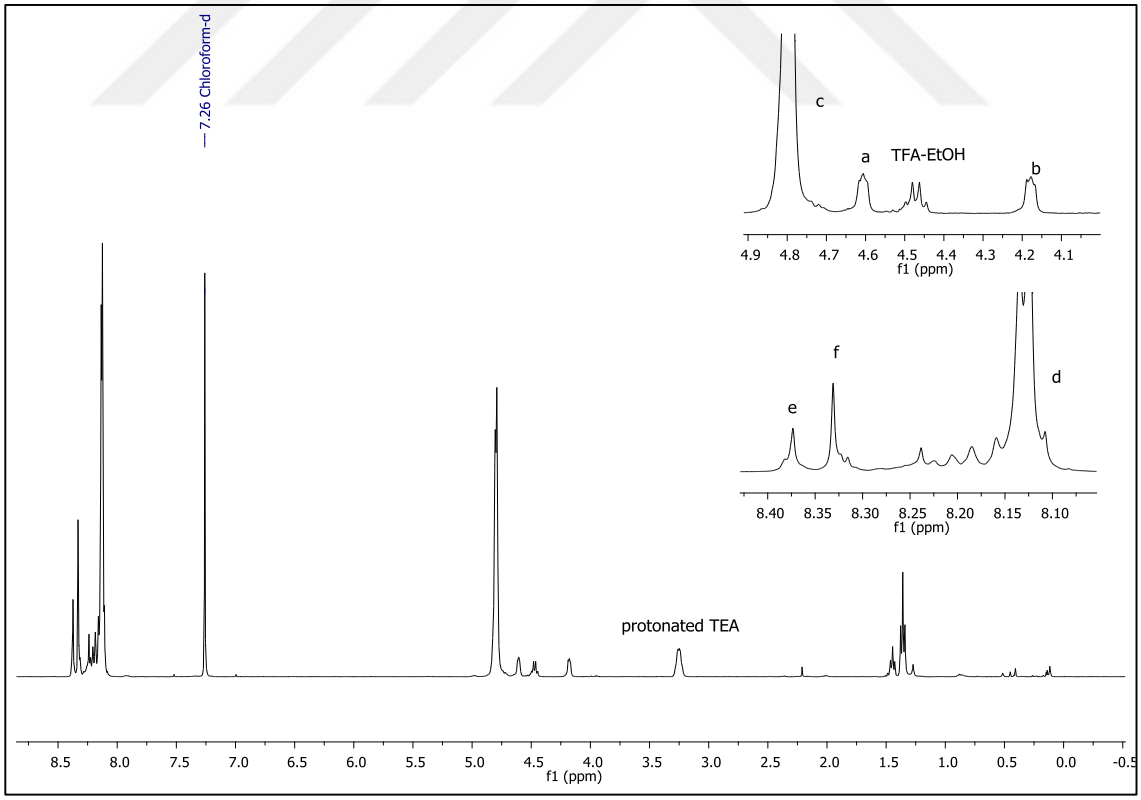



Figure A.15. $^{1}$H NMR of PET-5.

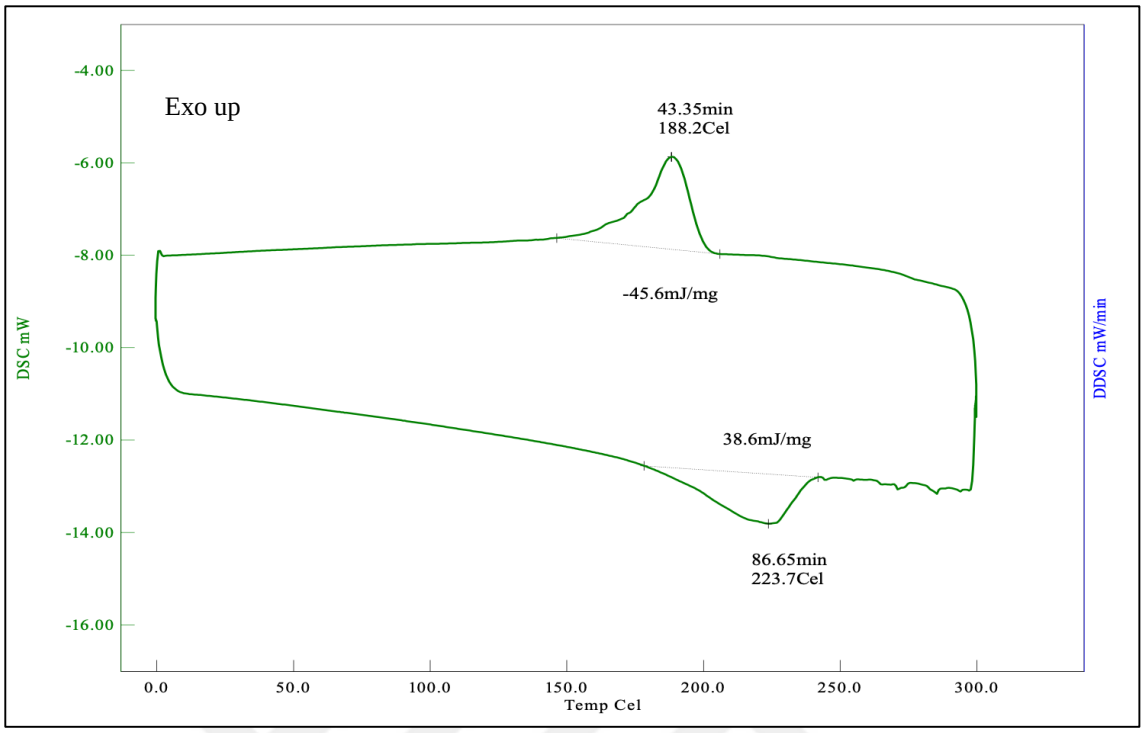



Figure A.16. DSC Analysis of PET-5.

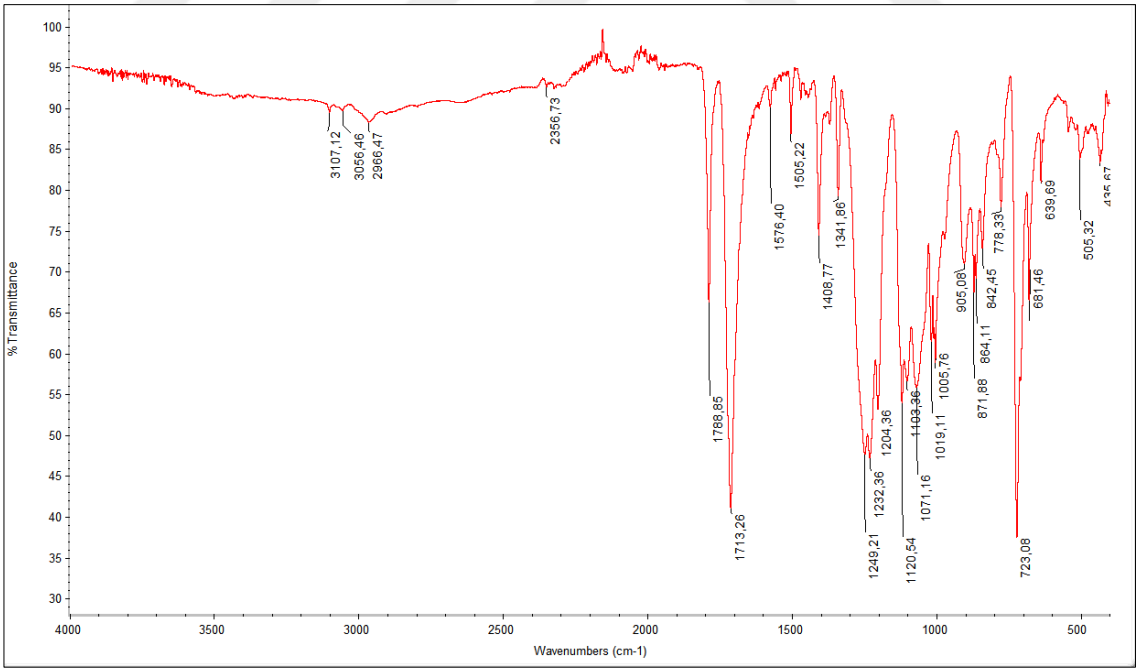



Figure A.17. FTIR Spectrum of PET-6.

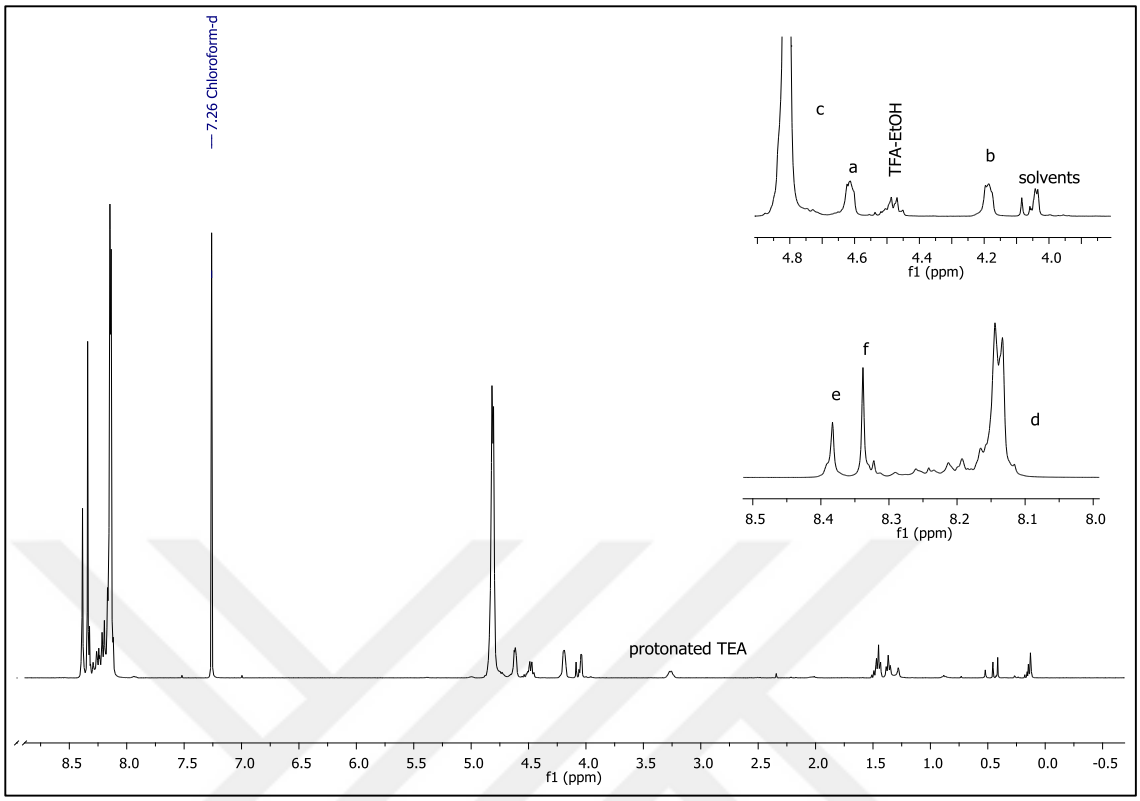



Figure A.18. $^{1}$H NMR of PET-6.

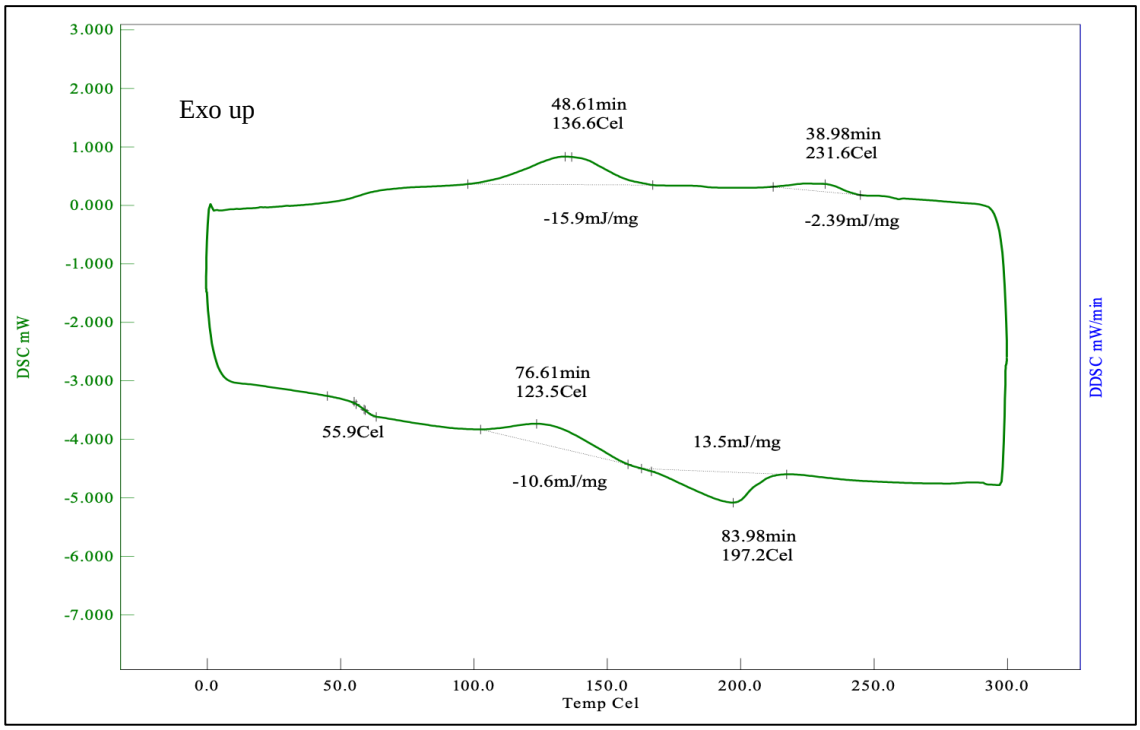



Figure A.19. DSC Analysis of PET-6.

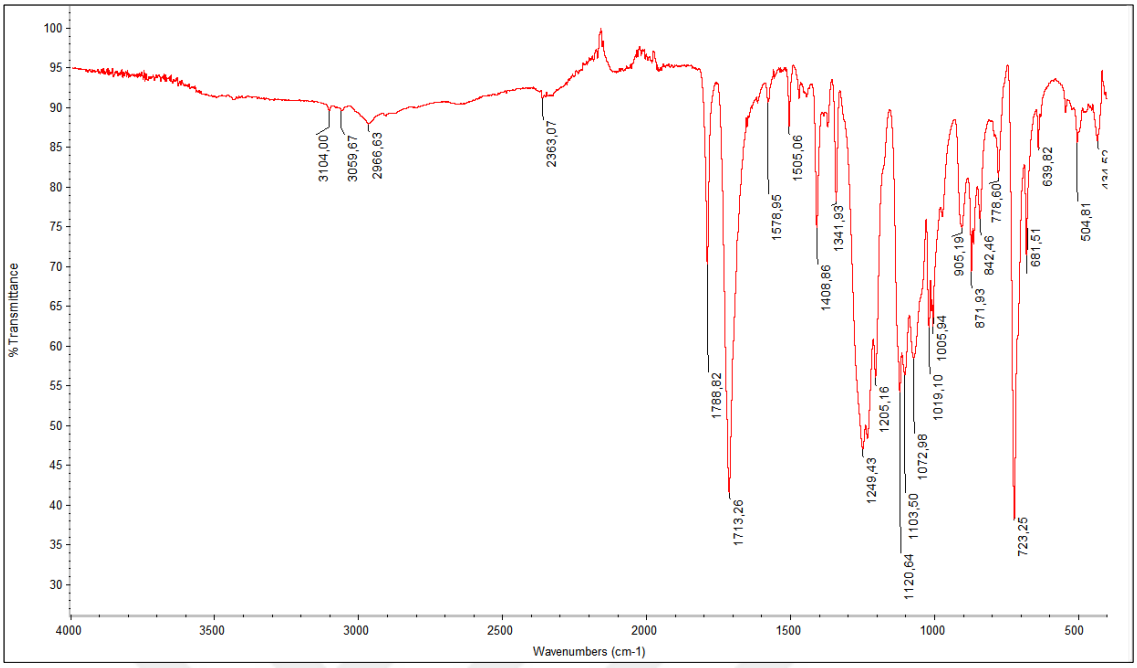



Figure A.20. FTIR Spectrum of PET-7

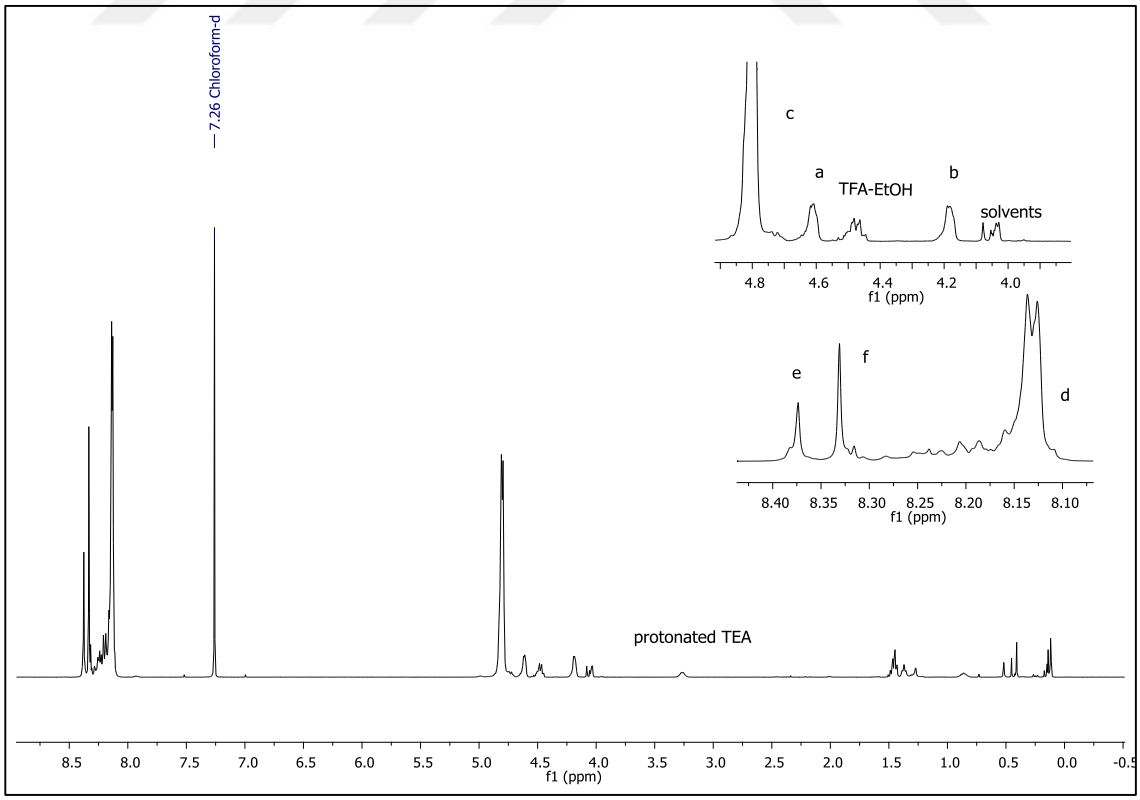



Figure A.21. $^{1}$H NMR of PET-7.

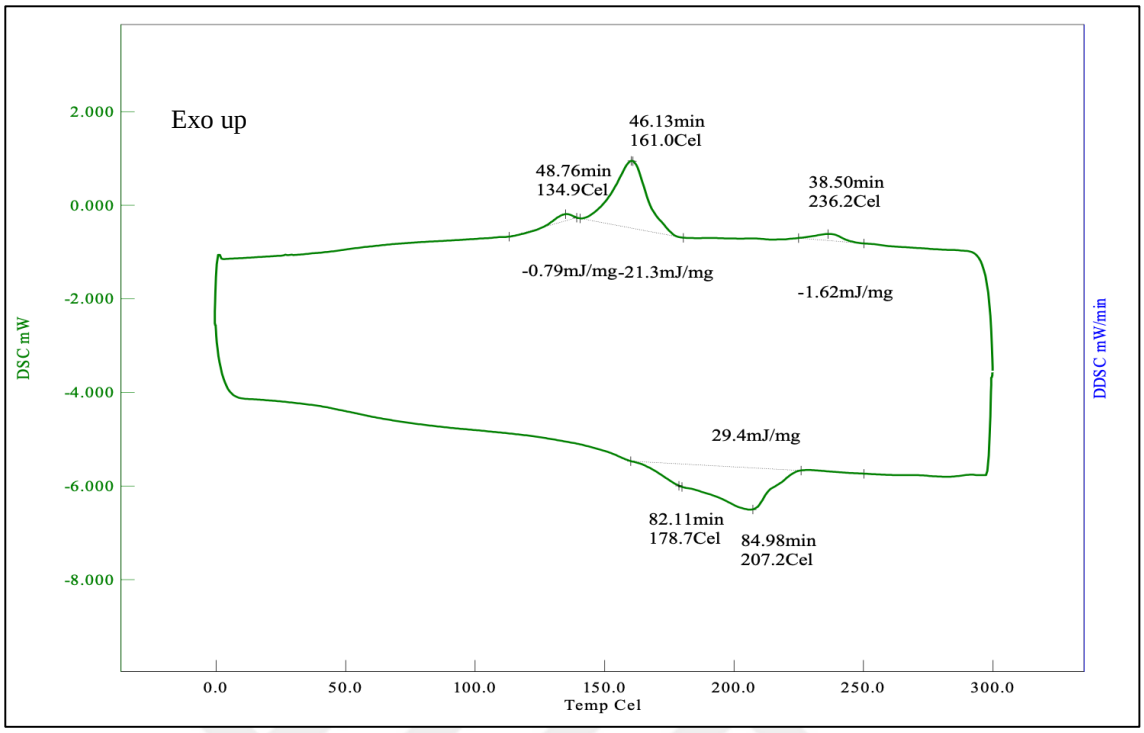



Figure A.22. DSC Analysis of PET-7.

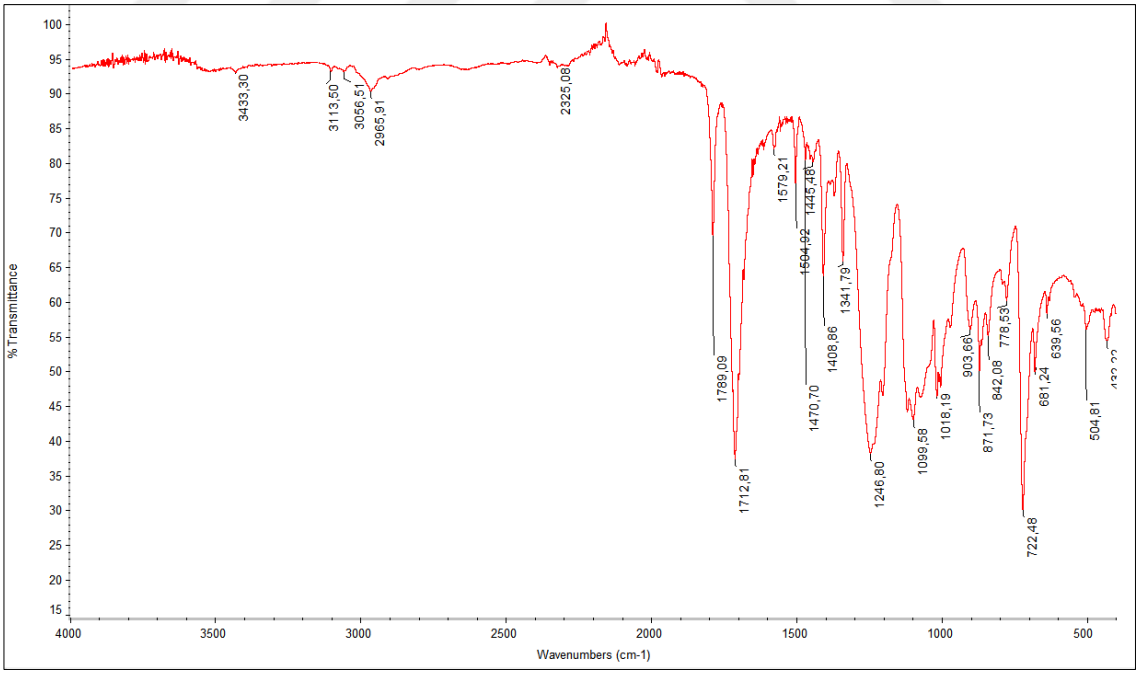



Figure A.23. FTIR Spectrum of PET-8.

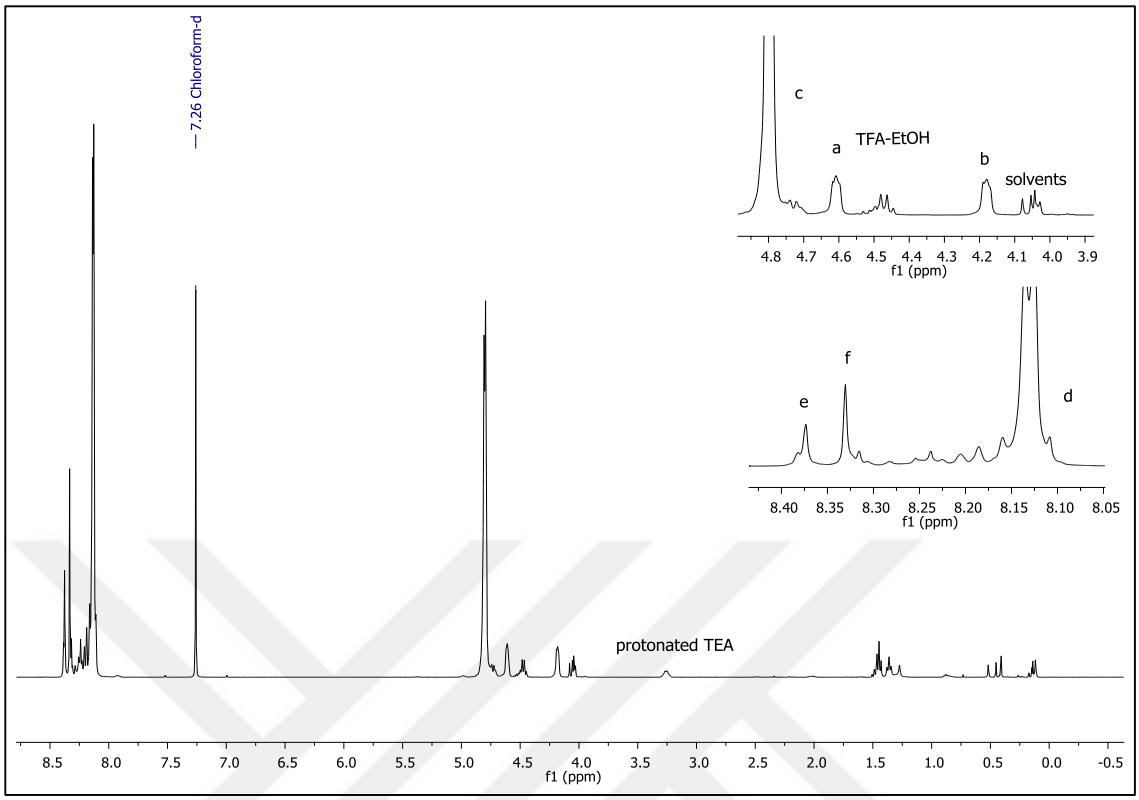



Figure A.24. $^{1}$H NMR of PET-8.

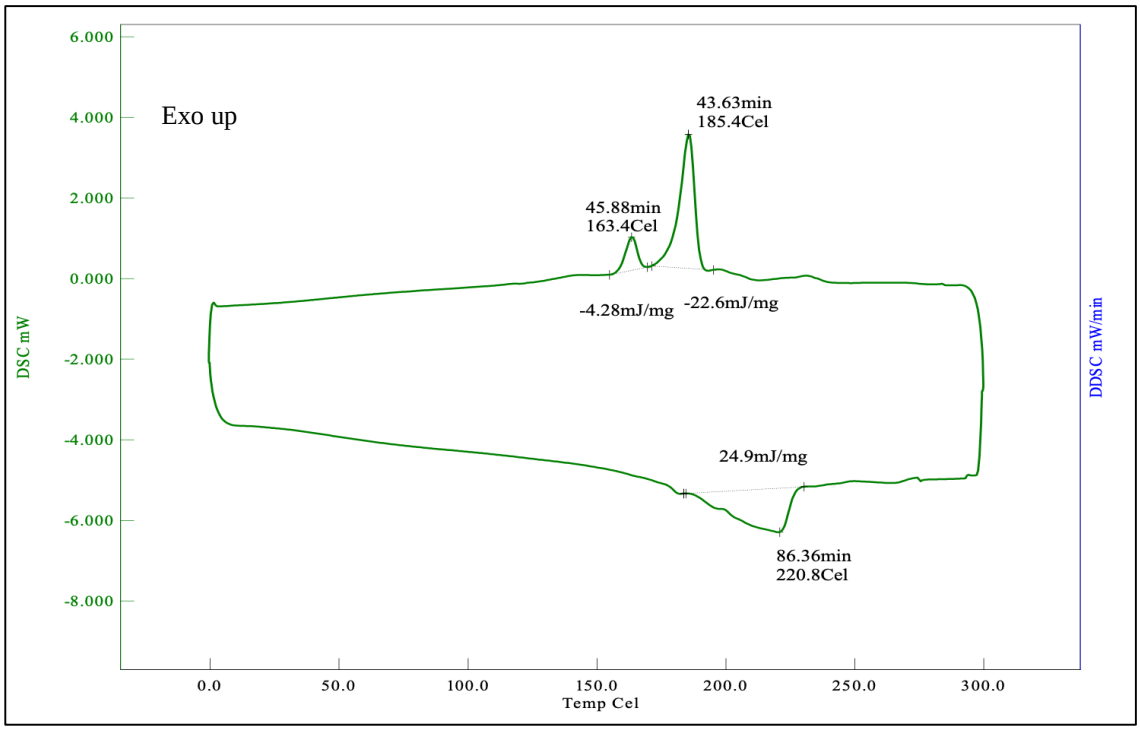



Figure A.25. DSC Analysis of PET-8.

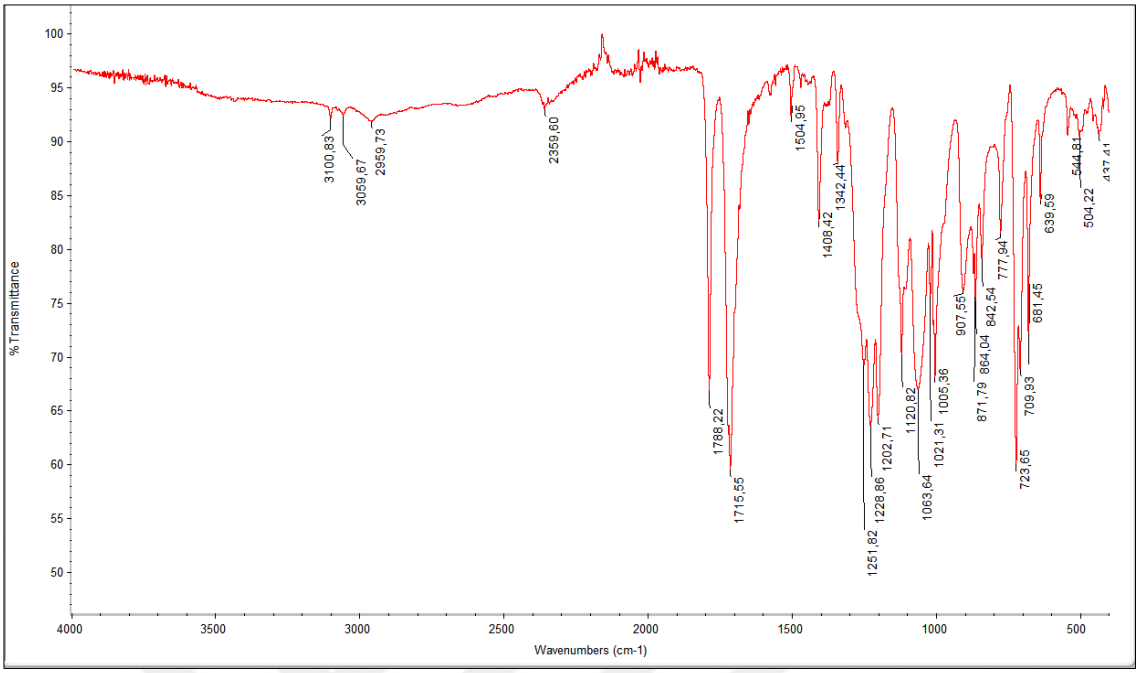



Figure A.26. FTIR Spectrum of PET-9.

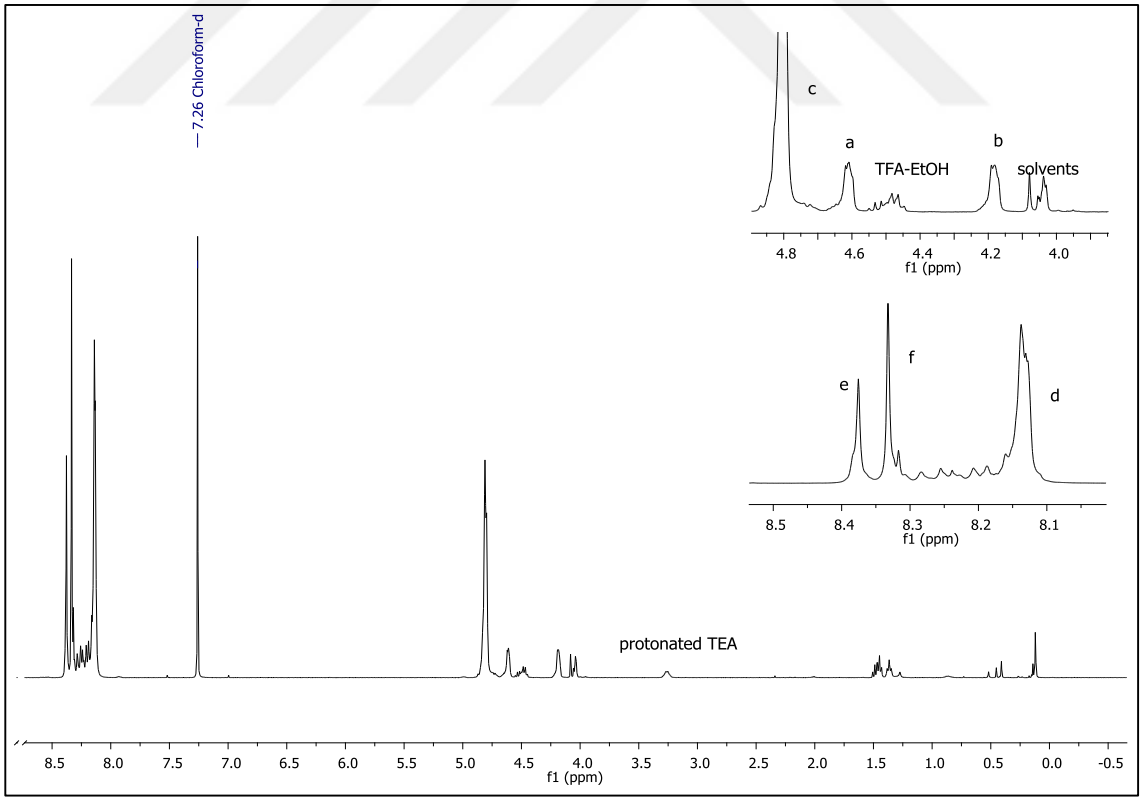



Figure A.27. $^{1}$H NMR of PET-9.

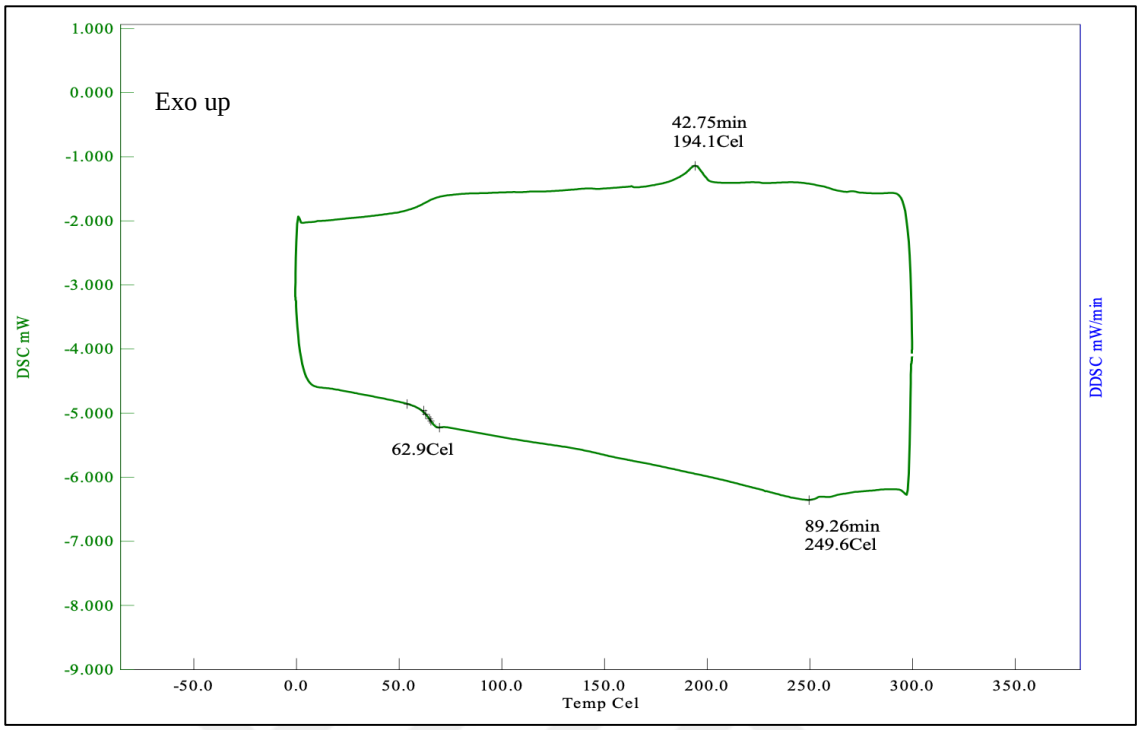



Figure A.28. DSC Analysis of PET-9.

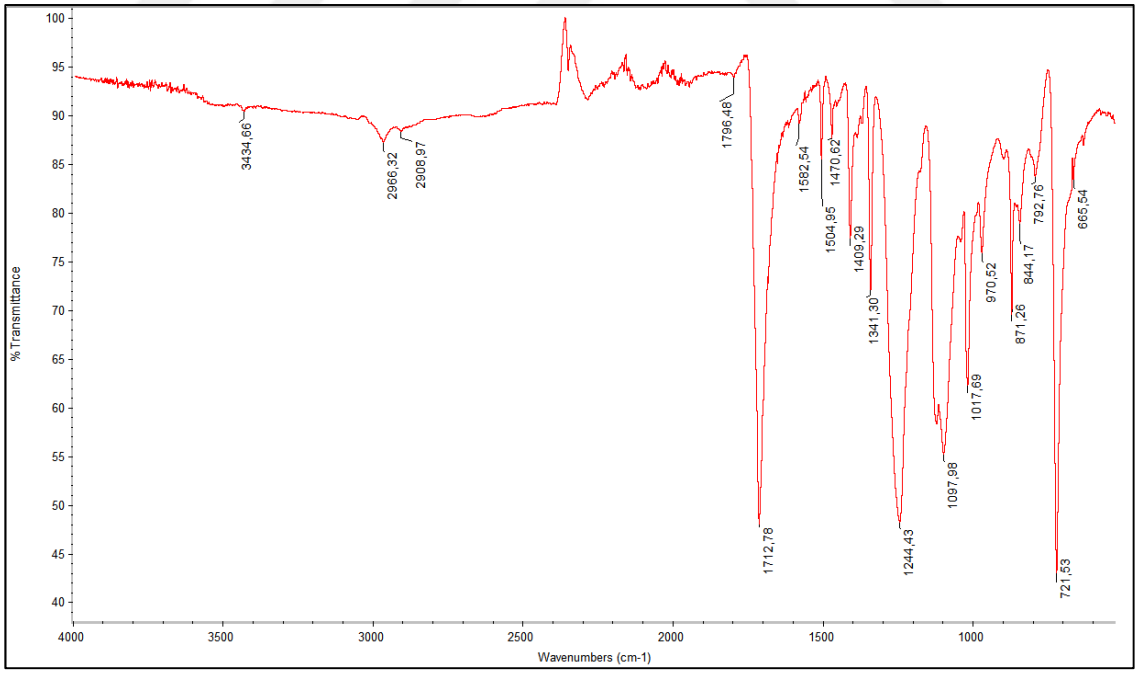



Figure A.29. FTIR Spectrum of PET-10.

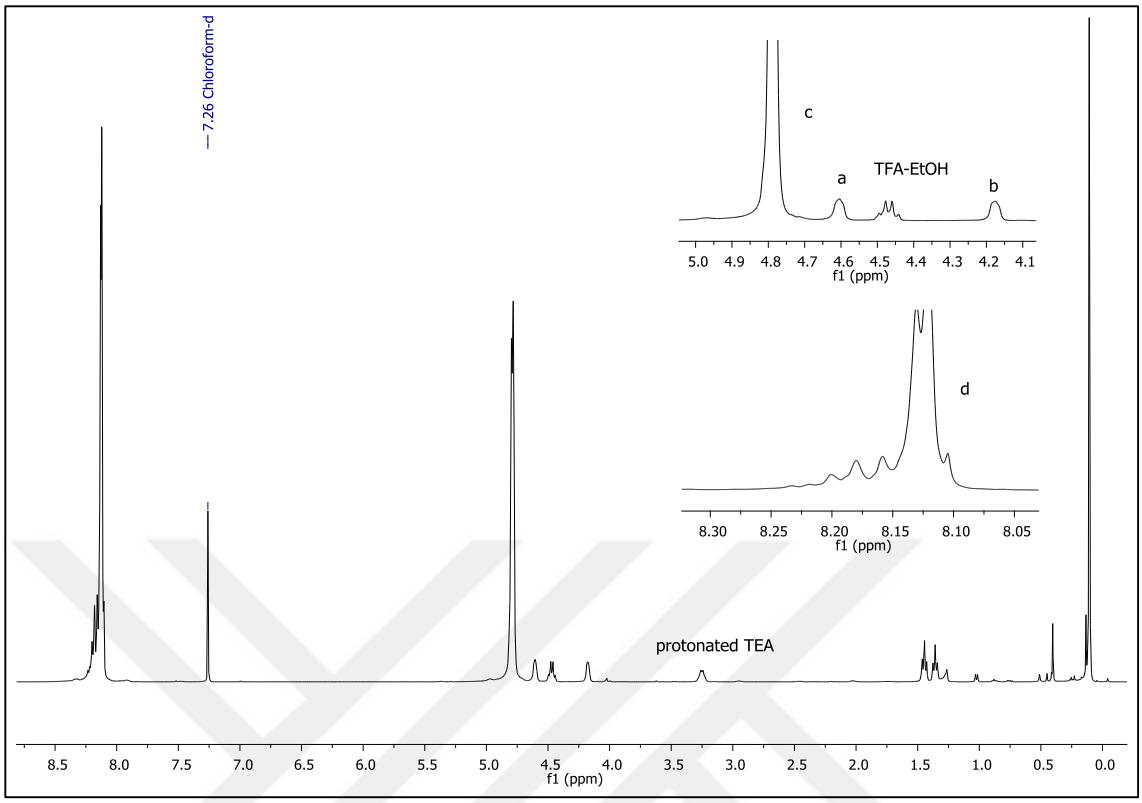



Figure A.30. $^{1}$H NMR of PET-10.

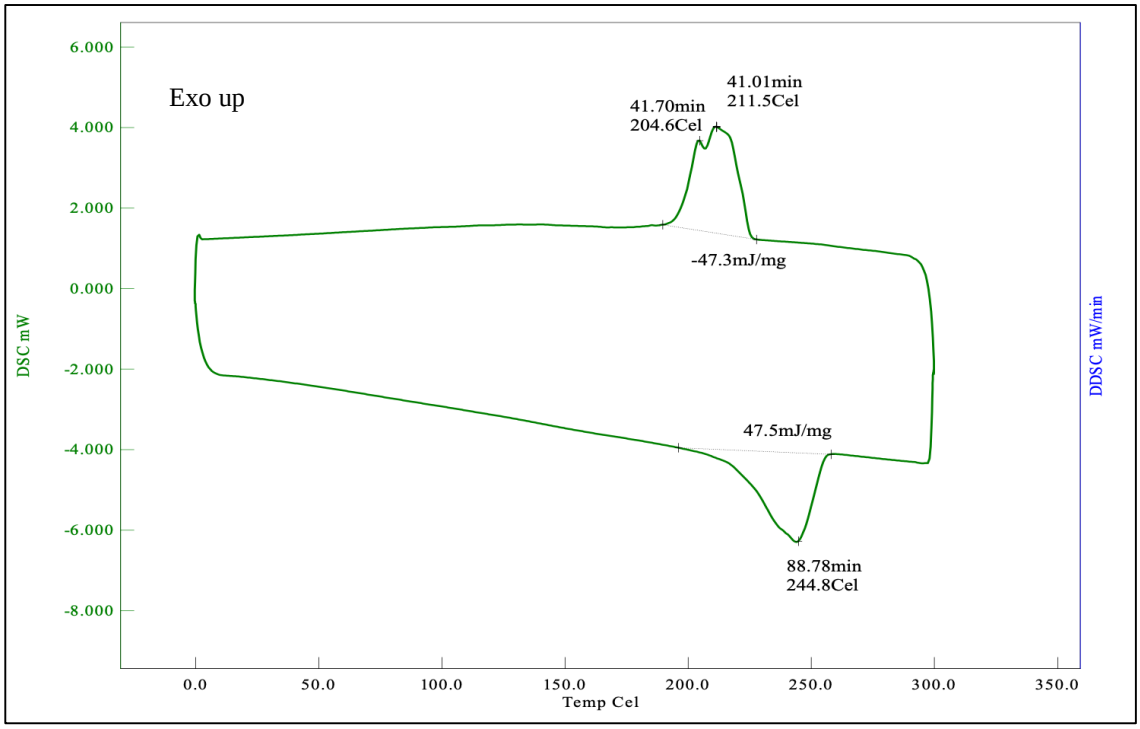



Figure A.31. DSC Analysis of PET-10.

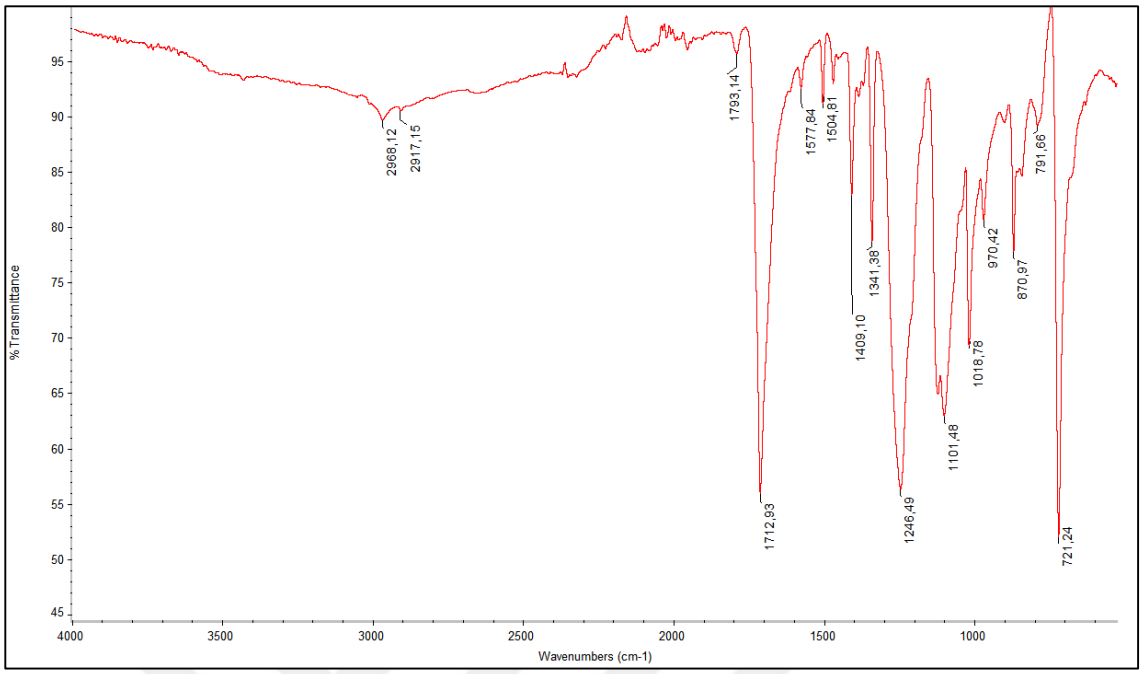



Figure A.32. FTIR Spectrum of PET-11.

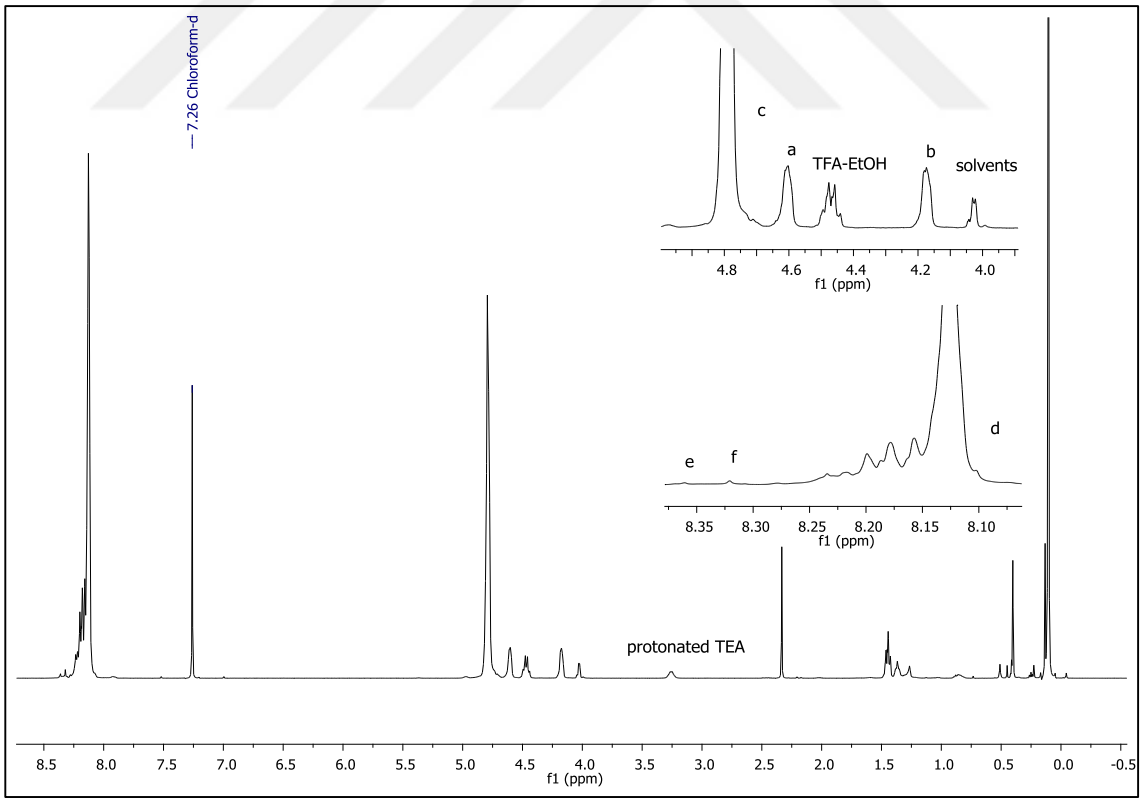



Figure A.33. $^{1}$H NMR of PET-11.

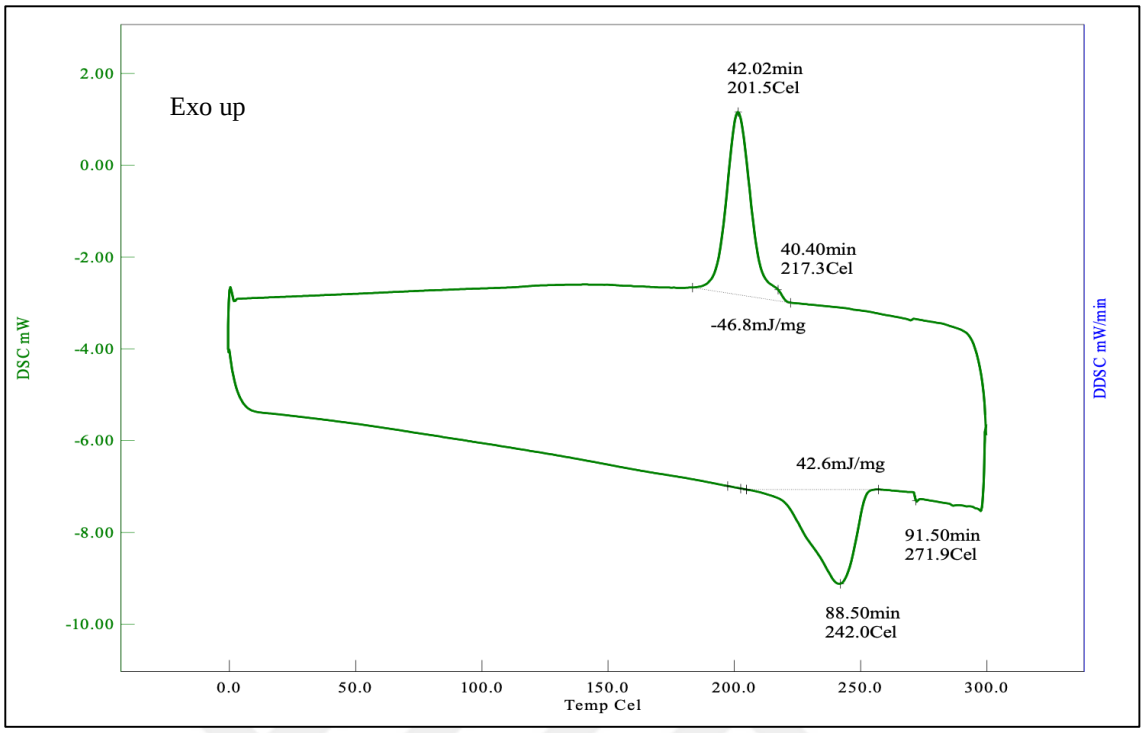



Figure A.34. DSC Analysis of PET-11.

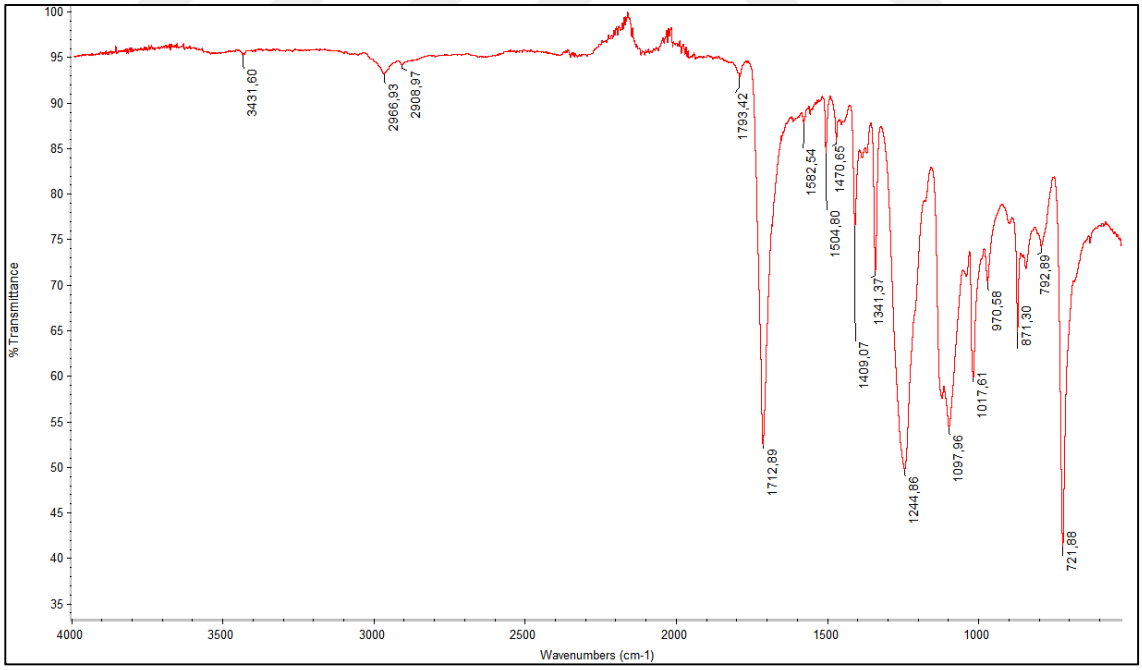



Figure A.35. FTIR Spectrum of PET-12.

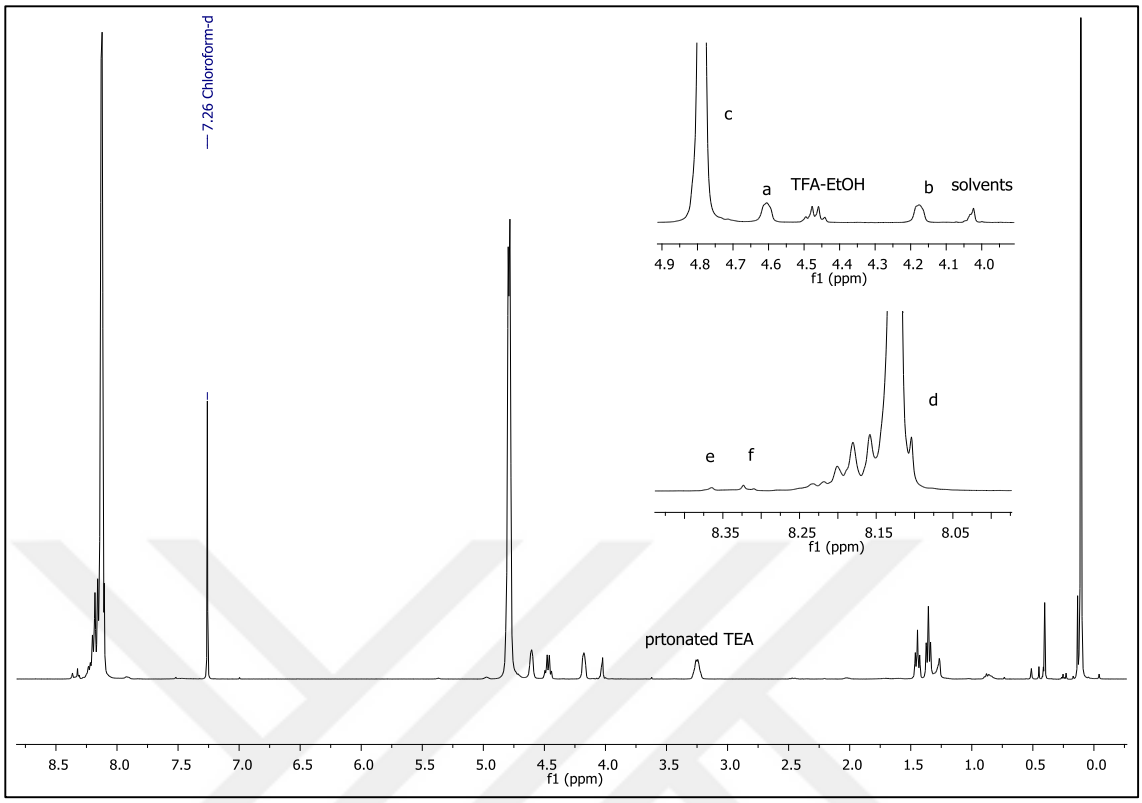



Figure A.36. $^{1}$H NMR of PET-12.

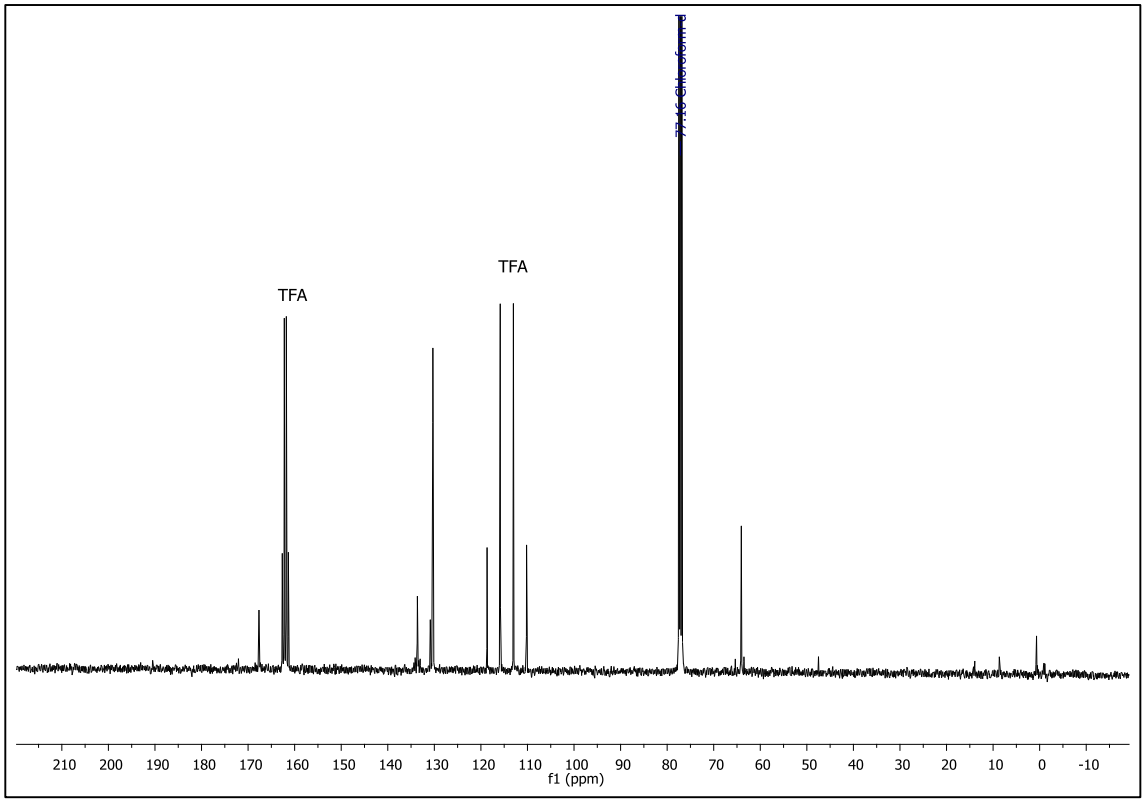



Figure A.37. $^{13}$C NMR of PET-12.

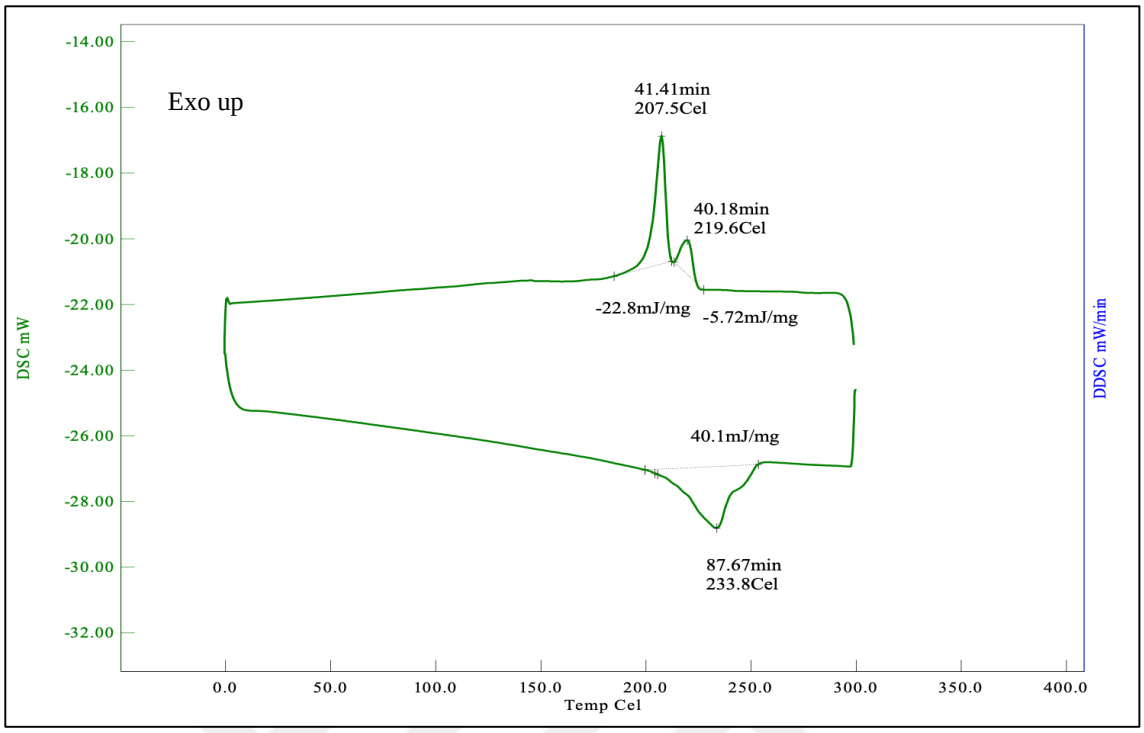



Figure A.38. DSC Analysis of PET-12.

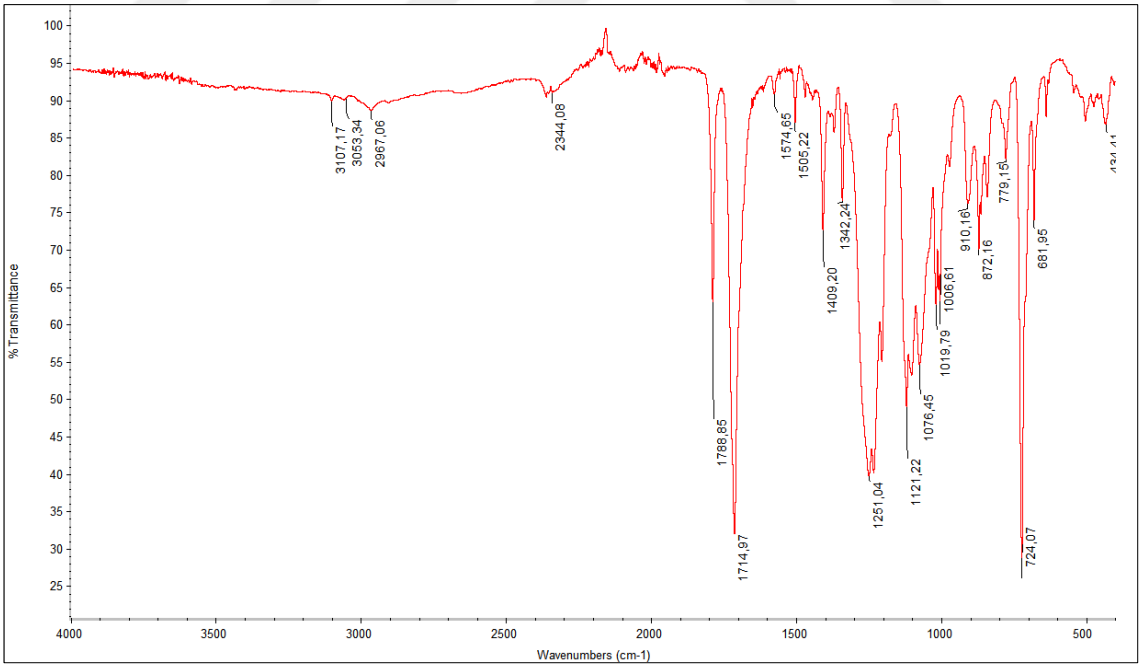



Figure A.39. FTIR Spectrum of PEA-1.

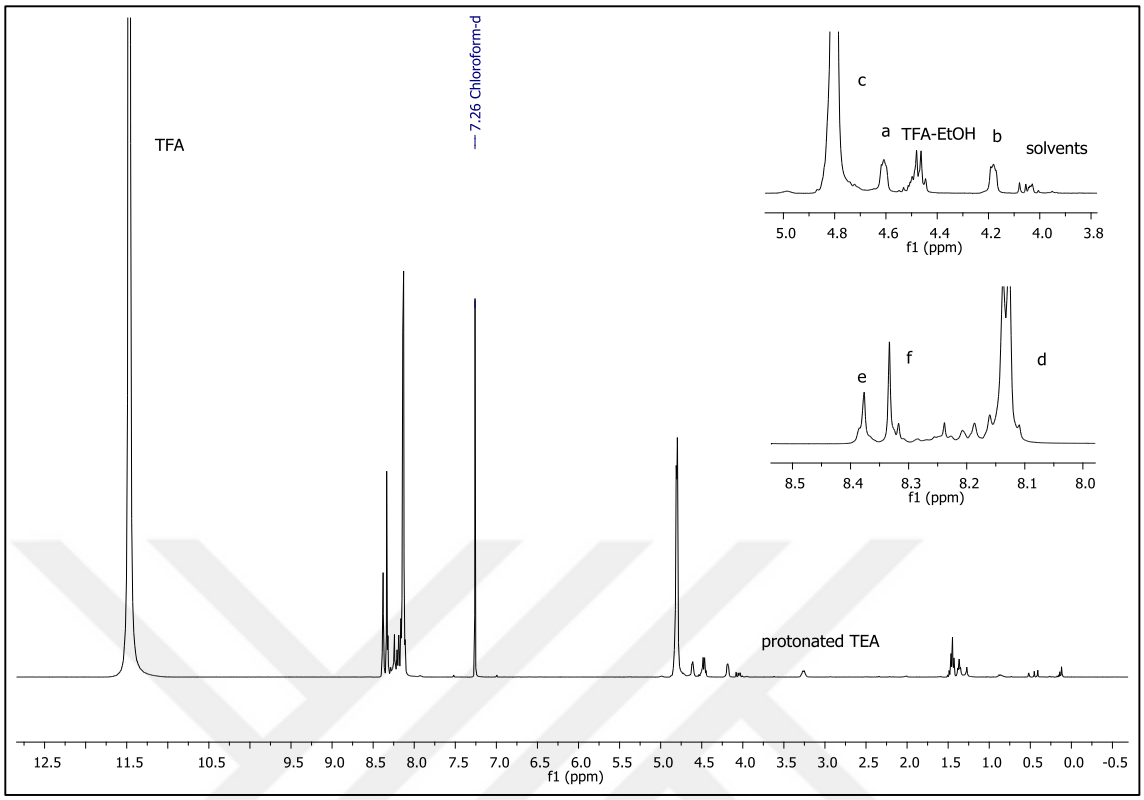



Figure A.40. $^{1}$H NMR of PEA-1.

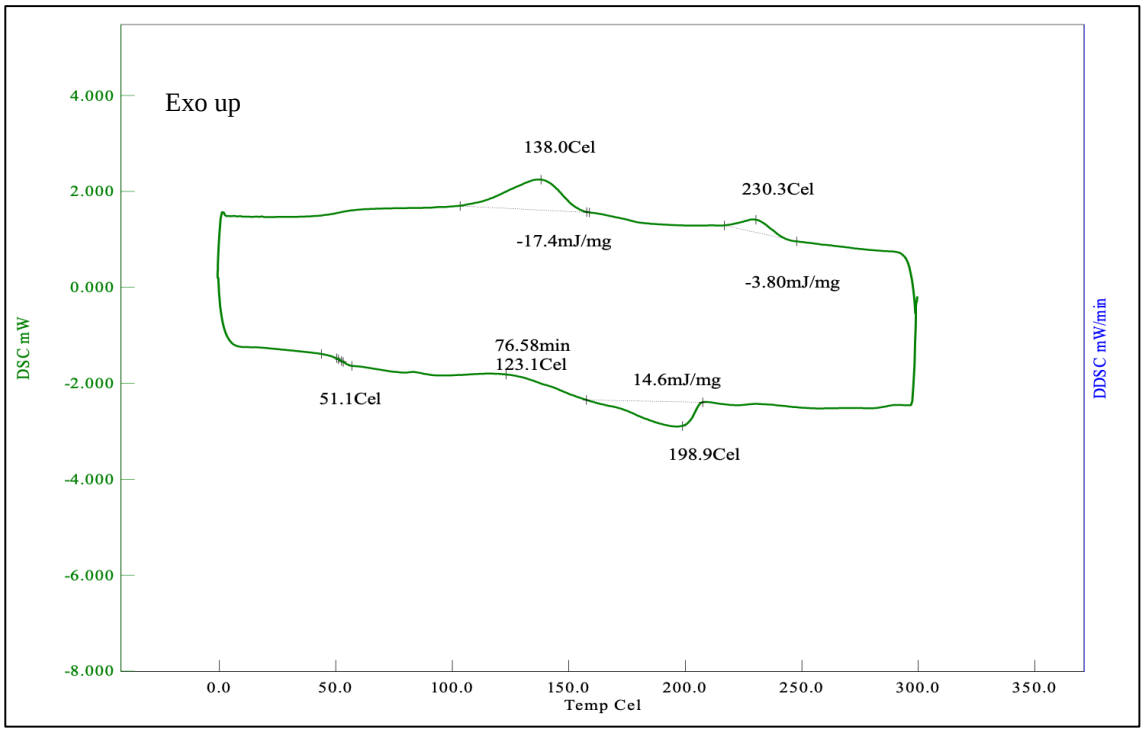



Figure A.41. DSC Analysis of PEA-1.

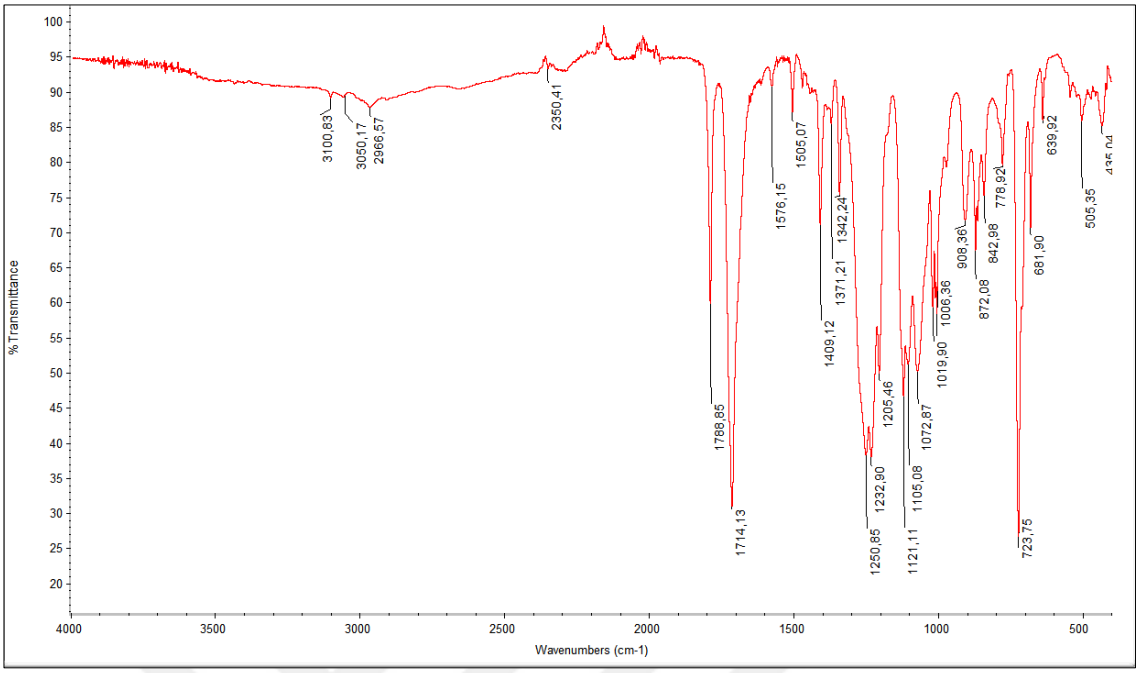



Figure A.42. FTIR Spectrum of PEA-2.

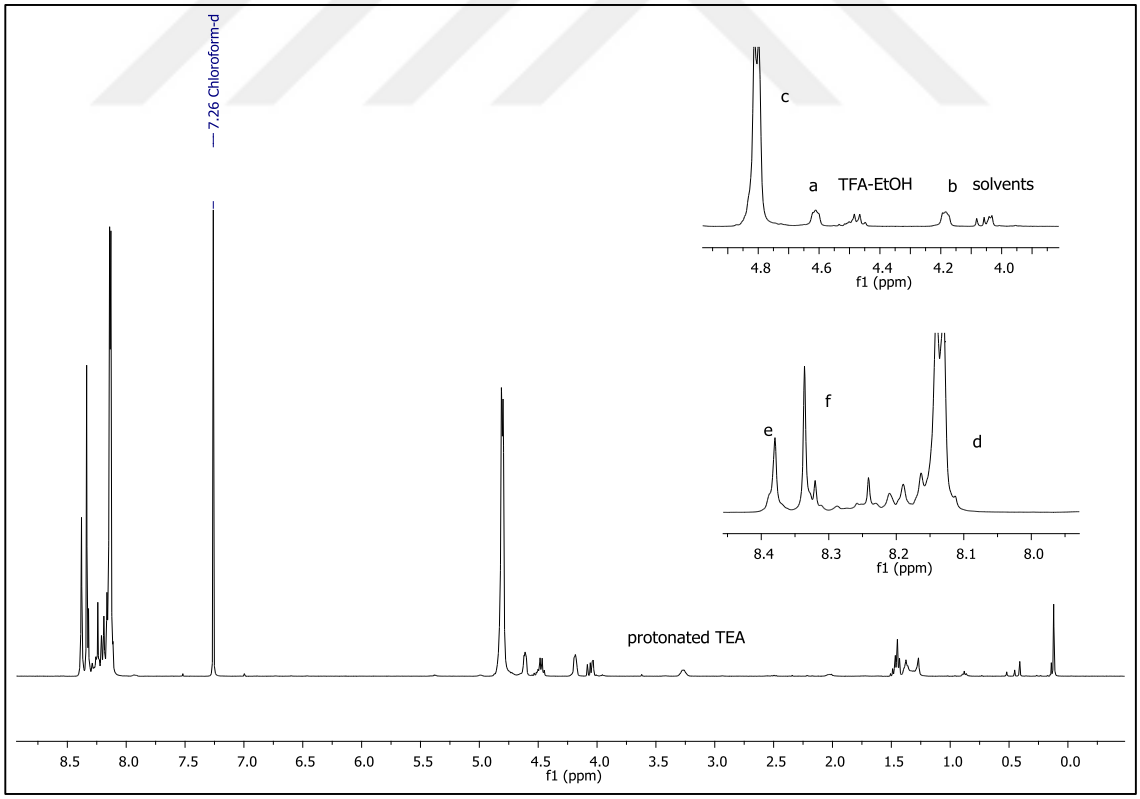



Figure A.43. $^{1}$H NMR of PEA-2.

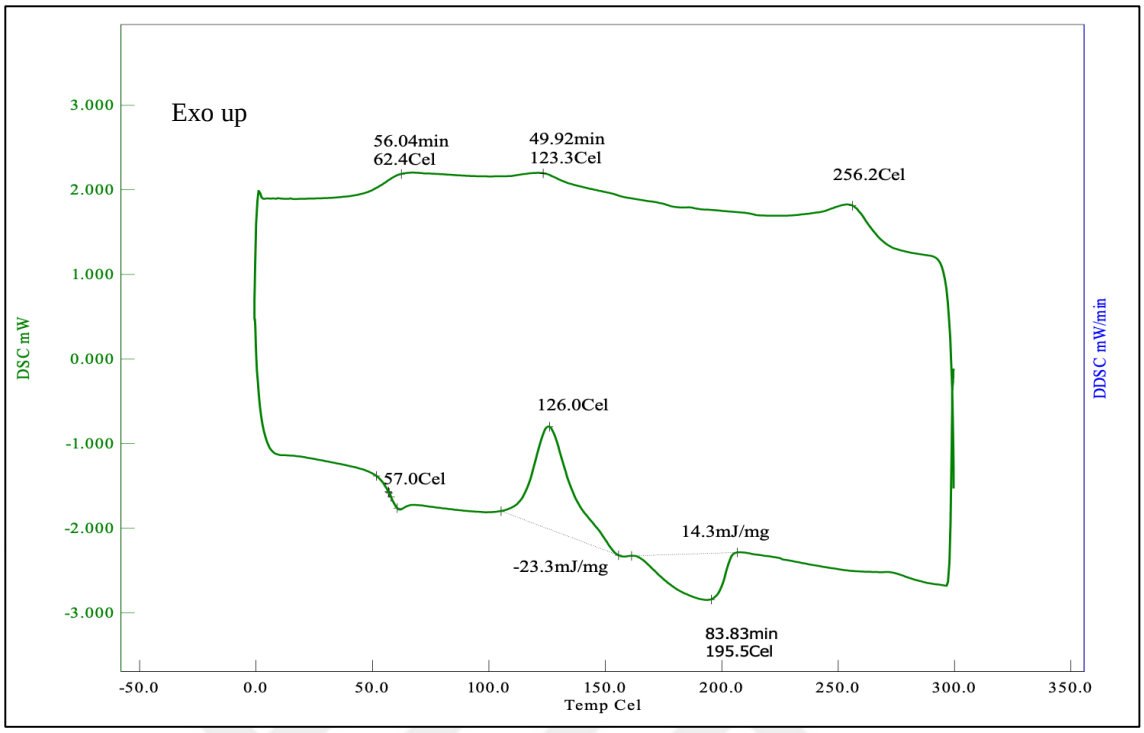



Figure A.44. DSC Analysis of PEA-2.

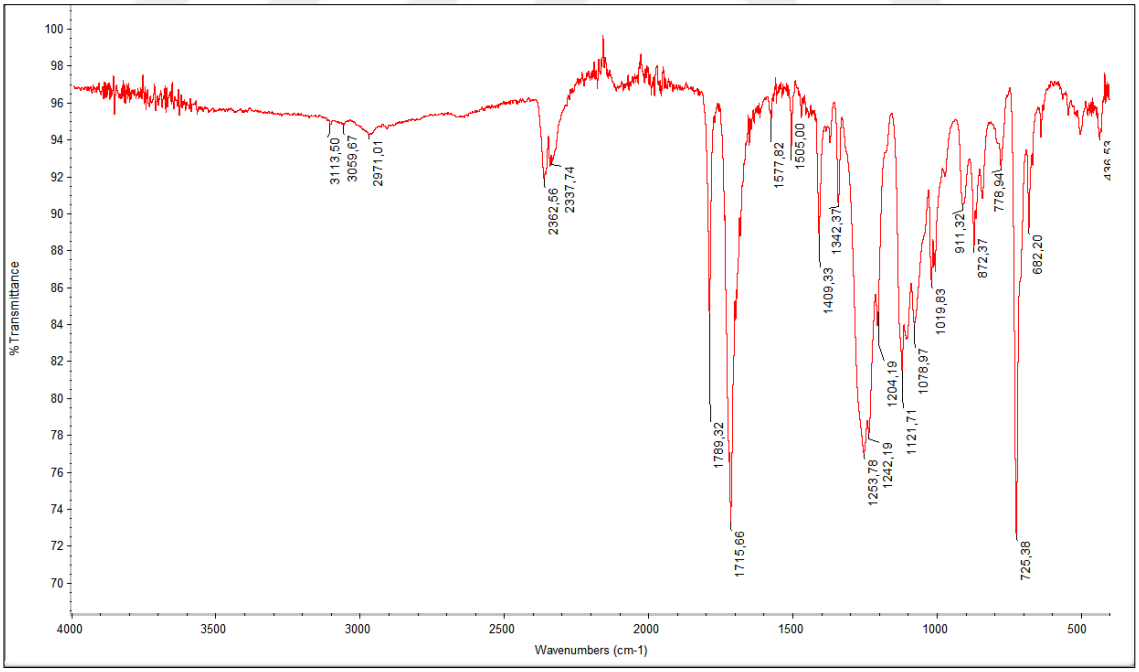



Figure A.45. FTIR Spectrum of PEA-3.

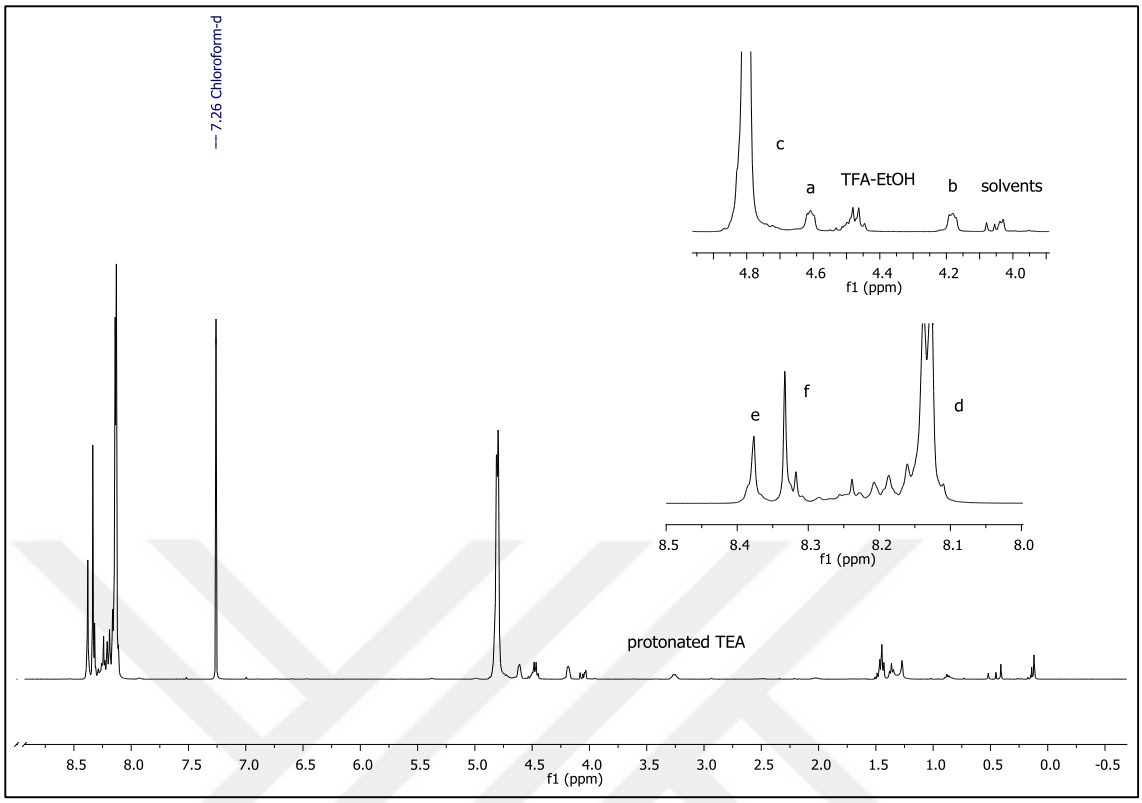



Figure A.46. $^{1}$H NMR of PEA-3.

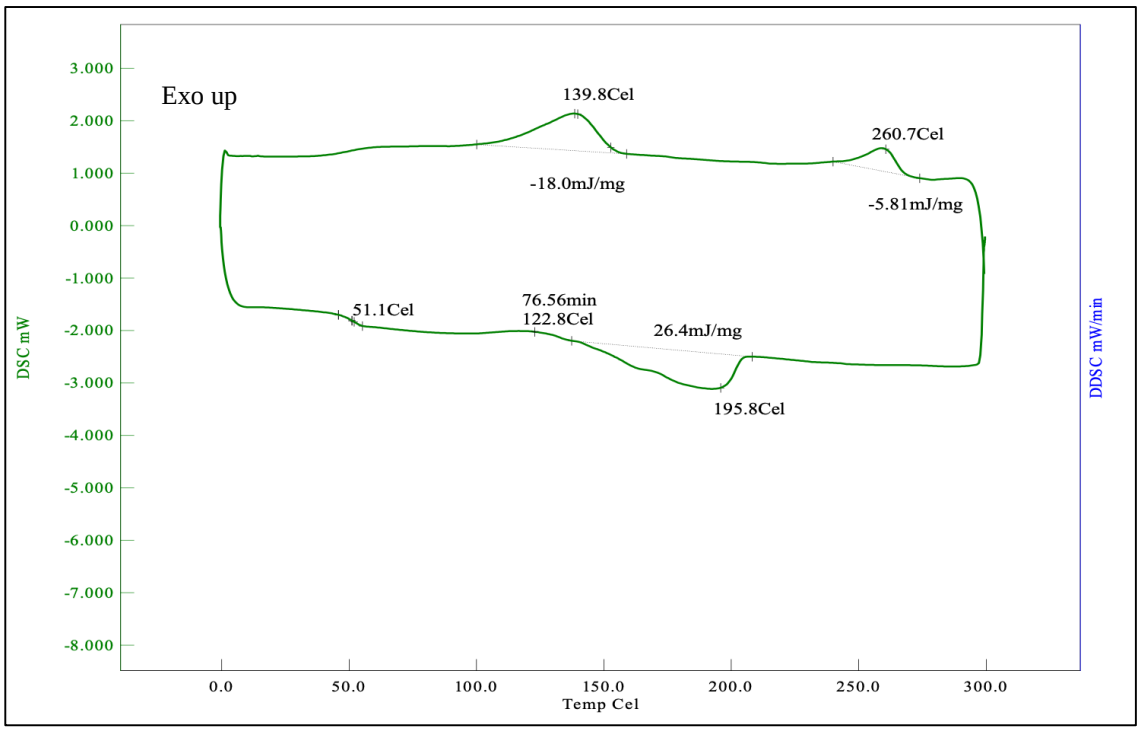



Figure A.47. DSC Analysis of PEA-3.

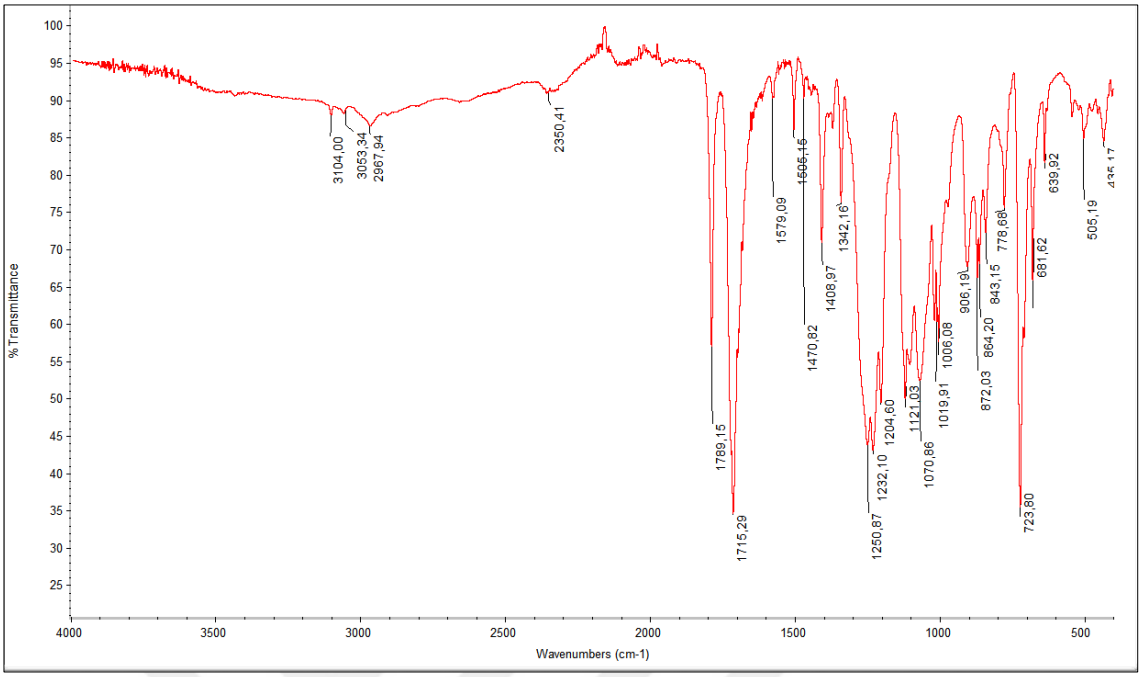



Figure A.48. FTIR Spectrum of PEA-4.

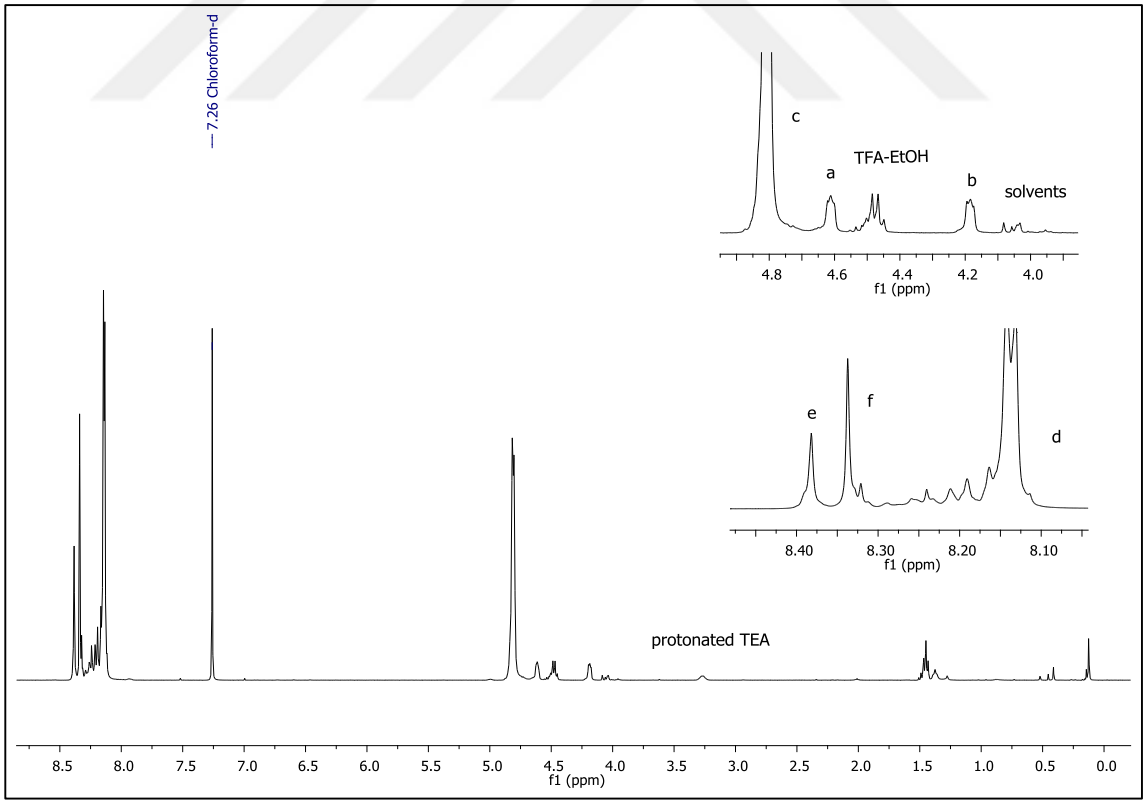



Figure A.49. $^{1}$H NMR of PEA-4.

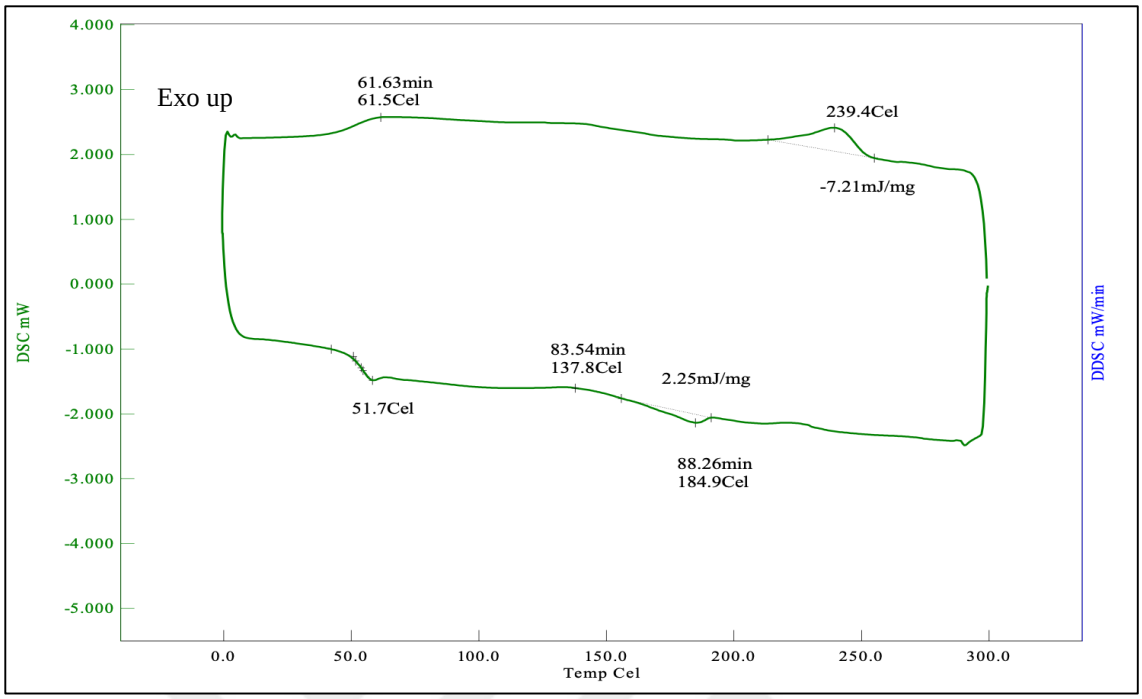



Figure A.50. DSC analysis of PEA-4.

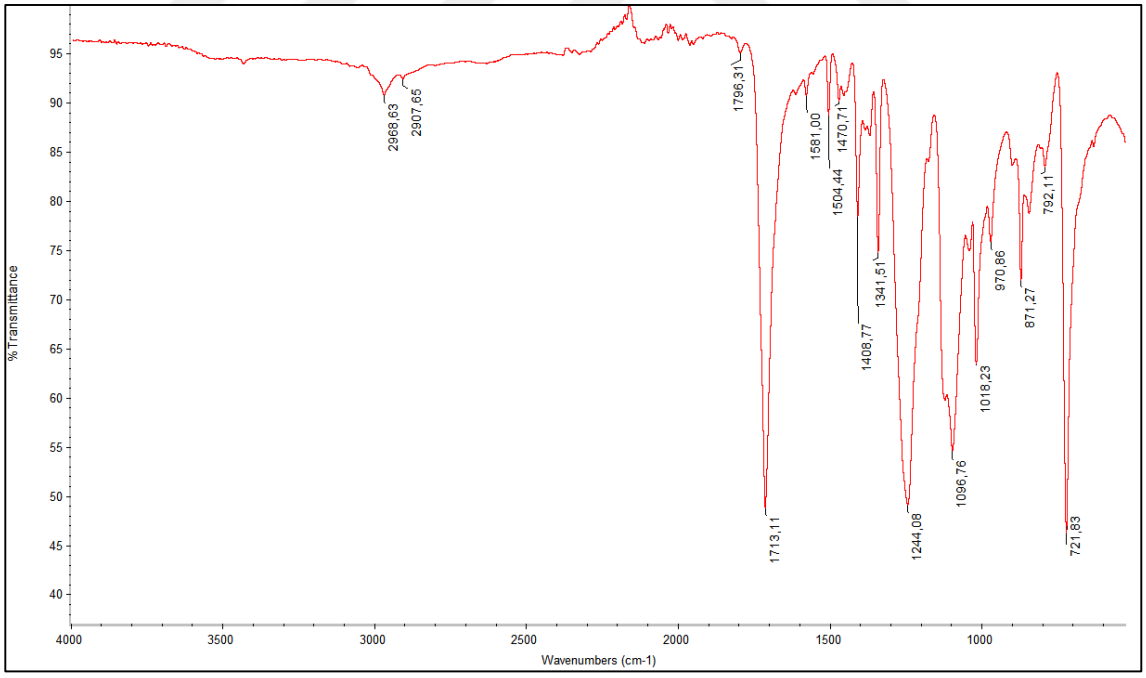



Figure A.51. FTIR Spectrum of PEA-5.

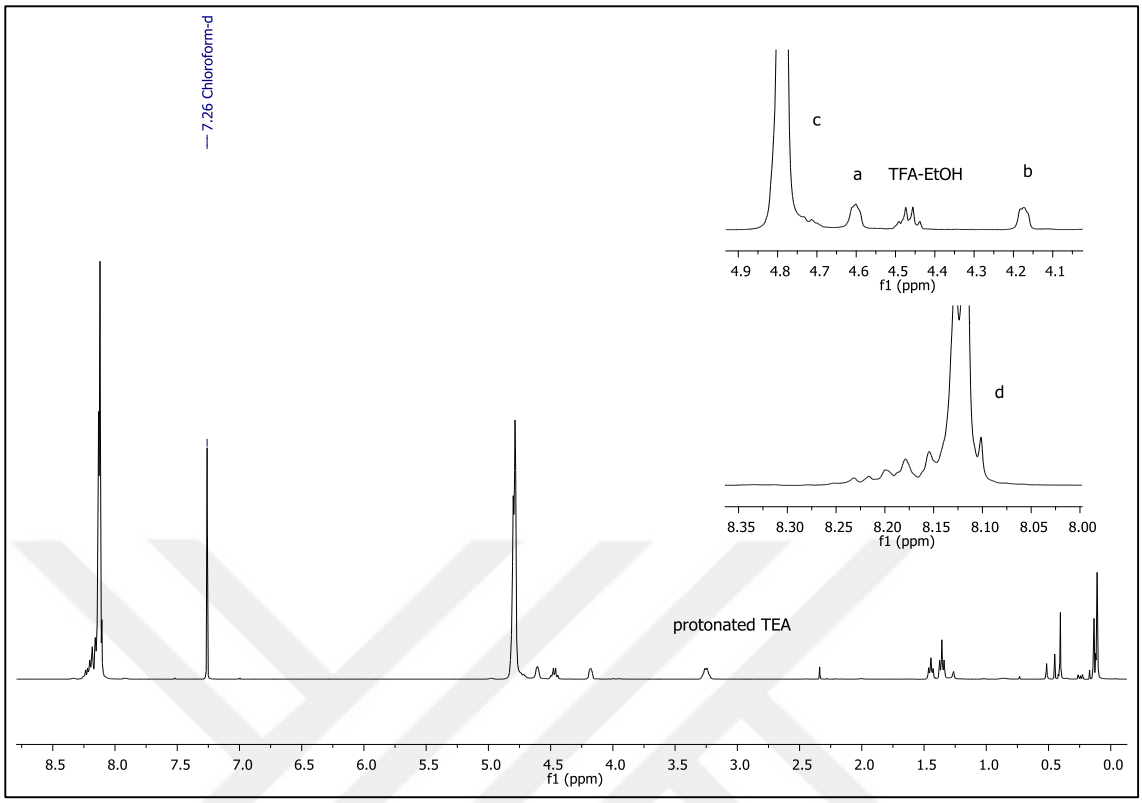



Figure A.52. $^{1}$H NMR of PEA-5.

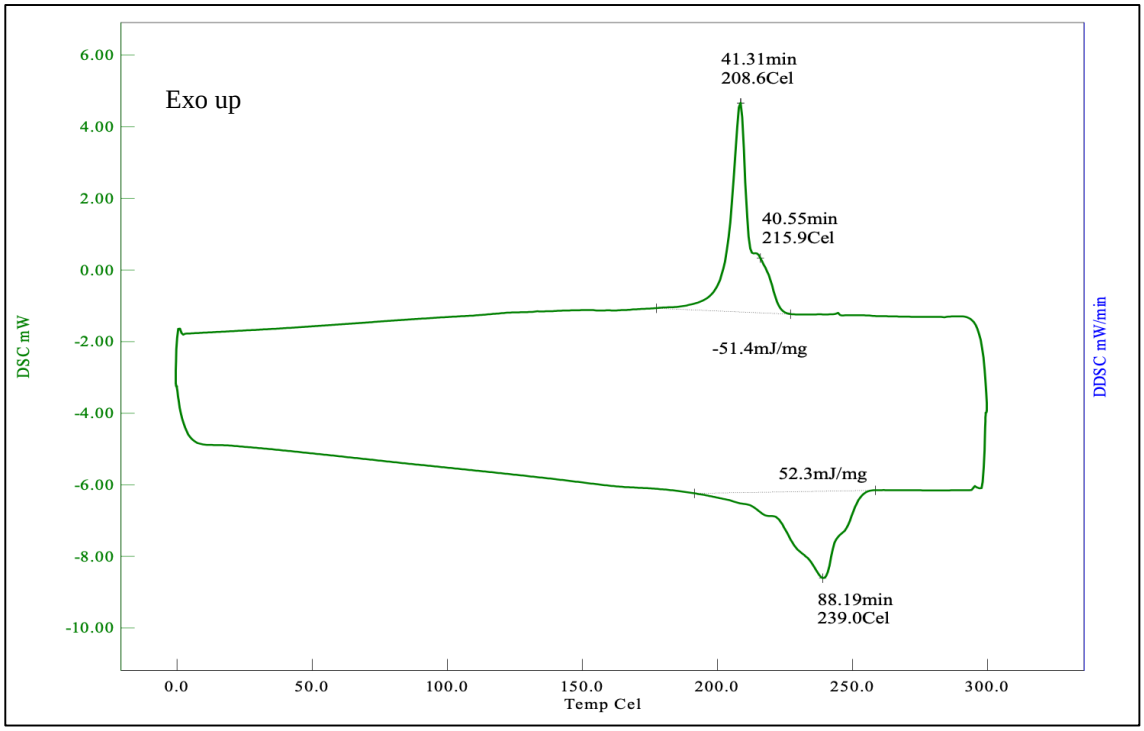



Figure A.53. DSC Analysis of PEA-5.

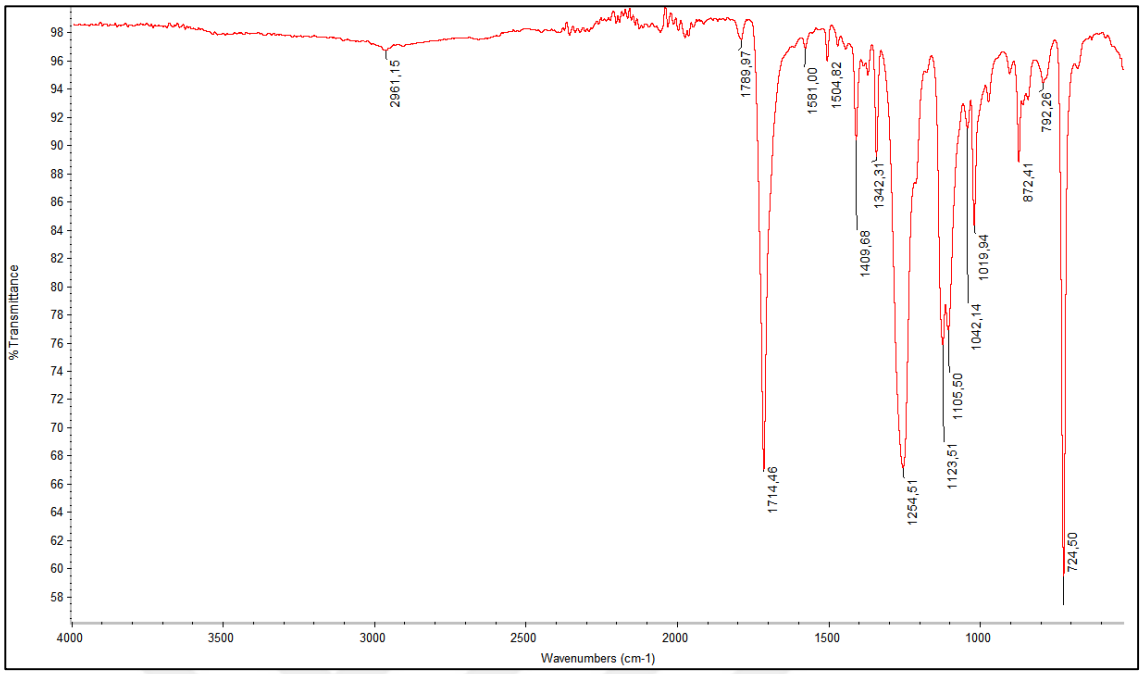



Figure A.54. FTIR Spectrum of PEA-6.

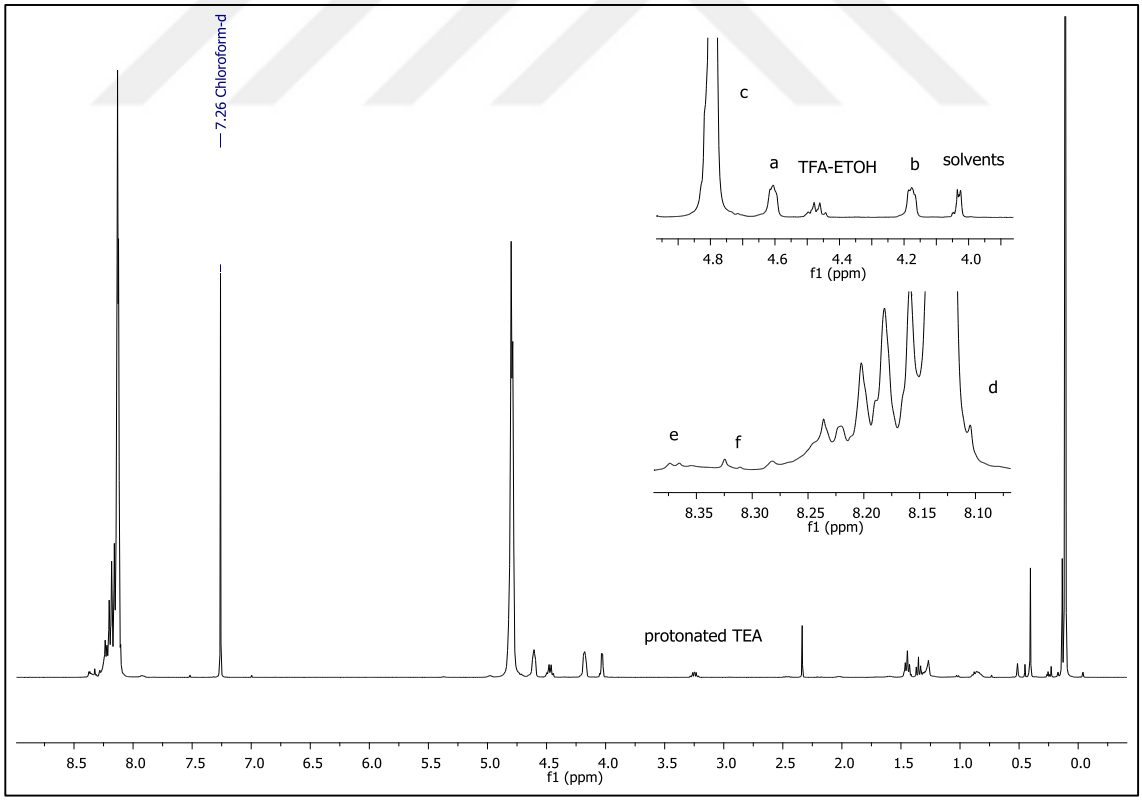



Figure A.55. $^{1}$H NMR of PEA-6.

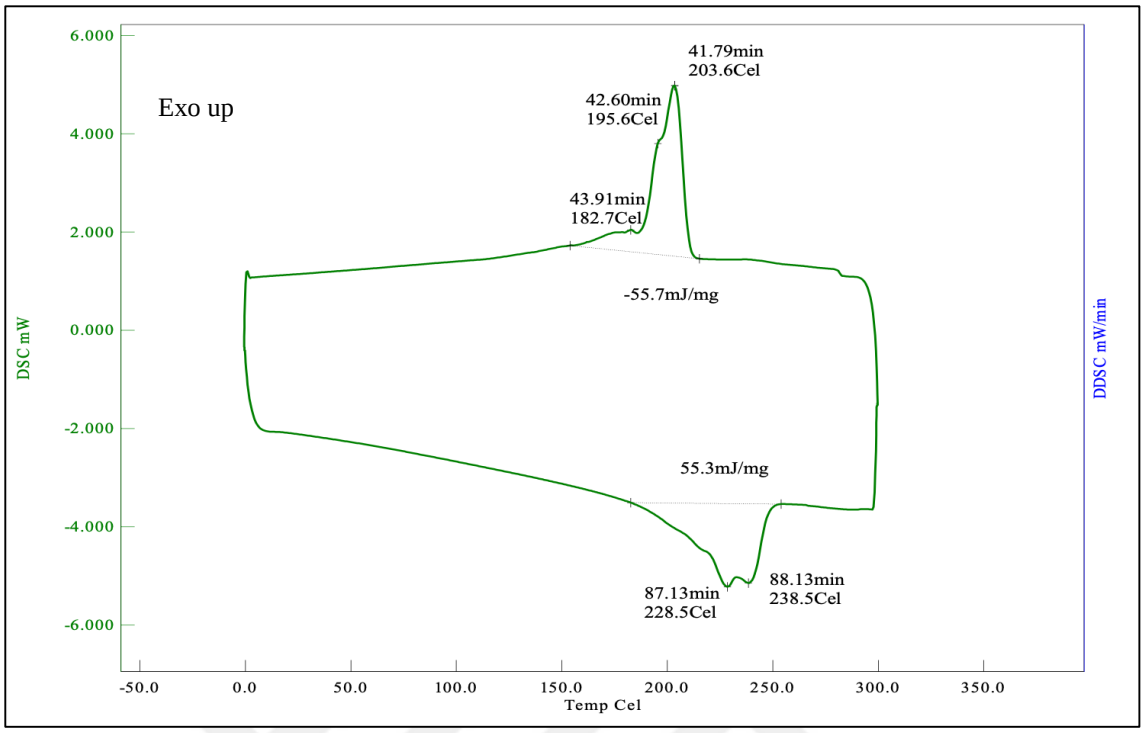



Figure A.56. DSC Analysis of PEA-6.

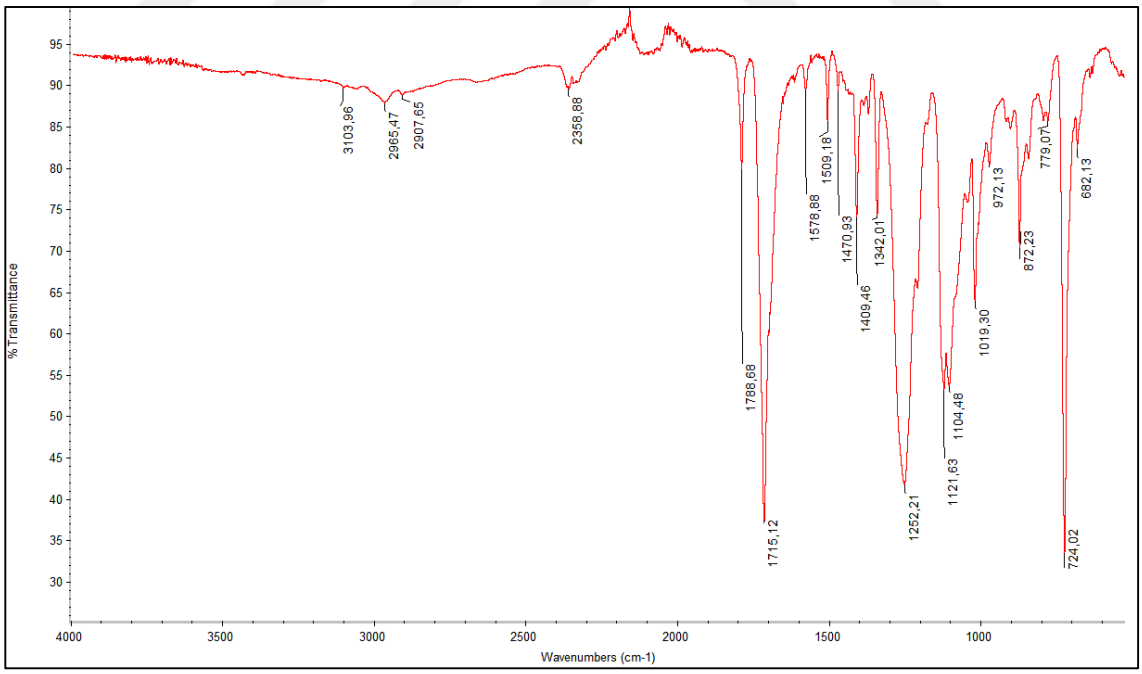



Figure A.57. FTIR Spectrum of PEA-7.

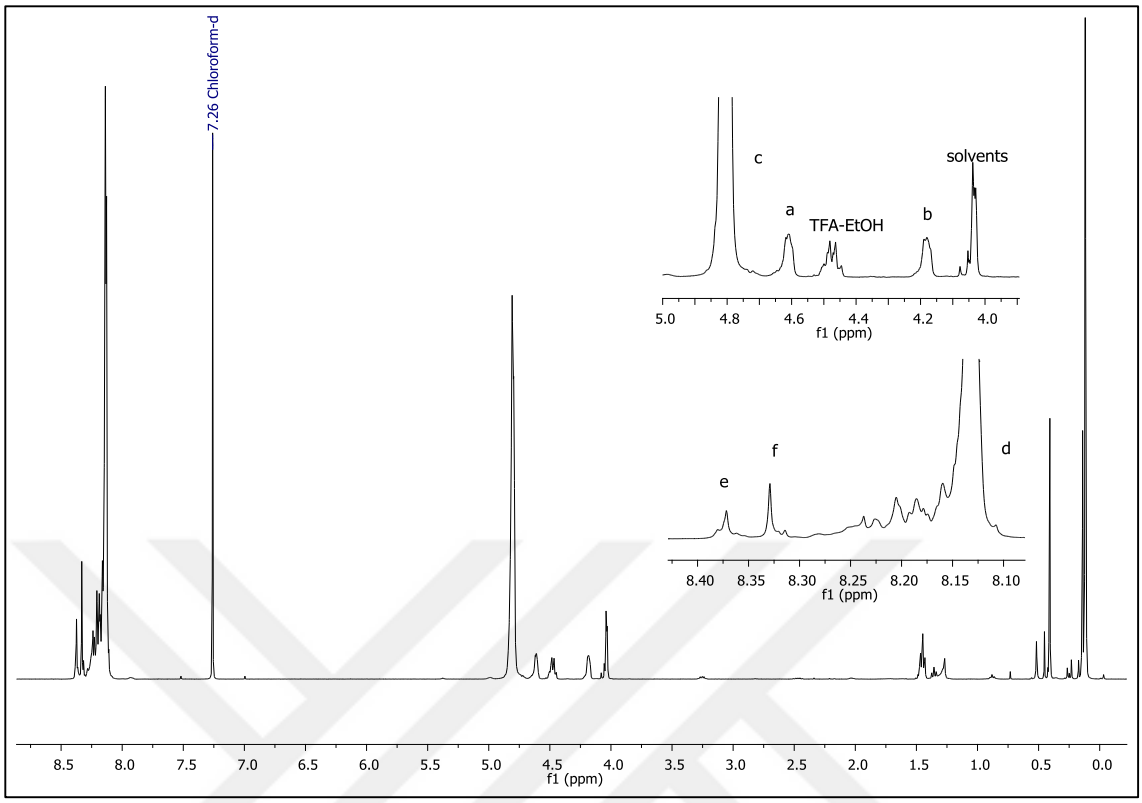



Figure A.58. $^{1}$H NMR of PEA-7.

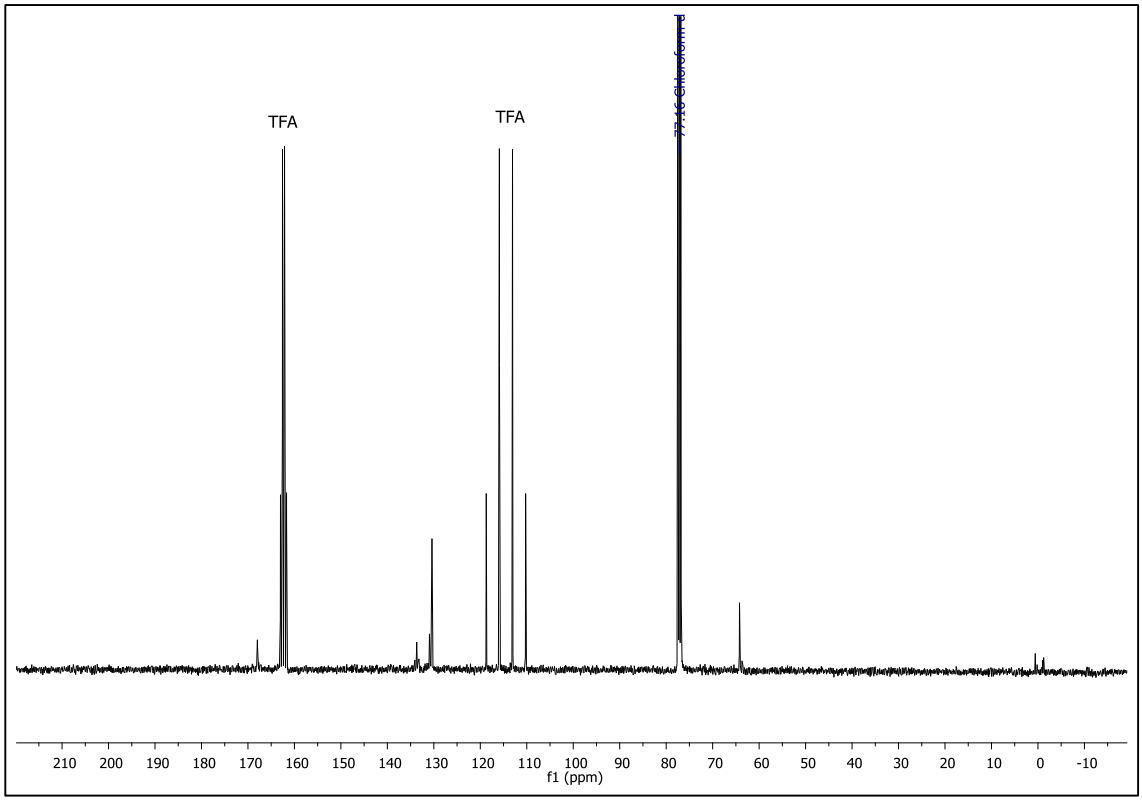



Figure A.59. $^{13}$C NMR of PEA-7.

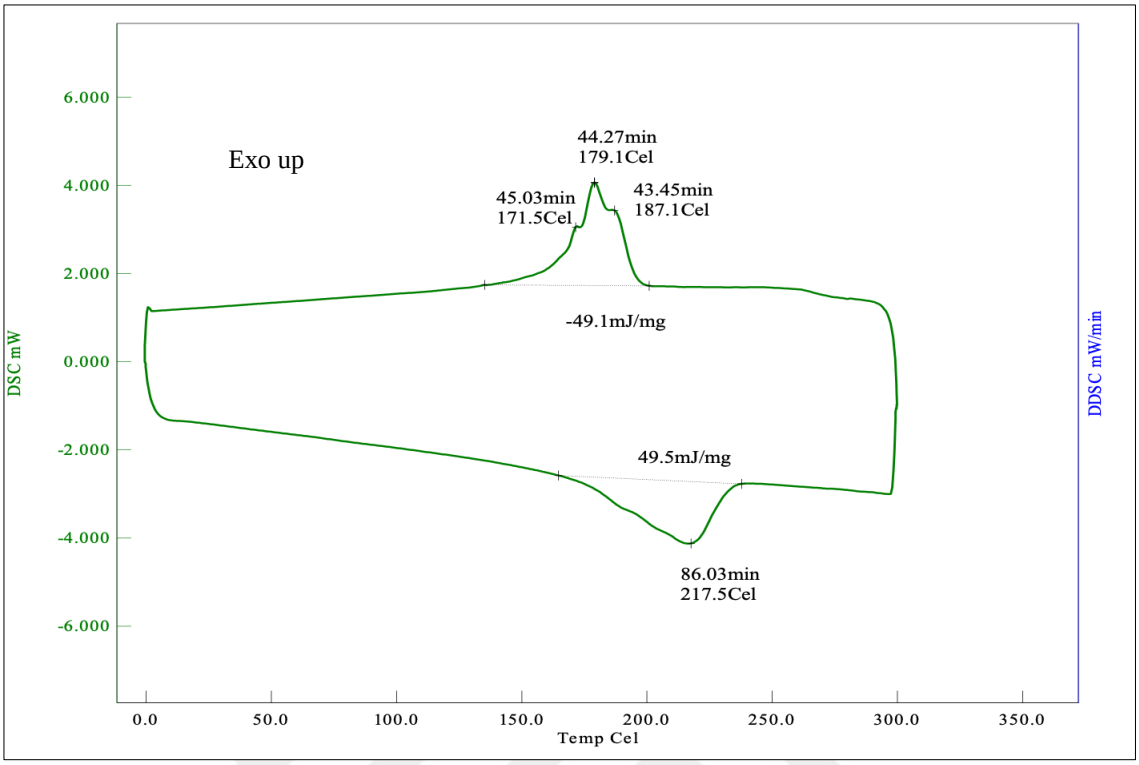



Figure A.60. DSC Analysis of PEA-7.

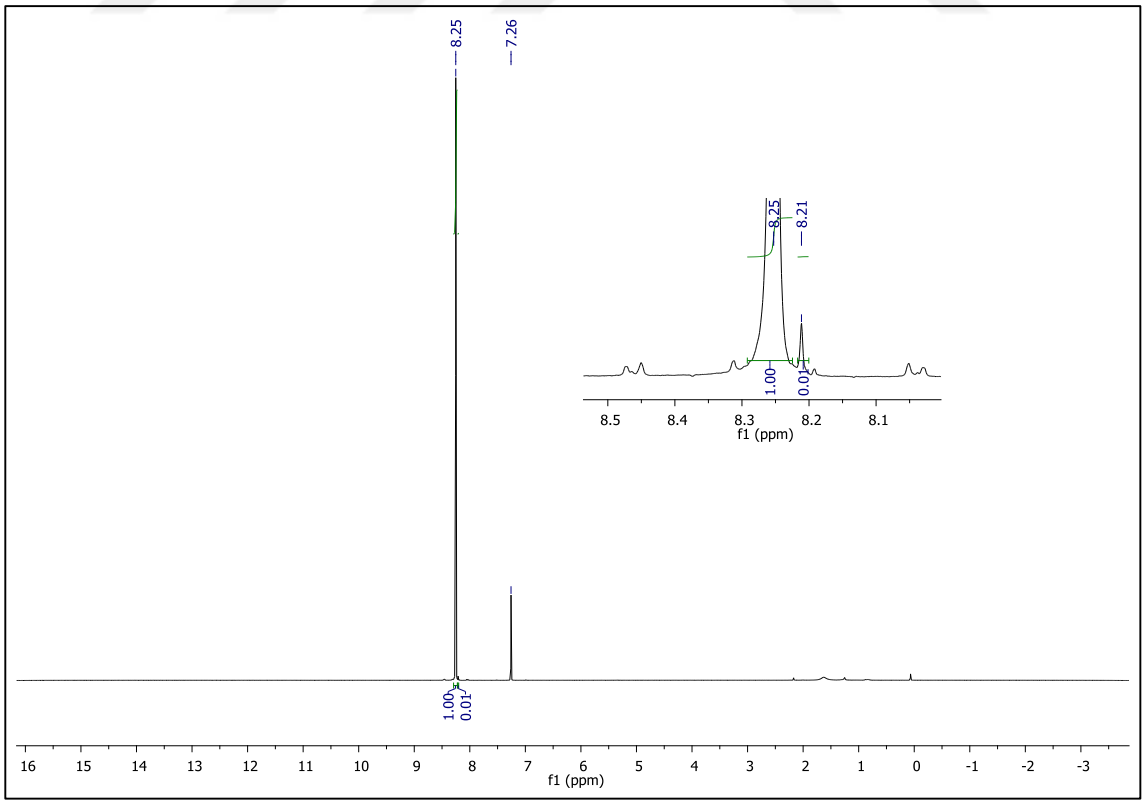



Figure A.61. $^{1}$H-NMR of the used old TPC.

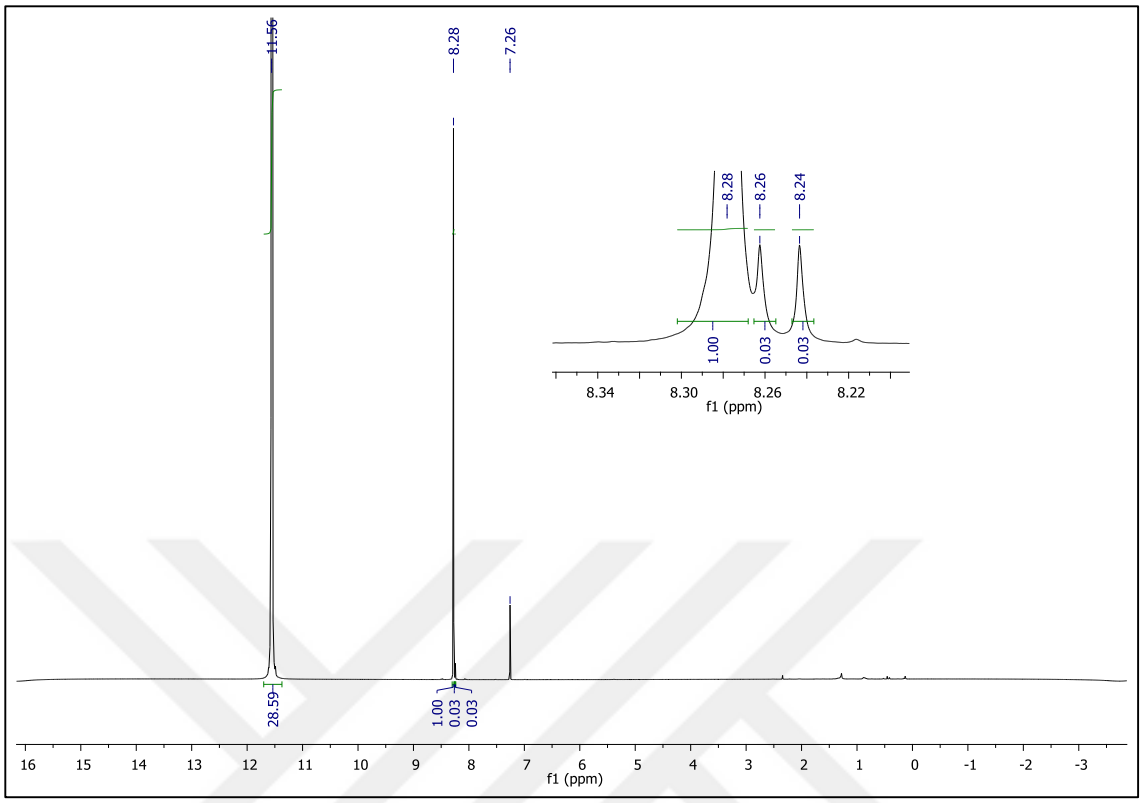



Figure A.62. $^{1}$H-NMR of the used old TPC with TFA.