SYNTHESES AND CHARACTERIZATION OF POLYESTERS DERIVED FROM RESORCINOL AND ISO/TEREPHTHALOYL CHLORIDE

by

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SYNTHESES AND CHARACTERIZATION OF POLYESTERS DERIVED FROM RESORCINOL AND ISO/TEREPHTHALOYL CHLORIDE

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Dedicated to my family

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ABSTRACT

SYNTHESES AND CHARACTERIZATION OF POLYESTERS DERIVED FROM RESORCINOL AND ISO/TEREPHTHALOYL CHLORIDE

Polyarylates are important class of polyesters, which are used for different application areas to improve thermal and mechanical properties of polymeric materials. They are also known as weatherable polymers that provide enhanced UV-protection.

The different monomer compositions and their ratios in the polyesters affect the physical properties of polymers, such as flexibility or rigidity of polymer chains. On the other hand, linear and symmetrical monomer units make ordered packing while non-linear and non-symmetrical monomer units may produce cyclic oligomers. Therefore, they influence the glass transition temperatures (T_g) and the melting point (T_m) of the polymers.

Previous studies performed in the literature involved the syntheses of polyarylates containing a composition of 1:1 ratio of 1,3 and 1,4 disubstituted acid chlorides. In this study, it was aimed to synthesize various polyesters with different ratios of these diacid chlorides to observe the structure-property relationship of the polymers. Furthermore, the syntheses of poly(ester-anhydrides) with the same monomers were performed to investigate the effect of anhydride linkages in the polymer backbone.

ÖZET

RESORSİNOL VE İZO/TEREFTALOİL KLORÜR'DEN OLUŞAN POLİESTER TÜREVLERİNİN SENTEZİ VE KARAKTERİZASYONU

Poliarilatlar, polimerik malzemelerin termal ve mekanik özelliklerini geliştirmek için çeşitli uygulamalarda kullanılan önemli bir poliester türüdür. Ayrıca poliarilatlar UV koruması sağlayan polimerler olarak da bilinirler.

Polimerlerdeki farklı monomer çeşitleri ve oranları, polimer zincirlerinin esnekliği veya sertliği gibi fiziksel özelliklerini etkiler. Örneğin polimer içindeki lineer ve simetrik monomer birimleri polimer zincirlerinin üst üste sıkı bir şekilde örtüşmesine sebep olur iken, lineer ve simetrik olmayan monomerler siklik halka oligomerlerin oluşumuna sebep olabilir. Sonuç olarak bu faktörler polimerlerin camsı geçiş sıcaklıklarını (T_g) ve erime noktalarını (T_m) etkiler.

Önceki akademik ve endüstriyel çalışmalarda, aromatik diasit klorür monomerleri (1,3 ve 1,4 pozisyonları) 1:1 mol oranlarında kullanılarak poliarilat sentezleri yapılmıştır. Bu projede aynı diasit klorürler farklı mol oranlarında kullanılarak farklı özellikte poliesterlerin sentezlenmesi amaçlanmıştır. Ayrıca, kullanılan monomerlerden kaynaklı sentezlenen polimerlerin yapı-özellik ilişkileri incelenmiştir. Son olarak, anhidrit bağlarının ürün üzerindeki etkilerini gözlemlemek için aynı monomerler kullanılarak poliester anhidrit sentezleri yapılmıştır.

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LIST OF ACRONYMS/ABBREVIATIONS

BPA	Bisphenol A
$CDCl_3$	Deuterated Chloroform
DSC	Differential Scanning Calorimetry
DCM	Dichloromethane
FTIR	Fourier-Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
H	Hydrogen
HFIP	Hexafluoro-2-propanol
IPC	Isophthaloyl chloride
IR	Infrared
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMR	Nuclear Magnetic Resonance
ODCB	*Ortho*-dichloro benzene
PDI	Polydispersity index
PE	Poly(ethylene)
PET	Poly(ethylene terephthalate)
PHEMA	Poly(hydroxyethyl methacrylate)
TEA	Triethyl amine

T_g	Glass transition temperature
TFA	Trifluoro acetic acid
THF	Tetrahydrofuran
T_m	Crystalline melting temperature
TPC	Terephthaloyl chloride
UV	Ultraviolet
UVA	Ultraviolet Absorber

1. INTRODUCTION

Polyesters are defined as condensation or step-growth polymers, which contain essential ester linkages through their chains. In addition, polyesters have a wide range of application areas such as textile industry, food packaging, fibers, films and various coating systems [1].

The physical properties of polyesters can be easily tuned by modifying the types and ratio of monomers and their reactive end groups. In fact, there are three factors to determine the essential nature of polymeric materials, which are the flexibility of macromolecule, the magnitude of the forces between molecules and the stereoregularity of the macromolecules. These factors can affect the glass transition temperature of polymers, the ability of polymers to crystallize and the melting point of polymers that are crystalline. At this point, the different types and ratios of monomers which are used for synthesizing polyesters have a great impact on changing the physical properties, such as glass transition temperature (T_g) [2]. The influences of polymer structure on their thermal transitions will be explained in the section 1.2.

Crosslinking is another significant parameter for polymeric materials since it has an effect on both chemical and mechanical properties of polymers. In fact, unlike the non-crosslinked thermoplastic polymers, crosslinked polymer networks are usually thermosets that cannot melt and flow at high temperatures. The polyesters containing carboxylic acid or hydroxyl end groups can be crosslinked by using appropriate multi-functional crosslinkers. These polymers have stronger mechanical strength and they are useful for many application areas, such as coatings. Therefore, the number and the nature of reactive end groups can easily influence the properties of polymers [2].

When comparing with all types of polyesters, polycarbonates are important class of thermoset polyesters since they have excellent physical and mechanical properties including higher impact strength, thermal and electrical stability with respect to other polyesters. In fact, polycarbonates, especially used for outdoor applications, should have UV stability, which is one of the most significant properties of polymeric materials. However, they have

the degradation problem of long-term color instability coming from the action of UV-light. It leads to occur yellowing of the polymers and lose their transparency and attractiveness [3], [4]. Polymer degradation mechanisms will be demonstrated in detail in the section 1.3.

Polyarylates or aromatic polyesters, which are one of the polyester types, consist of aromatic ester groups in their chain as seen in Figure 1.1. These polyesters can show some good thermal and mechanical properties such as high bond energies, low degree of reactivity and rigidity of polymer backbone structure. Furthermore, polyarylates have good toughness and weatherability properties as well as flammability and combustion resistance inherently [5]. Aromatic polyesters can be synthesized by using an aromatic dihydroxy compound and an aromatic dicarboxylic acid.

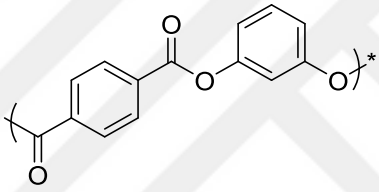


Figure 1.1. Poly(m-phenylene terephthalate).

There has been a great interest towards the synthesis of polyarylates and polyarylate block copolymers that provide enhanced UV-protection for decades. The first polyarylate was synthesized by using phthalate ester (iso/terephthalates) and bisphenol-A (BPA). It was marketed by General Electric Plastics Company with the 'Lexan PPC resins' trade name [3]. Moreover, Pickett *et al.* produced weatherable polyarylates, namely ITR polyesters, by using terephthaloyl dichloride and isophthaloyl dichloride as aromatic dicarboxylic acid derivatives and resorcinol as an aromatic dihydroxy compound [6]. In fact, resorcinol based arylate polymer blocks improve polycarbonate UV-stability and weatherability as seen in Figure 1.2. These polyarylates, in principle, can undergo Photo- Fries rearrangement that leads to the formation of hydroxy benzophenones which are known to produce protective UV-blocking moieties in the resin [7]. Further explanation on weatherable polymers and their features will be discussed in the section 1.4.

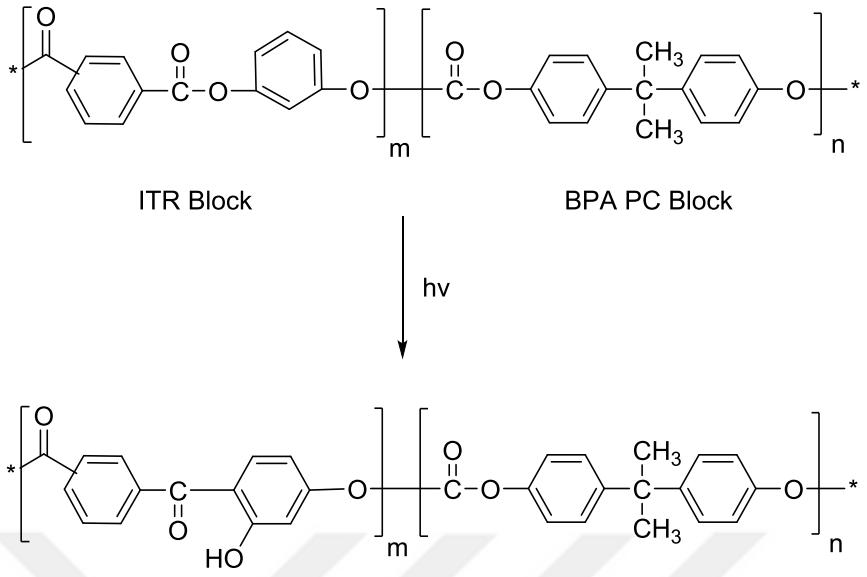


Figure 1.2. Photo-Fries rearrangement of ITR-PC block copolymer [7].

The arylate polyesters and poly(ester-anhydrides) synthesized by using solution polymerization in this study can be used for a potential application area, which is powder coating, due to their good mechanical properties and also their weatherability and high UV-resistance. Since monomer compositions, end groups and T_g values of the polyester resins are important factors for curing process; they should be tunable for these polyesters. Furthermore, the use of poly(ester-anhydrides), which is described in detail section 1.5, can be useful to obtain low curing temperature and also to prevent agglomeration during the storage of resins in the powder coating.

1.1. Synthesis of Polyesters

Polymers are synthesized by using two polymerization techniques, which are chain growth and chain addition. In the former, the double or triple bonds in the monomers react through the reaction and there is no by-product. In the polycondensation reaction, the bifunctional monomers, such as dicarboxylic acids, acid chlorides or methyl esters, react with alcohols and as a by-product low molecular weight condensates (e.g. water or methanol) are eliminated during the polymerization [8]. The formation of polyesters occurs by using typical polycondensation reaction.

$$HOOC\text{-}R^1\text{-}COOH + OH\text{-}R^2\text{-}OH \longrightarrow HO(\text{-}OC\text{-}R^1\text{-}COO\text{-}R^2\text{-}O\text{-})H + H_2O$$

1.1.1. Synthesis of Polyarylate Block (ITR) Polyesters

ITR block polyester is an aromatic polyester that is synthesized by using polycondensation reaction of both isophthaloyl chloride and terephthaloyl chloride as dicarboxylic acid chlorides and resorcinol as dihydroxy alcohol with the help of a catalyst such as triethyl amine. This polymer is known as a weatherable and self-UV-protective polyester which can be used for coating systems [9].

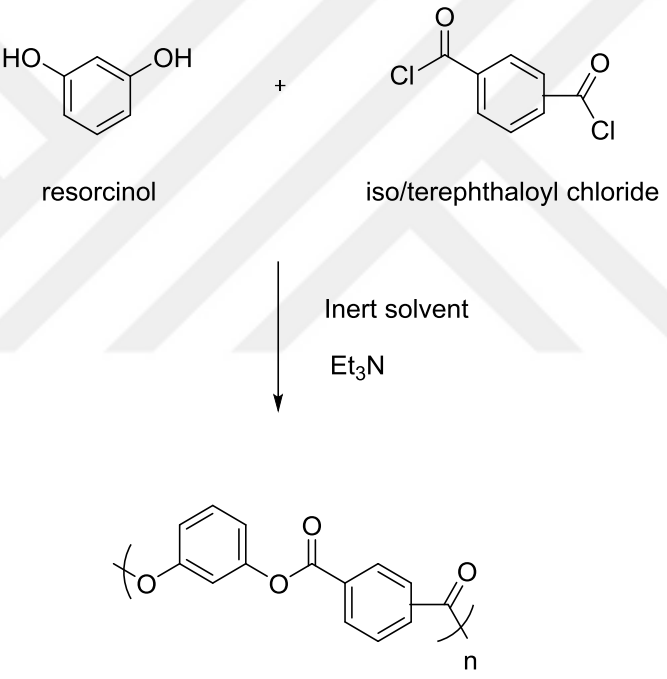


Figure 1.3. Synthesis of ITR Block Polyesters [5].

The ITR polyesters show better chemical and physical properties owing to their full aromatic structures when compared to the aliphatic polyesters. On the other hand, the arylate polyesters can have different packing and alignments due to the structural differences between dicarboxylic acid chloride monomers, which are isophthaloyl chloride and terephthaloyl chloride. It causes that the molecular weight and the glass transition

temperature values, which are related to physical states of the polyesters, to be changeable with the various ratio of monomers in the polymer chain [10].

1.2. Polymer Structure and Physical Properties

The structure of the polymer influences the thermal behavior of the materials under different conditions. For instance, while crystalline polymers such as tightly packed full aromatic polyesters or polyamides have only crystalline melting temperature (T_m) due to their molecular symmetry, the semicrystalline polymers such as linear polyethylene (PE) or polyethylene terephthalate (PET) can possess both T_g and T_m values due to their both flexible and crystalline natures [11]. As another example of the polymer structure effect, the mixtures of formed cyclic oligomers in the polymer have melting points considerably high [12]. Thermal transitions of polymers will be explained in the following sections.

1.2.1. Thermal Transitions of Polymers

Polymeric materials can be thermally characterized by mainly two essential transition temperatures, glass transition temperature (T_g) and crystalline melting point (T_m). The difference between these transition temperatures can be noticed more apparently *via* observing the behavior of polymeric materials in the liquid phase throughout a cooling process. The energies of the polymer molecules involving vibrational, rotational and translational energies reduce during cooling. In fact, when crystallization is possible at the point where the rotational and translational energies of the molecules are exactly zero, the temperature of melting (T_m) can occur. However, some polymers cannot pack into ordered state and get the symmetry needed for the crystallinity. The energies of molecules continue to fall with the decreasing temperature and during the molecular motion glass transition temperature (T_g) can be detected for these polymers [10].

1.2.1.1. The Crystalline Melting Point of Polymers. The crystalline melting point is the melting temperature of the polymers containing crystalline domains. While a fully crystalline polymer exhibits only T_m, semicrystalline polymers show both T_m and T_g transition temperatures, and also a completely amorphous polymer presents just T_g value as seen in the Figure 1.4. [10].

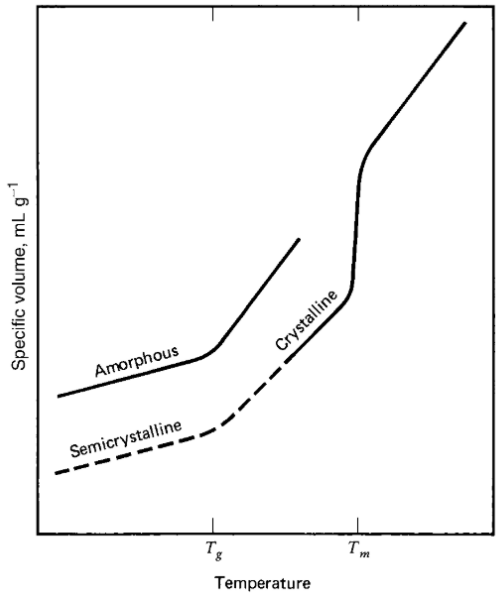


Figure 1.4. Determination of the crystalline melting point and the glass transition temperatures of polymers [10].

Some of the crystalline polymers do not have well-defined melting points when compared to the other conventional compounds. The reason for that is polymers are mostly mixtures containing different sizes of components that have a range of relative molecular mass, which melt, at different temperatures. Hence, homopolymers with the lower relative molecular mass melt at lower temperatures with respect to the higher relative molecular mass constituents. In addition, the size of crystalline polymer affects the range of the melting point, because the smaller crystallites melt before larger compounds. There are other factors that influence the range of the melting point, such as the presence of the co-monomer and traces of solvent or plasticizers in the polymer mixture. Among these factors, the first one

causes a decrease in the melting point due to shortening of the crystalline domains. The second one also is a reason for lowering the melting point, since the relative mobility of the polymer components increases and then the energy needed to melt reduces generally [2].

1.2.1.2. The Glass Transition Temperature of Polymers. Glass transition temperature (T_g) is a term that can be described as the temperature at which the state of hard and brittle polymeric materials becomes more rubbery owing to the molecular motion of the polymer chains within the materials. Some physical properties, such as the coefficient of thermal expansion, refractive index, heat capacity, mechanical damping and electrical properties, are related to the glass transition temperature where T_g is indicative of degree of freedom within a polymer matrix [2].

Molecular motion of polymer chains becomes easier when a polymeric material is heated to its glass transition temperature (T_g) or above. There are a number of factors that influence the glass transition temperature (T_g). First, the presence of pendant groups and rigid structures in the polymer backbone leads to a change in the mobility of the polymer chain hence it also changes T_g. Second, crosslinking and interaction between polymer chains such as hydrogen bonding cause restricted molecular motion of the polymer chains. Last but not the least, the relative molar mass is an important issue to be addressed. The higher molar mass contributes to more limitations in overall molecular freedom of the polymer when compared to the cases with lower molar mass. Finally, the presence of plasticizers influence T_g values expectedly because they reduce the stiffness, brittleness and hardness of polymers [2], [13].

1.2.1.3. Determination of Thermal Transitions of Polymers. Thermal transition temperatures of polymers are mostly determined by using differential scanning calorimetry (DSC) method. In DSC technique, the difference of heat flow rate into an inert reference material and a polymer sample is measured as a function of temperature under a specific temperature control [14].

DSC method can be applied to a variety of fields such as characterization of polymeric materials, purity determinations, phase diagram evaluations, kinetic investigations and determination of heat capacity and complex heat capacity [15].

1.2.2. Molecular Weight of Polymers

Molecular weight has a crucial importance in the synthesis and application of polymers. It is widely used to identify the size of a polymer. However, it is difficult to answer the question of the exact value of molecular weight of polymers because they are in a mixture constituted of different molecular weight chains [16].

The number-average molecular weight (M_n) can be determined to count the number of molecules in a mixture of polymer sample by using different experimental methods. M_n is described as the total weight of the polymer molecules (W) divided by the total mole number of the polymer [10]. Therefore, the equation that is necessary to obtain the number of average molecular weight is given as;

$$Mn = \frac{w}{\sum Nx} = \frac{\sum NxMx}{\sum Nx} \qquad (1.1)$$

where the M_x is molar mass of polymer molecules and N_x is the number of molecules in the sample [2]. In addition to that, the weight-average molecular weight (M_w) can be defined *via* the equation;

$$Mw = \frac{\sum NxMx^2}{\sum NxMx} \qquad (1.2)$$

Finally, the viscosity-average molecular weight (M_v), which is less widely used, can be calculated by using the equation;

$$Mv = \frac{\sum NxMx^3}{\sum NxMx^2} \qquad (1.3)$$

The ratio of the number average molecular weight and the weight average molar mass gives the polydispersity index for the polymers. The polymer is called *homo-* or *mono-*

dispersed when the ratio M_w to M_n is equal to 1. For a polydisperse polymer, the molecular weight distribution Mw/Mn broadens [10].

$$Mw > Mv > Mn \qquad (1.4)$$

The relationship between M_n, M_w and M_v values in a typical polymer is shown in Figure 1.5.

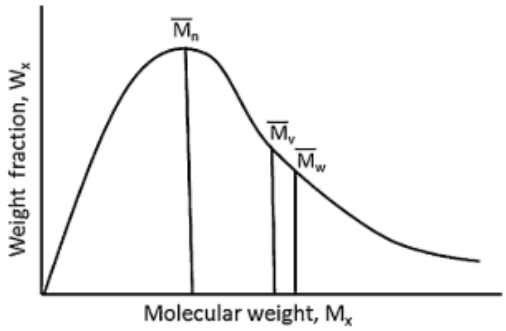


Figure 1.5. Molecular weight distribution of the polymer [16].

The mechanical properties of a given polymer can be usually predicted by its molecular weight. As it can be seen in Figure 1.6., the strength of the polymer increases from the point A to the critical point B. After that, the mechanical strength improves slowly until reaching a limiting value C. High molecular weight polymers give rise to high viscosity as well as poor processability.

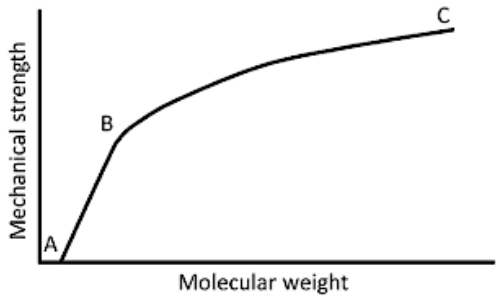


Figure 1.6. The dependency of mechanical strength on polymer molecular weight [10].

1.2.2.1. Determination of Molecular Weight of Polymers. There are various methods for the measurement of molecular weights of polymers such as end group analysis, membrane osmometry, mass spectroscopy, light scattering method and gel permeation chromatography (GPC) [16].

Gel permeation chromatography (GPC) is the technique that is widely used for determining molecular weight and molecular weight distribution of polymers. In principle, GPC is based on the exclusion of polymer molecules above a certain size from entering particular pores through the column packing, which is made up of a cross-linked polystyrene gel or a special porous material such as glass. The polymer mixture in solution depending on the size of the molecules is able to permeate pores that have different volume throughout the packing. The smaller molecules can come into proportion through each pore slowly. In some extreme cases, the largest molecules cannot permeate any pores at all and they pass thorough the packing easily with the solvent [2].

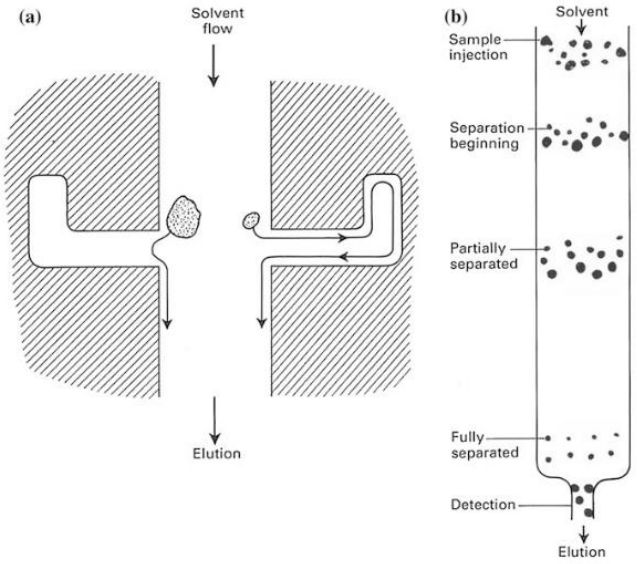


Figure 1.7. Simple illustrations of gel permeation chromatography principle [16].

1.2.3. The Relationship between M_n and T_g of Polymers

The number average molecular weight (M_n) influences the glass transition temperature (T_g). It can be derived from the Flory-Fox equation shown below;

$$Tg = Tg^{\infty} - \frac{k}{Mn} \qquad (1.5)$$

where $T_g \infty$ is the glass transition temperature at infinite molecular weight of polymer and k is the constant that depends on the polymer structure [13].

For example, the relationship between the molecular weight and glass transition temperature of polystyrene has been investigated widely. According to the Figure 1.8., as the number average molecular weight increases, T_g value also increases until it reaches a certain temperature [17].

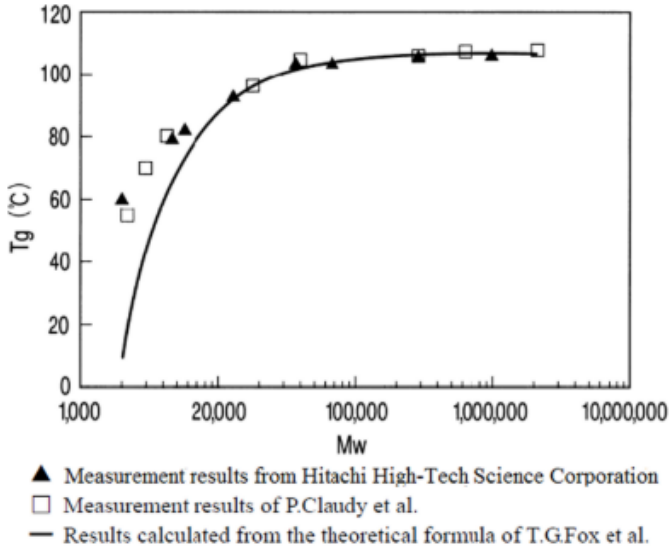


Figure 1.8. Dependence of glass transition temperature on molecular weight [18].

1.3. Polymer Degradation

Degradation of polymers involves some kinds of changes in the chemical structure and mechanical properties of polymeric materials due to external chemical or physical factors. For example, polymers are vulnerable to harmful effects that are originated from outdoor conditions such as oxygen and its reactive forms, humidity, atmospheric pollutants such as sulfur dioxide, nitrogen oxides and ozone. In addition to these effects, many physical stresses such as heat, radiation and mechanical forces may contribute to polymer degradation. There are different types of polymer degradation types such as thermal-, chemical- and photo- degradation [19].

The thermal degradation of polymers can be defined as the chemical changes in the polymer at the elevated temperatures without any other external involvement. Thermal degradation has a great importance in developing fire-retardant materials and high performance polymers [19]. An example on possible thermal degradation mechanisms is given for the polymer poly(2-hydroxyethyl methacrylate) (PHEMA) in Figure 1.9.

Apart from thermal degradation, polymers erode by typical ways, which are hydrolysis and enzymatic reactions. In fact, the latter option is generally appropriate for natural biopolymers such as proteins and polysaccharides, where suitable enzymes are available.

Hydrolysis is a significant reaction for the polyester and polyalkylacrylate degradations and there are several factors that affect the reaction speed, which are the type of the chemical bond to be formed, the composition of copolymer and pH value [20]. Among these, the chemical bond type within the polymer chain is a main factor that influences the reaction rate. In Figure 1.10., reactivity order of some polymer class is investigated. According to this information, anhydride and ortho ester groups can degrade in a shorter time than ester and amide bonds.

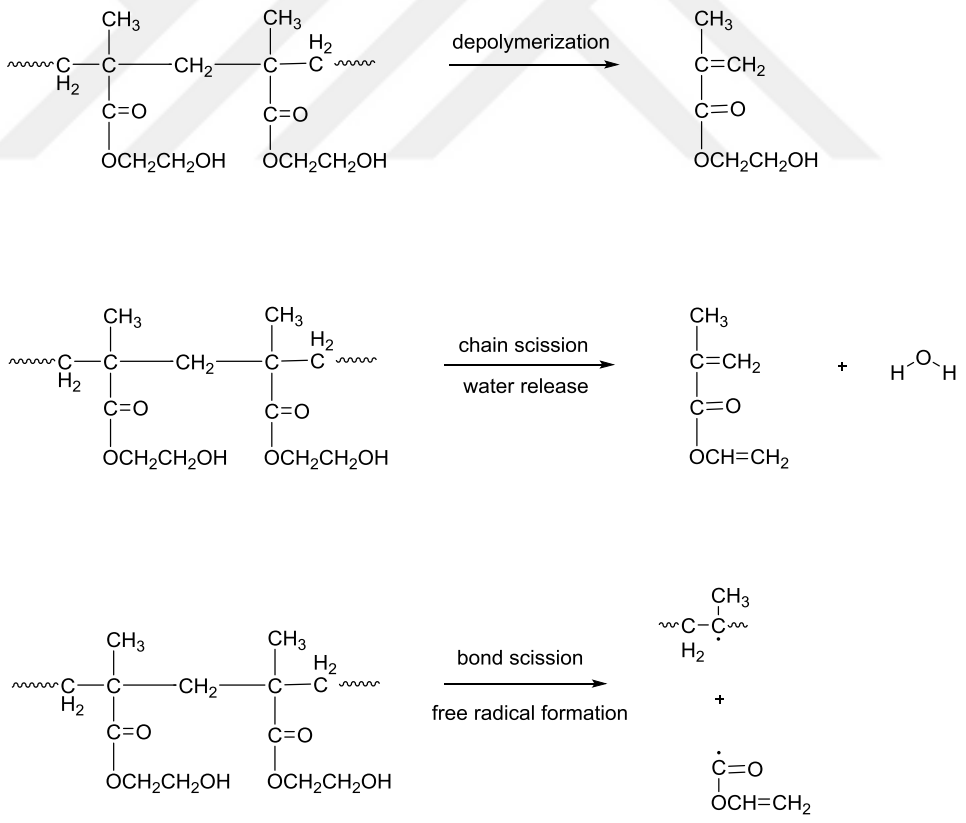


Figure 1.9. Reactions proposed for the thermal degradation of PHEMA [21].

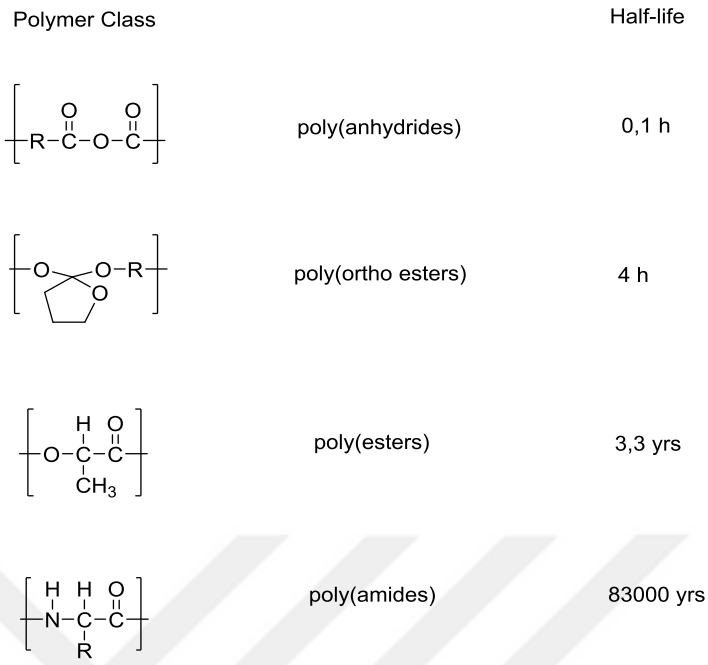


Figure 1.10. Classes of hydrolysable bonds with half-lives [20].

All polymers degrade remarkably under the ultraviolet (UV) light or γ-radiation. For example, aromatic polycarbonates change their color from colorless to yellow under the UV-light by photodegradation [5]. The main effect of UV-light on polymers is free radical formation because of homolytic breaking of chemical bonds. Once the free radicals are formed, they react with the atmospheric oxygen to form peroxy radicals. Then, the peroxy radicals abstract a hydrogen from the polymer chain, hence create hydroperoxides and also more free radicals. Through the process of formation of free radicals, they contribute to breaking bonds in the polymer chains. A plausible photo-degradation mechanism poly(ethylene terephthalate) (PET) is given in Figure 1.11. As a result, deterioration of physical and mechanical properties of the polymers becomes highly possible. In order to overcome these problems, UV-inhibitors have been used to stabilize the effect of UV-radiation on polymeric materials [5].

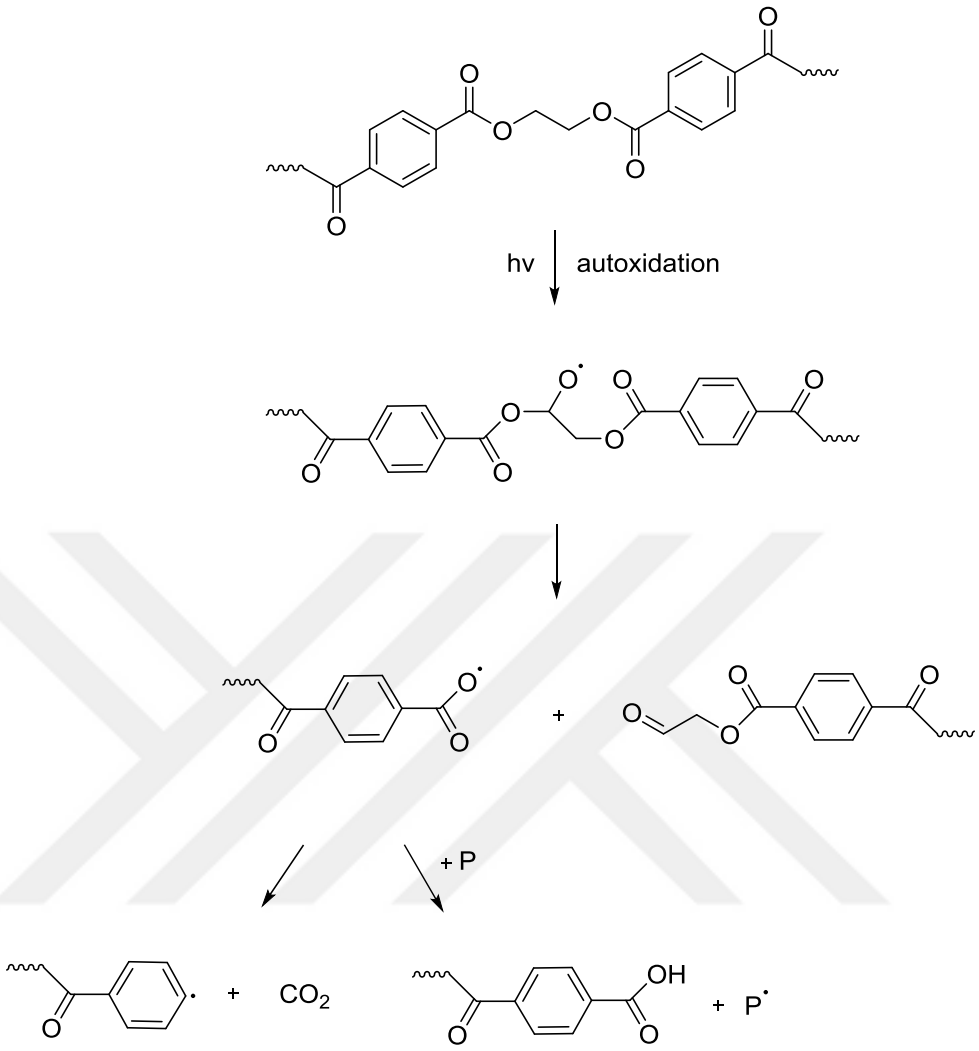


Figure 1.11. Photo-induced autooxidation for poly(ethylene terephthalate) [22].

1.4. UV Stabilizers and Weatherable Polymers

Polymeric materials have been used widely in the buildings in the form of coating and thermoplastic products. However, the coating exposed to sunlight or UV- radiation source in the atmosphere is able to face with severe degradation and deformation as proved by changes in their physical properties. The photo-degradation in polymer coatings can be probably understood when some outcomes such as increased brittleness; discoloration, surface cracking and loss of mechanical strength are observed.

The UV-absorbers (UVA) are able to protect the polymers against the possible photo-degradation by absorbing the UV radiation. The most significant commercial UV absorbers are based on benzotriazole, triazine and benzophenone (Figure 1.12).

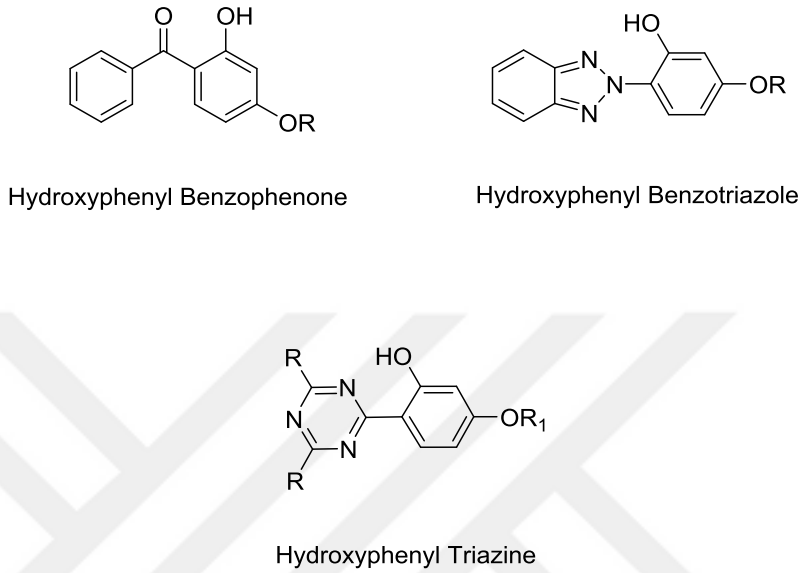


Figure 1.12. Samples of commercial UV-absorbers [5].

These UV-absorbers are capable of converting the energy that they absorbed from UV-radiation to the thermal energy in the form of heat, which is shown in Figure 1.13.

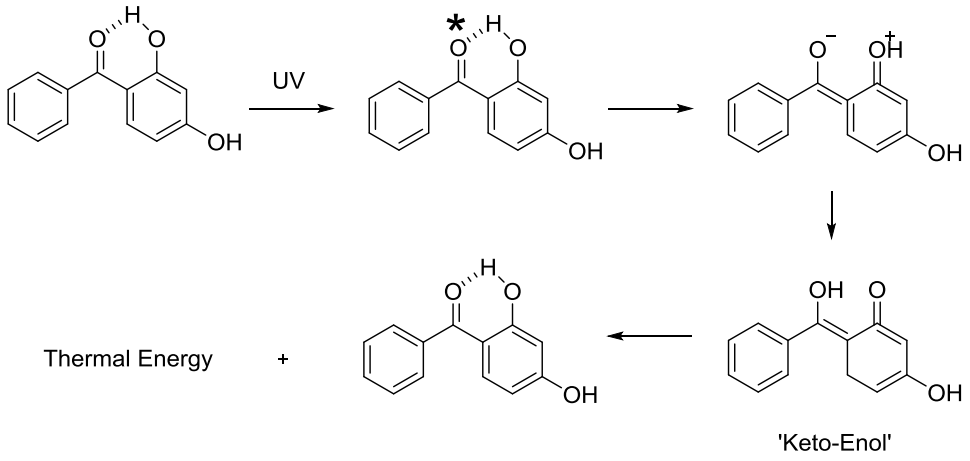


Figure 1.13. Possible UV stabilization mechanism for resorcinol benzophenone absorbers [5].

Apart from UV-absorbers, the synthesis of weatherable polymers has drawn great attention to prevent the yellowing of polymers by weathering. It has been found that resorcinol based polyarylates comprising isophthalic and terephthalic acid monomers show excellent weatherability with very low yellowing [6]. The resorcinol based polyarylates are able to undergo Photo-Fries rearrangement to form *o*-hydroxybenzophenones as shown in Figure 1.14. These structures help polyarylates to improve their UV-stabilities. A thin uniformed skin, which is opaque into UV-radiation but transparent to visible light, may occur at the top of the layers in the coating. [23].

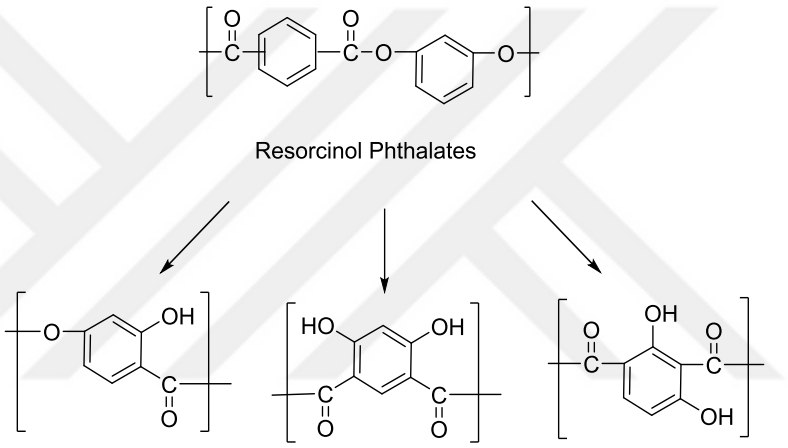


Figure 1.14. Photo-Fries rearrangement and o-hydroxybenzophenone structures [5].

1.5. Polyanhydrides

Polyanhydrides have shown remarkable performances as crucial biomaterials for short-term drug release, due to high reactivity of anhydride functionality towards water that caused to hydrolysis either in the polymer backbone or side chains. Due to the hydrolytic instability of anhydride linkages, polyanhydrides can easily degrade when compared to the other hydrolysable polymers such as polyesters and polyamides [24].

Firstly, polyanhydrides were studied by Bucher and Slade. Their actual work was to synthesize aromatic polyanhydrides containing meta and para positions. And then, aliphatic polyanhydrides and the behavior of diacid monomers for anhydride formation were reported by Hill and Carothers. Moreover, Conex was investigated new polyanhydrides that have

been synthesized by using different synthetic methods. Over these years, there are several studies about physical, chemical and degradation properties of polyanhydrides in order to enlarge their application areas in industry and academia [25].

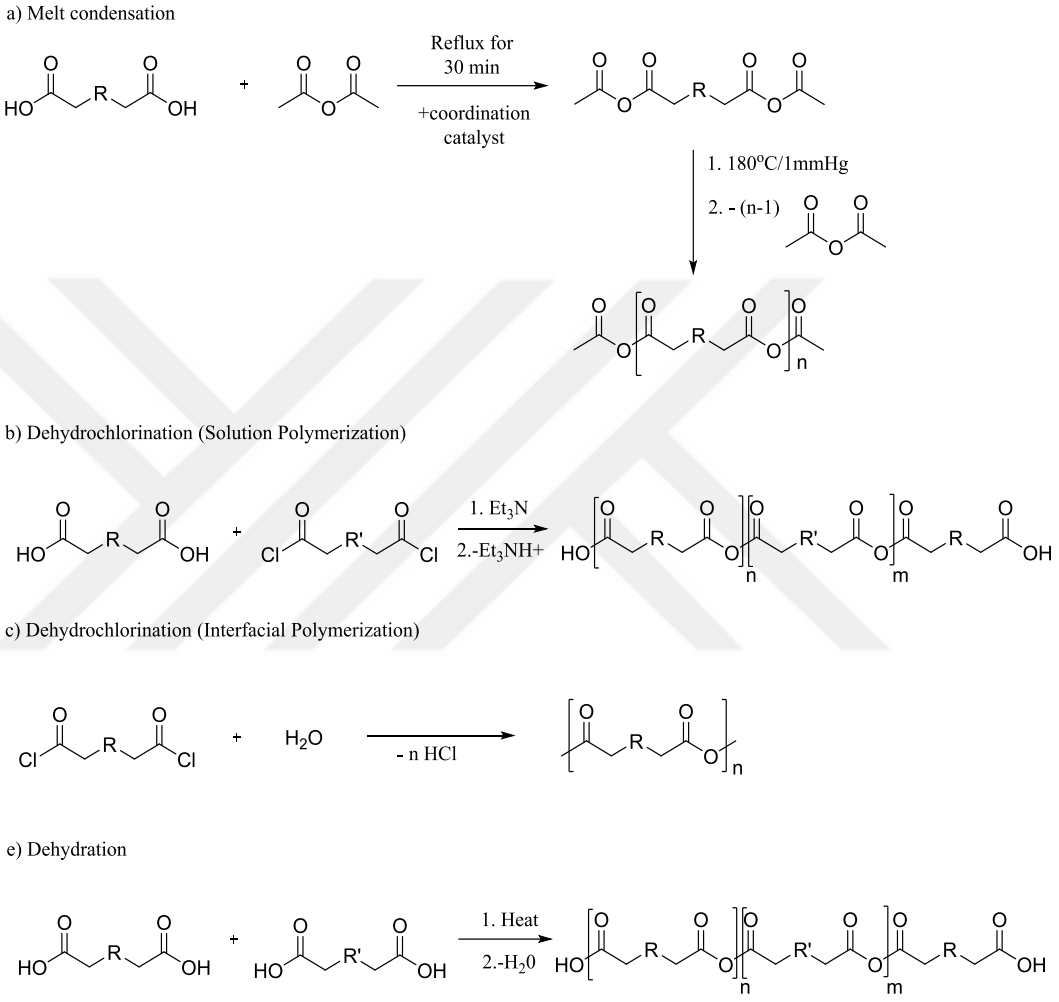


Figure 1.15. General schemes for polyanhydride condensation polymerizations [24].

Polycondensation method has been commonly used in synthesis of polyanhydrides. In fact, polycondensation reaction has a number of requirements such as organic solvents, halogenated compounds, high temperatures or low pressures. As acid scavengers, some bases such as pyridine and triethylamine are used when carrying out a condensation reactions of acid chlorides. Polycondensation reactions can be performed by means of various ways such as melt polycondensation, dehydrochlorination, interfacial polycondensation and

dehydrative coupling [8], [24]. In Figure 1.15., there are examples of condensation reactions of polyanhydrides.

However, in order to incorporate the useful degradation properties of polyanhydrides and to make the mechanical properties of polyesters better, poly(ester-anhydrides) have been synthesized for different kinds of applications such as pharmaceutical ingredients, biomaterials and tissue engineering [26]. Therefore, these poly(ester-anhydrides) may be useful for different application areas with the help of changing the ratio of anhydride or ester linkages in the polymer backbones.

1.6. Solution Polymerization

Solution polymerization is a method that is generally used in industry. In fact, polymerization of monomer in an appropriate solvent is more advantageous compared to bulk polymerization. In solution polymerization, the solvent behaves like a diluent and helps the transfer of heat during the polymerization. In addition, since the viscosity is reduced, the reaction mixture can easily be mixed and homogenous in the solvent. On the other hand, it is important to choose a solvent used in the polymerization, because the needed reaction temperature depends on the boiling point of the solvent. Moreover, if there is a solvent removal problem, it is difficult to obtain a pure product from the solution polymerization. Finally, owing to the continuing chain transfer in the solvent, there is a restriction of molar mass of the polymers in solution polymerization [2], [10].

2. AIM OF THE STUDY

The aim of this study is to synthesize weatherable arylate ITR polyesters and poly(ester-anhydrides) that can be used in powder coating resins by using solution polymerization method in one step. In order to reach this goal, diacid chlorides which are terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were reacted with the resorcinol in the presence of triethyl amine (TEA). The effects of the diacid monomer ratios and end groups on the physical properties of the polyesters were investigated. Moreover, the anhydride linkage was aimed to obtain arylate ITR based poly(ester-anhydrides). The influences of different monomer ratios and the amount of catalyst TEA on the polymerization were investigated. Finally, both arylate ITR polyesters and poly(ester-anhydrides) were analyzed by using FTIR, DSC, NMR and GPC measurement techniques.

3. EXPERIMENTAL

3.1. Materials

Terephthaloyl dichloride and isophthaloyl dichloride with ~ 99% pure content were obtained from Aldrich. Resorcinol was obtained from Kordsa. Triethyl amine and dichloromethane were obtained from Merck and used as received.

3.2. Synthesis of Polyesters

3.2.1. Synthesis of Carboxylic Acid-Terminated ITR Polyesters

Terephthaloyl dichloride and isophthaloyl dichloride (0.0197 mole, 4.00 g) were mixed in different ratios in a five-necked reactor flask. (Table 3.1) As a solvent, dichloromethane (DCM) (30 mL) was used, and also condenser that provide water flow inside was set to the reaction system in order to prevent reduce the amount of DCM. Other two necks of the flask were closed by using the two different septa. In addition, DCM (12 mL) was added to the resorcinol (0.0193 mole, 2.12 g) that weighed into any small glass flask and mixed about approximately 2 minutes. After the addition of DCM to the resorcinol, triethylamine (TEA) (0.0386 mole, 5.38 mL) as a catalyst was added to the mixture and stirred. The resorcinol that completely dissolved in DCM and TEA was added to the diacid solution by means of additional funnel within 10 minutes. The molar ratio of diacid monomers to resorcinol was defined as 1.02 with the aim of obtaining carboxylic acid-terminated polyesters. And also, one more molar ratio such as 1.2 and the different amount of TEA were investigated during the period of hydroxyl-terminated polyesters syntheses. (Table 3.2) Polymerization reaction was performed in 60 minutes at 195 rpm and room temperature. When completing polymerization duration, the organic phase which obtained as polymer solution was extracted with the help of distilled water, 2M hydrochloric acid (HCl) solution, distilled water, sodium bicarbonate ($NaHCO_3$) (pH=8) solution and distilled

water respectively. After the extraction process, the organic phase was precipitated in the mixture compromising methanol and water (5:2 v/v).

It was obtained 3.14 g weight yield of white powder polyester from iso/terephthaloyl dichlorides (4.00 g) and resorcinol (2.12 g) monomers at the end of the condensation polymerization for ITR-11. The percentage of conversion was calculated as 58%.

Table 3.1. Carboxylic acid terminated ITR polyesters with different diacid ratios.

Samples	Alcohol/ Diacids (mole)	Diacids feed ratios (IPC:TPC) (mole)
ITR-1	1.02	100:0
ITR-2	1.02	95:5
ITR-3	1.02	90:10
ITR-4	1.02	85:15
ITR-5	1.02	80:20
ITR-6	1.02	75:25
ITR-7	1.02	70:30
ITR-8	1.02	65:35
ITR-9	1.02	60:40
ITR-10	1.02	55:45
ITR-11	1.02	50:50
ITR-12	1.02	45:55
ITR-13	1.02	40:60
ITR-14	1.02	35:65
ITR-15	1.02	30:70
ITR-16	1.02	25:75
ITR-17	1.02	20:80
ITR-18	1.02	15:85
ITR-19	1.02	10:90
ITR-20	1.02	5:95
ITR-21	1.02	0:100

Table 3.2. Carboxylic acid terminated ITR polyesters with different the ratio of alcohol to diacids and different amount of TEA.

Samples	Diacid/ Alcohol (mole)	Diacids feed ratios (IPC:TPC) (mole)	total mole of diacids	mole of alcohol	mole of TEA
ITR-11	1.02	50:50	0.0197	0.0193	0.0386
ITR-22	1.20	50:50	0.0197	0.0164	0.0328
ITR-23	1.02	50:50	0.0197	0.0193	0.0492
ITR-24	1.02	50:50	0.0197	0.0193	0.0414

3.2.2. Synthesis of Resorcinol-Terminated ITR Polyesters

Terephthaloyl dichloride (TPC) and isophthaloyl dichloride (IPC) (0.0197 mole, 4.00 g) were mixed in different ratios in a five-necked reactor flask. (Table 3.4) As a solvent, dichloromethane (DCM) (30mL) was used, and also condenser that provide water flow inside was set to the reaction system in order to prevent reduce the amount of DCM. Other two necks of the flask were closed by using the two different septa. In addition, DCM (12 mL) was added to the resorcinol (0.0207 mole, 2.28 g) that weighed into any small glass flask and mixed about approximately 2 minutes. After the addition of DCM to the resorcinol, triethylamine (TEA) (0.0394 mole, 5.49 mL) as a catalyst was added to the mixture and stirred. The resorcinol that completely dissolved in DCM and TEA was added to the diacid solution by means of additional funnel within 10 minutes. The molar ratio of resorcinol to total diacid monomers was defined as 1.05 with the aim of obtaining resorcinol-terminated polyesters. And also, different molar ratio such as 1.2 was investigated during the period of resorcinol-terminated polyesters syntheses as shown in Table 3.5. Polymerization reaction was performed in 60 minutes at 195 rpm and room temperature. When completed polymerization duration, the organic phase which obtained as polymer solution was extracted with the help of distilled water, 2M hydrochloric acid (HCl) solution, distilled water, sodium bicarbonate ($NaHCO_3$) (pH=8) solution and distilled water respectively. After the extraction process, the organic phase was precipitated in the mixture compromising methanol and water (5:2 v/v).

Table 3.3. Resorcinol terminated ITR polyesters with different ratio of diacid to alcohol and the amount of TEA.

Samples	Diacid/ Alcohol (mole)	Diacids feed ratios (IPC:TPC) (mole)
ITR-25	1.05	100:0
ITR-26	1.05	95:5
ITR-27	1.05	90:10
ITR-28	1.05	85:15
ITR-29	1.05	80:20
ITR-30	1.05	75:25
ITR-31	1.05	70:30
ITR-32	1.05	65:35
ITR-33	1.05	60:40
ITR-34	1.05	55:45
ITR-35	1.05	50:50
ITR-36	1.05	45:55
ITR-37	1.05	40:60
ITR-38	1.05	35:65
ITR-39	1.05	30:70
ITR-40	1.05	25:75
ITR-41	1.05	20:80
ITR-42	1.05	15:85
ITR-43	1.05	10:90
ITR-44	1.05	5:95
ITR-45	1.05	0:100

Table 3.4. Resorcinol terminated ITR polyesters with different the ratio of alcohol to diacids and different amount of TEA.

Samples	Monomer feed ratios		total mole of diacids	mole of alcohol	mole of TEA
	Alcohol/ Acid	molar ratio of IPC:TPC			
ITR-35	1.05	50:50	0.0197	0.0207	0.0394
ITR-46	1.20	50:50	0.0197	0.0236	0.0394

3.3.3. Synthesis of Poly(ester-anhydrides)

Terephthaloyl dichloride and isophthaloyl dichloride (0.0363 mole, 7.37 g) were mixed in different ratios in a five-necked reactor flask. (Table 3.6) As a solvent, dichloromethane (DCM) (36 mL) was used, and also condenser that provide water flow inside was set to the reaction system in order to prevent reduce the amount of DCM. Other two necks of the flask were closed by using the two different septa. Triethyl amine (TEA) (0.00363 mole, 0.500 mL) and dichloromethane (DCM) (11.1 mL) was stirred about 2 minutes in another glass flask. This solution was added to the diacid mixture within 10 minutes with the help of additional funnel. At the same time, resorcinol (0.0303 mole, 3.33 g) was mixed with the DCM (11.1 mL) and then TEA (0.0650 mole, 8.85 mL). After addition of the mixture of TEA and DCM, distilled water (130 μl) was added to the solution as gradually (two times 65.0 μl). Thereafter, the resorcinol that completely dissolved in DCM and TEA was added to the diacid solution by means of additional funnel within 10 minutes. Polymerization reaction was performed in 60 minutes at 195 rpm and room temperature. When completing polymerization duration, the organic phase which obtained as polymer solution was extracted with the help of distilled water, 2M hydrochloric acid (HCl) solution, distilled water, sodium bicarbonate ($NaHCO_3$) (pH=8) solution and distilled water respectively. After the extraction process, the organic phase was precipitated in the mixture compromising methanol and water (5:2 v/v).

It was obtained 6.23 g weight yield of white powder polyester from iso/terephthaloyl dichlorides (7.37 g) and resorcinol (3.33 g) monomers at the end of the condensation polymerization for ITR-36. The percentage of conversion was calculated as 58%.

Table 3.5. Poly(ester-anhydrides) that contain different amount of TEA and different diacid to alcohol ratio.

Samples	**Diacid/ Alcohol (mole)**	**Diacids feed ratios (IPC:TPC) (mole)**	**TEA (1) (mL)**	**TEA (2) (mL)**	**water (μL)**
ITR-A-1	1.2	50:50	0.50	8.85	65
ITR-A-2	1.20	50:50	0.86	8.85	65
ITR-A-3	1.02	50:50	0.50	8.85	65

3.3.3.1. Anhydride test and hydrolysis process for poly(esteranhydrides). First of all, 0.10 g sample was dissolved in 6 mL DCM and checked the pH value of organic phase (pH 3). After that, 3 drops of 2M NaOH base solution was added to the sample and observed that pH value was about 10. And then, 4 drops of diisobutyl amine was added (pH 7). Finally, 2.5 mL of 2M HCl acid solution added immadiately. The pH value of the aqeous phase was about 4. After extraction of water, the solvent in the organic phase was evaporated by using rotary evaporator.

Secondly, in hydrolysis, 0.20 g sample was dissolved in 12 mL DCM solvent. The pH value of polymer in the solvent was about 5. And then, 3 drops of 2M NaOH base solution was added to the polymer. (pH 10) After mixing the polymer with NaOH, 15 mL distilled water was added to the polymer solution and stirred the mixture for 2 hours.

3.3. Analysis

3.3.1. 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.

3.3.2. NMR Analysis

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

3.3.3. Gel Permeation Chromatography (GPC) Analysis

Viscotek VE2001 GPC instrument was used for the measurements. Samples were prepared by dissolving 4 mg of polyester samples in 1 mL THF and 3 mg of poly(ester-anhydrides) samples in 1.5 mL the mixture of ODCB/HFIP/THF.

3.3.4. Differential Scanning Calorimetry (DSC) Analysis

The samples were analyzed by DSC with the two different method for various polyesters and poly(ester-anhydrides) in Table 3.3. and 3.4.

Table 3.6. DSC run method. (1)

Initial T (ºC)	Final T (ºC)	Rate (ºC /min)	Hold time (min)
-20	280	10	2
280	-20	10	2
-20	280	10	2

Table 3.7. DSC run method. (2)

Initial T (ºC)	Final T (ºC)	Rate (ºC /min)	Hold time (min)
-20	300	10	2
300	-20	10	2
-20	300	10	2

4. RESULTS AND DISCUSSION

The main goal of the present work was the syntheses of polyesters using resorcinol, iso- and terephthaloyl chloride in solution. The literature contains a lot of information on the syntheses of such polymers, however, almost all of them are fixed to a composition where the iso/tere phthaloyl chloride ratio is 1:1 and many of the process parameters are kept constant [27]. The reason for that, this ratio is the ratio directly obtained by the manufacturing process of the mentioned diacid chlorides, and therefore is commercially available in large industrial scale. Also, most of the polymers reported are -OH terminated since they were initially synthesized to be incorporated into the manufacturing process of BPA-polycarbonates during the phosgenation step. Therefore, our research was mostly focused on three main points.

(i) First of all, the carboxylic acid terminated ITR polyester containing 50:50 mole ratio of diacid monomers, IPC and TPC, were synthesized by the condensation polymerization with resorcinol. Under this title two main investigations were carried out. First, the effects of diacids to alcohol feed ratios together with the amount of TEA on the efficiency of polymerization were investigated. Second, the influence of different diacids mole ratios (IPC/TPC) on the properties of polyesters were examined.

(ii) Second, the syntheses of resorcinol terminated ITR polyesters were performed to compare their properties to the carboxylic acid terminated ITR polyesters. Similar to the above study various alcohol to diacid monomers and IPC/TPC mole ratios were used to obtain different resorcinol terminated ITR polyesters and their properties were analyzed.

(iii) The poly(ester-anhydrides) of ITR were obtained by using solution polymerization. The outcome of using different diacids to alcohol feed ratios and the amount of TEA were investigated.

During the characterizations of the synthesized polyesters, a major solubility problem was encountered which seemed to depend on the IPC/TPC ratio and thus the polymer structure. As a side work, factors governing the solubility and other properties were investigated. Thus, the first three subject will be discussed in these orders, and our findings about the solubility and other physical properties will be discussed at each section.

4.1. Syntheses and Characterization of Carboxylic Acid-Terminated ITR Polyesters

As a first step in this study, the synthesis of carboxylic acid terminated ITR polyesters were targeted in dichloromethane (Figure 4.1). The IPC/TPC mole ratio was kept constant at 1:1. The molar ratio of acid chlorides to alcohol was tuned as 1.02.

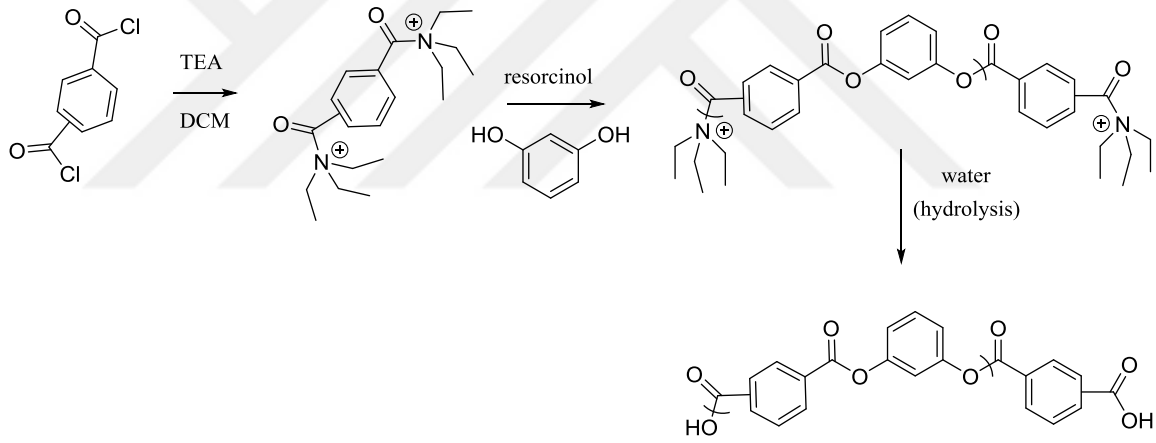


Figure 4.1. Polymerization mechanism of carboxylic acid terminated ITR polyesters.

ITR polyesters that were synthesized are shown in Table 4.1. The effect of diacid chloride to resorcinol ratio was investigated first. The syntheses of the polyesters which are ITR-11 and ITR-22 were carried out by two different ratios of acid to alcohol. Theoretically, when the molar acid to alcohol monomer ratio is close to 1, polymers with higher M_n values are obtained [28]. Thus, as expected, ITR-11 (1.02 feed ratio) has higher M_n and T_g values compared to ITR-22 (1.20 feed ratio).

Table 4.1. The overall results of carboxylic acid terminated ITR polyesters.

Samples	Monomer feed ratios		M_n (g/mole)	M_w (g/mole)	PDI	T_g (°C)
	Acid/Alcohol	molar ratio of IPC:TPC				
ITR-11	1.02	50:50	9544	15023	1.573	139
ITR-22	1.20	50:50	2214	4063	1.835	103
ITR-23	1.02	50:50	6178	8110	1.313	123.6
ITR-24	1.02	50:50	6560	8677	1.323	125.9

Second, the effect of TEA amount was examined. It is important to state that resorcinol is not soluble in DCM alone, however when TEA is added, which contains three relatively hydrophobic ethyl groups, it becomes soluble most probably due to the complexation to resorcinol -OH groups (slightly acidic) through TEA's nitrogen (slightly basic). One equivalent TEA, used in ITR-11 and ITR-22 experiments, was found to be the minimum amount necessary to dissolve the resorcinol in DCM efficiently. Other polyesters (ITR-23 and 24) were synthesized by using 1.25 and 1.05 equivalent TEA with respect to diacid chlorides.

Triethylamine (TEA) serves as a catalyst and also an acid scavenger in the condensation reactions. It is known to enhance the reaction rate through the formation of acyl ammonium intermediates [5]. One should note that a very special equilibrium must be present for the reaction to occur. When the reaction condition is too acidic, TEA can be protonated which leads almost impossible catalytic activity. In contrast, too basic conditions may open the possibility of acid chloride hydrolysis under slightly humid conditions. At the end of the syntheses of ITR-11 and ITR-22 polyesters, it was observed that the aqueous phase of the polyesters was acidic (pH=6) when performing the extraction process by using distilled water. Whereas, the pH value of aqueous phase was about 9-10 for the trials of ITR-23 and ITR-24.

The ^{1}H-NMR spectrum belonging to ITR-11 is presented in Figure 4.2. With the help of precipitation and extraction methods, there are almost no monomer peaks in the NMR spectrum. Thus, it is apparent that the monomers used in the synthesis of the polyesters were

considerably reactive through the reaction to form the intended polyester. While ITR-11 and ITR-22 were soluble deuterated chloroform ($CDCl_3$) which is the common solvent used for NMR analysis, there was a solubility problem with ITR-23, 24, and 25. Hence, the mixture comprising d-chloroform (0.5 mL) ($CDCl_3$) and 10% trifluoro acetic acid (0.05 mL) (TFA) was used for these polyesters as NMR solvent.

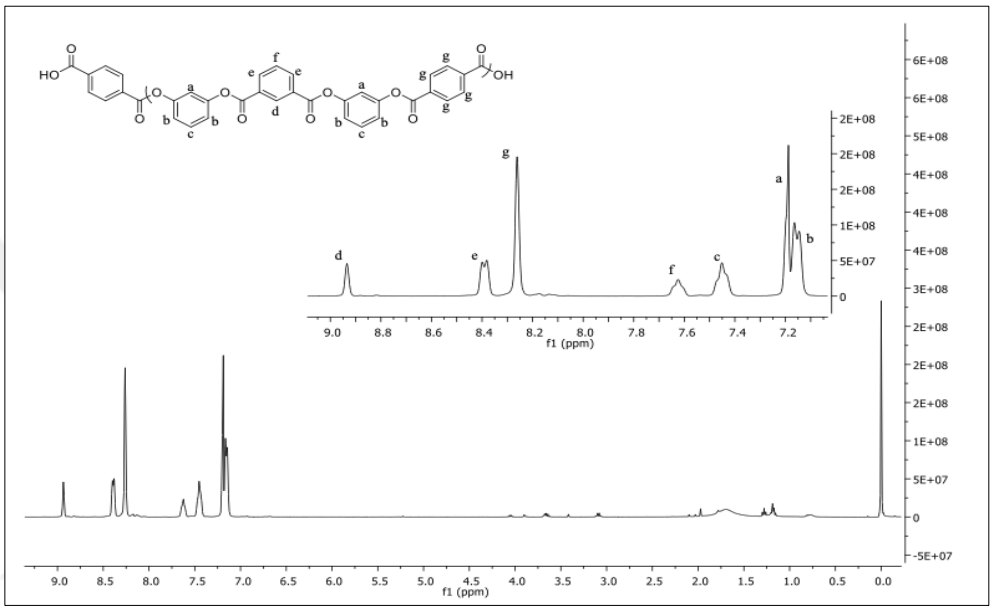


Figure 4.2. ^{1}H-NMR spectrum of ITR-11.

Molecular weight determinations of polyesters were obtained by means of gel permeation chromatography (GPC). As an alternative, molecular weights and repeating units of polymers can be calculated *via* the end group analysis from their ^{1}H-NMR spectra [29]. Nonetheless, when the ^{1}H-NMR spectra of carboxylic acid terminated ITR polyesters were analyzed, no peak belonging to carboxylic acid end groups could be resolved. The GPC result of ITR-11 polyester is shown in Figure 4.3 as an example for molecular weight determination.

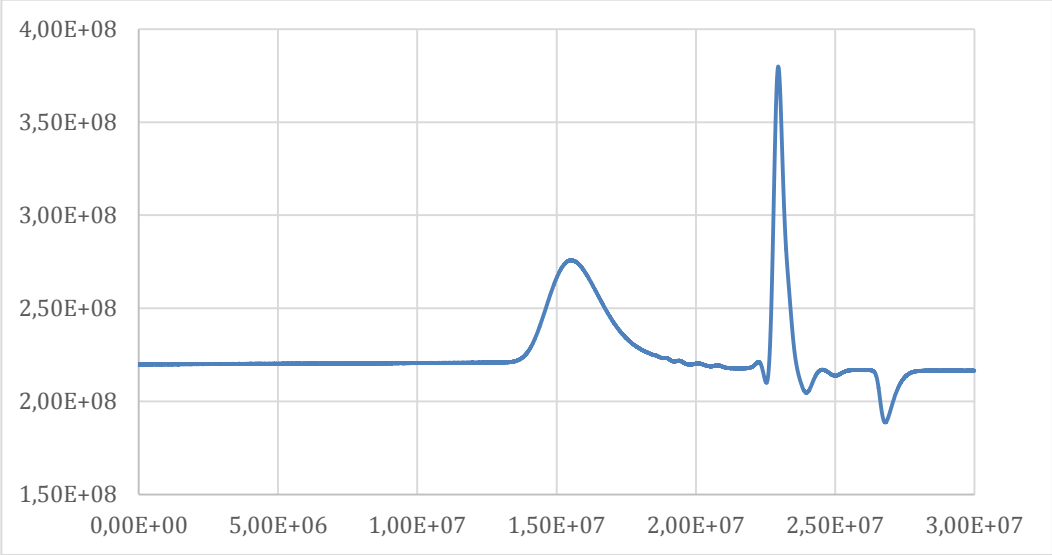


Figure 4.3. GPC result of ITR-11.

Furthermore, all polyesters were also analyzed by DSC to determine their thermal transition temperatures. As an example, DSC thermogram of ITR-11 is shown in Figure 4.4. In the thermogram, there is no melting and crystallization temperatures. It can be concluded that this polyester behaves like an amorphous polymer.

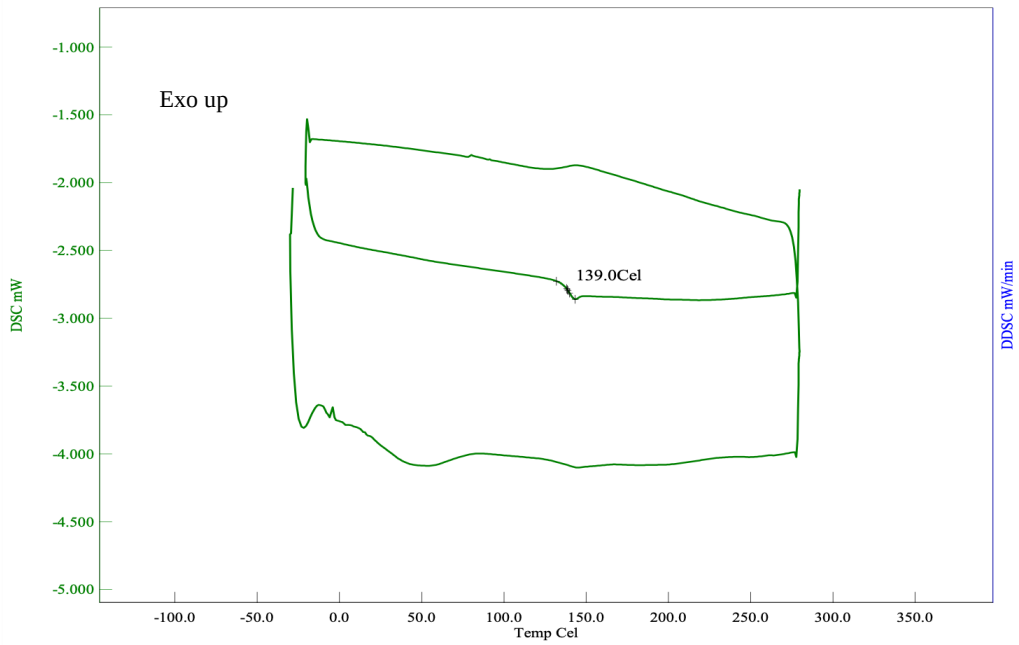


Figure 4.4. DSC thermogram of ITR-11.

The relationship between the T_g and M_n values of the polyesters is shown in Figure 4.5.

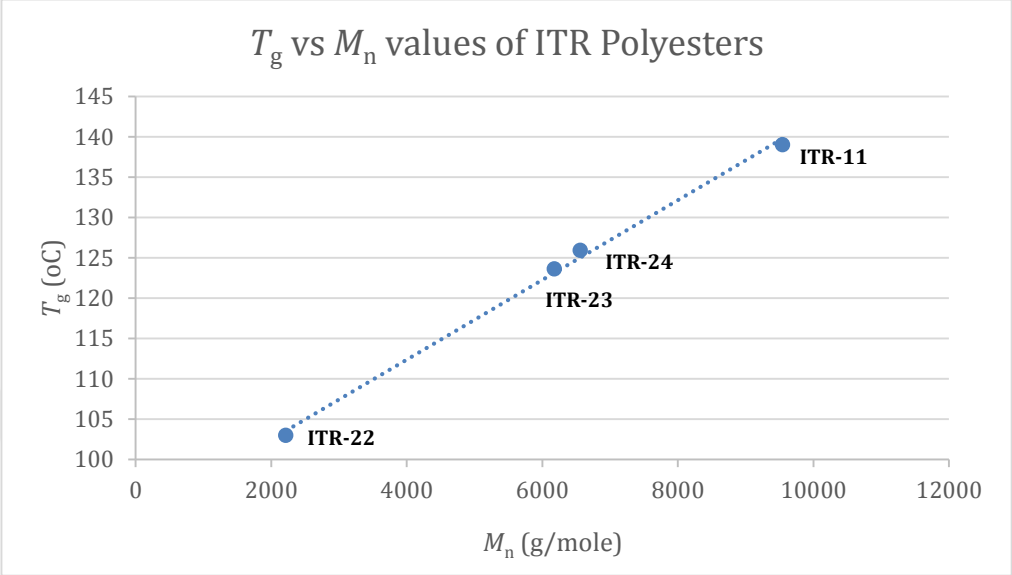


Figure 4.5. The T_g vs M_n values of carboxylic acid terminated ITR polyesters.

4.1.1. Carboxylic Acid-Terminated ITR Polyesters with Different IPC/TPC Ratios

Carboxyl terminated ITR polyesters with varying *iso/tere* diacid chloride ratios were synthesized and their properties were investigated. The syntheses were performed by using the optimized amount of TEA and the diacid chloride/alcohol ratio was kept constant at 1.02. The main purpose for the synthesis of these polyesters was to observe the influence of the IPC/TPC ratio, thus the polymer structure on the physical properties.

As seen in Table 4.2, the observed ratios of IPC/TPC in the polymers by NMR are relatively close to their feed ratios. Polyesters with feed ratios close to 1/1 could be dissolved mostly in pure $CHCl_3$, however 10% TFA was added to $CHCl_3$ in order to solubilize the other polyesters which have diacid feed ratios higher than 85% for IPC or 60% for TPC.

Table 4.2. ITR Polymers synthesized and their NMR, DSC and GPC analyses.

Samples	Monomer feed ratios	NMR analysis	T_g (ºC)	M_n (g/mole)	M_w (g/mole)	PDI
	molar ratio of IPC:TPC	observed ratio of IPC:TPC				
ITR-1	100:0	-	129.2	n/a	n/a	n/a
ITR-2	95:5	94:6	130.0	n/a	n/a	n/a
ITR-3	90:10	88:11	126.7	n/a	n/a	n/a
ITR-4	85:15	83:17	131.0	n/a	n/a	n/a
ITR-5	80:20	78:22	135.6	n/a	n/a	n/a
ITR-6	75:25	73:27	135.0	n/a	n/a	n/a
ITR-7	70:30	68:32	131.8	5869	9144	1.557
ITR-8	65:35	60:40	122.9	5421	9580	1.767
ITR-9	60:40	55:44	130.2	8552	13734	1.606
ITR-10	55:45	50:50	128.9	7753	12592	1.624
ITR-11	50:50	48:52	139.0	9544	15023	1.573
ITR-12	45:55	40:60	135.2	9524	14751	1.549
ITR-13	40:60	36:64	127.7	n/a	n/a	n/a
ITR-14	35:65	31:69	135.9	n/a	n/a	n/a
ITR-15	30:70	36:64	125.9	n/a	n/a	n/a
ITR-16	25:75	26:74	127.5	n/a	n/a	n/a
ITR-17	20:80	20:80	136.2	n/a	n/a	n/a
ITR-18	15:85	14:86	131.7	n/a	n/a	n/a
ITR-19	10:90	9:91	-	n/a	n/a	n/a
ITR-20	5:95	5:95	-	n/a	n/a	n/a
ITR-21	0:100	-	-	n/a	n/a	n/a

**Acid/alcohol feed ratio is 1.02 for all carboxylic acid terminated ITR polyesters.*

Thermal transition temperatures and molecular weights of the polyesters are important points to show the relationship between polymer structure and physical properties. Considering the different substitution patterns varying IPC/TPC ratio should in principle have different packings and alignments due to 1,3 and 1,4 substitutions, respectively.

The T_g of the polyesters were found around 125 ºC and higher, depending on the molecular weight and the *iso/tere* ratio. However, not all polyesters showed T_g values in the first heating cycle, the polyesters with high amount of TPC and IPC had only crystalline melting curves in the first cycle. Detailed thermal analyses of the polyesters will be demonstrated in the Table 4.3 and discussed in the following sections.

When M_n values of the polyesters are compared (Table 4.2), it can be seen that the polyesters with TPC/IPC feed ratios close to 1/1 have higher M_n. GPC measurements were not done on all polyester samples, because some polyesters were partially soluble in tetrahydrofuran (THF) and hexafluoro-2-propanol (HFIP) solvents that are used for GPC analysis. The partial solubility was observed in two types of polymers; the ones rich in IPC or TPC. For TPC excess polyesters, this is most probably related to the close packing of polymer chains due to the more symmetrical nature of 1,4 substitution. One should also note that the polyesters formed are fully aromatic. For polyesters rich in IPC, the partial solubility is observed most likely due to the possible cyclic oligomers which are known to have very high crystallinity and poor solubility [30]. The cyclics are formed mostly from the condensation reaction of 1,3 disubstituted IPC and resorcinol.

The existence of cyclic oligomers in the polyesters with higher IPC ratio is also somewhat detected in the GPC results, but with limited resolution (Figures 4.6 and 4.7). In the literature, the sequential small peaks at the low molecular regions are often considered as a proof for cyclic oligomers when such structures are possible [31]. Further efforts on the analysis of the cyclic structures is ongoing with GPC systems that have low molecular weight columns.

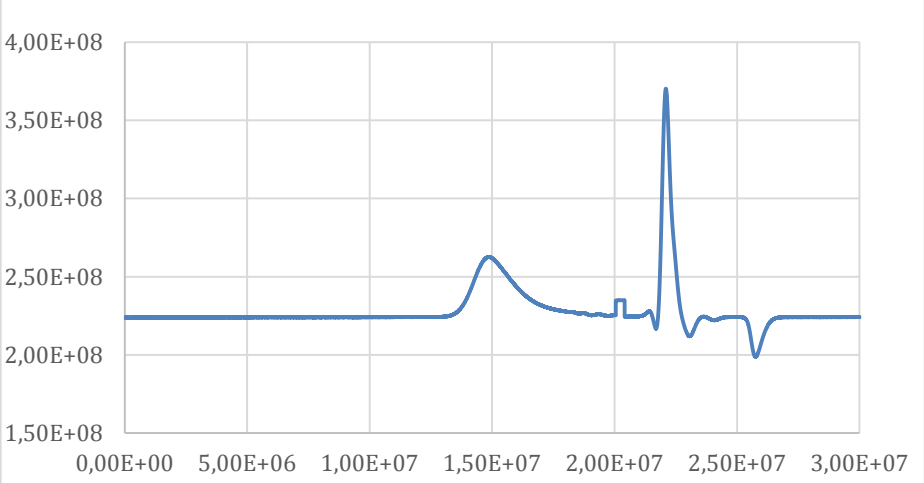


Figure 4.6. GPC analysis result of ITR-7.

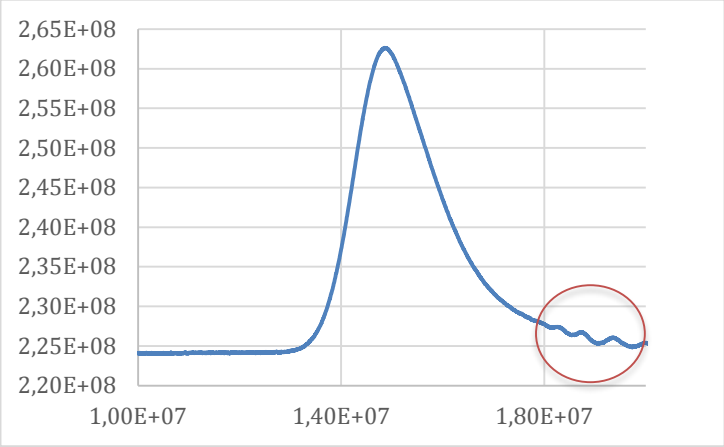


Figure 4.7. GPC analysis result of ITR-7.

The presence of cyclic oligomers is also indirectly observed in the DSC analyses of polyesters. The polyesters with higher IPC ratio (the range between 85% to 100%) have both T_m and T_g values. As mentioned in the introduction part, cyclic oligomers have high melting temperatures [12]. Therefore, it was thought that the observation of T_m is indicative of the presence of cyclic oligomers in IPC rich polyesters (Table 4.3).

Table 4.3. DSC results of carboxylic acid terminated ITR polyesters rich in IPC or TPC.

Samples	**molar feed ratio of IPC:TPC**	**1st cycle (heating)**		**1st cycle (cooling)**	**2nd cycle (heating)**	
		***T*g (ºC)**	***T*m (ºC)**	***T*c (ºC)**	***T*g (ºC)**	***T*m (ºC)**
ITR-1	100:0	-	217.1	_	129.2	-
ITR-2	95:5	-	215.9	_	130.0	-
ITR-3	90:10	-	212.5	_	126.7	-
ITR-4	85:15	-	208.0	_	131.0	-
ITR-17	20:80	-	248.4	_	136.2	-
ITR-18	15:85	-	263.1	_	131.7	265.0
ITR-19	10:90	-	271.6	224.3	-	273.2
ITR-20	5:95	-	277.1	265.9	-	277.0
ITR-21	0:100	-	297.6	272.8	-	295.5

**Those samples are insoluble in THF for GPC analysis.*

In the polyesters with moderately higher TPC ratios (80% and 85%) both T_g and T_m can be detected in the first or second cycle. However, the polyesters with 90%, 95% and 100% TPC have only melting and crystallization temperatures. It is most likely that these polyesters are almost fully crystalline due to the better and stronger packing caused by the more symmetrical 1,4 disubstituted TPC monomer and the full aromaticity of the polyester. (Table 4.3)

The synthesized polyesters were analyzed by NMR. The polyesters that are not soluble in $CDCl_3$ were dissolved in the $CDCl_3$ containing 10% (v/v) TFA. On the other hand, the presence of the TFA in the $CDCl_3$ affected the result. For example, as seen in the Figure 4.8, the ^{1}H-NMR spectrum of ITR-17 (20 IPC:80 TPC), the peak of the carboxylic acid proton of TFA was observed more intensely in the spectrum. Thus, the acidic hydrogen peaks belonging to the polymer chain ends were not detectable.

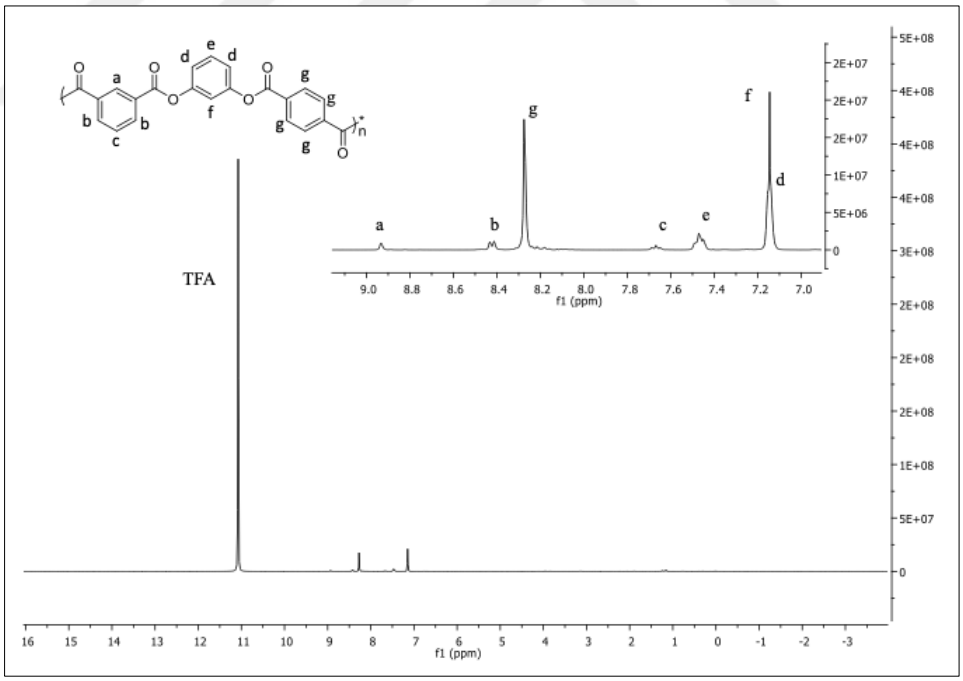


Figure 4.8. The ^{1}H-NMR spectrum of ITR-17.

4.1.2. Photo-Fries Rearrangement of ITR polyesters

In order to observe the Photo-Fries rearrangement of ITR polyesters, a sample solution (ITR-22 in THF) was held under the UV-light for one hour. The characterization of ITR-22 was performed by using UV-VIS spectrophotometer.

As seen in Figure 4.9, once the sample was exposed to UV-irradiation, its absorption peaks shifted towards longer wavelength region, with a bimodal distribution where a tail in the visible region (380 to 450 nm) is observed. This is a typical spectrum for hydroxyl-benzophenone type of UV-absorbers. Thus, results indicate that ITR underwent Photo-Fries rearrangement where the formation of hydroxyl-benzophenones was proven.

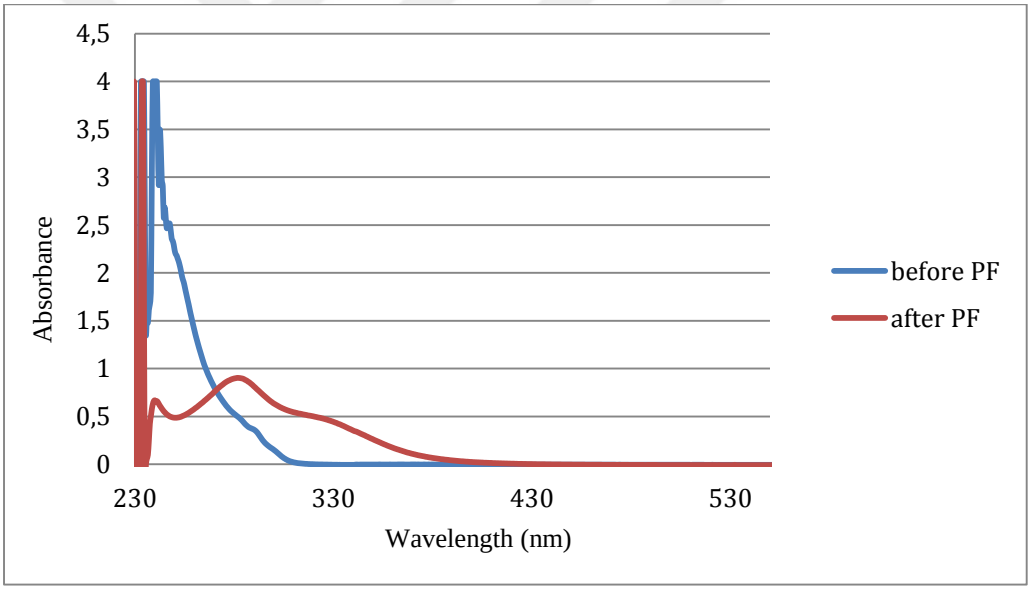


Figure 4.9. UV/VIS spectrum of ITR-22 polyester before and after Photo-Fries rearrangement.

4.2. Syntheses and Characterization of Resorcinol-Terminated ITR Polyesters

In this part, the syntheses of resorcinol-terminated polyesters (Figure 4.10) by various diacid chloride ratios were performed and their properties against the carboxylic acid terminated polyesters were compared. Firstly, the molar ratio of alcohol to diacid was

optimized (1.05) to get resorcinol-terminated polyesters (Table 4.4). And then, the TPC/IPC ratio was altered.

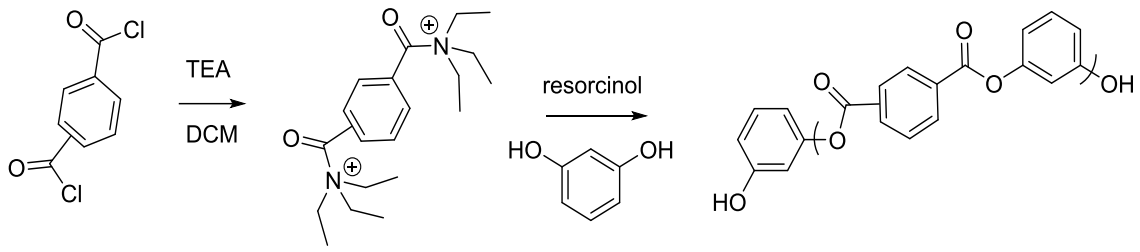


Figure 4.10. The reaction mechanism of resorcinol terminated polyesters.

Table 4.4. The overall results of resorcinol terminated ITR polyesters.

Samples	**Monomer feed ratios**		M_n **(g/mole)**	M_w **(g/mole)**	**PDI**	T_g **(°C)**
	Alcohol/ Acid	**molar ratio of IPC:TPC**				
ITR-35	1.05	50:50	6354	10140	1.596	128.1
ITR-46	1.20	50:50	4423	7779	1.759	118.9

In Figure 4.11, there is ^{1}H NMR spectrum of ITR-35 polyester. Similar to ITR-11 carboxylic acid terminated ITR polyester, the protons belonging to the polyester were assigned in the spectrum. However, end group analysis from ^{1}H NMR spectrum was not possible for resorcinol terminated polyesters. Protons on the resorcinol end groups were not detectable by either ^{1}H or ^{13}C NMR. Therefore, indirect M_n calculations could not be carried out using the NMR techniques.

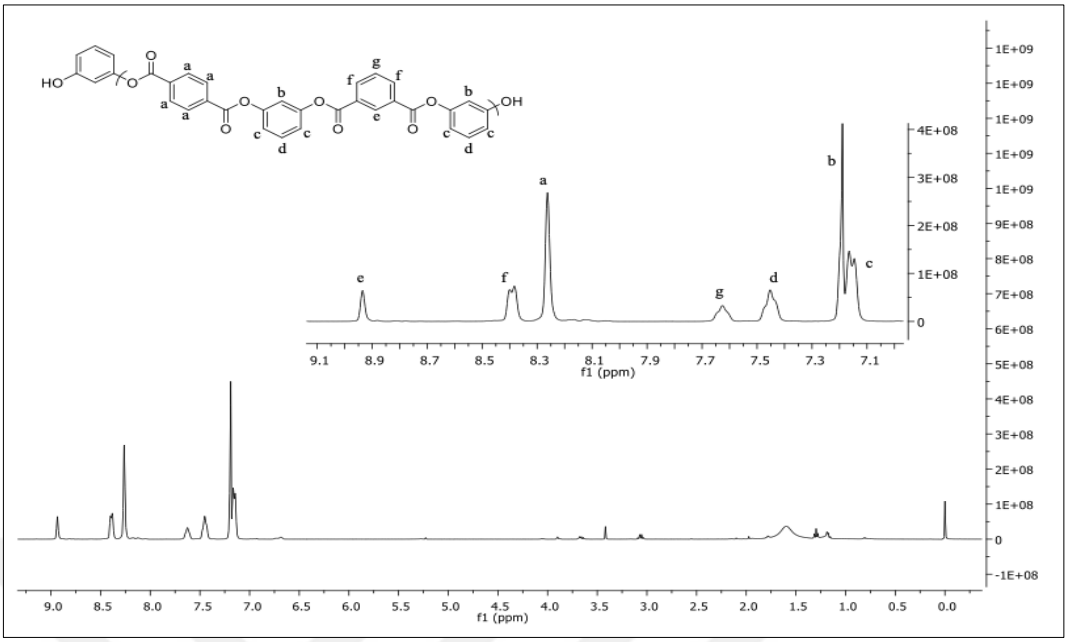


Figure 4.11. ^{1}H NMR spectrum of ITR-35.

Thus, molecular weight measurements were carried out by GPC analysis when proper solubility was achieved (Figure 4.12, Table 4.5).

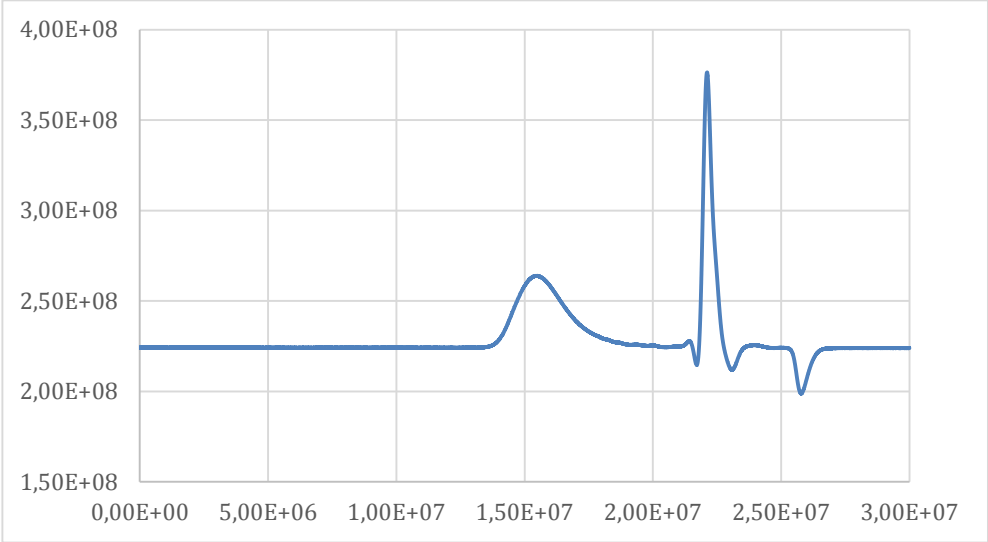


Figure 4.12. GPC analysis result of ITR-35.

As mentioned in section 4.1, thermal transition temperatures were analyzed by using DSC method. For example, ITR-35 polyester shows only T_g value rather than the melting or crystallization temperatures (Figure 4.13). This shows that when IPC and TPC are equimolar, the resulting ITR shows more amorphous behavior.

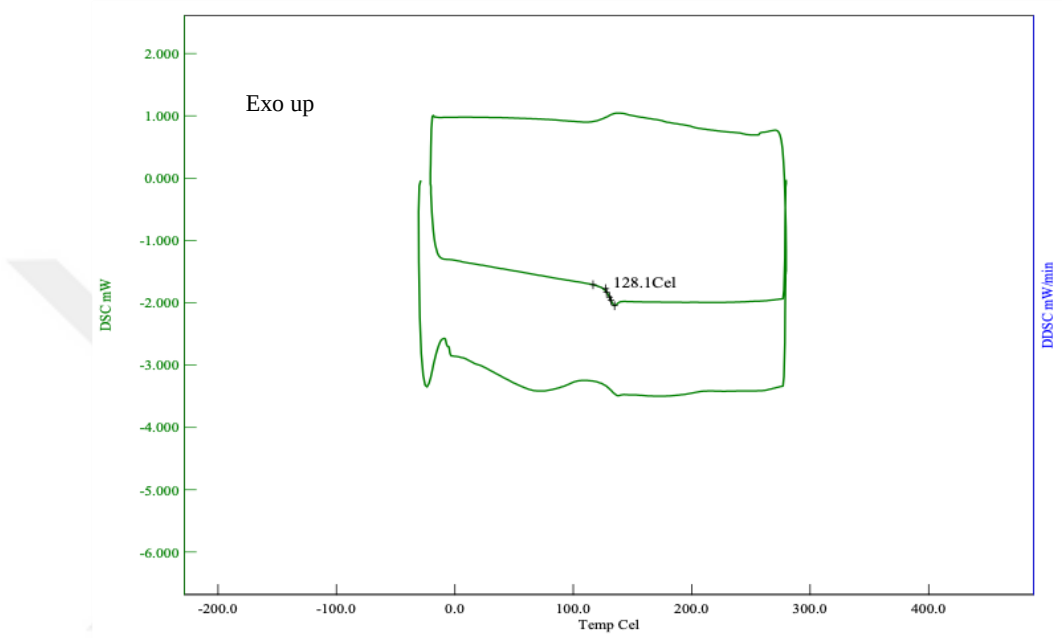


Figure 4.13. DSC thermogram of ITR-35.

4.2.1. Resorcinol-terminated ITR Polyesters with Different IPC/TPC Ratios

Resorcinol terminated ITR polyesters with various *iso/tere* diacid chloride ratios were synthesized and their properties were investigated.

Molar feed ratios of diacid chlorides were compared against the observed ratios in the ^{1}H-NMR spectra (Table 4.5). The observed ratios were close to the feed ratios. As in the case of carboxylic acid terminated ITR polyesters, some of resorcinol-terminated ones were not soluble in $CHCl_3$. Likewise, the chloroform solvent mixture containing 10% TFA was used to dissolve polyesters with 60% and more TPC, or 80% and more IPC.

Table 4.5. ITR Polymers synthesized and their NMR, DSC and GPC analyses.

Samples	Monomer feed ratios	NMR analysis	T_g (°C)	M_n (g/mole)	M_w (g/mole)	PDI
	molar ratio of IPC:TPC	observed ratio of IPC:TPC				
ITR-25	100:0	-	127.6	n/a	n/a	n/a
ITR-26	95:5	93:7	133.4	n/a	n/a	n/a
ITR-27	90:10	89:11	134.5	n/a	n/a	n/a
ITR-28	85:15	84:16	131.9	n/a	n/a	n/a
ITR-29	80:20	75:25	123.5	n/a	n/a	n/a
ITR-30	75:25	73:27	125.7	n/a	n/a	n/a
ITR-31	70:30	69:31	127.7	6082	9505	1.563
ITR-32	65:35	63:37	128.7	6407	9859	1.539
ITR-33	60:40	58:42	132.8	7469	11611	1.554
ITR-34	55:45	53:47	123.6	5109	8165	1.598
ITR-35	50:50	47:53	128.1	6354	10140	1.596
ITR-36	45:55	43:57	120.8	3868	5809	1.502
ITR-37	40:60	38:62	135.7	n/a	n/a	n/a
ITR-38	35:65	32:68	135.8	n/a	n/a	n/a
ITR-39	30:70	28:72	133.6	n/a	n/a	n/a
ITR-40	25:75	24:76	134.8	n/a	n/a	n/a
ITR-41	20:80	18:82	134.0	n/a	n/a	n/a
ITR-42	15:85	14:86	133.3	n/a	n/a	n/a
ITR-43	10:90	8:92	132.5	n/a	n/a	n/a
ITR-44	5:95	6:94	-	n/a	n/a	n/a
ITR-45	0:100	-	-	n/a	n/a	n/a

**Alcohol/acid feed ratio is 1.05 for all resorcinol terminated ITR polyesters.*

The T_g and M_n, M_w and PDI values of synthesized resorcinol terminated polyesters with various diacid chloride monomer ratios are shown in Table 4.5.

As it is seen in Table 4.5, M_n values of some polyesters were not measured because these polyesters were not soluble in THF and HFIP due to their crystallinity as discussed earlier in section 4.1.1.

In the DSC results, T_g values were measured for all polyesters except those with high TPC (Table 4.5). On the other hand, some of the polyesters with higher ratio of IPC and TPC showed only T_m and T_c values which were attributed to the presence of cyclic oligomers (for IPC rich polyesters) and higher crystalline packing (for TPC rich polyesters).

When IPC or TPC ratios were increased in polyesters, they showed melting points in their DSC thermograms. Their melting temperatures are over 200 °C, as can be seen in Table 4.6. ITR-45 and ITR-46 polyesters have melting temperatures in both first and second heating cycles and they also have crystallization temperatures in their first cooling cycle.

Table 4.6. DSC results of resorcinol terminated ITR polyesters.

Samples	**molar feed ratio of IPC:TPC**	**1st cycle (heating)**		**1st cycle (cooling)**	**2nd cycle (heating)**	
		T_g (ºC)	**T_m (ºC)**	**T_c (ºC)**	**T_g (ºC)**	**T_m (ºC)**
ITR-26	100:0	-	237.2	-	127.6	-
ITR-27	95:5	-	216.5	-	133.4	-
ITR-28	90:10	-	209.1	-	134.5	-
ITR-29	85:15	-	206.6	-	131.9	-
ITR-41	20:80	-	255.7	-	134.0	-
ITR-42	15:85	-	263.3	-	133.3	-
ITR-43	10:90	-	275.0	-	132.5	275.9
ITR-44	5:95	-	283.8	228.7	-	284.8
ITR-45	0:100	-	296.7	267.7	-	296.5

**Those samples are insoluble in THF for GPC analysis.*

On the other hand, for the other resorcinol terminated polyesters (Appendix A), the lower melting temperatures, which were at around 130 ºC and 180 ºC, were observed in their first heating cycle. The reason for the existence of the melting temperatures belonging to these polyesters could be related to the crystallinity of short chains in the polymers. It was assumed that these crystalline domains melted in the first heating and then mixed with the long chains properly. Finally, these polyesters demonstrated T_g values in the second heating cycle.

4.3. Poly(ester-anhydrides)

The final step of this study was to synthesize ITR based poly(ester-anhydrides) with carboxylic acid terminal groups. The process and the proposed mechanism for the formation of polyester anhydride is given in Figure 4.14.

The process is very similar to the polyester process in terms of chemicals used, their role etc. The main difference is that, prior to the addition of resorcinol, a portion of the diacid chloride is mono-hydrolyzed to carboxylic acid which then react *in situ* with the excess diacid chloride present to form a dimeric diacid chloride anhydride. Thus, through the process, pH control is important since it affects the formation and the durability of the anhydride linkages formed. The partial hydrolysis of the acid chloride is achieved by adding a given amount of water in the presence of TEA, which acts as a catalyst and acid scavenger.

The synthesized poly(ester-anhydrides) are shown in Table 4.7. First, these products were synthesized to investigate the plausible effects of different molar ratio of diacids to resorcinol on the formation and degradation mechanisms of the poly(ester-anhydrides). Second, during the syntheses, samples taken from the reaction medium at specific time intervals were analyzed by FTIR. The amount of TEA added before the addition of water seemed the most influential factor and had to be optimized to get anhydride bonds in the polyesters. The amount was found to be around 0.16 equivalent w.r.t the acid chloride.

Table 4.7. The synthesized poly(ester-anhydrides).

Samples	**Diacid/ Alcohol (mole)**	**Diacids feed ratios (IPC:TPC) (mole)**	**TEA (1) (mole)**	**TEA (2) (mole)**	**water (mole)**
ITR-A-1	1.20	50:50	0.0036	0.063	0.0036
ITR-A-2	1.20	50:50	0.0062	0.063	0.0036
ITR-A-3	1.02	50:50	0.0036	0.063	0.0036

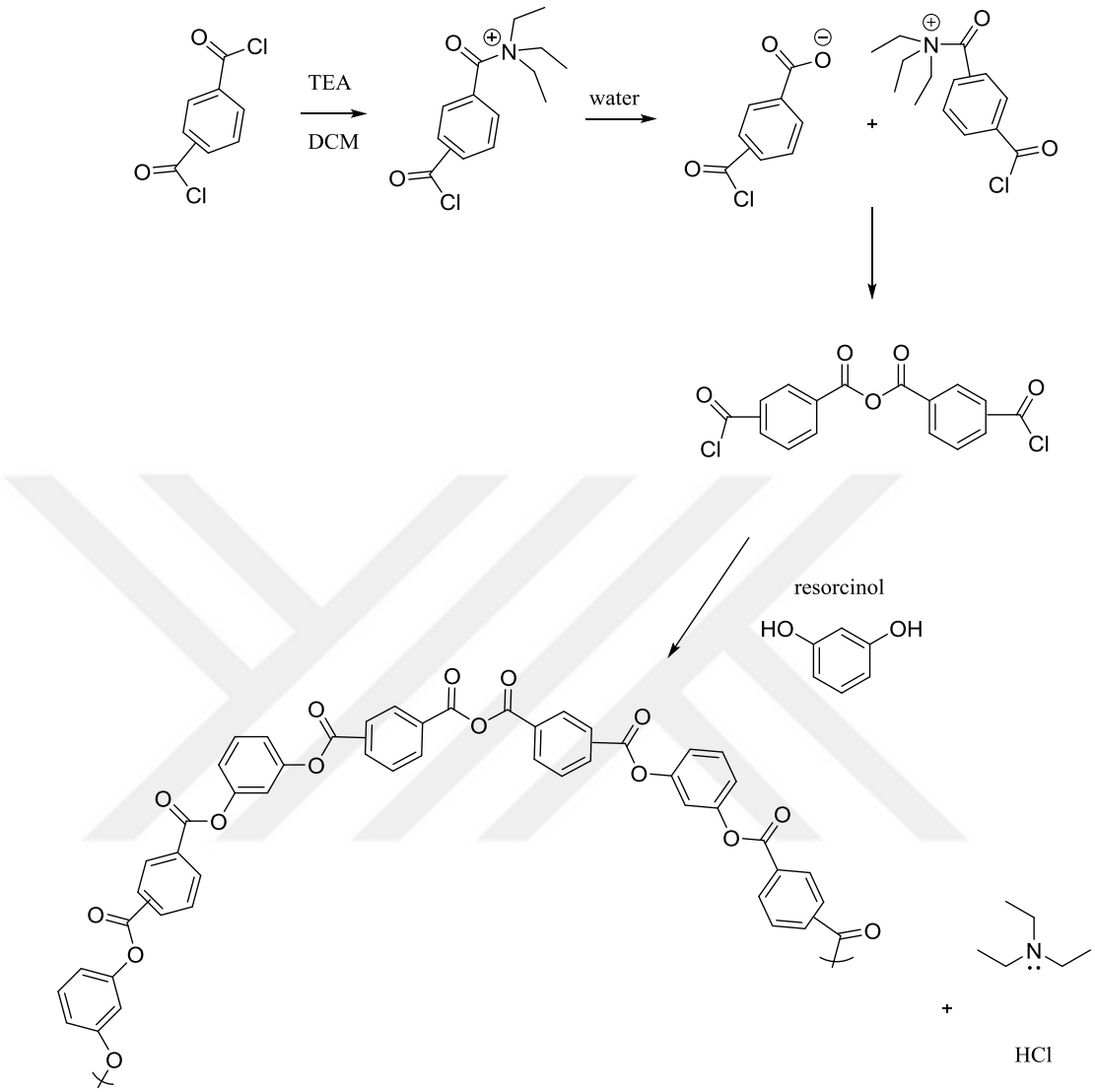


Figure 4.14. The proposed reaction mechanism of ITR poly(ester-anhydrides).

According to the literature, for anhydrides, there are two main carbonyl peaks that results from symmetric and asymmetric stretching in FTIR spectrum [32]. Based on this knowledge, the anhydride bond formation for each product was confirmed by using FTIR spectroscopy. As seen in Figure 4.15, the FTIR spectrum of the product, ITR-A-1 has anhydride characteristic peaks at 1794 cm^{-1} and 1732 cm^{-1}.

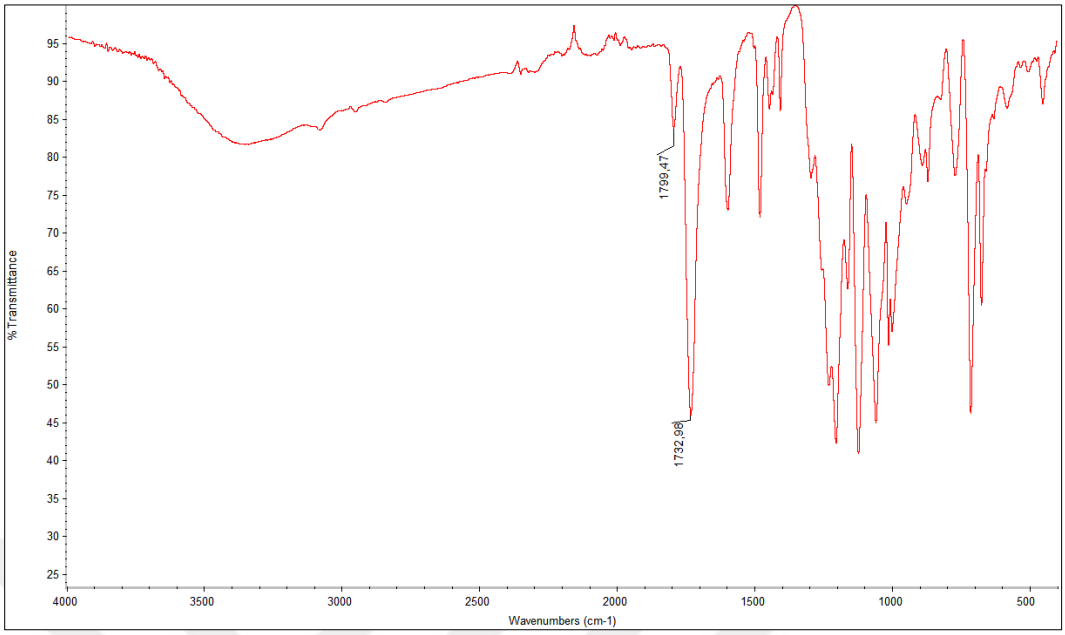


Figure 4.15. FTIR spectrum of ITR-A-1.

As explained in the experimental part, the anhydride test and hydrolyses were performed for each product to break the anhydride linkages in the poly(ester-anhydrides) backbones. In the anhydride test the polyester anhydrides are broken by a secondary amine (di-isobutyl amine) to produce carboxylic and amide terminated shorter polyesters. In the hydrolysis, the anhydrides are broken by hydrolysis with water to produce carboxylic acid terminated shorter polyester chains. The FTIR spectra associated with the three products, which are named as ITR-A-1, ITR-A-1 after hydrolysis and ITR-A-1 after anhydride test are compared in Figure 4.16. While ITR-A-1 product has two anhydride carbonyl peaks in the FTIR spectrum, there is just one peak belonging to carbonyl groups of polyesters after amine test or hydrolysis. Meanwhile, the obtained product after anhydride test has an amide peak at 1628 cm^{-1}. These results are important evidences for the presence of anhydride bond formations in the ITR-A-1.

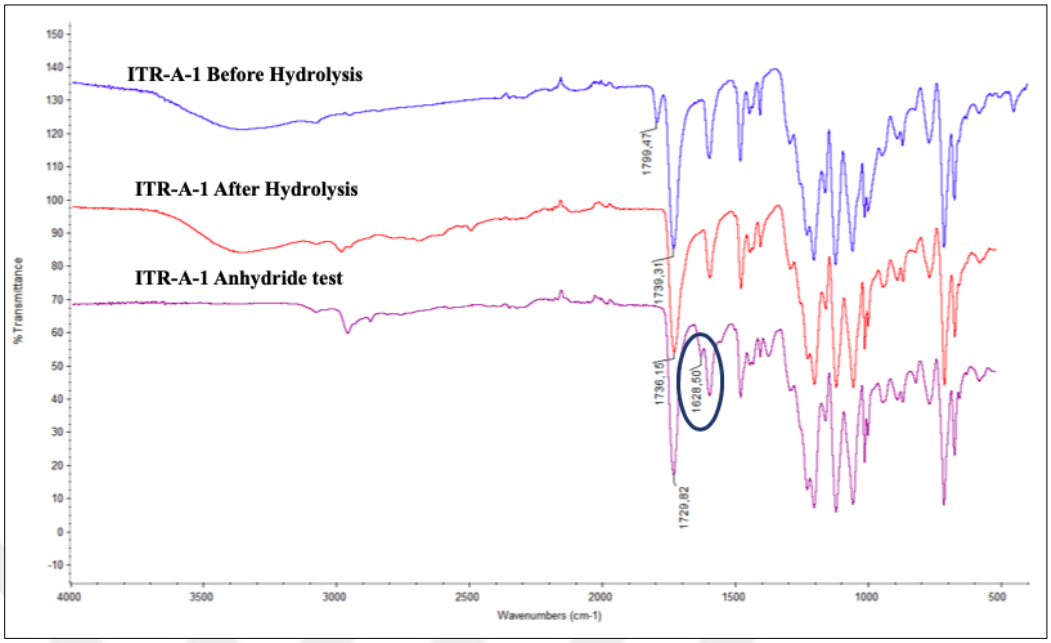


Figure 4.16. The comparison of FTIR results of ITR-A-1 before hydrolysis, after hydrolysis and after anhydride test.

When the ^{1}H NMR spectrum of ITR-1-A (Figure 4.17) is analyzed, short polymer chain peaks can be seen near the main peaks belonging to the polymer in the aromatic range between 7-9 ppm. When compared to the previous polyester products, these peaks are more detectable in poly(ester-anhydrides). It is possible that these peaks might belong to short chains of polyesters and poly(ester-anhydrides) formed during the polymerization process. Furthermore, this product was not soluble in $CHCl_3$. For NMR analysis, $CDCl_3$ containing 5% HFIP (v/v) was used as NMR solvent.

These short polymer chains are also observed in the GPC result of ITR-A-1 sample. The small peaks at the end of the line show the existence of low molecular weights oligomers which may also contain some cyclics. The polymer peak in GPC is barely detectable since a very low concentration (2 mg/mL) is dissolved in THF/HFIP mixture and *ortho*-dichloro benzene (ODCB). When trying higher concentration of the polymer to dissolve in this mixture, the precipitation of dissolved polymer was clearly observed. Figure 4.18 shows the GPC graph of ITR-1-A and Figure 4.19 indicates only the polymer peak.

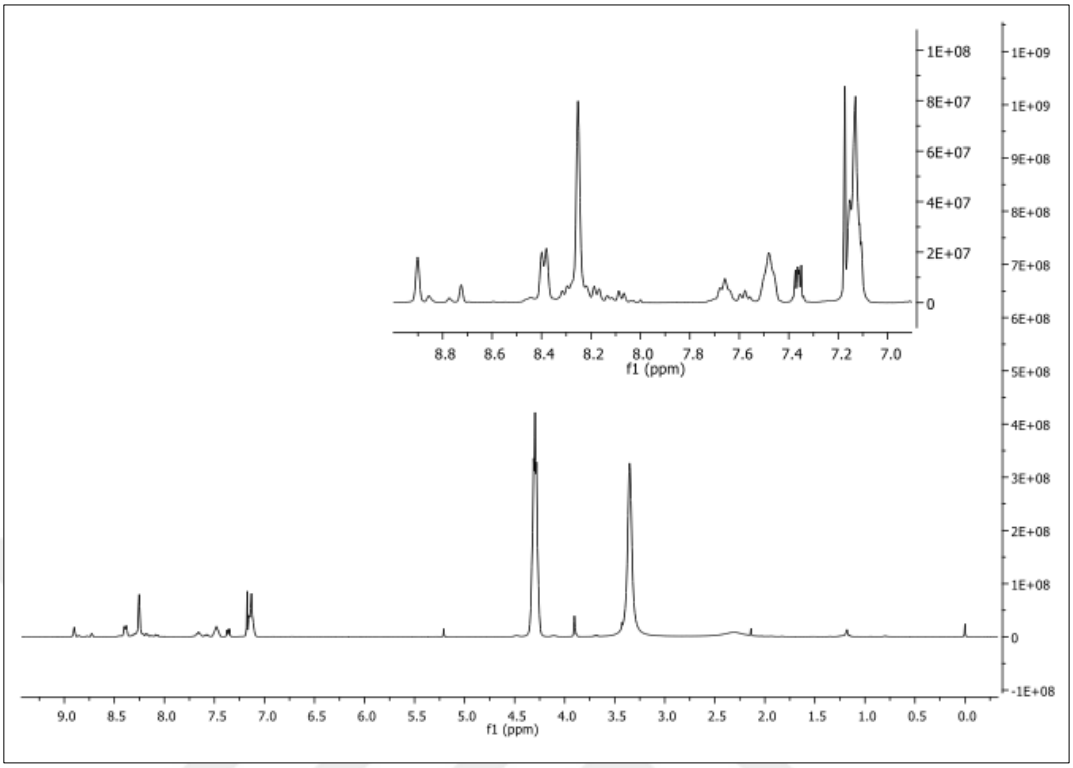


Figure 4.17. ^{1}H NMR spectrum of ITR-1-A before anhydride test.

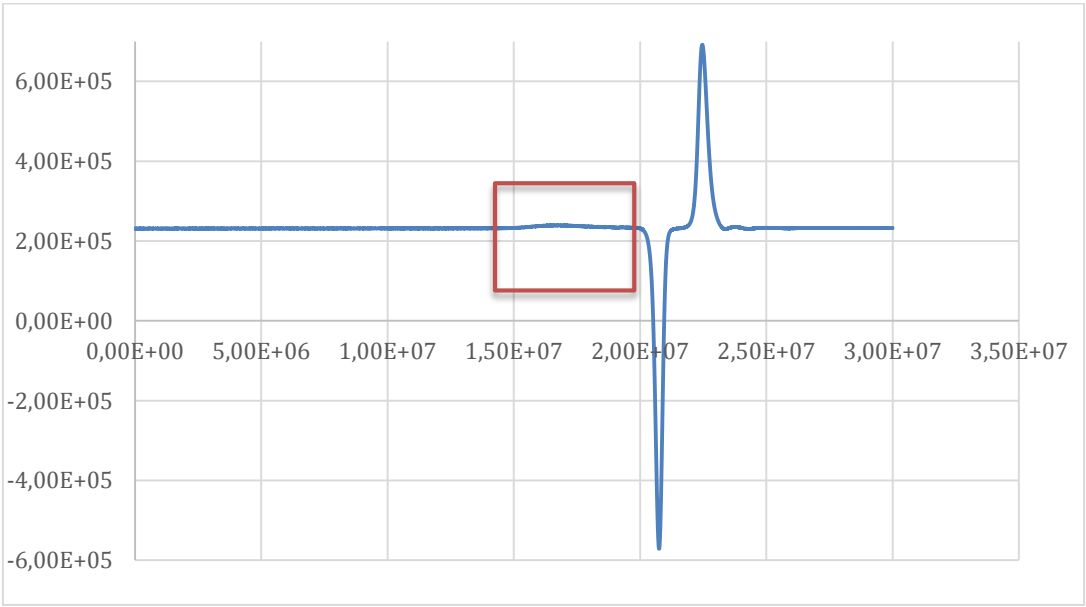


Figure 4.18. GPC analysis result of ITR-1-A.

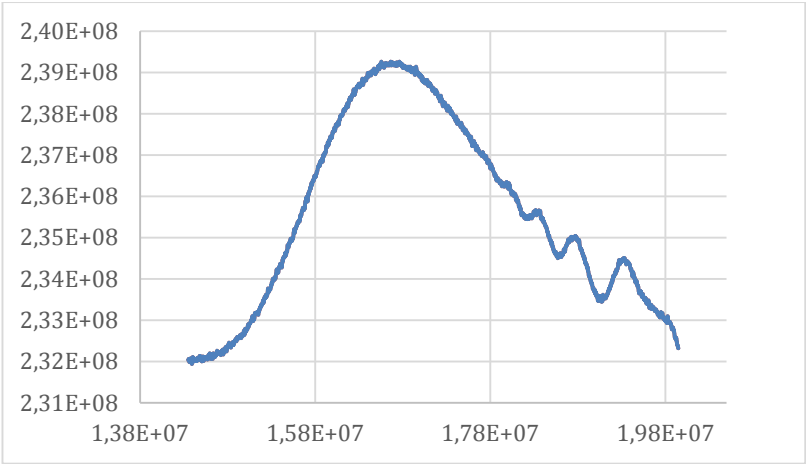


Figure 4.19. GPC analysis result of ITR-A-1

In order to detect hydrogens of IPC and TPC bonded with anhydride linkages, the ^{1}H NMR spectra of ITR-A-1 before and after anhydride tests were compared in Figure 4.20. It was observed that the peaks which were at 8.95 ppm, 8.45 ppm and 7.70 ppm in the ^{1}H NMR spectra of ITR-A-1 disappeared when the anhydride test was performed to the ITR-A-1 product. It was assumed that these peaks might be associated with the protons of IPC, which is connected to IPC or TPC monomers by anhydride linkages to the polymer.

Furthermore, the peak at 8.05 ppm might belong to the protons of TPC, which is near to anhydride bond, since this peak cannot be seen in the ^{1}H NMR spectra of ITR-A-1 after anhydride test (Figure 4.20).

The presence of anhydride bond formation in the polymers were also proven by the anhydride test in addition to FTIR and NMR analyses (Table 4.8 and 4.9). When anhydride test was implemented for each product, both T_g and M_n values decreased due to the breakage of anhydride linkages.

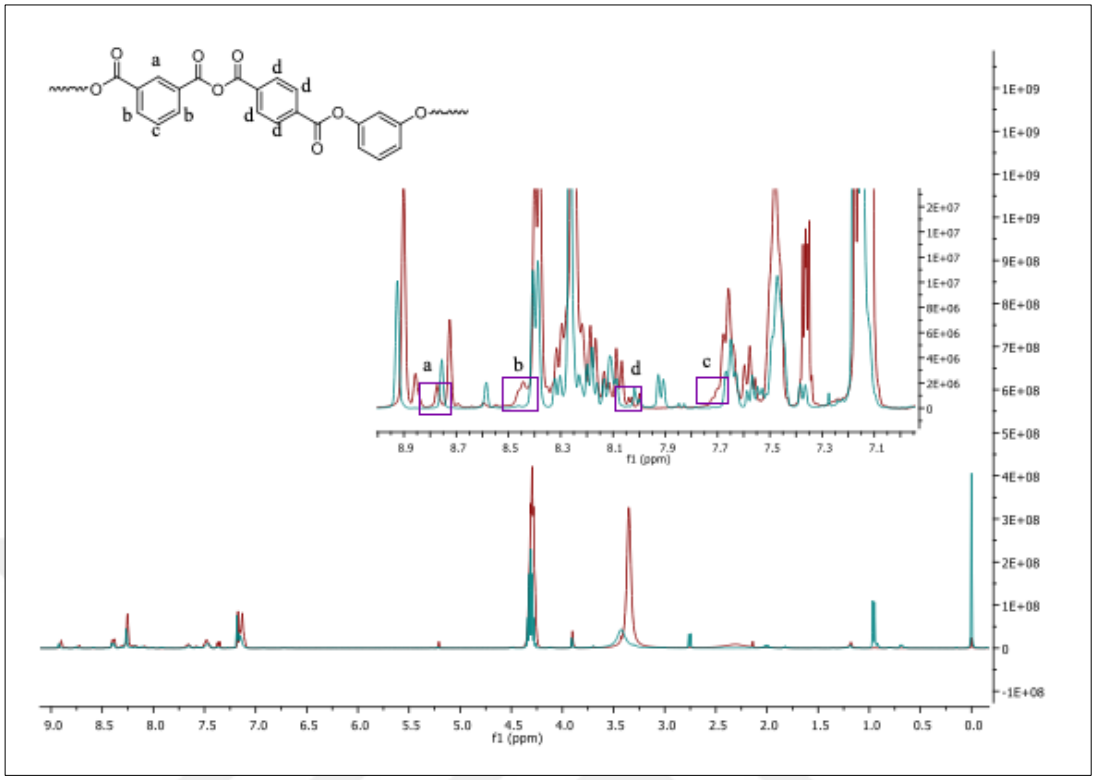


Figure 4.20. The comparison of ^{1}H NMR spectra of ITR-A-1 before and after amine test (blue line: amine test, red line: before anhydride test).

Table 4.8. The overall results of poly(ester-anhydrides) before and after anhydride test.

Samples	**Diacid/Alcohol (mole)**	**Before Anhydride Test**			**After Anhydride Test**		
		M_n **(g/mole)**	M_w **(g/mole)**	**PDI**	M_n **(g/mole)**	M_w **(g/mole)**	**PDI**
ITR-A-1	1.20	5456	13389	2.454	2842	3253	1.145
ITR-A-2	1.20	8408	12098	1.439	4299	5736	1.334
ITR-A-3	1.02	6650	9690	1.457	4397	6690	1.522

Table 4.9. DSC results of poly(ester-anhydrides) before and after anhydride test.

Samples	**Diacid/ Alcohol (mole)**	**T_g (ºC)**	**T_g (ºC) (anhydride test)**
ITR-A-1	1.20	95.7	68.1
ITR-A-2	1.20	115.8	84.3
ITR-A-3	1.02	110.0	89.1

Thus, the decreases in number average molecular weights by a factor of ½ show that the synthesized polyester anhydrides had in average at least one anhydride linkage in the polyester backbone.

5. CONCLUSIONS

In this study, the syntheses of ITR polyester and poly(ester-anhydrides) were carried out by solution polymerization and their characterizations were conducted.

First of all, the carboxylic acid terminated ITR polyesters with different diacid chloride (IPC/TPC) ratio were synthesized to observe the effect of polymer structure on the polymer properties. Secondly, the syntheses of resorcinol terminated polyesters containing various diacid chloride ratios were performed to compare their properties with the carboxylic acid terminated polyesters.

In their characterizations, it was found that some of these polyesters, which comprised higher ratio of IPC or TPC, had T_m and T_c values coming from their crystalline domains. It is well known that the crystallinity of the polyesters with higher ratio of TPC might be related to the molecular symmetry. On the other hand, the reason for the polyesters with higher ratio of IPC have melting temperatures was attributed to the possible formation of cyclic oligomers.

Finally, the poly(ester-anhydrides) were synthesized to investigate the mechanism of the formation of anhydride linkages. The effects of the diacid to alcohol molar feed ratio and the amount of TEA on the polymerization efficiency and degradation of the poly(ester-anhydrides) were investigated. The presence of anhydride bonds in the backbones of synthesized poly(ester-anhydrides) was proven successfully.

6. FUTURE WORK

The end group characterization of the synthesized polyesters by NMR analysis can be performed *via* phosphorus derivatization of the ITR -OH and -COOH end groups. Furthermore, the effects of end groups on the thermal and mechanical properties of polyesters will be investigated. GPC measurements will be repeated with using low molecular weight columns to obtain more accurate results for the polyesters, especially for IPC rich polyesters, and poly(ester-anhydrides). Moreover, the syntheses of poly(ester-anhydrides) might be performed by using the interfacial polymerization method.

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APPENDİX A: SPECTROSCOPY DATA

This section includes ^{1}H-NMR Spectroscopy and DSC Analysis of synthesized polymers. Necessary expansions were made on the data for easy interpretation.

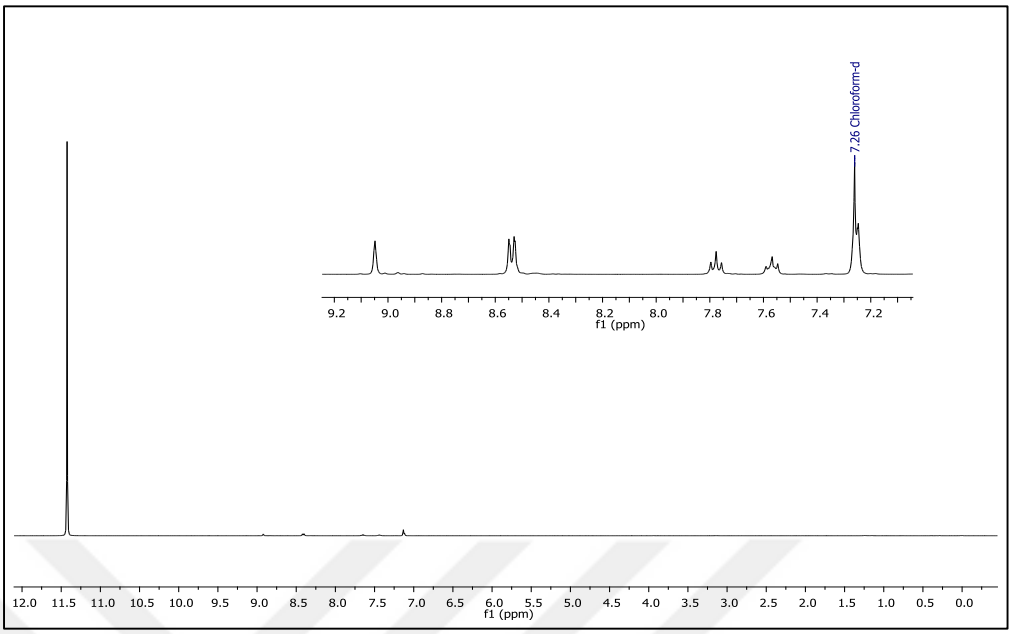


Figure A.1. ^{1}H NMR of ITR-1.

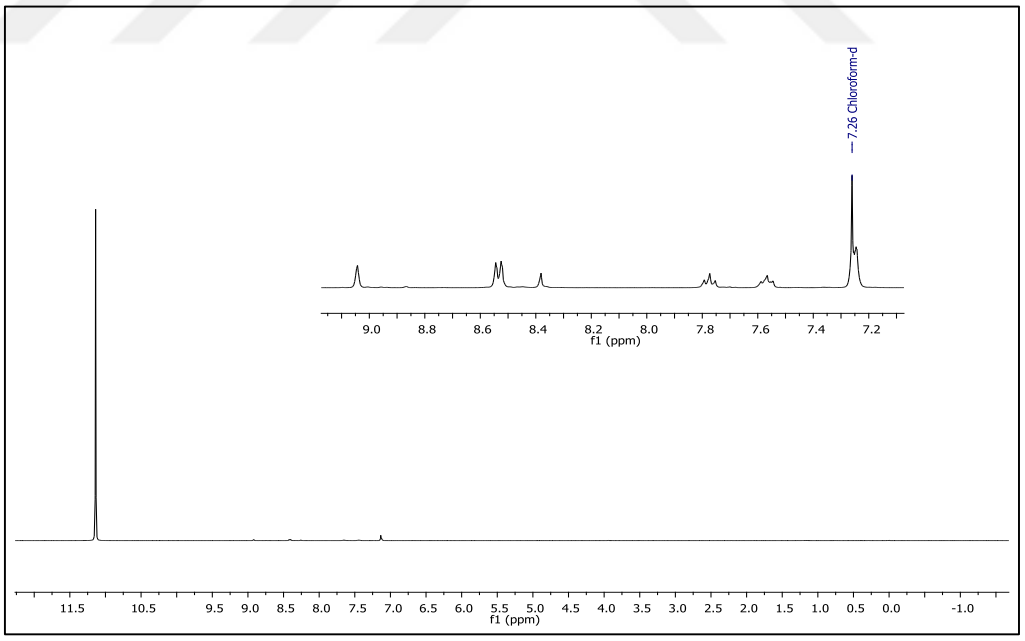


Figure A.2. ^{1}H NMR of ITR-3.

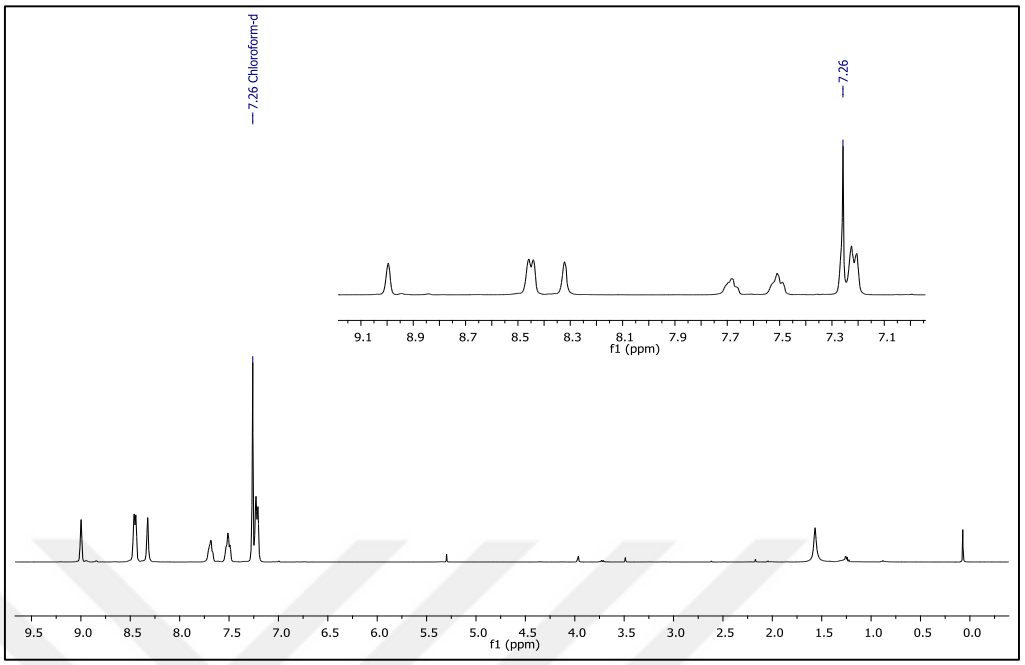


Figure A.3. ^{1}H NMR of ITR-5.

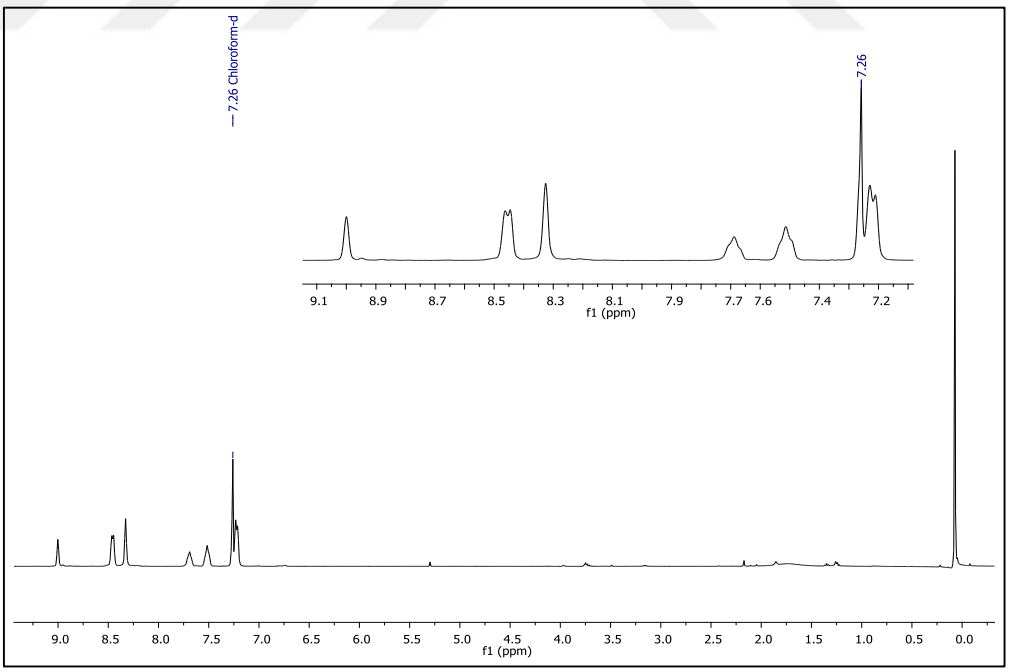


Figure A.4. ^{1}H NMR of ITR-7.

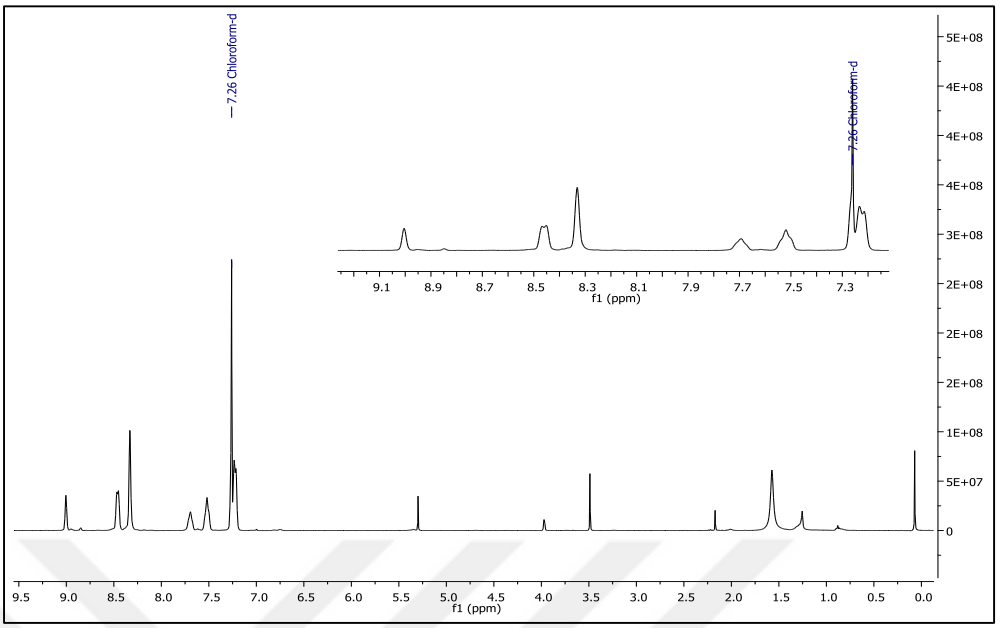


Figure A.5. ^{1}H NMR of ITR-9.

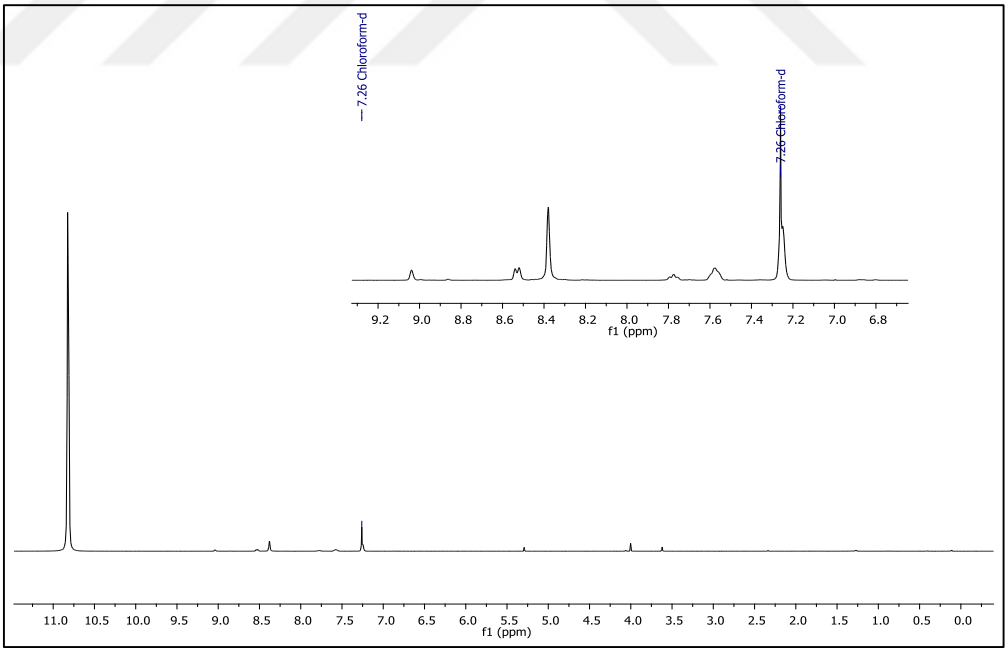


Figure A.6. ^{1}H NMR of ITR-13.

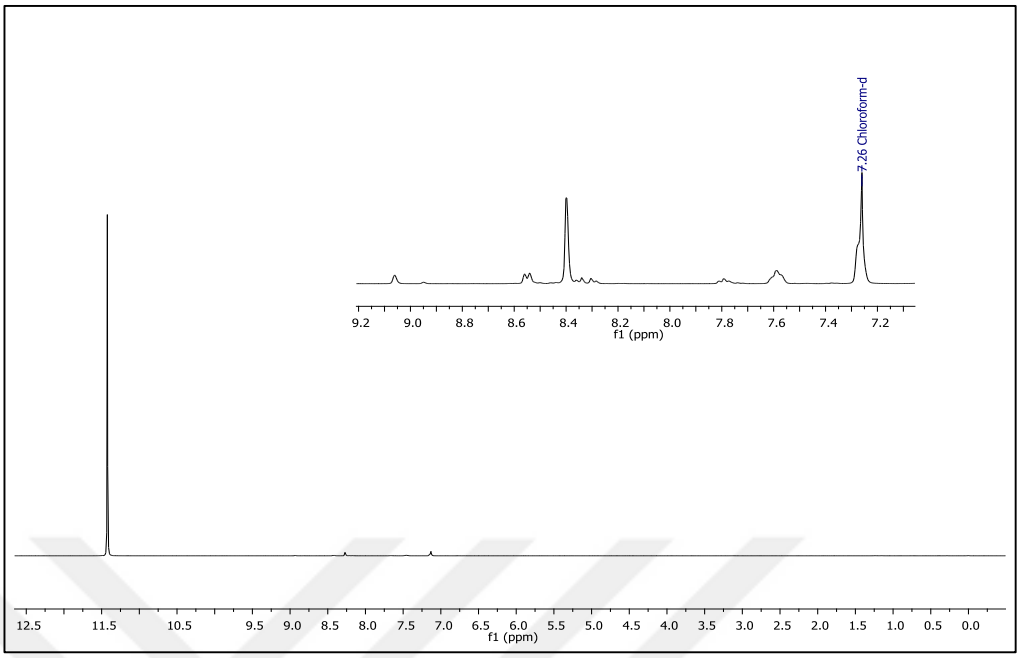


Figure A.7. ^{1}H NMR of ITR-15.

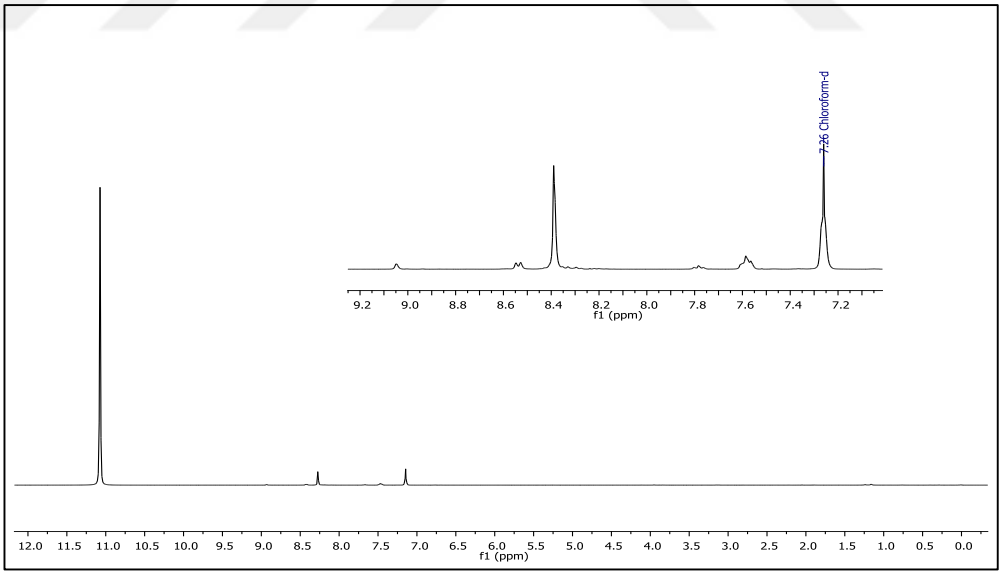


Figure A.8. ^{1}H NMR of ITR-17.

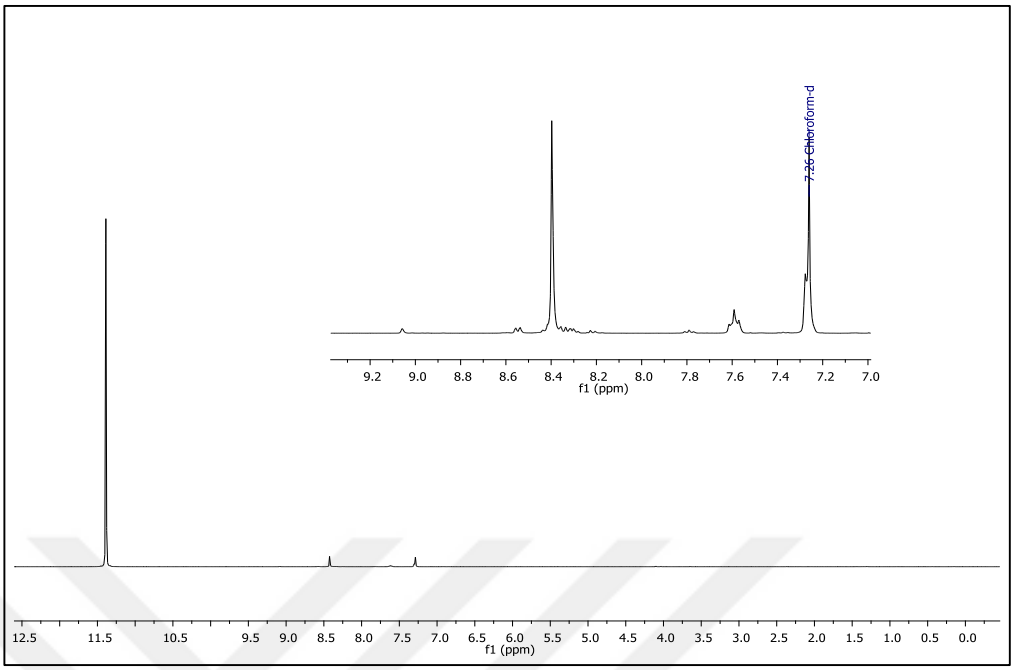


Figure A.9. ^{1}H NMR of ITR-19.

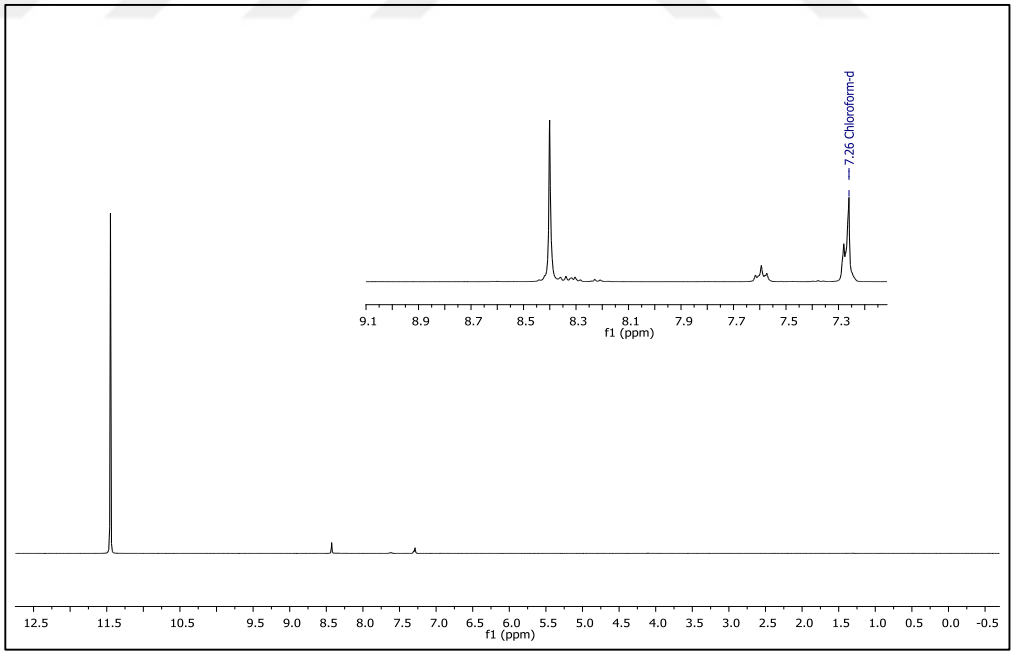


Figure A.10. ^{1}H NMR of ITR-21.

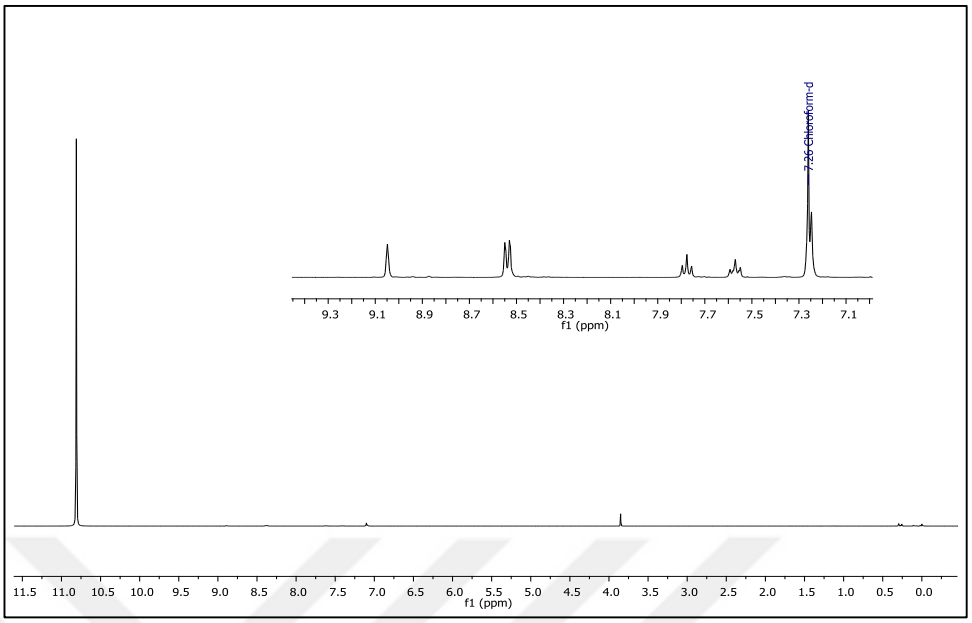


Figure A.11. ^{1}H NMR of ITR-25.

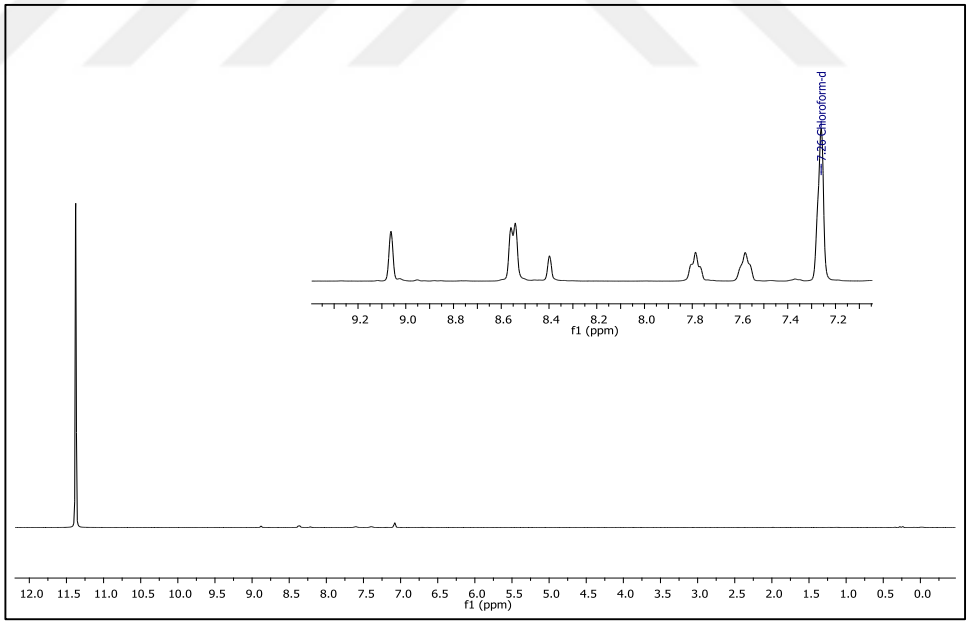


Figure A.12. ^{1}H NMR of ITR-27.

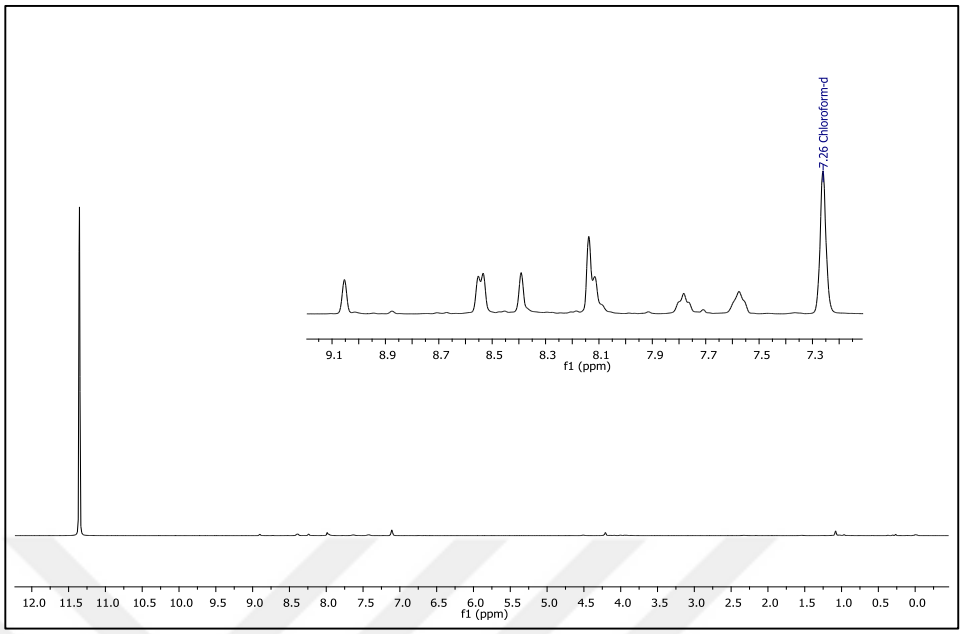


Figure A.13. ^{1}H NMR of ITR-29.

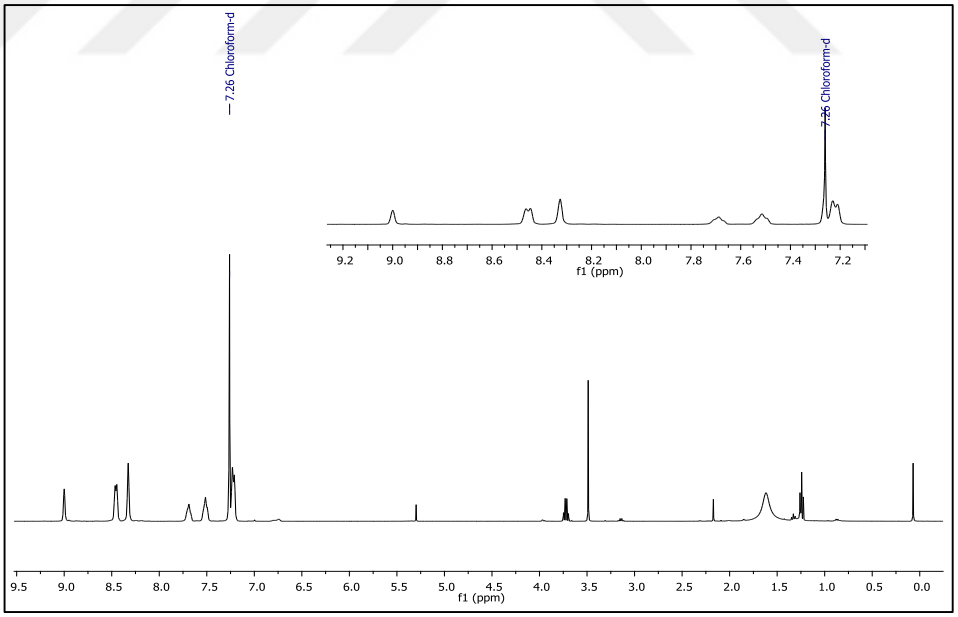


Figure A.14. ^{1}H NMR of ITR-31.

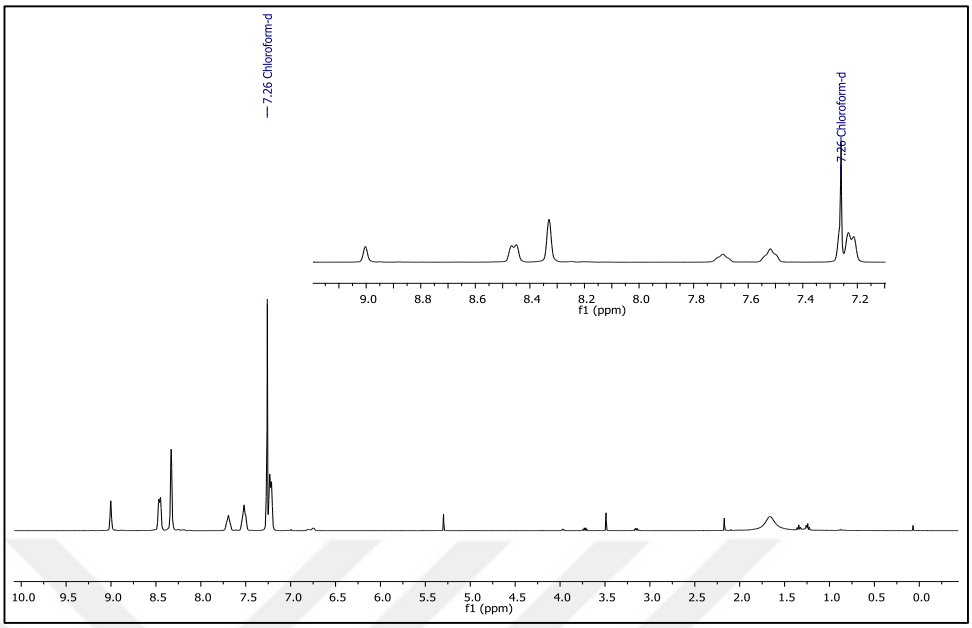


Figure A.15. ^{1}H NMR of ITR-33.

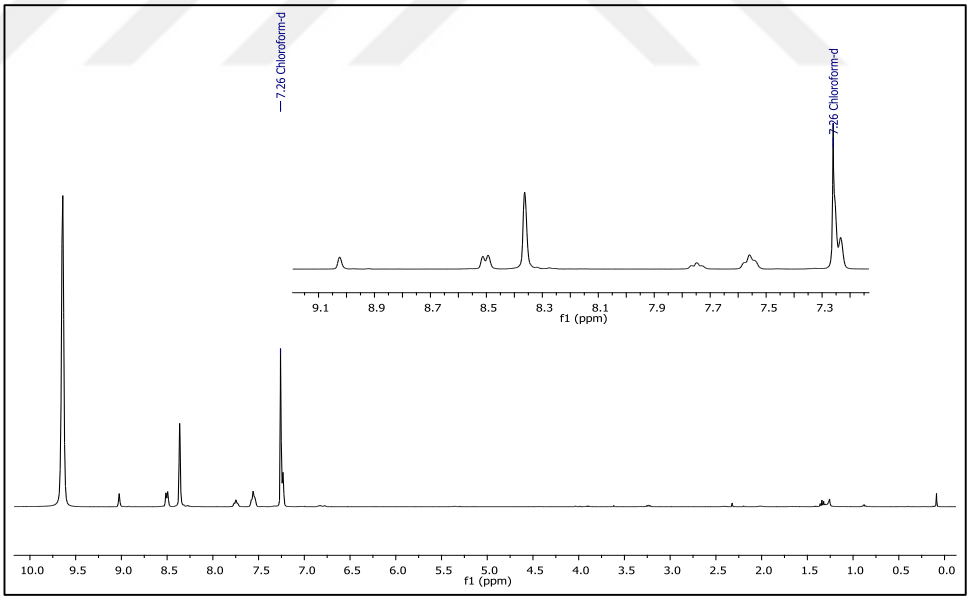


Figure A.16. ^{1}H NMR of ITR-37.

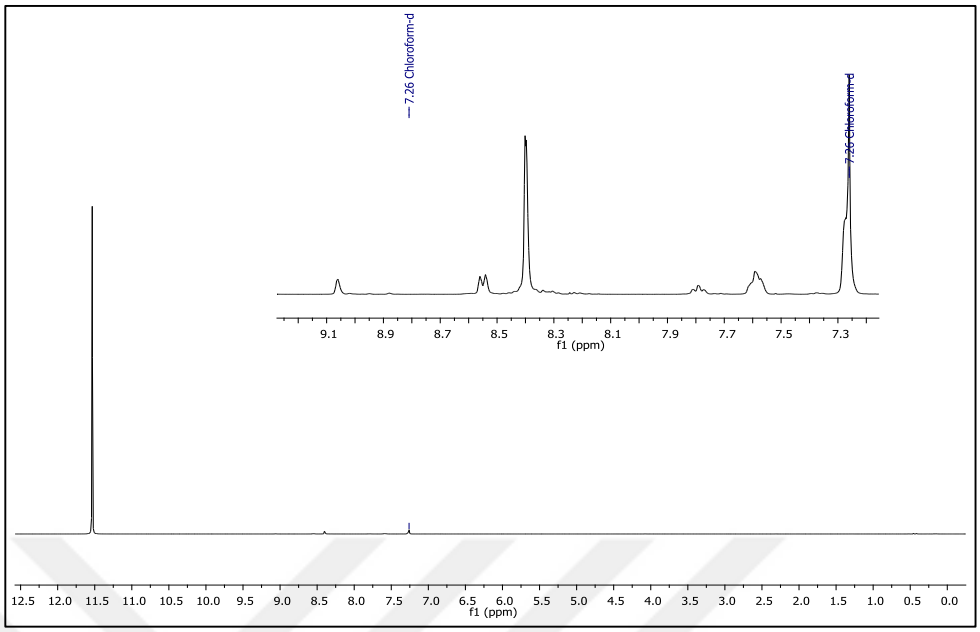


Figure A.17. ^{1}H NMR of ITR-39.

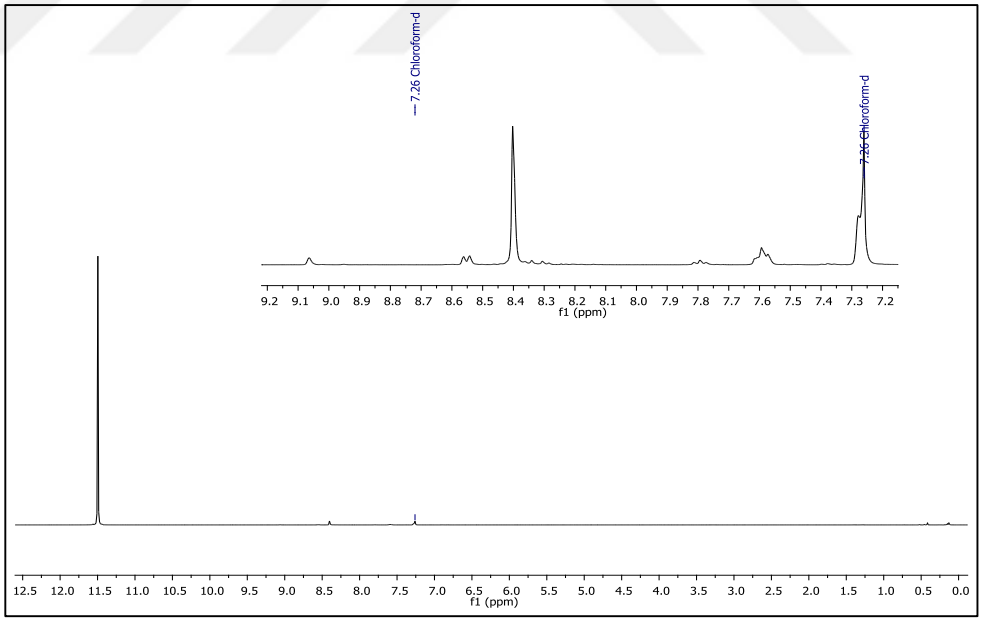


Figure A.18. ^{1}H NMR of ITR-41.

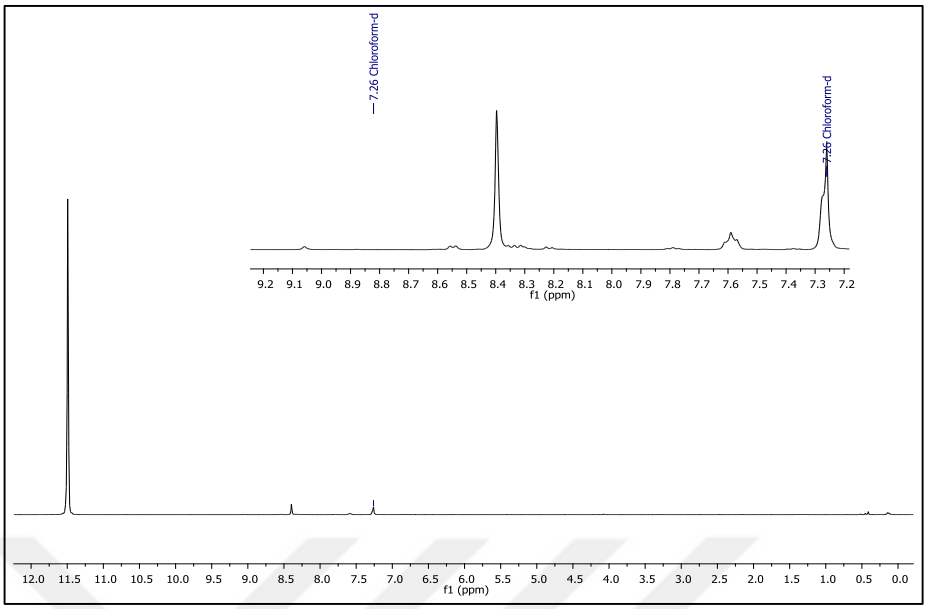


Figure A.19. ^{1}H NMR of ITR-43.

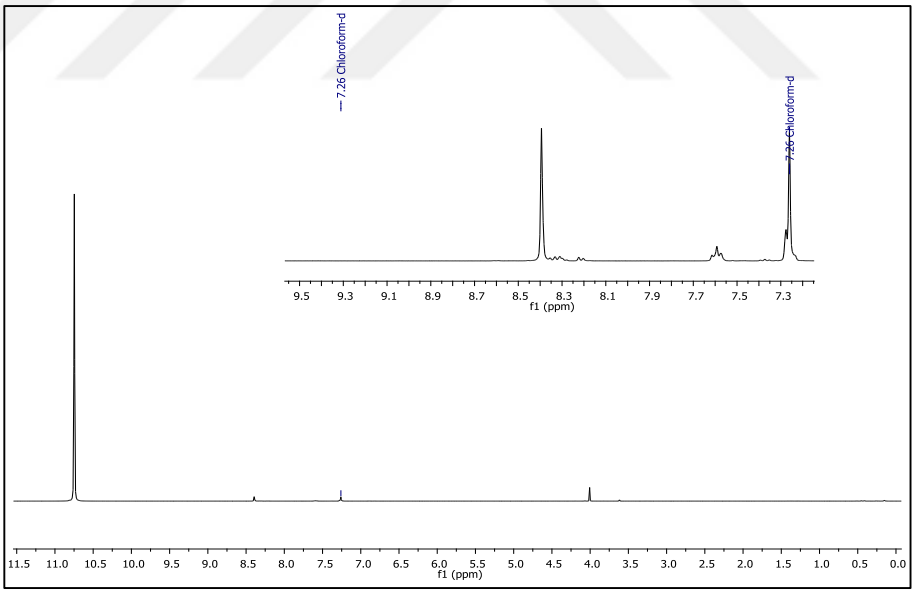


Figure A.20. ^{1}H NMR of ITR-45.

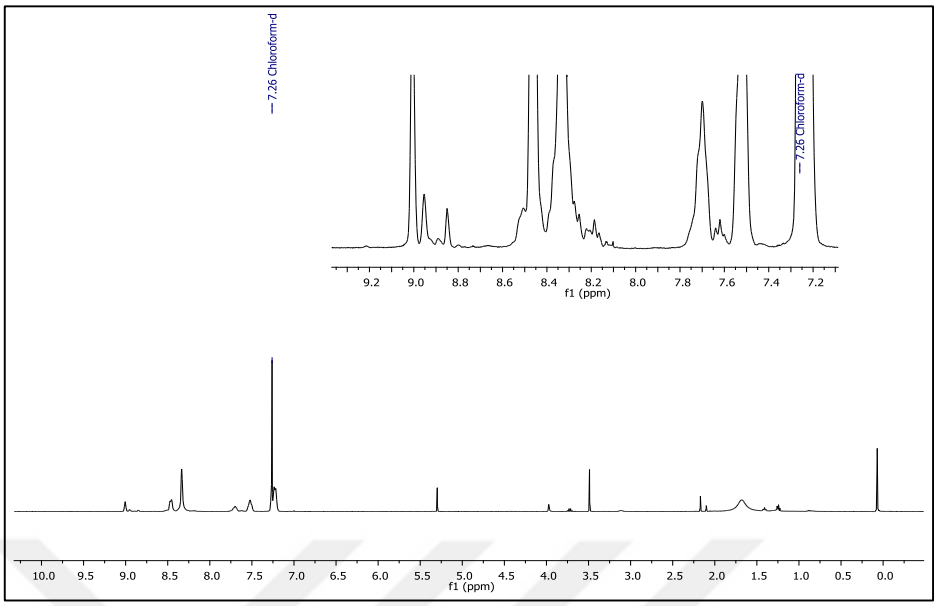


Figure A.21. ^{1}H NMR of ITR-A-2 Before Anhydride Test.

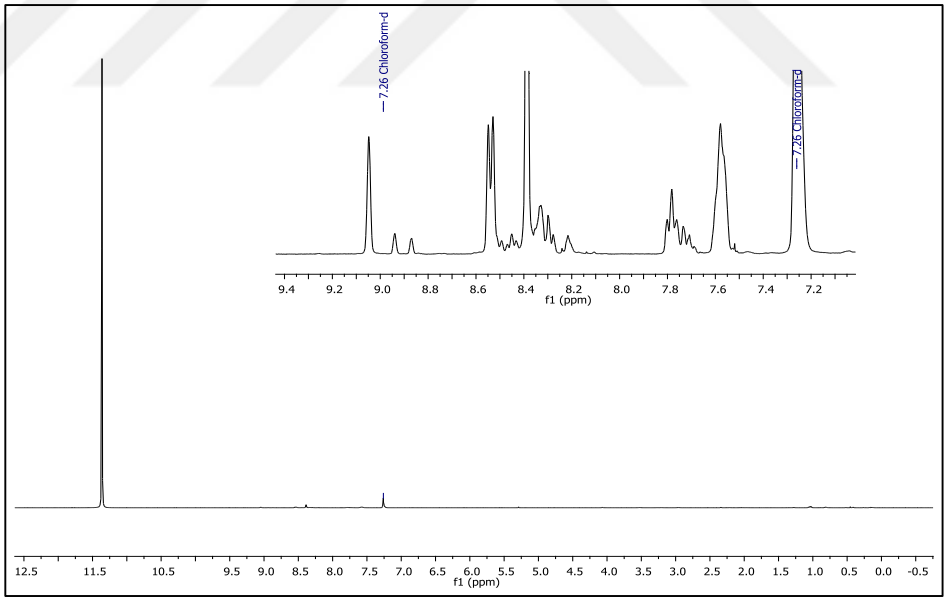


Figure A.22. ^{1}H NMR of ITR-A-2 After Anhydride Test.

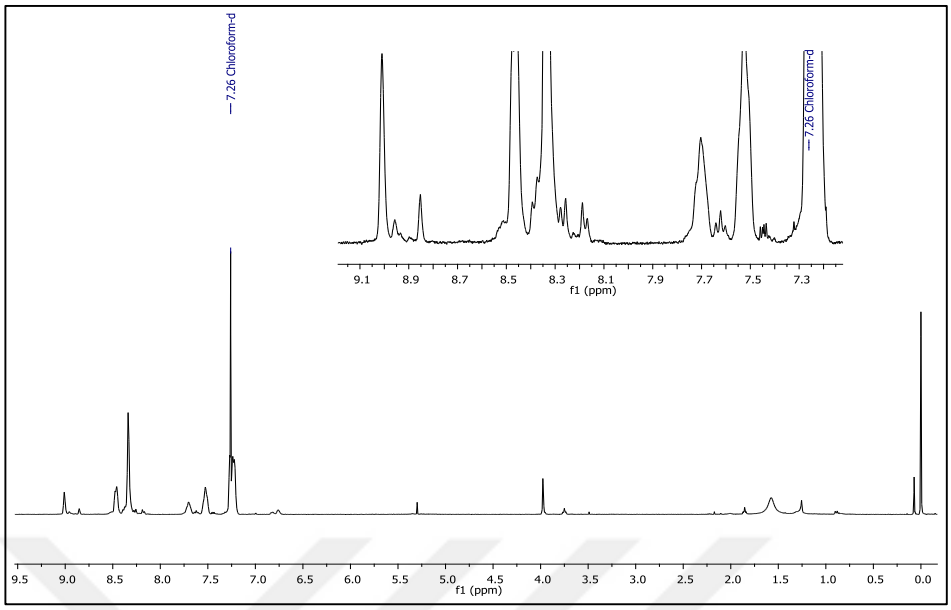


Figure A.23. ^{1}H NMR of ITR-A-3 Before Anhydride Test.

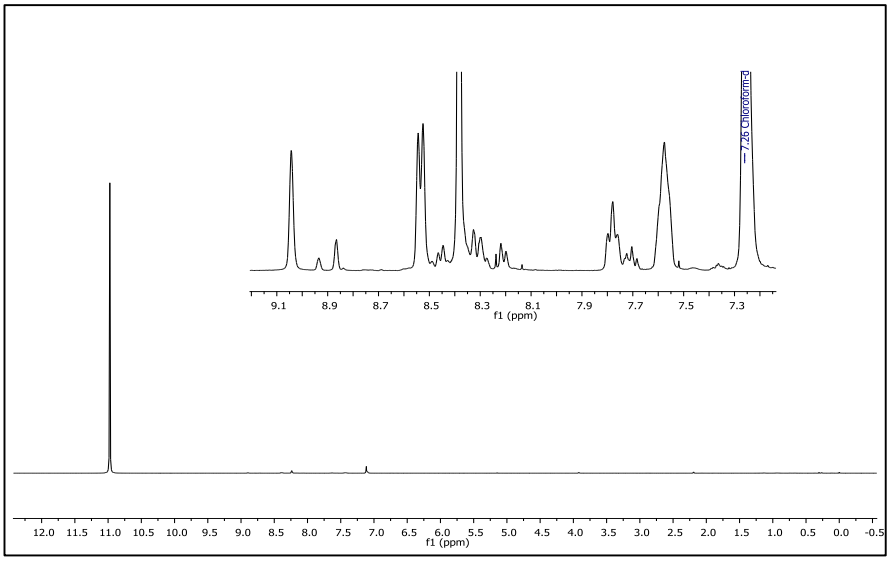


Figure A.24. ^{1}H NMR of ITR-A-3 After Anhydride Test.

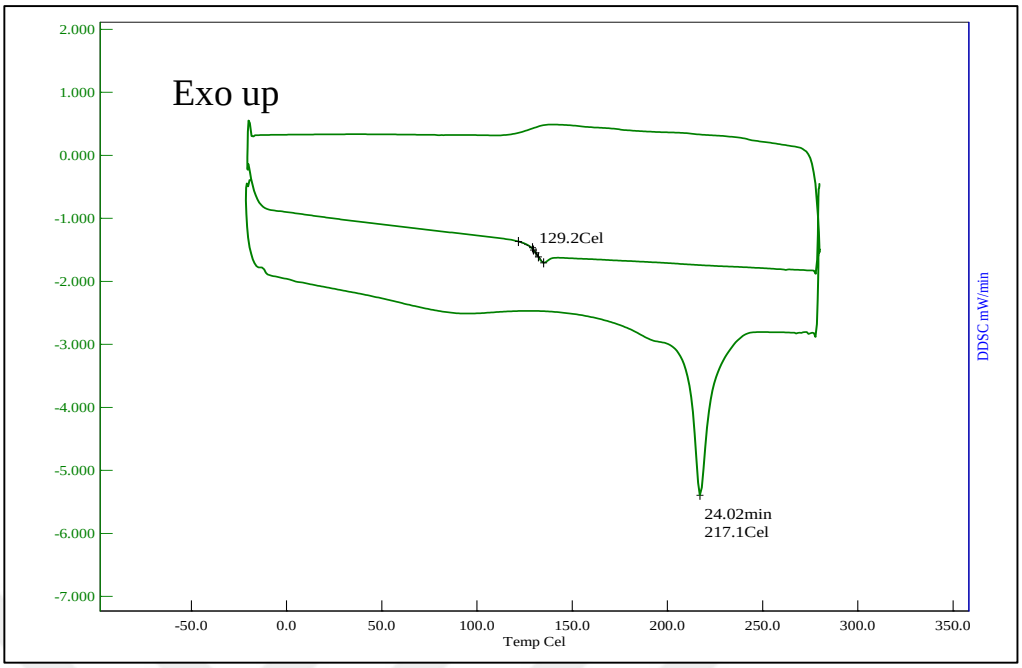


Figure A.25. DSC Analysis of ITR-1.

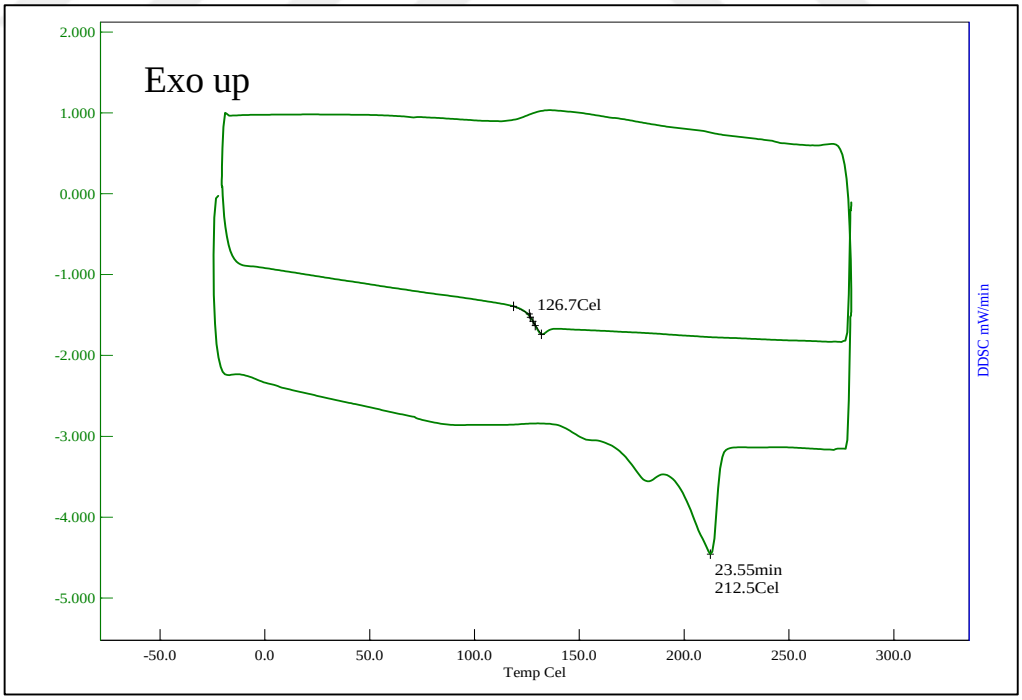


Figure A.26. DSC Analysis of ITR-3.

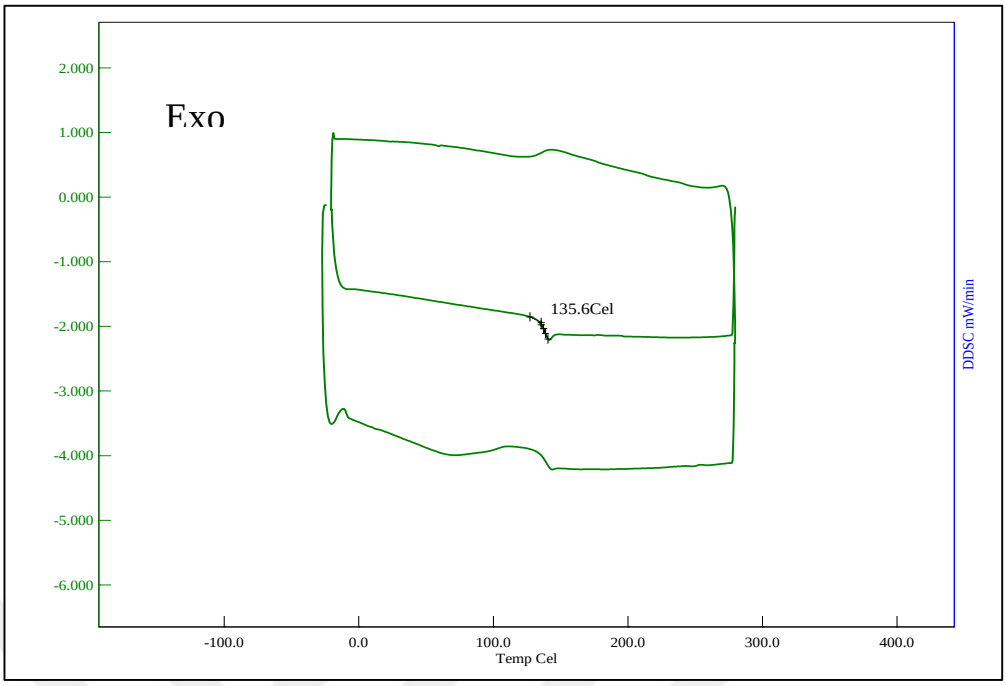


Figure A.27. DSC Analysis of ITR-5.

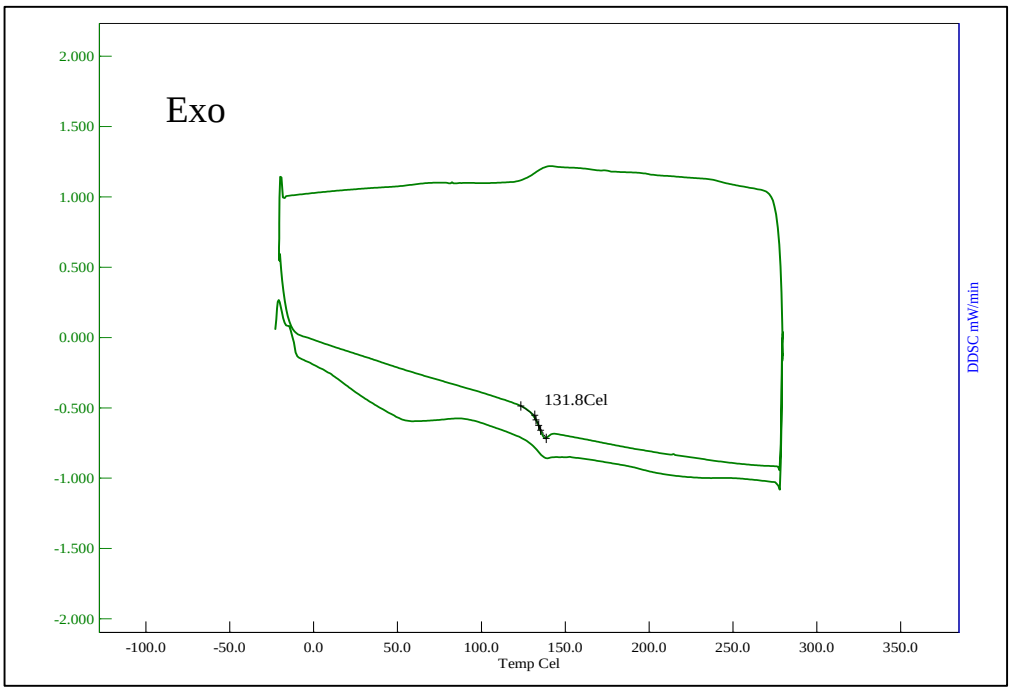


Figure A.28. DSC Analysis of ITR-7.

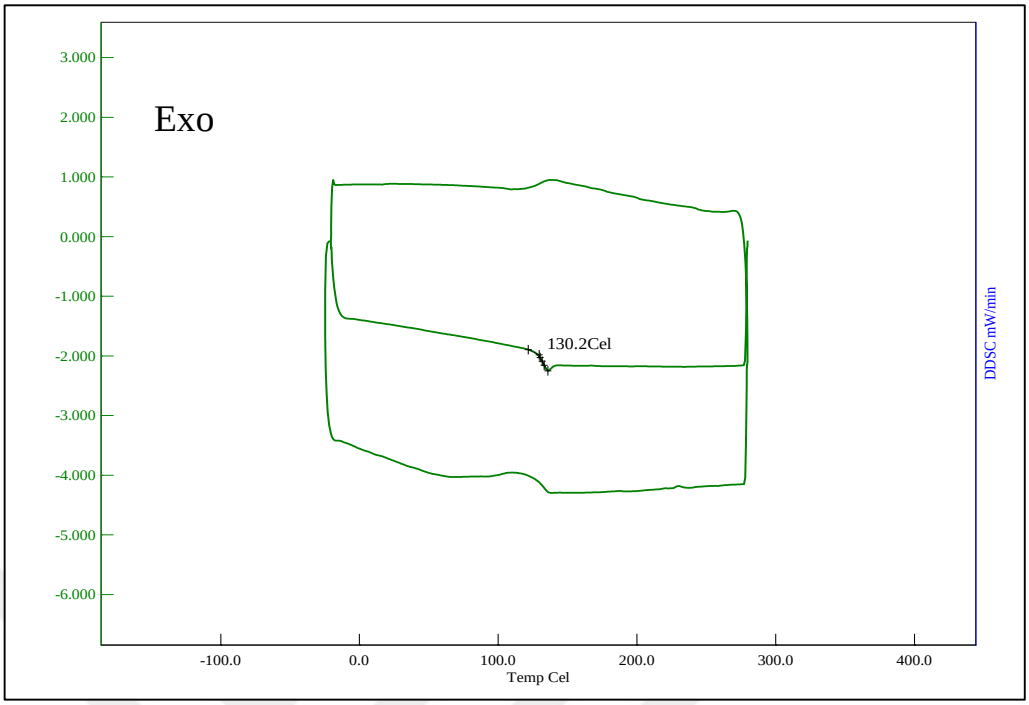


Figure A.29. DSC Analysis of ITR-9.

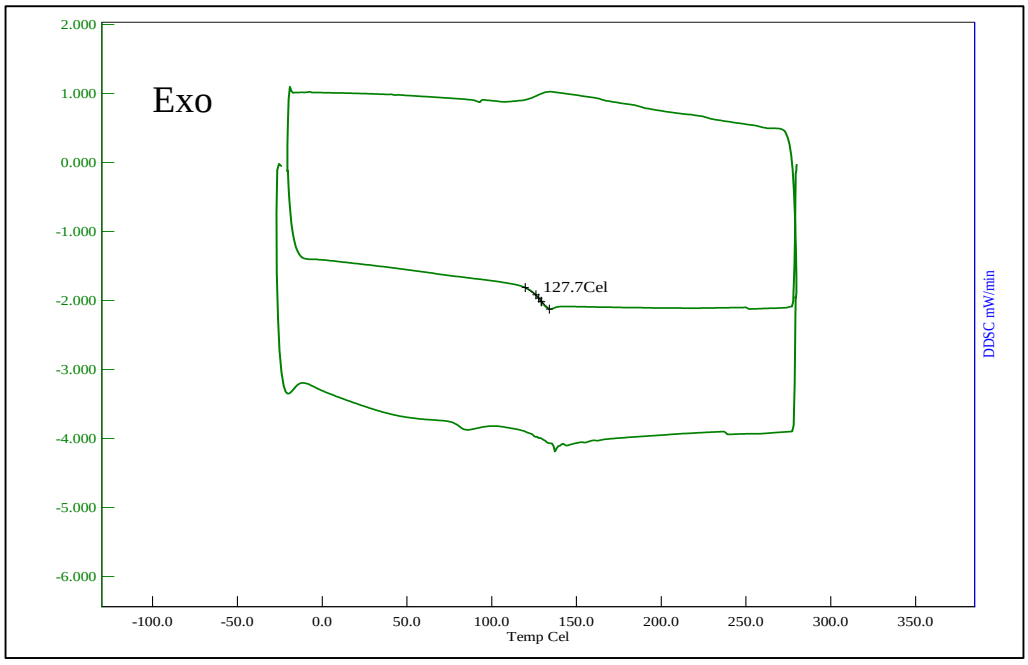


Figure A.30. DSC Analysis of ITR-13.

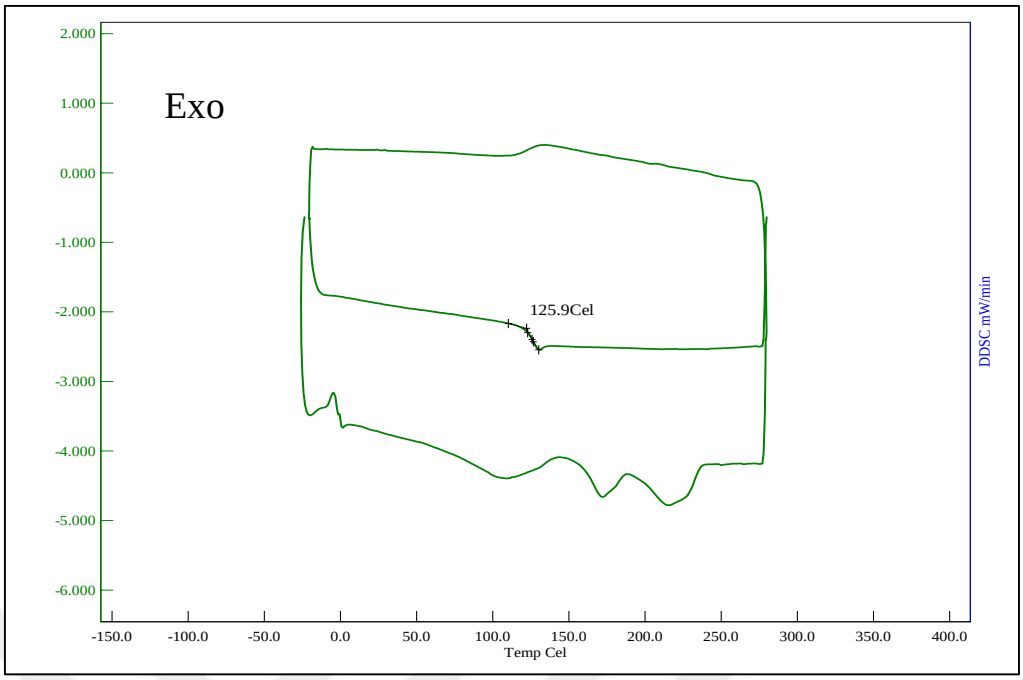


Figure A.31. DSC Analysis of ITR-15.

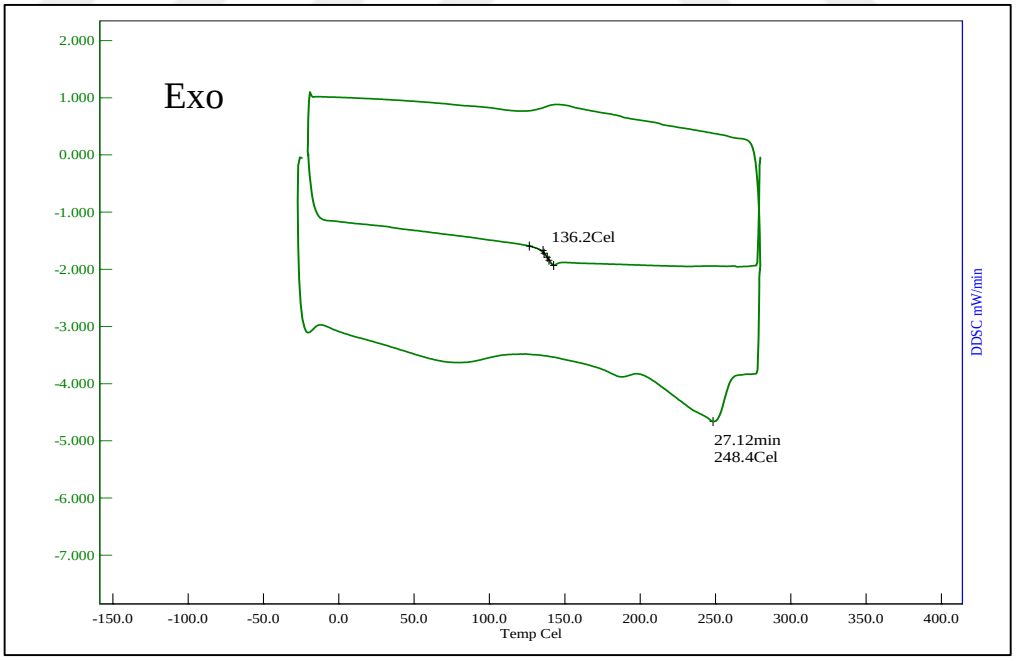


Figure A.32. DSC Analysis of ITR-17.

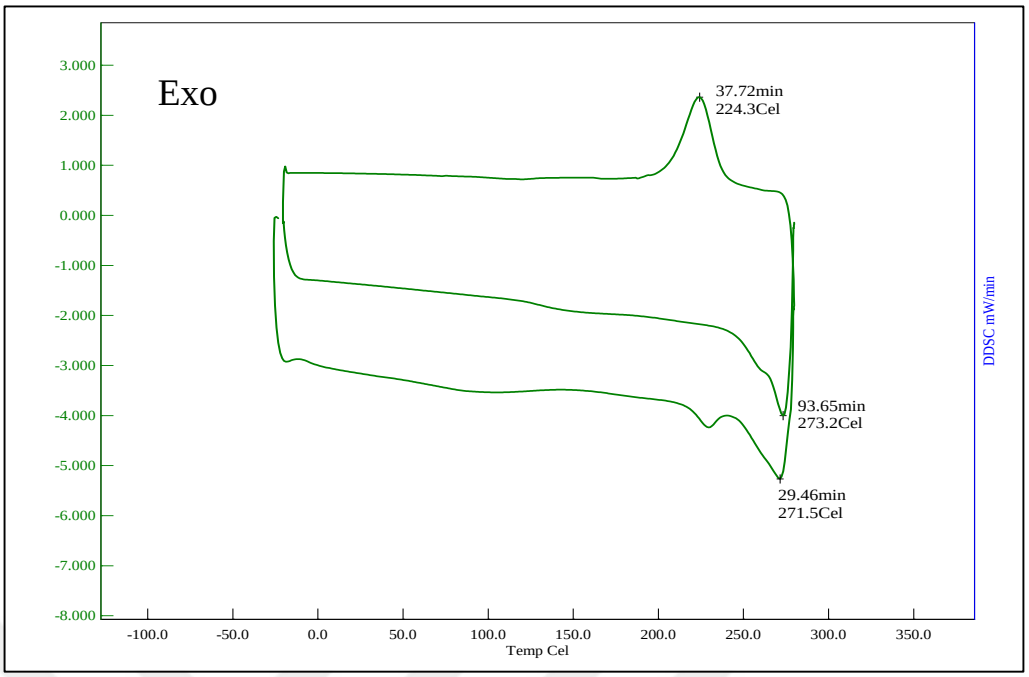


Figure A.33. DSC Analysis of ITR-19.

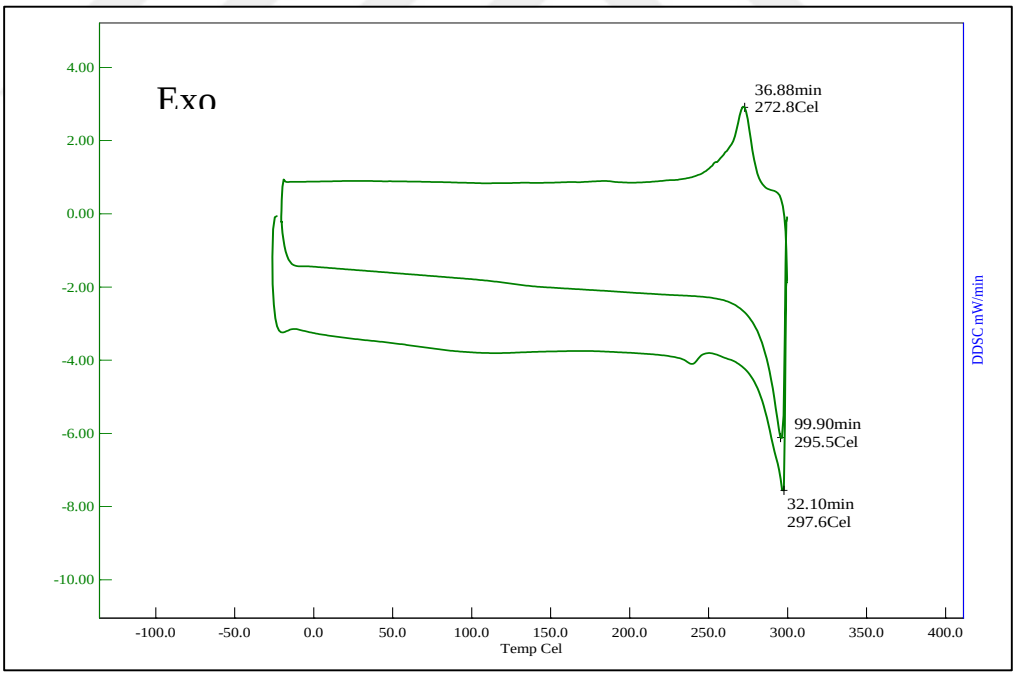


Figure A.34. DSC Analysis of ITR-21.

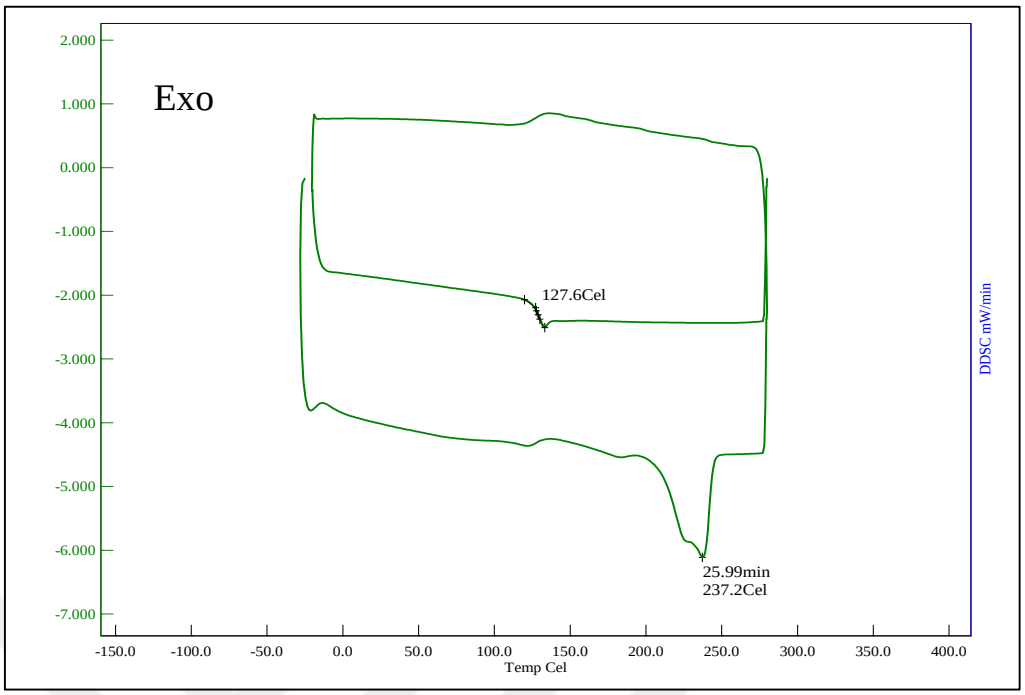


Figure A.35. DSC Analysis of ITR-25.

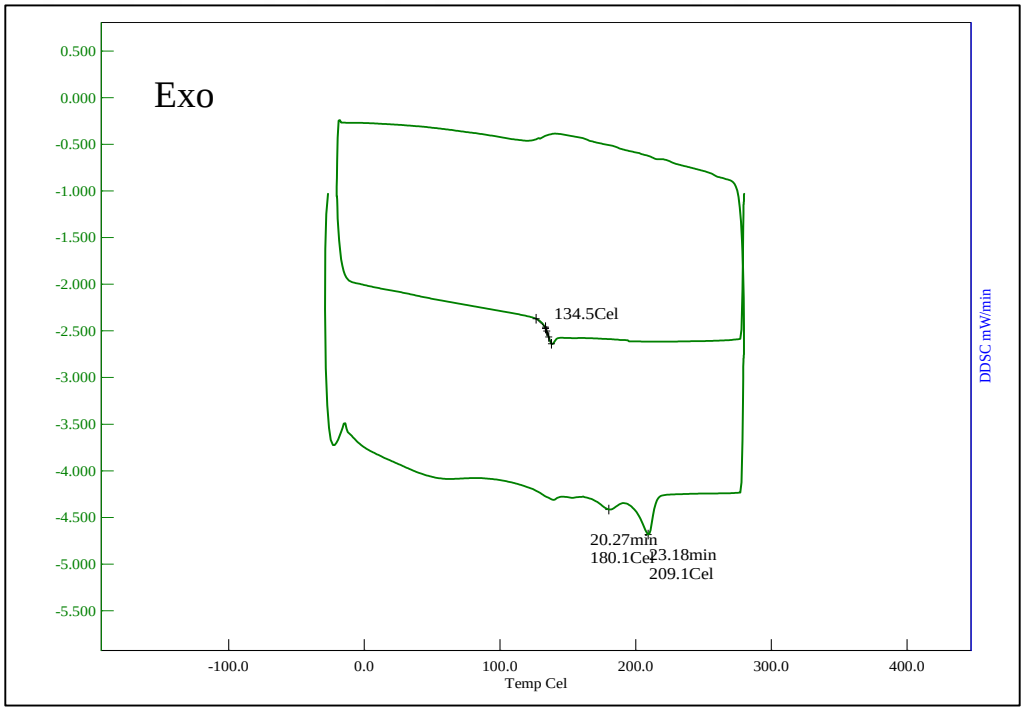


Figure A.36. DSC Analysis of ITR-27.

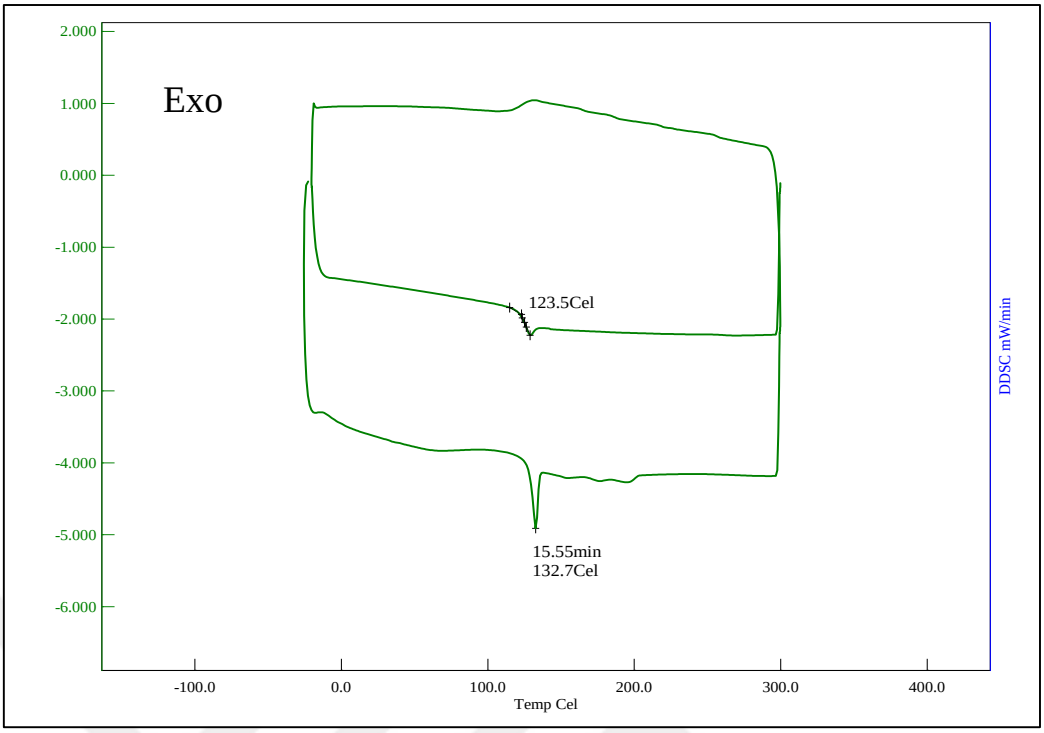


Figure A.37. DSC Analysis of ITR-29.

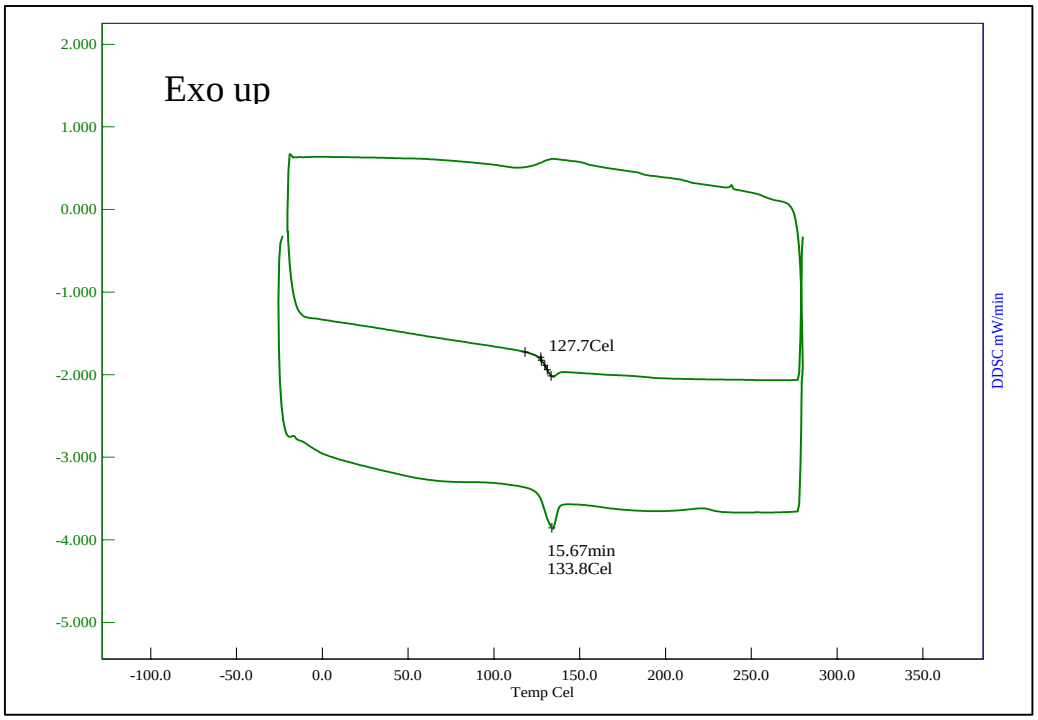


Figure A.38. DSC Analysis of ITR-31.

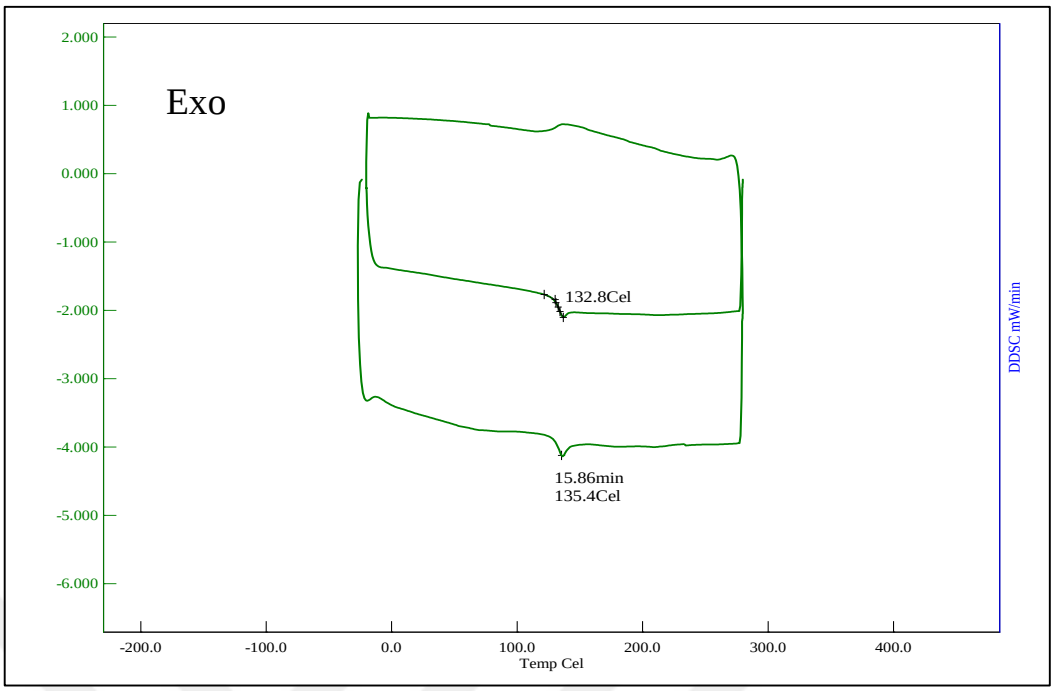


Figure A.39. DSC Analysis of ITR-33.

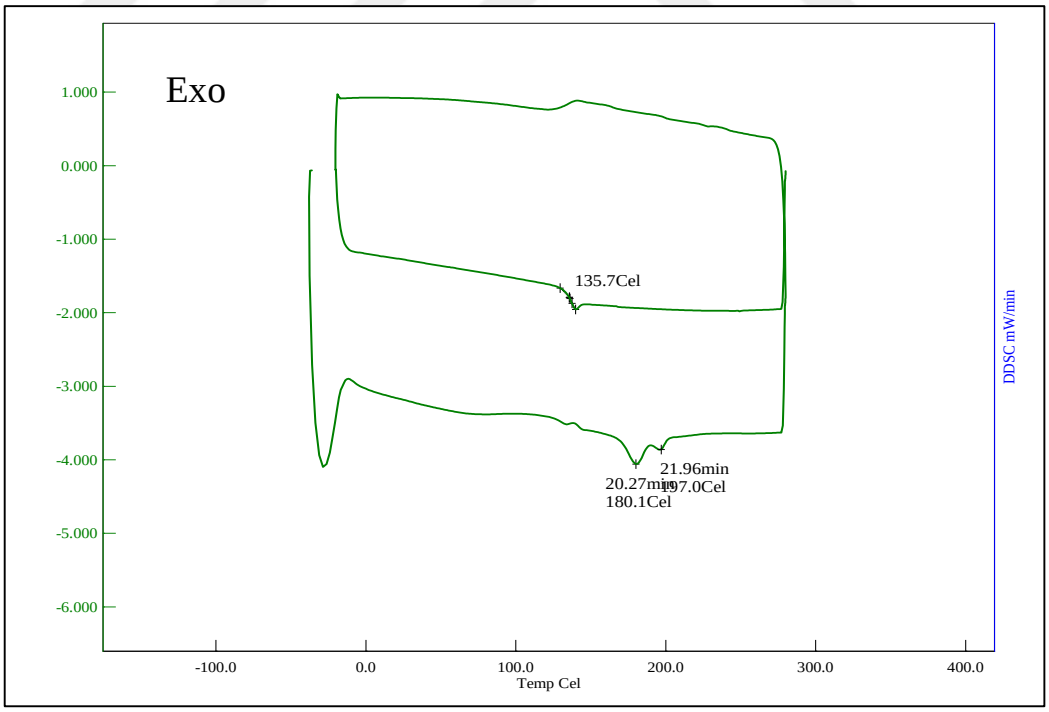


Figure A.40. DSC Analysis of ITR-37.

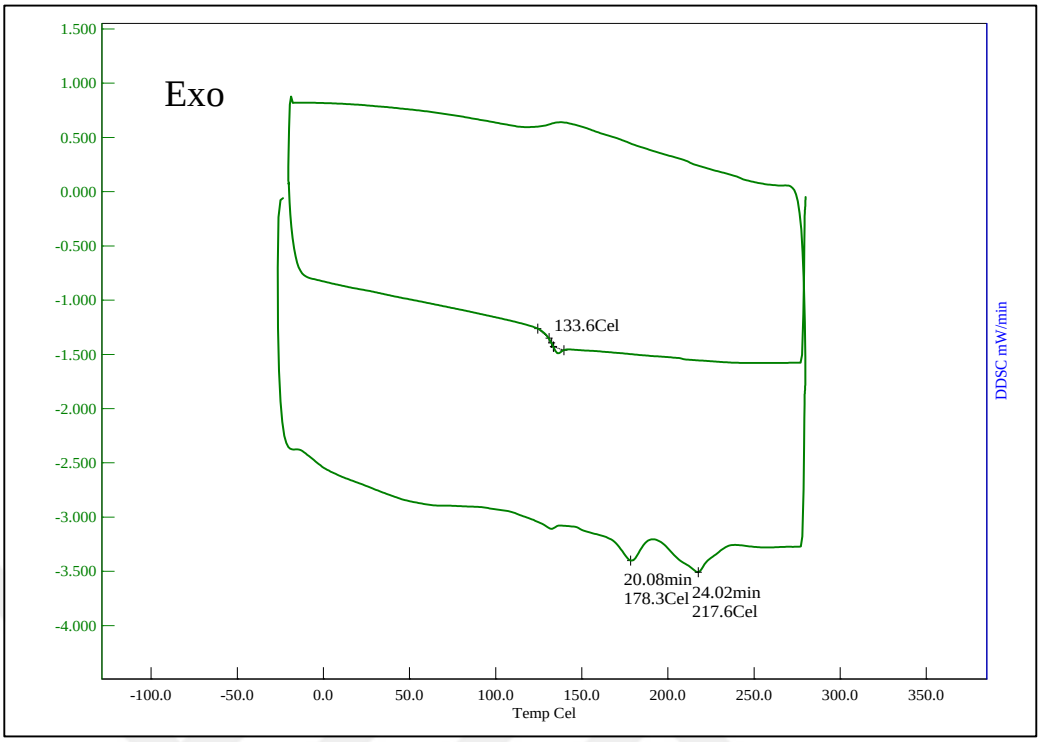


Figure A.41. DSC Analysis of ITR-39.

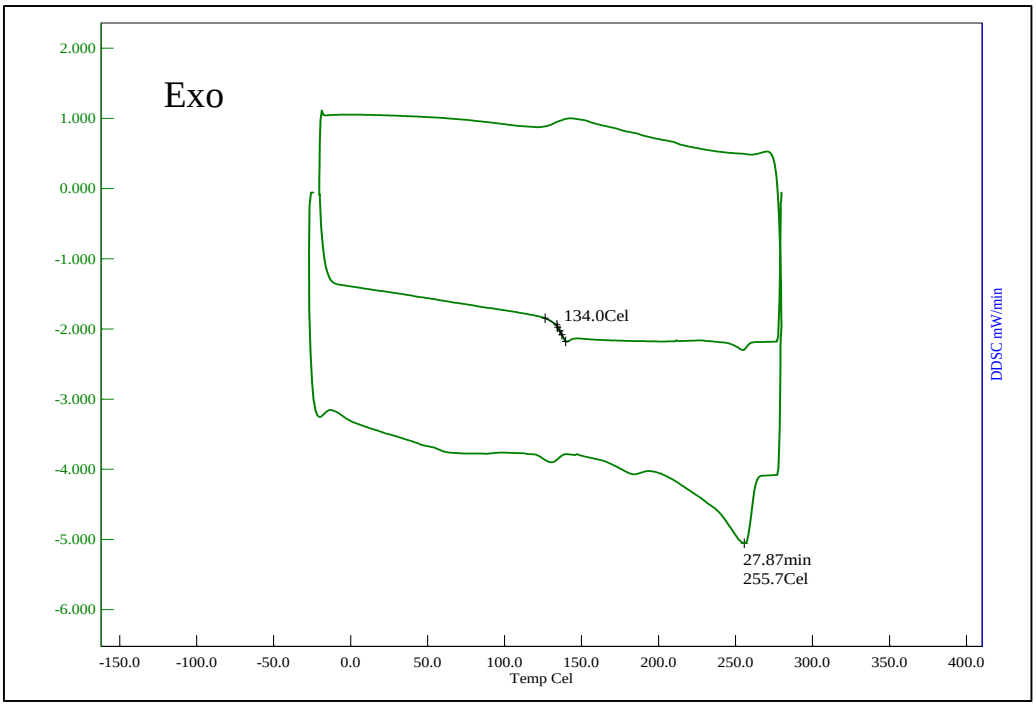


Figure A.42. DSC Analysis of ITR-41.

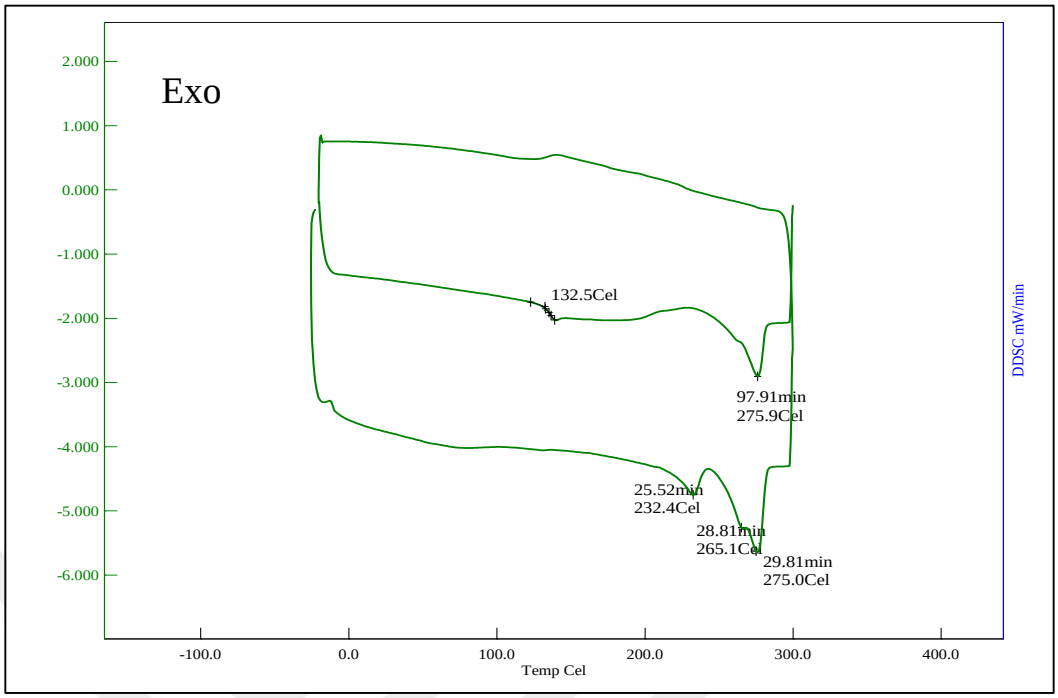


Figure A.43. DSC Analysis of ITR-43.

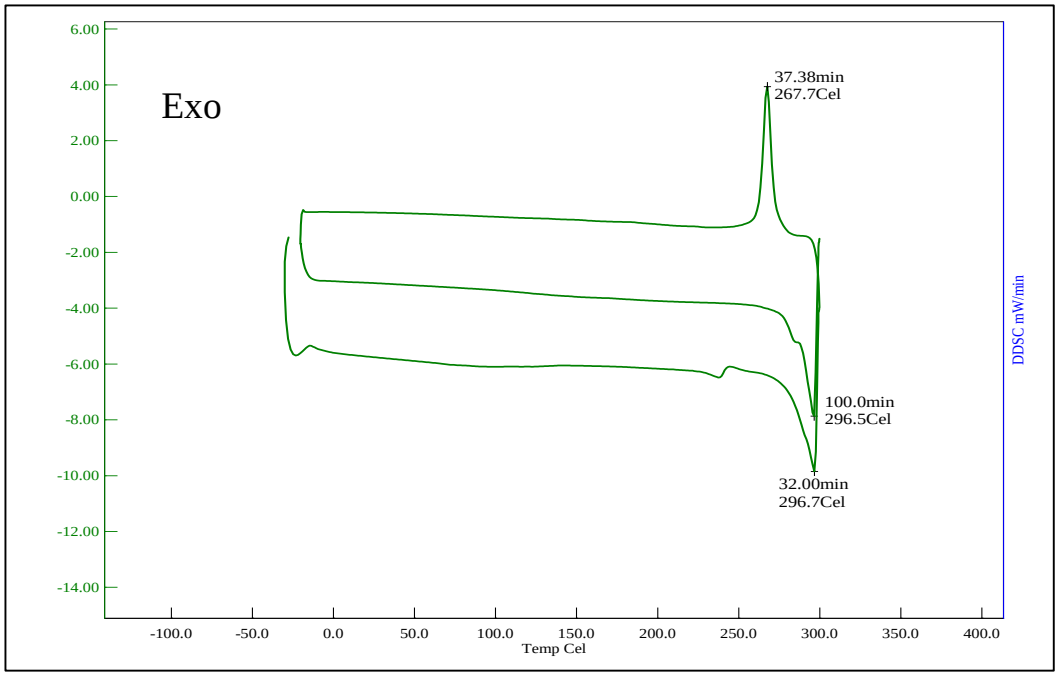


Figure A.44. DSC Analysis of ITR-45.