SYNTHESES OF FUNCTIONAL POLYESTERS WITH TUNABLE GLASS TRANSITION TEMPERATURES

by

Kübra Kalaycı

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Dedicated to my family

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ABSTRACT

SYNTHESES OF FUNCTIONAL POLYESTERS WITH TUNABLE GLASS TRANSITION TEMPERATURES

Polyesters are important polymers for many applications and one of them is powder coatings. They meet the required properties of powder coating resins. Furthermore, the ease of altering physical properties of polyesters opens a huge area to be studied. One of the important properties of polyesters is their glass transition temperature (T_g) which is the temperature that polymers change from rubbery to brittle structure. T_g can be affected by many factors related to the structure of polymers. Number average molecular weight (M_n) is one of the factors that has a great effect on it. It is also a critical feature for powder coating applications since powder coating resins undergo curing reactions in which crosslinking between chains occur and the coating takes its final form by applying heat. Therefore, the curing temperature is highly dependent on the T_g of powder coating resin. It is challenging to control T_g values of polyesters that are used as powder coating resins since it changes curing temperature. In order to study the effect of molecular structure, end group and molecular weight on T_g, various polyesters were synthesized with hydroxyl and carboxyl end groups. Polyesters with the same molecular weight but different end groups showed different T_g values. Higher T_g value was observed in carboxyl terminated polyesters probably because of hydrogen bonding between chains. On the other hand, changing one of the monomers to less sterically hindered one caused a big decrease on T_g. From the polyesters synthesized before, poly(ester-anhydride)s were tried to be obtained by using different anhydrides. Thus, it was achieved to increase M_n and T_g by increasing number of functional groups. Increasing T_g by this way, it was aimed to keep curing temperature low since these functional groups can also form crosslinks during curing reactions. Some reactions were successful with the formation of anhydride linkages, others ended up with the formation of anhydrides and chain scission at the same time. Formation of anhydride linkages between chains increased the molecular weight and T_g as expected.

ÖZET

AYARLANABİLİR CAMSI GEÇİŞ SICAKLIĞINA SAHİP FONKSİYONEL POLİESTERLERİN SENTEZLERİ

Poliesterler bir çok önemli uygulama alanına sahiptir ve bunlardan biri de toz boyalardır. Toz boya reçinelerinin gerek duyulan özelliklerini karşılarlar. Dahası, polyesterlerin fiziksel özelliklerinin kolayca değiştirilebilmesi, büyük bir araştırma alanıdır. Poliesterlerin önemli özelliklerin birisi camsı geçiş sıcaklığı (T_g) denen, polimerlerin elastikten kırılgan bir yapıya geçtikleri sıcaklıktır. T_g, polimerin yapısına bağlı olan birçok faktörden etkilenebilir. Sayısal ortalamalı mol kütlesi (M_n) T_g'ye büyük etkisi olan faktörlerden biridir. T_g aynı zamanda toz boya uygulamaları için de kritik bir özelliktir, çünkü toz boyalar sıcaklık uygulanarak son şekillerini aldıkları ve zincirler arası çapraz bağların oluştuğu kürlenme reaksiyonları verirler. Bu nedenle, kürlenme sıcaklığı büyük ölçüde toz boya reçinesinin Tg'sine bağlıdır. Toz boya reçinesi olarak kullanılacak polyesterlerin T_g değerlerini kontrol edebilmek, T_g değerinin kürlenme sıcaklığının da değişmesine neden olacağı için çetrefillidir, Molekül yapısı, uç gurup ve mol kütlesinin T_g üzerindeki etkilerini incelemek amacıyla farklı uç gruplara sahip çeşitli poliesterler sentezlendi. Aynı mol kütlesine ama farklı uç guruplara sahip polyesterler farklı T_g değerleri gösterdiler. Muhtemelen zincirler arası hidrojen bağına neden olması sebebiyle, karboksil uçlu polyesterlerde daha yüksek T_g değeri gözlendi. Diğer bir yandan, monomerlerin birini daha az sterik engele sahip monomerle değiştirmek T_g üzerinde büyük bir düşüşe neden oldu. Sentezlenen poliesterlerden, poliesteranhidrit elde etmek için farklı anhidritler kullanıldı. Böylece polimer yapısındaki fonksiyonel grupları arttırarak mol kütlesinin ve T_g değerinin artması sağlandı. Bu şekide T_g değerini arttırmakla, kürlenme sırasında fonksiyonel grupların da çapraz bağ yapabilecek olması sayesinde düşük kürlenme sıcaklığının korunması amaçlandı. Bazı reaksiyonlar anhidrit bağlarının oluşmasıyla başarıya ulaştı, diğerlerinde ise anhidrit oluşumu ve zincir kopması aynı anda gerçekleşti. Beklendiği gibi, anhidrit bağlarının oluşması mol kütlesinde ve T_g değerinde artışa yol açtı.

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BPADE	Bisphenol A diglycidyl ether
CHDA	1,4- Cyclohexanedicarboxylic acid
CHDM	1,4- Cyclohexanedimethanol
$CDCl_3$	Deuterated Chloroform
DSC	Differential Scanning Calorimetry
GPC	Gel Permeation Chromatography
H	Hydrogen
IPA	Isophthalic acid
IR	Infrared
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMR	Nuclear Magnetic Resonance
NPG	Neopentyl glycol
PA	Phthalic anhydride
PCCD	Poly (1,4-cyclohexylidenecyclohexane- 1,4-dicarboxylate)
PCL	Poly (ε- caprolactone)
PDO	1,3 propanediol
PG	Propylene glycol
PIN	Polyester of Isophthalic acid and Neopentyl glycol

PIP	Polyester of Isophthalic acid and Propanediol
PLA	Polylactide
PLS	Poly (sebacic acid)
PTN	Polyester of Terephthalic acid and Neopentyl glycol
RA	Ricinoleic acid
SA	Succinic anhydride
TEA	Triethyl amine
T_g	Glass transition temperature
THF	Tetrahydrofuran
$Ti(i\text{-}OPr)_4$	Titanium isopropoxide
T_m	Crystalline melting temperature
TPA	Terephthalic acid
UV	Ultraviolet
VOC	Volatile organic compounds

1. INTRODUCTION

Polyesters are among the most important polymers, since they have a very large range of application area such as clothing and home textile, food packaging, bottles, fibers, films and coatings. Polyester fibers have low water absorption, high heat resistance, high tenacity and less shrinkage when compared to other industrial polymer fibers [1]. Polyesters can be obtained via condensation of diols with diacids, diacid halides or diesters. The detailed synthesis of polyesters is mentioned in section 1.1.

The physical properties of polyesters can be easily changed by changing the type and ratio of monomers and reactive end groups. Carboxylic or alcoholic end groups can be used to obtain crosslinked polymer networks, in other words thermoset resins. Crosslinking can occur during polymerization or after polymerization by adding the necessary chemicals. It increases mechanical strength of the polymers which is a required property for some application areas such as coatings [2]. Crosslinking density and extend of reactions are also important to determine physical properties and it is basically related to reactive group concentration in the polymer chain and conversion of the end groups. Further explanation on reactive groups and crosslinking will be discussed in section 1.1.3.

The monomer composition of polyesters and the end groups have a great impact on some physical properties such as molecular weight and glass transition temperature which is mentioned in detail in sections 1.3 and 1.4. Determining of the molecular weight of polymers is not as easy as determining the molecular weights of small molecules, since not all the polymer chains are in the same length and it is only possible to calculate an average value of their size [3]. On the other hand, glass transition temperature (T_g) is also a critical property for polyesters in some application areas and there is an important relationship between T_g and number average molecular weight of polymers which is described in detail in section 1.4.2.

The potential application area of polyesters and poly(ester-anhydride)s synthesized in this study could be powder coatings since T_g is critical for powder coating resins. For the curing process which is explained in detail in section 1.5.1 low curing temperature is a desired feature and it depends on T_g. To achieve low curing temperature T_g should also be low, on the other hand it should not be too low to cause agglomeration during storage of resins. It seems to be possible to keep this balance using polyesters with tunable T_g.

1.1. Synthesis of Polyesters

The synthesis of polyesters proceeds through a typical condensation reaction between difunctional carboxylic acids or methyl esters and diols with the elimination of water or methanol respectively. Condensation polymerization mechanism is based on a step-wise condensation of reactive end groups [3].

OH-R-OH + HOOC-R'-COOH → OH-R-OOC-R'-COOH + H_2O

1.1.1. Polyesters Based on 1,4- Cyclohexanedimethanol (CHDM) and 1,4-Cyclohexanedicarboxylic Acid (CHDA)

Poly (1,4-cyclohexylidenecyclohexane- 1,4-dicarboxylate) (PCCD) is an aliphatic polyster that is obtained by the condensation reaction of 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexane dimethanol in the presence of a catalyst such as titanium(IV). This polyester is known for its good weatherability properties due to the lack of any significant UV-chromophore [4].

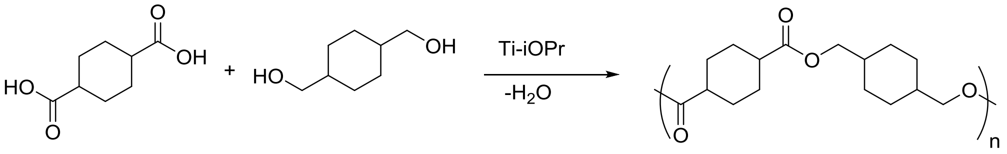


Figure 1.1. Synthesis of PCCD.

Aliphatic polyesters have some disadvantages such as low chemical stability and low Tg compared to aromatic ones. However, cycloaliphatic polyesters compared to acyclic ones show improved chemical stability and higher Tg and among those PCCD has gained an interest thanks to its good processability while retaining good impact resistance, solvent resistance and UV stability [4].

The stereochemistry of monomers (both the diol and the diacid) has a great effect on the molecular weight and glass transition temperature of the resulting polyesters. Therefore it is important to determine *-cis* to *-trans* ratio in such polyesters [4].

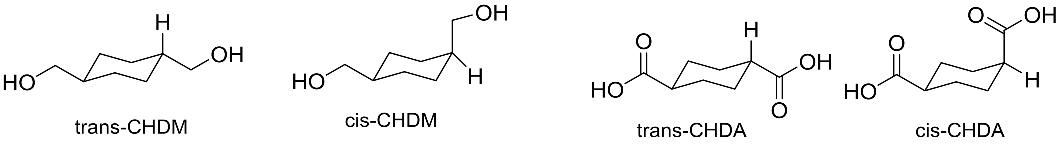


Figure 1.2. Different Conformations of CHDM and CHDA.

1.1.2. Polyesters Based on Isophthalic and Terephthalic Acid

Polyesters that are made from aromatic acids such as isophthalic acid (IPA) and terephthalic acid (TPA) can be semi-aromatic or fully-aromatic depending on the choice of the diol. Aromatic structures usually increase rigidity and thus the heat resistance [1]. However, low weathering stability is one of the problems in most of the fully aromatic polyesters.

The example illustrated in Figure 1.3 shows a semi-aromatic copolyester synthesis based on isophthalic acid (IPA), 2,2-dimethyl,1,3-propanediol (NPG) and propylene glycol (PG). In this corresponding study, relative monomer ratios were altered to observe the effect of molecular architecture on the polyester properties [5].

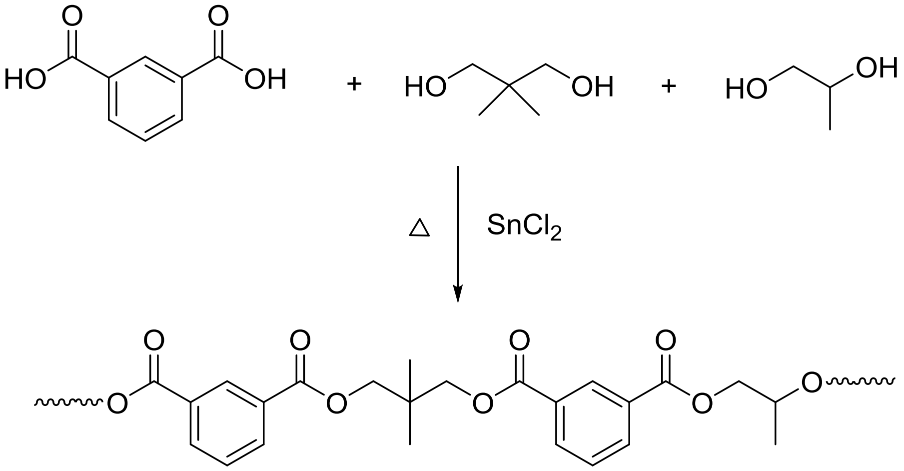


Figure 1.3. Synthesis of Semi-aromatic Copolyester.

1.1.3. End Group Modification of Polyesters

End group modification is an important process for polyesters, since end groups play a key role in cross-linking reactions and degradation mechanism. Polyesters should have reactive end groups to react with cross-linkers and to form bonds between polymer chains which helps to achieve a given required physical strength and resistance. Furthermore, the properties of cross-linked polyesters can be modified for different applications by changing the chemical composition and the architecture [6].

It is a common procedure to synthesize prepolymers with hydroxyl end groups and then modifying these end groups to synthesize carboxyl terminated polyesters. The modification of hydroxyl terminated end groups can be done in various methods. One example for this is using anhydrides such as succinic or phthalic anhydride. A study suggests end group modification of polyesters based on poly(ε- caprolactone) (PCL) and polylactide oligomers (PLA) with succinic anhydride to obtain cross-linkable poly(ester-anhydride) networks as shown in Figure 1.4 [7].

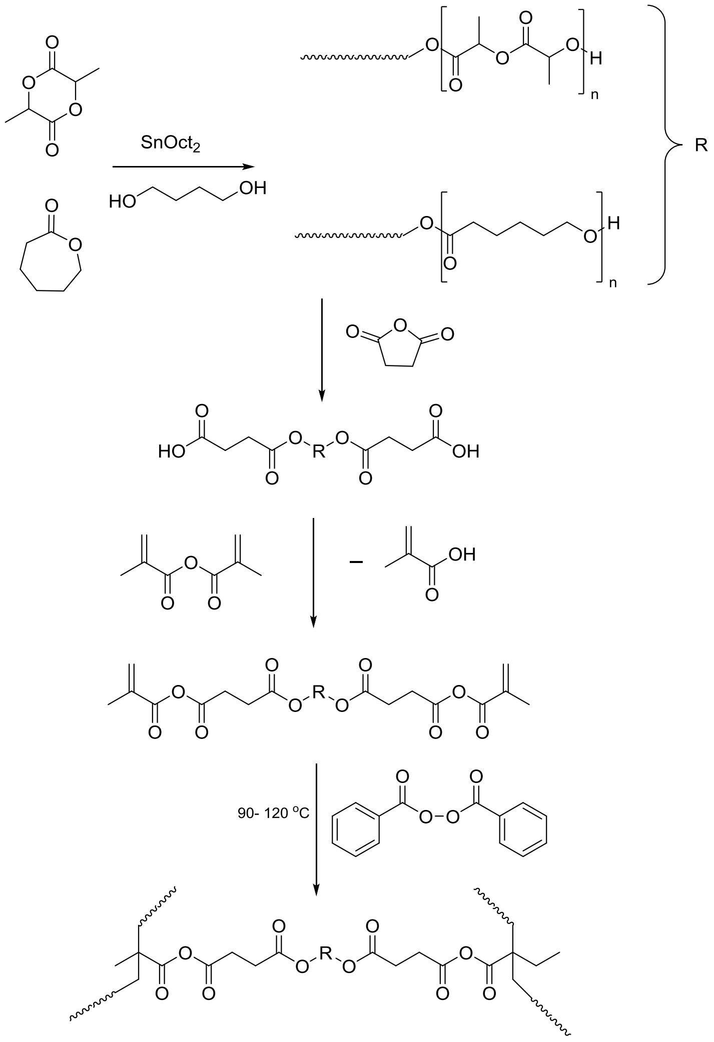


Figure 1.4. An Example of End Group Modification of Hydroxyl Terminated Cross-linkable Polyesters.

1.1.4. Melt Polymerization Method for Polyester Synthesis

In melt polymerization method, simply the reactants are put in a vessel and then heat is applied to melt and to achieve the condensation reaction. The main characteristic of melt polycondensation method is that reaction is run without solvents. Therefore, it is not necessary to purify the polymer at the end of the reaction unless some side products are formed. Since there is no solvent used, almost nothing escapes into the air which makes the process environmentally friendly. The condensate that are distilled can be collected and reused again. The conversion rate in melt polycondensation is very high; almost 100 %. However, this method requires high temperatures such as 200 – 270 ^{o}C. The monomers and the target polymers should be stable at those temperatures. It is also possible to produce large amounts of polymers with high molecular weights by using this method [8].

The other polyesterification techniques have some disadvantages when compared to melt polymerization. For instance, it is difficult to obtain high molecular weight polymers by solution polymerization. Therefore, polyesters would not have good impact strength [9]. On the other hand, excess solvent must be removed to obtain the pure polymer once the desired conversions are reached [1]. For interfacial polymerization moisture is an important problem which can cause polymer to degrade [9]. Furthermore, in this method large amounts of water are always present and it may react with diacid halide monomer and decrease the yield [9]. The industrial yield in interfacial method is also very low which is about 3-20% polymer solids per batch. Both solution and interfacial polymerization techniques are often preferred when the starting monomers or the final polyesters are sensitive to high temperatures. In the present study melt polycondensation technique was used for the synthesis of polyesters.

The melt polycondensation equipment consists of a glass reactor, a mixer that measures the torque, heater, vacuum pump and a condenser which helps collect the distillate. A reactor vessel is placed in an oil bath. There is an inlet for nitrogen and vacuum pump and outlet for the distillate (Figure 1.5).

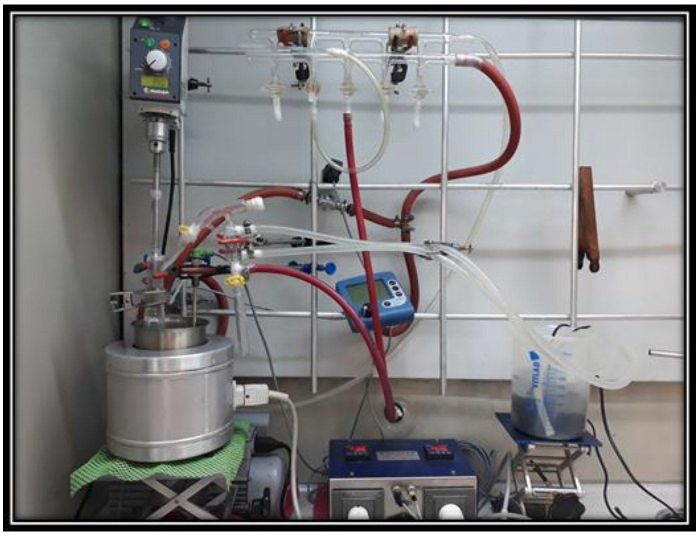


Figure 1.5. Melt Polymerization Set-up.

1.2. Poly(ester-anhydride)s

Poly(ester-anhydride)s have gained interest in recent years for many polymer applications because of their high amount of functionality [10]. An example that shows introduction of anhydride linkages into polyesters is the synthesis of poly(lactic acid) (PLA)-terminated poly(sebacic acid) (PLS) by melt condensation to yield ester-anhydride ABA type triblock copolymers as shown in Figure 1.6 [11].

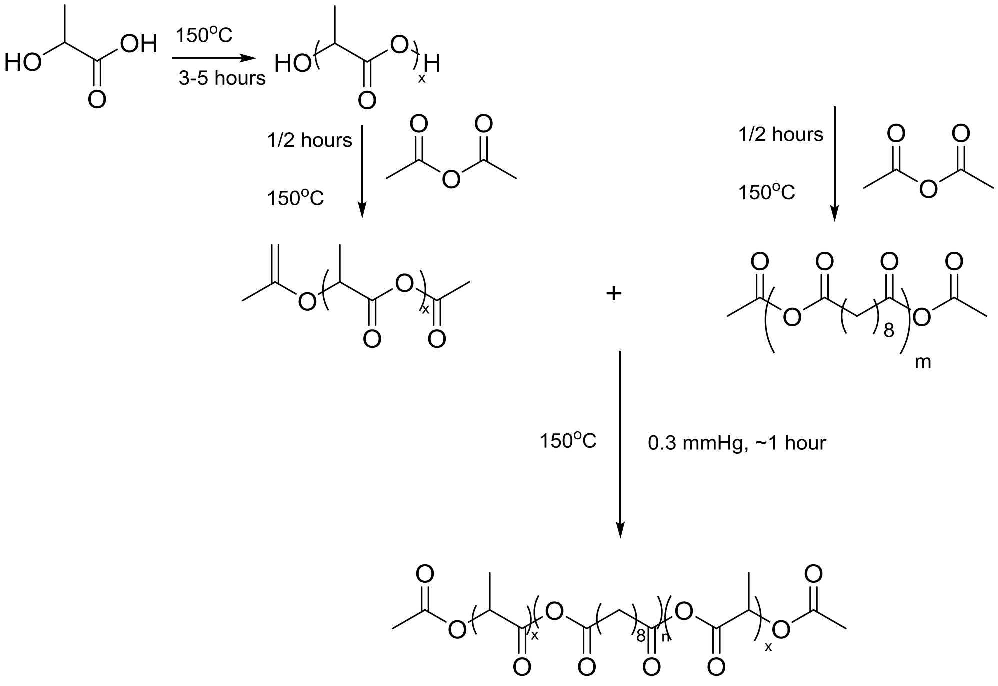


Figure 1.6. Synthesis of ABA Type Poly(ester-anhydride) Copolymers.

Another example that is related to poly(ester-anhydride)s synthesis describes the insertion of ricinoleic acid (RA) into diacid oligomers of poly(sebacic acid) (PSA) to synthesize degradable poly(ester-anhydrides) by melt polycondensation as shown in Figure 1.7 [12].

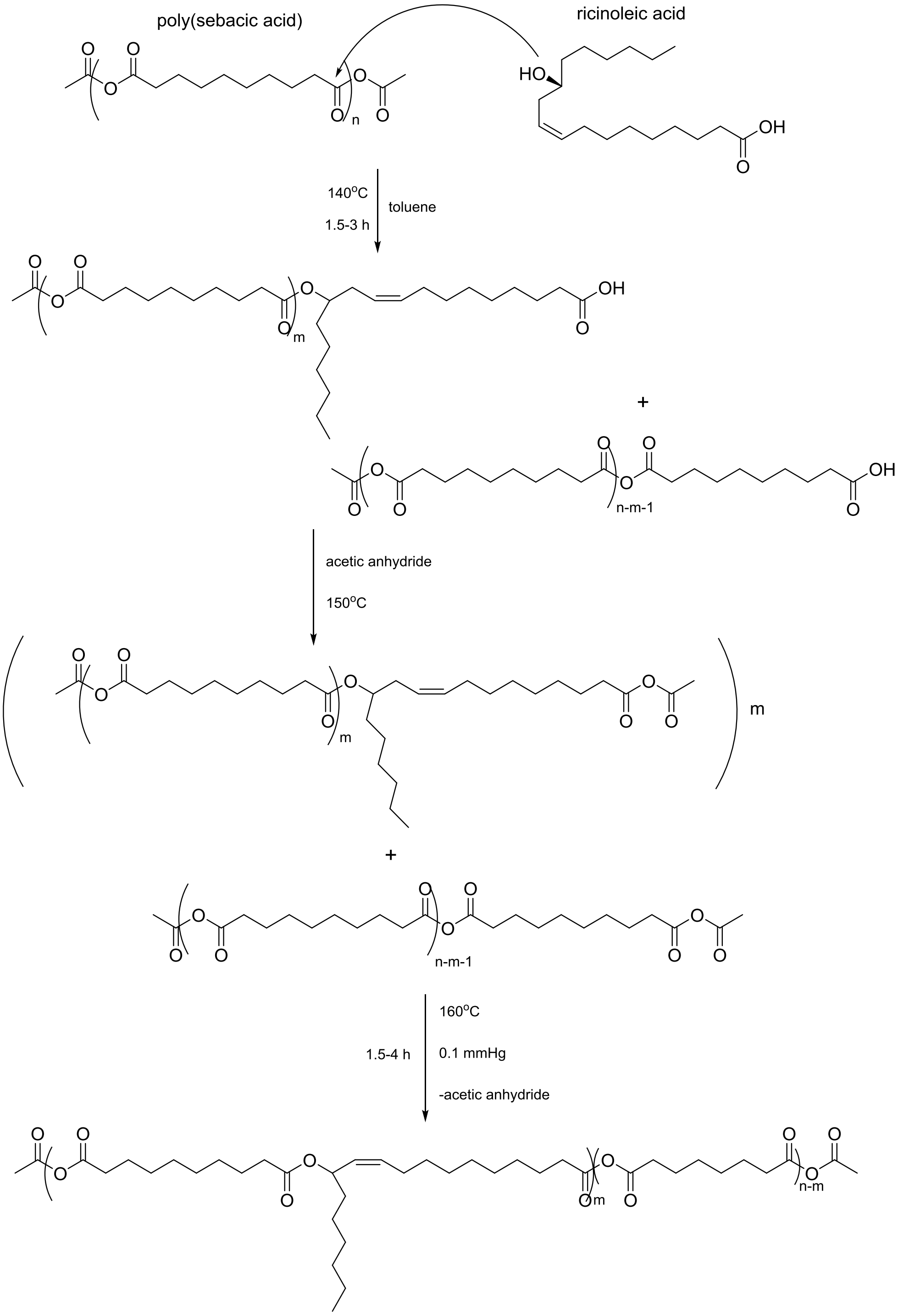


Figure 1.7. Synthesis of Degradable Poly(ester-anhydride)s.

Anhydride linkages can also be used for the application in powder coatings by converting polyester (PCCD) oligomers to poly(ester-anhydride) resins, using 1,4-cyclohexane dicarboxylic (CHDA) acid and 1,4-cyclohexane dimethanol (CHDM) as monomers as shown in Figure 1.8 [10]. However, the release of acetic acid is a problem for industrial applications.

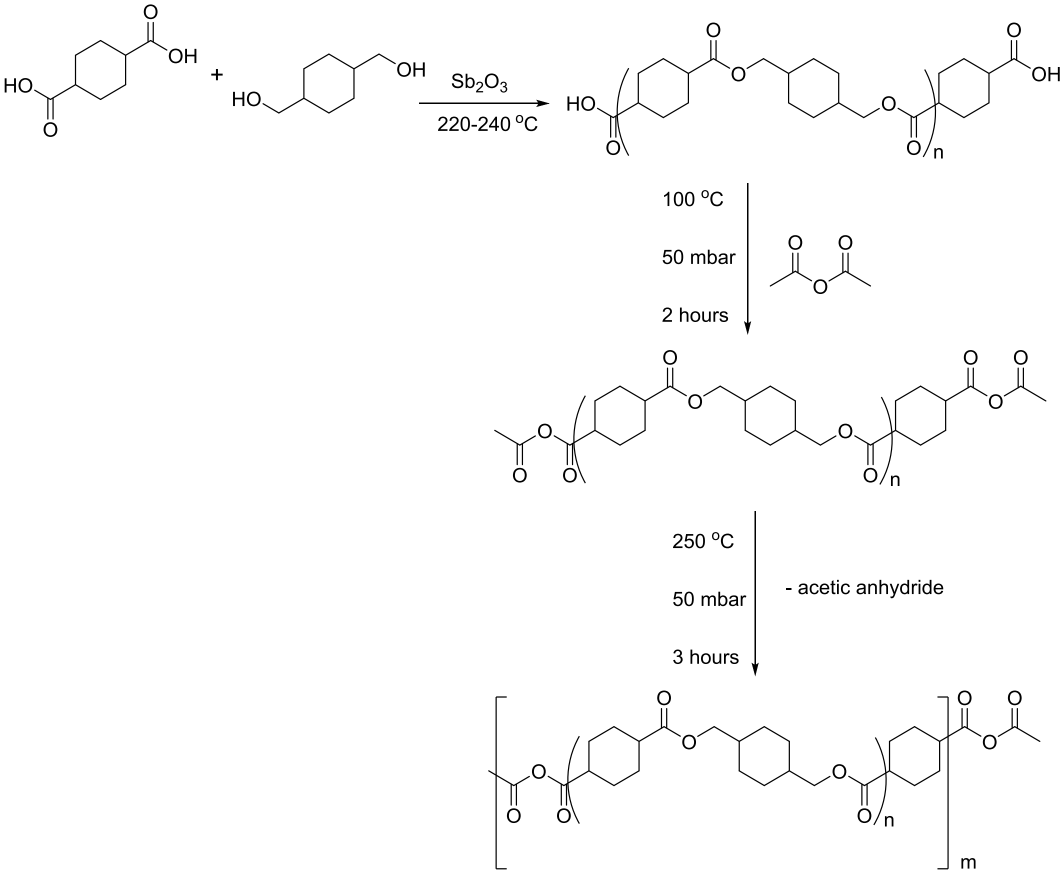


Figure 1.8. Synthesis of Poly(ester-anhydride)s from PCCD Oligomers.

1.3. The Glass Transition Temperature (T_g) of Polymers

Glass transition temperature is the temperature at which polymeric structures change from brittle and glassy character to less rigid and more rubbery ones. At this temperature properties such as thermal expansion, heat capacity, refractive index, change, since all of them are related to the degree of freedom for molecular motion [2].

The glass transition is a second-order transition which differs from phase transitions such as melting or boiling which are known as first-order transitions. Crystalline polymers where polymer chains are packed in a regular way show crystalline melting temperature

(T_m). The difference between these thermal transitions is related to the molecular motion. At crystalline melting temperature, the translational, rotational and vibrational energies of the molecules increase and they show long-range motions. However, slightly above glass transition temperatures amorphous polymers which have random chain arrangement show only small segmental motion [13].

Polymer morphology determines whether the sample exhibits T_g or T_m; completely amorphous polymers show only T_g while completely crystalline polymers show only T_m. On the other hand, semi-crystalline polymers exhibit both T_g and T_m. Figure 1.9 illustrates the changes in specific volume with temperature for completely amorphous, completely crystalline and semi-crystalline polymers [13].

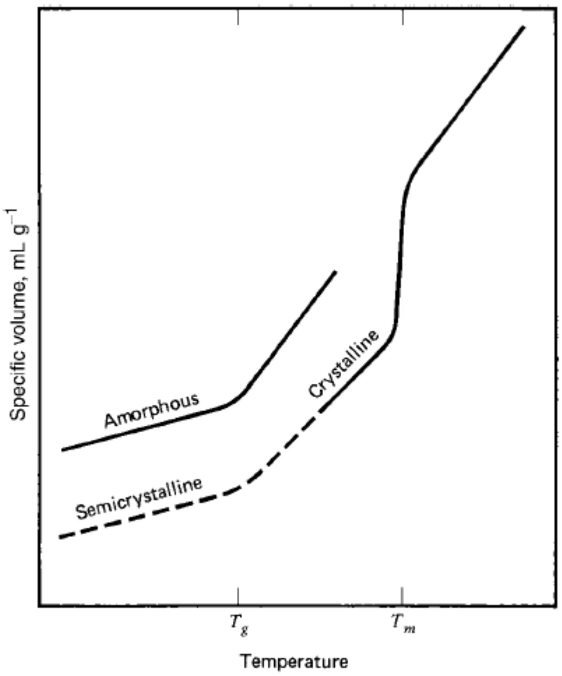


Figure 1.9. Determination of Glass Transition and Crystalline Melting Temperature.

The glass transition temperature is influenced by some specific features such as;

- The pendant groups to polymer chain which increase the energy required to rotate the molecule around the bonds in the main chain. Branches and side chains have also the same effect.
- The rigid groups such as benzene ring in the polymer backbone.
- Crosslinking
- Physical interactions such as hydrogen bonds between polymer chains.
- Number average molecular weight since higher molar mass polymers have less ease of movement and more restriction of their overall molecular freedom.
- The existence of plasticisers [2].

1.3.1. Determination of Tg

The glass transition temperature, Tg, is most widely determined by using Differential Scanning Calorimetry (DSC) technique. It basically measures the heat flow into (endothermic) or out (exothermic) of a sample as a function of temperature and time [14].

In a DSC instrument a sample and reference are both subjected to nearly the same heating/cooling rate throughout the experiment. By measuring the difference in heat flow between reference and sample cell, amount of heat released or absorbed during such transitions can be calculated [15].

1.4. Molecular Weight of Polymers

The term molecular weight is usually used to describe the size of a polymer. Compared to other molecules, the molecular weight of a polymer is not a certain value since the chain lengths varies. It is rather a distribution of molecular weight of polymer chains [3]. This distribution can be illustrated as in Figure 1.10.

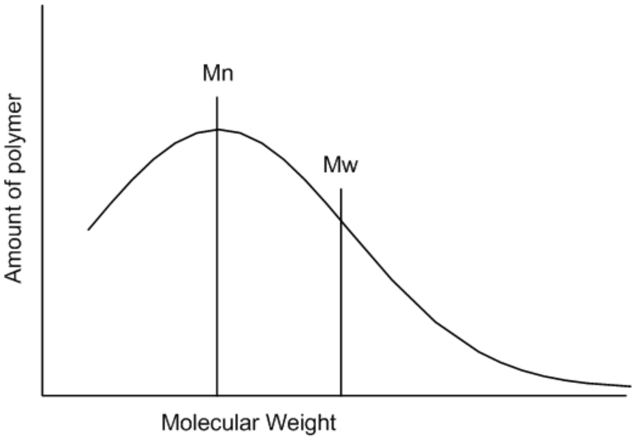


Figure 1.10. Distribution of a Molecular Weight in a Typical Polymer.

Due to this distribution of molecular weight, measurements can give only average values. Different averages such as number average (M_n) or weight average (M_w) molecular weight can be calculated [13]. The most general is the simple arithmetic mean which gives M_n and this is defined by the equation;

$$Mn = \frac{\sum NiMi}{\sum Ni}$$

where Mi is the molar mass of the molecular species I and Ni is the number of molecules of I in the sample [2]. Furthermore, M_w can be calculated from the equation;

$$Mw = \frac{\sum NiMi^2}{\sum NiMi}$$

The ratio of M_w to M_n gives the information about the spread of molar masses in a particular polymer sample and it is called *polydispersity* (PDI) of the polymer [2].

1.4.1. Determination of Molecular Weight

There are many methods to calculate the molecular weight of polymers such as end group analysis, light scattering, measurement of viscosity or ultracentrifugation. However the most common and easy method is the Gel Permeation Chromatography (GPC), also referred as Size Exclusion Chromatography (SEC) [2].

GPC is based on the permeation of a polymer solution through a column in which contains microporous beads of a crosslinked polymer which is usually polystyrene. These beads have different pore diameters. When polymer molecules pass through the column, depending on their size they migrate at different rates through the pores [2]. The small-sized polymers penetrate more beads in the column, so they pass through more slowly and leave the column last. The larger polymer molecules on the other hand, can penetrate fewer beads and leave the column earlier. A detector located at the end of the column measures the amount of polymer leaving the column as a function of time and it gives a plot which shows the molecular weight distribution. M_n and M_w are also calculated automatically [13].

It is also possible to calculate M_n by end group analysis of polymers using ^{1}H-NMR [14]. End group proton signals can usually be distinguished from the proton signals at the repeating units. Therefore, after identifying these signals, simple calculations can be done. First molecular weight of end groups and repeating unit is calculated. Then the integral of proton signals is determined and integrals per proton are calculated. By dividing integral per proton of repeating unit to integral per proton of end groups, the number of repeating units is obtained. Finally, the number of repeating units is multiplied by the molecular weight of repeating units and the molecular weight of the end groups is added to this number. The result gives the M_n of the polymer [16].

1.4.2. Relationship Between Mn and Tg

Number average molecular weight, M_n, and the glass transition temperature, T_g, are related by the *Flory-Fox equation* as shown below;

$$Tg = Tg,\infty - \frac{K}{Mn}$$

where Tg,∞ is the highest glass transition temperature that can be achieved at an infinite molecular weight and K is a constant related to the free volume present in the polymer [17]. The equation basically shows the dependence of the glass transition temperature on free space available for molecular motions.

As the free volume increases, it becomes easier for the polymer chains to move and change its physical conformations. Upon cooling, free volume decreases until the glass transition temperature is reached and at this point the polymer chains cannot achieve segmental motions. The number of polymer chain ends also determine the free volume in a polymer. Polymers with longer chains, in other words high molecular weights, would have less chain ends per total units and less free volume than polymers with shorter chains and polymers with less free volume results in a higher T_g.

To sum up, glass transition temperature depends on free volume, which in turn depends on the number average molecular weight of the polymer. As the molecular weight increases, the glass transition temperature increases asymptotically up to a certain value as illustrated in Figure 1.11.

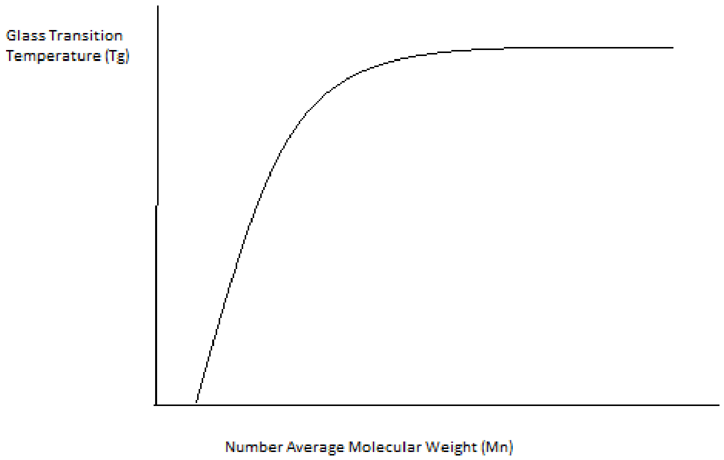


Figure 1.11 Molecular Weight-Glass Transition Temperature Relationship.

1.5. Potential Application Area: Powder Coatings

Powder coatings are separated from solution-based coatings by their dry finished form that does not emit any volatile organic compounds (VOC) during the application and curing. Powder coatings are durable and have a wide variety of applications. They involve finely ground particles of pigment and resin which are charged electrostatically and sprayed onto a metal surface that is ground. They adhere to the surface and are held there until heated in an oven [18]. During the heating process, powder melts and forms a uniform, continuous coating. Depending on the type of powder coating, the coating can be thermoplastic or thermoset. For thermoset powder coatings, which constitutes almost 95% of all powder coatings, the heating/curing step is the most crucial process since the crosslinking reactions take place in this step[19].

1.5.1. Curing of Thermoset Powder Coatings

Thermoset powder coatings must be heated to provide the desired properties such as mechanical, chemical or decorative properties. Since the production of powder coating is a high-speed production, the heating process must be efficient, cost- and energy-effective. Therefore, the curing temperature is critical for powder coating applications [19].

So far, powder coating resins that can be cured at 120◦C have been developed [20]. However, when decreasing curing temperature, one must be careful about the glass transition temperature. Because low temperature curing systems also contain polyesters with low glass transition temperature and this may result in agglomeration during storage. In order to prevent this problem, T_g of powder coating resins should be around 50◦C.

Using anhydride linkages in powder coating resins could be a solution to this problem as shown in Figure 1.12. Instead of using polyester resins, polyester-anhydrides which have the same molecular weight as polyesters could be used. Moreover, they would have higher number of functional groups which can react during curing process. In this way, resins will have high M_n value as well as high T_g during storage, and easy breakage of anhydride bonds during curing process will enable higher crosslink densities at low temperatures.

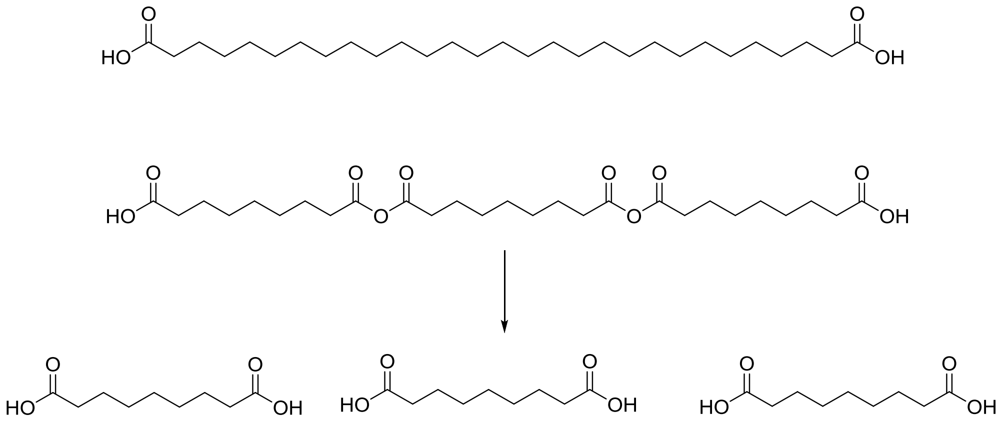


Figure 1.12. Usage of Anhydride Linkages.

1.5.2. Curing Reactions of Powder Coatings

Curing reactions of powder coatings involves chemical crosslinking of powder coating resins. Epoxides are the most common type of curing agents in powder coating industry and one of the most common one among them is the polymer of Bisphenol A diglycidyl ether (BPADE) as seen in Figure 1.13 [21].

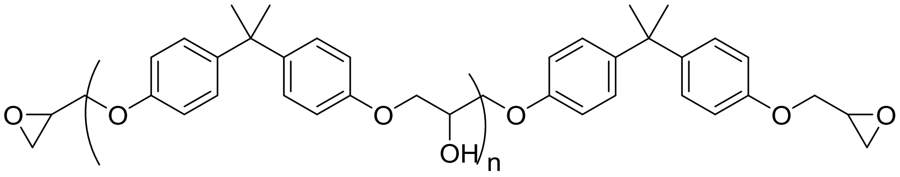


Figure 1.13. Molecular Structure of Poly (bisphenol A diglycidyl ether).

The reaction between poly(ester-anhydride) resins and crosslinking agent during curing process would be breaking anhydride linkages and formation of new bonds with epoxide. An example in Figure 1.14 shows the possible reaction between anhydrides and epoxides [21].

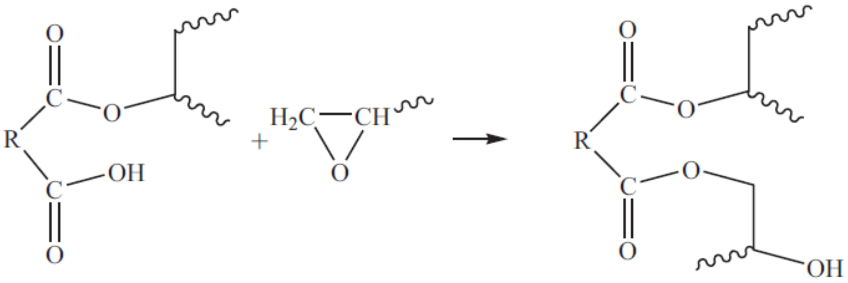


Figure 1.14. An Example of Anhydride-epoxy Curing Reaction.

2. AIM OF THE STUDY

The aim of this study is to synthesize polyesters that can be used as powder coating resins by melt polycondensation method and to examine the relationship between end groups, molecular weight (M_n) and glass transition temperature (T_g) by using ^{1}H-NMR, GPC and DSC analysis. Moreover, the synthesis of poly(ester-anhydride)s by using these polyesters or modification of the end groups of polyesters and the effect of these reactions on T_g were investigated. By using anhydride linkages, it is aimed to increase the number of reactive functional groups in chain. By this way high molecular weight powder coating resins with high enough T_g for storage can be obtained and since anhydride linkages are reactive they will be broken during the curing process and low curing temperature could be achieved despite the high T_g.

3. EXPERIMENTAL

3.1. Materials

1,4-Cyclohexane dicarboxylic acid (CHDA) with ~70% trans content was obtained from Acros Organics. 1,4-Cyclohexane dimethanol (CHDM), isophthalic acid (IPA), 2,2-dimethyl-1,3-propanediol (NPG), 1,3-propanediol (PDO), succinic anhydride (SA), phthalic anhydride (PA) and titanium isopropoxide (Ti(i-OPr)$_4$) were obtained from Aldrich. Terephthalic acid (TPA) was obtained from Merc.

3.2. Synthesis of Polyesters

3.2.1. Synthesis of Poly (1,4-cyclohexylidenecyclohexane- 1,4-dicarboxylate) (PCCD)

1,4-Cyclohexanedicarboxylic acid and 1,4-Cyclohexanedimethanol were mixed in different ratios in a melt reactor as shown in Figure 3.1 and Table 3.1. Ti(i-OPr)$_4$ was used as catalyst at 0.5 mol-% ratio (0,3465 mmol). Heat was applied, and the torque was recorded throughout the reaction. The distilled water was collected to favour the equilibrium towards products. The reaction was run under nitrogen atmosphere and then vacuum was applied. Reaction temperatures, pressures and total times used in various reactions are depicted in Table 3.2.

Table 3.1. Mole ratios of monomers for PCCD synthesis.

Sample Name	CHDA:CHDM (mole ratio)	CHDA		CHDM	
		mole	weight (g)	Mole	weight (g)
PCCD_1	1 : 1	0,0690	12,0000	0,0690	10,1000
PCCD_2	1,0 : 1,1	0,0695	11,9760	0,0765	11,0330
PCCD_3	1,1 : 1,0	0,0765	13,2000	0,0695	10,1000
PCCD_4	1 : 1	0,0690	11,8873	0,0690	9,9956
PCCD_5	1,05 : 1,00	0,0720	12,4021	0,0686	9,8982
PCCD_6	1,02 : 1,00	0,0693	11,9370	0,0680	9,8018
PCCD_7	1,00 : 1,05	0,0602	10,3658	0,0632	9,1190
PCCD_8	1,00: 1,05	0,1321	27,7420	0,1387	20,000

Table 3.2. Reaction conditions for PCCD synthesis.

Sample Name	Temp (◦C)	Vacuum (mbar)	Total Time (hour)
PCCD_1	200-->240	30	4
PCCD_2	200-->240	30	4
PCCD_3	200-->240	15	4
PCCD_4	180-->245	25 (2 hours)	6
PCCD_5	180-->245	3 (2 hours)	6
PCCD_6	180-->245	4 (2 hours)	6,5
PCCD_7	180-->245	6 (1.5 hour)	6,5
PCCD_8	180-->245	5-3 (1 hour)	6,5

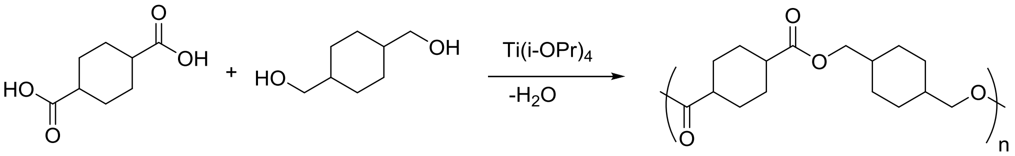


Figure 3.1. Synthesis of PCCD.

3.2.2. Synthesis of Polyesters Based on Terephthalic Acid and Neopentyl Glycol: PTN

Terephthalic acid and neopentyl glycol were mixed in a melt reactor at different ratios as shown in Figure 3.2 and Table 1.3. Ti(i-OPr)$_4$ was used as catalyst in 1 mol-% ratio. Reaction was run under nitrogen atmosphere, vacuum was applied for 1.5 hours as illustrated in Table 3.4. A similar melt polymerization procedure to the above one was followed.

Table 3.3. Mole ratios of terephthalic acid and neopentyl glycol.

Sample Name	TPA: NPG (mole ratio)	TPA		NPG	
		mole	weight (g)	mole	weight (g)
PTN_1	1,0: 1,1	0,09	14,9526	0,10	10,4084
PTN_2	1,00: 1,15	0,10	16,6140	0,15	15,6126

Table 3.4. Reaction conditions for the synthesis of PE from TPA and NPG.

Sample Name	Temp (◦C)	Vacuum (mbar)	Total Time (hour)
PTN_1	160-->230	13 (1.5 hours)	6
PTN_2	180-->250	4 (1.5 hours)	7

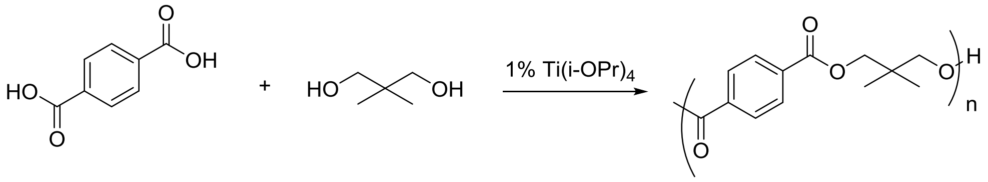


Figure 3.2. Synthesis of Polyester (PTN) from TPA and NPG.

3.2.3. Synthesis of Polyesters Based on Isophthalic Acid and 1,3-propanediol :PIP

Isophthalic acid and 1,3 propanediol (Figure 3.3) were mixed in a mole ratio of 1:1.8 (0,05 mole, 8,307 g IPA; 0,075 mole, 5,708 g PDO). 1.0 mol-% of Ti-(iOPr)$_4$ was used. Reaction was started at 160 ◦C and then temperature was raised to 240◦C in 6 hours. 80 mbar of vacuum was applied for 1 hour. The reaction was run under nitrogen atmosphere and above melt polymerization procedure was applied.

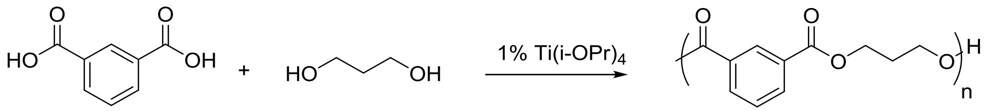


Figure 3.3. Synthesis of Polyester (PIP) from IPA and PDO.

3.2.4. Synthesis of Polyesters Based on Isophthalic Acid and Neopentyl Glycol :PIN

Isophthalic acid and neopentyl glycol were mixed in a melt reactor in different ratios as shown in Figure 3.4 and Table 3.5. The same reaction procedures were applied as described above and reaction conditions were depicted in Table 3.6.

Table 3.5. Mole ratios of IPA and NPG.

Sample Name	IPA : NPG (mole ratio)	IPA		NPG	
		mole	weight (g)	mole	weight (g)
PIN_1	1,0 : 1,5	0,05	8,3070	0,075	7,8063
PIN_2	1,0 : 1,8	0,05	8,3070	0,090	9,3676
PIN_3	1,0 : 1,8	0,12	19,9368	0,216	22,4821

Table 3.6. Reaction conditions for the synthesis of PE from IPA and NPG.

Sample Name	Temp (◦C)	Vacuum (mbar)	Total Time (hour)
PIN_1	160-->250	100 (1.5 hours)	6
PIN_2	140-->250	5-3 (2 hours)	9
PIN_3	140-->250	5 (1 hour)	9

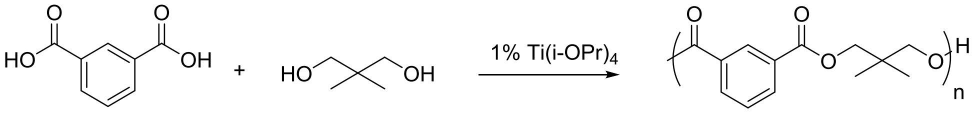


Figure 3.4. Synthesis of Polyester (PIN) from IPA and NPG.

3.3. Synthesis of Poly(ester-anhydride)s

3.3.1. Synthesis of Poly(ester-anhydride)s from PCCD and Phthalic Anhydride (PA)

Previously synthesized PCCD polymers with hydroxyl end groups were mixed with phthalic anhydride in different monomer ratios in a melt reactor as shown in Table 3.7 and Figure 3.5. Reactions carried out in inert atmosphere. Vacuum was not applied during reactions. Reaction conditions were illustrated in Table 3.8.

Table 3.7. Mole ratios of PCCD and PA.

Sample Name	PCCD-OH : PA	PCCD-OH		PA	
		mole	weight (g)	mole	weight (g)
PCCD_2_PA_1	1 : 2	0,0051	23,4933	0,0102	1,5065
PCCD_7_PA_1	1,0 : 2,2	0,0006	3,0000	0,0132	0,2000
PCCD_7_PA_2	1 : 3	0,0006	3,0000	0,0018	0,3000
PCCD_7_PA_3	1 : 3	0,0006	3,0000	0,0018	0,3000
PCCD_7_PA_4	1 : 4	0,0004	2,1000	0,0016	0,2400

Table 3.8. Reaction conditions for polyester-anhydrides of PCCD and PA.

Sample Name	TEA	Temp (◦C)	Total Time (hour)
PCCD_2_PA_1		180-->220	5
PCCD_7_PA_1		180-->210	4
PCCD_7_PA_2		160-->210	4
PCCD_7_PA_3	10%	160-->210	4
PCCD_7_PA_4		160-->210	4

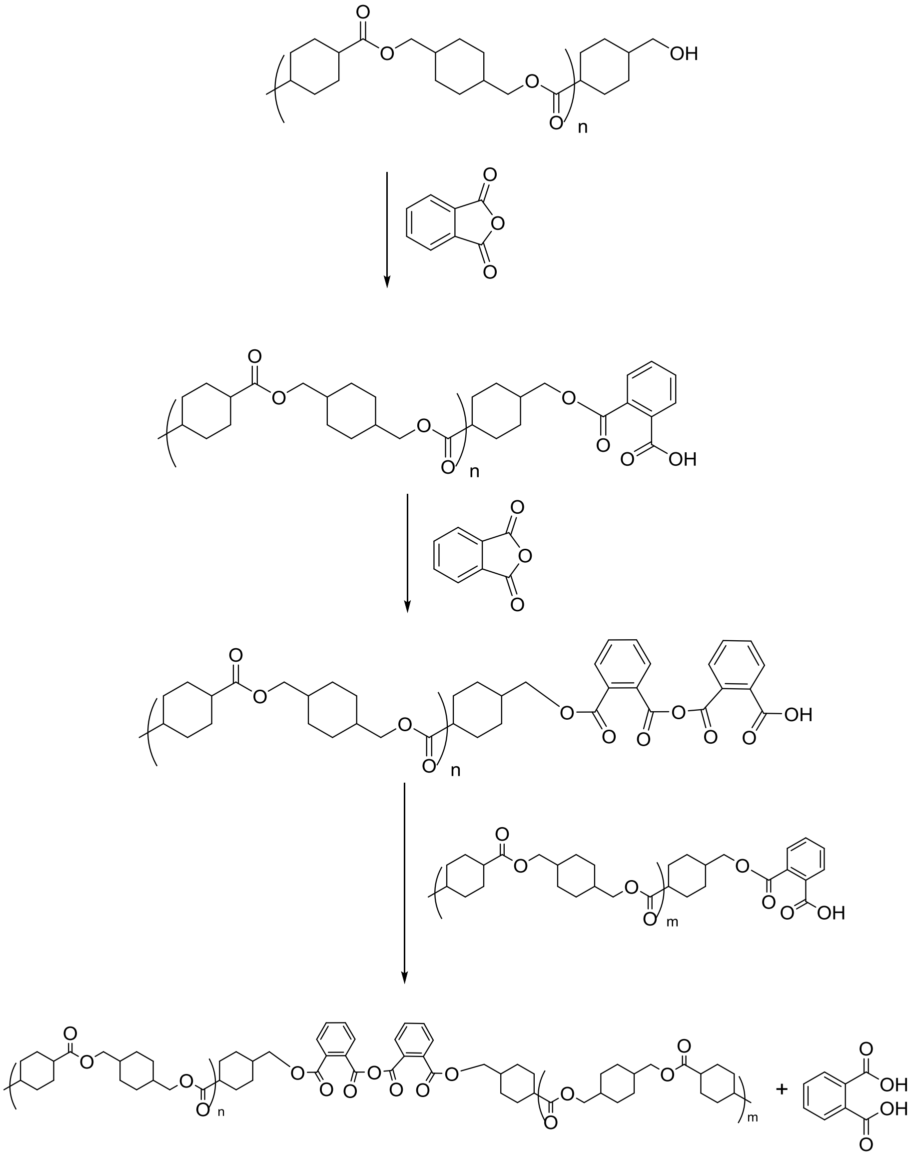


Figure 3.5. Synthesis of Poly(ester-anhydride)s from PCCD and PA.

3.3.2. Synthesis of Poly(ester-anhydride)s from PCCD and Succinic Anhydride (SA)

A hydroxyl terminated PCCD (PCCD_8) polymer was mixed with succinic anhydride in 1:4 mole ratio (0,001 mole, 8,152 g PCCD; 0,004 mole, 0,4 g SA) in a melt reactor under nitrogen atmosphere as shown in Figure 3.6. Catalyst was not used in this reaction. Reaction was started at 160◦C and raised up to 200◦C in 4 hours. 10 mbar of vacuum was applied for 2 hours.

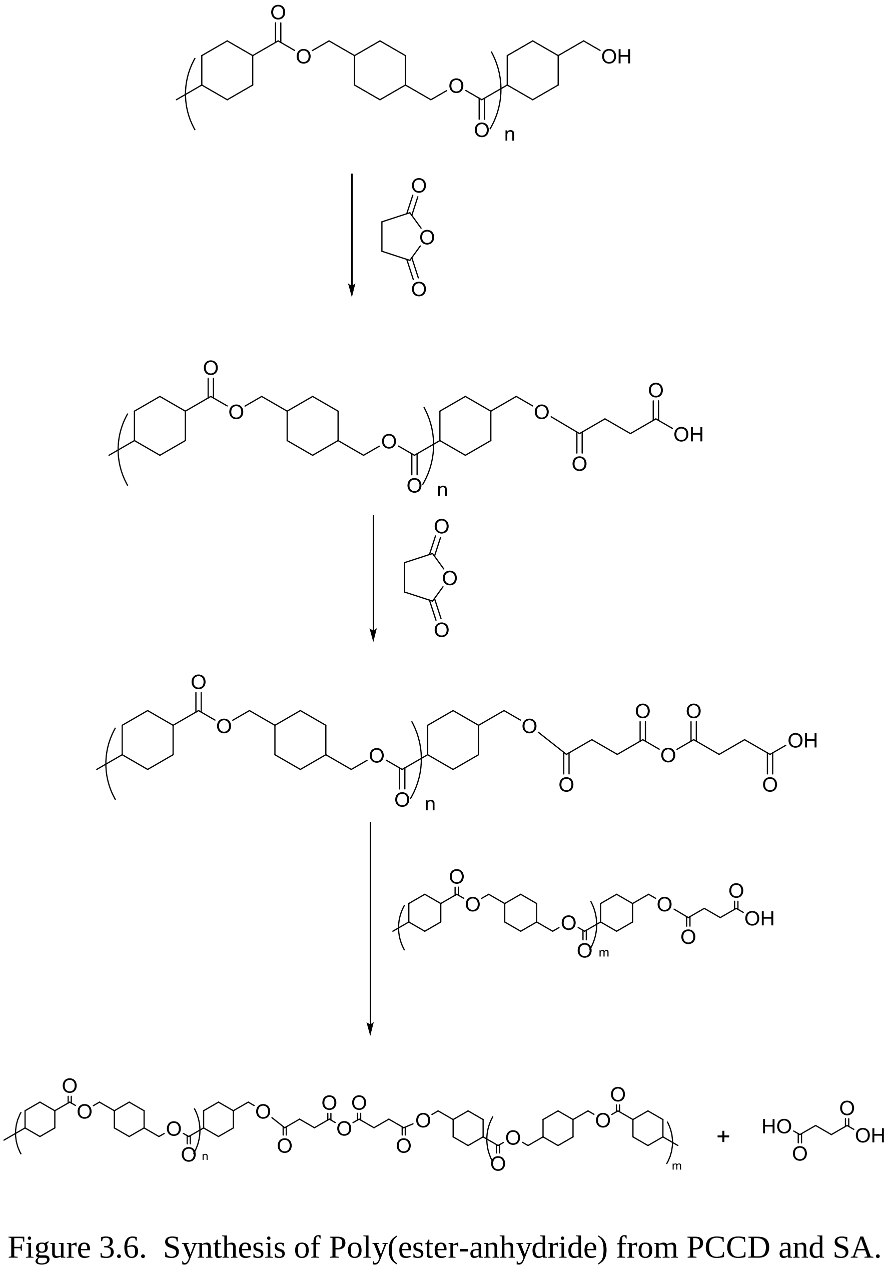


Figure 3.6. Synthesis of Poly(ester-anhydride) from PCCD and SA.

3.3.3. Synthesis of Poly(ester-anhydride)s from PIN and Succinic Anhydride (SA)

Polyesters (PIN) of isophthalic acid and neopentyl glycol and succinic anhydride (SA) were mixed in a melt reactor in 1 to 3 mole ratio (0,0028 mole, 8,0 g PIN; 0,0080 mole, 0,84 g SA). Temperature was set to 160◦C at the beginning and increased to 200◦C in 4 hours. 10 mbar of vacuum was applied for the last 2 hours of the reaction. Same melt condensation procedure as above was followed. Figure 3.7 illustrates the reaction mechanism.

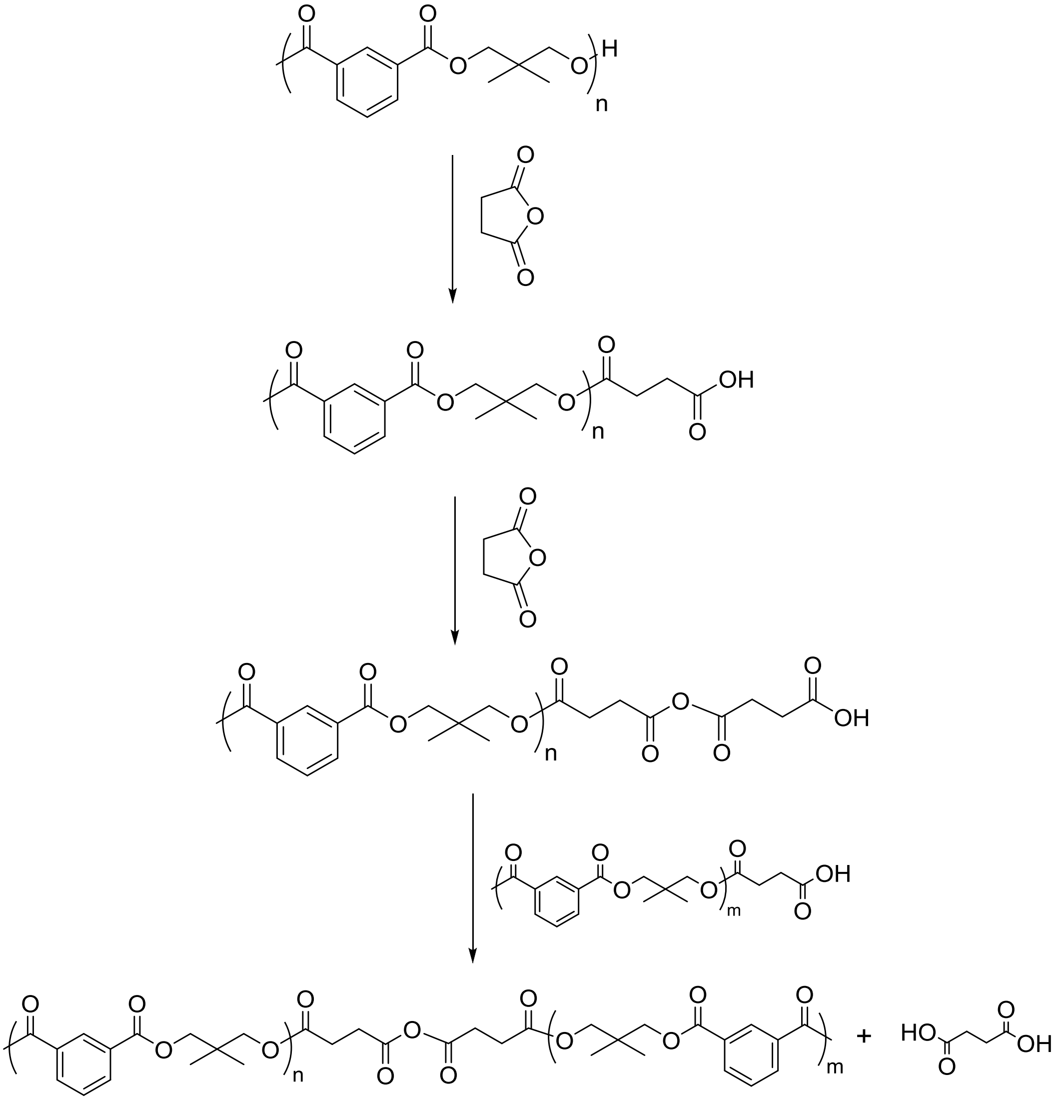


Figure 3.7. Synthesis of Poly(ester-anhydride) from PIN and SA.

3.4. Detection of Anhydride Linkages in Poly(ester-anhydride)s

3 g of poly(ester-anhydride)s were dissolved in 12 mL EtOAc. 1 mL of 1N NaOH was added to this solution and pH was adjusted to 11-12. Then 3-4 drops of diisobutylamine was also added. Finally, pH was lowered to 6-7 by adding 3 mL of 1N HCl. The mixture was extracted, organic layer was collected and then the solution was precipitated into Hexane.

3.5. Characterization

3.5.1. GPC Analysis

Viscotek VE2001 GPC instrument was used for the measurements. Samples were prepared by dissolving 4 mg of polymer samples in 1 mL THF.

3.5.2. DSC Analysis

Exstar SII DSC 7020 instrument was used for thermal analysis. As a method starting temperature was set to -20◦C and maximum temperature was 300◦C for polyesters and 250◦C for poly(ester-anhydride)s. The rate was set to 20 ^{o}C/min.

3.5.3. ^{1}H-NMR Analysis

Varian Gemini 400 MHz spectrometer was used in $CDCl_3$ for ^{1}H-NMR analysis.

3.5.4. IR Analysis

Nicolet 380 FT-IR spectrometer was used for analysis.

4. RESULTS AND DISCUSSION

In the first section of this part, the synthesis of various polyesters using cycloaliphatic and aromatic monomers is discussed. Cycloaliphatic monomers were preferred since they provide high glass transition temperature. Aromatic monomers were chosen because of their high rigidity. Two aromatic diacids, TPA and IPA were compared, since their physical properties differ significantly. Polyesters synthesized from TPA are more linear and better packed due to the 1,4 positions of carboxylic acids which makes it very difficult to melt and dissolve or process. Moreover, the effect of steric hindrance and restricted motion on glass transition temperature was also studied by comparing 1,3 propane diol and neopentyl glycol which has 2 more germinal methyl groups. Then, end group modification and synthesis of poly(ester-anhydride)s from previously synthesized polyesters and their characterization were studied. In the following sections the results will be presented in the order cited herein.

4.1. Synthesis of Poly (1,4-cyclohexylidenecyclohexane- 1,4-dicarboxylate) (PCCD)

As a first step, the relationships between the molecular weight of polyesters, the end groups and T_g were investigated. Therefore, hydroxyl and carboxyl terminated PCCD polymers with various molecular weights were synthesized using different monomer ratios.

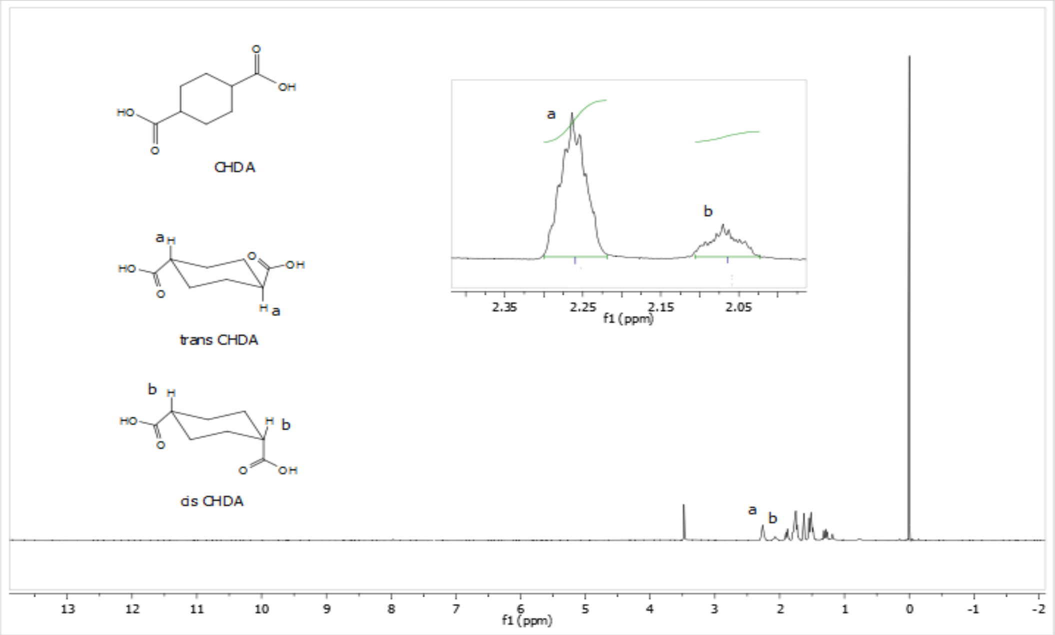


Figure 4.1. ^{1}H-NMR Spectrum of CHDA Monomer.

The molecular weight of polyesters was tuned by adjusting the monomer ratios, increasing reaction time and vacuum. Polyesters with various molecular weights were synthesized. ^{1}H-NMR results show that monomers that have *cis* or *trans* conformation (both the diacid and diol monomers exist in *trans* or *cis* form) give different signals in spectra (Figure 4.1). It can be seen that *trans* conformation appears at higher chemical shifts since axial hydrogens appear at higher field than the corresponding equatorial hydrogens [16]. From ^{1}H-NMR spectra of CHDA, we calculated *cis* to *trans* ratio as 30% to 70%.

Protons that are close to the end groups enabled to calculate the number average molecular weight from the ^{1}H-NMR (Figure 4.2). However, this was possible only for the PCCD polymers with hydroxyl end groups. The protons that are close to carboxyl end groups were not or barely detectable on ^{1}H-NMR (Figure 4.3). So, it was not possible to calculate the molecular weights of these carboxyl terminated PCCD polymers with precision. The calculation of molecular weight of hydroxyl terminated PCCD polymer (PCCD_2) is shown below as an example.

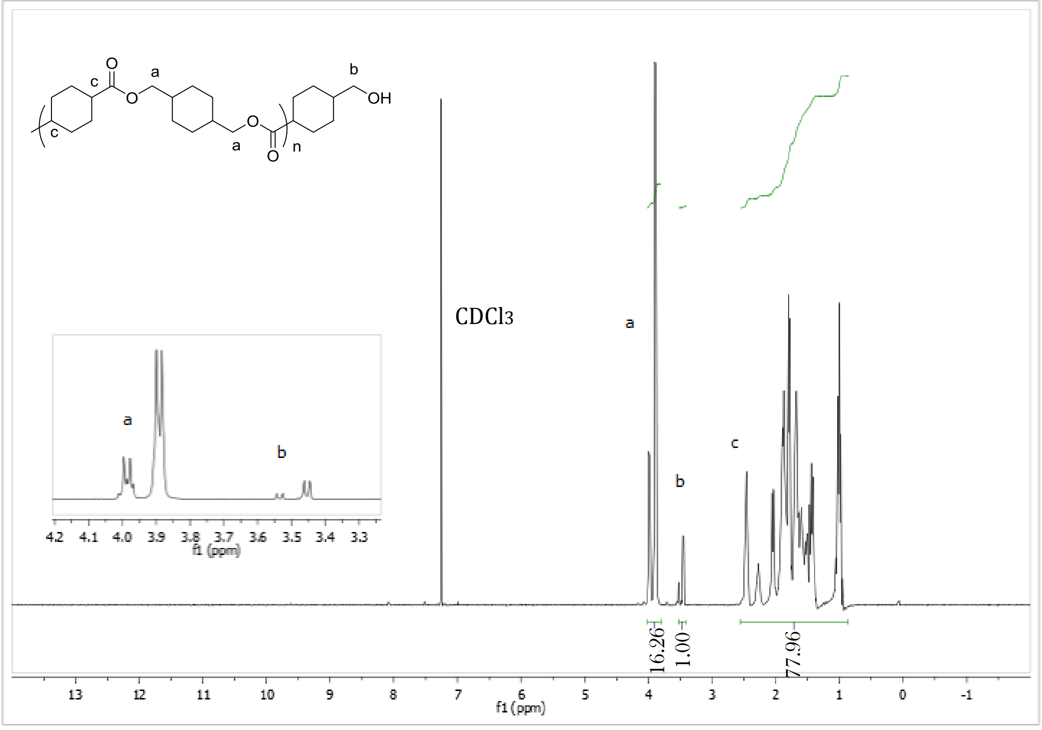


Figure 4.2 ^{1}H-NMR Spectrum of PCCD_2.

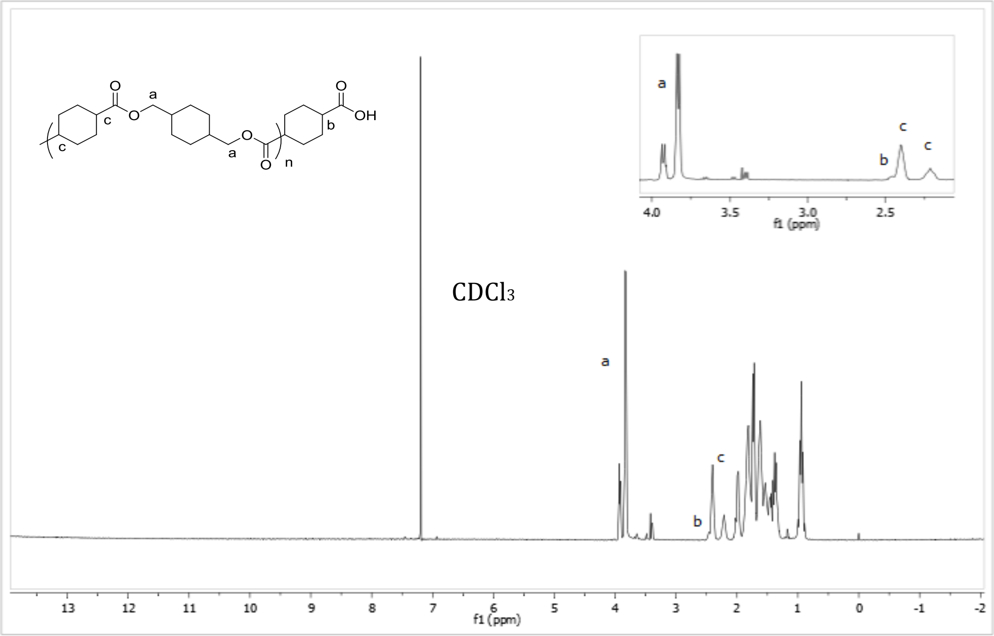
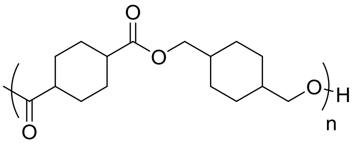


Figure 4.3 ^{1}H-NMR Spectrum of PCCD_3.

First molecular weights of end groups and repeating unit were calculated as shown below.



– $C_{16}O_4H_{22}$ – CH_3OH

– 266 g/mol – 32 g/mol

The integral of the peak area at about 3.5 ppm belongs to protons of -CH_2-OH near end groups and assuming there are 2 protons at the both ends, by dividing this area by 4, the area per proton can be calculated:

1 / 4 = 0,25

The other peaks belong to protons in repeating unit. Since there are 22 protons in each repeating unit, dividing the total integral of the peak areas to 22, gives the area per proton. Then number of repeating unit is obtained by dividing this value to the value above.

(16,26+77,96) / 22 = 4,28

4,28 / 0,25 = 17,12 (number of repeating units)

Finally, by multiplying molecular weight of repeating unit by the number of repeating unit and adding this value to the sum of molecular weights of two end groups number average molecular weight of polymer can be obtained.

$$[32+ (266*17,12)] = 4619 \text{ g/mol}$$

The molecular weights were also measured by GPC. The ^{1}H-NMR and the GPC results were close to each other (PCCD_7 and _8). Slight deviation in PCCD_2 may be attributed to the presence of minor amount of carboxylic acid end groups which were not accounted in the molecular weight calculation by ^{1}H-NMR (Proton NMR with high resolution will be investigated in the future for more accurate calculations).

DSC results showed that PCCD polymers with almost similar molecular weights but different end groups have different glass transition temperatures. It was observed that hydroxyl terminated PCCD polymers in general have lower T_g than carboxyl terminated PCCD polymers at similar molecular weights. The reason for this could be a physical network formation due to hydrogen bonding between carboxyl end groups of polymer chains. The M_n and T_g values of polyesters are shown in Table 4.1 (Experimental data in Table 3.1 and 3.2).

Table 4.1. M_n and T_g values of PCCDs.

Sample Name	End Group	M_n(NMR)	M_n(GPC)	T_g (◦C)
PCCD_1	-COOH & -OH	n/a	6200	37,4
PCCD_2	-OH	4619	3825	31,2
PCCD_3	-COOH	n/a	4498	35,7
PCCD_4	-COOH & -OH	n/a	6207	35,6
PCCD_5	-COOH	n/a	6420	41,2
PCCD_6	-COOH	n/a	8444	41,8
PCCD_7	-OH	4601	4595	35,7
PCCD_8	-OH	8152	8788	39,5

4.2. Synthesis of Polyesters Based on Terephthalic Acid (TPA) and Neopentyl Glycol (NPG) : PTN

Different polyesters were targeted using different diols and diacids. TPA being aromatic and 1,4 substituted and NPG having decreased mobility are known to increase the T_g of the polyesters that they are incorporated in. Thus, as a next study, TPA and NPG were used as the starting diacid and diol respectively. However, the polymerization could not be observed under the polymerization conditions used. The reaction mixture was not homogenous. Although a shift of the carbonyl peak on IR spectra was observed, the ^{1}H-NMR results showed a large number of unreacted monomer as well. The reason of the carbonyl peak shift is due to the formation of an adduct that contains NPG at the two end groups and one TPA unit in the middle. The NMR spectra confirms this structure (Figure 4.4). The peak a at 4.06 ppm and the peak b at 3.26 ppm belong to 4 H atoms separately as shown on the spectra. The ratio of the integrals (3.71 and 3.76 respectively) is ~1 which is also equal to the ratio of number of protons. The peak c at 0.91 ppm has the integral of 11.06 which is approximately 3 times higher than the integrals of the peaks a and b. Again, this ratio is identical with the ratio of number of H atoms. Furthermore, there are 4 H atoms in aromatic ring and the peak f which belongs to these H atoms has the integral of 3.68 which

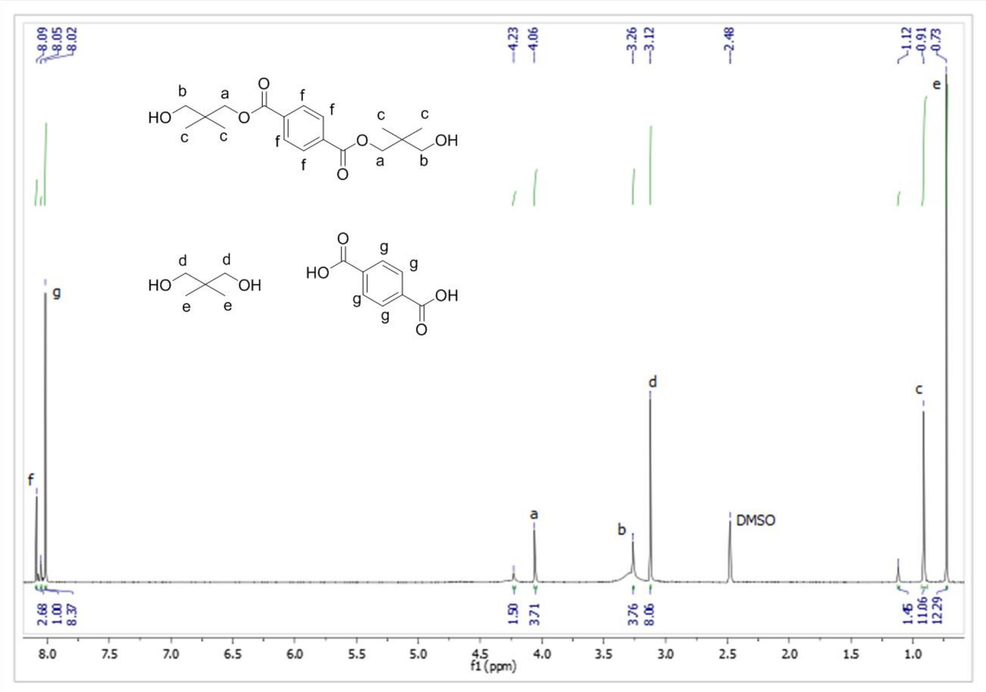


Figure 4.4. ^{1}H-NMR Spectrum of TPA and NPG adduct.

is almost the same value of the integral of peaks a and b. On the other hand, the peak g which belongs to terephthalic acid and peaks d and e which belong to neopentyl glycol confirms the incomplete polymerization. The integrals of peak d and e give the ratio of ~2/3 which is also corresponds to the ratio of protons (4 and 6 Hs respectively) that belong to these peaks.

^{1}H-NMR analysis proves that polymerization of TPA and NPG was not successful and the reason for this is probably the low reactivity of TPA which results from poor melting and solubility due to the symmetrical character of TPA. TPA structure favors both π - π stacking and H-bonding between TPA molecules. Therefore, it was concluded that TPA as a sole diacid monomer is not suitable to synthesize polyesters by melt polycondensation. It requires probably much higher temperatures and vacuum conditions or higher reaction time which are not preferable for industrial applications.

4.3. Synthesis of Polyesters Based on Isophthalic Acid (IPA) and Neopentyl glycol (NPG) : PIN

Since TPA was not reactive enough to obtain polyesters, it was decided to change it with its more soluble and reactive isomer, IPA. As expected, polymerization was achieved this time. NPG was used in excess amount since it evaporates during reaction and lost during the transesterification process. The excess of alcohol also allowed us to obtain hydroxyl terminated polyesters. The shift of carbonyl peak from 1683 cm^{-1} to 1716 cm^{-1} in IR spectra confirms the formation of ester bonds. Increasing reaction time and vacuum had a significant effect on M_n and T_g of polyesters (Table 4.2), (Experimental data in Table 3.5, 3.6). PIN_2 and PIN_3 were both synthesized in 9 hours and under high vacuum conditions, as a result their M_n values are 5 times higher than the M_n of PIN_1. On the other hand, when we compare the T_g values of aromatic polyesters such as PIN_2 and PIN_3 with an aliphatic polyester i.e. PCCD_8 whose M_n is greater than both samples (8152 g/mol), a ~15◦C difference is seen in favour of the aromatic polyester. This difference indicates the importance of the flat, rigid aromatic structure on the polyesters's T_g.

Table 4.2. M_n and T_g values of PINs.

Sample Name	End Group	M_n(g/mol)	T_g (◦C)
PIN_1	-OH	1107	29,0
PIN_2	-OH	5109	56,1
PIN_3	-OH	5298	56,5

4.4. Synthesis of Polyesters Based on Isophthalic Acid (IPA) and 1,3-Propanediol (PDO) :PIP

In order to understand the effect of molecular structure of monomers on T_g, PDO was used instead of NPG. The latter is a sterically more hindered diol with diminished degree of freedom due to the germinal methyl groups. The comparison as expected indicated a significant decrease in T_g. The T_g of PIP is way below room temperature (~5◦C) and the polymer was a viscous honey like material compared to polyester PIN_1 (M_n= 1107 g/mol) which has almost same molecular weight with PIP_1 (M_n=1175 g/mol). Again, the product was analysed by IR. The IR spectra of IPA and PDO was compared and a shift of carbonyl peak from 1683 cm^{-1} to 1712 cm^{-1} was observed (Figure 4.5).

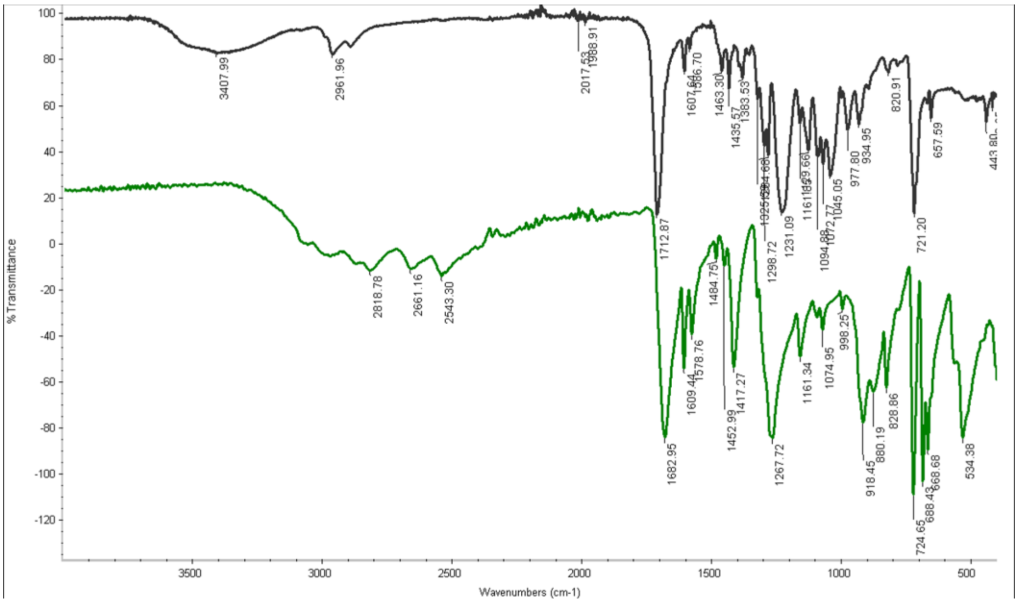


Figure 4.5. IR Spectrum of IPA and PIP.

4.5. Synthesis of Poly(ester-anhydride)s from PCCD and Phthalic Anhydride (PA)

As a next step, previously synthesized polyesters were modified using different anhydrides. First PCCD polyesters and PA were reacted. Among their reactions only the first reaction (PCCD_2_PA_1) resulted in a significant increase in molecular weight (M_n increased from 3825 g/mol to 5875 g/mol). The other reactions in which a different PCCD was used, did not show an increase in molecular weight except the PCCD_7_PA_4 (M_n increased from 4595 g/mol to 5096 g/mol) which was synthesized with the excess amount of PA in 1:4 ratio (Table 4.3).

Table 4.3. M_n and T_g values of PCCD_PA's and PCCD's.

Parent PCCD	M_n(g/mol)	T_g (◦C)	Anhydride Sample Name	M_n(g/mol)	T_g (◦C)	M_n(g/mol) (Anhydride test)
PCCD_2	3825	31,2	PCCD_2_PA_1	5875	36,8	3244
PCCD_7	4595	35,7	PCCD_7_PA_1	4719	36,1	-
PCCD_7	4595	35,7	PCCD_7_PA_2	4288	32,8	-
PCCD_7	4595	35,7	PCCD_7_PA_3	4737	33,0	-
PCCD_7	4595	35,7	PCCD_7_PA_4	5096	33,4	-

The formation of ester bonds (peak a) between PA and PCCD was observed from ^{1}H-NMR for all the products (Figure 4.6). However, since anhydrides could not be detected by ^{13}C-NMR or IR because of their low concentration in the polymer structure, anhydride test which is explained in experimental section 3.4 was applied in order to break the anhydride linkages if there were any. Except for the product PCCD_2_PA_1, M_n values could not have been detected after anhydride test because of the very poor solubility. The M_n of PCCD_2_PA_1 was measured as 3244 g/mol after the anhydride test. This result proves the existence of anhydride linkages in the mid-section of polyesters. It is assumed that there could be two possible explanation for the unchanged M_n values; either formation of anhydride linkages and chain scission occur simultaneously or PA reacts only once with the end groups and reaction does not proceed further. The results later in section 4.7 prove that anhydride formation and chain scission may occur at the same time.

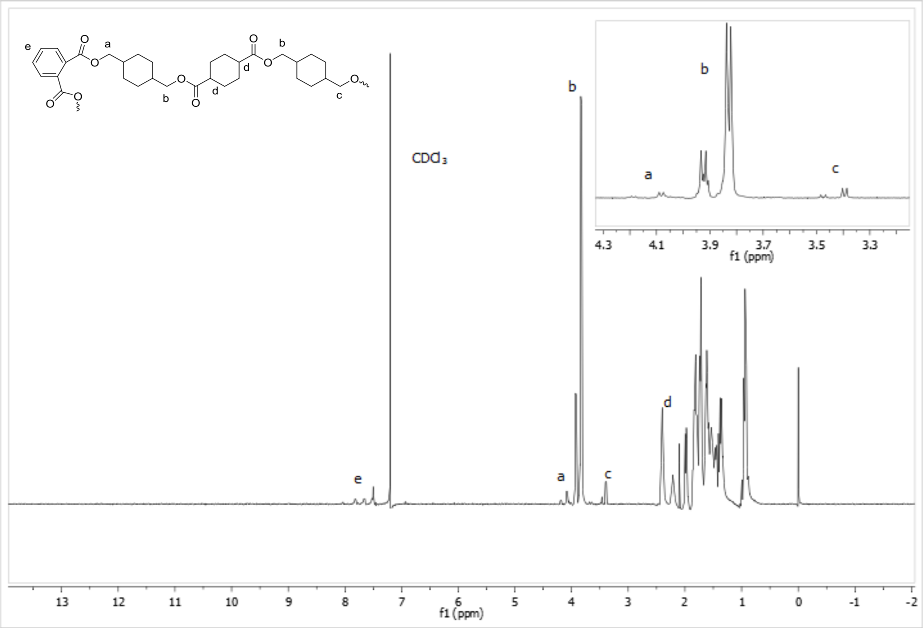


Figure 4.6. ^{1}H-NMR Spectrum of PCCD_2_PA_1.

The increase in T_g value of PCCD_2_PA_1 is noticeable with a rise from 31,2◦C to 36,8◦C. This result proves that formation of anhydride linkages between polymer chains increases molecular weight and thus the T_g of polymers (Table 4.3).

Lastly, TEA was used as catalyst in one of the reactions to understand if it changes the reactivity of anhydrides with the end groups of polyesters. However, it did not show an influence on the proceeding of the reaction. For PCCD_7_PA_2 and PCCD_7_PA_3 exactly same reaction conditions were performed only with the difference of using catalyst. In the case of PCCD_7_PA_3 10 % of TEA was used as catalyst, but the results did not show any significant difference. The results show that the most important parameter to obtain anhydride linkages is probably the reaction time.

4.6. Synthesis of Poly(ester-anhydride)s from PCCD and Succinic Anhydride (SA)

Further, PCCD_8 (M_n=8788 g/mol, T_g=39,5 ◦C) was reacted with SA and formation of anhydride linkages was observed again. GPC result showed an increase in molecular weight (M_n=10027 g/mol) and after performing anhydride test as described in section 3.4 the molecular weight decreased (M_n=6122 g/mol) which indicates the breakage of anhydride links and proves the existence of them. However, contrary to expectations the increase in T_g (40,4◦C) was very low.

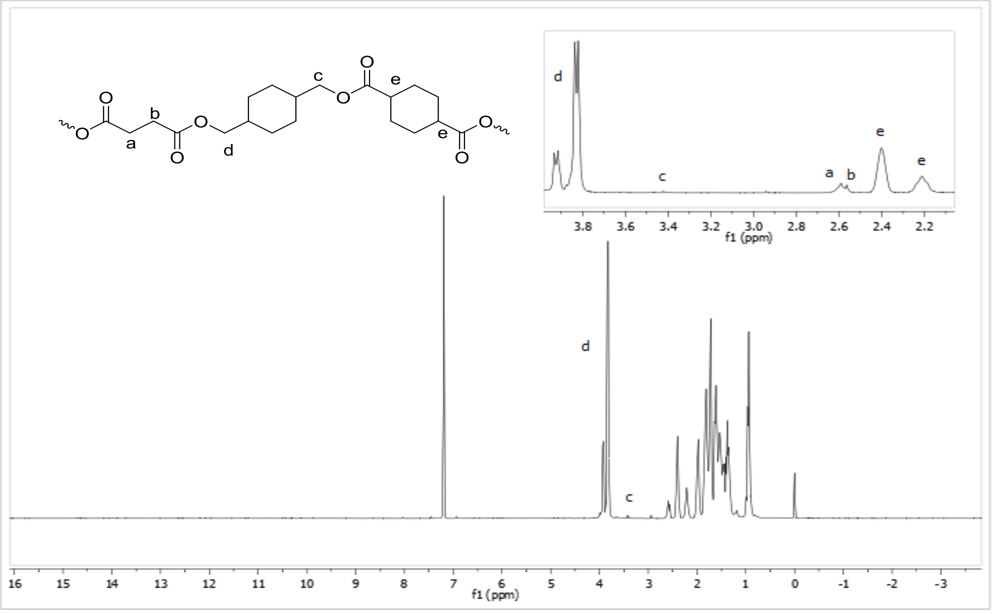


Figure 4.7. ^{1}H-NMR Spectrum of PCCD_8_SA_1.

The reason for this could be that T_g in this molecular weight range did not change too much by the increasing molecular weight. Moreover, this significant decrease in molecular weight after anhydride test could be the indication of simultaneous presence of anhydride formation and chain scission.

^{1}H-NMR results also prove the formation of new ester bonds (peak c) between SA and PCCD (Figure 4.7). On the other hand, the proton peaks which belong to SA monomer still exist. Therefore, it could have been better to run the reaction for longer time to get a higher conversion.

4.7. Synthesis of Poly(ester-anhydride)s from PIN and Succinic Anhydride (SA)

Lastly, the reaction of PIN_3 (M_n=5259 g/mol, T_g=56,5 ◦C) and SA was performed. Although formation of ester bonds can be observed between SA and PIN by ^{1}H-NMR (Figure 4.8), T_g value (50,5◦C) and M_n (4805 g/mol) of PIN_3_SA_1 decreased unexpectedly. Anhydride test was performed in order to understand whether any anhydride linkages were formed or not. A decrease in M_n (3519 g/mol) was observed again after anhydride test, which proves the existence and breakage of anhydride linkages. Therefore, it can be concluded that during anhydride formation SA also caused chain scission which led to decrease in M_n and T_g values.

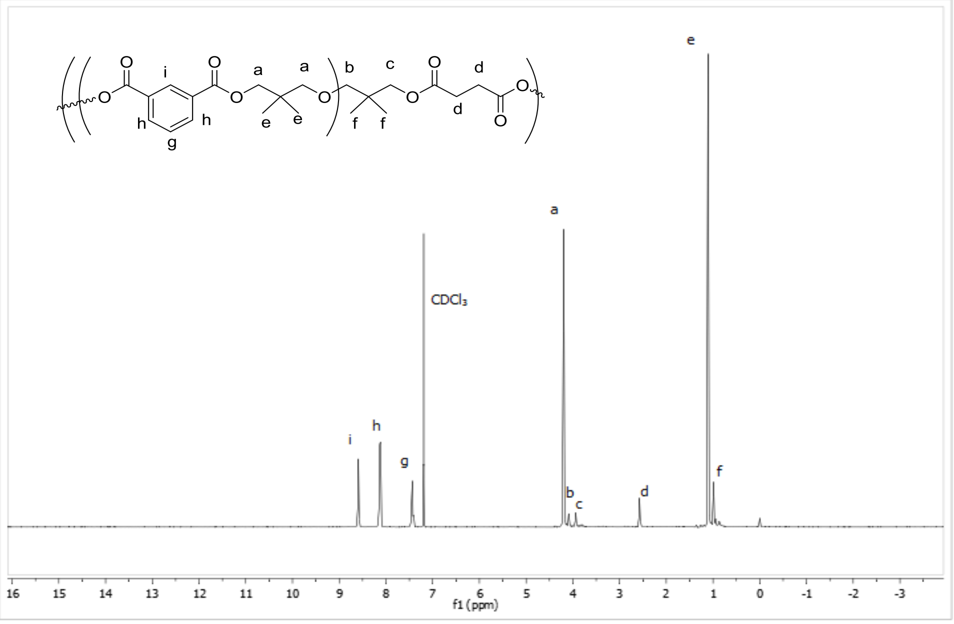


Figure 4.8. ^{1}H-NMR Spectrum of PIN_3_SA_1.

5. CONCLUSIONS

As a conclusion, it was showed that by formation of anhydride linkages between polyester chains, it is possible to increase M_n and T_g values. However, in some cases, during anhydride formation chain scission can occur at the same time and this prevents increase of M_n and T_g. Moreover, the relationship between M_n and T_g as well as, effect of end groups and molecular structure on T_g were studied. The relationship between M_n and T_g was confirmed as polymers with higher M_n have also higher T_g values. It was observed that the steric hindrance and aromaticity in molecular structure increase T_g and carboxylic acid terminated polyester have higher T_g values compared to the ones with hydroxyl terminated ends due to the physical crosslinking between polyester chains.

6. FUTURE WORK

The reaction conditions for the poly(ester-anhydride) formation need to be optimized. In-depth characterization of end groups should be done since only ^{1}H-NMR analysis is insufficient to detect end groups precisely. GPC measurements might be repeated with low molecular weight columns using the same device to get more precise results since some of the measurements were done using different GPC devices. Synthesis of polyesters and poly(ester-anhydride)s with higher molecular weights and higher T_g values could be studied as a future work. Moreover, the crosslinking reactions of these polyesters and poly(ester-anhydride)s are still an issue to be investigated.

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APPENDIX 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.

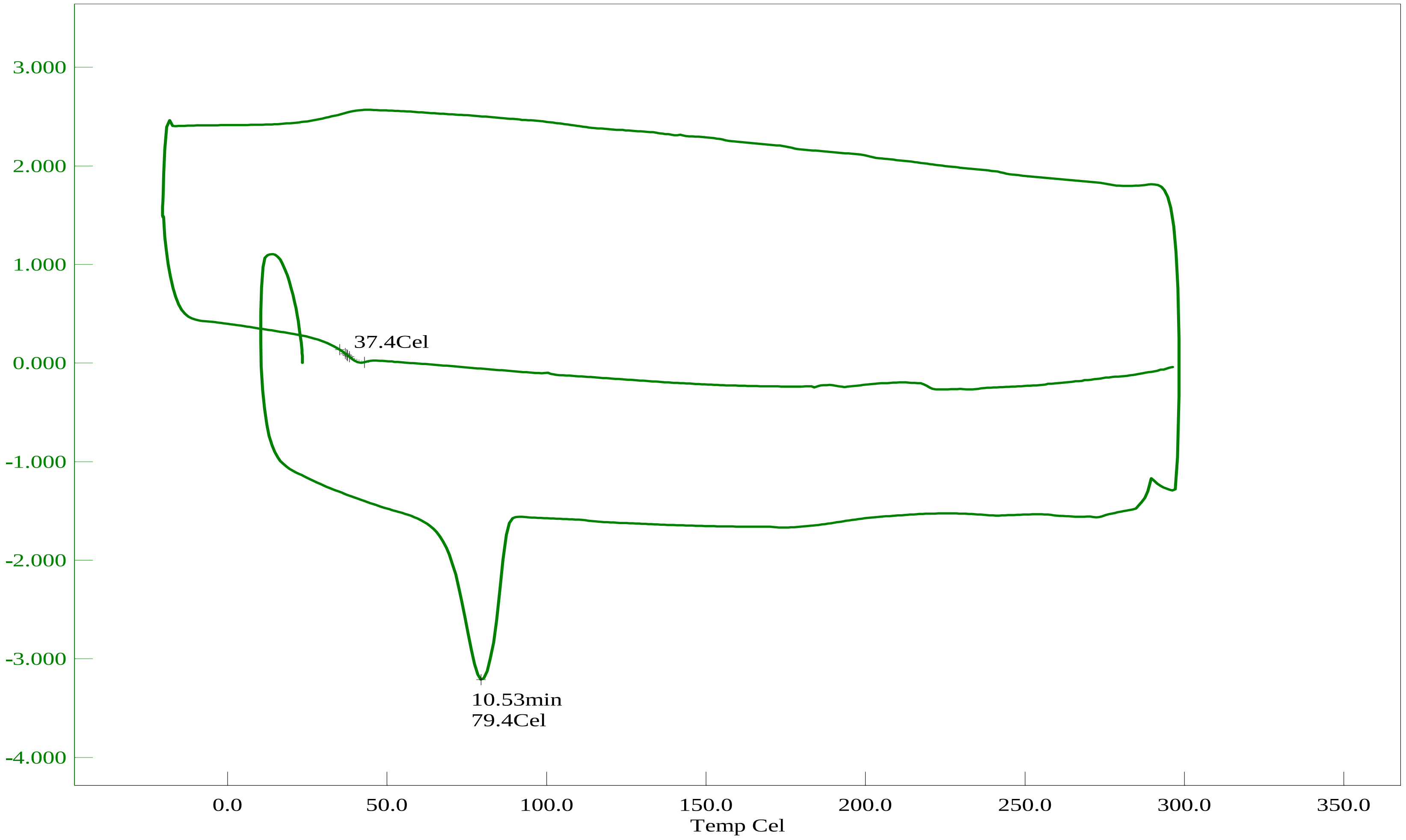


Figure A. 1. DSC Analysis of PCCD_1.

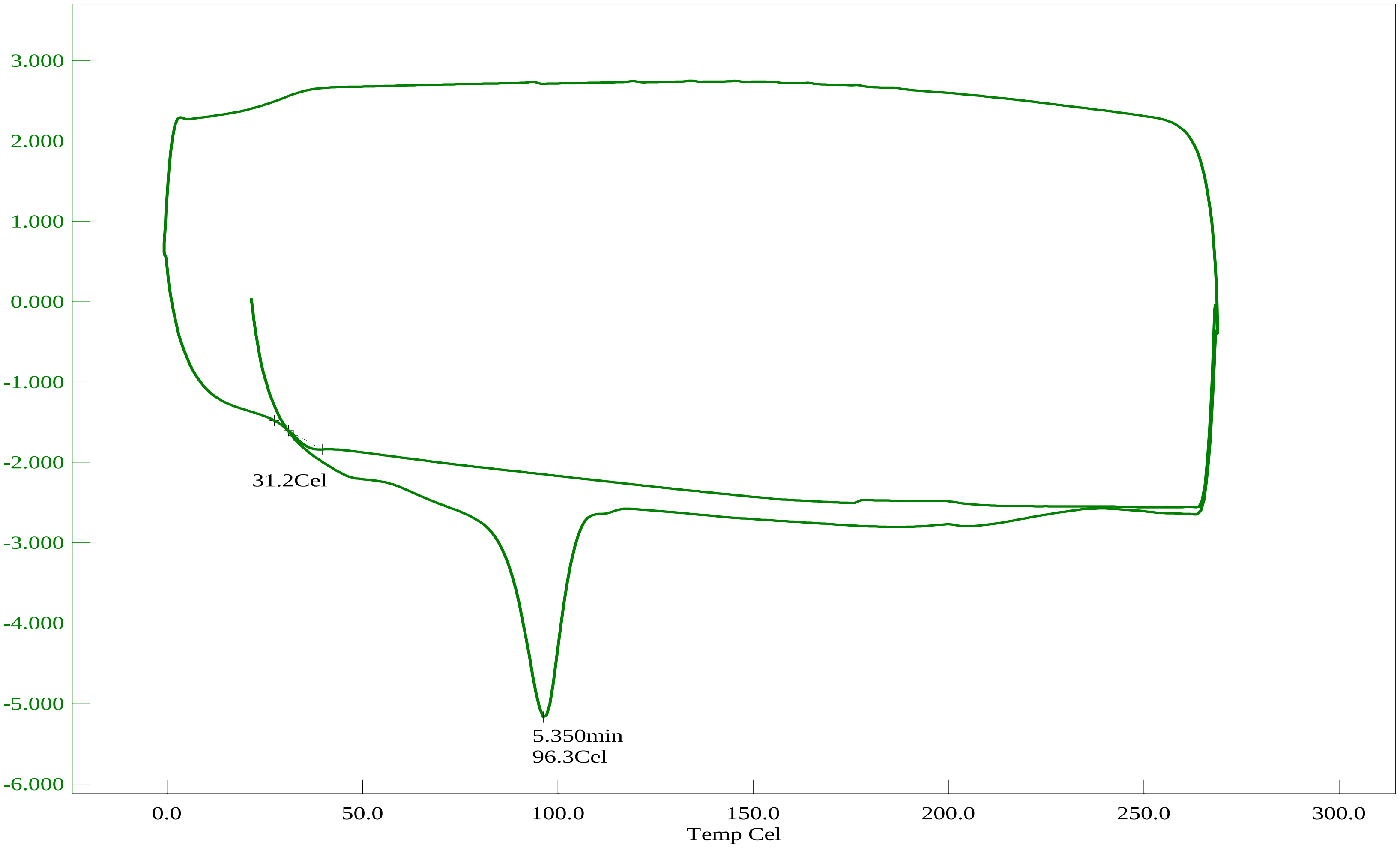


Figure A. 2. DSC Analysis of PCCD_2.

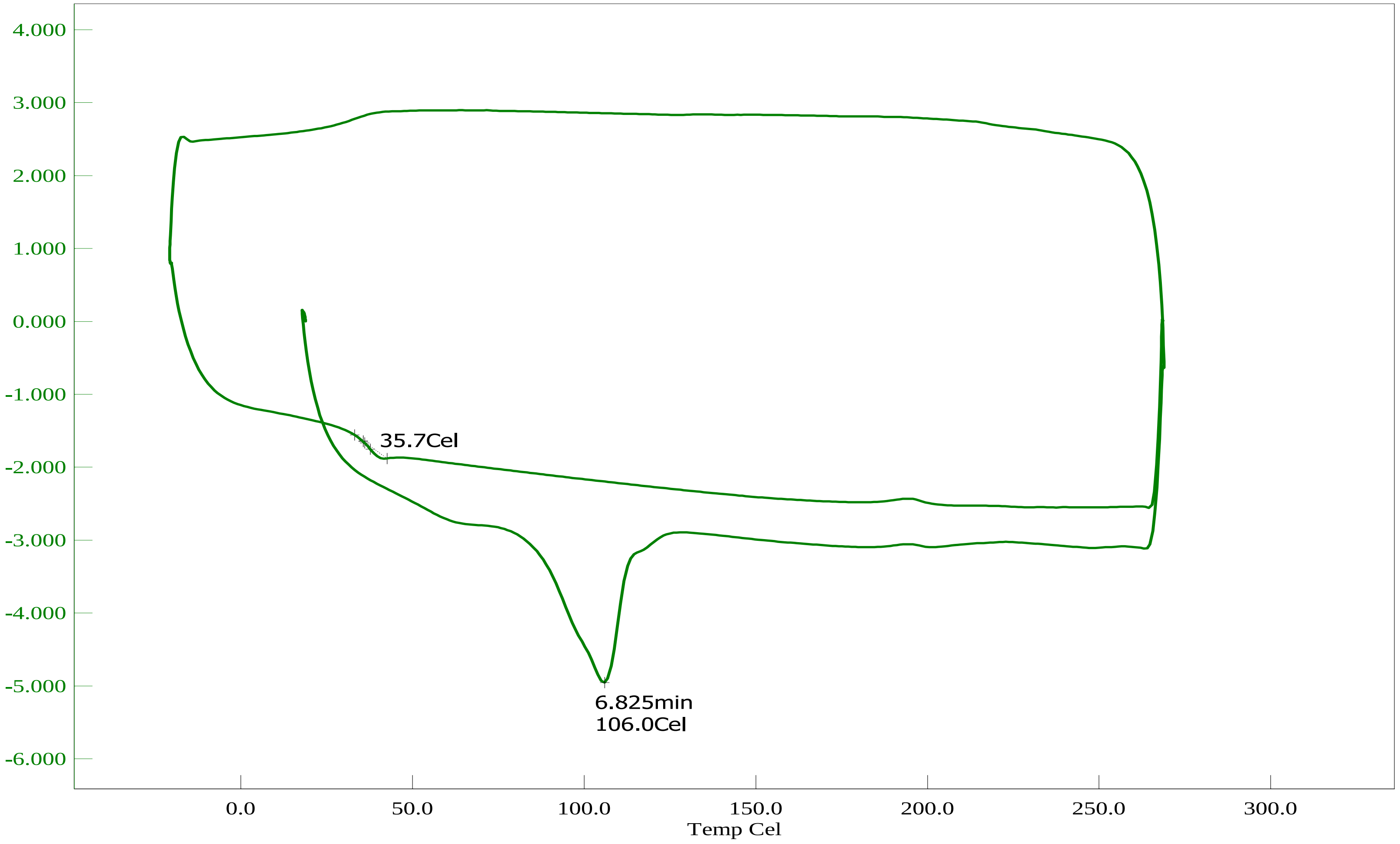


Figure A. 3. DSC Analysis of PCCD_3.

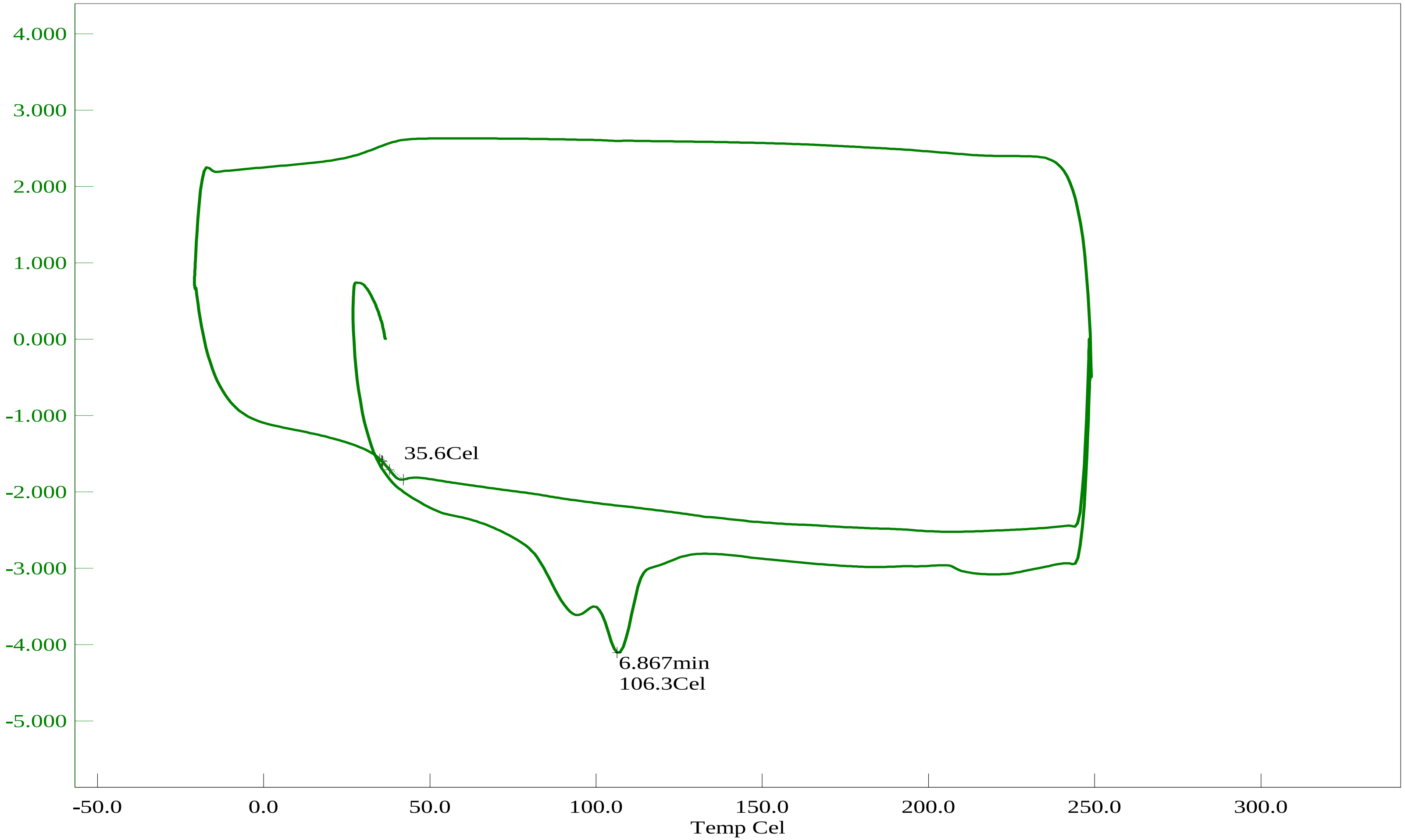


Figure A. 4. DSC Analysis of PCCD_4.

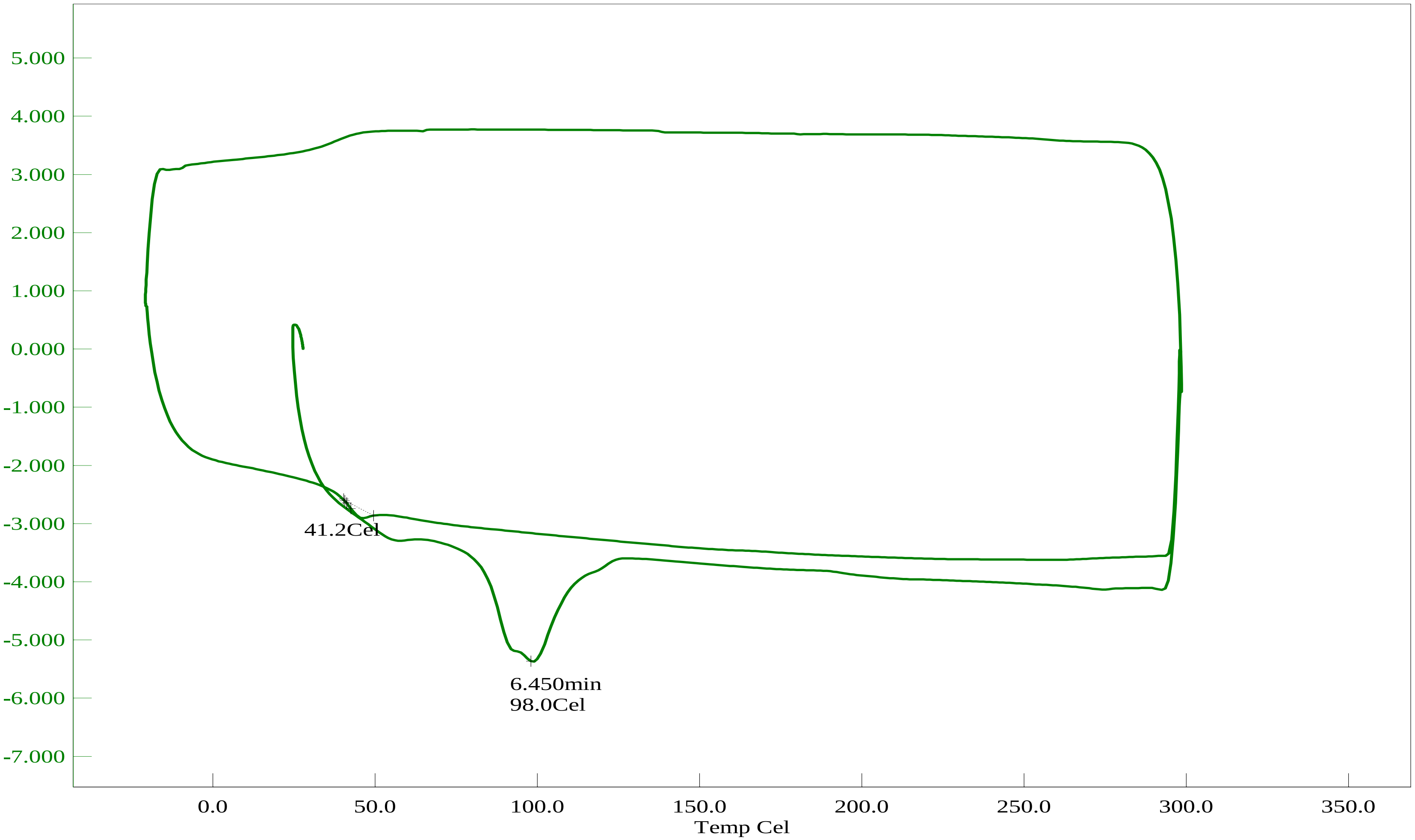


Figure A. 5. DSC Analysis of PCCD_5.

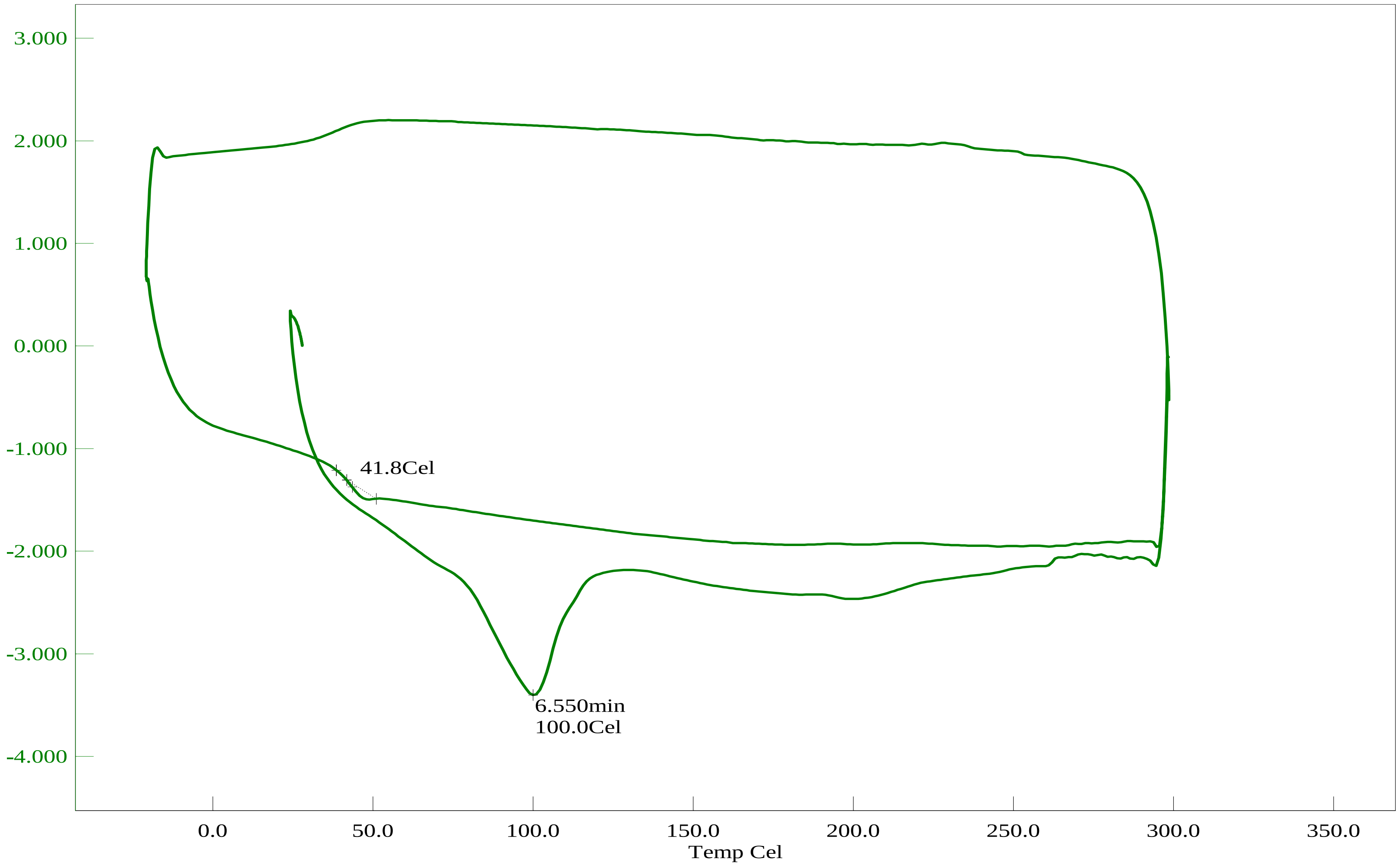


Figure A. 6. DSC Analysis of PCCD_6.

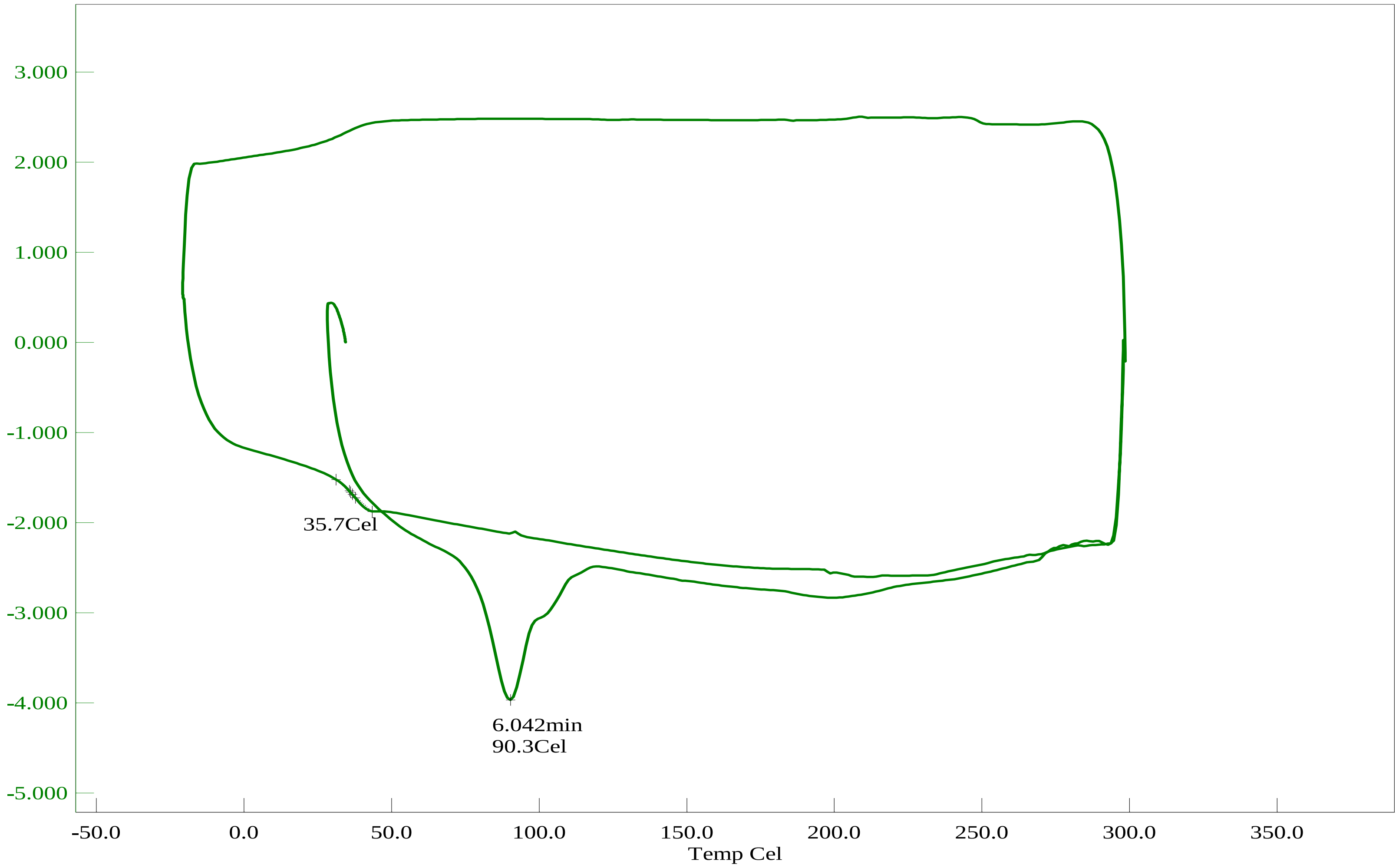


Figure A. 7. DSC Analysis of PCCD_7.

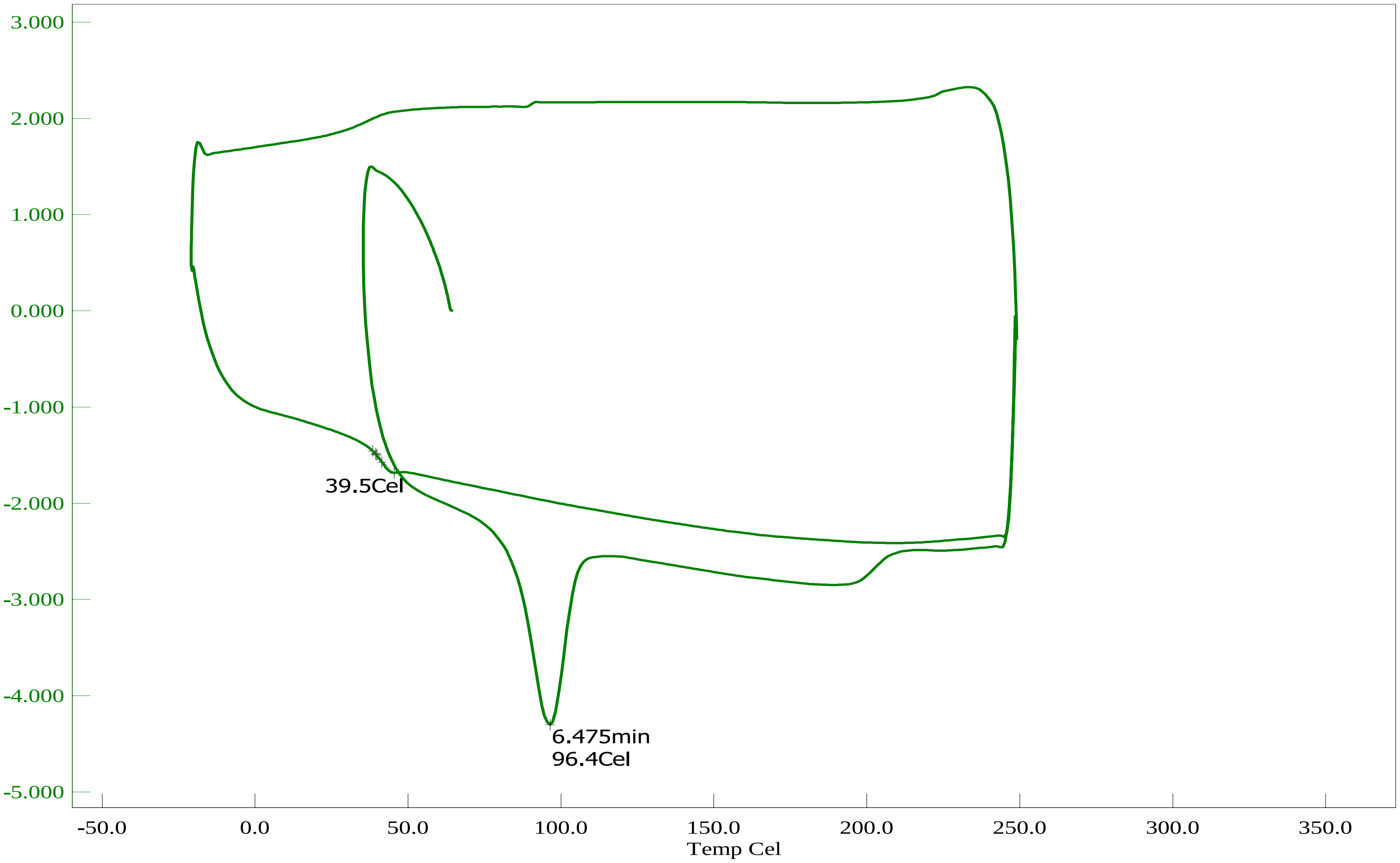


Figure A. 8. DSC Analysis of PCCD_8.

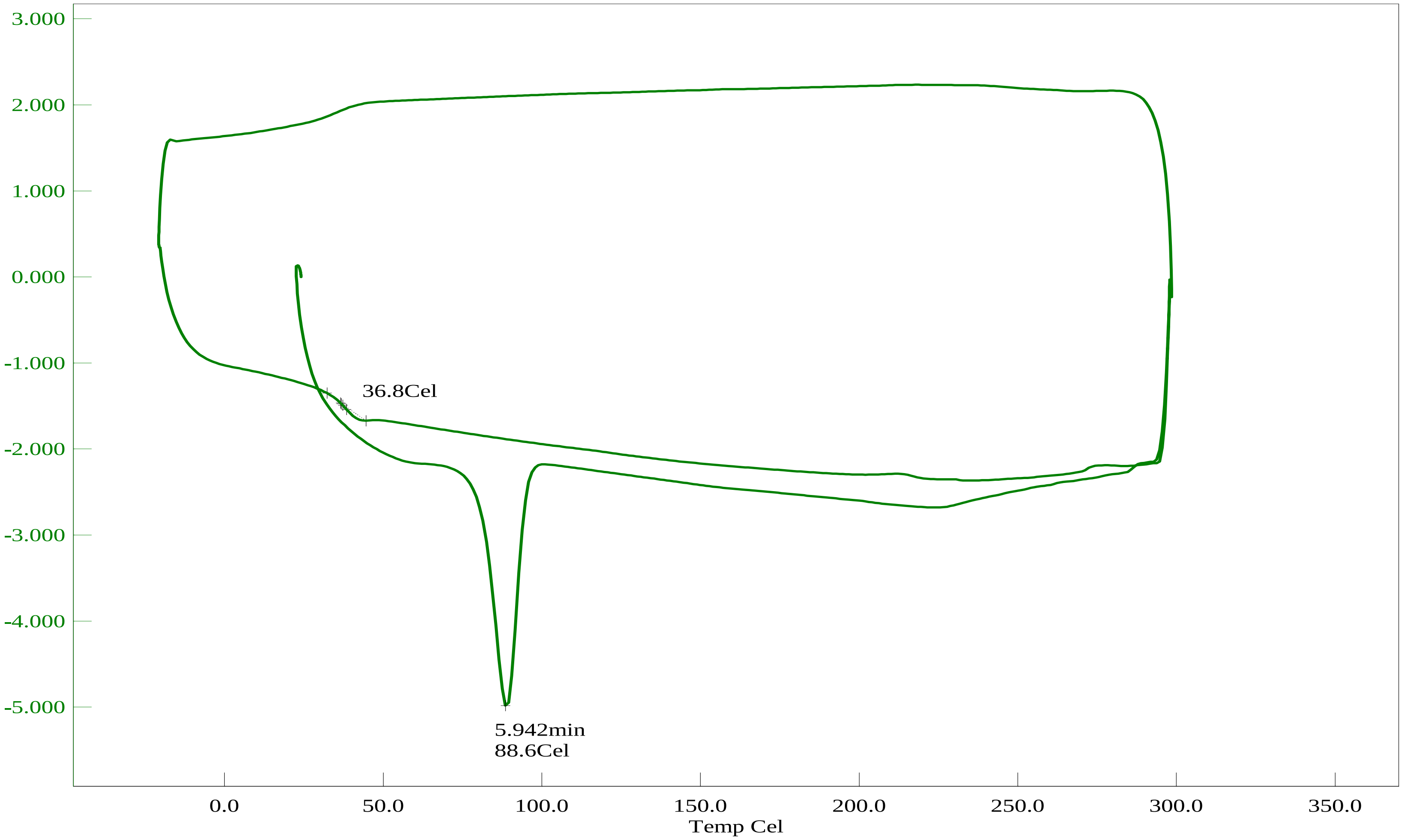


Figure A. 9. DSC Analysis of PCCD_2_PA_1.

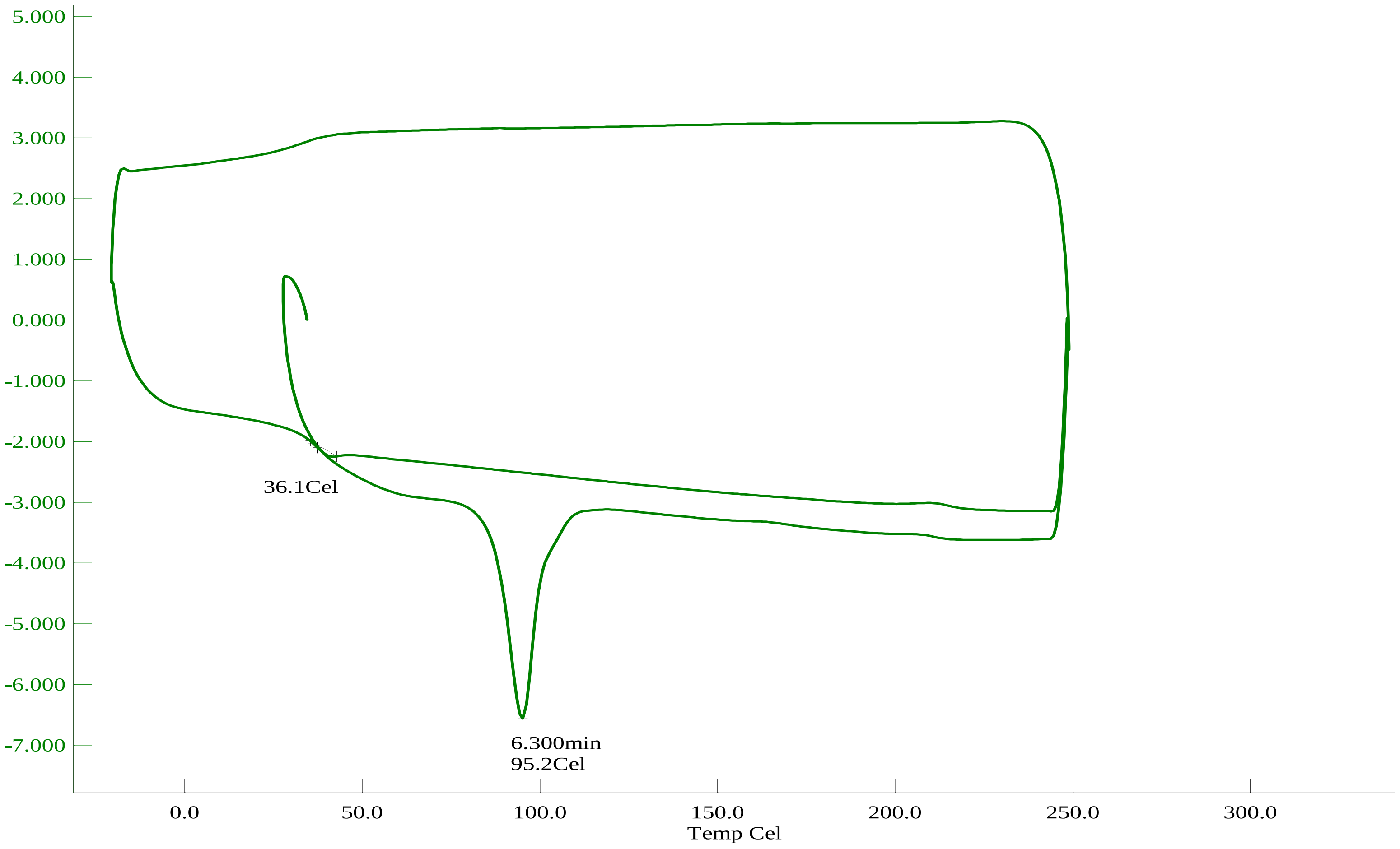


Figure A. 10. DSC Analysis of PCCD_7_PA_1.

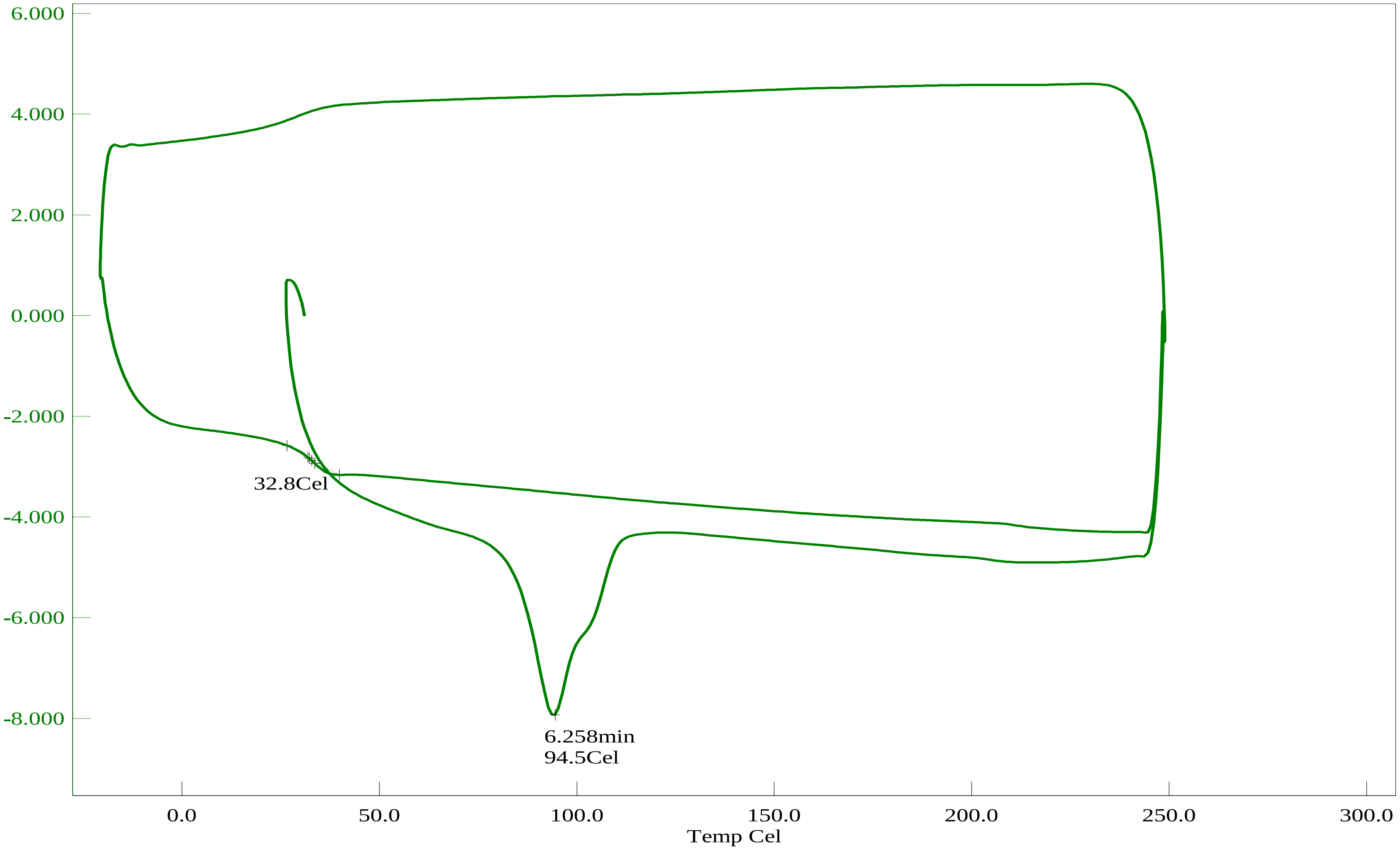
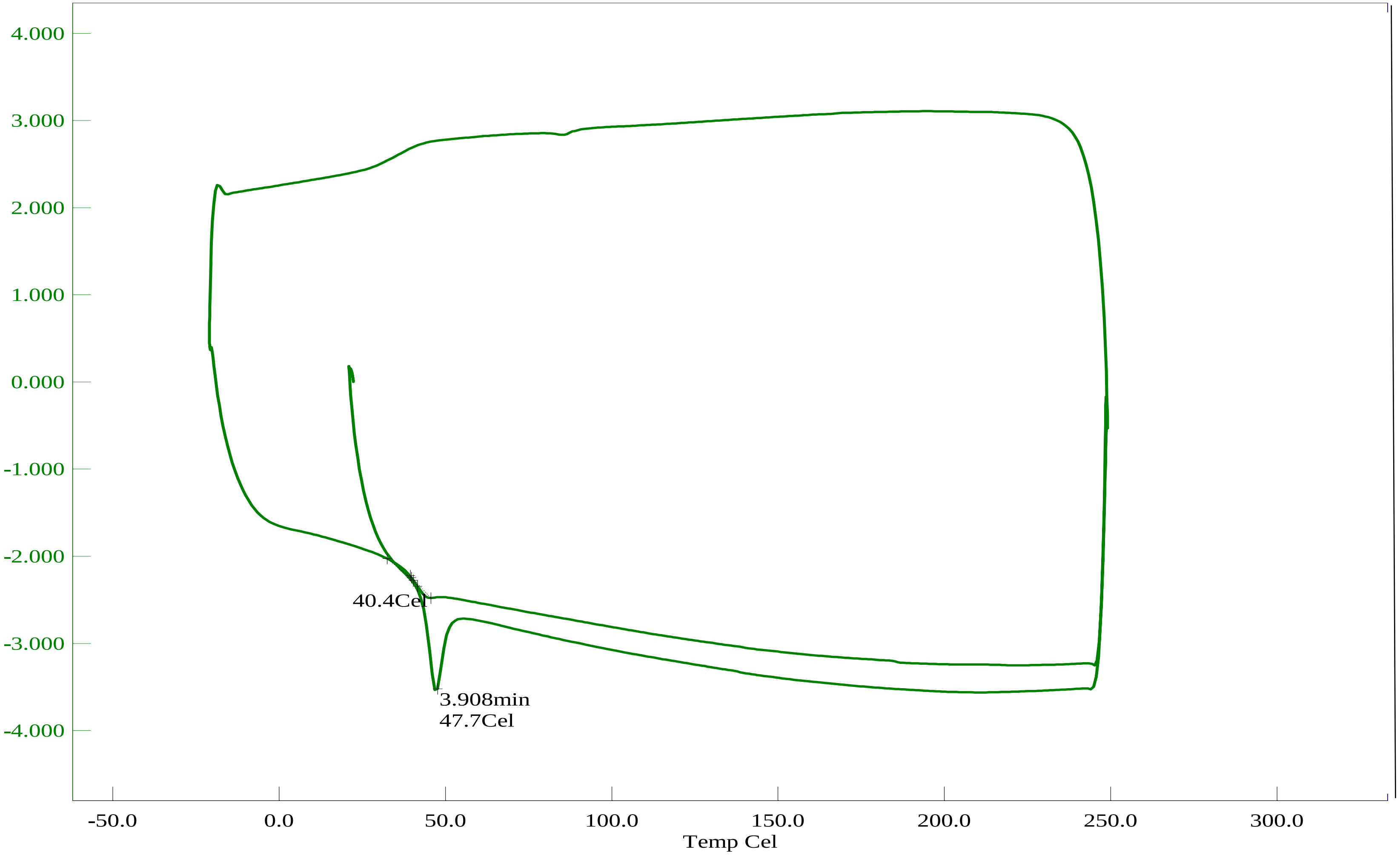


Figure A. 11. DSC Analysis of PCCD_7_PA_2.

Figure A. 12. DSC Analysis of PCCD_7_PA_3.

Figure A. 13. DSC Analysis of PCCD_7_PA_4.



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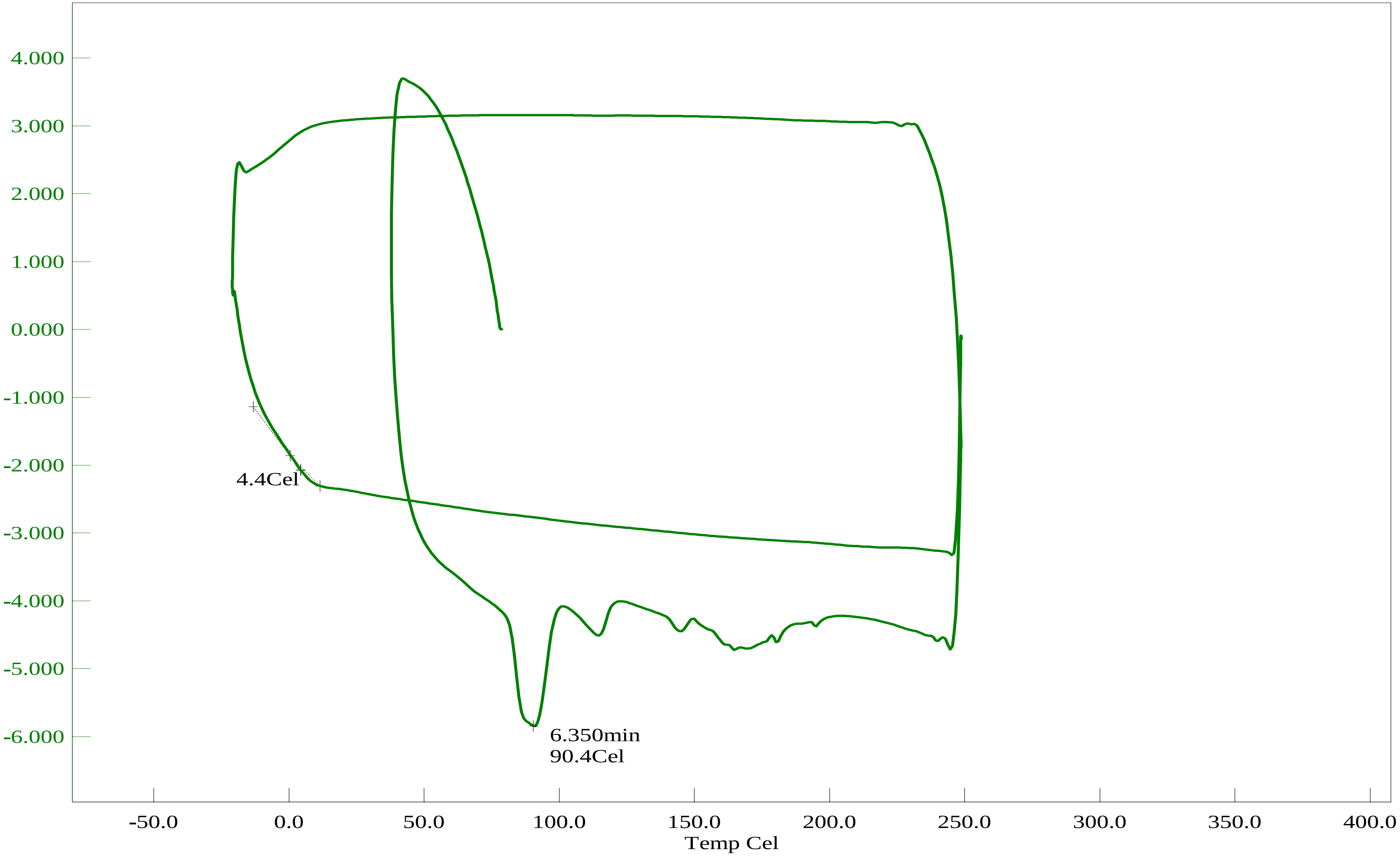


Figure A. 15. DSC Analysis of PIP_1.

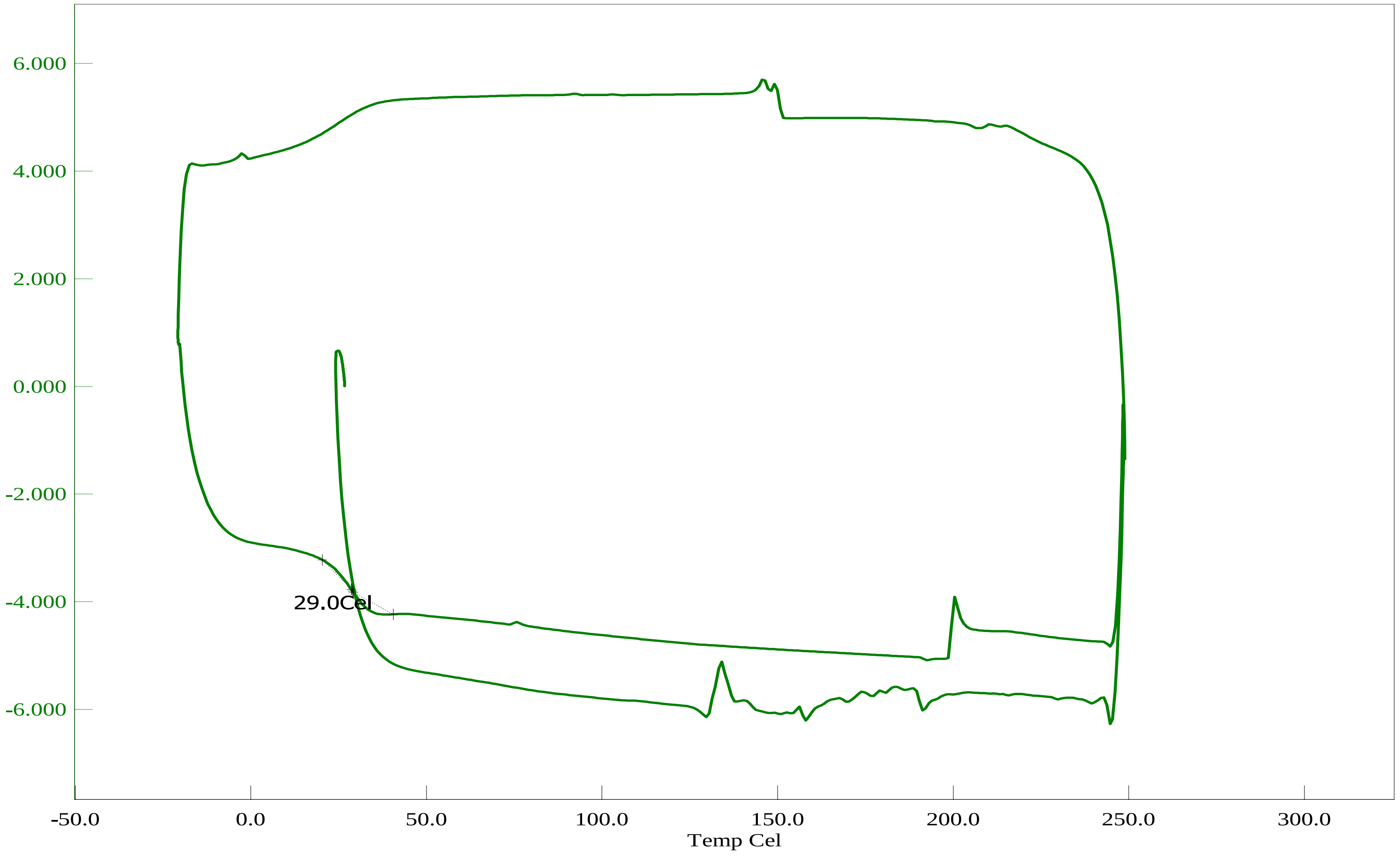


Figure A. 16. DSC Analysis of PIN_1.

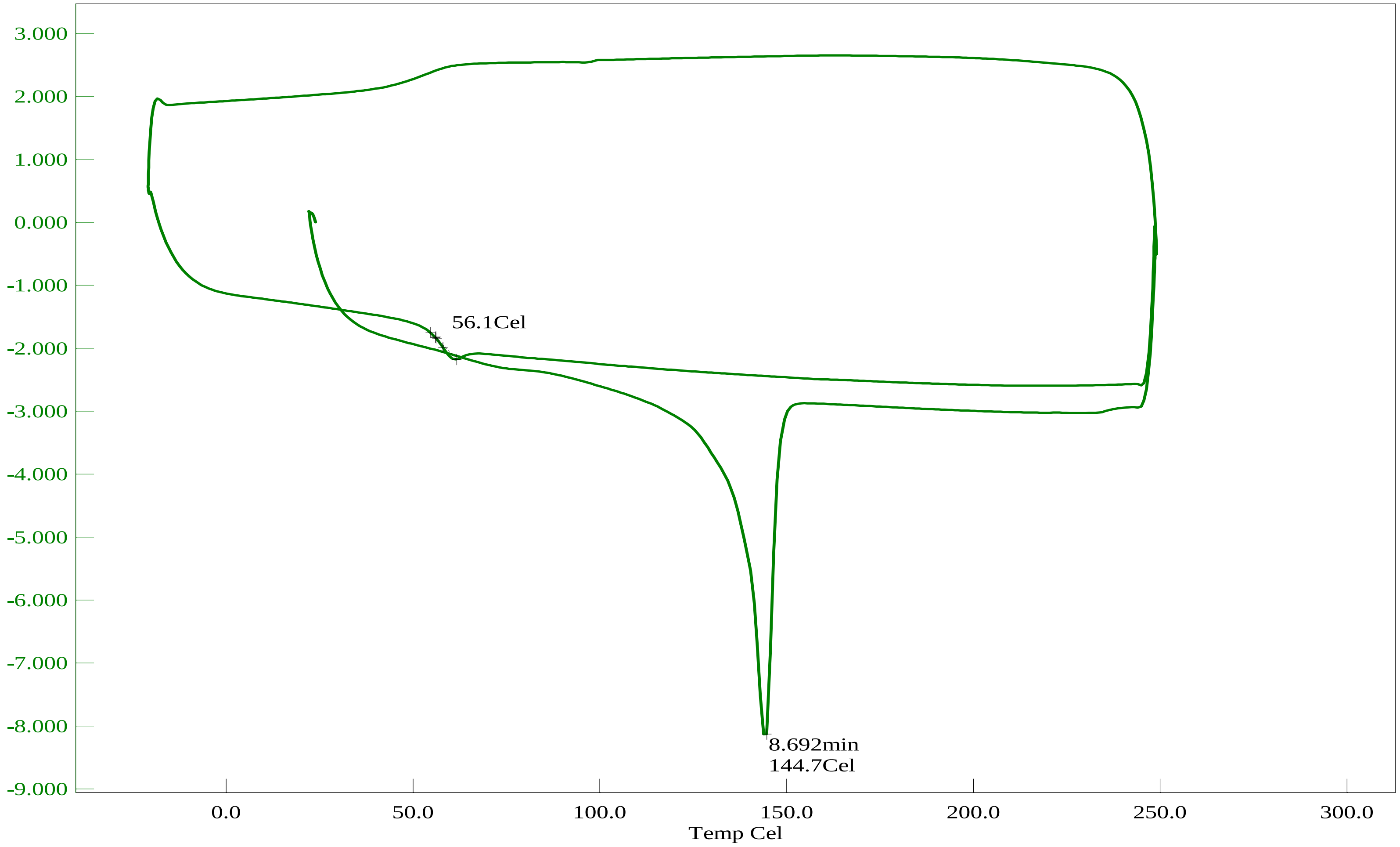


Figure A. 17. DSC Analysis of PIN_2.

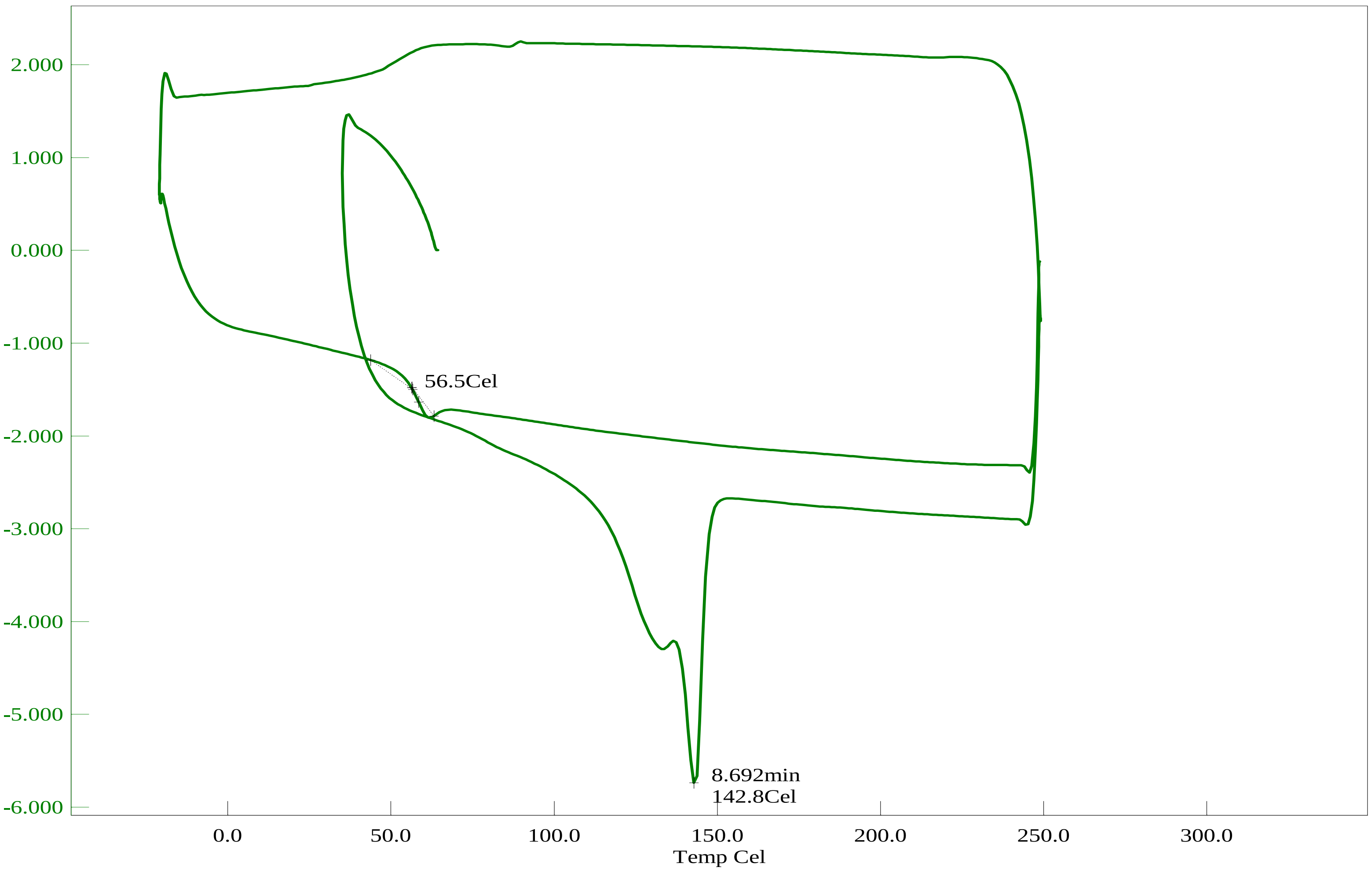


Figure A. 18. DSC Analysis of PIN_3.

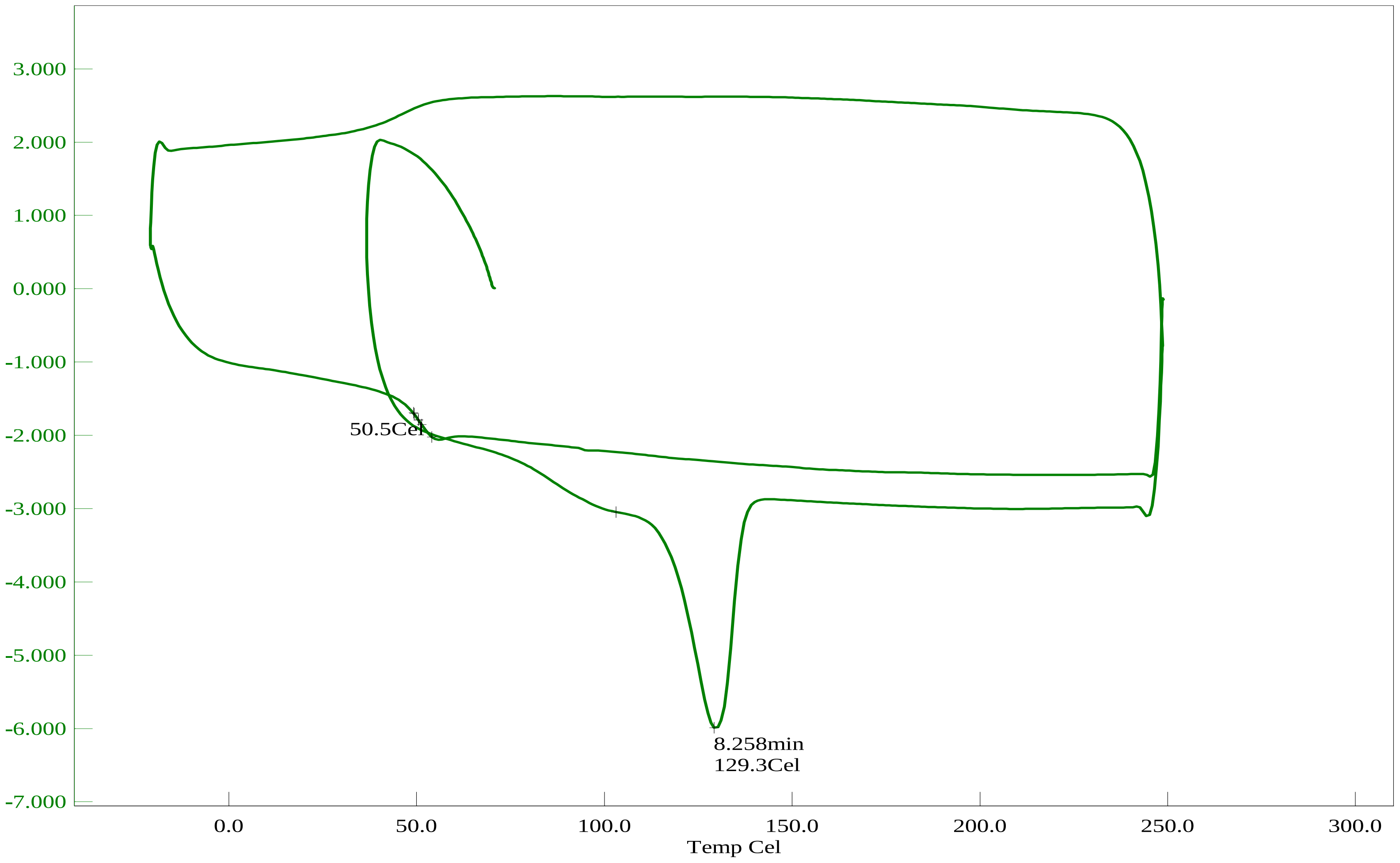


Figure A. 19. DSC Analysis of PIN_3_SA_1.

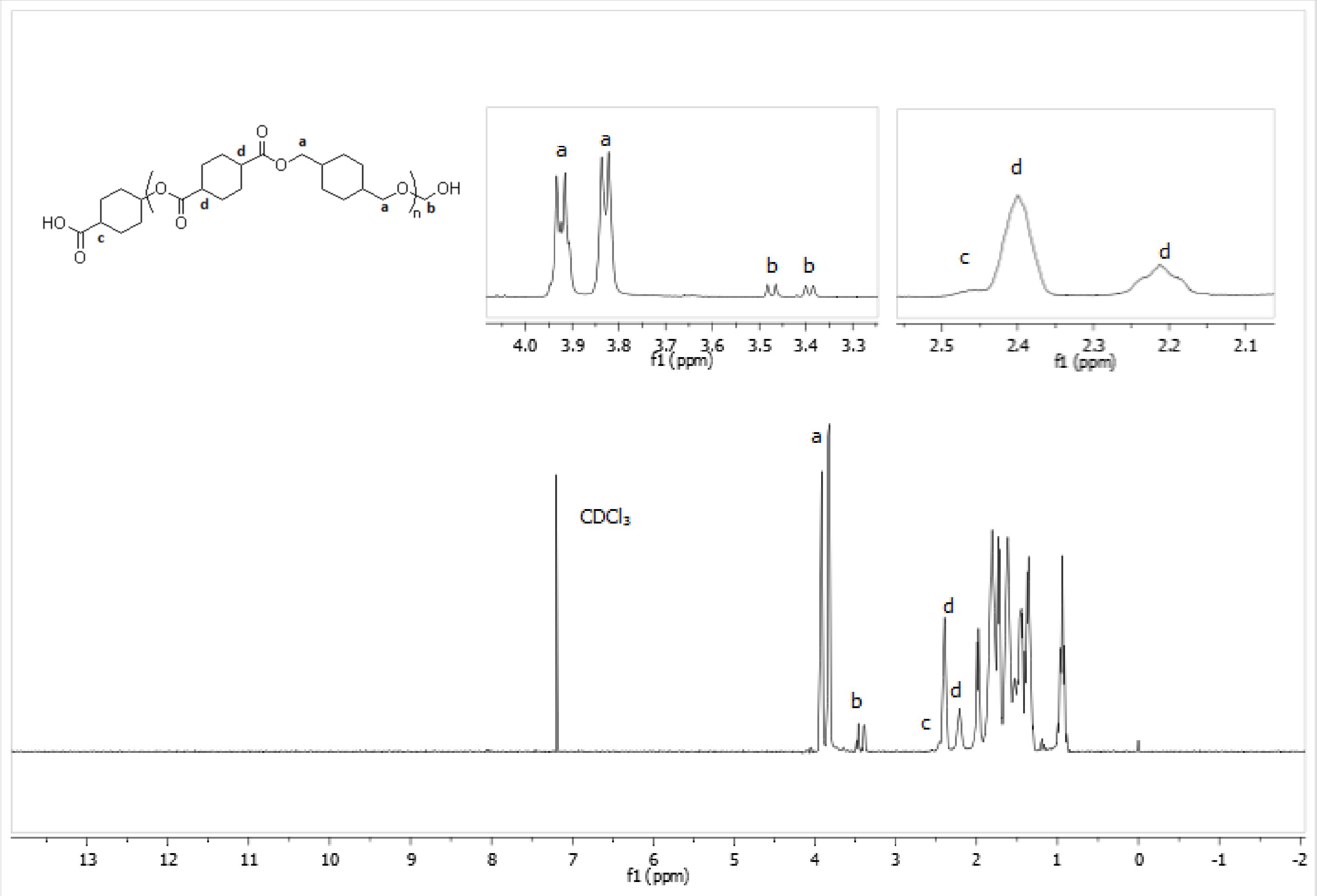


Figure A. 20. ^{1}H-NMR Spectra of PCCD_1.

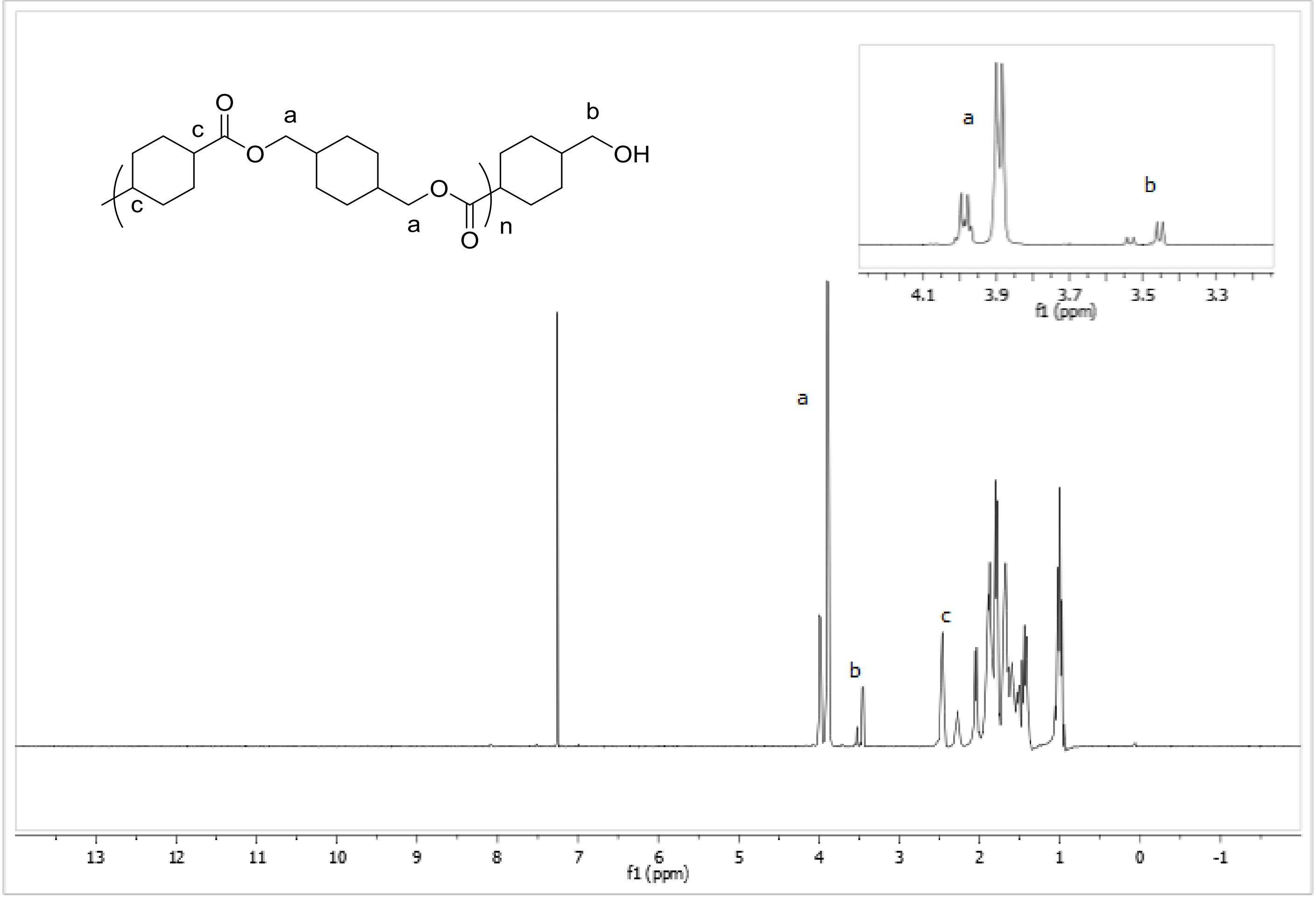


Figure A. 21. ^{1}H-NMR Spectra of PCCD_2.

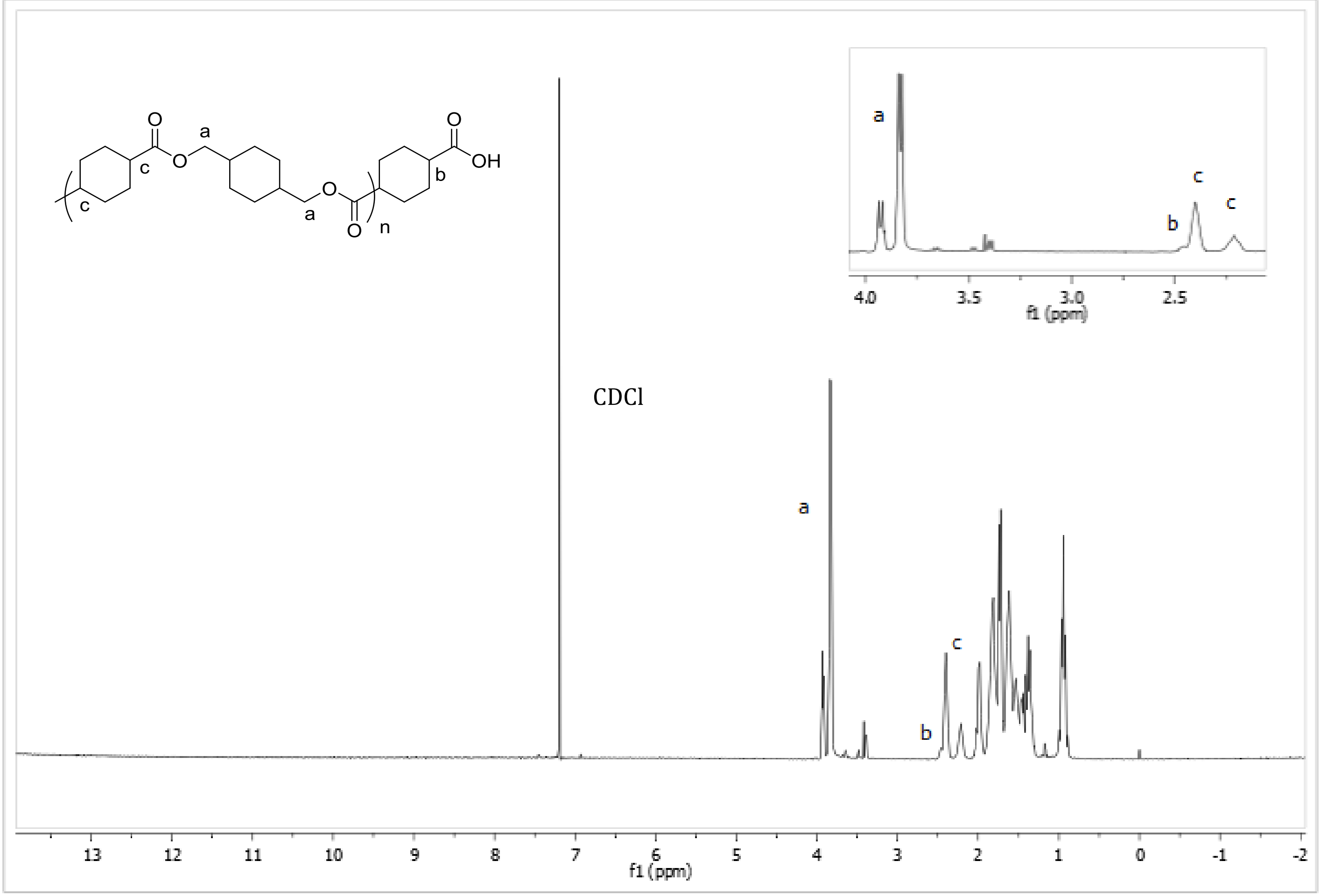


Figure A. 22. ^{1}H-NMR Spectra of PCCD_3.

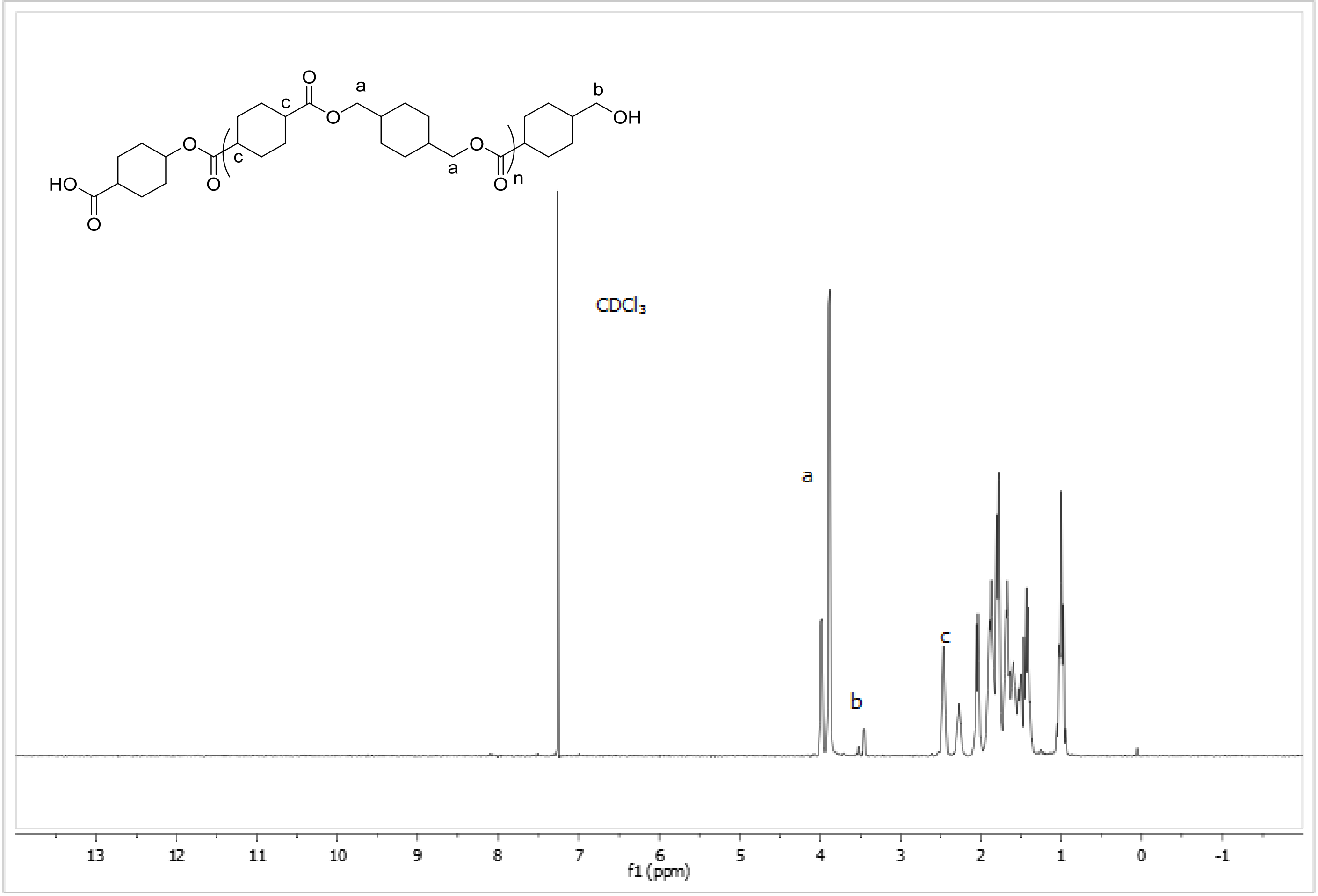


Figure A. 23. ^{1}H-NMR Spectra of PCCD_4.

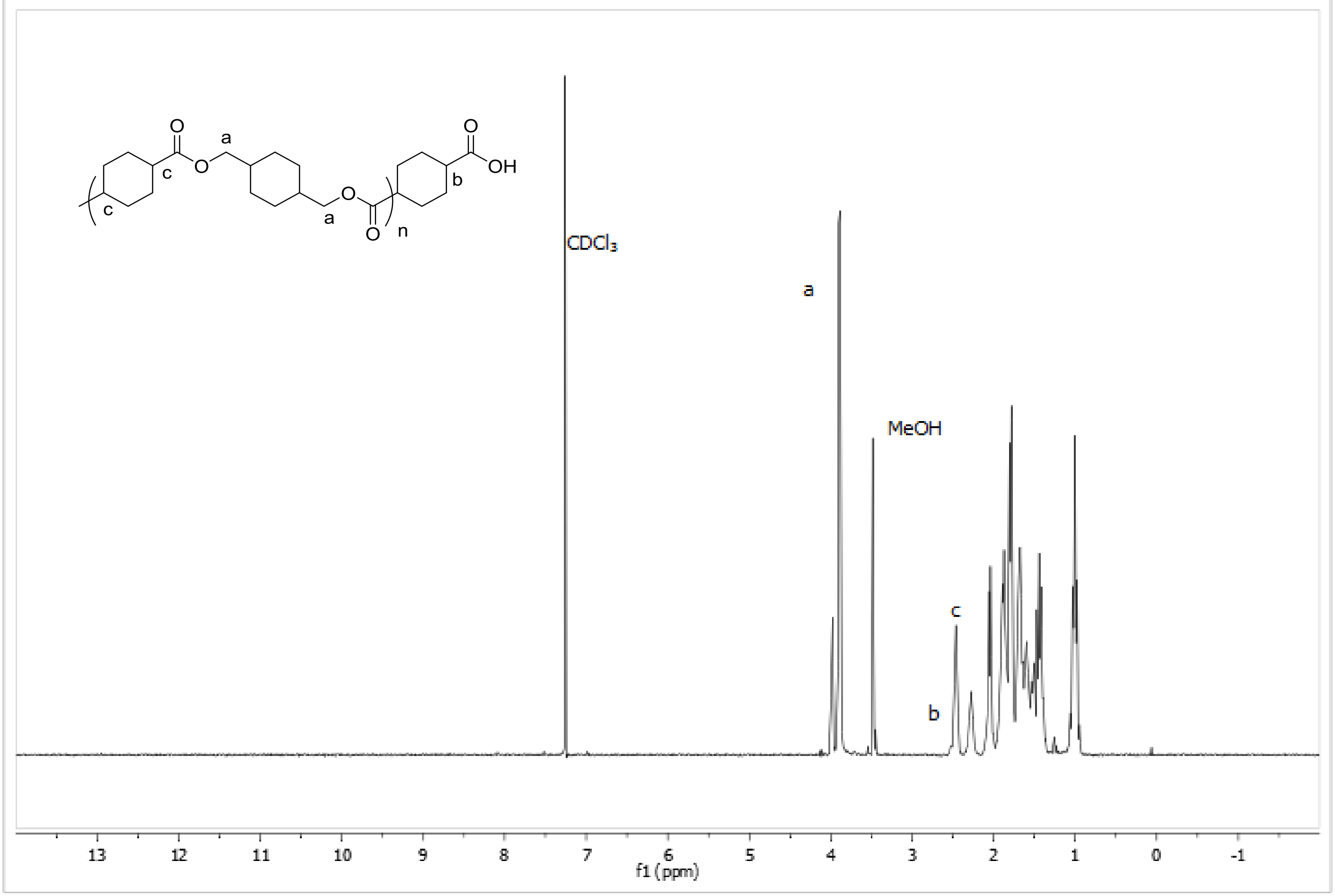


Figure A. 24. ^{1}H-NMR Spectra of PCCD_5.

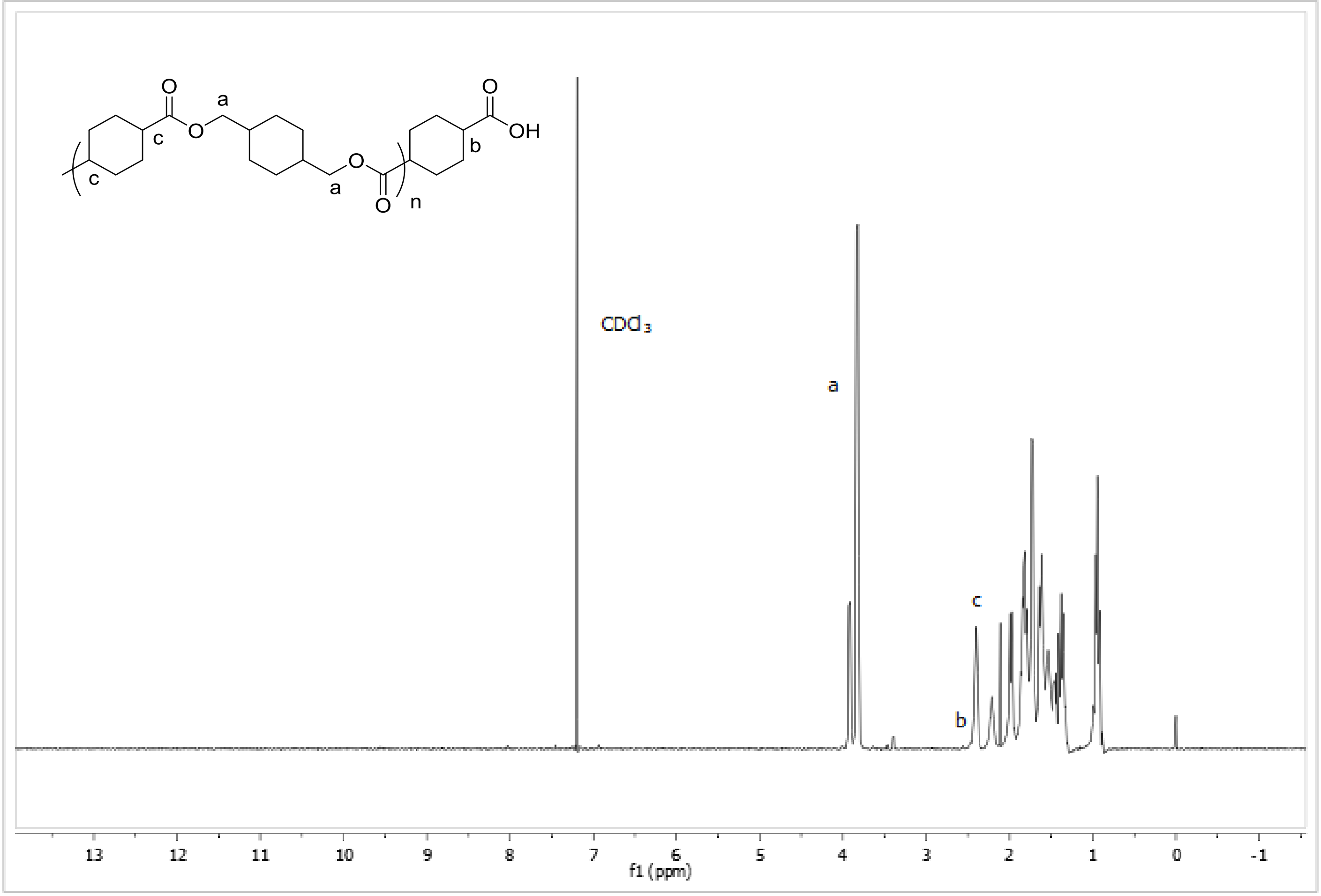
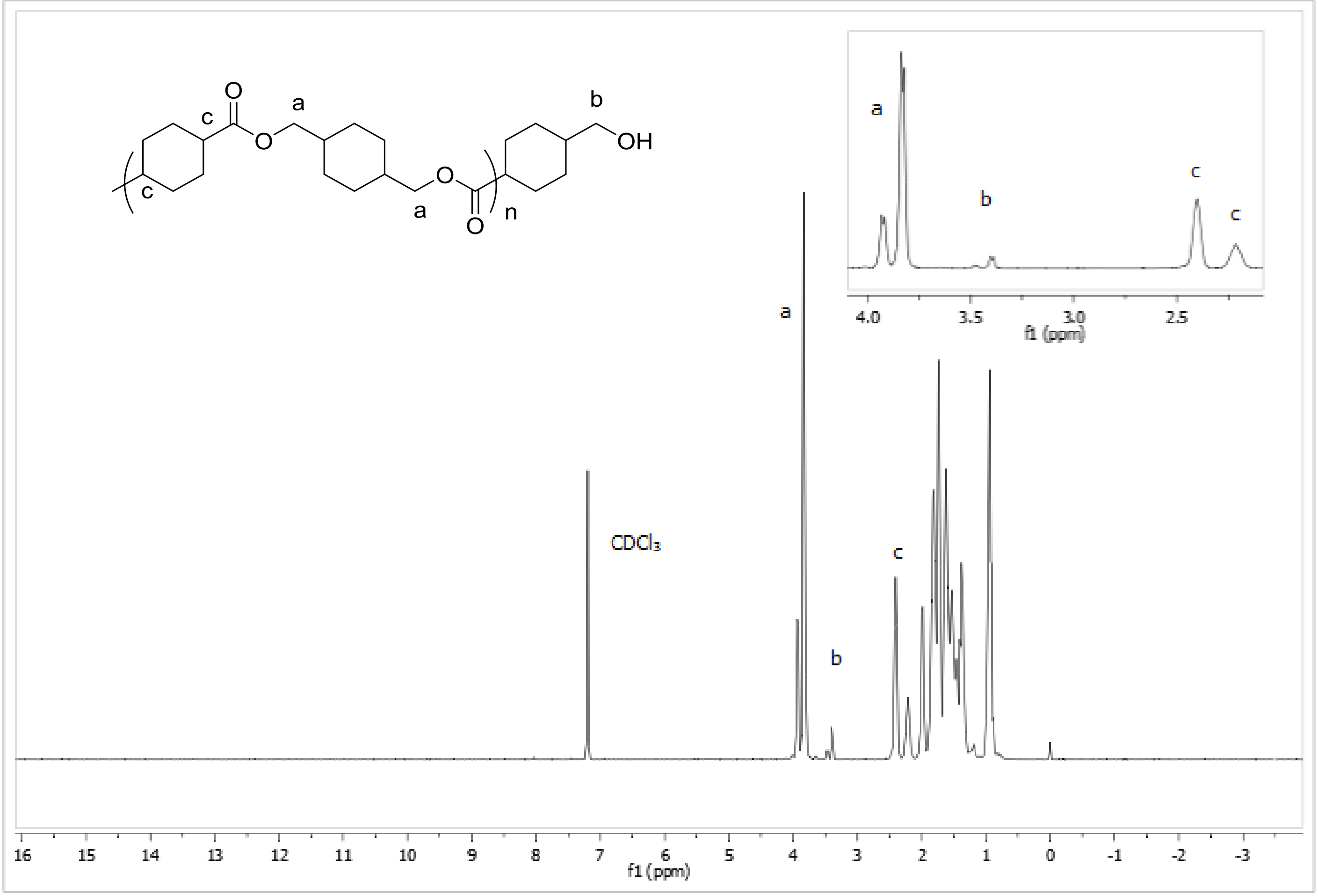


Figure A. 25. ^{1}H-NMR Spectra of PCCD_6.



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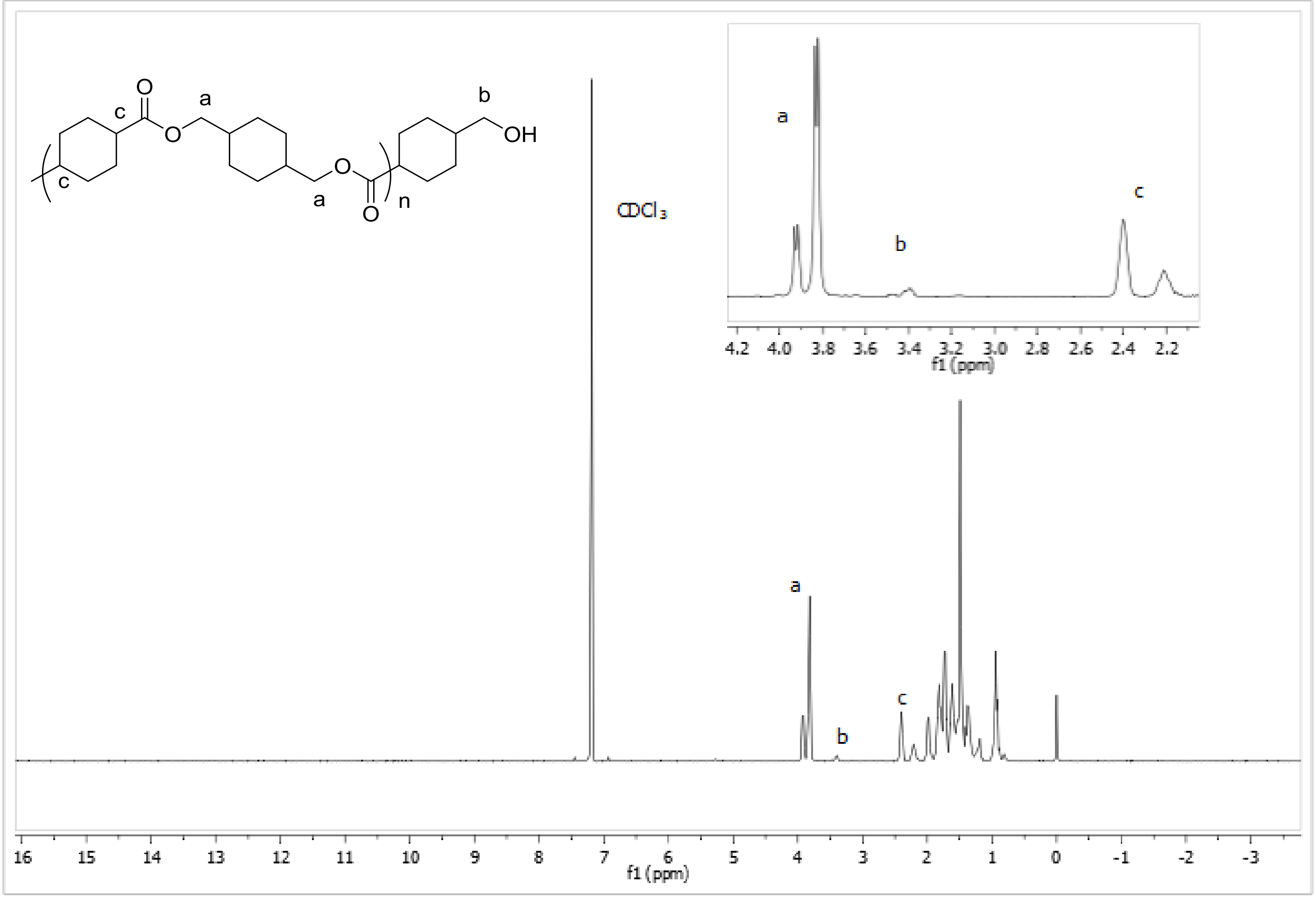


Figure A. 27. ^{1}H-NMR Spectra of PCCD_8.

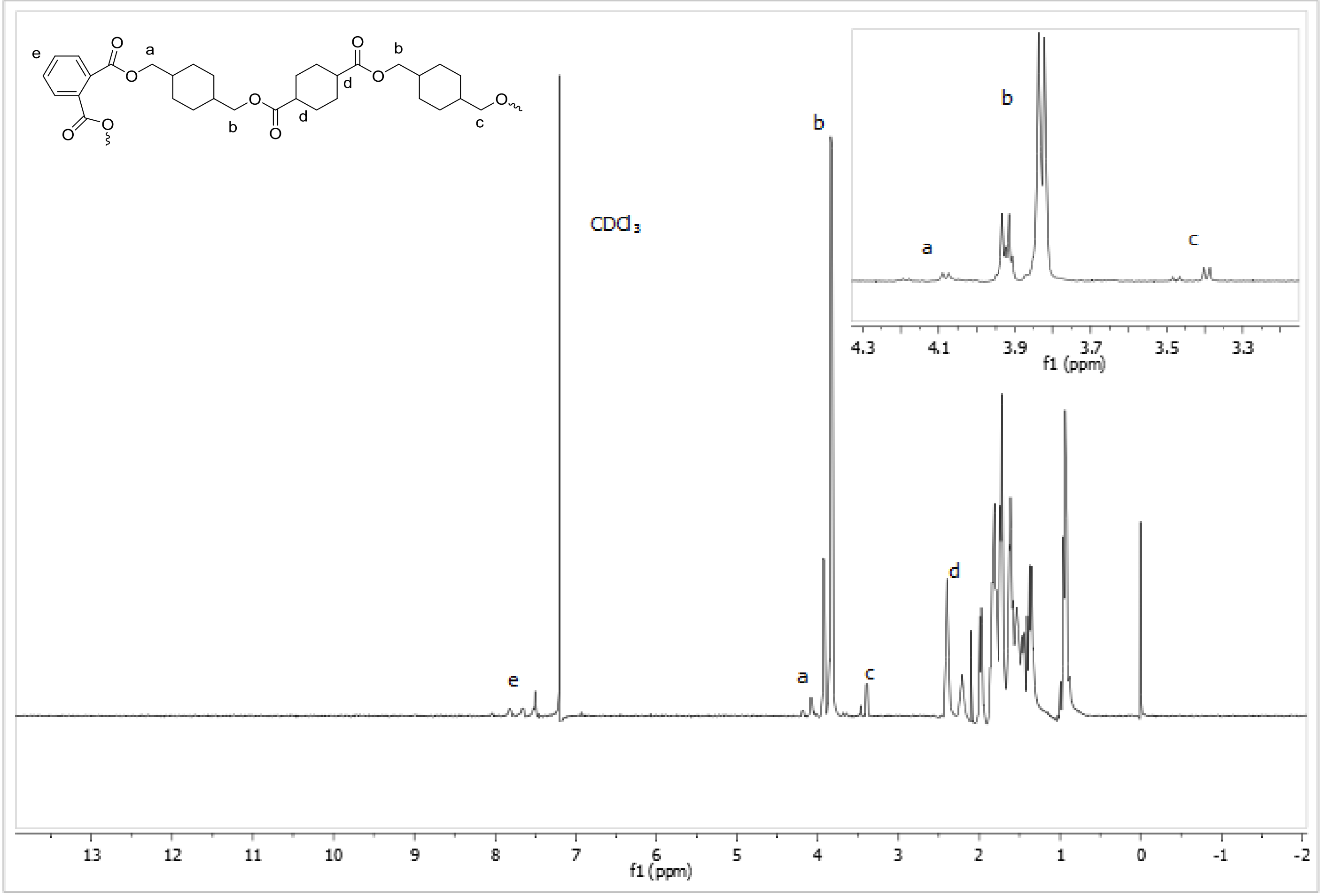


Figure A. 28. ^{1}H-NMR Spectra of PCCD_2_PA_1.

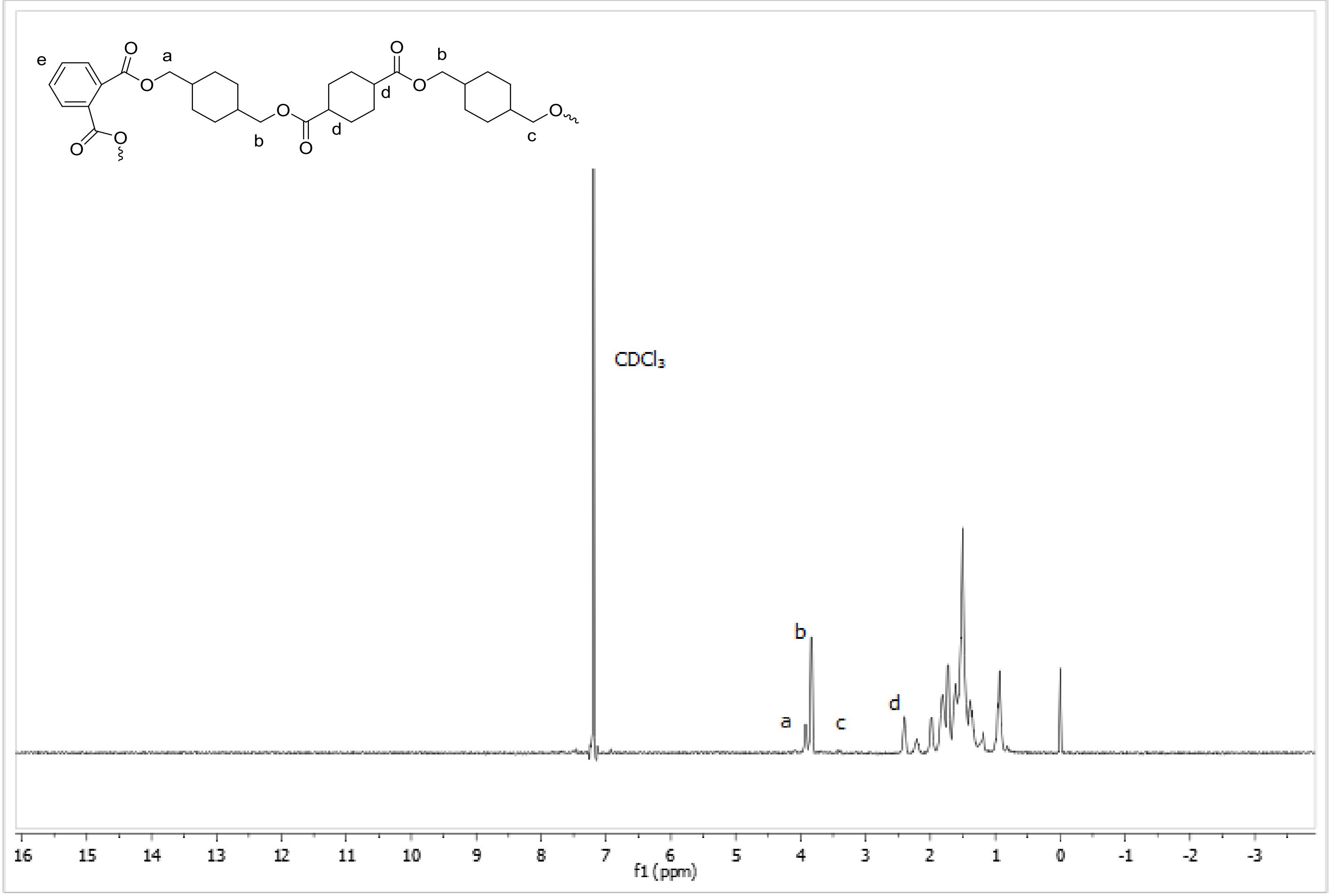


Figure A. 29. ^{1}H-NMR Spectra of PCCD_7_PA_1.

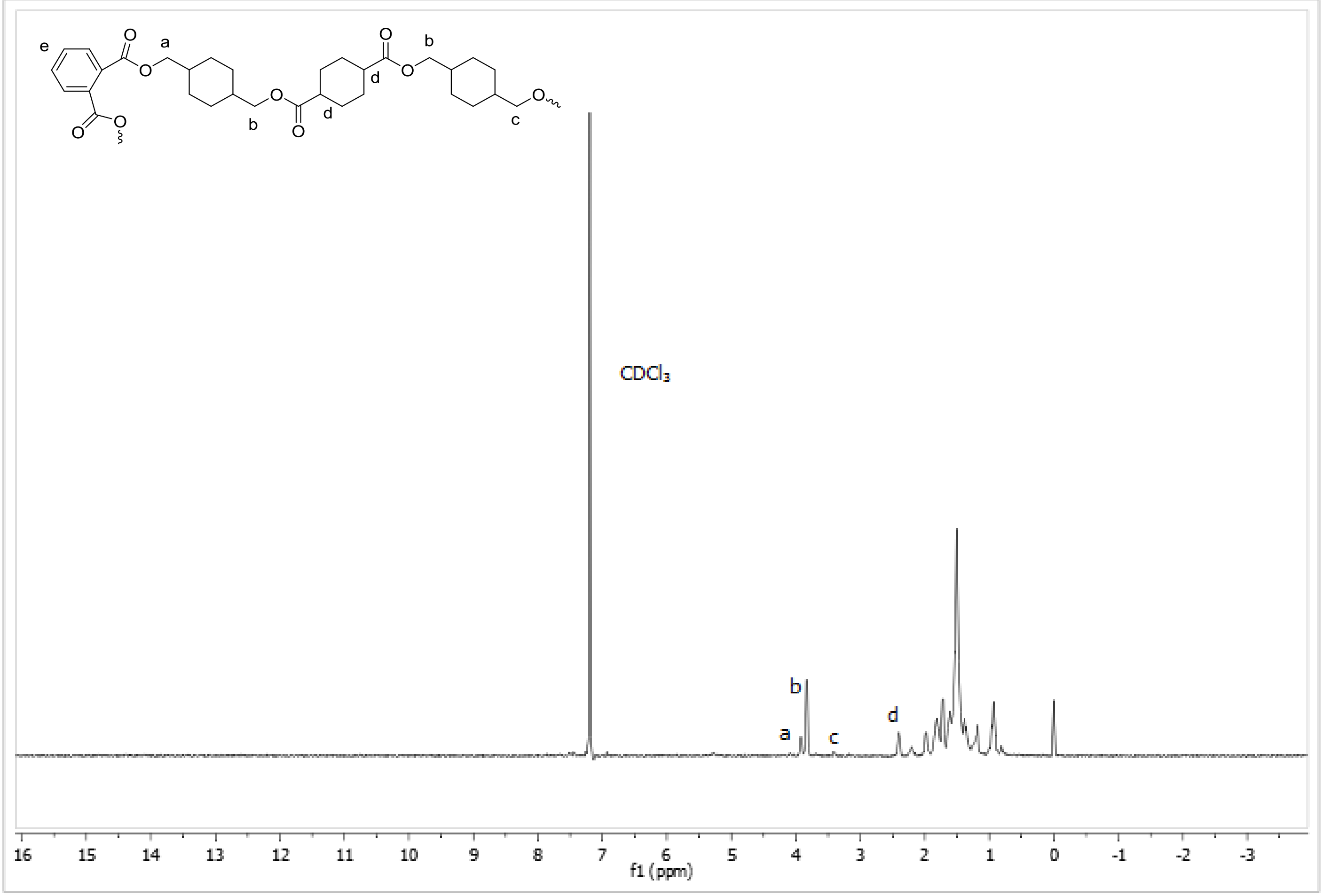
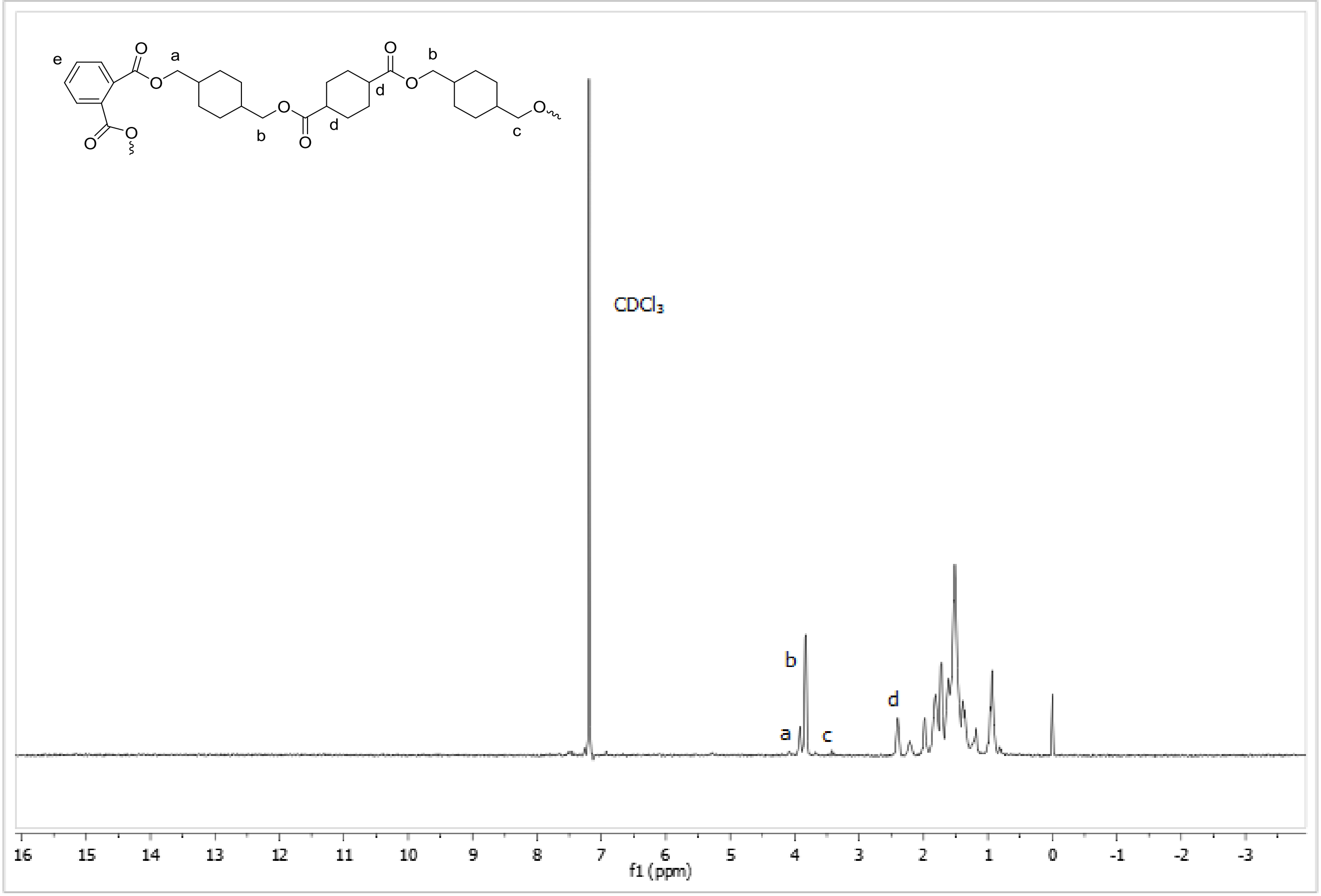


Figure A. 30. ^{1}H-NMR Spectra of PCCD_7_PA_2.



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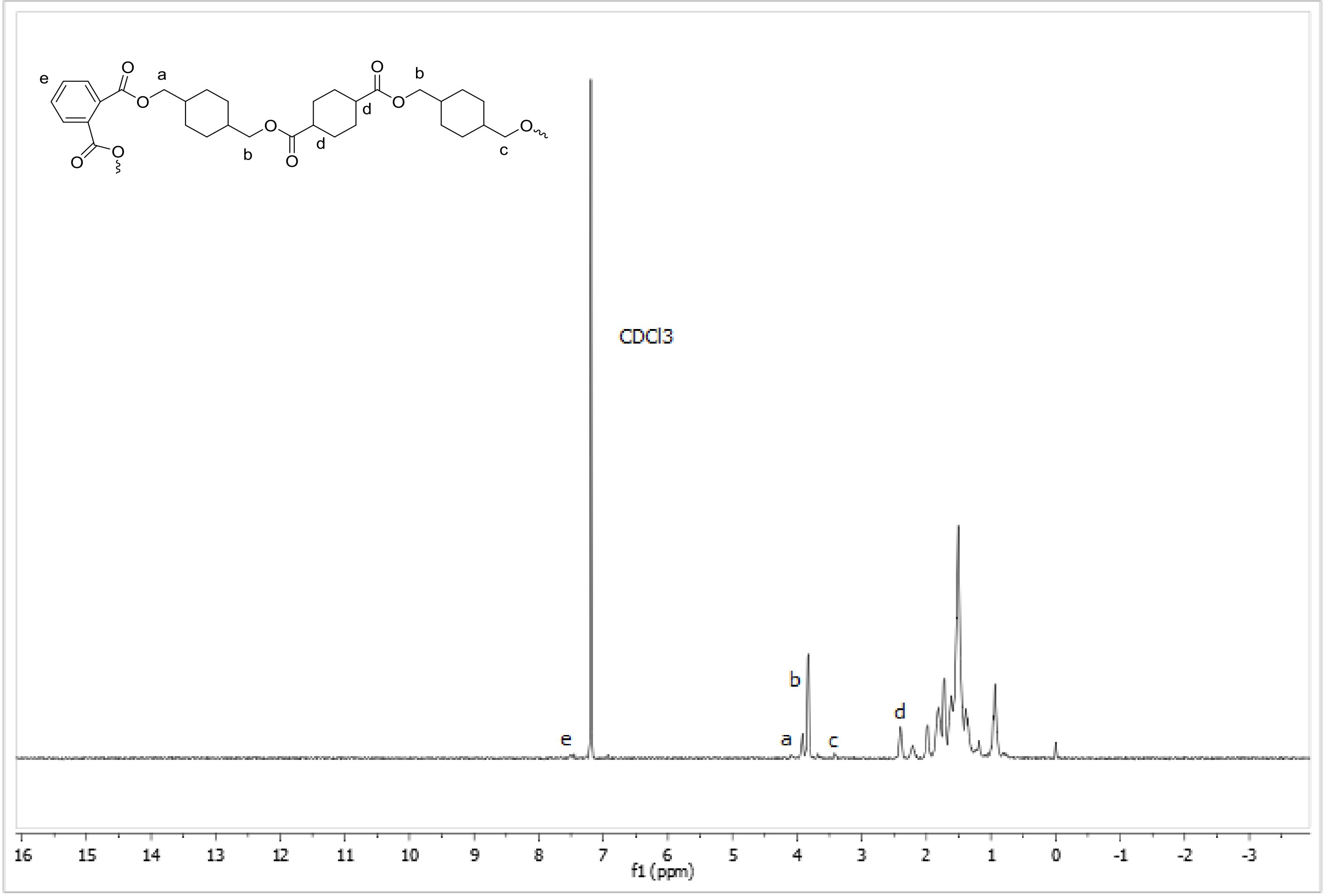


Figure A. 32. ^{1}H-NMR Spectra of PCCD_7_PA_4.

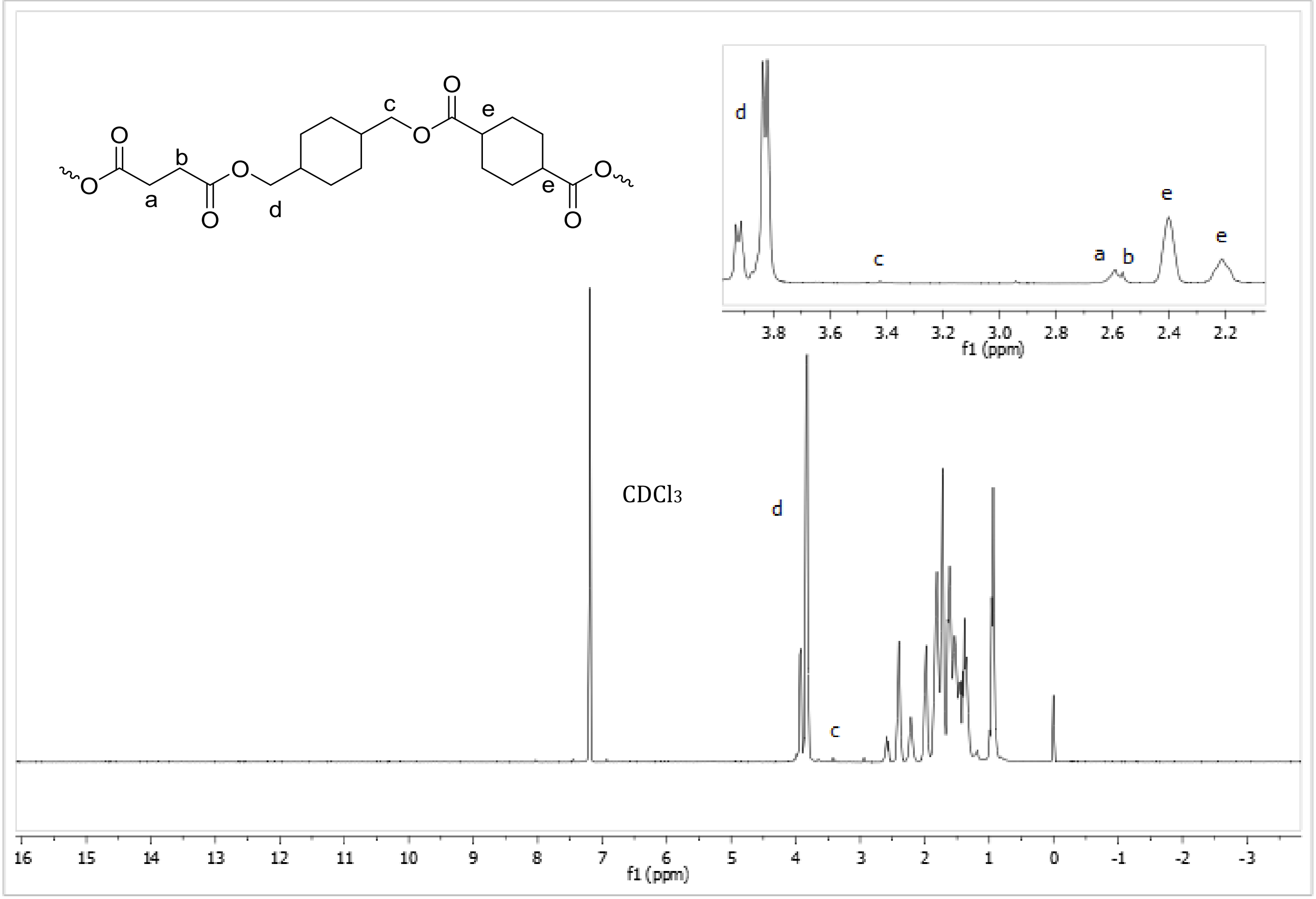


Figure A. 33. ^{1}H-NMR Spectra of PCCD_8_SA_1.

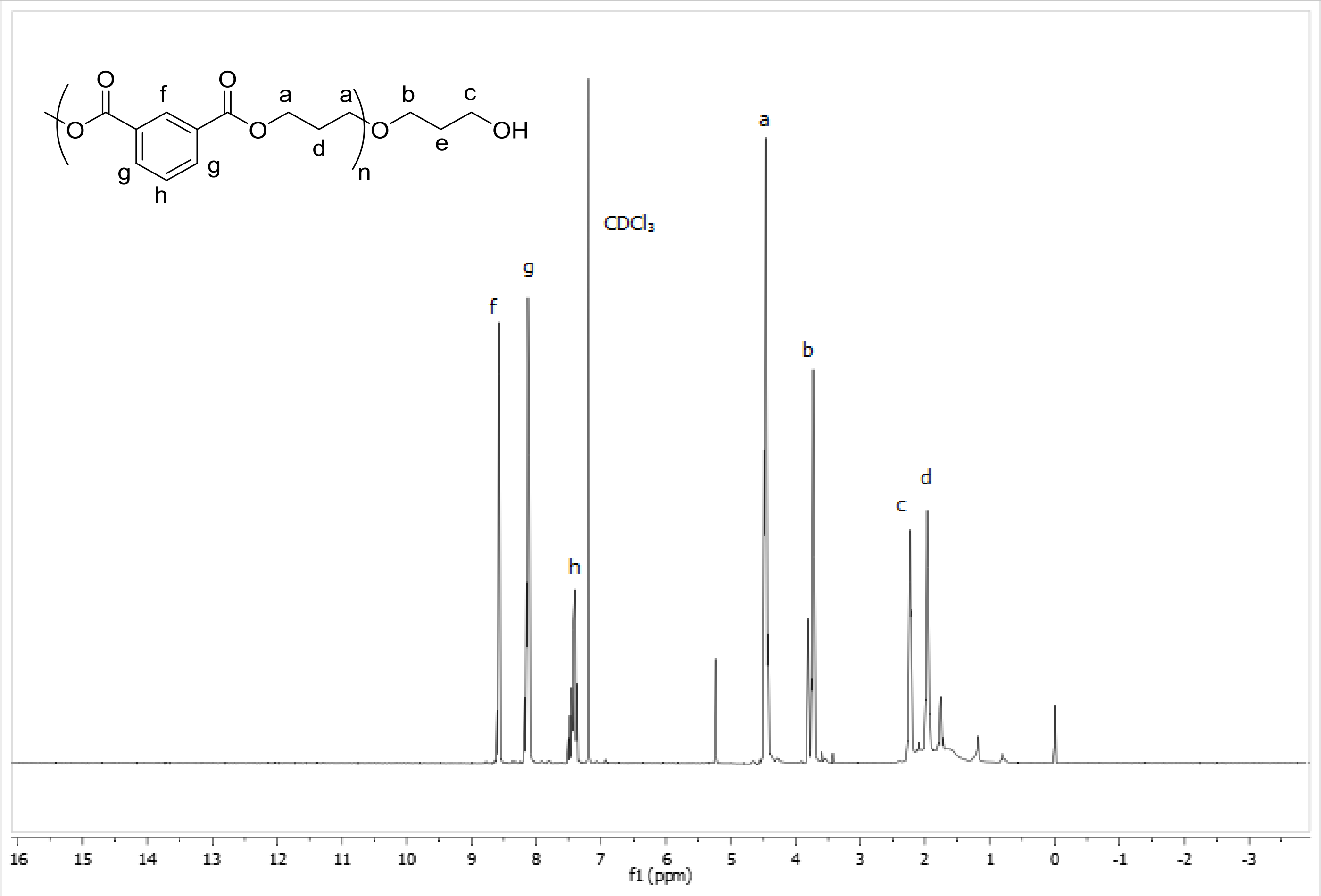
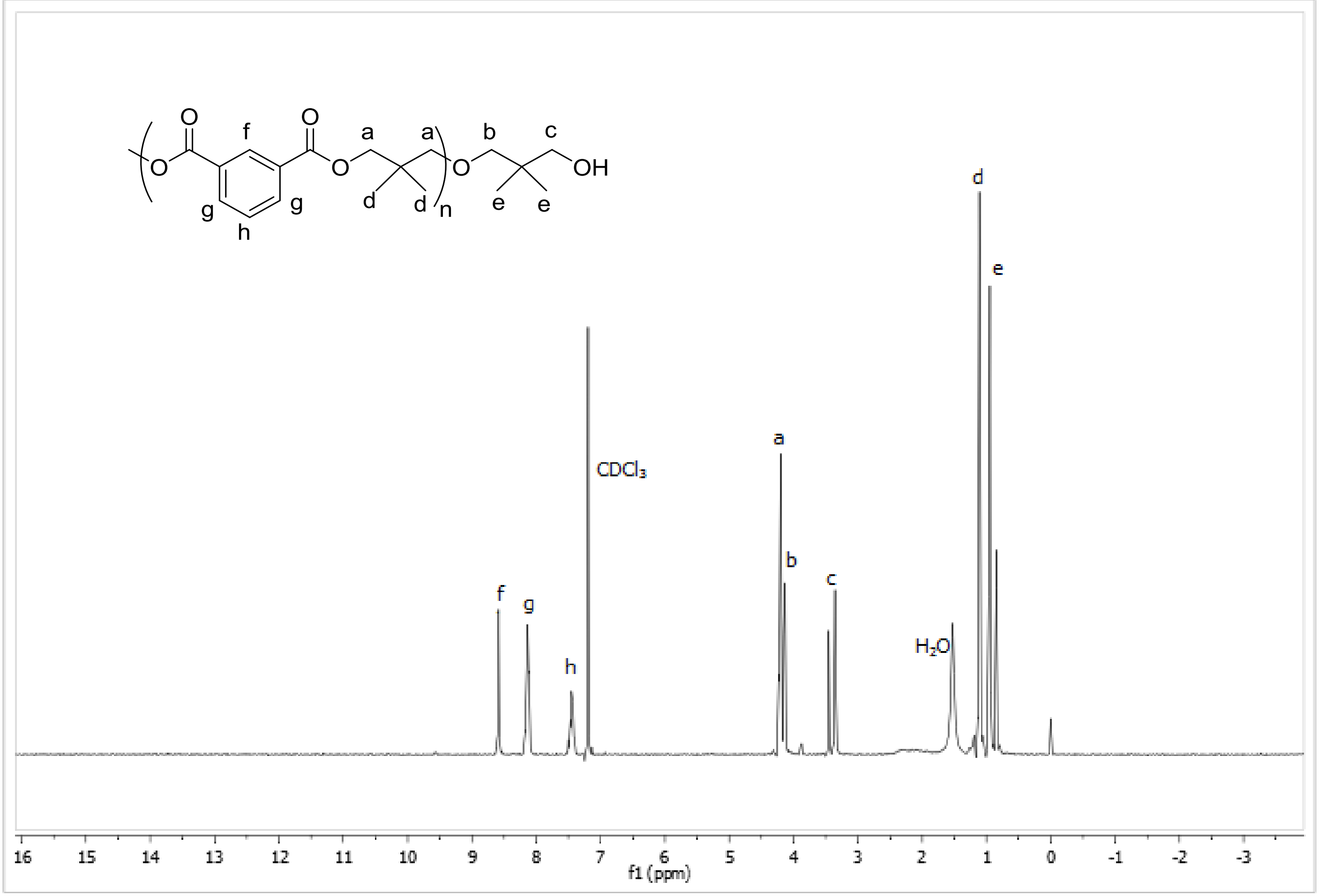


Figure A. 34. ^{1}H-NMR Spectra of PIP_1.



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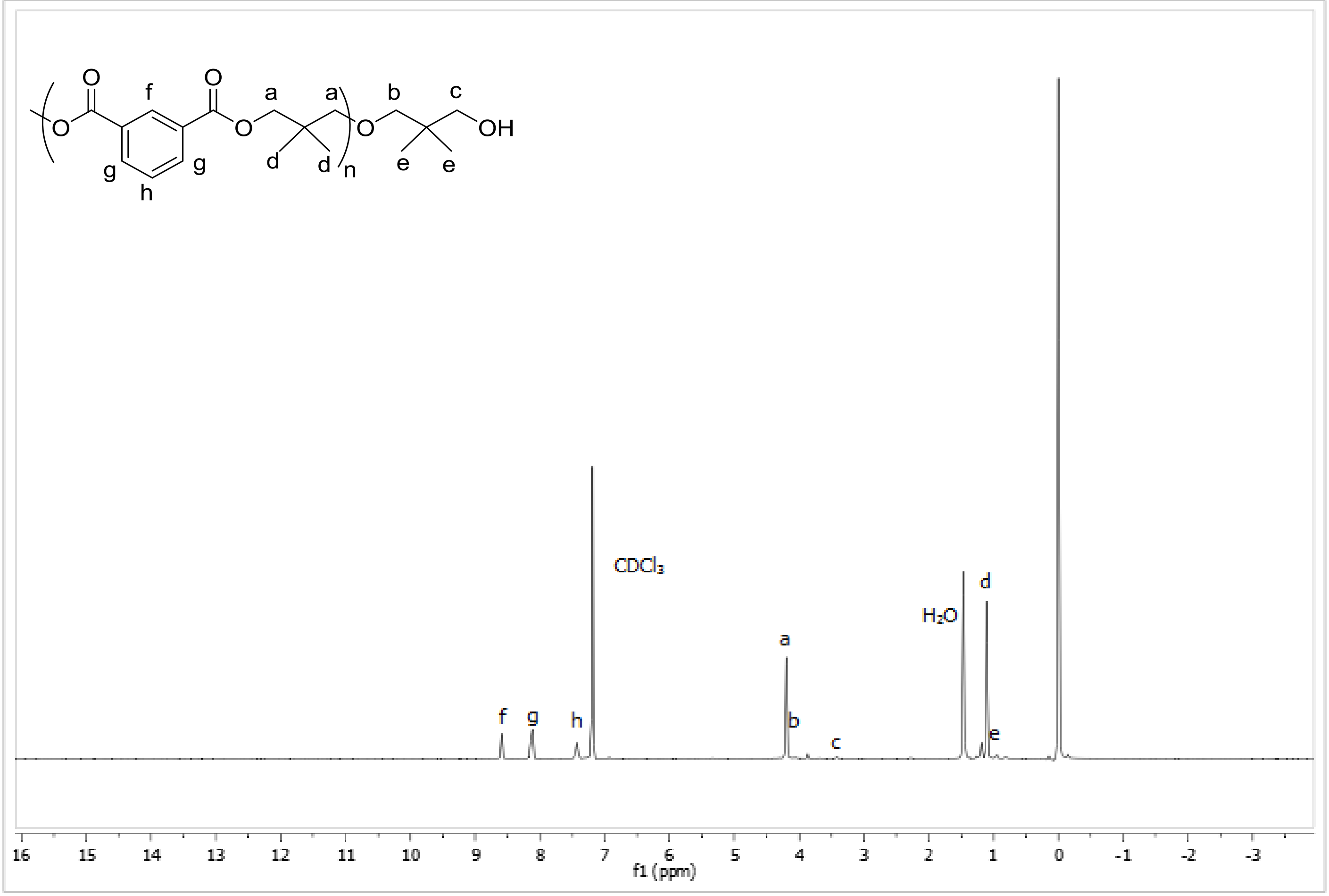

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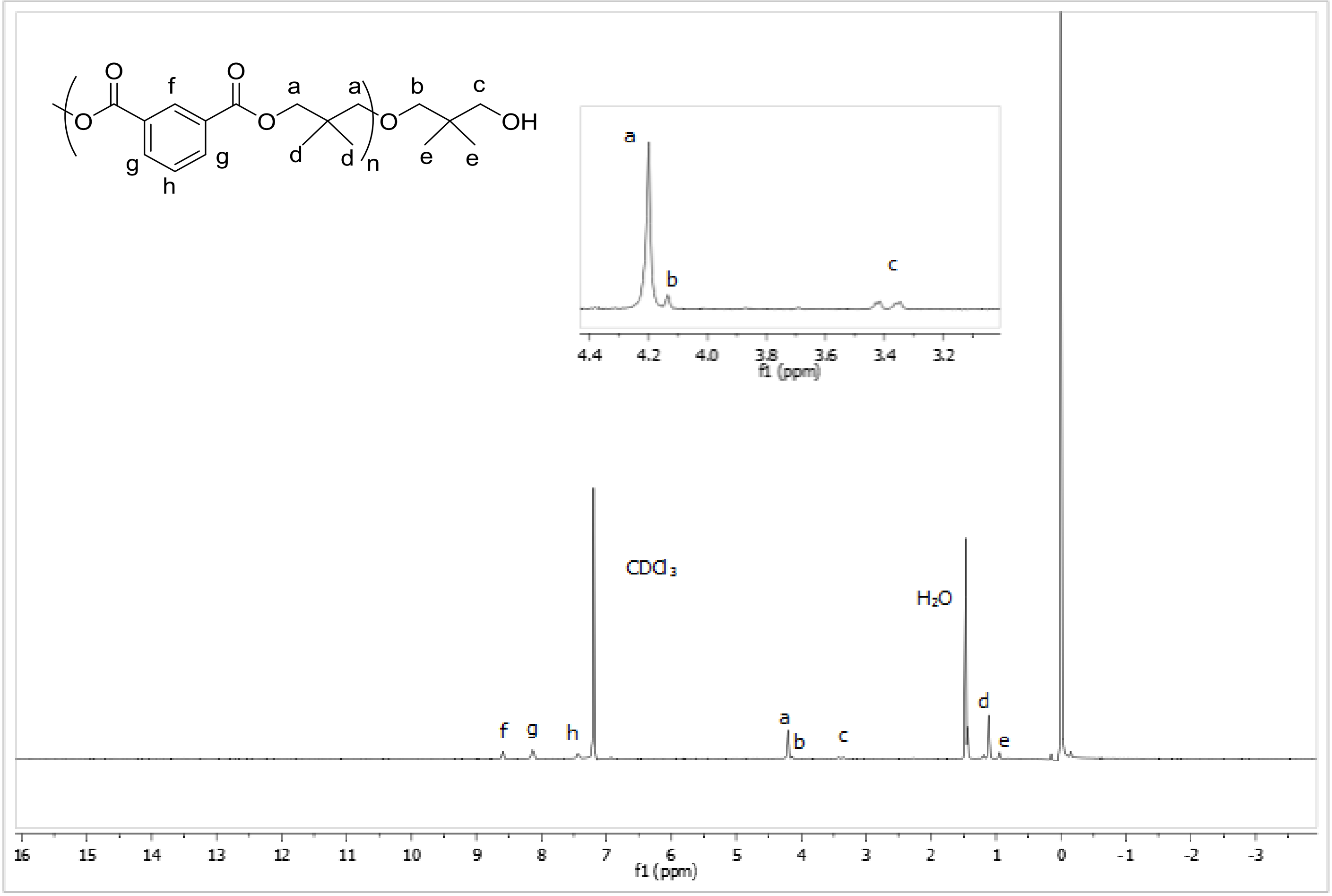

Figure A. 37. ^{1}H-NMR Spectra of PIN_3.

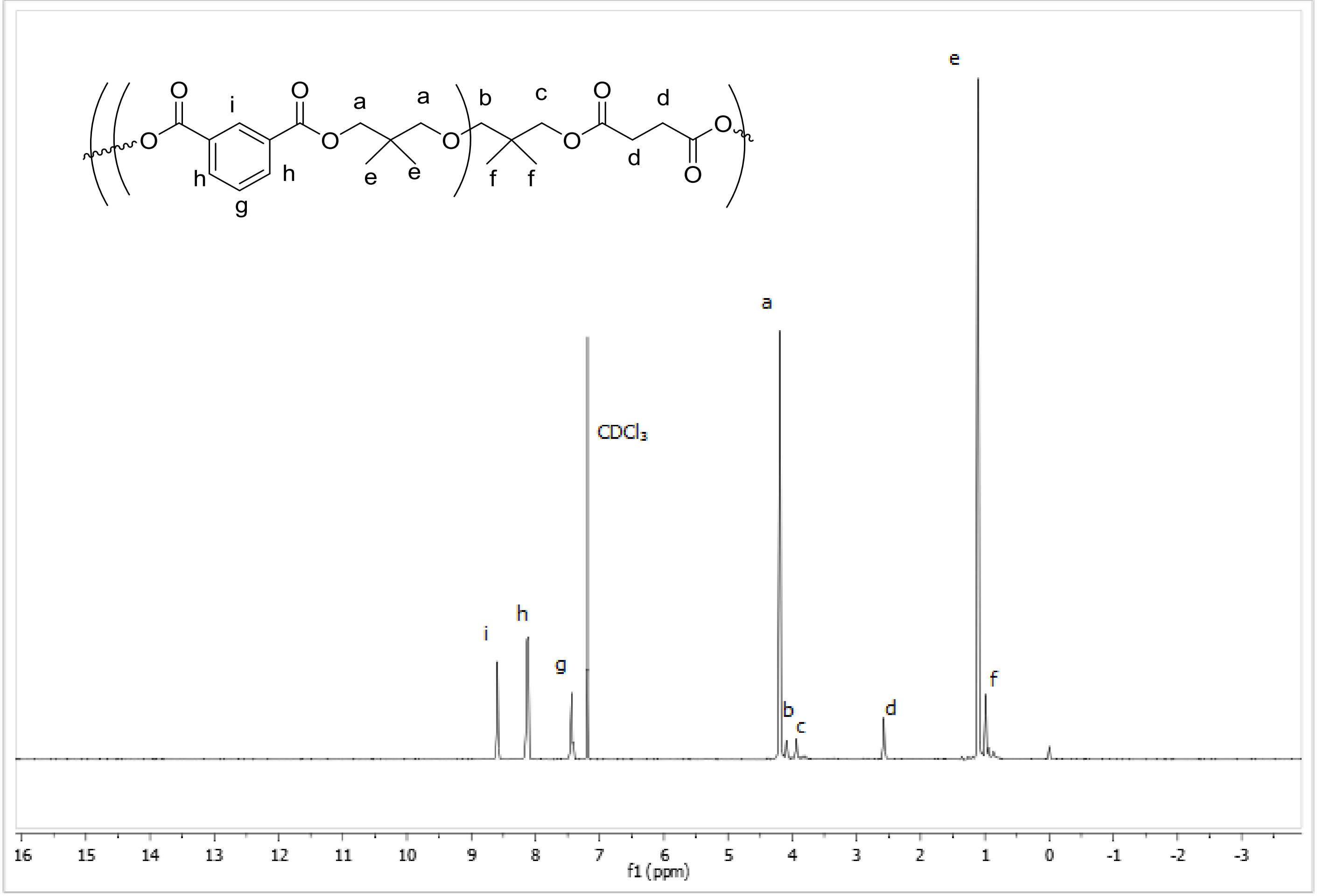

Figure A. 38. ^{1}H-NMR Spectra of PIN_3_SA_1.