SYNTHESIS OF SULFONATED POLYETHYLENE TEREPHTHALATE *VIA* MELT POLYCONDENSATION

by

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Dedicated to my family and my dear nephew Atlas

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ABSTRACT

SYNTHESIS OF SULFONATED POLYETHYLENE TEREPHTHALATE *VIA* MELT POLYCONDENSATION

Polyethylene terephthalate (PET) is an essential thermoplastic polyester that used in many industrial applications. The synthesis of PET has two pathways, which are the esterification of terephthalic acid (TPA) and ethylene glycol (EG) or transesterification of dimethyl terephthalate (DMT) and EG. PET can be produced *via* melt polymerization to obtain low to medium molecular weight. High molecular weight PET requires one additional step, solid-state polymerization (SSP). PET has distinctive properties such as high mechanical strength and solvent resistance. The hydrophobic nature of PET restricts its use in some applications, such as textile, dyeing, adhesion, and water absorption, in which polarity is necessary. Modifying the surface of the PET is necessary to enhance its wettability.

In this study, to alter the hydrophobic nature of PET and introduce hydrophilicity, the effect of incorporation of the ionic monomers, SM_1 and SM_2, was investigated. The copolymers were synthesized *via* melt polycondensation, and their wettability were investigated by using contact angle measurements. The impact of incorporating additional monomers such as diethylene glycol (DEG) and triethylene glycol (TEG) on PET hydrophilicity was studied. Sulfonated copolymers of PET were synthesized on a large scale. Surface modification of PET with sulfonated monomers, DEG and TEG exhibited better hydrophilic properties than the pure PET.

ÖZET

SÜLFONLU POLİETİLEN TEREFTALATIN ERİYİK POLİKONDENZASYON İLE SENTEZLENMESİ

Polietilen tereftalat (PET) temel bir termoplastik polyesterdir ve birçok endüstriyel uygulamada kullanılmaktadır. PET'in sentezi, tereftalik asit (TPA) ve etilen glikolün (EG) esterleştirilmesi veya dimetil tereftalat (DMT) ve EG'nin transesterifikasyonu olmak üzere iki yoldan gerçekleşir. PET, düşük ve orta moleküler ağırlık elde etmek için eriyik polimerizasyonu yoluyla üretilebilir. Yüksek moleküler ağırlıklı PET'in elde edilmesi katı hal polimerizasyonu (SSP) yoluyla sentezlenebilir. PET, mekanik mukavemet ve birçok çözücüye karşı direnç gibi ayırt edici özelliklere sahiptir. PET'in hidrofobik yapısı, polaritenin gerekli olduğu tekstil, boyama, yapışma ve absorpsiyon gibi bazı uygulamalarda kullanımını kısıtlamaktadır. PET'in ıslanabilirliğini arttırmak için yüzeyinin modifiye edilmesi gereklidir. Bu çalışmada, PET'in hidrofobik yapısını değiştirmek ve yüzeyinde polarite sağlamak için, sülfonlu monomer_1 ve sülfonlu monomer_2 olan iyon eşleştirme içeren monomerlerin PET'in hidrofilikliği üzerindeki etkisi ve kopolimerleri eriyik polikondensasyon yoluyla sentezlenmiş ve temas açısı ölçümü kullanılarak ıslanabilirlikleri araştırılmıştır. Ayrıca, DEG ve TEG'in yumuşak blok segmentleri olarak PET kopolimerlerinin yüzeyine eklenmesinin etkisi incelenmiştir. Ayrıca, PET'in sülfonlanmış kopolimerleri büyük ölçekte sentezlenmiştir. PET ve kopolimerinin sülfonlanmış monomerler ve yumuşak blok segmentleri ile yüzey modifikasyonu, saf PET'e göre daha iyi hidrofilik özellikler sergilemiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

M_n	Number Average Molecular Weight
T_c	Crystallization Temperature
T_m	Melting Temperature
T_g	Glass Transition Temperature

LIST OF ACRONYMS/ABBREVIATIONS

DEG	Diethylene Glycol
DMT	Dimethyl Terephthalate
DSC	Differential Scanning Calorimetry
EG	Ethylene Glycol
FT-IR	Fourier Transform-Infrared
GPC	Gel Permeation Chromatography
^{1}H-NMR	Proton NMR
HFIP	Hexafluoroisopropanol
IPA	Isophthalic Acid
IV	Intrinsic Viscosity
NMR	Nuclear Magnetic Resonance
PDI	Polydispersity Index
PET	Polyethylene Terephthalate
PETI	Poly (ethylene terephthalate-co-isophthalate)
Sb_2O_3	Antimony trioxide
SM_1	Sulfonated Monomer_1
SM_2	Sulfonated Monomer_2
TEG	Triethylene glycol
TFA	Trifluoroacetic acıd
TPA	Terephthalic acid
TTIP	Titanium tetraisopropoxide

1. INTRODUCTION

1.1. Background of Poly (ethylene terephthalate)

Polyesters are fundamental polymers worldwide and are manufactured by the condensation reaction of difunctional monomers [1]. Polyethylene terephthalate, shortly known as PET, is an essential thermoplastic polyester and primarily spread in marketplaces for decades. In 1941, the original PET was synthesized by J.T. Dickson and Rex Whinfield at the Calico Printers Association Laboratories. Afterward, PET was developed by Imperial Chemical Industries (ICI) with Terylene trade name, and later Dupont manufactured PET as fiber in 1953 [2,3].

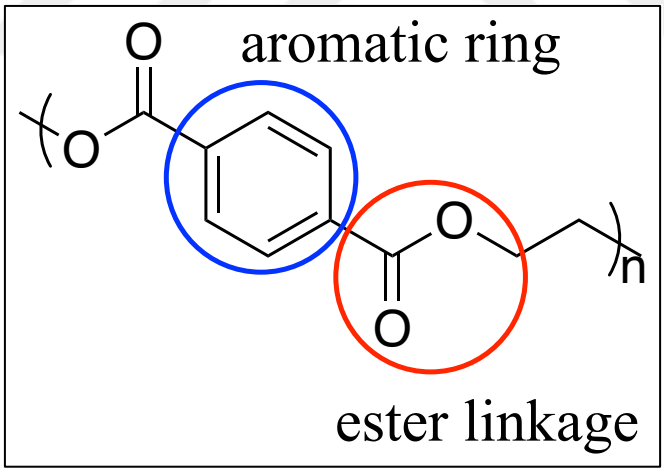

Figure 1.1. Repeating unit of PET [4].

PET is an example of semi-crystalline polyesters. The repeating unit of its structure has an aromatic ring and short ethylene group (Figure 1.1). Due to π-π stacking of aromatic rings, the chain mobility of PET diminishes [4]. Therefore, restriction of the chains leads to enhanced crystallinity [5]. The supremacy in physical and chemical properties results from the high crystallinity (Table 1.1). Consequently, there are many different applications of PET because of its outstanding properties [5,6]

Table 1.1. Physical and chemical properties of PET [7].

Property	Value
Molecular weight of repeating unit ($g.mol^{-1}$)	192
Weight-average (M_w) ($g.mol^{-1}$)	30000-80000
Glass Transition Temperature (°C) (T_g)	69 - 115
Melting Temperature (°C) (T_m)	250 - 265
Crystallization Temperature (°C)	150 - 190
Breaking Strength (MPa)	50
Tensile Strength (Young's Modulus) (MPa)	1700
Yield strength (%)	4
Impact Strength ($J\ m^{-1}$)	90
Density ($g.cm^{-3}$)	1.41
Permeability to hydrogen at ($25\ cm^3.cm.cm^{-2}s^{-1}Pa^{-1}$)	0.4 x 10 13
Permeability to nitrogen at ($25\ cm^3.cm.cm^{-2}s^{-1}Pa^{-1}$)	0.004 x 10 13
Permeability to oxygen at ($25\ cm^3.cm.cm^{-2}s^{-1}Pa^{-1}$)	0.03 x 10 13
Water absorption (after 24 h) (%)	0.5

1.2. Synthesis Methods of PET

Melt polymerization is a technique that surpasses the melting points of both monomers and the polymer in the polymerization process [6]. PET manufacturing has two steps. The first step is called pre-polymerization where bis (2-hydroxyethyl terephthalate) (BHET) and oligomers are produced. In the second step, known as polycondensation, oligomers and pre-polymers are reacted further to obtain high molecular weight polymers [4], [6] .

As seen in Figure 1.2., PET can be synthesized *via* two alternative pathways. One pathway is the esterification reaction of terephthalic acid (TPA) with ethylene glycol (EG). The other pathway is the transesterification reaction of dimethyl terephthalate (DMT) and EG [8]. There exist some distinctions between the two pathways. For example, in the esterification process, water is distilled off. On the other hand, in transesterification, methanol is eliminated as the *by*-product. When TPA is used, the rate of esterification is higher, and the requirement of catalyst is lower than DMT. Generally, germanium, antimony, and titanium-based catalysts are preferred for TPA, whereas zinc, lead, and mercury-based catalysts are chosen for DMT. Also, the esterification reaction is more manageable for PET synthesis than the transesterification reaction since methanol's flammability necessitates extra precautions. However, TPA is more difficult to dissolve and melt. Hence, to get outstanding products effective reactions of the monomers and oligomers are necessary [5,6].

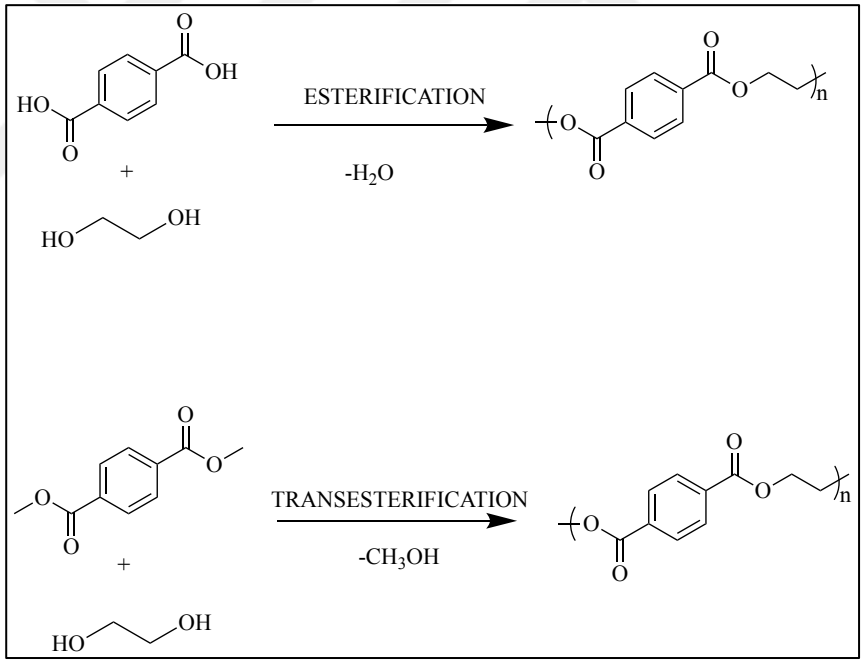

Figure 1.2. PET synthesis pathways [9].

Various requirements exist for the melt polymerization of PET. The reaction temperature ranges from 150°C to 210°C for the pre-polymerization and from 260°C to 290°C for the subsequent polycondensation process. Also, to distill off EG from the medium, 0.5-1 torr or 0.13 kPa vacuum is employed during the polycondensation [6].

When the reaction progresses, increase in the melt viscosity of PET is observed. The reaction between the end groups, -OH and -COOH or –COOMe, becomes more challenging as the viscosity and chain lengths increase. Thus, the rate of condensation diminishes. Therefore, the temperature of the reaction is increased to reduce the melt viscosity. Conversely, long exposure to high temperatures, exceeding the melting temperature of PET gives rise to thermal degradation. Therefore, PET's molecular weight and IV reduce, forming by-products such as diethylene glycol (DEG), as illustrated in Figure 1.3. [10].

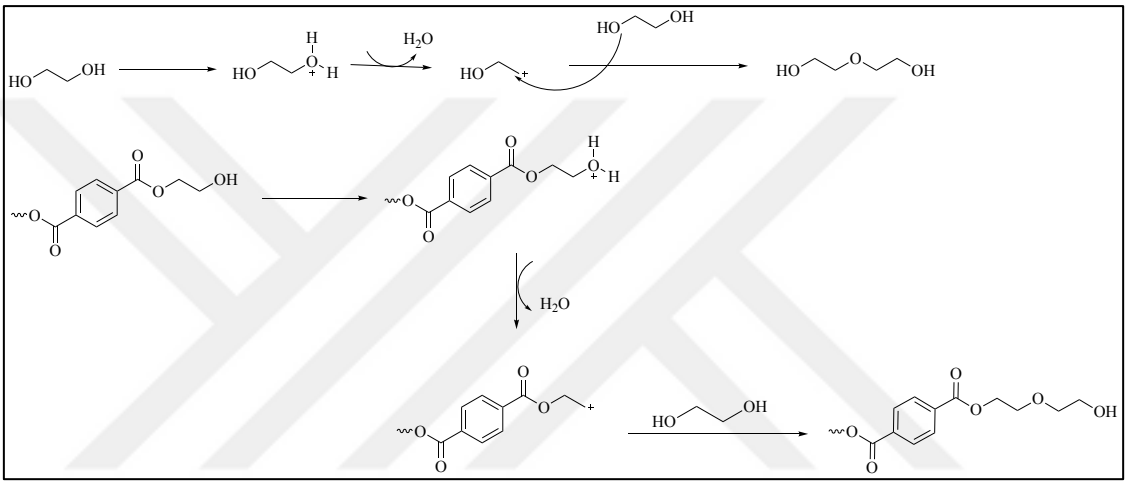

Figure 1.3. DEG formation [10].

DEG can be formed *via* the etherification reaction of EG and PET chains-OH end groups or between EG molecules in the medium. Formation of DEG in the backbone of PET increases its chain mobility, hence reduces the melting point [10].

IV of PET produced *via* melt polymerization roughly ranges from 0.5 dl/g to 0.7 dl/g. Therefore, melt polymerization is suitable for obtaining PET with low to medium IV's [9]. Solid-state polymerization is necessary to obtain higher molecular weight and viscosity PET's [2].

1.3. Applications Areas of PET

PET is dominating the thermoplastic industry due to its distinctive properties such as mechanical strength, resistance to many solvents, gas barrier, and heat resistance, which have expanded its field of applications [6], [11].

PET is used primarily as fiber in textile manufacturing for clothes, sportswear, and furniture due to its elasticity, transparency, lightweight character, and resilience to environmental conditions [12].

Furthermore, PET is applicable for packaging due to its impact resistance, enhanced biaxial drawing [13]. In addition, PET is suitable for the carbonated beverage bottles thanks to its high gas barrier property especially for carbon dioxide (CO_2) and oxygen (O_2). Disposable PET vessels are used in medical centers in wound drainage systems [14]. Moreover, PET is used for non-food packaging, such as cosmetics, toiletries, and household items. Most global PET packaging consumption contains carbonated soft drinks and water. [5,6], [11]. PET is also usable for manufacturing photographic film and magnetic tapes [15]. Additionally, PET is used in the automotive sector, electrical-electronic, medicine, and mechanical engineering thanks to its benefits and effortless processing methods and low cost [3], [11].

The diverse application of PET requires different molecular weights and intrinsic viscosities. Low carboxylic acid end group concentration (CEG) in PET enhances its thermal durability, therefore high molecular weight PET shows better chemically durability [16]. Table 1.2 illustrates PET applications in different areas based on intrinsic viscosity.

Table 1.2. IV Values of PET based on application areas [9].

Application Area	IV (dl/g)
Textile	0.40 - 0.70
Technical	0.72 - 0.98
Biaxially oriented film	0.60 - 0.70
Sheet grade for thermoforming	0.70 - 1.00
Water Bottle	0.70 - 0.78
Carbonated soft drink grade	0.78 - 0.85

1.4. Hydrophobicity and Hydrophilicity of PET

The tendency of the surface to repulse water is called hydrophobicity, whereas drawing water is referred to as its hydrophilicity. The interaction between polar substances, such as water and alcohols, and hydrophilic surfaces is strong. On the other hand, non-polar substances such as oil-based solvents exhibit an improved tendency to hydrophobic surfaces [17].

Like many polymers, PET is used across different industries thanks to its cost-effectiveness, preferred thermal, mechanical, and physical properties, as described earlier. The structure of PET lacks hydrogen bonding forming groups such as -OH or -NH_2 which leads to low surface energy, giving PET its hydrophobic nature . [18]. The hydrophobicity of PET provides extraordinary barrier properties against moisture and water vapor. Therefore, PET is a favorable polymer, especially for the packaging of beverages and foods, where it is essential to preserve the integrity of products and prolong the shelf life [3], [19].

However, the hydrophobic nature of PET fabric, predominantly used in synthetic fibers, leads to a deficiency in moisture absorption along with notable properties such as dimensional durability and resistance to wear. This deficiency causes comfortlessness and

extreme heat absorption, which is especially problematic in hot environments and limits its applications in sportswear and activewear. Therefore, enhancing the moisture permeability is critical to develop fabrics that wick sweat away and dry rapidly. Furthermore, failing to eliminate sweat adequately can cause bacterial growth and odor that threaten human health [20].

In addition, PET's low polarity and wettability limit its use in many applications, such as biomaterials, protective coatings, and membranes [21]. Also, PET's capability to print, dye, and adhere is weak. Hence, modifying the surface of PET is necessary to provide polarity for applications demanding hydrophilicity and adhesion [18].

1.4.1. Methods to Modify PET's Hydrophilicity

As mentioned before, the composition of polymer surfaces affects their wettability. The management of surface wettability has become the main focus of interest because of its value in diverse applications such as dyeing, printing, adhesion, absorption, and product comfort. Like many polymers, PET demonstrates low surface energy owing to its inherent structure, deficiency of hydrophilicity, and polar functional groups [18].

There is extensive research in the literature to alter the chemical and physical performance of the PET surface , especially for fabrics, and improve its wetting property without changing its intrinsic character [12]. Numerous chemical and physical methods exist to manufacture hydrophilic PET fabrics, such as graft copolymerization [22], copolymerization with hydrophilic monomers and polymers, and plasma treatment [23-25].

Grafting onto PET: Graft polymerization is mainly used for surface modification of PET due to its capacity for incorporating desired functional groups onto the surface [26]. For example, in a recent study, grafting of hydrophilic polyvinyl alcohol (PVA) onto PET was investigated. Although the results showed a successful wettability on grafted-PET fabrics, a decrease in their mechanical strength was observed [24]. Moreover, there have been other studies to enhance the hydrophilicity of PET fibers by grafting hydrophilic monomers which contain hydroxyl or amide group onto them [27]. However, because of the hydrophobic nature of PET, to obtain high grafting ratio is not easy [28].

Plasma Treatment: Plasma treatment is widely employed to change PET's surface while protecting its bulk characteristics [29]. Plasma treatment is conducted under low-pressure conditions to incorporate a stable plasma by introducing ranges of gaseous into the reaction chamber [30]. It is used to generate polar groups that contain oxygen on the PET surface [19]. The formation of polar functional groups or short graft chains in the medium and roughening of the surface enhances water absorption [12]. Nevertheless, after plasma treatment over time, the polymers revert to a hydrophobic state because the generated polar groups on the surface are not permanent. Therefore, hydrophilic properties on the polymer surface may diminish with prolonged storage [31]. Moreover, atmospheric pressure plasma which is formed in ambient air instead of a vacuum chamber, is investigated for its effect on the wettability of PET. This method can produce numerous high-density active species such as free radicals and ions that can disrupt covalent bonds within polymers [32,33]. However, there have been studies showing that atmospheric plasma treatment frequently leads to damage in polymer surfaces during the processing [32], [34].

Copolymerization with Hydrophilic Monomers and Polymers: The hydrophobicity of PET can be altered by incorporating hydrophilic monomers or polymer segments into its backbone [35]. According to a recent study, surface modification can be achieved by copolymerizing polyethylene glycol (PEG) with the PET monomers [18] which introduces a hydrophilic segment that facilitates the formation of hydrogen bonding with the water [36]. Another effective method to improve the hydrophilicity of PET is incorporating ionic groups such as sulfonated sodium salts into PET by copolymerization. Adding ionic groups is essential, especially in imparting cationic dyeability to PET fibers [37].

1.5. Sulfonated PET

Ion-containing polymers are used in numerous essential areas, such as water purification, drug delivery and conductive materials [38].

Incorporating a proportionally small number of ionic functional groups into the main structure shows a tendency to aggregate, which behaves as a different phase or thermolabile crosslink because of the low dielectric constants of the matrices. Hence, numerous properties

of both the bulk material and polymer solutions may be altered thanks to the modified chain polarity, elasticity, and ion-ion or ion-dipole interactions [39]. Therefore, adding ionic groups into the polymers enables customization of the structure that can affect the characteristics of the polymer, such as crystallization rate, toughness, melt viscosity, and solubility [40].

Studies show the hydrolytic durability of sodium sulfonate groups (SPET) incorporated PET co-polymers. According to these results, the hydrolytic degradation of SPET is higher than regular PET [41]. SPETs can demonstrate water-dispersible properties because of ionic functional groups in the polymer's structure [42]. SPETs become valuable because of their utility, especially in the textile area, which improves PET's dyeability with cationic dyes [43]. Cationic dyeable polyester (CDP) is a characteristic polyester fiber that undergoes modification during the polymerization. The modification is achieved by inserting sulfonated monomer to form an anionic medium that does not exist in regular PET fiber. The metal sulfonate group linked with the aromatic ring behaves as an ionomer with a rigid backbone chain. Also, recent research shows that the bonding of ionic functions in metal sulfonate polymers is robust, and aggregation of the sulfonate group can be observed in ionic polymers derived from PET [44].

2. AIM OF THE STUDY

In the broadest sense, the study aims to alter and tune the hydrophilicity of PET by using different amount of catalysts, monomers, and oligomers *via* melt polycondensation reaction. As catalysts antimony trioxide (Sb_2O_3), titanium tetraisopropoxide (TTIP) were used. Terephthalic acid (TPA), isophthalic acid (IPA), sulfonated monomer_1 (SM_1), sulfonated monomer_2 (SM_2) were employed as the diacid monomers and ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) were used as the diols. The main target was to increase the hydrophilicity of PET.

3. EXPERIMENTAL

3.1. Materials

Terephthalic acid (TPA), isophthalic acid (IPA), SM_1, SM_2, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), titanium tetraisopropoxide (TTIP), antimony trioxide (Sb_2O_3), and sodium acetate (NaOAc) were received from SASA Polyester A.Ş.

3.2. Instrumentation and Methods

The samples' characteristics were analyzed using a Thermo Fisher Scientific Nicolet 380 FTIR instrument. For the samples, 32 scans were performed with a resolution of 2.

For the proton (^1H) and carbon (^{13}C) NMR spectroscopies, a Brucker 400 MHz spectrometer was used, a mixture of deuterated chloroform ($CDCl_3$) and trifluoro acetic acid (*d*-TFA) at a ratio of 8/1 was used to dissolve the samples.

For GPC analysis, Wyatt Gel Permeation Chromatography was utilized; the column temperature was set to 40°C with 0.7 mL/min flow rate. Hexafluoroisopropanol (HFIP) was used as the mobile phase and was employed as well to dissolve the samples. All samples were filtered with 0.45 μm filter.

For thermal analysis, the Exstar SII differential scanning calorimetry (DSC) 7020 instrument was used with the methods shown in Table 3.1. Approximately 7.0 mg samples were heated in the first cycle to remove thermal history. The results of the second heating cycle were recorded.

Table 3.1. Method for DSC.

Initial T (^{0}C)	Final T (^{0}C)	Rate (^{0}C/min)	Hold (min)
-30	300	10	2
300	-30	10	3
-30	300	10	2

The contact angle of co-polymers was analyzed by the KSV CAM 101 instrument (Finland), which recorded images of water drops at room temperature. The polymer films were prepared by placing them in a silicon mold *via* hot pressing to measure the contact angle. Approximately two μL distilled water drops with a micro syringe were set on the surface of the films. The images of the water droplets on the surface, with ten different points, were captured for 5 seconds. The contact angles were measured three times to provide accuracy. The water contact angles of the co-polymers were calculated by taking mean values of the measurements.

The intrinsic viscosity (IV) measurements were analyzed by the miniPC-HX (Cannon Instrument) according to ASTM D4603 and ISO1628-5 standards.

3.3. Polymer Syntheses

The melt polycondensation reactions were carried out in a glass melt reactor (Figure 3.1). The temperature of the reactions was raised by ESM4450 48x48 1/16 DIN Universal Input PID Process Controller with Smart I/O Module System, and the transfer of heat to the glass reactor was done by silicon oil. Experiments were done under a nitrogen (N_2) atmosphere. Heidolph overhead stirrer set to 50 rpm was used. The polymerization of the reactions was monitored by the torque changes.

Figure 3.1. Glass melt polycondensation set-up.

3.3.1. Syntheses of PET and PET-*co*-Sulfonated Monomers

This study was conducted in collaboration with SASA Polyester A.Ş. Therefore, the name of the added sulfonated monomer has been kept confidential and is referred to as sulfonated monomer_1 and sulfonated monomer_2. Moreover, the added molar ratios are shown as low, medium, and high and are referred as L-SM_1, M-SM_1, and H-SM_1.

The co-polyesters were synthesized with different ratio of sulfonated monomers. The composition of the polyesters and reaction conditions are shown in Table 3.2. The samples were labeled according to the amount of SM_1 with respect to the total acids. For example, L-PET-co-SM_1 indicates low mole SM_1 in copolymer, M- PET-co-SM_1 indicates medium mole SM_1 in copolymer, and H- PET-co-SM_1 indicates high mole SM_1 in copolymer with respect to the total mole of TPA and SM_1.

Synthesis of PET (blank): 10.8 g. TPA, 0.106 g NaOAc, 8 g. EG, and 3.13 µL TTIP in 184 µL EG were mixed inside a dry glass reactor, and the reaction was under a nitrogen atmosphere. The speed of the stirrer was set to 50 rpm. The reaction started at 170°C and was kept there for 1 hour. The temperature of the reaction was gradually raised from 170°C to 275°C in 9 hours. After 9 hours, the vacuum was gradually decreased from 1000 mbar to

1 mbar in 1 hour. Then, the vacuum continued for 1 hour at 1 mbar, and the reaction was maintained at 1 mbar for 1 hour. Throughout the reaction, torque was noted. Then the reaction was terminated. The glass reactor was kept on Teflon paper for 20 minutes, and the polyester was removed.

Synthesis of PET-co-L-SM_1: TPA, L-SM_1, 0.1 g NaOAc, 7.44 g. EG, and 3.6 µL TTIP in 184 µL EG were placed into a glass reactor, and the reaction was under a nitrogen atmosphere. The speed of the stirrer was set to 50 rpm. The reaction started at 170°C and was kept for 1 hour. The temperature of the reaction was gradually elevated from 170°C to 275°C in 9 hours. After 9 hours, the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour. Then, the vacuum continued for 1 hour at 1 mbar, and the reaction was maintained at 1 mbar for 1 hour. Throughout the reaction, torque was noted. Then the reaction was terminated. The glass reactor was kept on Teflon paper for 20 minutes, and the polyester was removed.

Synthesis of PET-co-M-SM_1: TPA, M-Sulfonated Monomer, 0.102 g. NaOAc, 7.44 g. EG, and 3.6 µL TTIP in 184 µL EG were placed into a glass reactor. The reaction was under a nitrogen atmosphere. The speed of the stirrer was set to 50 rpm. The reaction started at 170°C and was kept for 1 hour. The temperature of the reaction was gradually increased from 170°C to 275°C in 9 hours. After 9 hours, the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour. Then, the vacuum continued for 1 hour at 1 mbar, and the reaction was maintained at 1 mbar for 1 hour. Throughout the reaction, torque was noted. Then the reaction was terminated. The glass reactor was kept on Teflon paper for 20 minutes, and the polyester was removed.

Synthesis of PET-co-H-SM_1: TPA, H-SM_1, 0.103 g. NaOAc, 7.44 g. EG, and 3.6 µL TTIP in 184 µL EG were mixed into a glass reactor. The reaction was under a nitrogen atmosphere. The speed of the stirrer was set to 50 rpm. The reaction started at 170°C and was kept for 1 hour. The temperature of the reaction was gradually increased from 170°C to 275°C in 9 hours. After 9 hours, the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour. Then, the vacuum continued for 1 hour at 1 mbar, and the reaction was maintained at 1 mbar for 1 hour. Throughout the reaction, torque was noted. Then the

reaction was terminated. The glass reactor was kept on Teflon paper for 20 minutes, and the polyester was removed.

Table 3.2. Reaction conditions of PET-*co*-sulfonated monomers.

Entry No	**Polyester**	**TPA mol%**	**SM_1 mol%**	**EG mol%**	**Catalyst mol%**	**NaOAc mol%**
1	PET (blank)	32.7	0	66.5	0.01 TTIP	0.79
2	PET-*co*-L-SM_1	X mole	Low mole	66.4	0.01 TTIP	0.79
3	PET-*co*-M-SM_1	X mole	Medium mole	65	0.01 TTIP	0.79
4	PET-*co*-H-SM_1	X mole	High mole	64.3	0.01 TTIP	0.79

Reaction Conditions:

PET: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 2hr. 1000 mbar → 1 mbar, 50 rpm, 1 hr.

PET-*co*-L-SM_1: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.

PET-*co*-M-SM_1: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.

PET-*co*-H-SM_1: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.

3.3.2. Syntheses of S-PETI with Different Amount of Catalyst

Sulfonated copolyesters were synthesized by a one-pot method with the same mole ratio of TPA, IPA, H-SM_1, but different mole ratios of the catalyst. The composition of the polyesters and reaction conditions are shown in Table 3.3. The samples were labeled as S-

PETI_0.005, S-PETI_0.01, and S-PETI_0.02, which imply copolymerization of H-SM_1, TPA, EG, and IPA with dissimilar mol ratios of catalyst.

Table 3.3. Reaction conditions of S-PETI with different amount of catalyst.

Entry No	Polyester	TPA mol%	IPA mol%	H-SM_1mol%	EG mol%	Catalyst mol%	NaOAc mol%
1	S-PETI_0.005	X mole	Y mole	High mole	67.5	0.005 TTIP	0.795
2	S-PETI_0.01	X mole	Y mole	High mole	67.5	0.01 TTIP	0.79
3	S-PETI_0.02	X mole	Y mole	High mole	67.5	0.02 TTIP	0.79
Reaction Conditions: S-PETI_0.005: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr. S-PETI_0.01: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr. S-PETI_0.02: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.							

3.3.3. Syntheses of Sulfonated Copolyesters with Different Monomers

Firstly, the copolyesters were synthesized by using different acids. The composition of the polyesters and reaction conditions of them were shown in Table 3.4. PETI indicates copolymerization of TPA, IPA, and EG. Also, the samples labeled as S-PETI- 4, implying the copolymerization of TPA, IPA, SM_2, and EG, whereas S-PETI is the copolymerization of TPA, IPA, SM_1, and EG.

Synthesis of PETI (blank): TPA, IPA, 0.083 g NaOAc, 6.1 g. EG, and 0.4 µL TTIP in 184 µL EG were mixed inside a dry glass reactor, and the reaction was under a nitrogen atmosphere. The speed of the stirrer was set to 50 rpm. The reaction started at 170°C and was kept for 1 hour. The temperature of the reaction was gradually increased from 170°C to 275°C in 9 hours. After 9 hours, atmospheric pressure was stopped, and the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour, and the reaction was maintained at 1 mbar for 1 hour. Then the reaction was terminated, and the polymer was removed by the discharge valve.

Synthesis of PETI-co-SM_2: TPA, IPA, H-SM_2, 0.104 g NaOAc, 7.9 g. EG, and 3.2 µL TTIP in 184 µL EG were mixed inside a dry glass reactor, and the reaction was under a nitrogen atmosphere. The speed of the stirrer was set to 50 rpm. The reaction started at 170°C and was kept for 1 hour. The temperature of the reaction was gradually increased from 170°C to 275°C in 9 hours. After 9 hours, atmospheric pressure was stopped, and the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour, and the reaction was maintained at 1 mbar for 1 hour. Then the reaction was terminated, and the polymer was removed by the discharge valve.

Synthesis of PETI-co-SM_1: TPA, IPA, H-SM_1, 0.105 g NaOAc, 7.9 g. EG, and 3.2 µL TTIP in 184 µL EG were mixed inside a dry glass reactor, and the reaction was under a nitrogen atmosphere. The following procedure was the same as above.

Table 3.4. Reaction conditions of S-PETI with different acids.

Entry No	Polyester	TPA mol%	IPA mol%	SM_1mol%	SM_2 mol%	EG mol%	DEG mol%	TEG mol%	Catalyst mol%	NaOAc mol%
1	PETI	X mole	Y mole	0	0	65.7	0	0	0.005 TTIP	0.79
2	PETI-*co*-SM_2	X mole	Y mole	0	High mole	67.1	0	0	0.005 TTIP	0.79
3	PETI-*co*-SM_1	X mole	Y mole	High mole	0	67.5	0	0	0.005 TTIP	0.79

Reaction Conditions:

PETI: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.

PETI-*co*-SM_2: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.

PETI-*co*-SM_1: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.

Secondly, the co-polyesters were synthesized by using different diols. The composition of the polyesters and reaction conditions of them were shown in Table 3.5. The samples labeled as S-PETDI indicated the copolymerization of TPA, IPA, SM_1, EG, and DEG, whereas S-PETTI indicated the copolymerization of TPA, IPA, SM_1, EG and TEG.

The synthesis of S-PETDI and S-PETTI, except for adding TPA, IPA, SM_1, and EG, differed by adding DEG to the former and TEG to the latter. The procedure was the same.

Table 3.5. Reaction conditions of S-PETI with different diols.

Entry No	Polyester	TPA mol%	IPA mol%	SM_1mol%	EG mol%	DEG mol%	TEG mol%	Catalyst mol%	NaOAc mol%
1	PETI	X mole	Y mole	0	65.7	0	0	0.005 TTIP	0.795
2	S-PETI	X mole	Y mole	High mole	67.5	0	0	0.005 TTIP	0.795
3	S-PETDI	X mole	Y mole	High mole	63	6.6	0	0.005 TTIP	0.795
4	S-PETTI	X mole	Y mole	High mole	63	0	6.6	0.005 TTIP	0.795

Reaction Conditions:

PETI: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 1 hr.

S-PETI: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 1 hr.

S-PETDI: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 1 hr.

S-PETTI: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 1 hr.

3.3.4. Large Scale Syntheses

Sulfonated copolyesters were synthesized by a one-pot method with the same mole ratio of monomers, but different catalysts, which were TTIP and Sb_2O_3 in a large scale. The composition of the polyesters and reaction conditions are shown in Table 3.6. The samples were labeled as S-PETI_TTIP, and S-PETI_Sb_2O_3, which imply copolymerization of SM_1, TPA, EG, and IPA with similar mol ratios, but different catalysts.

Synthesis of S-PETI_TTIP in Large Scale: S-PETI was synthesized in a 5L stainless steel reactor (Juchheim GmbH, Bernkastel Kues, Germany) in SASA Polyester A.Ş. TPA, IPA, H-SM_1, 936.1 g EG NaOAc, and 0. 69 g. TTIP were mixed inside the 5L reactor, and the reaction was under a nitrogen atmosphere. The reaction started at 170°C and was kept there for 1 hour. The temperature of the reaction was gradually raised from 170°C to 275°C in 9 hours. After 9 hours, atmospheric pressure was stopped, and the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour, and the reaction was maintained at 1 mbar for 1 hour. Then the reaction was terminated, and the polymer was removed by the discharge valve.

Synthesis of S-PETI_Sb_2O_3 in Large Scale: S-PETI was synthesized in a 5L stainless steel reactor (Juchheim GmbH, Bernkastel Kues, Germany) in SASA Polyester A.Ş. TPA, IPA, H-SM_1, 936.1 g EG NaOAc, and 0. 69 g. Sb_2O_3 were mixed inside the 5L reactor, and the reaction was under a nitrogen atmosphere. The reaction started at 170°C and was kept there for 1 hour. The temperature of the reaction was gradually raised from 170°C to 275°C in 9 hours. After 9 hours, atmospheric pressure was stopped, and the vacuum was gradually decreased from 1000 mbar to 1 mbar in 1 hour, and the reaction was maintained at 1 mbar for 1 hour. Then the reaction was terminated, and the polymer was removed by the discharge valve.

Table 3.6. Reaction conditions of S-PETI with different catalysts in large scale.

Entry No	**Polyester**	**TPA mol%**	**IPA mol%**	**SM_1mol%**	**EG mol%**	**Catalyst mol%**	**NaOAc mol%**
1	*S-PETI_TTIP*	X mole	Y mole	High mole	67.3	0.01 TTIP	0.79
2	*S-PETI_Sb_2O_3*	X mole	Y mole	High mole	67.3	0.01 Sb_2O_3	0.79
Reaction Conditions: *S-PETI_TTIP*: 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr. *S-PETI_Sb_2O_3:* 170°C 1 hr.: 180°C 1.5 hr.: 200°C 1.5 hr.: 215°C 1hr.: 240°C 3hr.: 275°C 1hr. 1000 mbar → 1 mbar, 50 rpm, 2 hr.							

4. RESULTS AND DISCUSSION

This study mainly aims to investigate the effect of incorporating SM_1 and SM_2 and various glycols on the hydrophilicity of PET.

In the first section, the effect of SM_1 on PET was investigated. The incorporation of SM_1 was studied using FTIR and NMR. Then, the contact angle, DSC, and GPC analyses PET-*co*-Sulfonated Monomers were compared where the mole percent of SM_1 was altered.

In the second section, isophthalic acid (IPA) was added as a third monomer into PET, labeled as PETI. The properties and contact angle of PETI copolymers were compared by adding different monomers, such as H-SM_1, H-SM_2, DEG, and TEG.

In the third section, the copolymers were synthesized by incorporating SM_1 into the PETI copolymers, labeled as S-PETI. The effect of the catalyst amount on the contact angle in the polymerization was investigated.

Finally, two S-PETI copolymers were synthesized in large-scale production in a 5L stainless steel reactor. S-PETI copolymers were conducted using a Sb_2O_3 catalyst and a TTIP catalyst. Their wettability and properties were investigated.

4.1. The Effect of SM_1 on PET

First, the incorporation of SM_1 with other monomers was investigated. All monomers, TPA, SM_1, and EG, were added at the beginning of the reaction. The samples were labeled according to the mole ratios of SM_1 in total diacids (i.e. PET-co-L-SM_1 has low mol% SM_1, PET-co-M-SM_1 medium mol%, and PET-co-H-SM_1 high mol% w.r.t total acids).

The incorporation of the SM_1 into the backbone was investigated by FTIR and NMR. In the FTIR, the PET ester groups gave absorption peaks around 1712 cm^{-1}. The SO_3^- group has a distinctive absorption peak at 626 cm^{-1} in the fingerprint region of the FTIR which became apparent after the incorporation of SM_1 into polymers (Figure 4.1). A broadening of the ester peak was observed when more SM_1 was incorporated. These results showed that the incorporation of sulfonate groups into the synthesized polymer chains was successful.

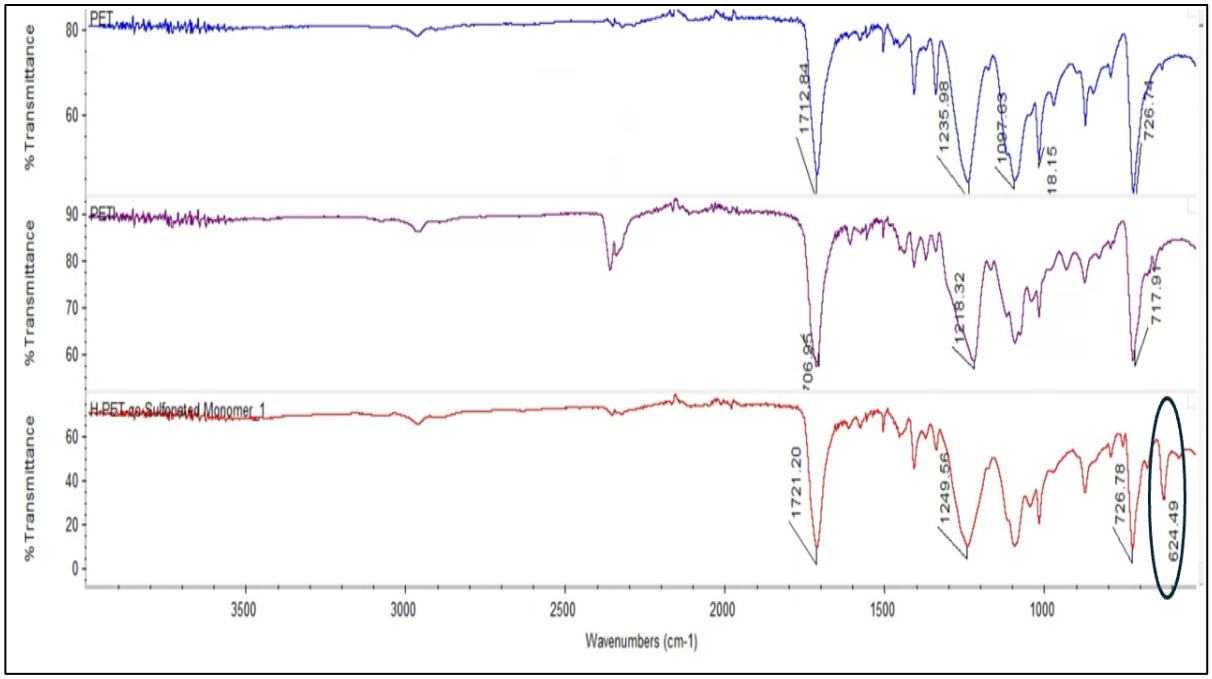

Figure 4.1. The FTIR spectra comparison between SM_1-based copolymer and neat copolymers.

Then the chemical structures of PET and PET-*co*-Sulfonated Monomers were examined by proton ^{1}H-NMR in Table 4.1., and Figure 4.2. (PET-*co*-H-SM_1). The peaks at around 8.7-8.8 ppm were attributed to aromatic hydrogens of the sulfonated monomer. It can be noted that the NMR calculated mole ratio of SM_1 in PET co-polymers was close to the molar feed ratios, indicating successful incorporation of sulfonated monomer. Thus, PET and PET-*co*-SM_1 was synthesized efficiently.

In addition to the expected peaks, the peaks at 4.1 and 4.6 ppm indicated the *in situ* formation of DEG, a well-known process in PET manufacturing [42].

Table 4.1. The compositions and found molar ratios in ^{1}H-NMR results of PET and PET-*co*-sulfonated monomers.

SAMPLE	Composition	
	Feed Molar Ratio (EG/DEG)	Found Molar Ratio[a] (EG/DEG)
PET	100/0	95/5
PET-*co*-L-SM_1	100/0	91/9
PET-*co*-M-SM_1	100/0	86/14
PET-*co*-H-SM_1	100/0	86/14
[a] Found molar ratio of DEG in total diol		

Table 4.2. Assignment of peaks.

δ(ppm)	Assignment
8.86	a (Sulfonated Monomer)
8.75	b (Sulfonated Monomer)
8.12	c (TPA)
4.78	d (EG)
4.62	e (DEG)
4.1	f (DEG)

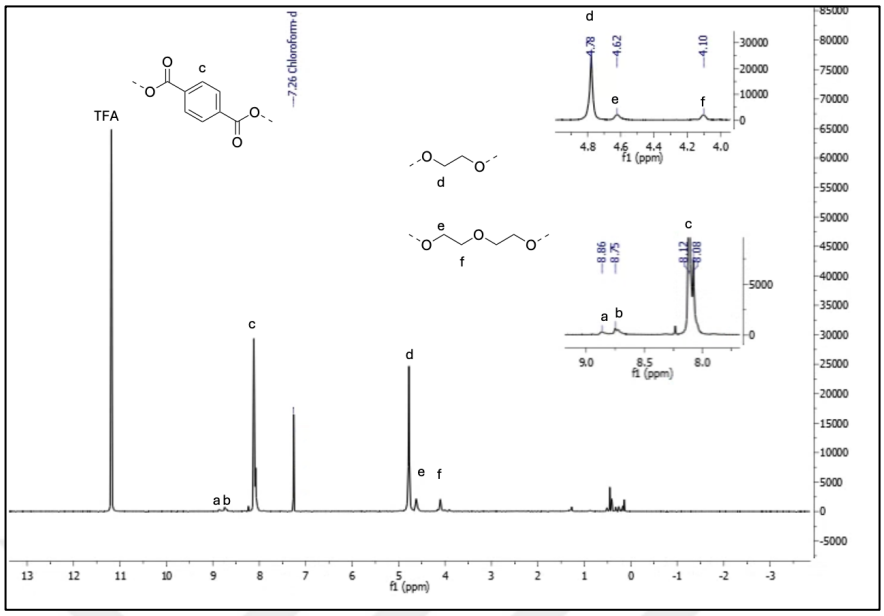

Figure 4.2. [1]H-NMR spectra of PET-*co*-H-SM_1.

The thermal properties of PET and PET-*co*-Sulfonated Monomers were analyzed by DSC. The results of are presented in Table 4.3. The results showed that as the mole percent of SM_1 increased from low mol% to high mol% in PET, T_m and T_c values decreased. Also, it should be noted that there were no T_m and T_c for PET-*co*-H-SM_1 (high mol% SM_1 with respect to diacids), possibly due to the intense ion group concentration which reduced the crystallization rate. No significant changes were observed in T_g with the increased SM_1 content.

Table 4.3. DSC results of PET and PET-co-sulfonated monomers.

SAMPLE	T_g (°C)	T_m (°C)	T_c (°C)	PDI	Mn
PET	76	253	219	-	-
PET-*co*-L-SM_1	72	251	201	2.9	6121
PET-*Co*-M-SM_1	70	223	161	3.2	5722
PET-*co*-H-SM_1	73	-	-	2.59	8021

Molecular weights were measured by GPC in HFIP as eluent. The results are shown in Table 4.4. However it should be noted that according to the literature, the GPC data for

ion-containing systems may not be reliable because of the polyelectrolyte effect that causes higher hydrodynamic volume within the polymer [45].

Table 4.4. GPC results of PET-*co*-sulfonated monomers.

SAMPLE	PDI	Mn	Tg (°C)
PET-*co*-L-SM_1	2.9	6121	72
PET-*co*-M-SM_1	3.2	5722	70
PET-*co*-H-SM_1	2.59	8021	73

The hydrophilicity of the PET and PET-*co*-SM_1 was examined by water contact angle measurement at various the SM_1 concentration. In theory, a hydrophilic surface must show a low contact angle, smaller than 90 degrees, whereas a hydrophobic surface a high contact angle, larger than 90 degrees [46]. Indeed, accordingly, as the amount of SM_1 increased, the contact angle of samples decreased from 91º to 65º, as shown in Figure 4.3. The results showed that the introduction of the SO_3^- group to the backbone increased the hydrophilicity of the PET. This improvement in wettability can potentially expand the application areas of PET, especially in the textile industry.

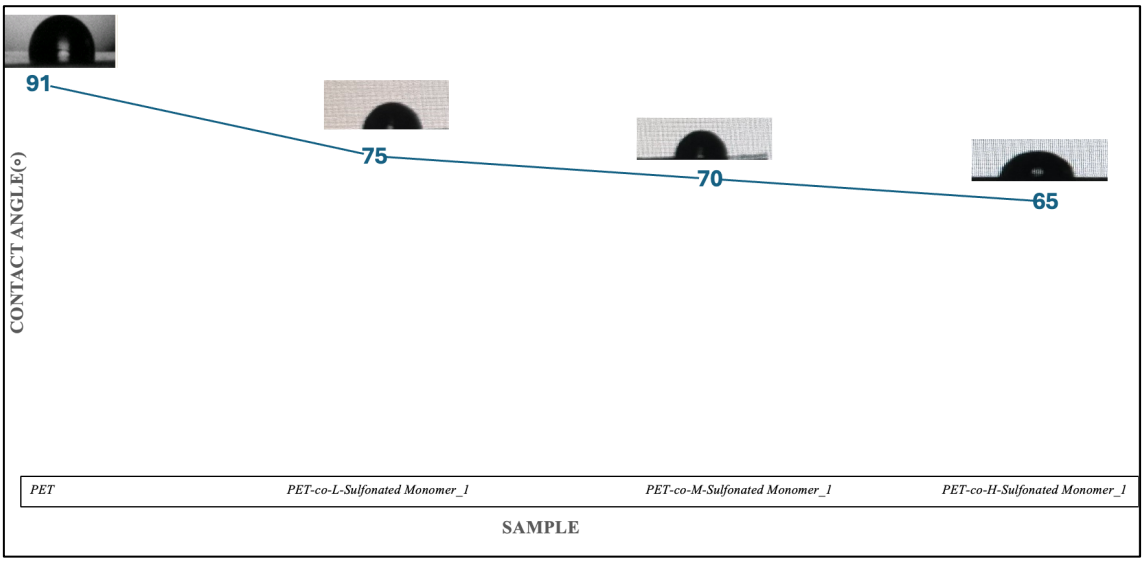

Figure 4.3. Water contact angles of PET and PET-co-SM_1s (From left to right the SM_1 content is increasing from none to high mol%).

4.2. The Effect of Different Monomers on Sulfonated PET-Copolymers

In this section, first isophthalic acid (IPA), as an additional diacid monomer, was added to PET and these copolymers were named as PETI. Then, H-SM_1 was incorporated to PETI and the resulting copolymers were named as S-PETI (S- for sulfonated). To change in hydrophilicity of S-PETIs further, diethylene glycol (DEG-the correspond PET was referred as S-PEDTI), and triethylene glycol (TEG, S-PETTI) were added.

Finally, H-SM_2 as the sulfonated monomer, instead of H-SM_1, PETI-*co*-H-SM_2 was investigated. Its properties were compared with S-PETI. However, in this section to make an understandable comparison, in the nomenclature, PETI-*co*-H-SM_1 instead of S-PETI was used. The results are shown in this order. In all the polymerizations, all monomers were added to the polymerization at the beginning of the polymerization process.

In the first part of this section, the chemical structures of the resulting copolymers S-PETIs with different diols were examined by ^{1}H-NMR. The peak assignments are shown in Table 4.6, and as an example, the ^{1}H -NMR spectra of S-PETTI, with TEG, is shown in Figure 4.4.

Table 4.5. Assignment of peaks for S-PETTI.

δ(ppm)	Assignment
8.86	a (Sulfonated Monomer)
8.72-8.68	b (Sulfonated Monomer); c (IPA)
8.26	d (IPA)
8.12	f (TPA)
7.57	e (IPA)
4.78	g(EG)
4.63-4.58	h (DEG); j (TEG)
4.12	i (DEG)
4.02	k (TEG)
3.92	l (TEG)

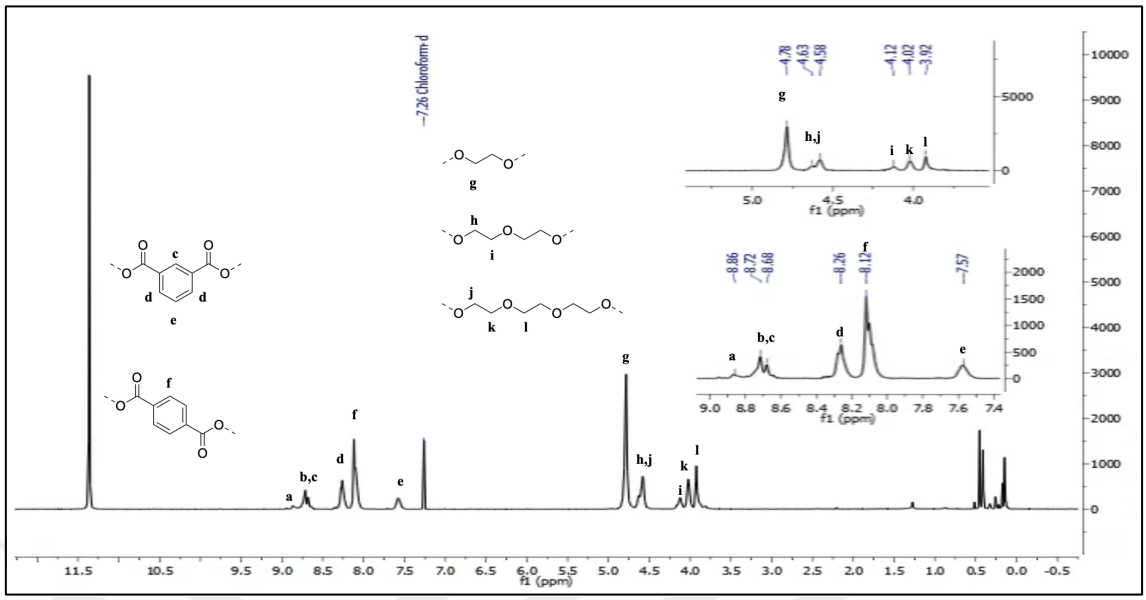

Figure 4.4. ^{1}H-NMR spectra of S-PETTI.

The compositions and found molar ratios of the resulting copolymers with different diols are shown in Table 4.5. It can be noted that the feed molar ratios of the new diols and IPA were close to the incorporated molar ratios. Thus, the diols and the acids were successfully incorporated into the PET backbone.

Table 4.6. The compositions and found molar ratios in ^{1}H-NMR of copolyesters with different diols.

SAMPLE	Composition	
	Feed Molar Ratio (EG/DEG [a] /TEG [b])	Found Molar Ratio (EG/DEG/TEG)
PETI	100/0/0	91/9/0
S-PETI	100/0/0	89/11/0
S-PEDTI	91/9/0	76/24/0
S-PETTI	91/0/9	71.1/9.5/19.4
[a] Molar ratio of DEG in total diols [b] Molar ratio of TEG in total diols		

The thermal properties of the resulting copolymers with different diols were analyzed by DSC, and their molecular weights were determined by GPC. The results of the copolymers are illustrated in Table 4.8.

Table 4.7. DSC and GPC results of copolymers with different diols.

SAMPLE	Mn (g/mol)	PDI	Tg (°C)
PETI	15390	2.5	61
S-PETI**	6306	2.9	67
S-PEDTI**	6265	2.8	57
S-PETTI**	19680	2	65
**Molar Ratio of DEG and TEG in total diols is 9.			

PETI which was synthesized without sulfonated monomers, served as a reference and the Mn of the obtained polymer was 15390 g/mol, and the T_g value was 61°C. When H-SM_1 was added, the polymer obtained under similar conditions had lower Mn, but higher T_g. It was noteworthy that the ionic groups in H-SM_1 most likely reduced the chain mobility, thereby forming restricted motion regions and thus higher T_g values.

When DEG was introduced into the S-PETI, the Mn value was almost the same as that of S-PETI, but the T_g value decreased. The decrease in the T_g could be attributed to the increased chain mobility and increased polarity. The latter may prevent the ionic groups from clustering where the addition of the high dielectric constant monomer into the polymer backbone, might increase the distance of ions from the rigid segments [47]. Dispersion of such ions may blocked the formation of multiplets, causing a less pronounced T_g increase [48].

The addition of TEG to S-PETI increased the Mn values obtained, which could be explained by the fact that TEG enhanced chain mobility allowing the polymer to go to higher molecular weights under the melt polymerization set-up.

Moreover, the hydrophilicity of the resulting S-PETIs copolymers was investigated by water contact angle measurements. The results show that as the sulfonated monomer, DEG and TEG are added to the polymer backbone the hydrophilicity is increased

significantly (Figure 4.5). As expected, the best result is obtained by adding the TEG which is a softer monomer. It should be noted that the latter, when added in same molar fraction, give rise to higher weight fraction of glycolic repeat units when compared to DEG.

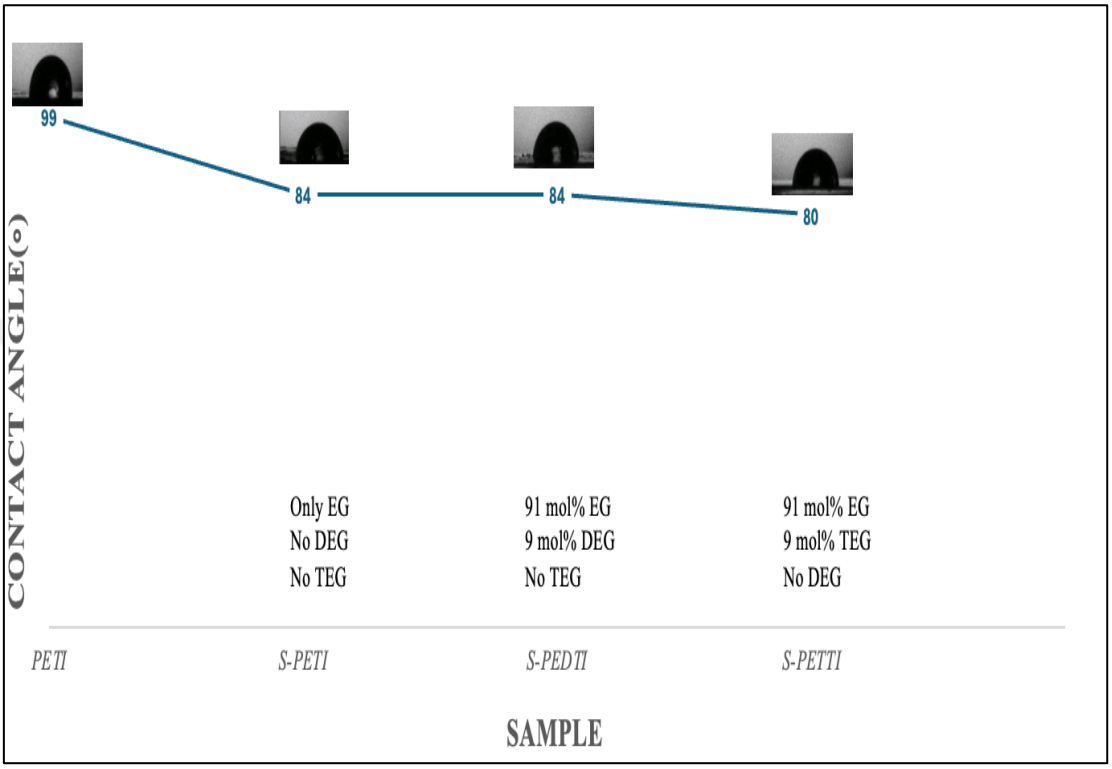

Figure 4.5. Water contact angle of PETI with different diols.

In the second part of this section, a comparison between SM_1 and SM_2 in PETI copolymers will be done. Firstly, the chemical analyses of PETI-co-SM_1 and PETI-co-SM_2 were examined by proton (^{1}H) -NMR spectroscopy. Their compositions and found molar ratios in ^{1}H-NMR are shown in Table 4.7. It can be noted that the incorporated molar ratios of both sulfonated monomers were close to their feed molar ratios. Thus, both monomers seem to be compatible with PET polymerization process. No significant difference was found between the two sulfonated monomers.

Table 4.8. The compositions and found molar ratios in ^{1}H-NMR of PETI-co-H-SM_1 and PETI-co-H-SM_2

SAMPLE	Composition	
	Feed Molar Ratio(EG/DEG)	Found Molar Ratio (EG/DEG[a])
PETI	100/0	89/11
PETI-*co*-H-SM_1 [a]	100/0	87/13
PETI-*co*-H-SM_2 [b]	100/0	88/12
[a] Found molar ratio of DEG in total diols		

The thermal properties of the PETI-co-SM_1 and PETI-co-SM_2 were analyzed by DSC, and their molecular weights were determined by GPC. The results are shown in Table 4.9.

Table 4.9. DSC and GPC results of PETI-co-H-SM_1 and PETI-co-H-SM_2.

SAMPLE	Mn (g/mol)	PDI	Tg (°C)
PETI	15390	2.5	61
PETI-*co*-H-SM_1*	6306	2.9	67
PETI-*co*-H-SM_2**	12770	1.82	66
* Molar Ratio of H-SM_1 in total diacids. ** Molar Ratio of H-SM_2 in total diacids.			

As seen from Table 4.9. the Mn value of PETI-co-H-SM_1 is lower than PETI. Although this might indicate a difference in the condensation reaction rate between the H-SM_1 and H-SM_2, the results are too preliminary to come to such conclusion.

Moreover, the hydrophilicity of PETI-co-H-SM_1 and PETI-co-H-SM_2 was studied by water contact angle measurement. The addition of high mol% SM_2 (concerning diacids) into the co-polymer although showed a slightly more hydrophilicity than the addition of high mol% SM_1 from the contact angle measurement (Figure 4.6), the results show that both monomers give rise more or less similar hydrophilicities.

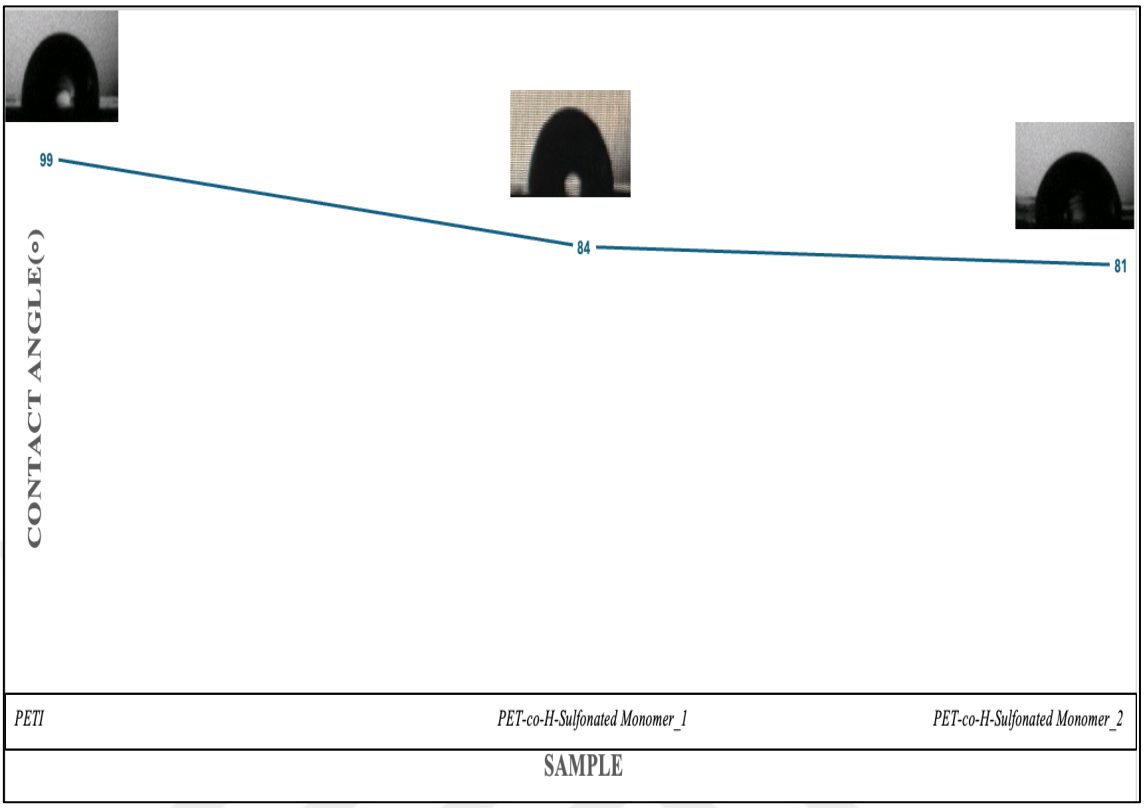

Figure 4.6. Water contact angle of PETI with SM_1 and SM_2.

4.3. The Effect of Amount of Catalyst on the Hydrophilicity of Sulfonated Copolymers

In this part, the effect of increasing amount of the catalyst on S-PETI wettability and properties was investigated. All sulfonated copolyesters were synthesized by a one-pot method with the X mol% TPA, Y mol% IPA, high mol% H-SM_1, but different mole ratios of the catalyst. The samples were labeled as S-PETI_0.005, S-PETI_0.01, and S-PETI_0.02 where the last numbers refer to mol% catalyst.

The chemical structures of S-PETIs with different amounts of catalyst were examined by proton (^{1}H) -NMR spectroscopy, and peak assignments are demonstrated in Table 4.10., and as an example, the ^{1}H -NMR result of S-PETI_0.01, with 0.01 mol% catalyst, is shown in Figure 4.7.

Table 4.10. Peak assignments of S-PETIs.

δ(ppm)	Assignment
8.86	a (Sulfonated Monomer)
8.72-8.68	b (Sulfonated Monomer); c (IPA)
8.26	d (IPA)
8.12	f (TPA)
7.57	e (IPA)
4.78	g(EG)
4.63	h (DEG)
4.12	i (DEG)

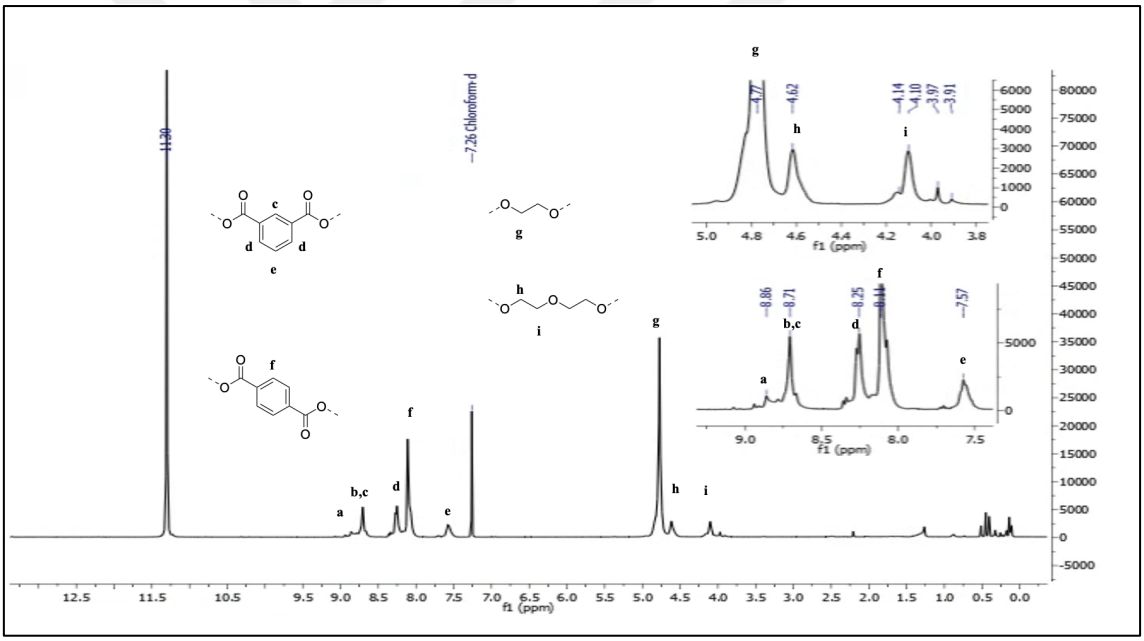

Figure 4.7. ^{1}H-NMR spectra of S-PETI_0.01.

The compositions and found molar ratios of the resulting copolymers S-PETIs with different amount of catalyst are shown in Table 4.11. It should be said that the feed molar ratio of synthesized S-PETIs was close to the incorporated molar ratio. Thus, there are no significant effect of the amount of the catalyst on incorporation. The DEG content seem also unaffected by the amount of the catalyst in these catalyst feed ratios. It is important to state that usually higher amounts of catalyst, especially acid catalyst, give rise to higher amount of DEG formation.

Table 4.11. The compositions and found molar ratios in ^{1}H-NMR results of S-PETI with different amount of catalyst.

SAMPLE		Composition	
	Amount of Catalyst (mol%)	Feed Molar Ratio (EG/DEG)	Found Molar Ratio[a] (EG/DEG)
S-PETI_0.005	0.005	100/0	89/11
S-PETI_0.01	0.01	100/0	87/13
S-PETI_0.02	0.02	100/0	88/12
[a] Found molar ratio of DEG in total diols			

As seen from Table 4.12., although higher Mn values of S-PETI copolymers were observed as the amount of the catalyst increased, the T_g values increased only slightly. This may be attributed to the T_g value reaching a particular threshold. According to Flory-Fox theory, as the Mn value of a polymer increases, the T_g value increases as the Mn increases up to a certain point, after which T_g is plateaued [49].

Table 4.12. GPC and DSC results of S-PETI with different amount of catalyst.

SAMPLE	Mn (g/mol)	PDI	Tg (°C)
S-PETI_0.005	6306	2.5	61
S-PETI_0.01	19080	1.32	67
S-PETI_0.02	52510	1.82	65

The hydrophilicity of the S-PETIs with different amounts of catalyst were examined by water contact angle measurement, as seen in Figure 4.8. The results showed that the S-PETI_0.02 exhibited a slightly more hydrophobicity. Although this may come from the lower end group concentration of the latter, the results are too preliminary to conclude.

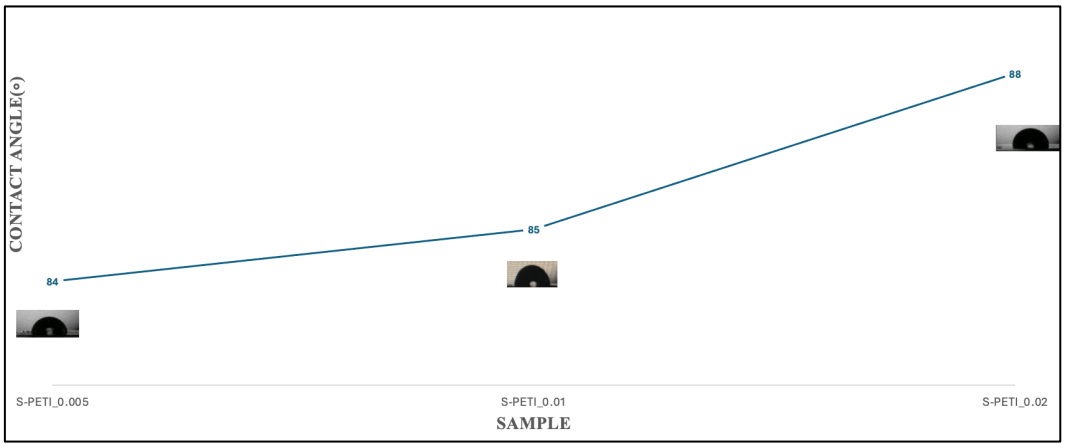

Figure 4.8. Water contact angle of S-PETIs with different amount of catalyst.

4.4. The Large Scale Results

The co-polymers synthesized for S-PETI samples in the laboratory were scaled up for large-scale production in a 5L stainless steel reactor. One of the S-PETI co-polymers was conducted by using an Sb_2O_3 catalyst, and the other was synthesized by a TTIP catalyst. They were labeled as S-PETI_Sb_2O_3 and S-PETI_TTIP.

The ^{1}H-NMR, IV, and DSC results are shown in the Table 4.13. From the incorporation part in Table 4.13., the molar feed ratios of the monomers with both Sb_2O_3 catalyst and TTIP catalyst were close to the incorporated molar ratios.

Table 4.13. Results of IV, DSC and the compositions and found molar ratios in ^{1}H-NMR.

SAMPLE	Composition		IV (dL/g)	Tg (°C)
	Feed Molar Ratio (EG/DEG)	Found Molar Ratio (EG/DEG [a])		
S-PETI_TTIP	100/0	86/14	0.31	67
S-PETI_Sb_2O_3	100/0	91/9	0.24	64
[a] Found molar ratio of DEG in total diol.				

It was observed that the syntheses of co-polymers with the two different catalysts on a large scale, titanium-based polyester, showed higher IV and Tg values than antimony-

based polyester. Furthermore, the contact angle of the copolymers showed no significant change.

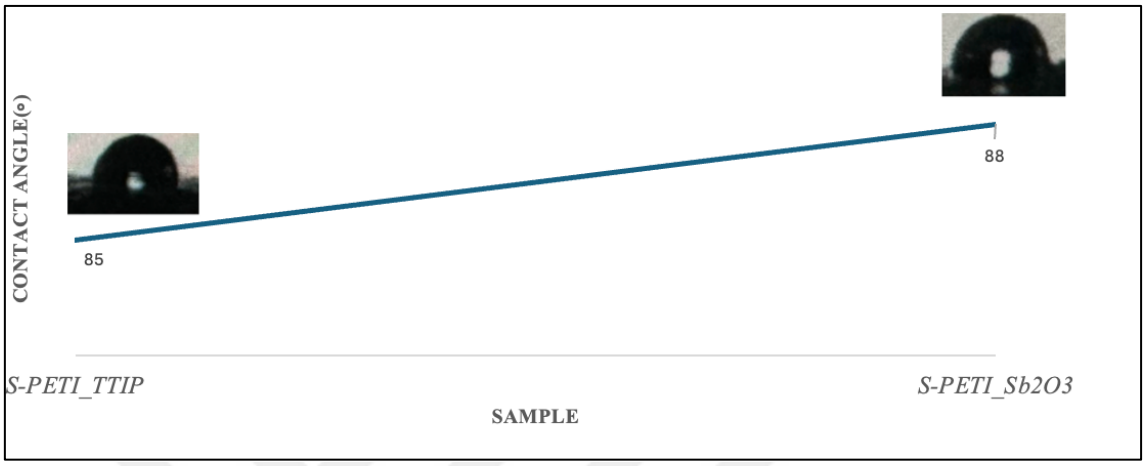

Figure 4.9. The contact angle results of polyester synthesized on large scale.

5. CONCLUSION

In this study, firstly, the hydrophilicity of PET was altered by adding SM_1 at changing amounts. The contact angles of the PETs decreased from 91º to 65º, which indicated a more hydrophilic character. However, as the mole percent of SM_1 increased in PET-co-SM_1 copolymers, the crystallinity of PET decreased.

Secondly, PETI copolymers were synthesized by incorporating IPA into the TPA and EG. Then, the effect of adding different monomers, such as SM_1, SM_2, DEG, and TEG, on the PET surface was studied. Once the SM_1was incorporated into the chain, the contact angle again decreased. Then, by adding soft block segments like TEG, the contact angle was decreased further.

Thirdly, the hydrophilicity of the S-PETIs with different amounts of catalyst was examined by water contact angle measurement. The experiments to compare the effect of the catalyst amount on surface wettability need to be studied further.

Finally, the contact angle of the copolymers synthesized with TTIP and Sb_2O_3 catalysts showed no significant change.

6. FUTURE WORK

As a future work, the hydrophilicity tests for the synthesized sulfonated polymers need to be expanded. In addition, the difference of a repeating unit in equal weight percent of DEG within a polymer need to be compared to that of an equal weight percentage of TEG to understand the effect on surface hydrophilicity.

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APPENDIX A: SPECTROSCOPY DATA

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

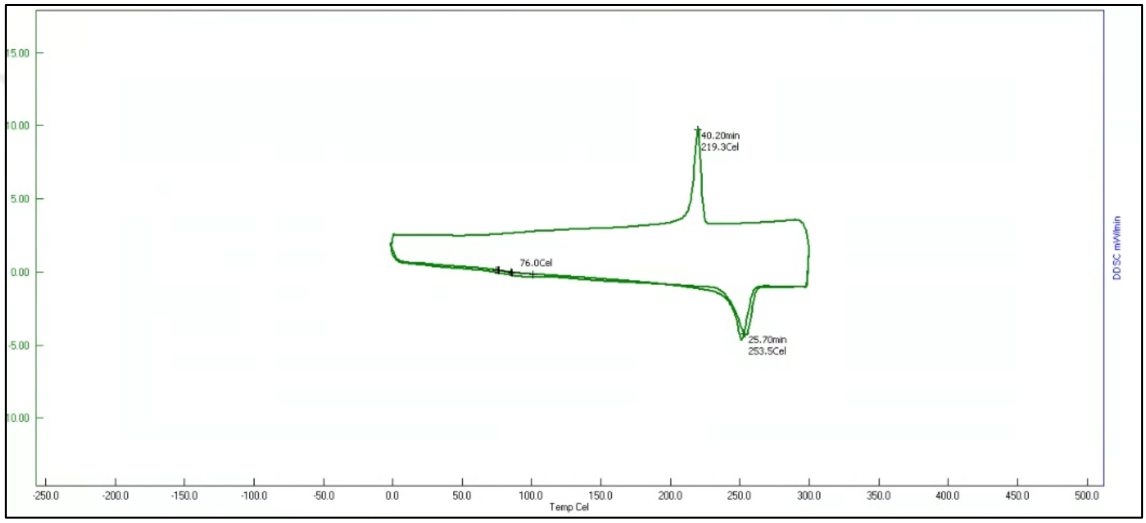


Figure A. 1. DSC result of PET.

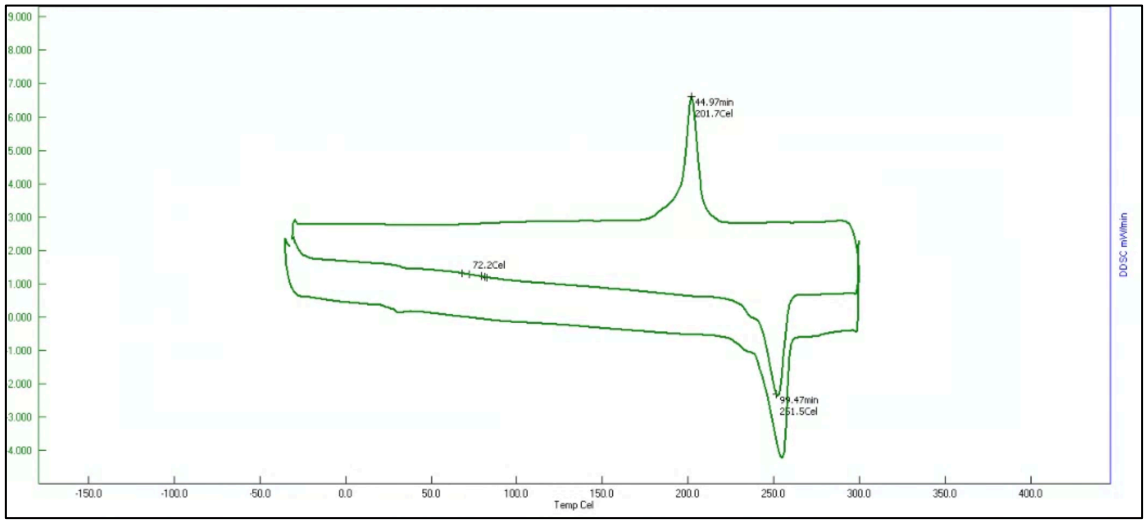


Figure A. 2. DSC result of PET-co-L-SM_1.

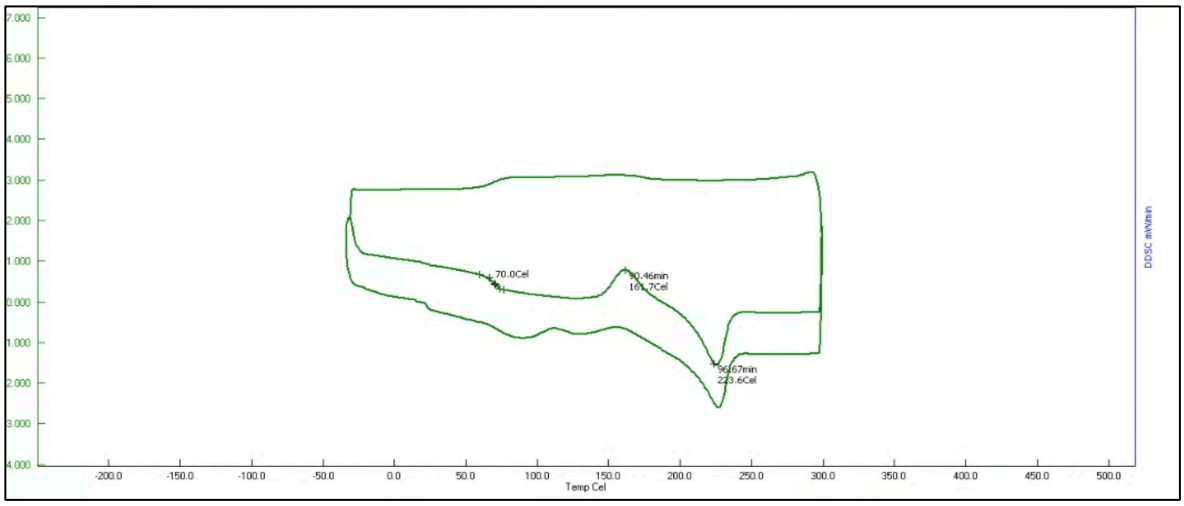


Figure A. 3. DSC result of PET-co-M-SM_1.

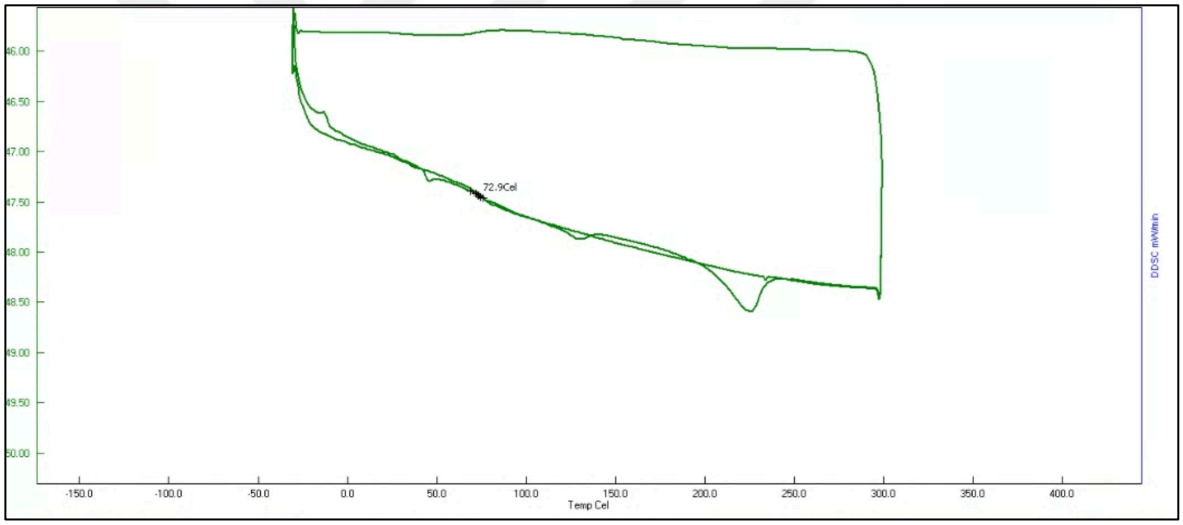


Figure A. 4. DSC result of PET-co-H-SM_1.

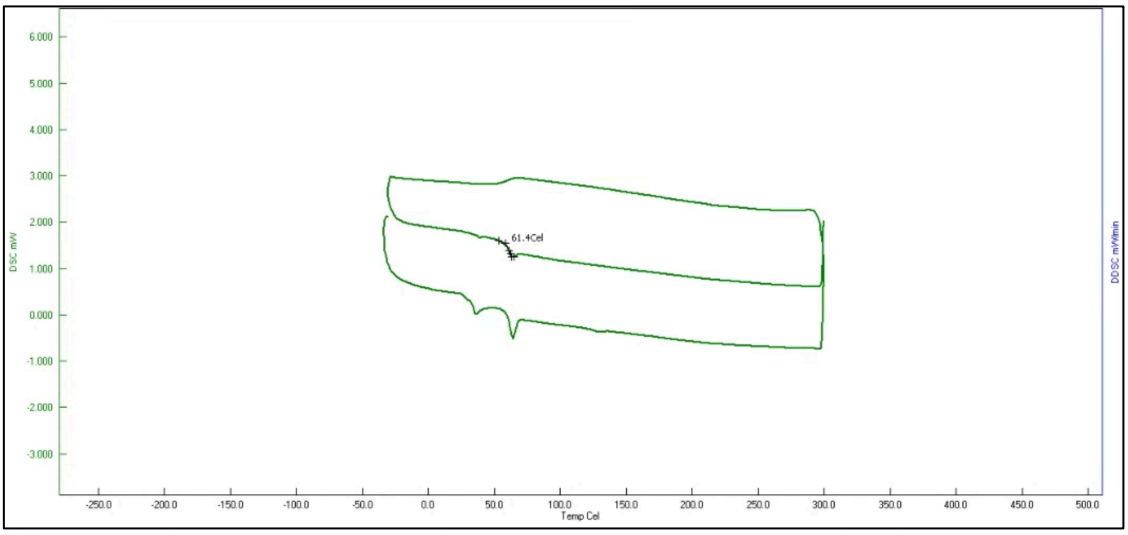


Figure A. 5. DSC result of PETI.

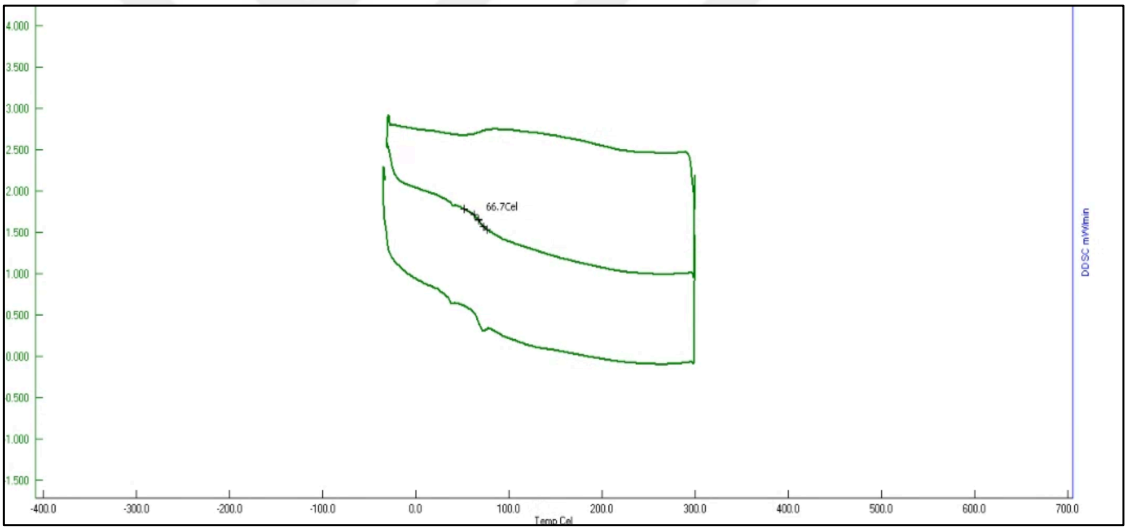


Figure A. 6. DSC result of PETI-co-H-SM_1.

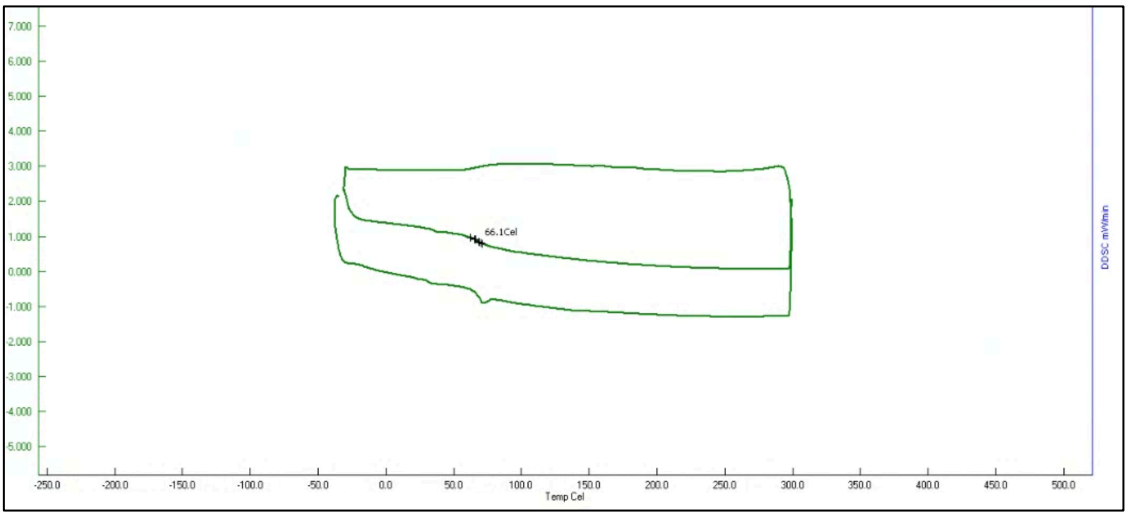


Figure A. 7. DSC result of PETI-co-H-SM_2.

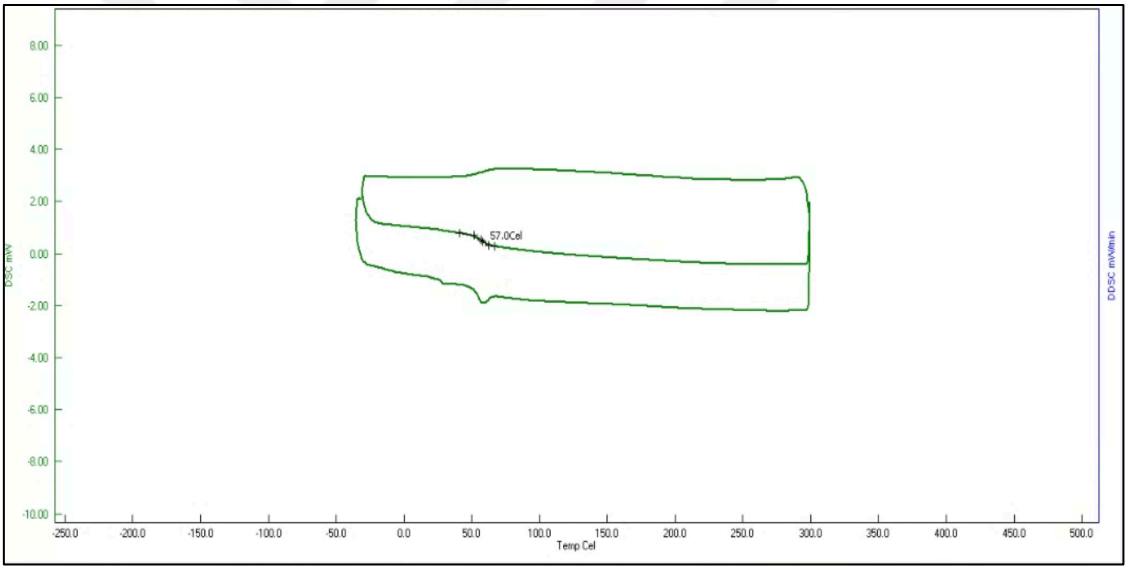
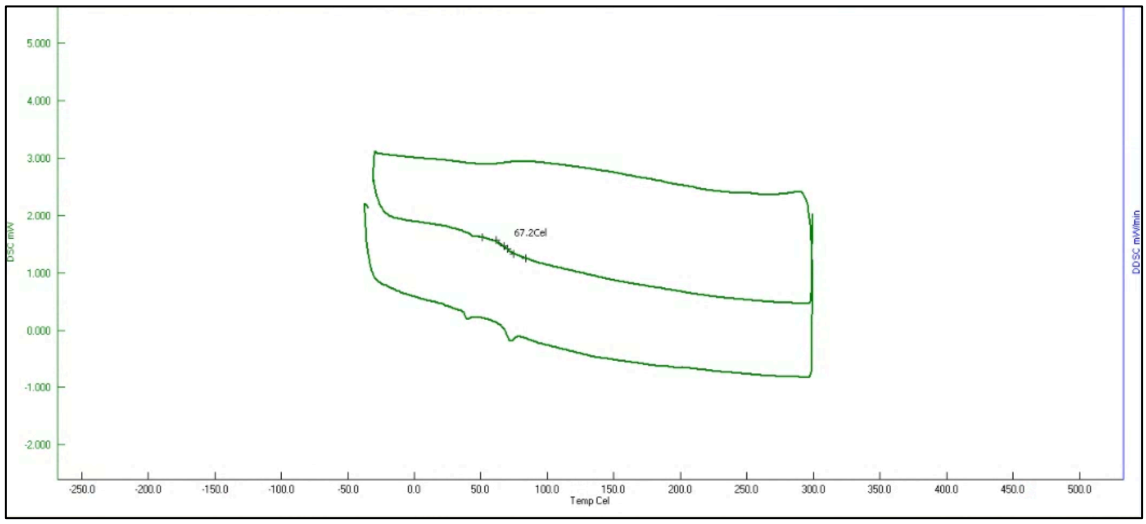


Figure A. 8. DSC result of S-PETDI



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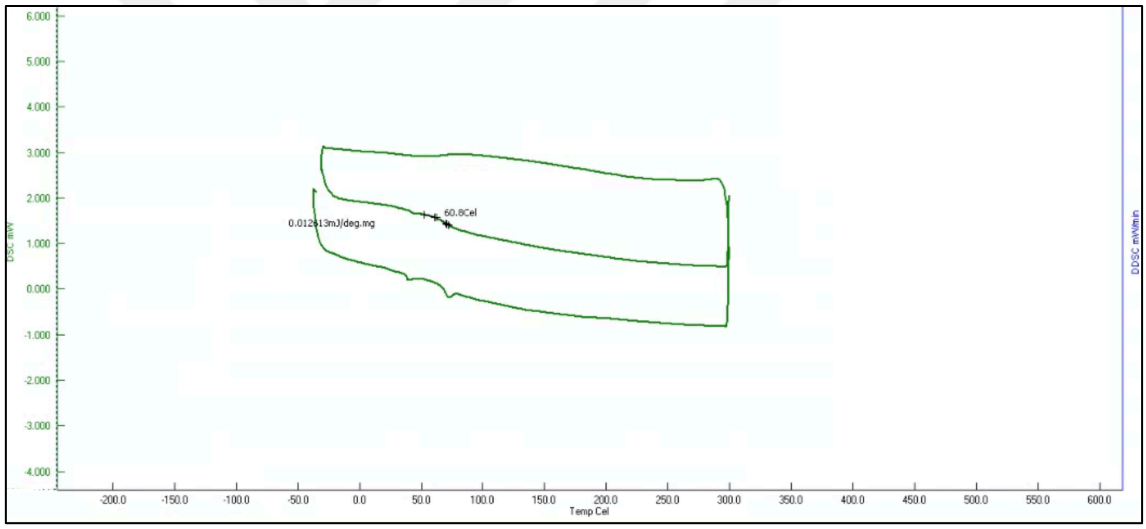
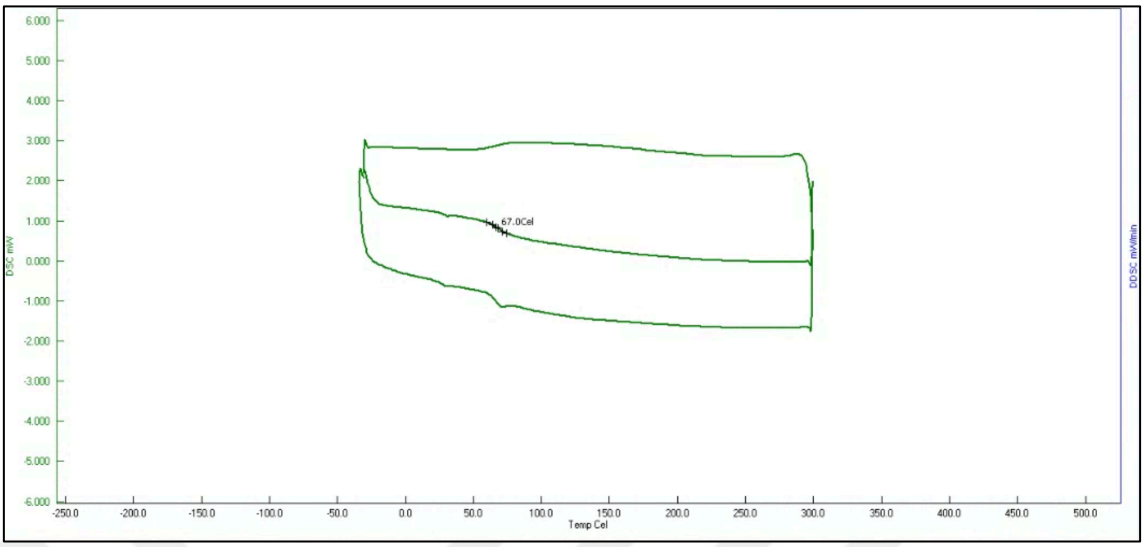


Figure A. 10. DSC result of S-PETI_0.005.



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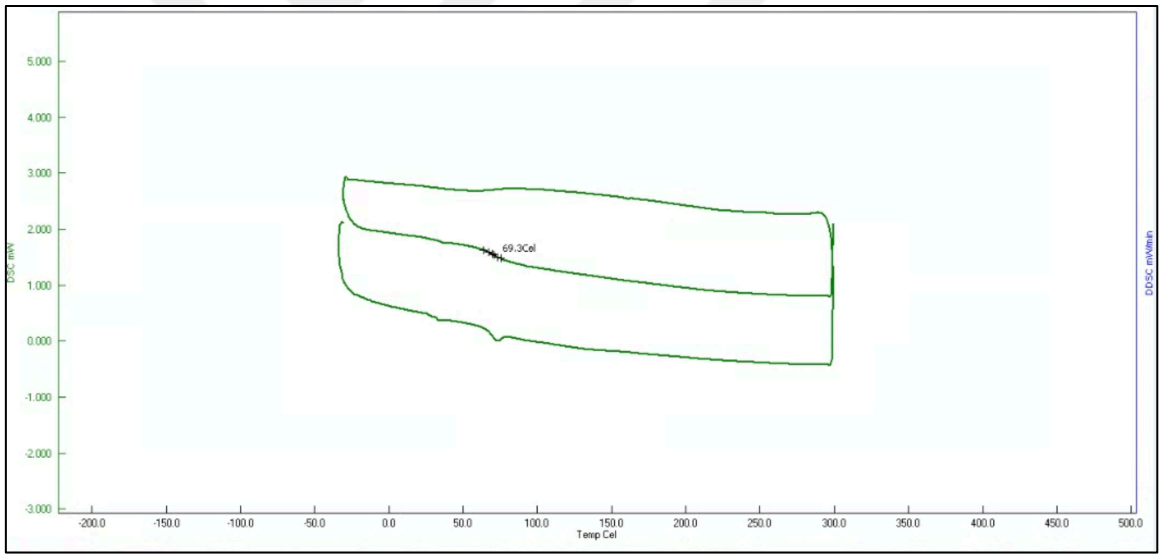

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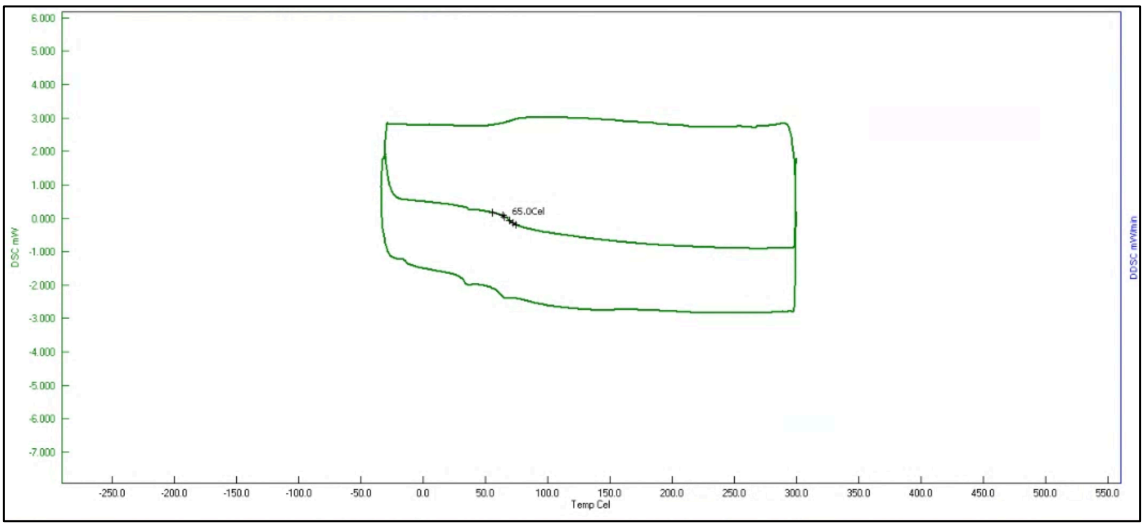

Figure A. 13. DSC result of S-PETTI.

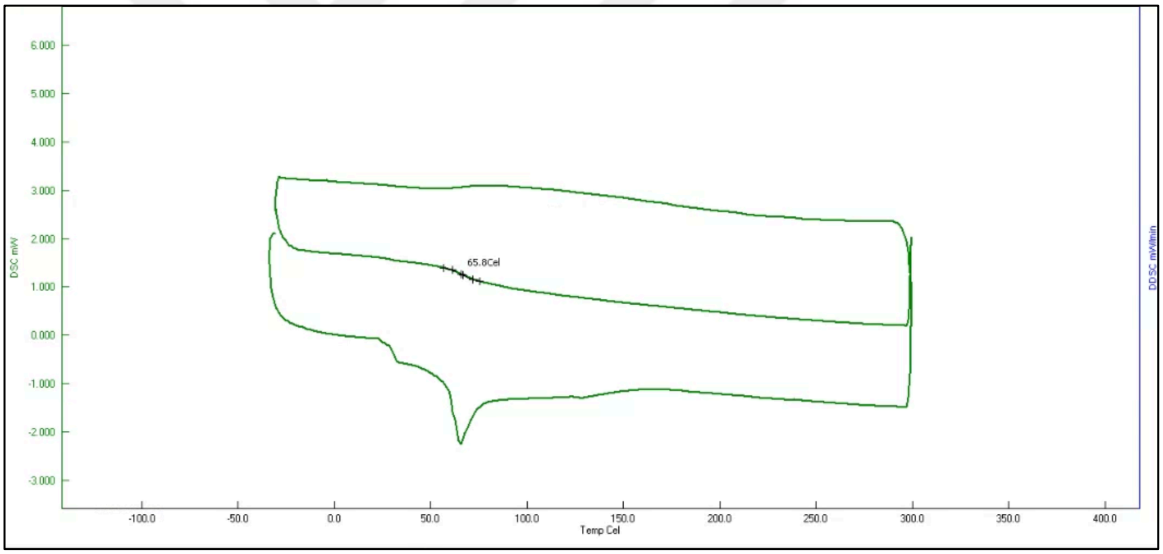

Figure A. 14. DSC result of S-PETI_Sb_2O_3.

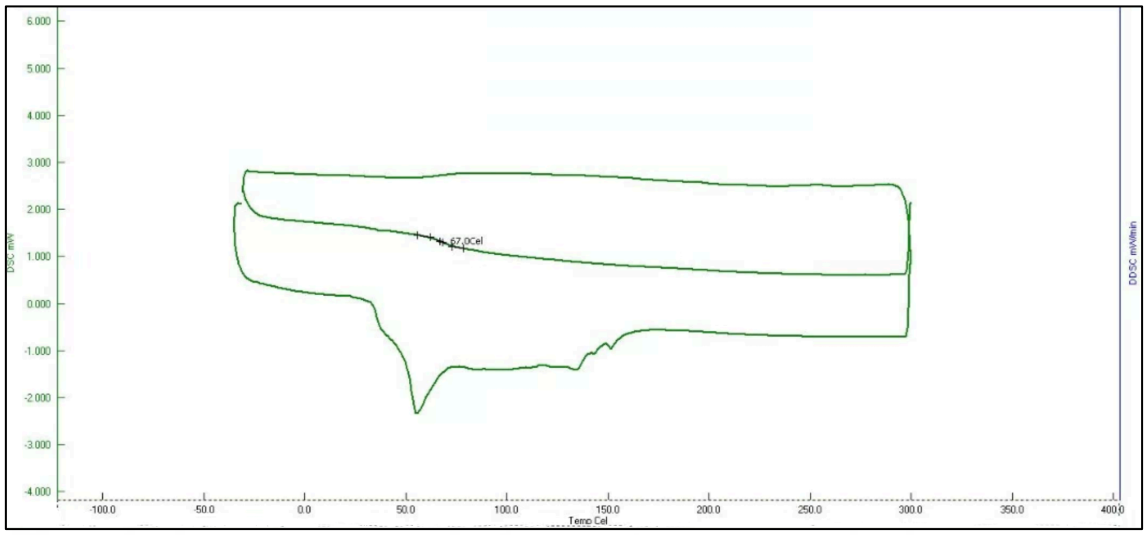

Figure A. 15. DSC result of S-PETI_TTIP.

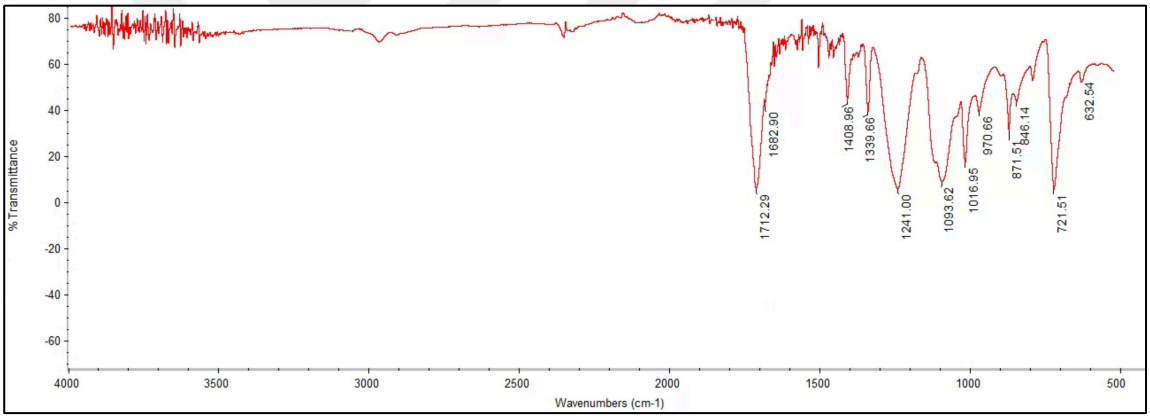

Figure A. 16. FTIR result of PET-co-L-SM_1.

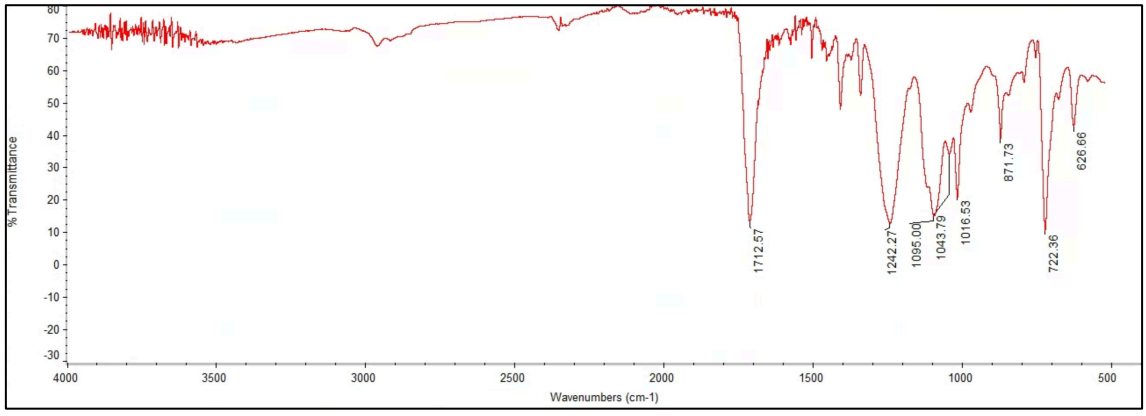

Figure A. 17. FTIR result of PET-co-M-SM_1.

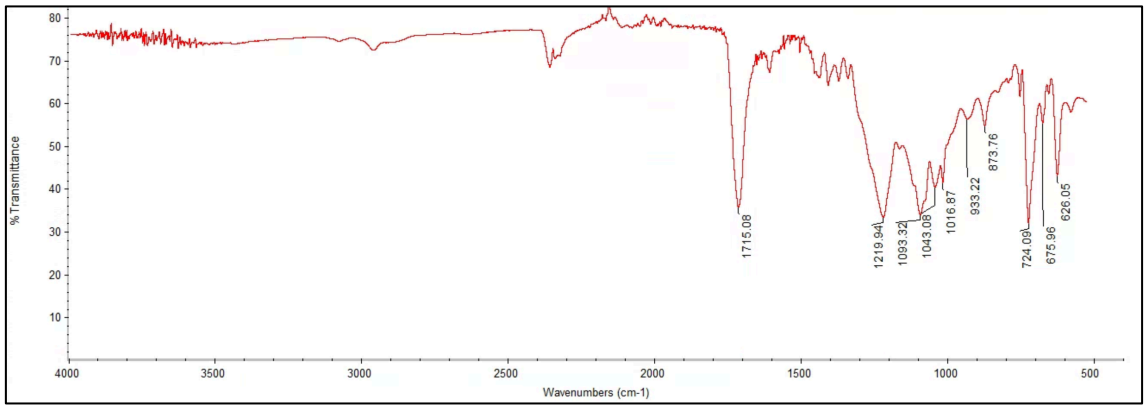

Figure A. 18. FTIR result of PETI-co-H-SM_1.

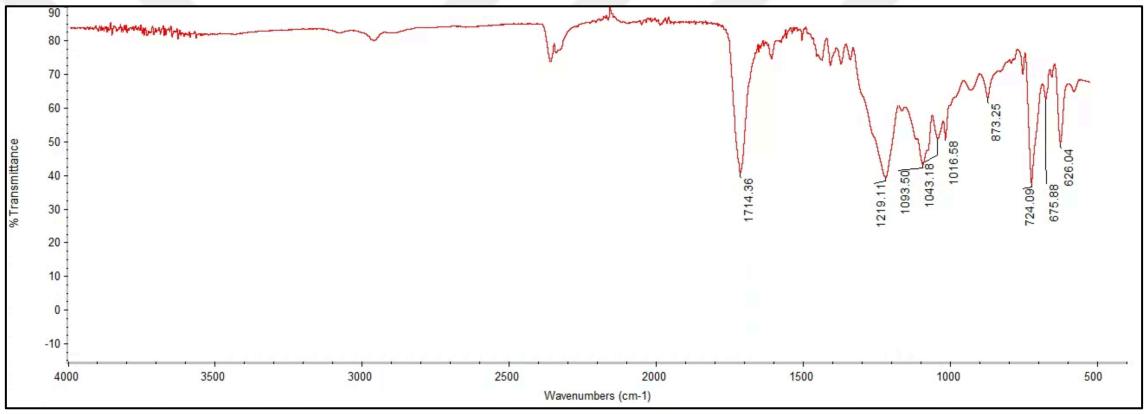

Figure A. 19. FTIR result of PETI-co-H-SM_2.

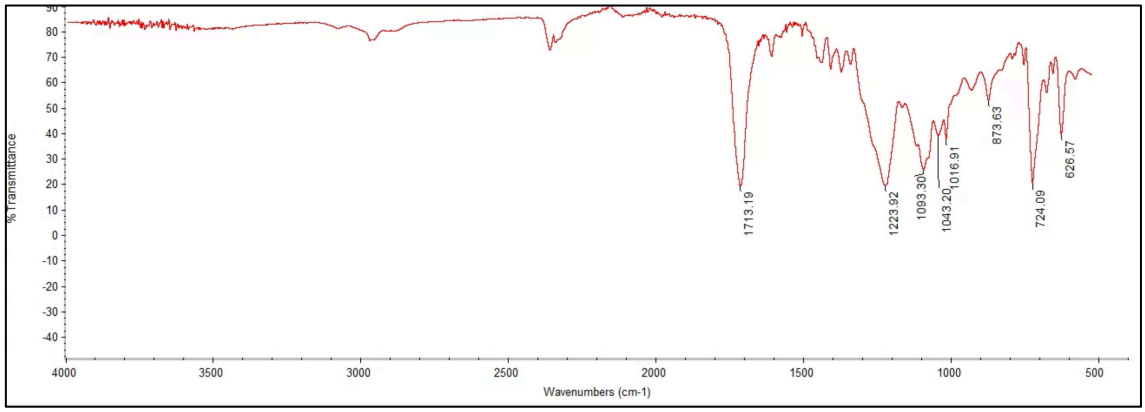

Figure A. 20. FTIR result of S-PETDI.

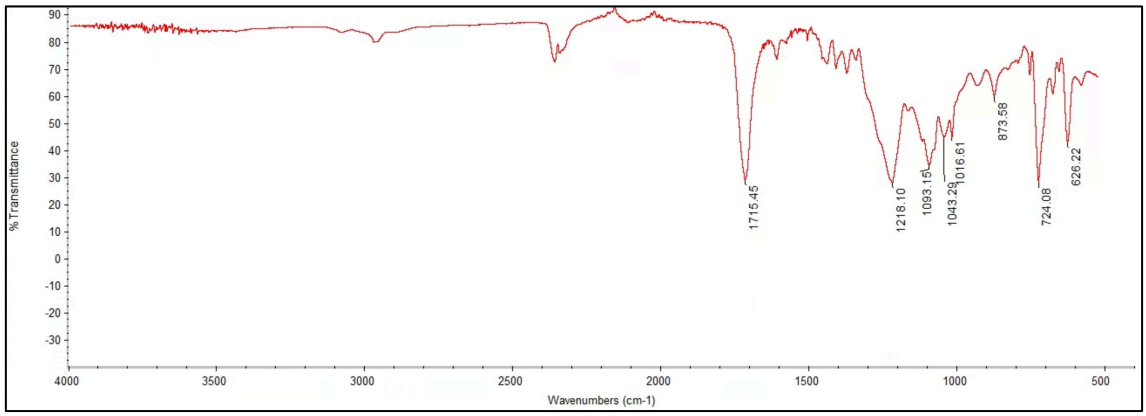

Figure A. 21. FTIR result of S-PETI.

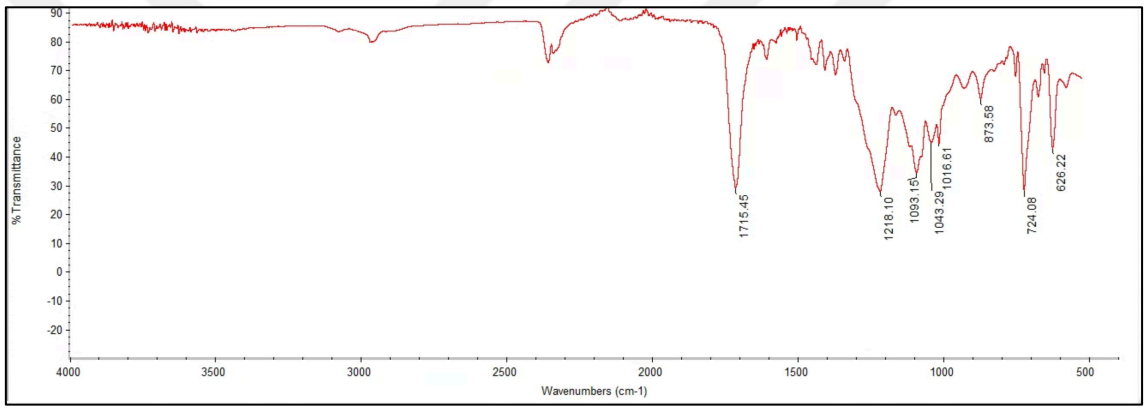

Figure A. 22. FTIR result of S-PETI_0.005.

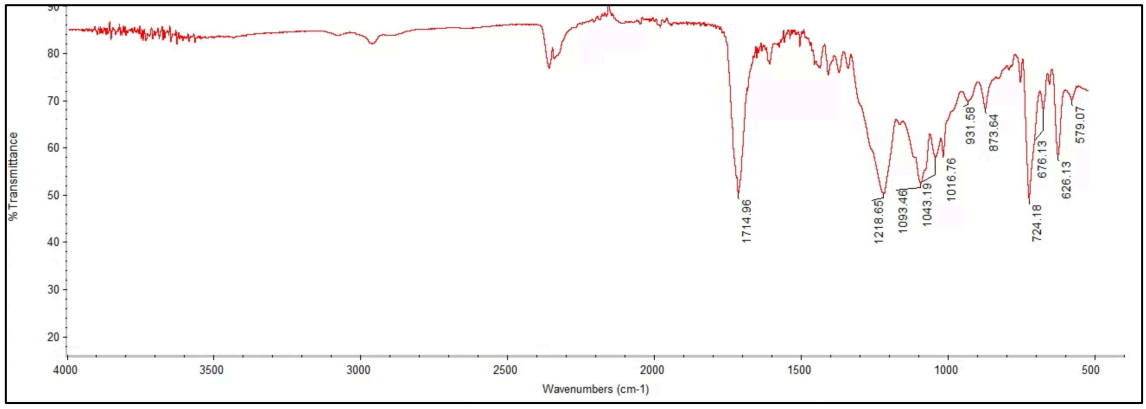

Figure A. 23. FTIR result of S-PETI_0.01.

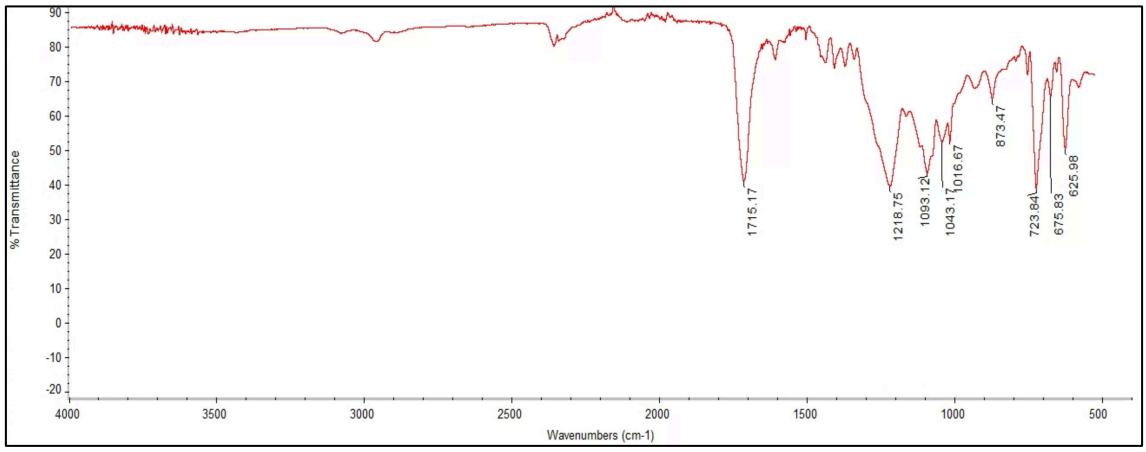

Figure A. 24. FTIR result of S-PETI_0.02.

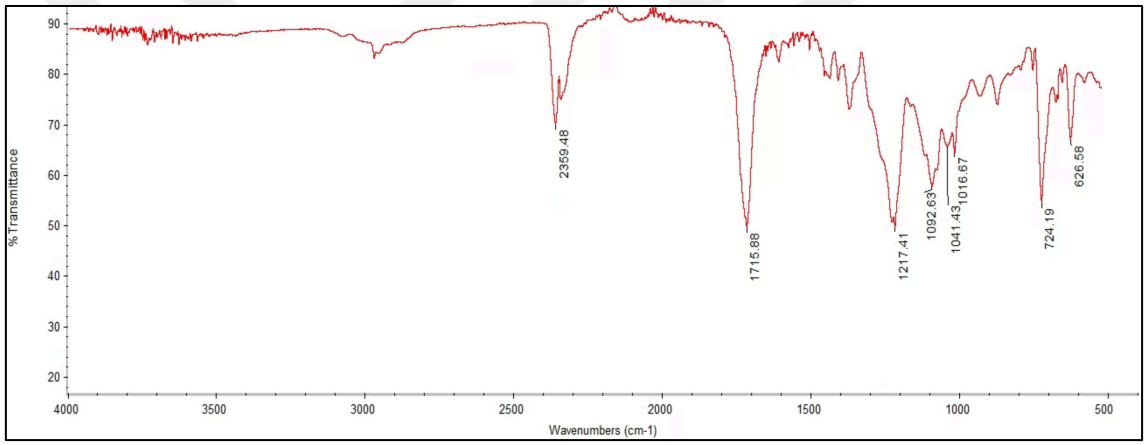

Figure A. 25. FTIR result of S-PETTI.

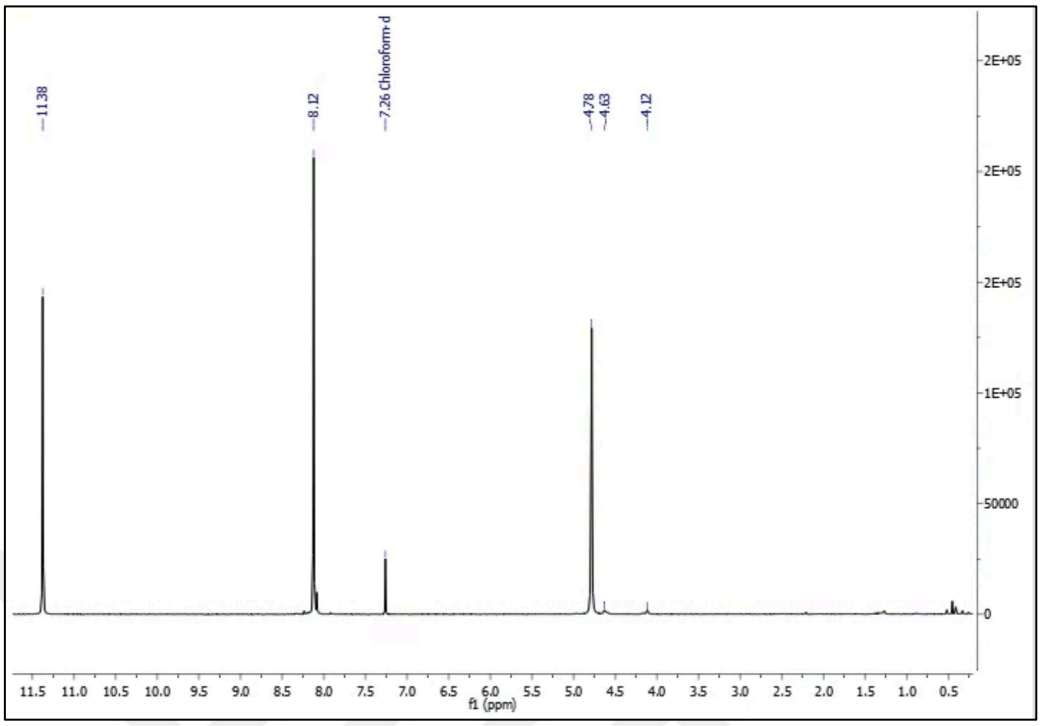

Figure A. 26. NMR result of PET.

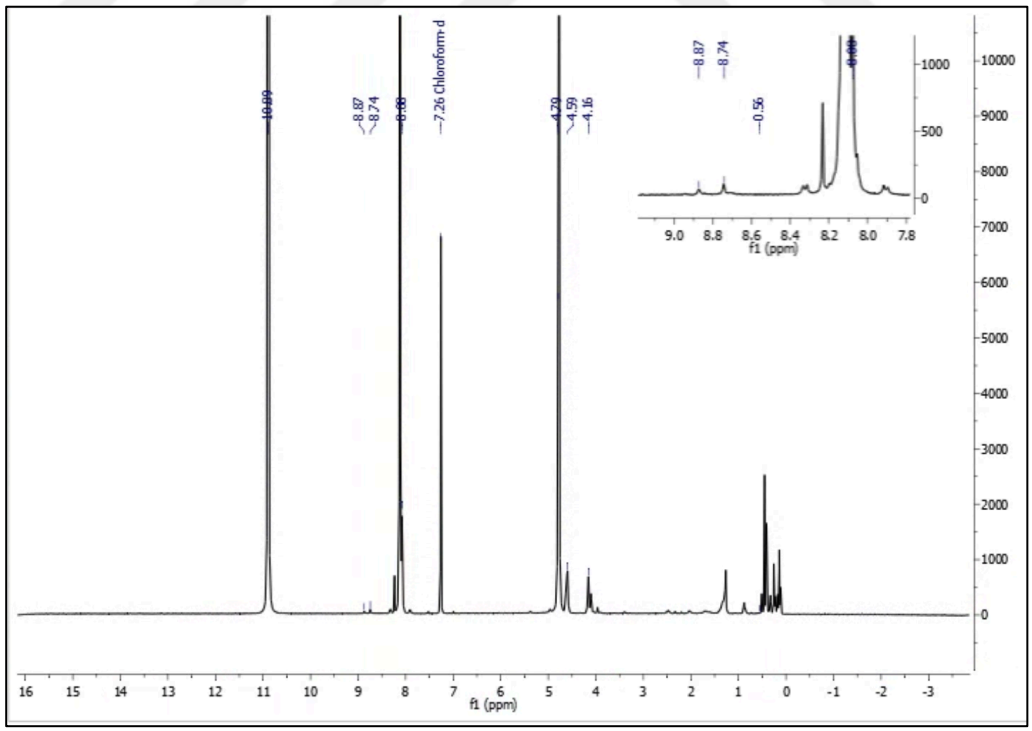

Figure A. 27. NMR result of PET-co-L-SM_1.

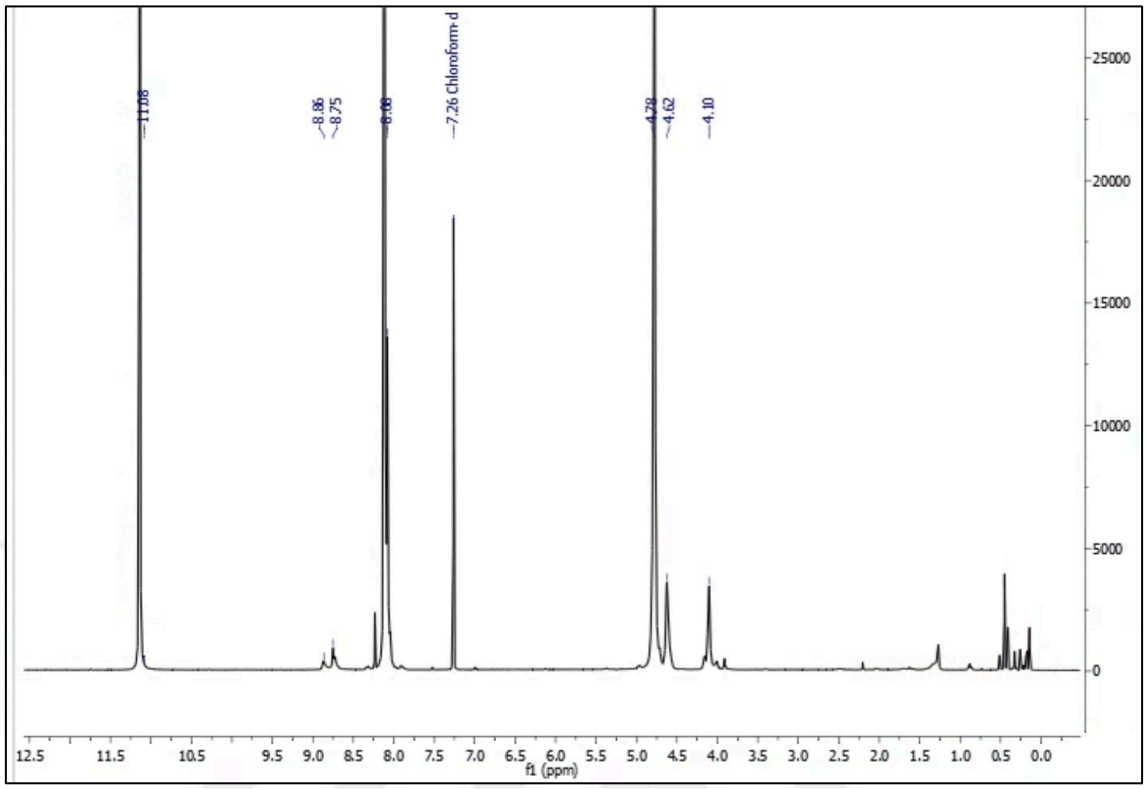

Figure A. 28. NMR result of PET-co-M-SM_1.

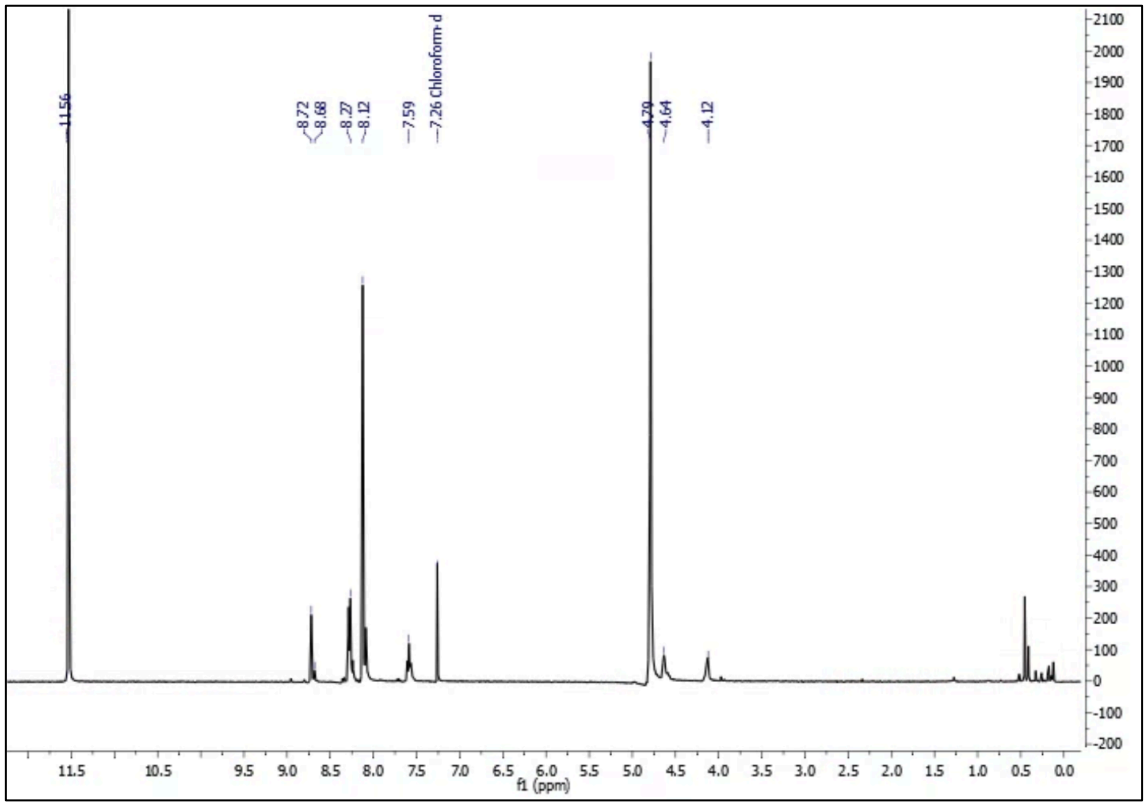

Figure A. 29. NMR result of PETI.

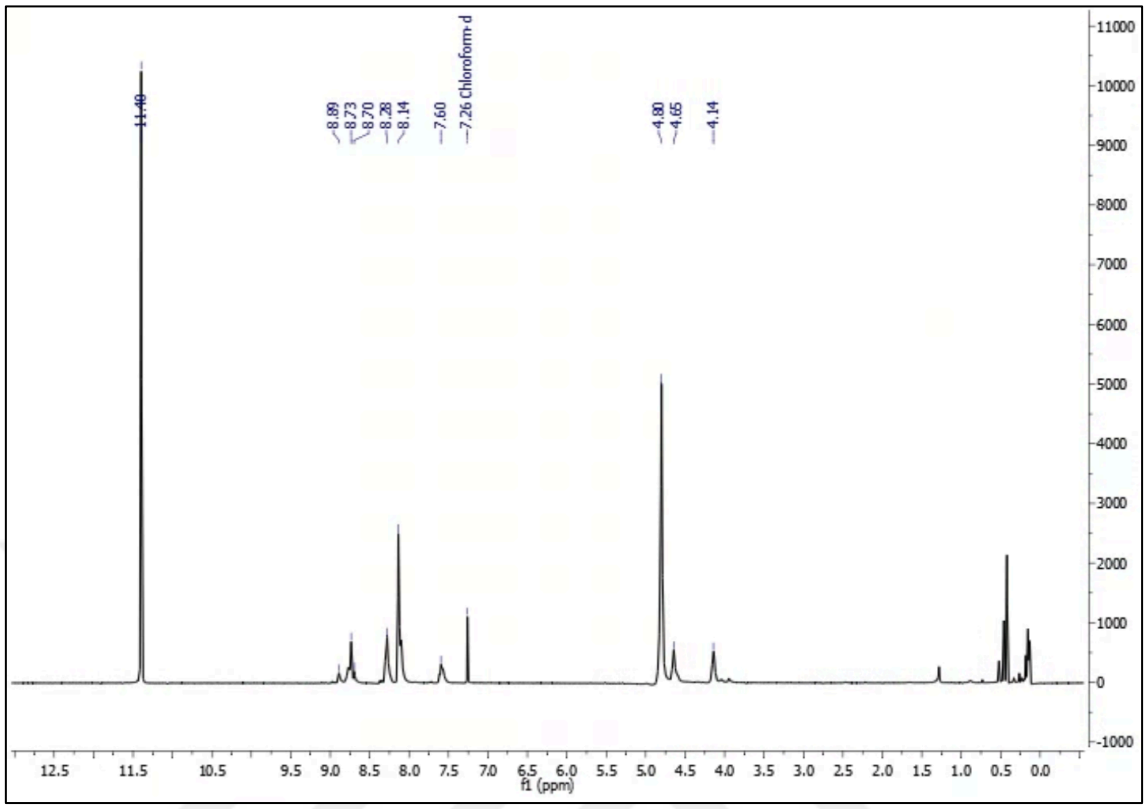

Figure A. 30. NMR result of PETI-co-H-SM_1.

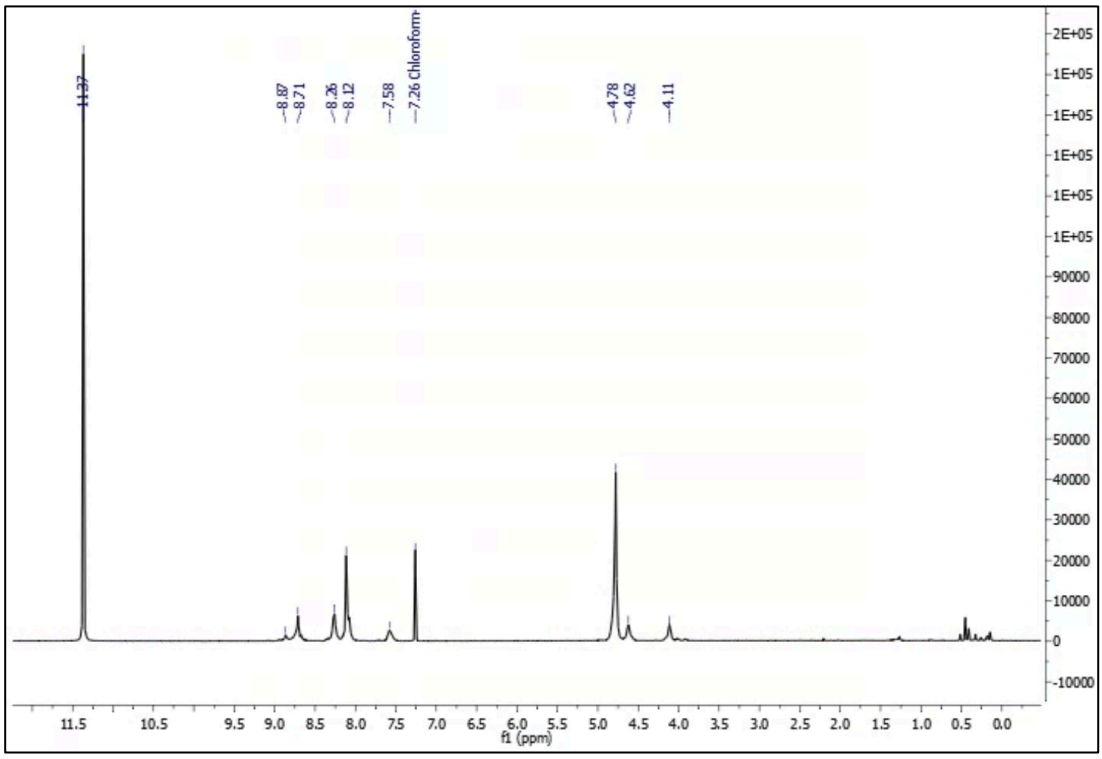

Figure A. 31. NMR result of PETI-co-H-SM_2.

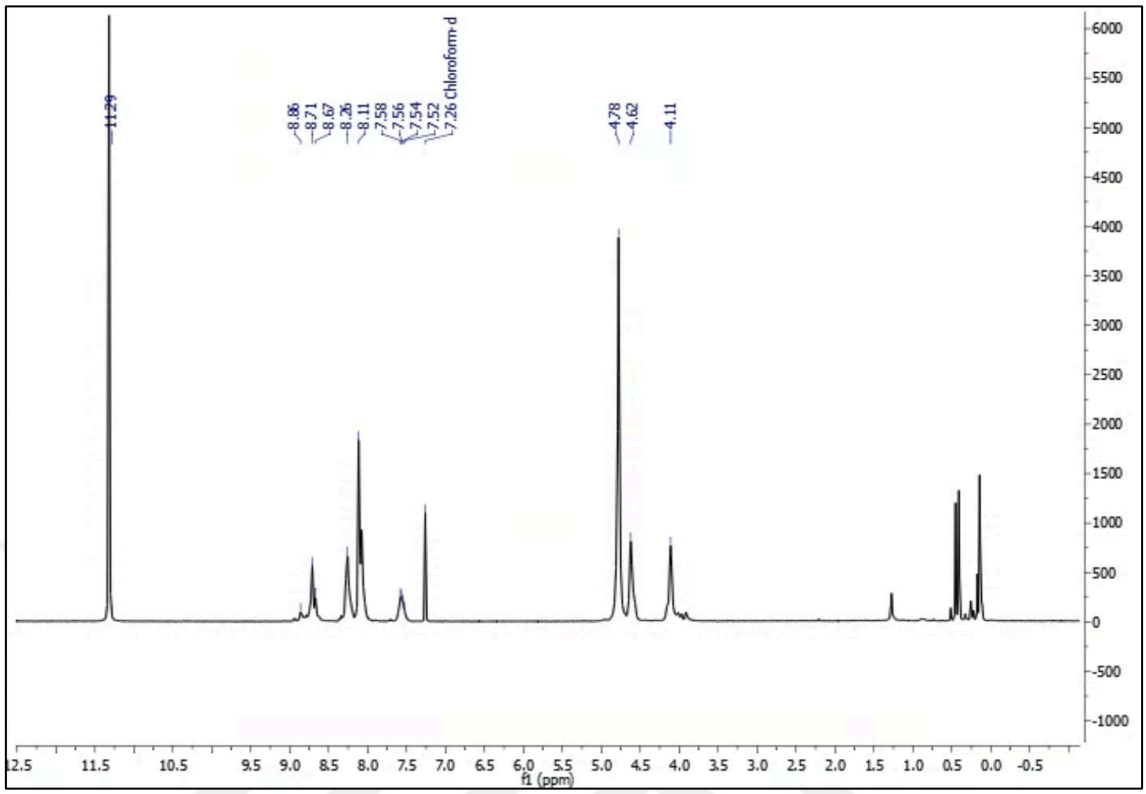

Figure A. 32. NMR result of S-PETDI.

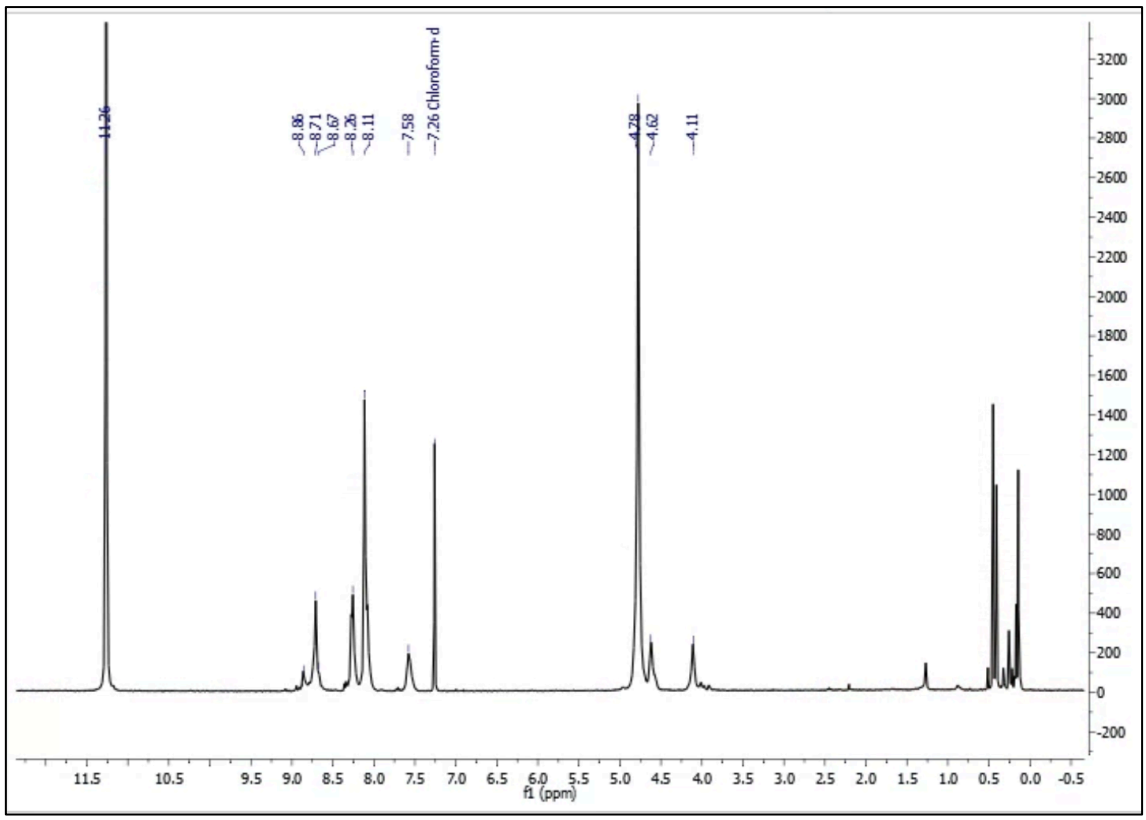

Figure A. 33. NMR result of S-PETI.

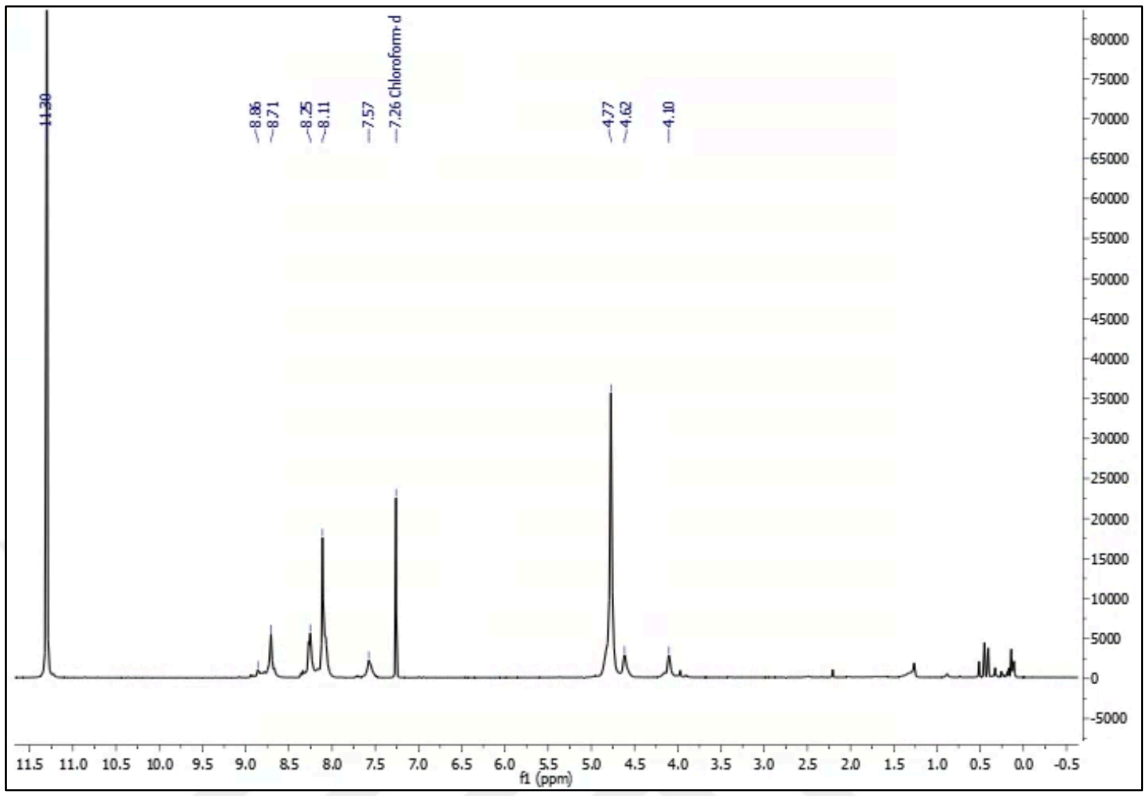

Figure A. 34. NMR result of S-PETI_0.02.

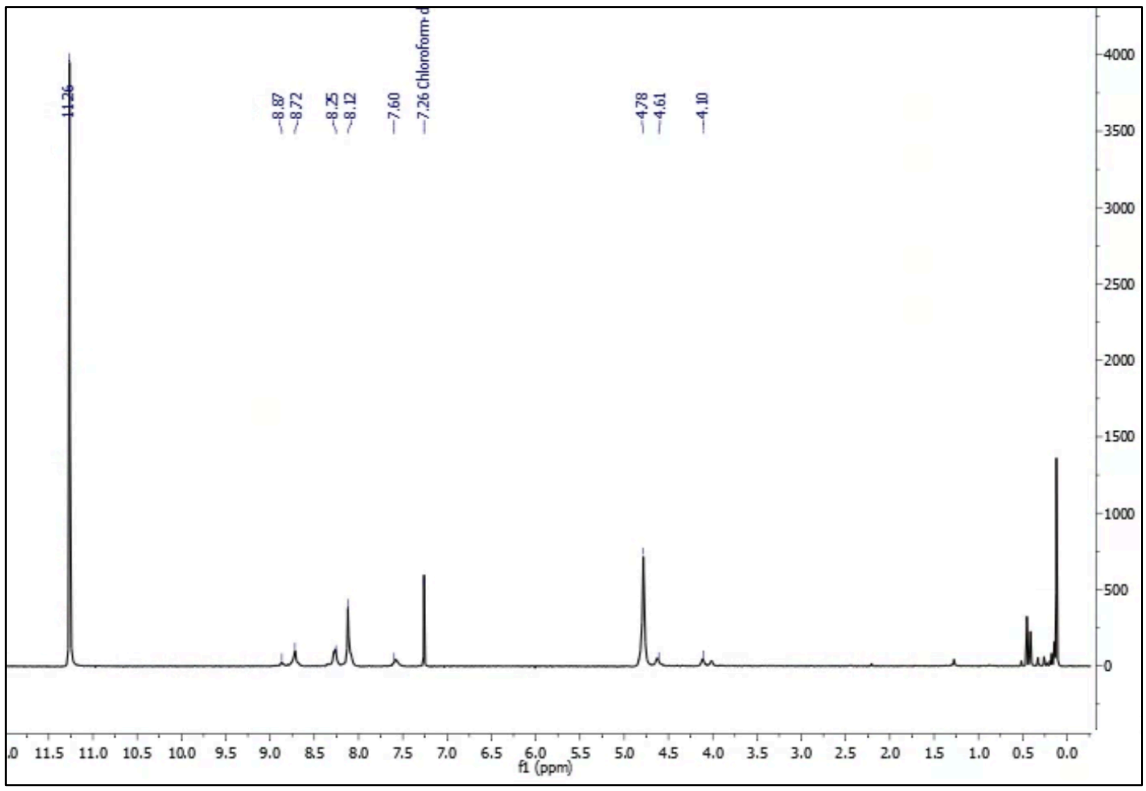

Figure A. 35. NMR result of S-PETI_Sb_2O_3.

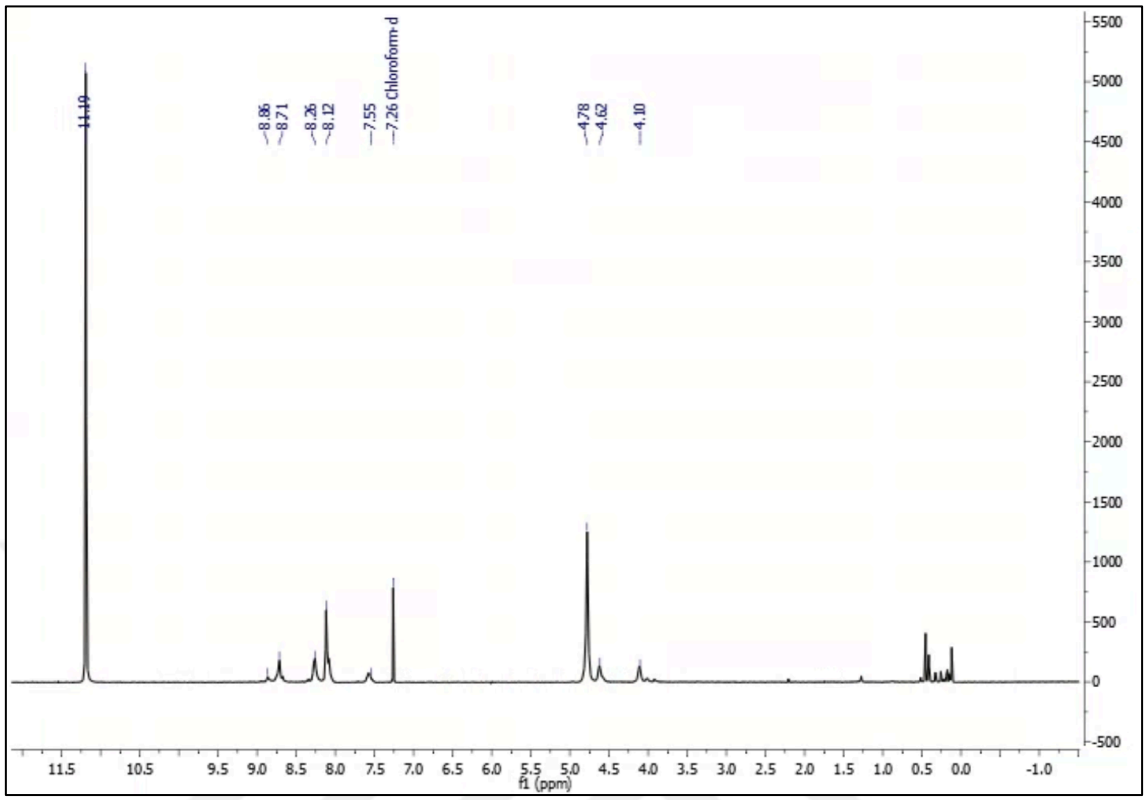

Figure A. 36. NMR result of S-PETI_TTIP.