

Synthesis and Characterization of Functionalized Polythiophene via Negishi Coupling



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By

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

*In the Name of Allah, the most
Gracious*

DRSML

*Dedicated To My Loving
Parents (Mr. and Mrs. Ameer Hassan Khan)*

&

My Uncle Awal Khan

*Whose prayers and encouragement have
helped in every moment of my life*

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All praises for **Almighty Allah**, the most beneficent, the most merciful who bestowed upon me with the sight to observe, the mind to think and the courage to work. Million time's peace and blessing of Allah be upon the **Holy Prophet (P.B.U.H)** who exhorted his followers to seek knowledge from cradle to grave.

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List of Abbreviations

CPs	Conducting Polymers
DCM	Dichloromethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
dppp	Diphenyl phosphino propane
E_g	Band gap
FETs	Field effect transistors
GC-MS	Gas chromatography – Mass spectrometry
HCl	Hydrochloric acid
m	Multiple
m.p	Melting point
NMR	Nuclear magnetic resonance
NBS	<i>N</i> -bromosuccinimide
PL	Photoluminescence
PTs	Polythiophenes
s	Singlet
t	Triplet
T_g	Glass transition temperature
TLC	Thin layer chromatography
THF	Tetrahydrofuran
UV-vis	Ultraviolet visible
XRD	X-ray diffraction

Abstract

Thiophene based conjugated polymers are a focal point for researchers across the globe because of their exceptional conductive properties and easy synthesis. The electronic properties of the conjugated backbone of polythiophenes can be tailored by the incorporation of different electron withdrawing and electron donating substituents. The present study aimed at synthesis and characterization of thiophene based polymers.

In the first part of this study, a novel ester functionalized polythiophene (**P1**) was synthesized, starting from thiophene-3-carboxylic acid (**1A**), which undergoes bromination by reacting with NBS to form 2,5-dibromothiophene-3-carboxylic acid (**2A**), which then undergoes esterification reaction with BnOH to form ester (**4A**). In the second part an amide functionalized polythiophene (**P2**) was synthesized where octadecyl phenyl amine (**1B**) by reacting with **1A** was converted into carboxamide (**4B**). The synthesized ester (**4A**) and amide (**4B**) were converted into organozinc reagent (**5A** and **5B**) by Knochel reaction that finally undergoes Negishi mediated self polymerization reaction to form polymer (**P1** and **P2**), in good yield of 48% and 52% respectively.

The synthesized monomers and polymers were characterized by NMR and GC-MS spectroscopic techniques which confirmed the presence of all the functional groups in proposed structures and their purity. XRD analysis of polymers suggested their amorphous nature. Both type of derivitized polythiophenes were found to be highly soluble in common organic solvents, such as CHCl₃, THF, MeOH and DMSO. The photophysical aspects of polymers were studied by UV-visible spectroscopy. The synthesized polymers exhibited broad and strong absorptions in the visible region (λ_{max} of **P1** = 325nm and λ_{max} of **P2** = 310nm). Small E_g values (2.5eV-2.9eV) suggested that these polymers are potential candidates for opto-electronic properties and can be used in solar cell films and in thin film transistors etc.

Chapter 1

Introduction

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1.1 Polymers

The term polymer was first described in 1833 by a Swedish chemist J. J. Berzelius for the structures containing ethyne (C_2H_2) unit¹. However, many people had been using polymers in their daily lives for a long time, but they did not realize until World War II², 1920. Hermann Staudinger defined polymers as “macromolecules formed by joining small molecules known as monomers”, and this concept gained attraction in the scientific community³.

The word polymer is originated from Greek word ‘poly’ mean many and ‘meros’ mean parts. Thus, Polymers are high-molecular-mass units, with each molecule made up of large number of individual structural units that are joined together in a regular pattern. In other words, polymers are large molecules with a high molecular weight, known as macromolecules, which are formed by linking together of large number of small molecules, known as monomers. Polymerization is the process by which monomers combine to form polymers³.

The polymer molecule is made up of a variety of structural units with high molecular weights in the 10000-1000000 g/mol range. Covalent bonds connect these structural units.

Polymers have existed in nature since the beginning of time, and polymers such as DNA, RNA, proteins, and polysaccharides play critical roles in plant and animal life. Natural polymers have been used by humans for clothing, decoration, shelter, tools, weapons, writing materials, and other purposes since the dawn of time. Life itself is connected to several macromolecules like DNA, RNA, and proteins which are essential and fundamental components to all forms of life⁴.

In the eighteenth century, Thomas Hancock proposed that natural rubber can be modified by blending it with certain additives. Charles Goodyear improved natural rubber properties by vulcanizing it with Sulphur. Bakelite was the first synthetic polymer to be manufactured in 1909, and it was quickly followed by rayon. In 1911, a synthetic fiber was invented. The systematic study of polymer science began only about a century ago, with Herman Staudinger's pioneering work. Staudinger has defined polymer in a new way. He was the first to publish the idea that, long covalently bonded molecules were used to create high molecular mass compounds in 1919⁵.

Thousands of natural polymers are there since the life began. Natural polymers are derived from animal and plant sources. Their benefits and utility are substantial. This category includes all polysaccharides (starch, cellulose etc.), protein (silk, wool etc.), and natural rubber families⁴.

Synthetic polymers are entirely the result of human invention. They are created as a result of the polymerization reaction of monomer molecules. For example nylon, polyethylene, polyester, Teflon, and epoxy. Some of the synthetic polymers were accidentally synthesized in the mid-19th century by chemists without knowing the chemical structure and composition of these materials⁶.

Due to the rapid increase in industrialized products, the impact of polymer materials on modern life is immense. More than half of the world's chemists and chemical engineers are involved in the polymer domain. Their widespread application has been discovered in the textile industry, medical appliances, automotive industry, electronics, civil engineering, agriculture, and many other fields⁷.

1.1.1. Synthesis of polymers:

In polymer chemistry, two types of polymerization methods are commonly used to convert monomer units into polymer⁸.

- a) Addition polymerization
- b) Condensation polymerization

1.1.1.1 a) Addition polymerization:

In addition polymerization, polymers are formed by the reaction of monomers without any by-product formation. Addition polymerization occurs in the presence of initiator (cation, anion or radical). Chain growth or chain reaction polymerization are the other names of addition polymerization. Examples include polystyrene, Figure 1.1 show commercially available polymer synthesized from styrene. It is hard, rigid, clear and amorphous polymer.

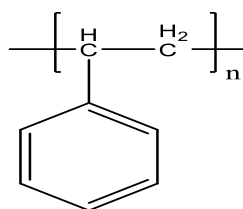


Figure 1.1: Polystyrene

1.1.1.2 b) Condensation polymerization:

When a condensation reaction between two bi-functional or tri-functional monomeric units is repeated, condensation polymerization occurs. Condensation polymerization is also called step growth or step reaction polymerization. As a result of these polymerization reactions, small molecules such as water, alcohol, hydrogen chloride, and so on are eliminated as byproducts. In 1907, an American chemist Leo H. Baekeland developed the very first sticky amber colored resin called "Bakelite" prepared through polycondensation reaction of phenol with formaldehyde⁹. It was first material to be synthesized by man, an important breakthrough in the field of polymers. Other examples include nylon 6,6, Figure 1.2(a), terylene (dacron) and nylon 6. When all of the condensing monomers are the same, the molecule is called a homopolymer for example polyvinylchloride, Figure 1.2(b).

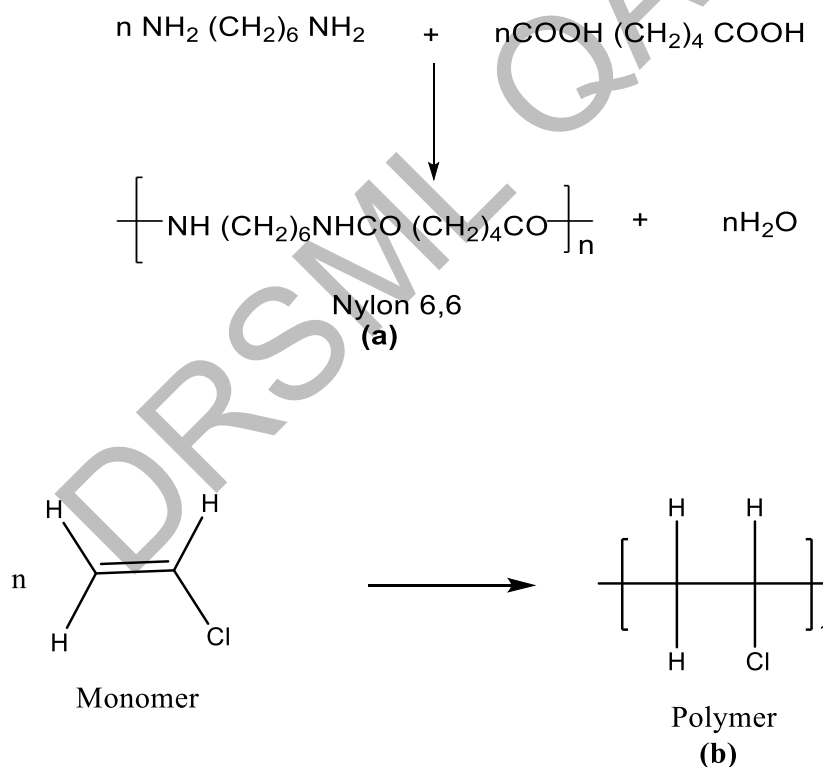


Figure 1.2: a) Nylon 6,6¹⁰

b) Polyvinylchloride¹⁰

1.2 Conjugated polymers

Those polymers which have alternate single and multiple bonds in their structure are known as conjugated polymers. The overlapping p-orbitals of conjugated polymers produce pi-electronic cloud, which led to their interesting optical and electronic properties, and vast range of application as shown in Figure 1.3.

The conjugated polymer were first developed by the addition polymerization of ethyne for the formation of polyacetylene^{11,12}. So, the first route for the formation of conjugated polymers was the addition polymerization of triple bond containing monomers. Alan Heeger and his coworkers were awarded Noble prize for describing conductive properties of polyacetylene in 2000¹³.

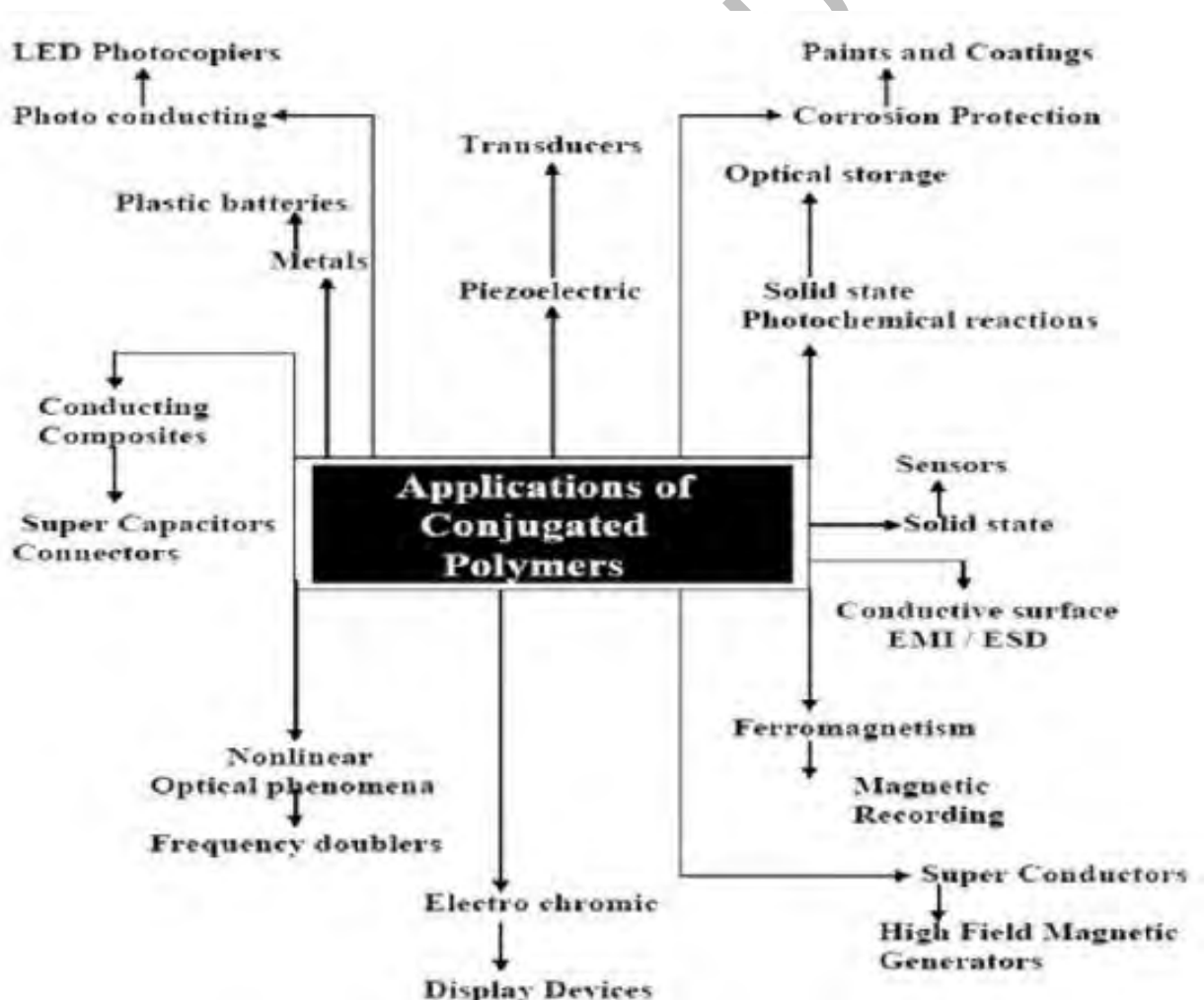


Figure 1.3: Applications of Conjugated Polymers

Thiophene based polymer show broad spectrum of applications in organic field-effect transistors (OFETs) ¹⁴⁻¹⁷, organic light emitting diode (OLEDs)^{18, 19} and organic photovoltaics (OPVs) ²⁰⁻²². These are also commonly used in sensor technology ^{23, 24}. Several methods have been reported for synthesizing oligothiophene but most commonly used methods are oxidative homo-coupling ²⁵⁻²⁷, ring closure ^{28, 29} and carbon-carbon coupling reaction catalyzed by different transition metals like Pd or Zn ³⁰⁻³².

Polythiophene based conjugated polymers are crucial topic of discussion. Conjugated polymer acting as donor show vast applications in transistors, LEDs and plastic solar cells ³³⁻³⁶. The extensive research and use of these polymers is due to their extraordinary optical and electrical characteristics. By tailoring conjugated substituents into backbone of polymer various properties can be altered. Among polythiophene poly(3-hexylthiophene) (P3HT) is well studied due to ease in synthesis and greater mobility of charge carriers³⁷. But unluckily HOMO level of this polymer is very high. Such drawback can be eliminated by substitution of group to stabilize resonance and attaching electron donating groups followed by electron withdrawing group results in formation of donor-acceptor type polymers ³⁸⁻⁴¹.

1.2.1 Thiophene

Thiophene is a five membered heterocyclic ring with sulfur as hetero atom. It is aromatic and have two pi-bonds in the ring. It is a colorless liquid with benzene like odor, and gives reactions similar to benzene⁴². Long ago, it was thought that it is just a contaminant in benzene. Victor Meyer was able to isolate it as a separate substance responsible for the blue dye formation on mixing isatin and benzene. Thiophene and its derivatives occur mainly in petroleum^{42, 43}.

The high stability of thiophene makes it possible to synthesize it in a number of ways. Initially it was synthesized by reacting acetylene with elemental sulfur by Victor who discovered it⁴². Now the classical synthesis involves reaction of 1,4 diketone, diester, dicarboxylates with sulfurizing agent such as P₄O₁₀ or Lawesson's reagent like in Paal Knorr synthesis, or in Gewald synthesis which involves condensation of carbonyl followed by cyclization, or Volhard-Erdmann cyclization etc.

As mentioned above, the reactivity of thiophene is similar to benzene. Thus, thiophene undergoes alkylation, acylation, oxidation, halogenation, desulfurization and most

importantly polymerization reactions. Thiophene also serves in coordination chemistry as it makes pi-ligand forming piano tool complexes.

Thiophenes are extensively used as building blocks in agrochemicals and pharmaceuticals^{44, 45}. Not only this, thiophene derivatives are known for anti-proliferative, anti-cancer, anti-mitotic activities etc⁴⁶.

1.2.1.1 Thiophene derivatives

Thiophene based small molecules (or derivatives) are in great number and widely used for their biological activities^{46, 47}. Benzene ring is replaced by thiophene in a number of drugs and similar activity has been shown by these drugs,^{44, 47-51} for example;

- a) Lornoxicam, also known as chlortenoxicam belongs to a class of oxicam drugs. It is a nonsteroidal anti-inflammatory drug (NSAID) used to reduce fever and relieve pain mainly caused by inflammatory infections⁴⁴. It was approved for medical use in 1997⁴⁸.
- b) Sufentanil is a thiophene analogue of fentanyl which contains a benzene ring (instead of thiophene). Sufentanil was first synthesized by Janssen Pharmaceutica in 1974⁴⁷. It is 500 times as potent as morphine and nearly 10 times than its parent drug fentanyl. Sufentanil is mostly used to relieve pain for a short period of time and has sedative properties which make it good anesthetic for use during operations^{43, 47}.
- c) Prasugrel is thienopyridine drug used to prevent blood clots and acts as a platelet inhibitor. Prasugrel was developed by Daiichi Sankyo Co. and produced by Ube, and approved for use in 2009⁵¹. Studies showed that prasugrel is more effective than the related clopidogre (c'), both inhibit platelets aggregations through active metabolite formation⁵⁰.
- d) Eprosartan is angiotensin II receptor antagonist used for the treatment of high blood pressure⁵². It blocks the binding of angiotensin II to AT₁ receptors in smooth muscle, followed by inhibition of production of sympathetic norepinephrine thus reducing blood pressure. Among other such inhibitors (e.g. enalapril), eprosartan is better tolerated especially among elders⁵³.

- e) Thifensulfuron-methyl is a thiophene based herbicide and its primary use is for soya beans and cereals⁵⁴. It is characterized by a rapid biodegradability in the soil.

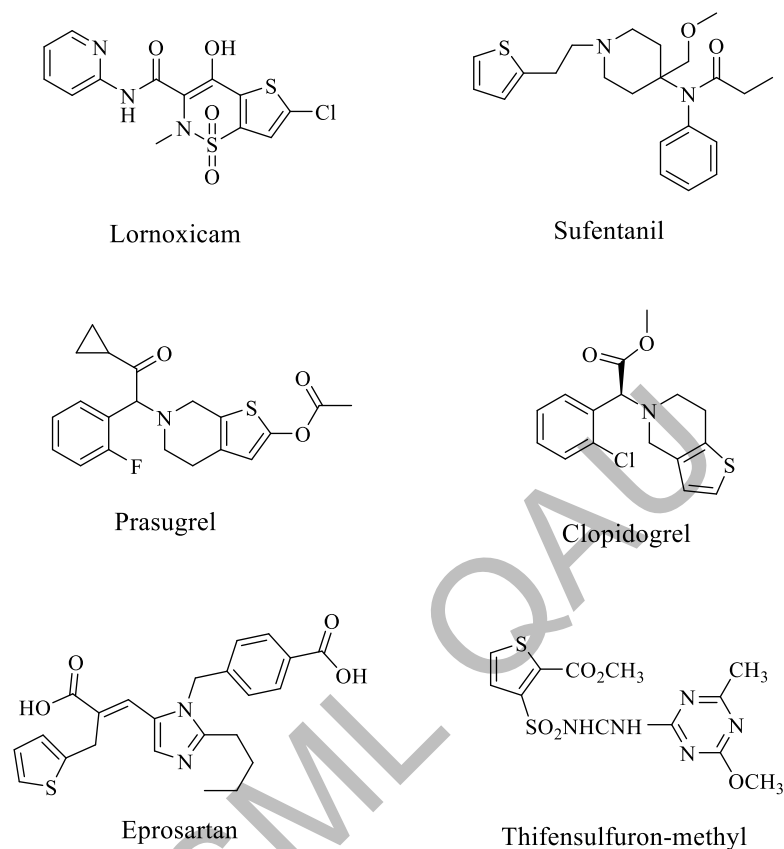


Figure 1.4 Chemical structures of thiophene derivatives

The less expensive class of 2-aminothiophene based azo dyes are known as disperse dyes for excellent brightness. This class became important after the development of 2-aminothiophene compounds by cyclization having azo intermediates⁵⁵. These dyestuffs exhibit superior properties when used for coloration of textile fabric materials including polyamide, cellulose acetate, and aromatic polyester. The colorations remain unaffected by wet and dry heat conditions^{43, 56}.

1.2.1.2 Thiophene based polymers

The search for conducting polymers has been an important task to have a possible substitute for inorganic (metallic) conductors and semiconductors⁵⁷. Characteristics associated with thiophene based organic polymers such as their mechanical flexibility, chemical stability, processability, resistance to corrosion, light weight, optical and

thermal properties led to the formation of a number of polyaromatics e.g. polypyrrole, polyacetylene, polyaniline, polythiophene etc⁵⁸.

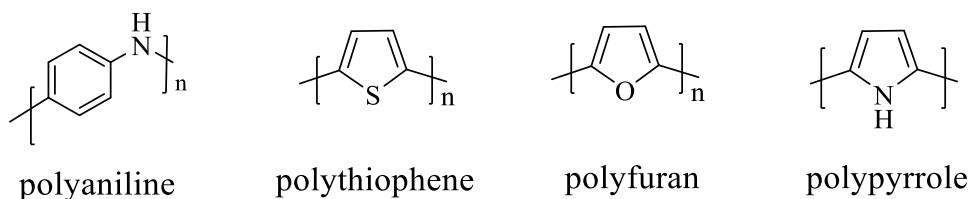


Figure 1.5 Important polyheterocycles

1.2.2 Background

The field of organic polymers has been under study for decades but their conductive nature was not so developed. One can assume that an organic polymer to have conducting properties must have unusual structure able to conduct electricity⁵⁹. There are numerous structural variations obtained up till now to achieve conductive properties in organic polymers but polyheterocycles are the most widely studied. The essential feature of conducting polymers (CPs) is their pi-conjugating system that extends over a chain through numerous monomer units. The modern era of CPs began in 1960s when polyacetylene was synthesized and was found that it can undergo 12 order of magnitude of conductivity compared to conventional conductors of that time^{59, 60}.

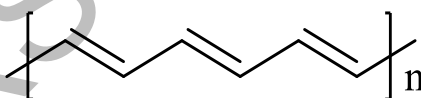


Figure 1.6 Structure of polyacetylene²⁸

Among poly heterocycles, polypyrroles were synthesized first in 1979 by oxidative polymerization of pyrroles after that interest shifted towards indole, thiophene, benzene, and furan to optimize electrical and optical properties of polymer films⁶⁰.

Polymers of thiophene (PTs) and its derivatives have a great potential for the new generation of display technology. Organic semiconducting polymers have been the subject of keen interest in recent 15 years due to their potential as alternatives to inorganic semi-conductors and other organic polymers in thin film transistors and photovoltaic cells. Polythiophenes are among these polymers due to attractive features like high charge carrier mobility, solubility, mechanical flexibility, variable band gaps, thermal and chemical stability and light weight⁵⁹. Extensive study on conducting

polymers and investigation of their properties for different applications started in 1980s
44, 47-50

Polymers of thiophenes have been considered best in terms of better stability against oxygen and moisture both in oxidation and reduction modes. Since then, thiophene is in limelight for being the best possible monomeric unit for conducting polymers (CPs)^{57, 59}.

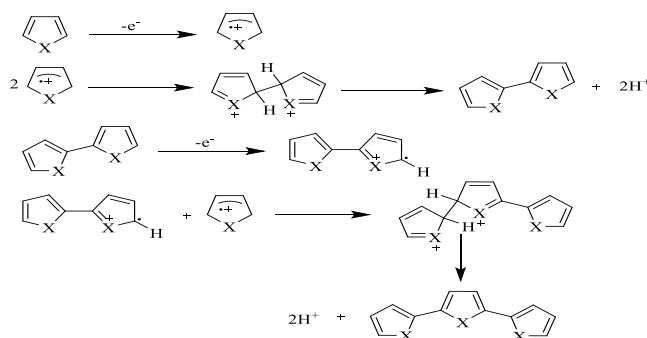
1.2.3 Synthesis of polythiophenes

Polythiophenes can be synthesized by three different ways⁶¹;

- Electrochemical (cathodic or anodic route) polymerization
- Oxidative polymerization
- Chemical (organometallic) synthesis

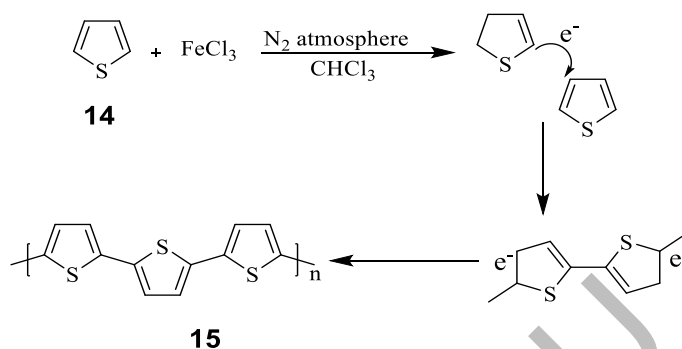
The first electrochemical synthesis dates back to 1981⁶⁰. In this process, the monomer is placed in an electrochemical cell with suitable electrodes connected to power supply. The radical reactions occurring in this cell can be controlled either by controlling the power supply (electrostatic) or the amount of current passing in the cell (galvanostatic). When the polymer is deposited on electrode, the reaction is stopped. Mechanically flexible polymer films which are easily removed from electrodes are considered good ones⁶²⁻⁶⁷. Despite the fact that a large number of PTs have been synthesized by electrochemical polymerization, the mechanism is still unclear. In general, it involves three major steps⁶⁴ shown in scheme 1.1.

- 1) Oxidation of monomer to its radical cation
- 2) Coupling of two radicals to form a dimer and
- 3) Oligomerization



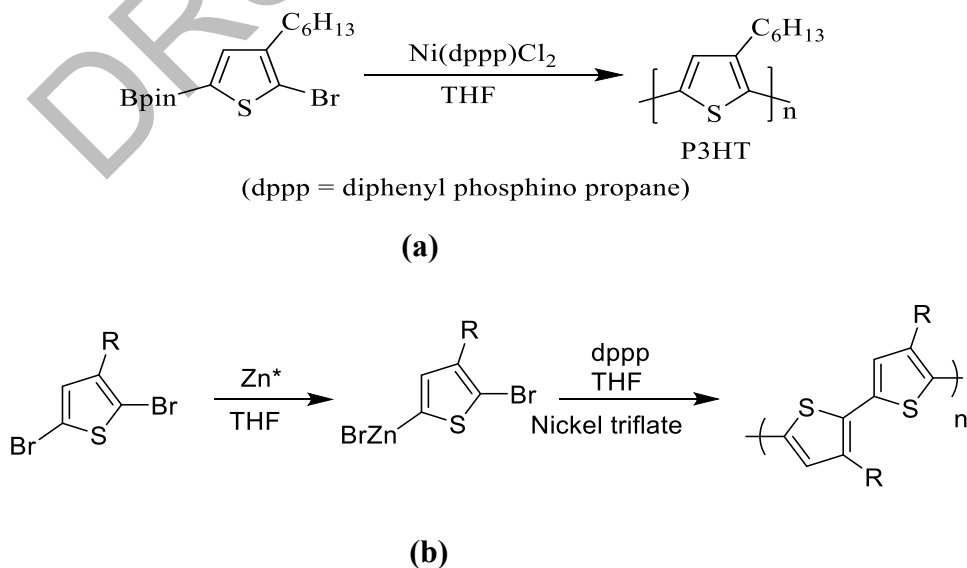
Scheme 1.1 Mechanism of electro-polymerization of five-membered heterocycles⁶⁰

The second type of synthesis is oxidative polymerization, which was reported by Sugimoto *et al.* in 1986. Oxidative polymerization of thiophene using ferric chloride as oxidant occur at room temperature shown in scheme 1.2. These substrates can also undergo oxidation by using nitrosonium salts with monomer in molar ratio of 1:1. The yields were high and good conductivity was achieved^{68, 69}.



Scheme 1.2 Mechanism of oxidative polymerization of thiophene⁷⁰

Chemical synthesis (Organometallic catalysis) involves the formation of oligomers starting with 2-halothiophene or 2,5-dihalothiophenes in the form of Grignard reagents, organoboranes and organotin compounds. Different nickel, palladium or copper catalyst along with a suitable ligand (if required) have been employed in this type of synthesis^{65, 66}. Polythiophene was chemically synthesized from 2,5-dibromothiophene using different coupling reactions⁷¹.



Scheme 1.3 (a) Organo-metallic polymerization of substituted thiophene⁷²

(b) Chemical synthesis of polythiophene from 2,5-dibromothiophene⁷³

Chemical synthesis of polythiophene offer two advantages compared with electrochemical synthesis⁷⁴.

- (1) A greater selection of monomers
- (2) Use of proper catalysts

1.2.4 Coupling Reactions

Coupling reactions are generally applied for a kind of reaction that involves joining of two fragments by the use of metal catalyst. In these reactions organometallic compounds react with an organic halide resulted in the formation of a new C-C bond of product⁷⁵.

There are two types of coupling reactions;

(1) Homocoupling reactions

These reactions occurs between two identical compounds.

Examples of homocoupling reaction are Glaser reaction, Ullmann reaction, Pinacol coupling and Wurtz reaction etc⁷⁶.

(2) Heterocoupling reactions

Heterocoupling reactions also known as cross coupling reaction involve coupling between two different partners. Examples of cross coupling reactions are Heck coupling, Sonogashira coupling, Stille coupling, Negishi coupling, Kumada coupling and Suzuki coupling etc⁷⁷.

Before the advent of Pd and other transition metal catalyst, cross coupling reactions were limited involving usually Grignard reagents and organo alkali species. These strong nucleophiles were good to react with unhindered sp^3 carbons but not for unsaturated sp^2 electrophiles. This problem was solved in 1970s by the discovery of organometallic catalyzed cross coupling reactions using a number of substrates with efficiency and high turnover number⁷⁸. These transition metal catalysts have the ability to activate C_{sp^2} -halogen bond. Since then the cross coupling reactions of organic halides and other electrophiles using organometallic reagents are well-known and among the few methods of C-C bond formation^{78, 79}.

In 1972, Kumada *et al.* succeeded in coupling alkenyl halide and aryl with Grignard reagent using nickel phosphine reagents⁷⁹. After this, series of synthetic methodologies were developed and named after the scientists. The use of Cu-alkenyl derivatives generated *in situ* paved a path for Pd-catalyzed C_{sp} nucleophiles and is known as Sonogashira Coupling^{78, 79}.

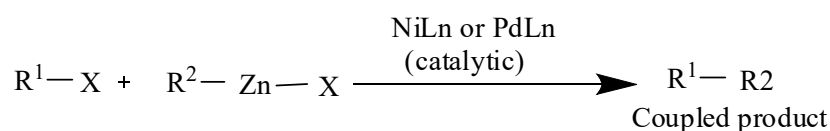
For functional group tolerance and compatibility, less nucleophilic yet reactive organozinc reagents were used in Negishi Coupling⁸⁰. The other important substrates include organostannanes in Stille coupling and organo-boranes in Suzuki coupling. All these coupling reactions are either catalyzed by Pd or Ni catalysts and the outcomes are different depending upon the catalyst activity⁷⁸⁻⁸⁰.

Palladium remains the catalyst of choice for cross coupling reaction, the main reason to replace it with other metals was its cost. Ni catalysts are less expensive than Pd catalyst. Ni catalysts also being more nucleophilic have higher activity and its functional group tolerance welcomes a number of substrates for coupling⁸⁰.

1.2.4.1 Negishi Coupling

Negishi Coupling (Scheme 1.4), published in 1977, is versatile nickel or palladium catalyzed coupling of organozinc compounds with various halides⁷⁹ (Scheme 1.4). Negishi *et al.* have reported the aryl-aryl coupling following a synthetic route that gives chemo as well as regioselectivity. Nickel-triphenyl phosphine ($\text{Ni}(\text{PPh}_3)_4$) was produced *in situ* using nickel acetylacetonate ($\text{Ni}(\text{acac})_2$), triphenyl phosphino propane (PPh_3) and diisobutylaluminium hydride ($i\text{-Bu}$)₂AlH. These reactions occur smoothly at lower temperature and result in higher yields. The aryl-aryl coupling is an attractive target for applications ranging from liquid crystals to pharmaceuticals hence they can be seen in use in industrial chemistry on high scale⁷⁸.

For aryl-alkyl coupling, Pd catalysis was employed between organohalides and pseudohalides. In 1988, Giovannini and Knochel developed Ni based alkyl-aryl coupling between arylzinc bromides and poly-functional alkyl iodides using 10% of $\text{Ni}(\text{acac})_2$ and 4-(trifluoromethyl) styrene in THF-NMP⁷⁹.



Scheme 1.4 Negishi coupling reaction⁷⁹

1.2.4.2 Cyclic mechanism

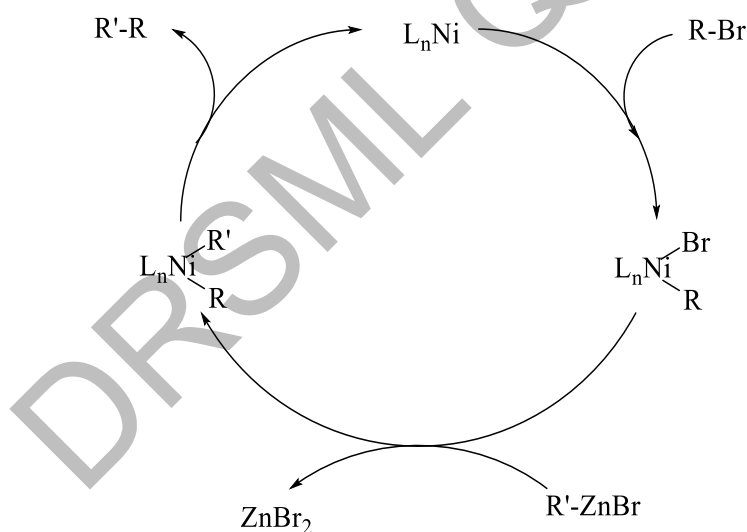
The mechanism of transition metal catalyzed cross coupling reactions is usually same in all cross coupling reactions. It involves three steps⁷⁹ (Scheme 1.5)

1) Oxidative addition – it involves the addition of organohalide to a low valent metal catalyst oxidatively giving an organo-metallic derivative with higher oxidation state of metal centre.

2) Transmetalation – in this step transmetalation of nucleophilic carbon takes place to the transition metal complex giving a diorgano metal specie.

3) Reductive elimination – carbon-carbon bond is formed and catalytic active specie is regenerated.

All these steps are essential for the cyclic mechanism of cross coupling reactions.



Scheme 1.5 Cyclic mechanism of Negishi coupling⁷⁹

1.2.4.3 Applications of Negishi coupling

Long ago, carbon carbon bond formation was thought to be a difficult task. There was no direct reaction ever discovered for C-C bond formation. This hindered the manufacturing of many simple and complex compounds which today are being synthesized on everyday basis and have applications in different areas. As soon as the first coupling reaction went successful, chemists entered into a never ending race to achieve the best possible combinations of substrate, counter halide, catalyst as well as ligand. This paved the path for

the synthesis of drugs people use today in their daily lives. The coupling reactions produce various coupled products like aryl-aryl, alky-aryl, or alkyl-alkyl^{78,79}.

Negishi coupling covers a wide range of industrial applications since the time of its invention. These coupling reactions have been the source of synthesis of a number of drugs on commercial scale^{81,82}. Talking about the synthetic applications of Negishi coupling, it is used where the two compounds are to be linked through carbon-carbon bond formation. There are a number of examples in which Negishi coupling is employed at one or more steps of total synthesis of drugs for industrial use⁸¹⁻⁸⁶. Some of the alkaloids and drugs which are formed through this coupling in their synthetic routes are shown in Figure 1.7.

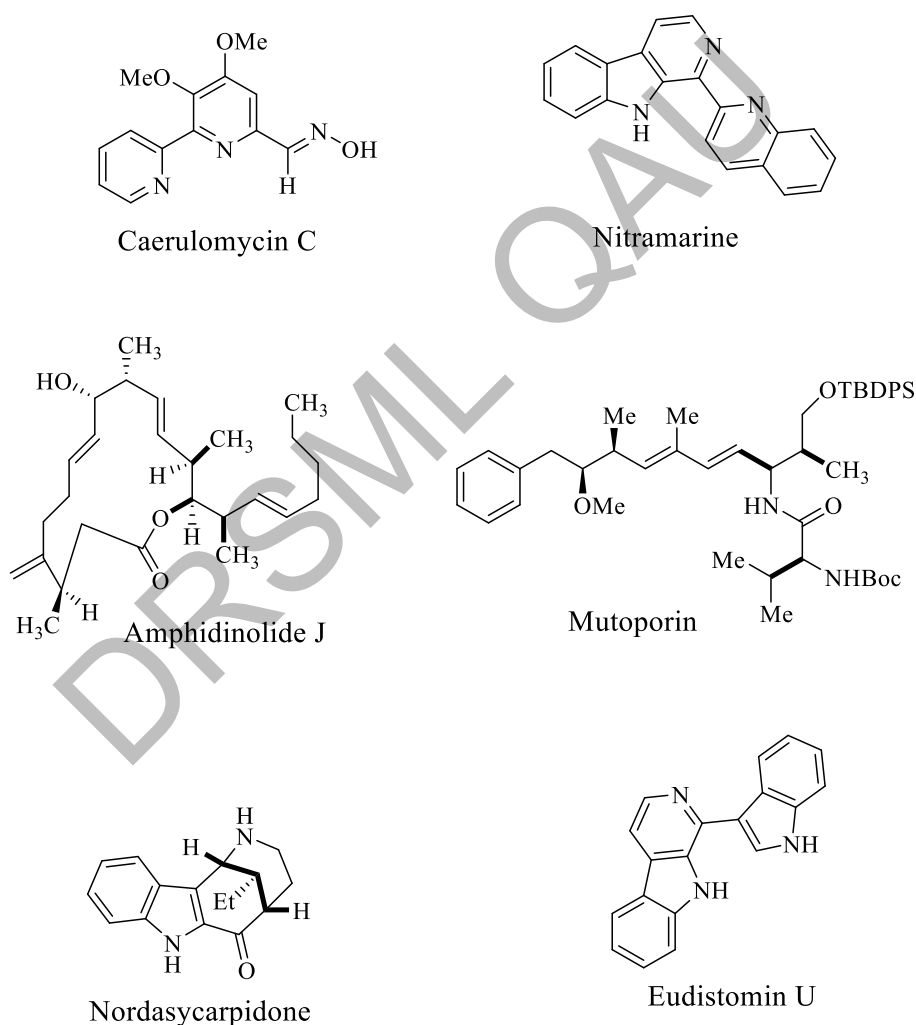


Figure 1.7 Synthetic applications of Negishi Coupling

1.2.4.4 Advantages of Negishi coupling over other coupling reactions

There are various cross coupling reactions for carbon-carbon bond formation. Negishi coupling has some advantages over Kumada, Suzuki, or Stille coupling. Organozinc halide is stable compared to other substrates. For example, Grignard reagent is not only difficult to synthesize but also being highly reactive and it has handling issues. Organozinc reagents are less expensive compared to stannanes. These reagents are less nucleophilic than Grignard reagents but are reactive to a limit which is required for the reaction, hence they do not attack on other electrophilic centre present in the counter substrate. This reaction possesses high functional group tolerance so are used in synthesis involving poly-functional compounds. The turn over number of organozinc substrates is high and give products in good yield. This reaction impose no impact on environment and are considered as friendly substrate for coupling reactions unlike tin reagents, organozinc also possesses a reasonable reactivity and activity towards electrophiles and the reaction time is less^{78-80, 87}.

1.3: Recent literature work on thiophene based materials

A brief review of literature related to the work in this study is presented herein;

In the last few years, thiophene based materials have become an important field of research because of their applications in semi-conductors, opto-electronic devices, fluorescent studies and selective detection of biopolymers⁴⁵.

Thiophene is among those heterocyclic compounds which are mostly studied as it is cheap, stable, processable and its synthetic applications have touched a number of important industries⁴⁵. The interest in thiophene started from the time it brightened the dye chemistry to drug design and now its tremendous performance in electronic and opto-electronic devices⁸⁸⁻⁹⁰.

Chemistry of thiophene is so versatile that its structure can be functionalized in a number of ways whether on alpha or beta positions of thiophene or on sulphur itself⁹¹. This strategy has been in use to prepare various regioregular oligomers or polymers with different functionalization⁹². The reason why thiophene is in continuous creation today in new forms is that its compounds provide fine tunable properties, and structure-property relationship varies greatly.

Because of various attractive features polythiophene is widely used in optoelectronic devices, these features include mechanical flexibility, less cost, excellent solubility, good film forming

property, high photoluminescent quantum yield and good stability (thermal and chemical) of polythiophenes. The most exploited reaction for the synthesis of these combination products has always been the Pd or Ni catalyzed coupling of halogenated thienyls substrates with metalated counterparts⁹³. In the last few years, new thiophene based materials such as thiophene-fluorene co-oligomers, fluorocarbon-substituted oligothiophene and alike polymers have been synthesized⁹⁴. Improved yields and high purity have been achieved using microwave-assisted methodologies which not only take less reaction time but also prevent the formation of undesirable by-products⁹⁵. Such a rate accelerated MW-assisted reaction was observed by Nehls *et al.* in the preparation of fluorine-bithiophene via Suzuki and Stille type reactions⁹⁶.

To obtain highly organized thin films many new thiophene oligomers have been synthesized for solution-processing deposition techniques. Murphy *et al.* reported the synthesis of soluble sexithiophene and casted it into thin films at room temperature⁹⁷. Another class of ruthenium based oligothiophenylacetylide was reported by Fillaut with high third-order optical properties tunable by changing the size of oligomers⁹⁸.

Improvements in terms of molecular weights and polydispersities were reported by Yokoyama *et al.* with synthesis of Ni-catalyzed polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene via chain growth mechanism and controlling the molecular weights by feed ratio of monomer to Ni catalysts⁹⁹.

Using the Stille coupling, Xia *et al.* prepared the dendrimers and dendrons of thiophene to study the self-organizing properties on different substrates which showed that they have ability to form nanostructures on surfaces and a great potential for opto-electronic devices¹⁰⁰. Calixarene quarter-thiophene based highly conductive polymer (on protonation) was synthesized by Yu *et al.*¹⁰¹.

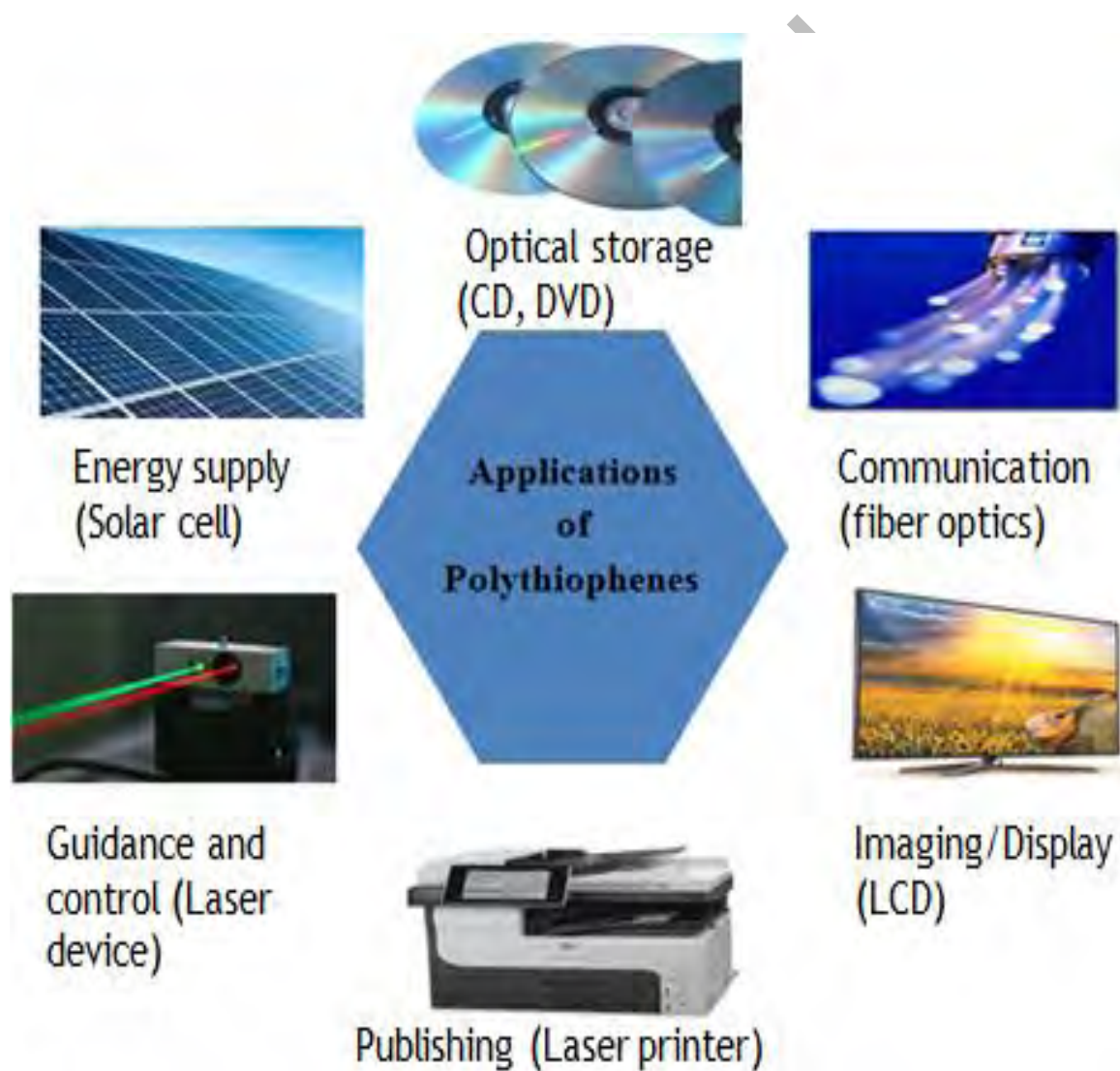
Thiophene derivatives give rise to polymorphism that is they are packed into different shapes in solid forms and can be characterized by electrical properties¹⁰². Block copolymers containing thiophene moieties have different morphologies e.g. lamellar, spherical, cylindrical¹⁰³. Large vesicles in this field have recently been synthesized having rod like copolymers of substituted thiophene and styrene¹⁰⁴.

Advances in the field of organic electronics have also been made through thiophene as semiconductors in field effect transistors FETs, lasers, photovoltaics and electrochromic devices and their remarkable performance in electronic devices¹⁰⁵. Morphology of the active

material is an important factor for the effective working of material and researchers are aware of the fact that morphology plays a key role in device performance.

Synthesis of light emitting devices made of organic and organometallic active materials is under progress, some commercial applications have been developed and many industries see a great potential in these devices for more applications¹⁰⁶.

This does not end here, infact there is a long list of developments and applications regarding thiophene materials which is in continuation and will bring a lot of advancements in organic electronics in the coming years.



1.4: Functionalization

Structural diversity of PTs is vast due to the number of possibilities of variations e.g. fused thiophenes, polymer composites, thiophene-metal composites, copolymers, poly-2,5-disubstitution, poly-3-substituted thiophene, poly-3,4-disubstituted thiophenes and then variation in the functional groups at these positions¹⁰⁷. Functional groups include alkyl chain, aryl group, electron donating or electron withdrawing groups etc. This modification of monomer requires the incorporation of a group which when couples to conjugated π -system does not affect the polymerization and π -system must also be conserved to show the same or even better electrical, optical and thermal properties. Among these the most studied poly-substituted thiophene is poly-3-methylthiophene^{60, 107}.

Functionalized polythiophenes are widely studied polymers. Processability of pure polythiophene is difficult that can be improved by adding different groups that results in increase of stability, easy processability and produce excellent optical properties¹⁰⁸.

1.5: Scope and objectives of work

It is concluded from the above cited literature review that thiophene based oligomers and polymers are extensively being studied for opto-electronic applications. Mostly thiophene based conjugated polymers are synthesized by coupling reactions till now.

Keeping this in view, this work was designed to combine the electron withdrawing ester and amide groups with long alkyl chain and study of its effect on opto-electronic properties of polythiophene. A systematic approach was considered to incorporate ester and amide functionality at position 3 of thiophene ring for investigating its thermal and electrical properties.

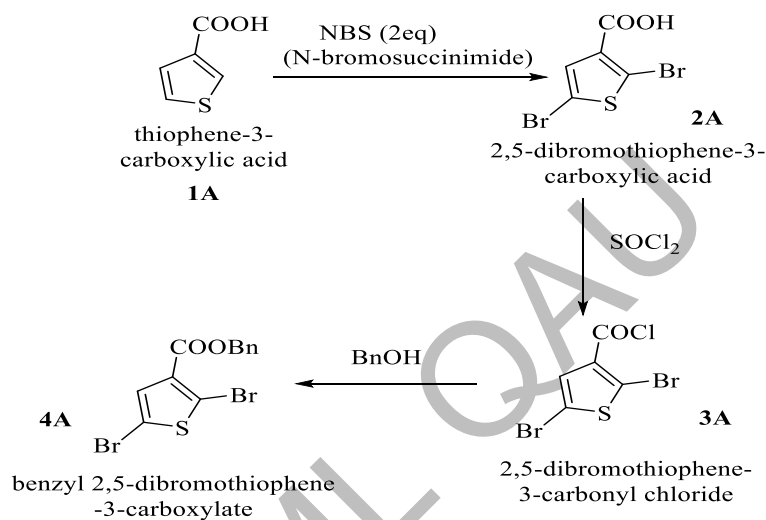
In this work, a new coupling route was employed to synthesize polythiophene and to appreciate this coupling over others in terms of less reaction time, stability and functional group tolerance.

1.6: Plan of Work

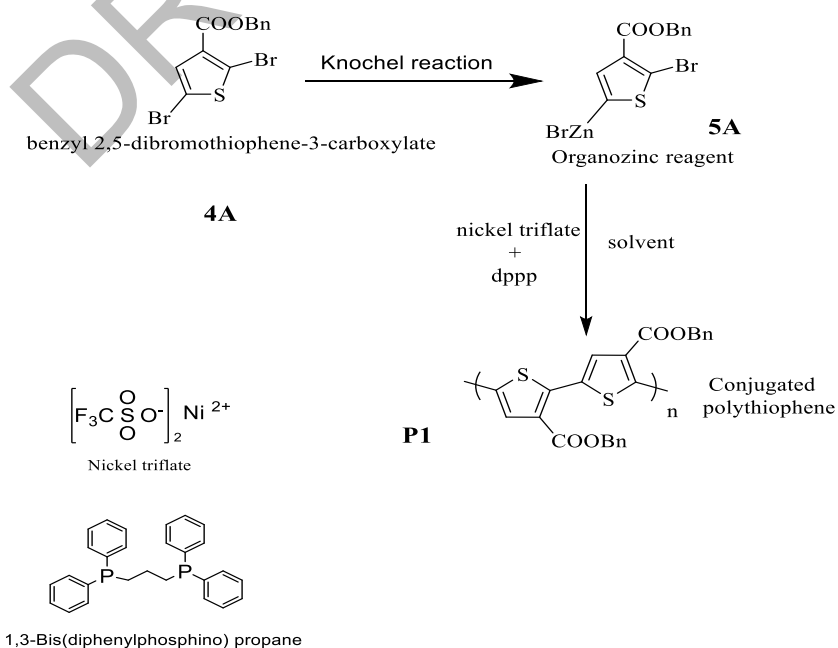
The present work was proposed to be done in two schemes;

1.6.1 Synthesis of Ester Functionalized Polythiophene (Scheme 1)

For the synthesis of dibromo precursor for polythiophene scheme 1.6 (a) was followed. Scheme 1.6 (b) shows the synthetic route for the Negishi coupling mediated self-polymerization of this monomer to form polymer P1.



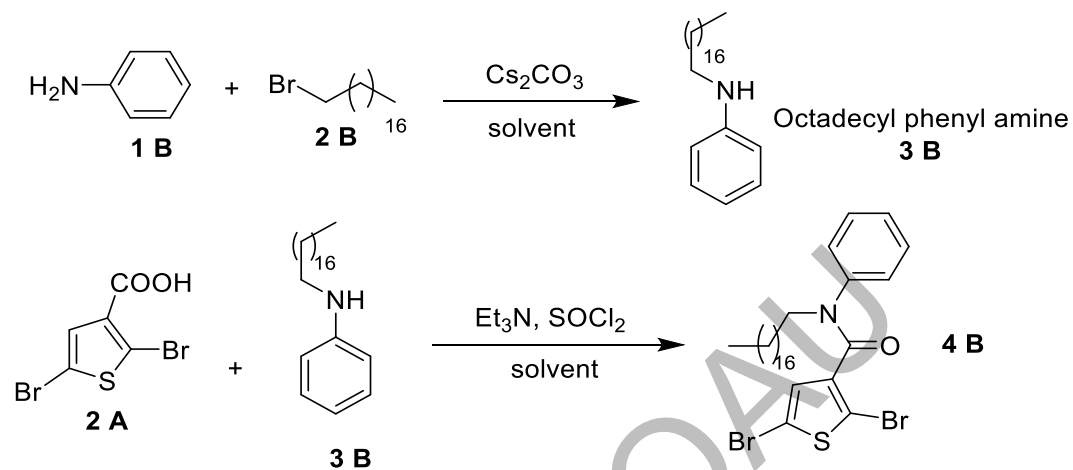
Scheme 1.6 (a) Synthesis of dibromo precursor (4A)



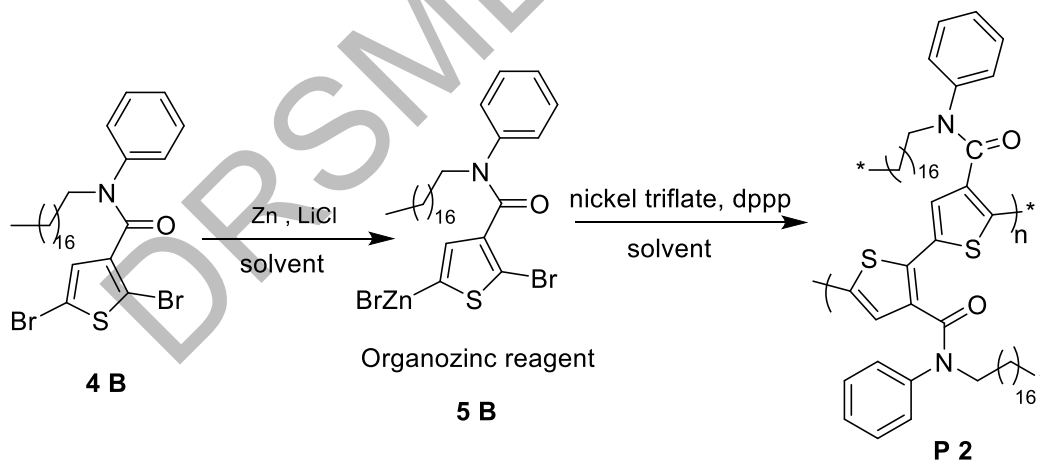
Scheme 1.6 (b) Negishi coupling mediated polymerization of 4

1.6.2 Synthesis of Amide Functionalized Polythiophene (Scheme 2)

Synthesis of amide functionalized polythiophene was also completed in two schemes. In scheme 1.7 (a) dibromoprecursor having amide functionality at position 3 of thiophene was synthesized followed by scheme 1.7 (b) where this dibromo compound undergoes Negishi mediated self polymerization to form polymer P2.



Scheme 1.7(a) Synthesis of dibromo precursor (4B)



Scheme 1.7(b) Negishi coupling mediated polymerization of 4B

Chapter 2
Experimental

DRSML QAU

The details for all kind of material used, procedure followed in order to synthesize the monomers (3-substituted thiophene) and polythiophenes are mentioned under this chapter.

2.1 Materials

All the chemicals and solvents used were of analytical grade, unless otherwise mentioned. The chemicals were purchased from various suppliers such as TCI-America, Fisher Scientific, Sigma-Aldrich, Fluka or Merck. These chemicals include benzyl alcohol (99%), 1-bromooctadecane (98%), triethyl amine (99%), aniline (98%), thiophene-3-carboxylic acid (99%), *N*-bromosuccinimide, thionyl chloride (99%), diphenyl phosphine propane (99%), nickel trifluoro methyl sulphonate (96%) and zinc powder.

Analytical grade solvents including ethyl acetate(99%), ethanol(>99.5%), *N,N*-dimethylformamide(DMF, 99.8%), *N*-methyl-2-pyrrolidone(NMP, 99%), Dichlorormethane (99%), dimethyl sulfoxide(DMSO, > 99.5%) , tetrahydrofuran(THF, 99.5%) and methanol(99%) were procured from Sigma-Aldrich and Fluka. Silica gel (230-400 mesh, grade 60) was utilized for the purification compounds.

2.2: Purifications of solvents

All solvents were dried and purified using standard distillation procedures¹⁰⁹. A short rundown of the approaches used is provided below;

- a) **Ethanol (EtOH)** (boiling point 78 °C) ethanol was refluxed for three hours with CaO for drying, it was distilled, and then preserved over molecular sieves.
- b) **n-hexane:** (boiling point 69 °C) n-hexane was stirred overnight in the presence of CaH₂ for drying purpose, distilled, and saved using a molecular sieve.
- c) **Ethyl acetate(EtOAc)** (boiling point 77 °C) was stirred for 24 hours in the presence of CaH₂ as drying agent before being distilled and saved using molecular sieves.
- d) **Triethylamine(Et₃N)** (boiling point 88 °C) was refluxed in the presence of KOH, distilled, and preserved using molecular sieves.

e) **Tetrahydrofuran (THF)** (b.p. 65 °C) was dried overnight by using CaH₂ as a drying agent. The mixture was then refluxed with sodium metal wires and benzophenone until the blue colour appeared. Following that, it was distilled.

f) ***N,N*-Dimethylformamide (DMF)** (b.p 153 °C) was dried using CaH₂ and stirred overnight before being distilled under vacuum and stored over molecular sieves.

2.3 Characterization techniques

Following analytical techniques were used to determine the structures of the synthesized compounds.

2.3.1 Thin layer chromatography (TLC)

Thin layer chromatography (TLC) was utilized to monitor the progress of various reactions and components present in the reaction mixture. Aluminum TLC plate, silica gel coated with fluorescent indicator F254 (E Merck), having 0.2 mm thickness were used for this purpose.

Following solvent systems in various ratios were used in the development of the chromatograms.

n-Hexane : ethyl acetate (1:1)

n-Hexane : ethyl acetate (9:1)

n-Hexane : ethyl acetate (8:2)

2.3.2 Column chromatography

The synthesized compounds were purified by employing column chromatography using silica gel (230-400 mesh, grade 60 Å) as the stationary phase and different ratios of n-hexane:ethyl acetate as mobile phase.

2.3.3 Melting point

Melting points of the synthesized compounds were determined in an open end capillary tube using Stuart SMP30 apparatus.

2.3.4. Powder X-ray Diffraction (XRD)

The X-ray diffraction technique is used to study the crystalline phases of sample materials. This analytical technique examines the phases of crystalline materials by using X-rays that are scattered at a specific angle from planes of atoms in a sample. It contains information about the unit cell. XRD spectra were obtained from 5^oC to 90^oC using Cu-K(alpha) radiation and an X-ray diffraction spectrometer. The samples for analysis are finely divided powder, but the sample surface is sufficient for determining diffraction. Hence, this technique was used to confirm the nature of polythiophenes i.e., whether these are of crystalline or amorphous nature. The Xpert PRO device was utilized to perform X-ray diffraction studies using Cu K(alpha) radiations at ambient temperature. The recording angle for XRD was $\theta=20-80^{\circ}$.

2.3.5 Ultraviolet-visible absorption spectroscopy

The UV-visible spectra of all synthesized compounds were obtained using a double beam Shimadzu UV-visible spectrophotometer equipped with a halogen lamp as a radiation source and a wavelength range of (200 nm-800 nm). To record the spectra, solutions of different molarity were prepared in CHCl₃ as solvent. The solution was collected in a quartz cell with a 1 cm path length. The energy gap was calculated from the UV-vis spectrum by using the following equation 2.1 (Planck's equation).

$$E = hc/\lambda \quad \text{Eq. 2.1}$$

E= Energy, h= Planck's constant, c=speed of light, λ =wavelength

2.3.6 Nuclear magnetic resonance spectroscopy

All the NMR spectra were recorded under ambient conditions. Bruker (300MHz) spectrometer was used to measure the ¹H-NMR and ¹³C-NMR spectra using deuterated chloroform and TMS (trimethyl silane) as an internal reference.

2.3.7 GC-MS analysis

GC-MS analysis of compounds was carried out for molecular mass determination. Analyses were performed using Agilent technologies GC-MS instrument (model number 6890N). Samples were passed through capillary column (Agilent JW Scientific DB-5MS) with film thickness of 0.25 μ m and an internal diameter of 30 m x 0.25 mm.

Stationary phase employed in column was molten silica packed with 5 % phenyl methyl polysiloxane. Splitless capillary inlet was used for manual injection (5 μL) of the sample at a pressure of 60-85 *psi*. The carrier gas (Helium) had a flow rate of 1.5 mL/min. The temperature of 120 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ was maintained during analyses with a gradual increase of 10 $^{\circ}\text{C}/\text{min}$ and run time for each analysis was 16 minutes. Molecular weight range was 50-800 *a.m.u.* Electron impact ionization mode was employed and 70 eV electron beam was used to produce 0-315 μA ionization current.

2.3.8: Differential scanning calorimetry (DSC)

The Mettler 823e DSC equipment was used for differential scanning calorimetry. Under inert atmosphere, the heat rate of sample was from -80 $^{\circ}\text{C}$ to 0 $^{\circ}\text{C}$ at a scan rate of 10 $^{\circ}\text{C}$ per min.

2.3.9: Photoluminescence spectroscopy (PL)

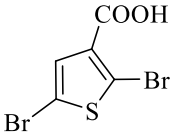
PL was performed at various excitation wavelengths using an F-7000 FL spectrophotometer. The emission wavelength spanned from 200 nm to 900 nm, with a scan rate of 1200 nm/min.

2.4 Synthesis of Ester Functionalized Polythiophene(Scheme 1)

In this study, poly-3-benzyl carboxylate thiophene was synthesized via Negishi coupling mediated polymerization for the first time.

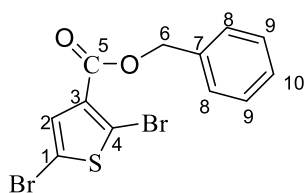
Polythiophene was synthesized in four steps. These steps include bromination of thiophene-3-carboxylic acid (2A), esterification to obtain benzyl ester (4A), organozinc halide formation (5A) and then coupling mediated self polymerization to form polymer P1.

2.4.1 Synthesis of 2,5-dibromothiophene-3-carboxylic acid (2A)

 In a 250 mL round bottom flask, 15.6 mmol (2.78 g) of *N*-bromosuccinimide was added in 10 mL of DMF in a moisture free environment. This solution was stirred for 30 minutes to dissolve NBS completely. To this, a solution of 7.80 mmol (1 g) thiophene-3-carboxylic acid in 5 mL of DMF was added drop wise at room temperature. The mixture was left on stirring at 60 $^{\circ}\text{C}$ overnight. After the completion of reaction, the mixture was extracted with aqueous

solution of sodium bicarbonate (3×30 mL) and chloroform. Now the product was in aqueous layer in the form of salt and this layer (pH=9) was acidified by adding dilute HCl and by continuously shaking. Filtration was carried out and product was washed with water thoroughly. White crystals were collected after drying. $R_f = 0.21$ in n-hexane and ethyl acetate (9:1). Yield: 86 %, m.p.: 175-178 °C (reported 177-180 °C).

2.4.2 Synthesis of benzyl 2,5-dibromothiophene-3-carboxylate (4A)



Dibromo acid (2A) was first converted to acid chloride (3A) by reaction of acid with thionyl chloride, which was then treated with benzyl alcohol to produce ester (4A). In a two neck round bottom flask 3.49 mmol (1 g) of 2A was taken in an inert atmosphere of nitrogen. Then, 8.7 mmol (1.04 g, 0.6 mL) of thionyl chloride was added drop wise carefully. This mixture was left on stirring at 60 °C for one hour. After 1 hour excess of thionyl chloride was removed by distillation. Afterwards, 4.37 mmol (0.47 g, 0.4 mL) of benzyl alcohol was added followed by 2 drops of pyridine and stirred for 24 hours at 120 °C. After the completion of reaction mixture was extracted with aq. NaHCO₃ and EtOAc. The organic layer containing product was dried with anhydrous sodium sulphate and then concentrated on vacuum evaporator. Brown oil obtained, which was then purified by column chromatography.

Physical appearance: Brown oil

$R_f = 0.65$ (mobile phase n-hexane: EtOAc (9:1))

Yield: 71 %,

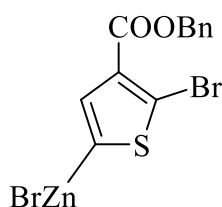
B.p.: 175-180 °C

¹H-NMR (CDCl₃): δ (ppm) = 7.37-7.48 (m, 6H, 2, 8, 8, 9, 9, 10) and 4.6 (s, 2H, 6).

¹³C-NMR (CDCl₃), δ (ppm) = 162 (5), 139 (7), 126-129 (2, 8, 9, 10), 132 (3), 123 (4), 121 (1), 66 (6).

GC-MS: molecular ion peak M⁺ (m/z = 376), base peak (m/z = 91).

2.4.3 Synthesis of organozinc bromide substrate (5A)



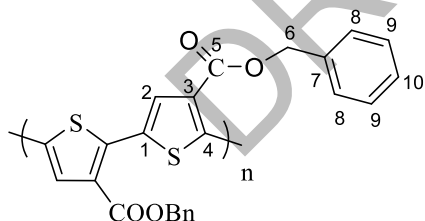
The glass apparatus i.e. flask and stoppers were dried on flame. The zinc powder was activated in a two neck flask using 8.5 mmol (360 mg) of LiCl in a solution of 8.5 mmol (555 mg) of zinc in 5 mL of

THF in a completely dry, inert atmosphere under vacuum at 140 °C for 2-3 hours. Afterwards, the mixture was cooled to room temperature and 0.21 mmol (39.9 mg, 18.39 μL) of 1,2-dibromoethane was added and the reaction mixture was heated at 60 °C for 20 minutes. Cooled to room temperature and 0.0425 mmol (4.6 mg, 5.3 μL) of TMSCl was added via syringe, followed by the addition of 5 drops of 1M iodine solution, reaction mixture was heated at 60 °C for 20 minutes. Cooled to room temperature. To this mixture, 4.25 mmol (1.6 g) of substrate (4A) was added carefully. The mixture was allowed to stir at 50 °C for 24 hours in N_2 atmosphere. Cooled to room temperature. Reaction mixture was allowed to stand for 24 hours without stirring. Blackish grey colour indicated that activation was successful.

Formation of organozinc was confirmed by titration using iodine solution, where 10 mL round bottom flask was equipped with magnetic stirrer. Flask was heated at reduced pressure and cooled to room temperature under argon atmosphere. 1 mmol (254 mg) of iodine was added in same flask, fitted with septum and flushed with argon.

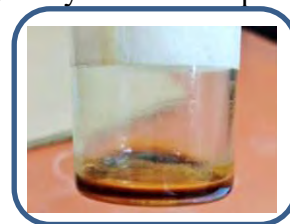
Saturated solution of LiCl in THF (3-5 mL) was added and reaction mixture was allowed to stir until iodine completely dissolved. Brown solution of iodine was cooled to 0 °C in ice bath, organozinc was added dropwise via 1 mL syringe. Brown colour of iodine disappeared which confirmed the formation of organozinc.

2.4.4 Synthesis of polythiophene (P1) via Negishi coupling



In a 25 mL one neck round bottom flask, 0.12 mmol (42.8 mg) of nickel trifluoromethane sulfonate (catalyst) and 0.12 mmol (65 mg) of diphenyl phosphino propane (dppp) ligand were added in 3-5 mL of THF under dry conditions. This reaction mixture was cooled to -20 °C and stirred for 15 minutes in nitrogen atmosphere. From the mixture of Negishi substrate (5A), 2.4 mmol (3 mL, 1 M) was added in the reaction mixture. After 24 hours of stirring at room temperature, 2 mL dilute HCl was added in the mixture and then extracted in water using chloroform. The organic layer was dried

using anhydrous sodium sulphate and concentrated on rotary to yield brown paste.



Polymer was found soluble in common organic solvents like;

THF, CHCl₃, DMSO and MeOH

¹H-NMR (CDCl₃): δ (ppm) = 7.11-8.17 (m, 6H, 2,8,9,10), 4.72 and 5.35 each for (s, 2H, 6).

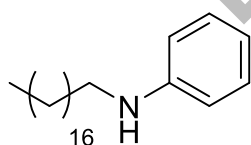
¹³C-NMR (CDCl₃), δ (ppm) = 162 (5), 126-140 (1, 2, 3, 4, 7, 8, 9, 10), 66, 65 (6).

2.5 Synthesis of Amide Functionalized Polythiophene (Scheme 2)

In this scheme, amide functionalized polythiophene having long 18 carbon alkyl chain was synthesized. Poly-3-thiophene-octadecyl phenyl carboxamide was synthesized via Negishi coupling mediated polymerization for the first time.

Polythiophene was synthesized in five steps. These steps include conversion of primary amine to secondary amine (3B), bromination of thiophene-3-carboxylic acid (2A), and amide bond formation to synthesized long chain carboxamide (4B), organozinc halide formation (5B) via Knochel reaction and then Negishi coupling mediated self polymerization to synthesize final polymer P2.

2.5.1 Synthesis of octadecyl phenyl amine (3B)



In a 250 mL round bottom flask, 6 mmol (1.94 g) of Cs₂CO₃ and 12 mmol (1000 mg, 1 mL) of aniline was added. To this mixture 15 mL of anhydrous DMF was added, and stirred at 25 °C for 30 minutes. White suspension was formed to which 6 mmol (2 mL) of 1-bromooctadecane was added. Reaction mixture was allowed to stir at 80-90 °C for 5-12 hours. Afterwards mixture was filtered and rinsed with EtOAc.

Filtrate was then taken into 1N NaOH (2x10ml) and extracted with EtOAc (4x10ml). Organic layer was washed by using brine (2x10ml), dried with anhydrous sod.sulphate, filtered and concentrated to give crude products.

Product was purified by column chromatography.

$R_f = 0.5$ (mobile phase= n-hexane:EtOAc 9:1)

Appearance: White powder

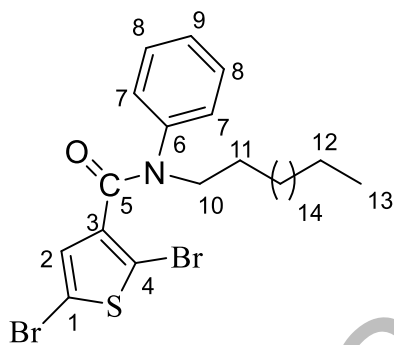
Yield: 70 %,

m.p.: 55-57 °C (reported 54-60 °C).

2.5.2 Synthesis of 2,5-dibromothiophene-3-carboxylic acid (2A)

2,5-dibromothiophene-3-carboxylic acid was synthesized by following method described above in section 2.4.1.

2.5.3 Synthesis of 2,5-dibromothiophene-3-octadecyl phenyl carboxamide (4B)



In a 250 mL round bottom flask, 7 mmol (2000 mg) of acid (2A) and 7 mmol (2400 mg) of amine (3B) was added. To this mixture 21 mmol (3 mL) of Et_3N and 25 mL of dry and distilled DCM was added. To the same reaction mixture 7 mmol (6 mL) thionyl chloride and 2 drops of pyridine were added and mixture was allowed to stir at room temperature for 30 minutes. Product was obtained by evaporating solvent at reduced pressure. Residue were taken up in DCM, washed with 1N HCl followed by washing with 1N NaOH. Product obtained was light brown powder.

$R_f = 0.3$ (mobile phase= n-hexane:EtOAc 9:1)

Appearance: Light brown powder

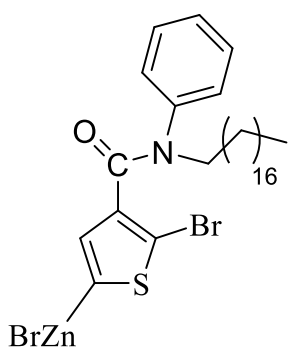
Yield: 72 %,

m.p.: 66-68 °C

$^1\text{H-NMR}$ (CDCl_3): δ (ppm) = 7.12-7.37 (4H, 7, 7, 8, 8), 7.11 (1 H, 2), 6.82 (1 H, 9), 3.87 (2H, 10), 1.65 (2H, 11), 1.27 (30 H, in between position 11 to 13), 0.91 (3H, 13).

$^{13}\text{C-NMR}$ (CDCl_3), δ (ppm) = 163 (5), 119-143 (all aromatic carbon), 50 (10), 31 (11), 26-29 (14 carbon of long alkyl chain), 22 (12), 14 (13).

2.5.4 Synthesis of organozinc bromide substrate (5B)

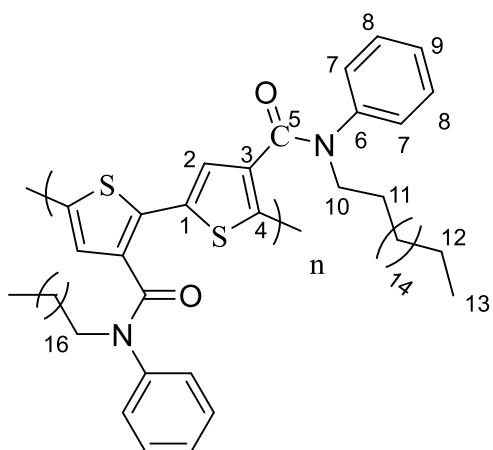


The glass apparatus i.e. flask and stoppers were dried in flame. The zinc powder was activated in a two neck flask using 8.5 mmol (354 mg) of LiCl in a solution of 8.5 mmol (546 mg) of zinc in 5 mL of THF in a completely dry, inert atmosphere under vacuum at 140 °C for 2-3 hours. Afterwards, the mixture was cooled to room temperature and 0.21 mmol (39.9 mg, 18 μ L) of dibromoethane was added and reaction mixture was heated at 60 °C for 20 minutes. Cooled to room temperature and 0.0425 mmol (4.6 mg, 5.3 μ L) of TMSCl was added via syringe, followed by the addition of 5 drops of 1M iodine solution, reaction mixture was heated at 60 °C for 20 minutes. Cooled to room temperature. To this mixture, 2.61 mmol (1.6 g) of substrate (4B) was added carefully. The mixture was allowed to stir at 50 °C for 24 hours in N₂ atmosphere. Cooled to room temperature. Reaction mixture was allowed to stand for 24 hours without stirring. Blackish grey color indicated that activation was successful.

Formation of organozinc was confirmed by titration using iodine solution, where 10 mL round bottom flask was equipped with magnetic stirrer. Flask was heated at reduced pressure and cooled to room temperature under argon atmosphere. 1 mmol (254 mg) of iodine was added in same flask, fitted with septum and flushed with argon.

Solution of LiCl in THF (3-5 mL) was added and reaction mixture was allowed to stir until iodine completely dissolved. Brown solution of iodine was cooled to 0 °C in ice bath, organozinc was added dropwise via 1 mL syringe. Brown colour of iodine disappeared which confirmed the formation of organozinc.

2.5.5 Synthesis of polythiophene (P2) via Negishi coupling



In a 25 mL one neck round bottom flask, 0.12 mmol (42.8 mg) of nickel trifluoromethane sulfonate (catalyst) and 0.12 mmol (65 mg) of diphenyl phosphine propane (dppp) ligand were added in 3-5 mL of THF under dry conditions. This reaction mixture was cooled to -20 °C and

stirred for 15 minutes in nitrogen atmosphere. From the mixture of Negishi substrate (5A), 2.4 mmol (3 mL, 1 M) was added in the reaction mixture. After 24 hours of stirring at room temperature, 2 mL dilute HCl was added in the mixture and then extracted in water using chloroform. The organic layer was dried using anhydrous sodium sulphate and concentrated on rotary to yield yellow gel.



Polymer P2 was found soluble in common organic solvents like; THF, CHCl₃, DMSO and MeOH

¹H-NMR (CDCl₃): δ (ppm) = 6.68-7.73 (all aromatic proton), 3.88 (4H, 2 H of position 10 of each unit), 1.6 (4 H , 2 H of position 11 of each unit), 1.26 (60H, corresponding to long alkyl chain of polymer), 0.86-0.90 (6 H, 13),.

¹³C-NMR (CDCl₃), δ (ppm) = 163 (C-5), 127-142 (all aromatic carbon), 44 and 50 (C-10), 31 (C-11), 26-29 (14 carbon of long alkyl chain), 22 (C-12), 14 (C-13).

Chapter 3

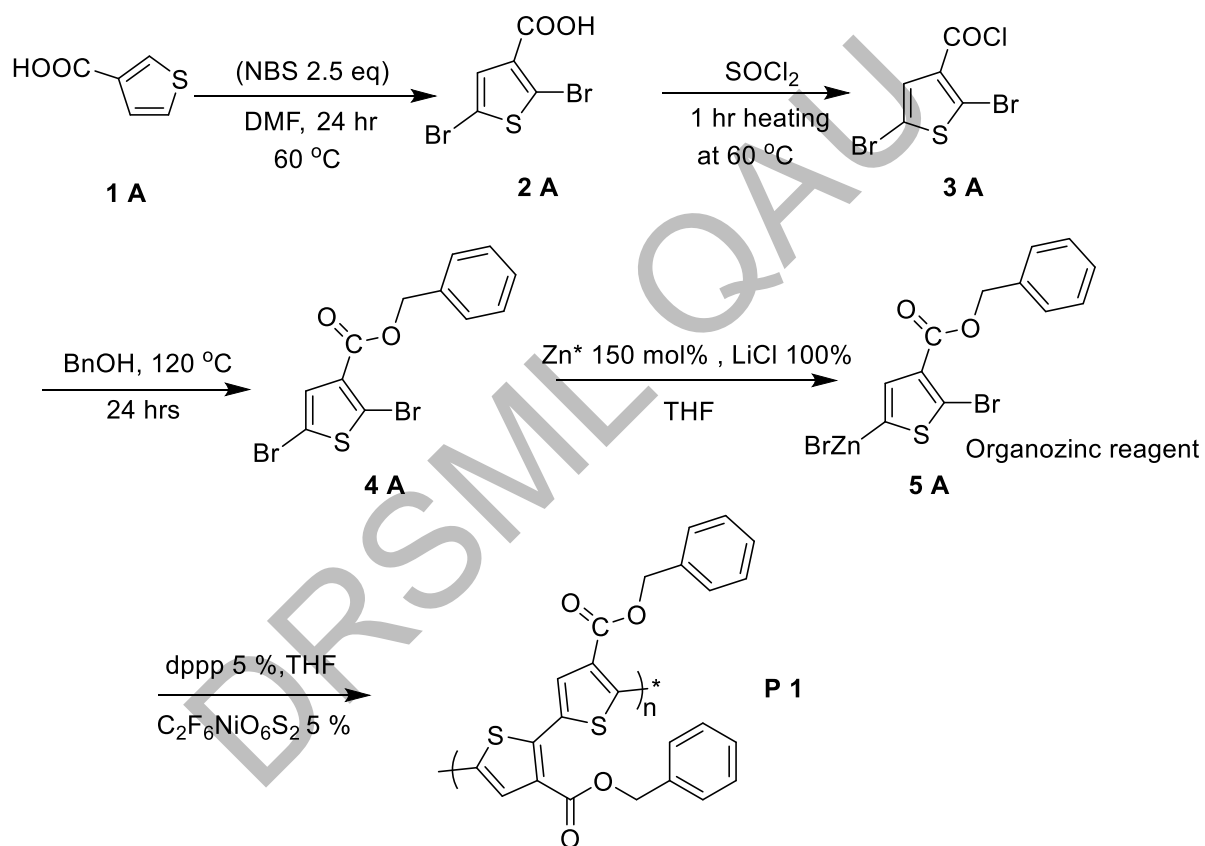
Results and Discussion

DRSML QAU

In this chapter all the results obtained from the characterization of synthesized monomers and polymers are discussed in detail.

3.1 Synthesis of Ester Functionalized Polythiophene (Scheme 1)

This section includes the characterization results of compounds synthesized in schemes 1; i.e. synthesis of thiophene-3-carboxylic acid, its benzyl ester and poly-3-benzyl thiophene carboxylate.



Scheme 3.1 Synthesis of ester functionalized polythiophene

3.1.1 Synthesis of benzyl-2,5-dibromo-thiophene-3-carboxylate (4A)

For Negishi coupling to occur in a single reactant, the compound must have dihalo groups. One of the halogen is first converted into zinc halide reagent which undergoes coupling using a catalyst and ligand. Therefore, thiophene-3-carboxylic acid (1A) was brominated using 2.5 eq of NBS in 10 mL of DMF on stirring at 60 °C overnight. The product was obtained by solvent extraction. White crystals were collected with 86% yield and melting point was observed in the range of 175-178 °C. The dibromo acid (2A) was converted into a benzyl ester (4A) by first reacting it with thionyl chloride which yielded acid chloride (3A). Then, 0.4 mL of benzyl alcohol was added in the mixture and an ester was successfully synthesized. After extracting with aqueous NaHCO₃ and EtOAc, crude product was purified by column chromatography, brown coloured oil was collected in 71% yield and its boiling point was observed in range of 175-180 °C.

The physical data of synthesized compounds is given in table 3.1.

Table 3.1 Physical data of 2A and 4A

Codes	Appearance	Yield %	m.p & b.p (°C)	R _f
2A	White crystals	86	175-178	0.21
4A	Brown oil	71	175-180	0.60

Mobile phase = n-hexane and ethyl acetate (9:1)

3.1.1.1 NMR spectroscopy of monomer (4A)

The ¹H-NMR spectrum of the compound 4A is shown in Figure 3.1, signals in the range of 7.37 ppm-7.48ppm corresponds to six aromatic protons (5 of benzene ring and 1 of thiophene ring) and signal at 4.6 ppm correspond to two methylene proton of benzyl moiety. This confirms the conversion of acid halide into benzyl ester.

Table 3.2 $^1\text{H-NMR}$ spectral data of 4A

Proton Number	Chemical shift δ (ppm)	Multiplicity	Integration
6	4.6	s	2H
2,8,9,10	7.37-7.48	m	6H

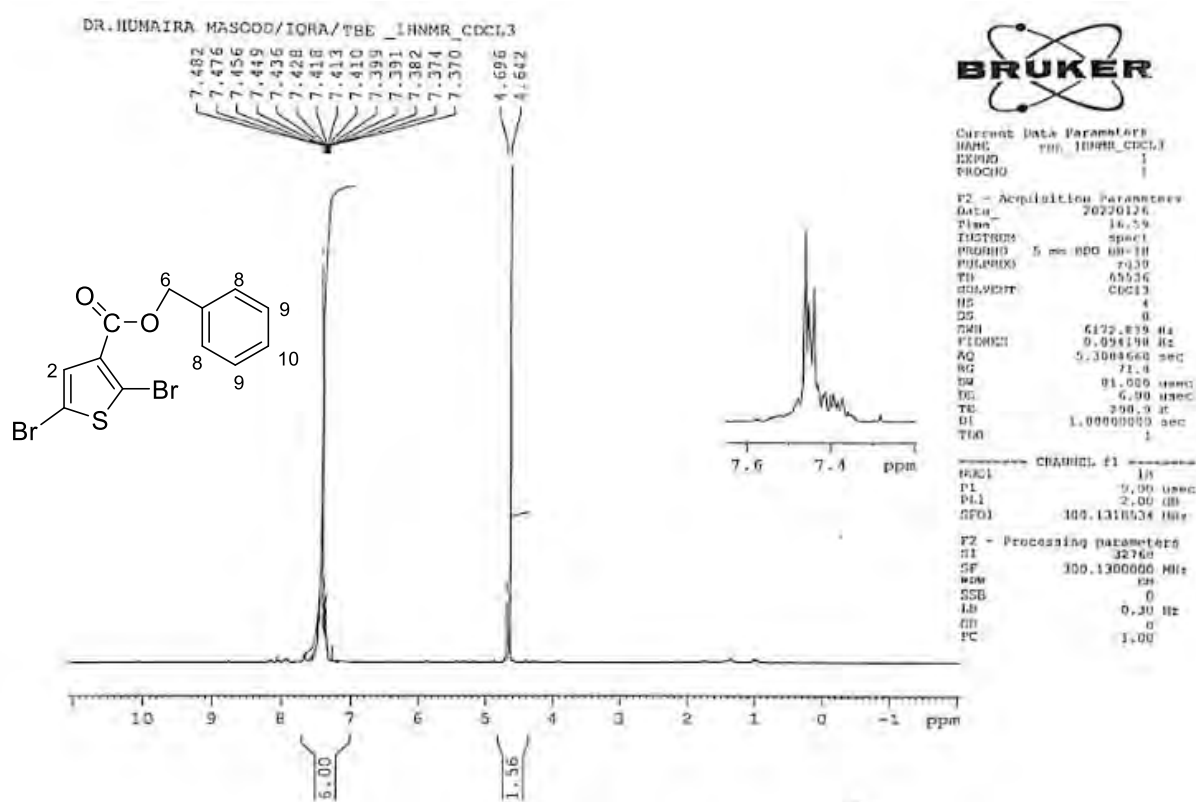


Figure 3.1 $^1\text{H-NMR}$ spectrum of 4A

$^{13}\text{C-NMR}$ spectrum of 4A is shown in figure 3.2, the most deshielded signal at 162 ppm correspond to carbonyl carbon (5) of ester functionality. The signals at 121 ppm and 123 ppm are of C-1 and C-4 of thiophene ring respectively. The signals appeared in the range of 126 ppm to 129 ppm were assigned to four carbons (2, 8, 9, 10). Signal at 132 ppm corresponds to carbon directly attached to carbonyl (3) and signal at 139 ppm is assigned to

ipso carbon (7), signal at 66 ppm in alkyl region is attributed to methylene carbon (6), listed in table 3.3.

Table 3.3 ^{13}C -NMR spectral data of 4A

Carbon no.	Chemical shift δ (ppm)	Carbon no.	Chemical shift δ (ppm)
5	162	4	123
7	139	1	121
3,7,8,9,10	132-126	6	66

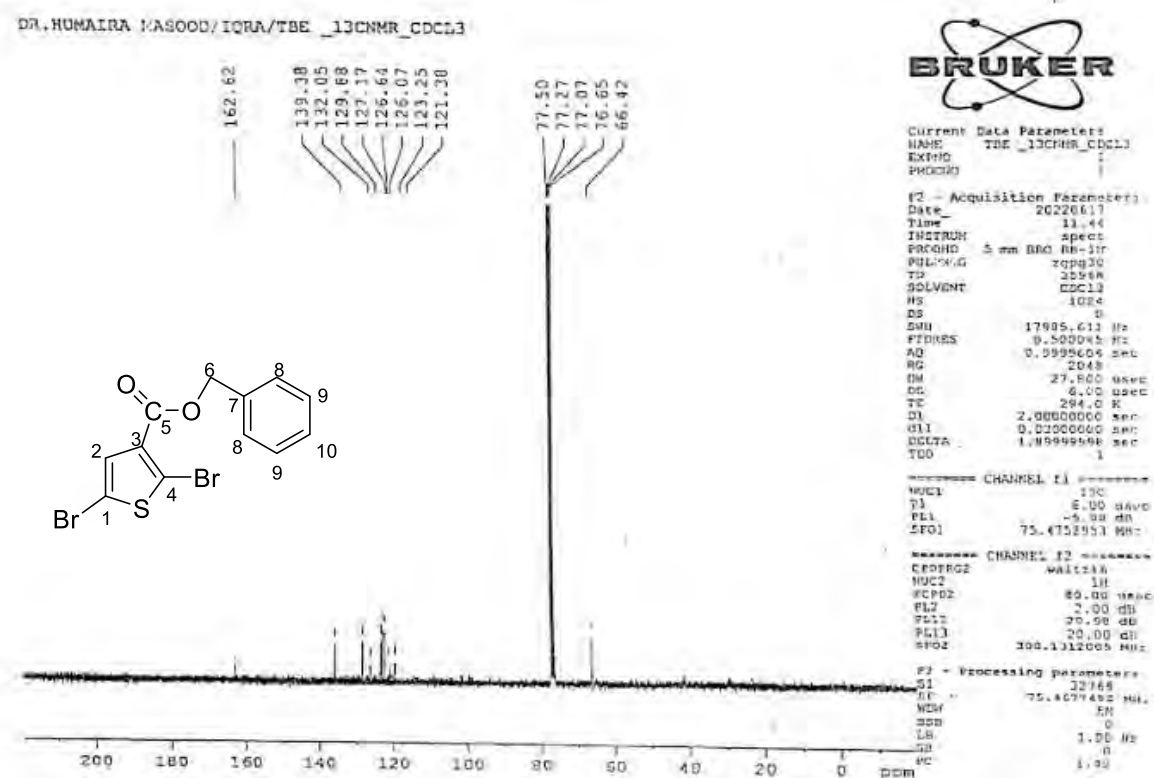


Figure 3.2 ^{13}C -NMR spectrum of 4A

3.1.1.2 GC-MS analysis of monomer (4A)

The GC-MS spectrum of compound 4A is shown in figure 3.3, which confirmed the formation of the product. Scheme 3.1 shows the fragmentation pattern. The TIC profile showed a single peak that confirmed the purity of the product. The molecular ion peak was observed at 376 m/z, equal to the molar mass of compound. The base peak appeared at 91 m/z for the tropylium cation, which is characteristics of benzyl esters. The second peak at 269 m/z appeared as a result of alpha cleavage of carbonyl, shown in scheme. Fragment appeared at m/z 79 and 81 are most likely due to bromo cation.

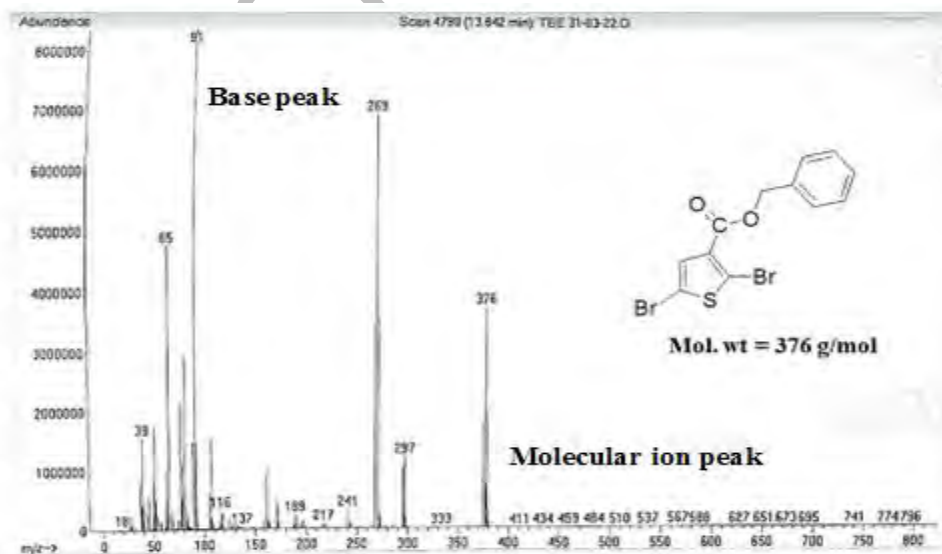
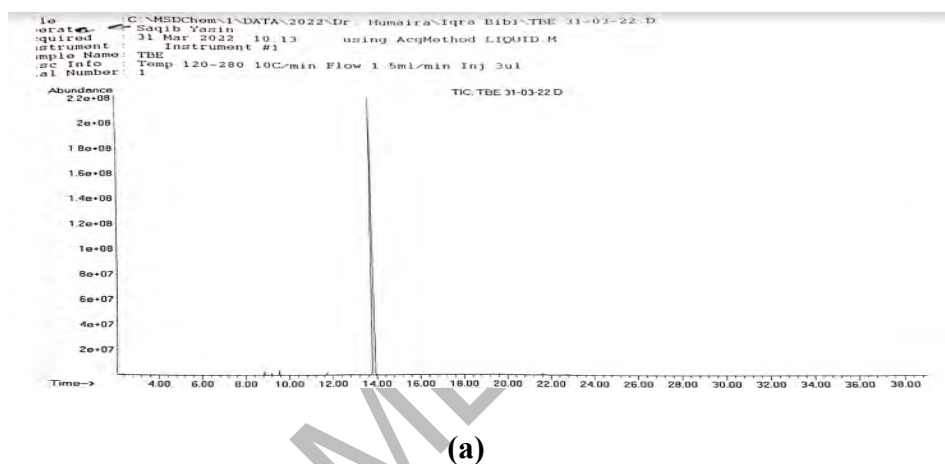
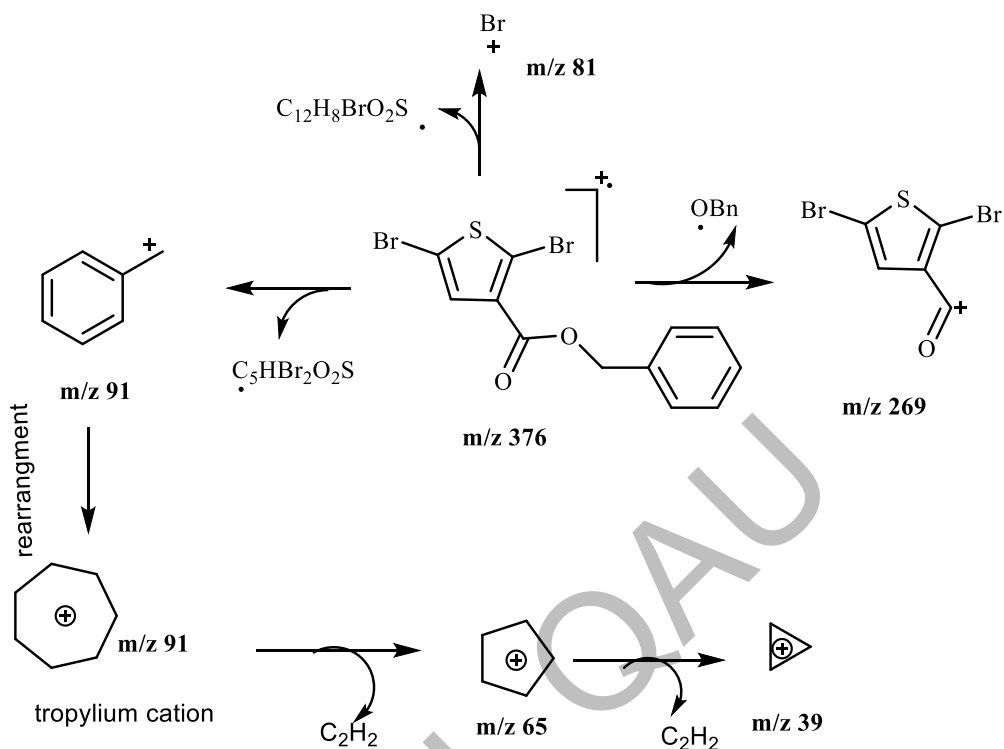


Figure 3.3 a) TIC profile of 4A b) GC-MS spectrum of 4A



Scheme 3.2 Mass fragmentation pattern of 4A

3.1.2 Synthesis of Negishi substrate monomer (5A)

The compound (4A) was reacted with zinc powder and LiCl in THF using iodine solution and dibromoethane for the activation of zinc to form organozinc compound (5A) via Knochel reaction. The formation of organozinc was confirmed by using iodometric titration as discussed in section 2.3.3.

3.1.3 Negishi mediated polymerization (P1)

Compound (5A) is an organozinc halide and was used as a Negishi substrate in the last step of scheme 1. This reagent was reacted with calculated amounts (5mol % each) of nickel trifluoromethane sulfonate (catalyst) and diphenyl phosphino propane (ligand) at $-20\text{ }^{\circ}\text{C}$ temperature in THF for 24 hours on stirring. The mixture obtained was extracted in water with chloroform and the organic layer was concentrated to obtain polymer as brown paste (P1).

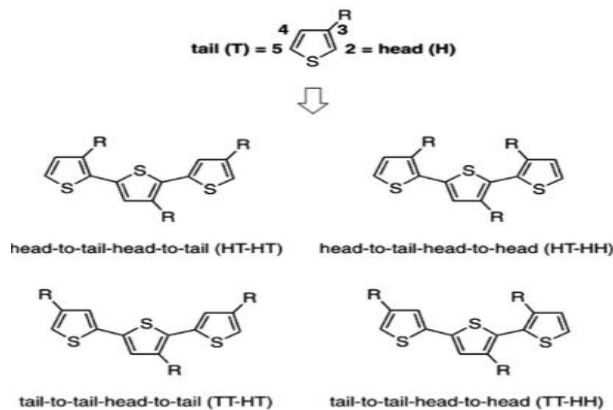
3.1.3.1 NMR spectroscopy of polymer P1

The ^1H -NMR spectrum of the polymer (P1) is shown in figure 3.4. Signals in the range of 7.11-8.17 ppm are attributed towards aromatic protons (5 of benzene ring and 1 of thiophene ring) of polymer. Signal at 4.7 and 5.3 ppm corresponds to methylene proton of benzyl moiety attached with the carbon (6). The integration increased while multiplicity and chemical shift value are same as that of reactant (4A). The signals appeared multiple times which is attributed to the fact that different chain lengths are produced in a polymerization reaction with different number of monomeric units. The chemical environment of methylene proton (6) is different in each chain so it resonates at different shift values, regio-isomers having different conformations change the chemical shift of the same proton to a small extent.

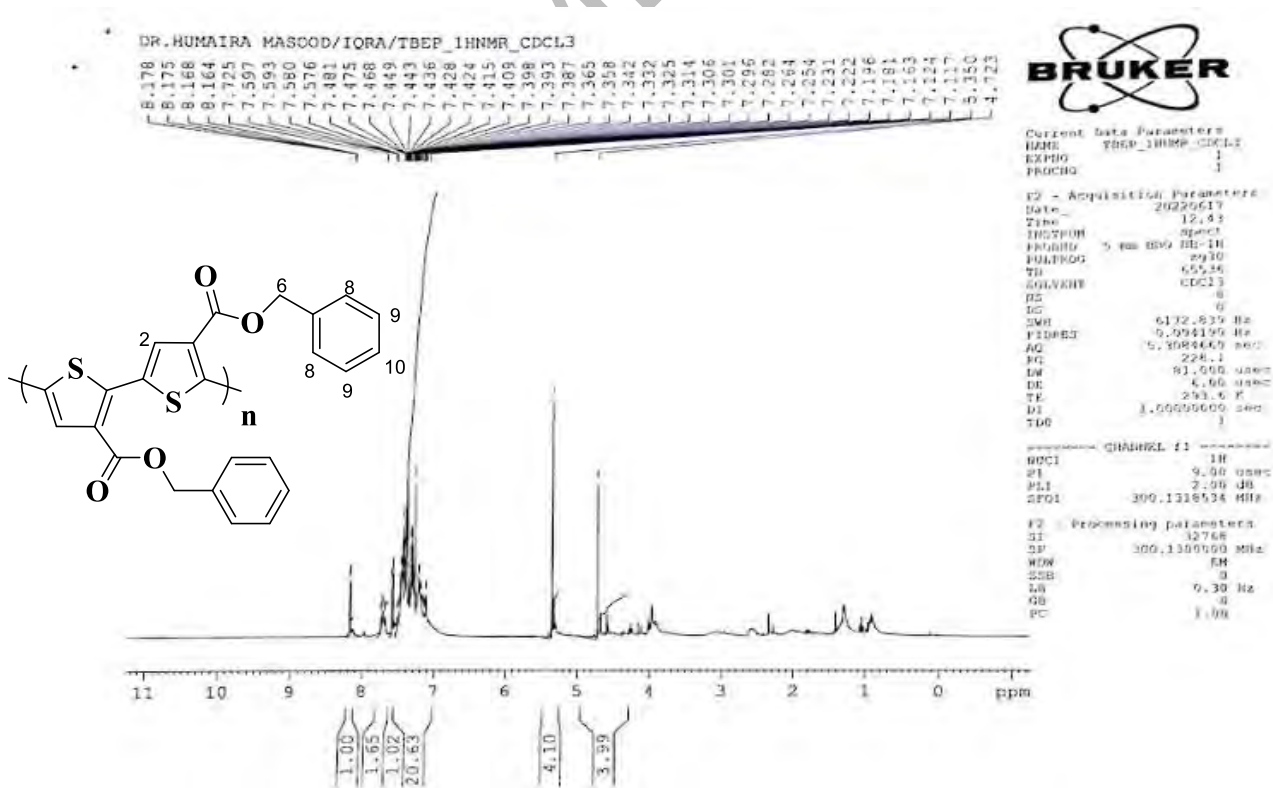
Table 3.4 ^1H -NMR spectral data of P1

Proton Number	Chemical shift δ (ppm)	Multiplicity	Integration
6	4.72	s	4H (for two methylene proton of C-6 2X)
	5.35	s	4H (for two methylene proton of C-6 2X)
2,8,9,10	7.11-8.17	m	20H (for 5 aromatic proton of benzene 4X) 1H (proton of C-2) 2H (proton of C-2 2X) 1H (proton of C-2)

The broadness of signals was observed which is due to number of protons resonating with same frequency, thus cluster is converted into a broad signal and formation of aromatic π -stacks. The ^1H and ^{13}C NMR spectra of polythiophene provide sensitive probes of the substitution pattern in the polymer backbone. In a mixture of the four possible triad regioisomers (HT-HT, TT-HT, HT-HH and TT-HH) four peaks for one aromatic proton of thiophene are theoretically possible and this is clearly demonstrated in the spectrum below.



(a)



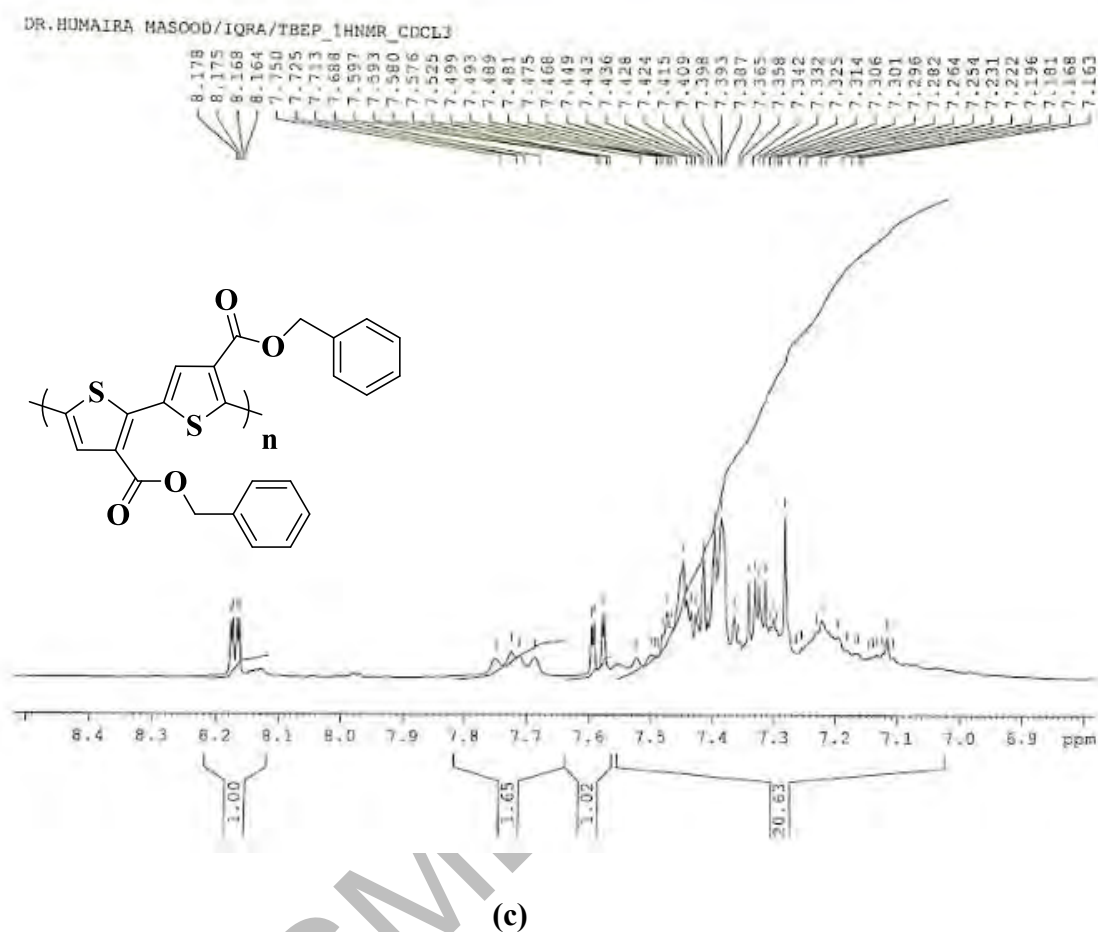


Figure 3.4 a) Coupling chemistry of 3-substituted thiophene

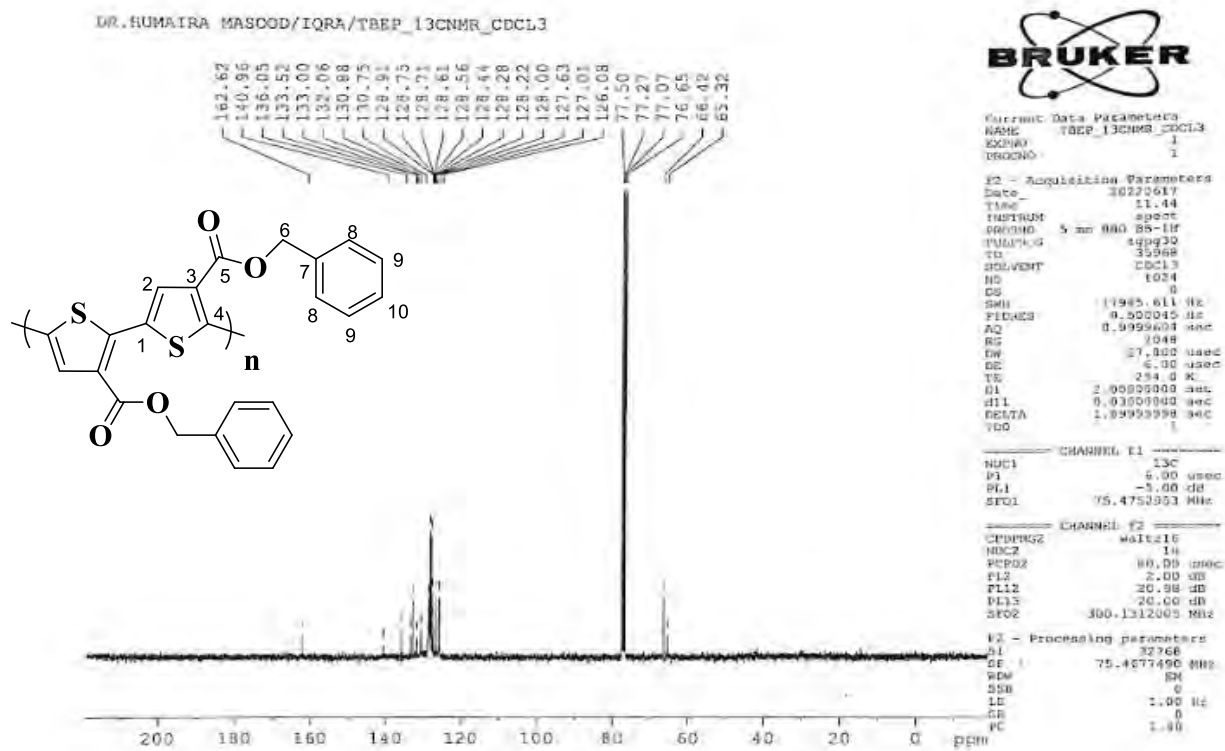
b) ¹H-NMR spectrum of P1

c) ¹H-NMR spectrum of P1 (expanded)

Same trends were observed in ¹³C-NMR spectrum. Each signal of carbon appeared multiple times. The chemical shift values are same as for compound (4B) except the shielded signal for C-Br appearing at 121 ppm in monomer disappeared in polymer which further confirmed that coupling reaction occurred. The most deshielded signals appearing at 162 ppm was attributed towards carbonyl carbon (C-5). Signals at 140 ppm corresponds to ipso carbon(C-7). Signals in the range of 136 ppm to 126 ppm are attributed to (C-1, 2, 3, 4, 8, 9, 10) and the signal at 66 ppm and 65 ppm are attributed to methylene carbon (6). This interpretation showed that the monomer was successfully polymerized to yield a polythiophene P1.

Table 3.5 ^{13}C -NMR spectral data of P1

Carbon no.	Chemical shift δ (ppm)	Carbon no.	Chemical shift δ (ppm)
5	162	6	66,65
7	140	1,2,3,4,8,9,10	136-126



(a)

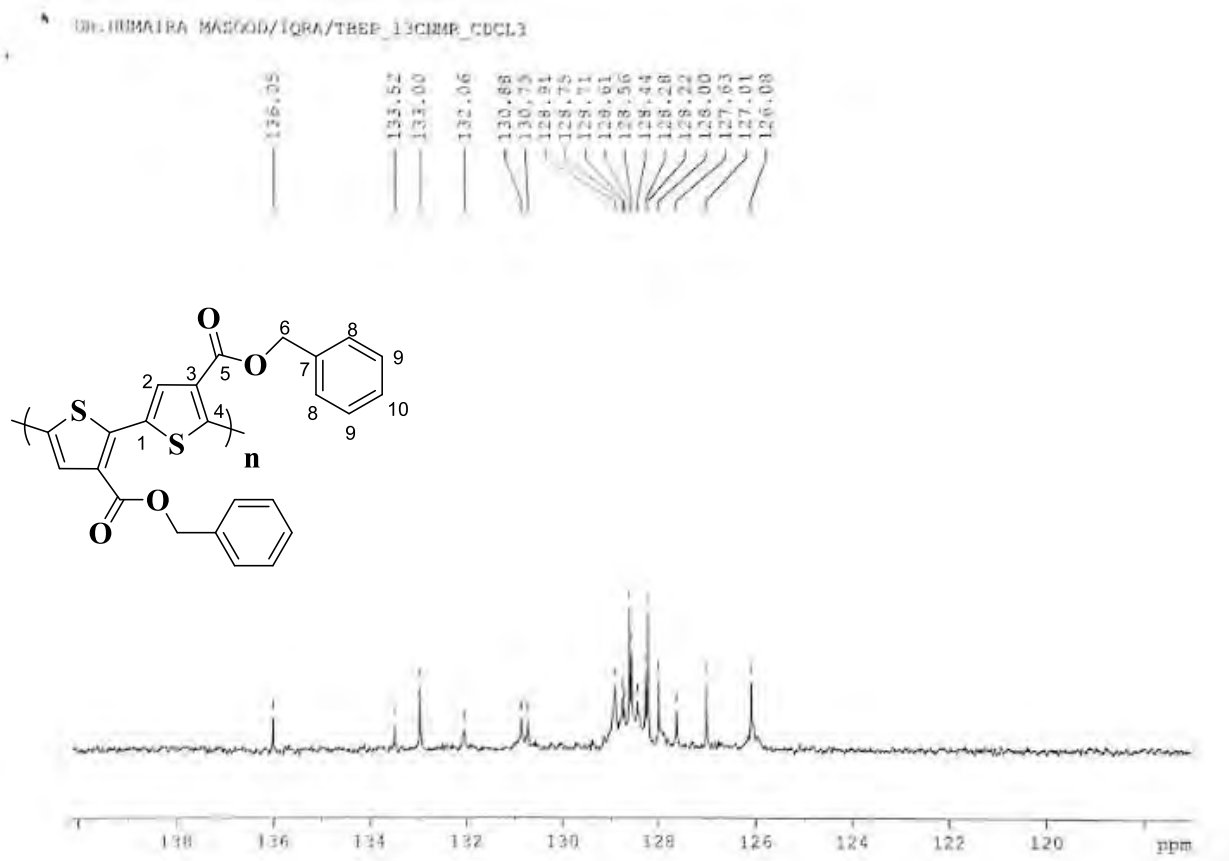


Figure 3.5 (a) ^{13}C -NMR spectrum of P1

(b) ^{13}C -NMR spectrum of P1 (expanded)

3.1.3.2 UV-visible spectroscopy of monomer 4A and polymer P1

UV-visible spectroscopy was performed using a solution of monomer and polythiophene in chloroform. The band observed at lower wavelength requiring more energy was due to π - π^* transitions, while band at higher wavelength requiring less energy is due to n - π^* transitions.

The benzyl ester substituted thiophene monomer showed two absorption band one at 298 nm and other at 367 nm in chloroform as shown in Figure 3.5 (chloroform having cut off wave length at 245nm). One absorption bands observed is due to π - π^* transitions of aromatic chromophore and the second band is because of n - π^* transition that is attributed to lone pair of sulphur and oxygen atom.

The HOMO-LUMO energy gaps (E_g) were calculated from the onset wavelength λ_{onset} employing the following Eq. 3.1

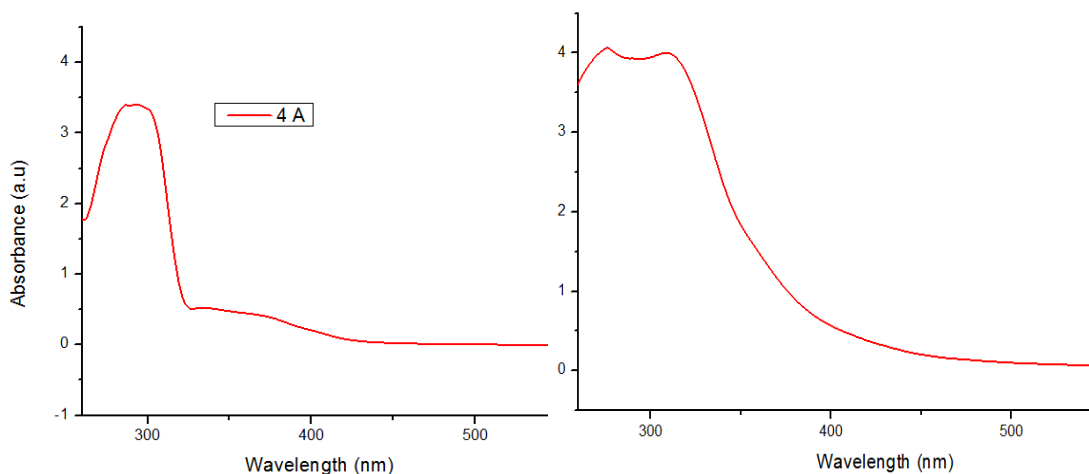
$$E_g = 1240/\lambda_{\text{onset}} \quad \text{Equation (3.1)}$$

The benzyl ester substituted polythiophene showed λ_{max} at 325 nm, this shift of absorption toward longer wavelength is attributed toward extended conjugation in case of polymer compared to monomer. The shift from 298 nm for monomer to 325 nm for polymer is known as bathochromic shift or red shift which further confirmed the formation of polymer. Two shoulder observed in the UV-Vis spectrum of polymer are characteristics of polymeric material¹¹⁰ which can be attributed as, due to presence of the different chain length absorption occurs at slight different wavelength.

The values of E_g of monomer was found 3eV while for polymer this value decreases to 2.3 eV. The values of E_g are plotted in table 3.6 and their absorption is shown in figure 3.6.

Table 3.6 UV-Vis spectral data of monomer 4A and polymer P1

Codes	λ_{max} $\pi - \pi^*$ nm	λ_{max} n- π^* nm	λ_{onset} nm	E_g $1240/\lambda_{\text{onset}}$ eV
4A	298	367	415	3.0
P1	325	-	529	2.3



(a)

(b)

Figure 3.6 (a) UV-Vis spectrum of monomer 4A

(b) UV-Vis spectrum of polymer P1

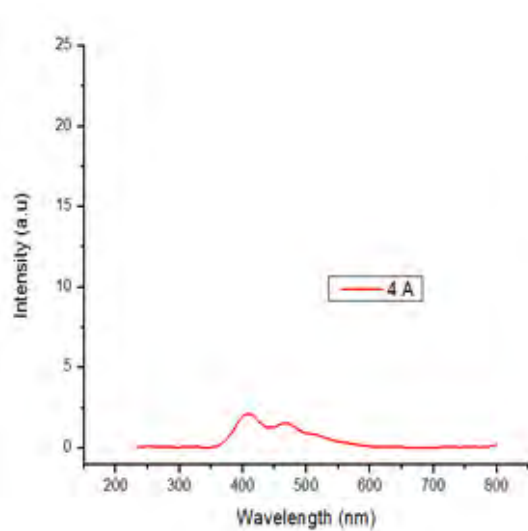
3.1.3.3 Photoluminescence (PL) spectroscopy of monomer 4A and Polymer P1

PL spectroscopy was performed at various excitation wavelengths using an F-7000 FL spectrophotometer. The emission wavelength spanned from 200 nm to 900 nm, with a scan rate of 1200 nm/min.

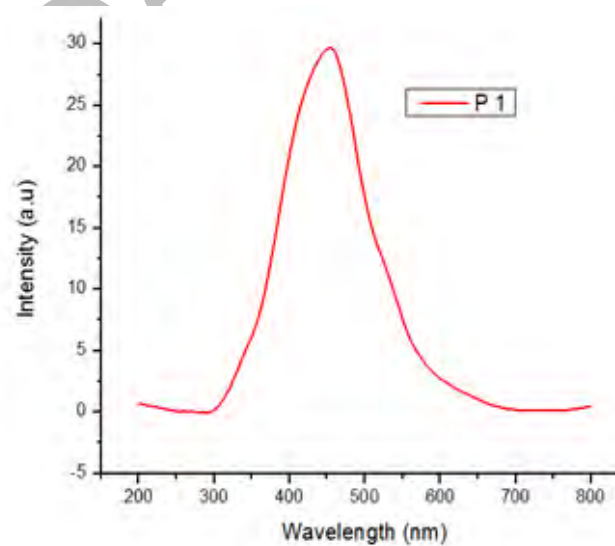
The photoluminescence spectral analysis of the synthesized monomer and polythiophene was performed in chloroform. PL graphs of synthesized monomer and polymer are depicted in figure 3.7 and data is presented in table 3.7. The sharper and more intense emission peaks is observed for polymer which is due to prolonged conjugation, two peaks at shorter and longer wavelengths are due to fluorescence and phosphorescence, which stabilize the singlet and triplet states, respectively. Their emission peaks also show that fluorescence has more energy than phosphorescence. The emission of light in the 405 and 453 nm area was designated as violet and blue in the PL spectra respectively, (fig. 3.7), and compounds showed their matching hues of yellow and orange.

Table 3.7 PL spectral data of monomer 4A and polymer P1

Codes	$\lambda_{\text{emis.}}$ nm	Color Region	Corresponding color
4A	395	violet	yellow
P1	453	blue	orange



(a)



(b)

Figure 3.7 (a) PL spectrum of monomer 4A

(b) PL spectrum of polymer P1

3.1.3.4 DSC Analysis of Polymer P1

The Mettler 823e DSC equipment was used for differential scanning calorimetry. Under inert circumstances, the heat rate for sample is employed from $-80\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ at a scan rate of $10\text{ }^{\circ}\text{C}$ per min. This analysis was performed for determining glass transition temperature (T_g) of polymer. T_g of polymers is the temperature at which amorphous polymer changes from hard glassy state to soft leathery state and vice versa and it is directly related to strength of material and very important for the uses of polymers. The DSC curve of polymer P1 is shown in Figure 3.8, which showed T_g of synthesized polythiophene as $-50\text{ }^{\circ}\text{C}$.

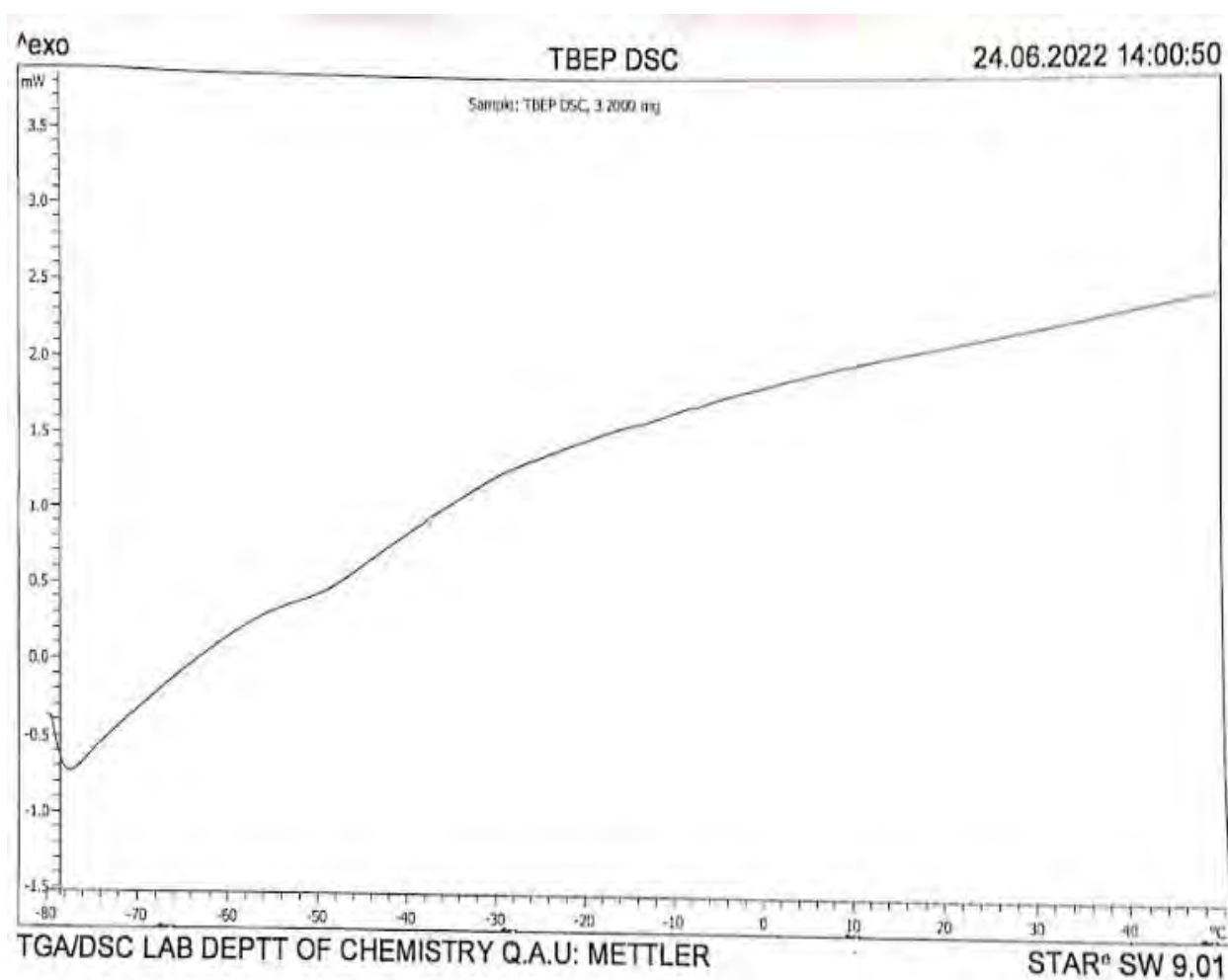


Figure 3.8 DSC curve of polymer P1

3.1.3.5 XRD Analysis of Polymer P1

The X-ray diffraction analysis was used to study the crystalline phases of polymer P1. This analytical technique examined the phases of crystalline materials by using X-rays that are scattered at a specific angle from planes of atoms in a sample. It contains information about the unit cell. XRD spectra were obtained from 5 °C to 90 °C using Copper K- α radiation and an X-ray diffraction spectrometer. The sample surface is sufficient for determining diffraction. Hence, this technique was used to confirm the nature of polythiophenes i.e., whether these are of crystalline or amorphous nature. The Xpert PRO device was utilized to perform X-ray diffraction studies. The recording angle for XRD was $2\theta=20-80^\circ$. Analysis of microstructure and morphology of polythiophene showed no crystalline peak in the region from $2\theta=19.9^\circ$ to 90° , hence concluded that synthesized polythiophene is amorphous in nature.

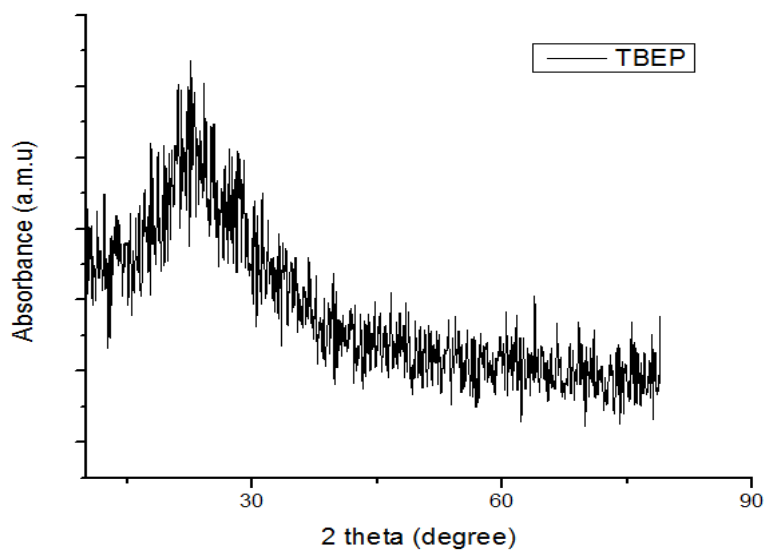
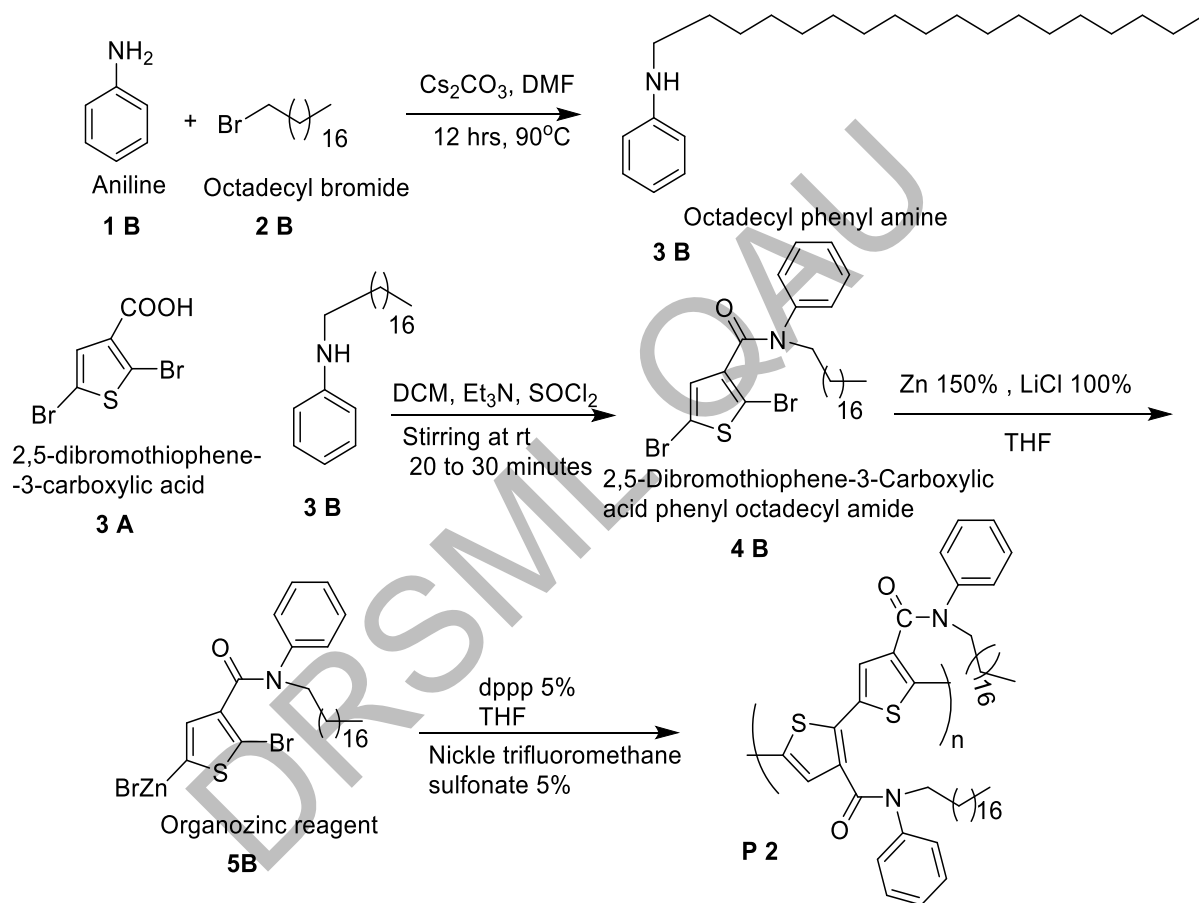


Figure 3.9 XRD plot of polymer P1

3.2 Synthesis of Amide Functionalized Polythiophene (Scheme 2)

This section includes the characterization results of compounds synthesized in schemes 2; i.e., synthesis of phenyl octadecyl amine (3B), 2,5 dibromothiophene-3-octadecyl phenyl carboxamide (4B) and poly-3-octadecyl phenyl thiophene carboxamide (P2).



Scheme 3.3 Synthesis of amide functionalized polythiophene

3.2.1 Synthesis of Amine (3B) and Amide (4B)

In a 250 mL round bottom flask, Cs_2CO_3 and aniline was added. To this mixture 15 mL of anhydrous DMF was added, and stirred at 25 °C for 30 minutes. White suspension was formed to which 1-bromooctadecane was added. Reaction mixture was allowed to stir at 80-90 °C for 5-12 hours. Afterwards mixture was filtered and rinsed with EtOAc. Filtrate was then taken into 1N NaOH (2x10mL) and extracted with EtOAc (4x10mL).

The organic layer was washed by using brine (2x10mL), dried with anhydrous sodium sulphate, filtered and concentrated to give crude product. Product was purified by column chromatography. White powder (3B) was collected with 70% yield and melting point was observed in the range 55-57 °C. The dibromo acid (2A) was converted into an amide (4B) by reacting it with amine (3B) in the presence of Et_3N as base and dry, distilled DCM as solvent. To the same reaction mixture thionyl chloride was added and mixture was allowed to stir at room temperature for 30 minutes. The product was obtained by evaporating solvent at reduced pressure.

Residue were taken up in DCM, washed with 1N HCl followed by washing with 1N NaOH. Product obtained was light brown powder (4B). The physical data of synthesized compounds is given in table 3.8. 3B and 4B appeared as white and light brown powder respectively. Yield = 70% (3B), 72% (4B), M.P = 55-57 °C (3B), 62-65 (4B), R_f Values = 0.5 (3B), 0.3 (4B)

Table 3.8 Physical data of 3B and 4B

Codes	Appearance	Yield %	M.p (°C)	R_f
3B	White powder	70	55-57 (54-60 reported)	0.5
4B	Light brown powder	72	62-65	0.3

Mobile phase = n-hexane and ethyl acetate (9:1)

3.2.1.1 NMR spectroscopy of monomer (4B)

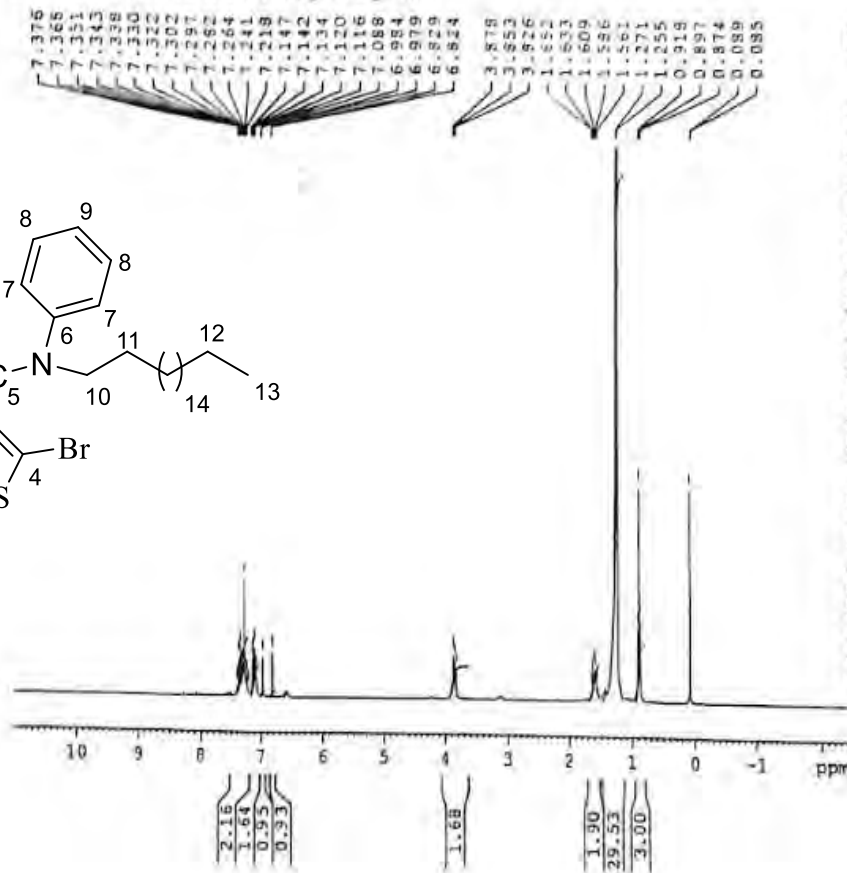
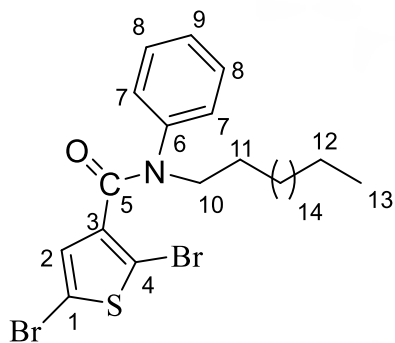
The ^1H -NMR spectrum of the compound 4B is shown in figure 3.10, signals in the range of 7.08 ppm-7.40 ppm are assigned to four aromatic proton (7, 7, 8, 8), signal at 6.9 ppm is attributed to one proton of thiophene ring (2) and signal at 6.8 ppm corresponds to one proton at para position of benzene (9). Triplet at 3.87 is assigned to two proton of carbon directly attached to nitrogen (10), signal at 1.65 ppm is attributed for two proton at position 11, signal at 1.2 ppm corresponds thirty proton of long alkyl chain. The most shielded signal at 0.8 ppm corresponds 3 methyl proton (13).

^1H -NMR spectral data of 4B is shown in table 3.9.

Table 3.9 ^1H -NMR spectral data of 4B

Proton Number	Chemical shift δ (ppm)	Multiplicity	Integration
7,8	7.08-7.40	m	4H
2, 9	6.9 and 6.8	s, d	H , H
10	3.87	t	2H
11	1.65	quint	2H
In b/w position 11 and 13	1.2	quint	30H
13	0.8	t	3H

DR. HUMAIRA MASOOD/IQRA/ODPAA_1HNMR_CDCL3



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PROCNO 1

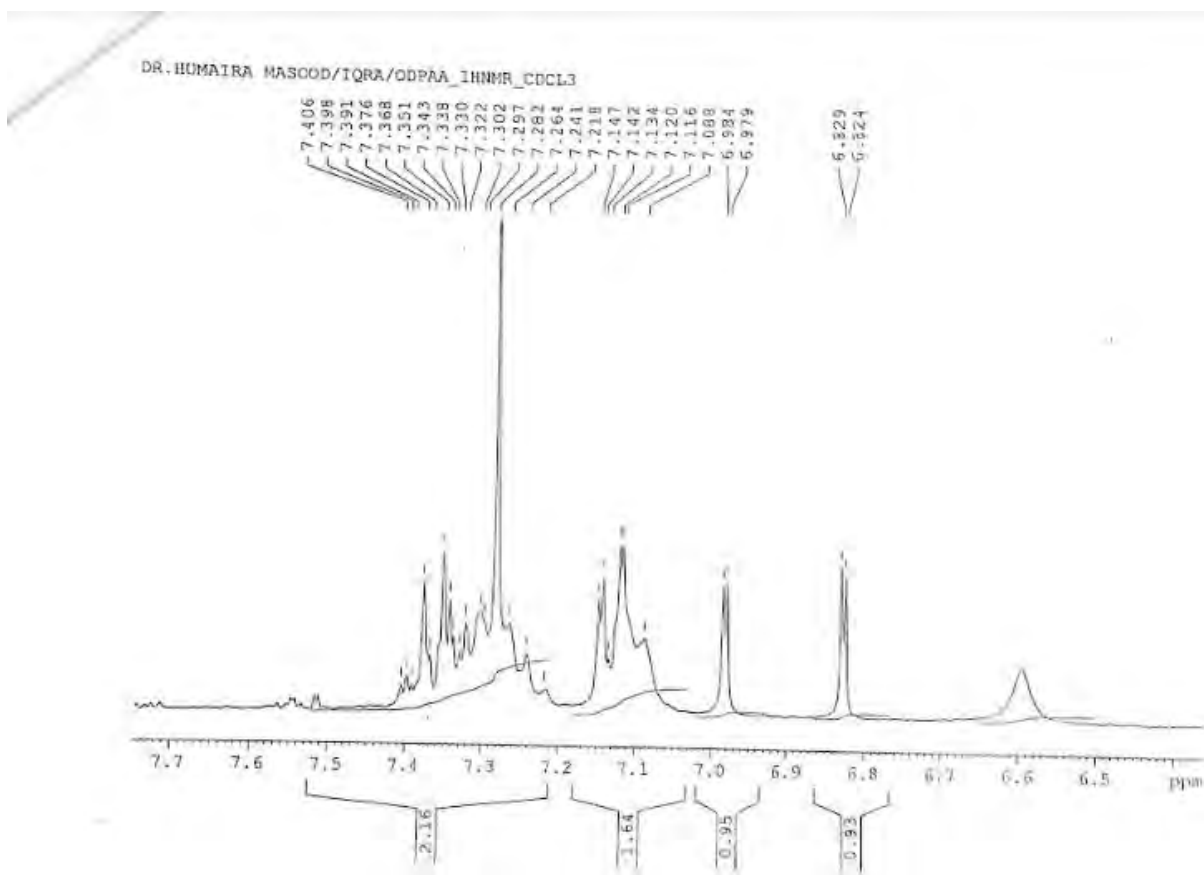
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DE 4.00 usec
TE 293.7 K
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T00 1

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P1 9.00 usec
PL1 2.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

DRS

(a)



(b)

Figure 3.10 (a) $^1\text{H-NMR}$ spectrum of 4B

(b) $^1\text{H-NMR}$ spectrum of 4B (expanded)

$^{13}\text{C-NMR}$ of 4B is shown in figure 3.11, the most deshielded signal at 163 ppm is assigned to the carbonyl carbon (5) of amide functionality. The signal in the range of 143 ppm to 127 ppm corresponds aromatic carbons, shielded signal in aromatic region at 119 ppm corresponds carbon attached to bromine (C-1), signal at 50 ppm is due to carbon directly attached to N (C-10). Signal at 31 ppm is due to C-11, signals in the range of 29 ppm to 26 ppm is due to carbon of long alkyl chain (b/w C-11 to C-12). Appearance of signal at 22 ppm and 14 ppm corresponds to C-12 and C-13 respectively. Appearance of signals in alkyl region further confirmed the formation of long chain containing amide.

Table 3.10 ^{13}C -NMR spectral data of 4B

Carbon no.	Chemical shift δ (ppm)	Carbon no.	Chemical shift δ (ppm)
5	163	10	50
1	119	11	31
2,3,4,6,	143-127	All C b/w C-	29-26
7,8,9		11 to C-12	
12	22	13	14

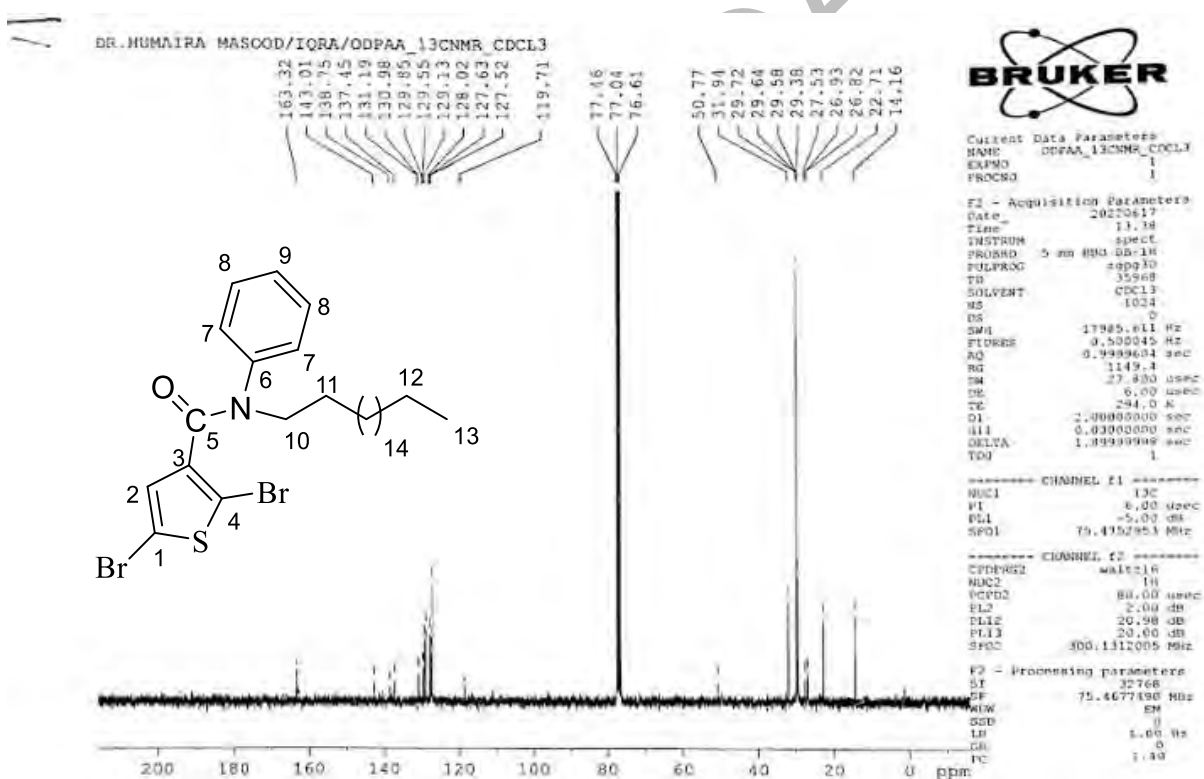


Figure 3.11 ^{13}C -NMR spectrum of 4B

3.2.2 Negishi mediated polymerization (P2)

Compound (5B) is an organozinc halide and was used as a Negishi substrate in the last step of scheme 2. This reagent was allowed to react with 5 mol % each of nickel trifluoromethane sulfonate (catalyst) and diphenyl phosphino propane (ligand) at -20 °C temperature in THF for 24 hours on stirring. The mixture obtained was extracted in water with chloroform and the organic layer was concentrated to obtain polymer as yellow gel (P2).

3.2.2.1 NMR spectroscopy of P2

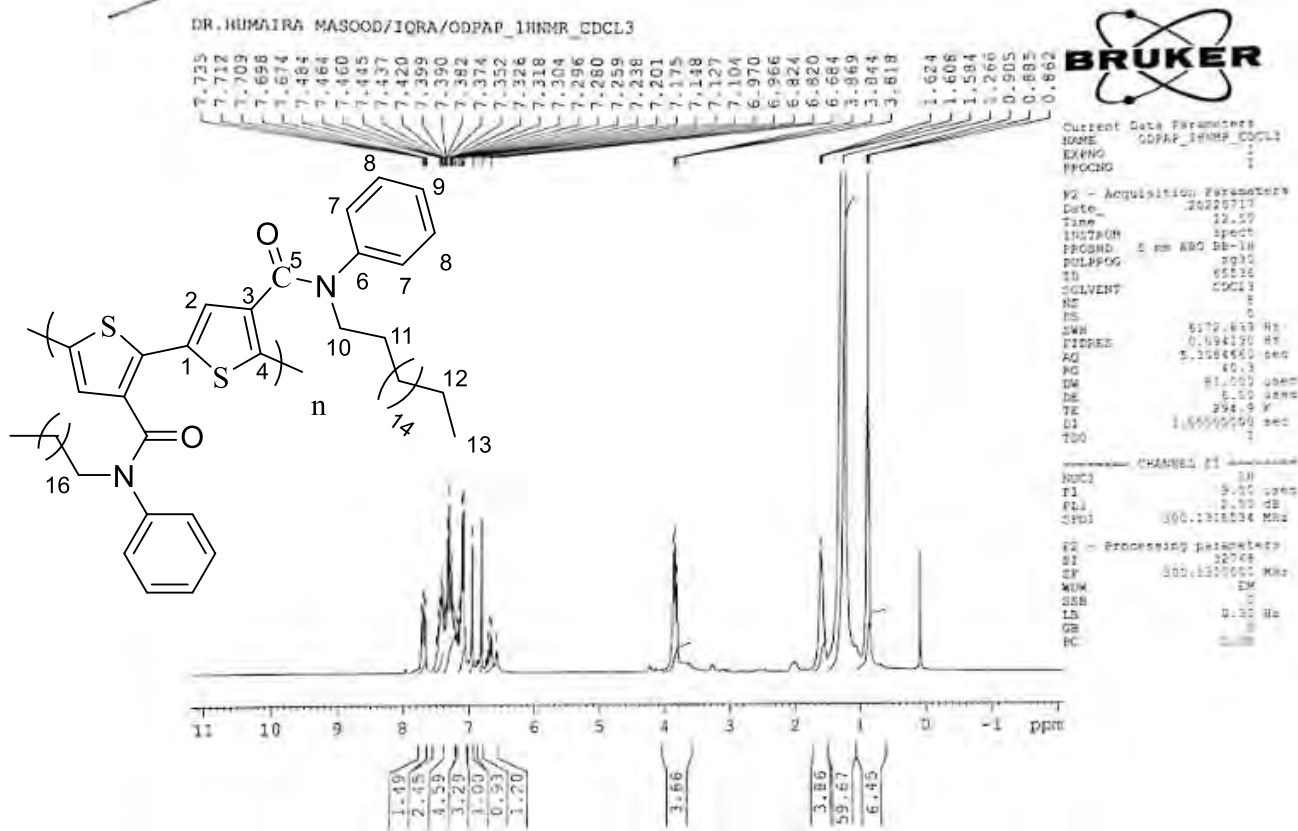
The ¹H-NMR spectrum of the polymer (P2) is shown in figure 3.12. The multiplet from 6.68 ppm-7.73 ppm corresponds to aromatic proton of benzene and thiophene ring. The signal appeared multiple times which is attributed to the fact that different chain lengths are produced in a polymerization reaction with different number of monomeric units. Triplet at 3.84 ppm is due to proton of C-10. Signal at 1.60 ppm is assigned to proton of C -11. Signal at 1.26 ppm is attributed to long 15 carbon alkyl chain. Triplet at 0.88 ppm corresponds methyl proton of carbon 13. The integration increased which is attributed toward successful polymerization reaction, while multiplicity and chemical shift value are almost same as that of reactant (4B). The chemical environment of proton is different in each chains so it resonates at different shift values, regio-isomers having different conformations changes the chemical shift of the same proton to a small extent. Similarly signal for aromatic protons (5 of benzene ring and 1 of thiophene ring also broaden and appears multiple time from 6.68 ppm-7.73 ppm .

Table 3.11 ¹H-NMR spectral data of P2

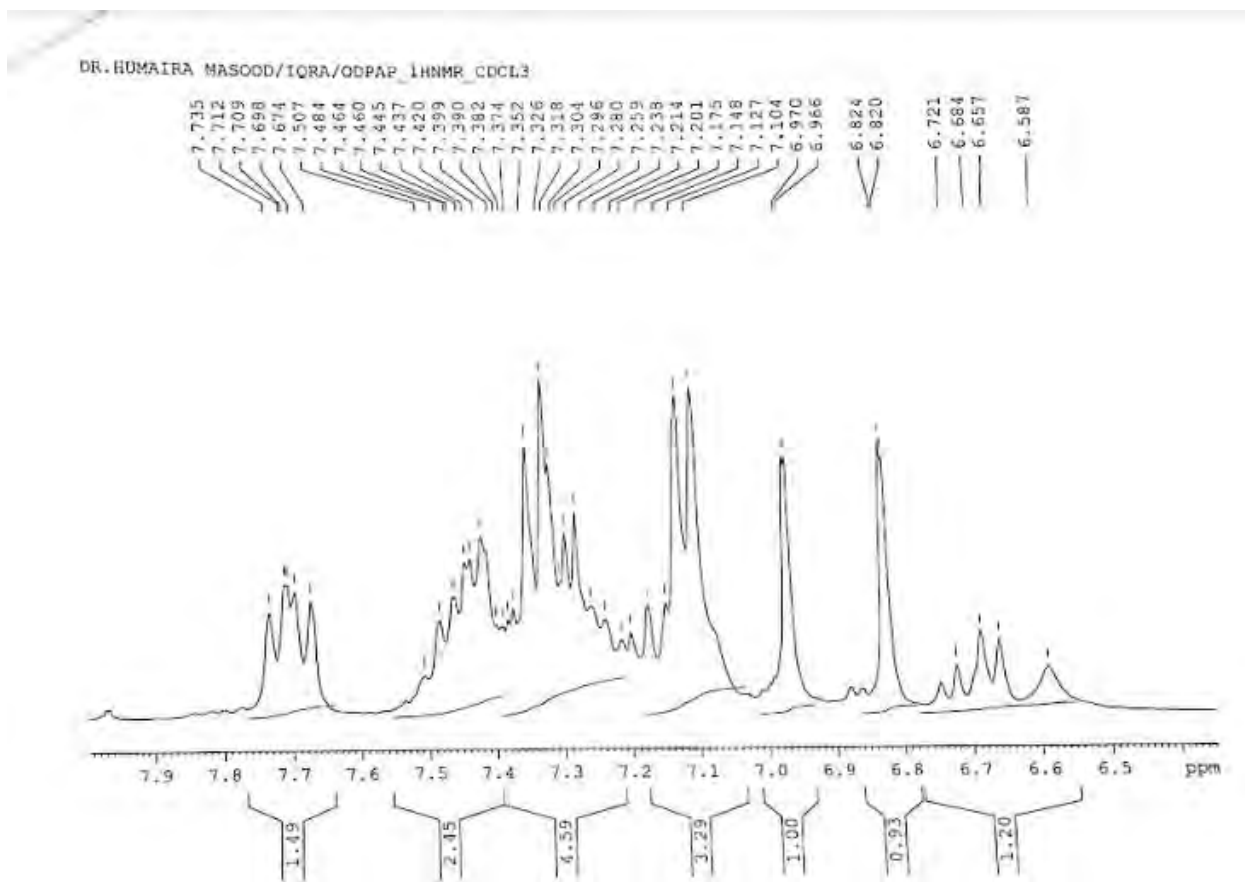
Proton Number	Chemical shift δ (ppm)	Multiplicity	Integration
11	1.60	quint	2H (2X)
10	3.84	t	2H (2X)
In b/w 11 to 13	1.26	quint	30 H (2X)

13	0.88	t	3H (2X)
2,6,7,8,9	6.684-7.735	m	Aromatic protons

The broadness in the signals was observed which is due to number of protons resonating with same frequency, thus cluster is converted into a broad signal and formation of aromatic π -stacks. The ^1H and ^{13}C NMR spectra of polythiophene provide sensitive probes of the substitution pattern in the polymer backbone.



(a)



(b)

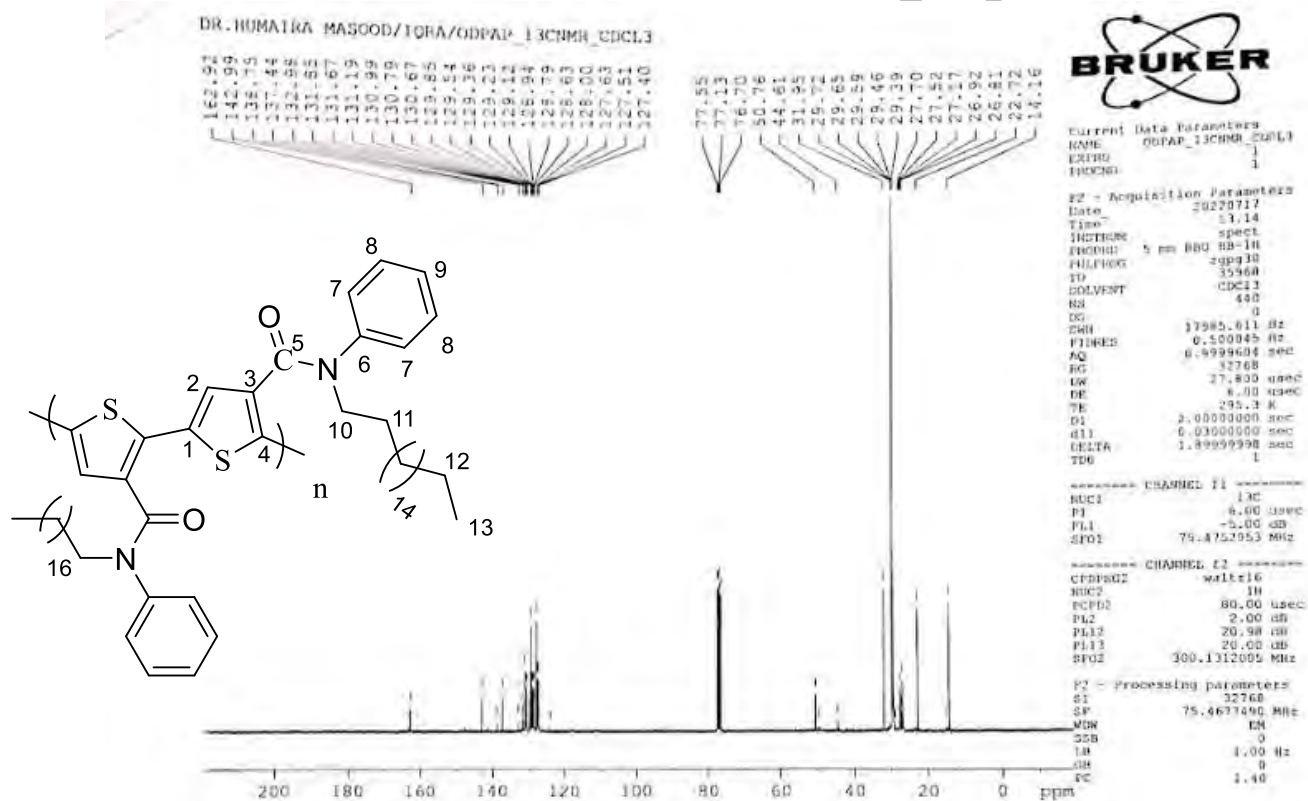
Figure 3.12 (a) $^1\text{H-NMR}$ spectrum of P2

(b) $^1\text{H-NMR}$ spectrum of P2 (expanded)

Same trends were observed in $^{13}\text{C-NMR}$ spectrum. Each signal of carbon appeared multiple times. The chemical shift values are same as for compound (4B) except the shielded signal for C-Br appearing at 119 ppm in monomer disappeared in polymer which further confirmed the successful coupling reaction. The most deshielded signals corresponding to carbonyl carbon of amide (C-5) appeared at 162.9 ppm. The signal from 142 ppm to 127 ppm corresponds aromatic carbons. Signal at 50 ppm and 44 ppm is due to carbon directly attached to N (C-10). Signal at 31 ppm is due to C-11, signals from 29 ppm to 26 ppm is due to carbon of long alkyl chain (b/w C-11 to C-12). Appearance of signal at 22 ppm and 14 ppm corresponds to C-12 and C-13 respectively.

Table 3.12 ^{13}C -NMR spectral data of P2

Carbon no.	Chemical shift δ (ppm)	Carbon no.	Chemical shift δ (ppm)
5	162.9	10,11	50,31
2,3,4,6, 7,8,9	142-127	All C b/w C- 11 to C-12	29-26
12	22	13	14



(a)

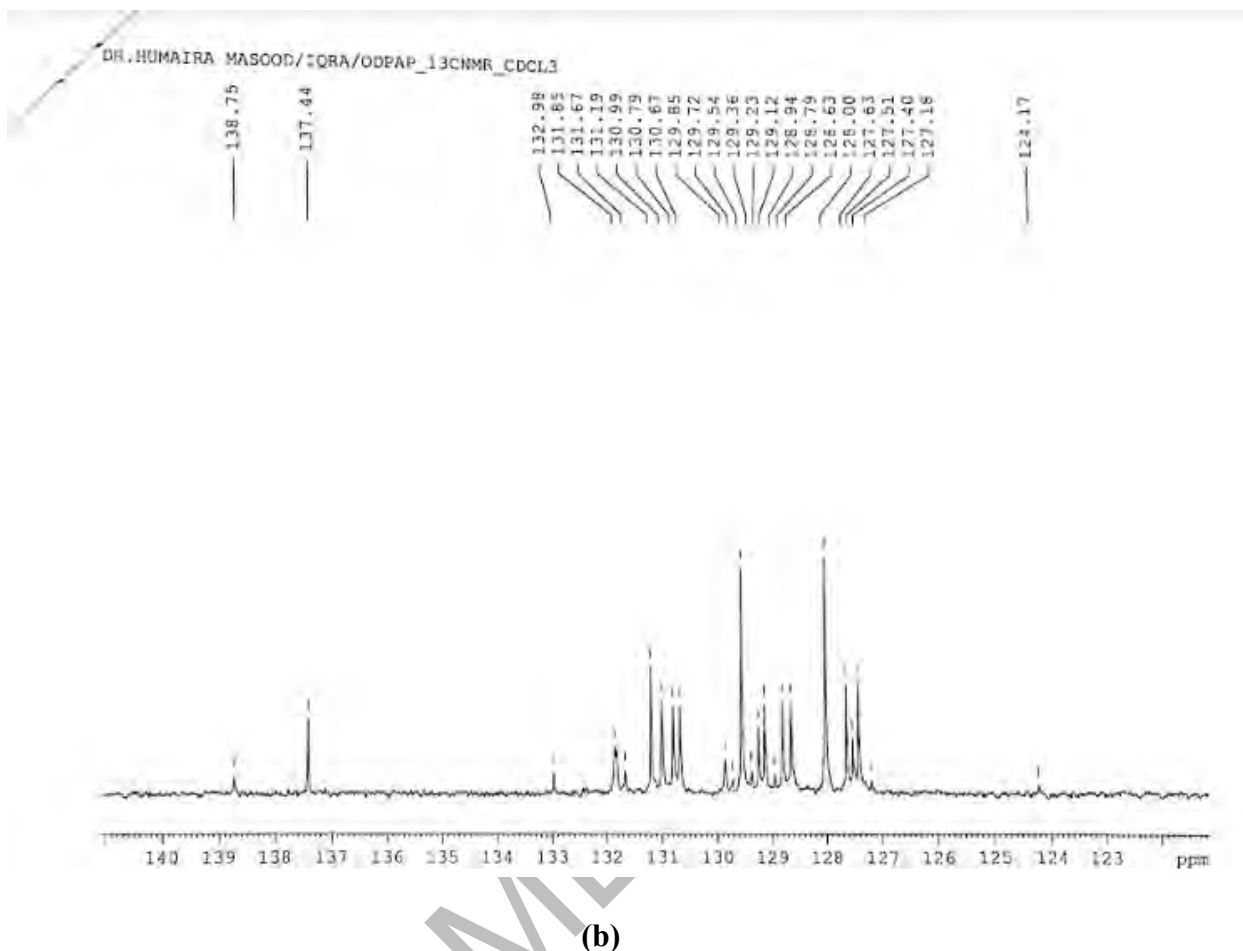


Figure 3.13 (a) ^{13}C -NMR spectrum of P2

(b) ^{13}C -NMR spectrum of P2 (expanded)

3.2.2.2 UV-visible spectroscopy of monomer 4B and polymer P2

UV-visible spectroscopy was performed using a solution of monomer 4B and polythiophene P2 in chloroform. The absorption band observed at lower wavelength requiring more energy was due to π - π^* transitions, while transition at higher wavelength are forbidden, are requiring less energy. Band due to n - π^* transitions does not appeared in this case.

The amide substituted thiophene monomer showed absorption band at 266 nm in chloroform as shown in figure 3.14 (chloroform having cut off wave length at 245nm). The absorption bands observed are due to π - π^* transitions of aromatic chromophore. The HOMO-LUMO energy gaps (E_g) were calculated from the onset wavelength λ_{onset} employing the following Eq. 3.2

$$E_g = 1240/\lambda_{\text{onset}}$$

eq 3.2

The value of E_g of monomer was found 4eV. The amide functionalized polythiophene showed λ_{max} at 310 nm, this shift of absorption toward longer wavelength is attributed toward extended conjugation in case of polymer compared to monomer. The shift from 266 nm for monomer to 310 nm for polymer is known as bathochromic shift or red shift which further confirmed the formation of polymer. Two shoulder observed in the UV-Vis spectrum are characteristics of polymeric material¹¹⁰ which can be attributed as due to presence of different chain length absorption occurs at slight different wavelength. The value of E_g of polymer was found 2.9eV.

The values of E_g are plotted in table 3.13 and their absorption is shown in figure 3.14.

Table 3.13 UV-Vis spectral data of monomer 4B and polymer P2

Codes	λ_{max} $\pi - \pi^*$ nm	λ_{onset} nm	E_g $1240/\lambda_{\text{onset}}$ eV
4A	266	305	4.0
P1	310	424	2.9

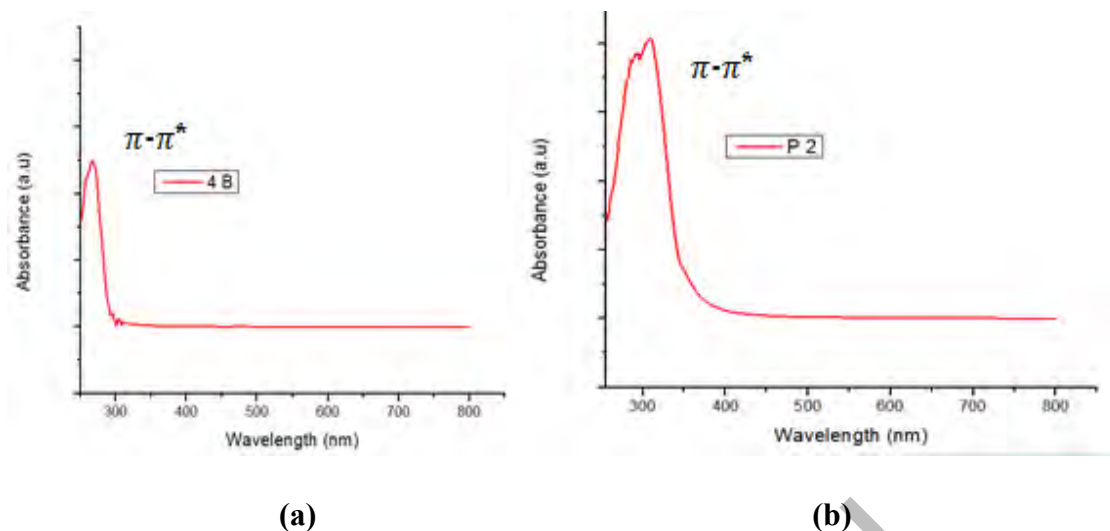


Figure 3.14 (a) UV-Vis spectrum of monomer 4B
(b) UV-Vis spectrum of polymer P2

3.2.2.3 Photoluminescence spectroscopy of monomer 4B and polymer P2

PL was performed at various excitation wavelengths using an F-7000 FL spectrophotometer. The emission wavelength spanned from 200 nm to 900 nm, with a scan rate of 1200 nm/min.

The photoluminescence spectral analysis of the synthesized amide substituted monomer and polymer was performed in chloroform. PL graphs of synthesized monomer and polymer are depicted in Figure 3.15 and data is presented in table 3.14. The sharper and more intense emission peak is observed for polymer which was due to prolonged conjugation, two peaks at shorter and longer wavelengths are due to fluorescence and phosphorescence, which stabilize the singlet and triplet states, respectively. The emission of light in the 390 nm and 470 nm area was designated as violet and blue in the PL spectra respectively, (Fig. 3.15), and compounds showed their matching hues of yellow and orange.

Table 3.14 PL spectral data of monomer 4B and polymer P2

Codes	$\lambda_{\text{emis.}}$ nm	Color Region	Corresponding color
4A	390	violet	yellow
P1	470	blue	orange

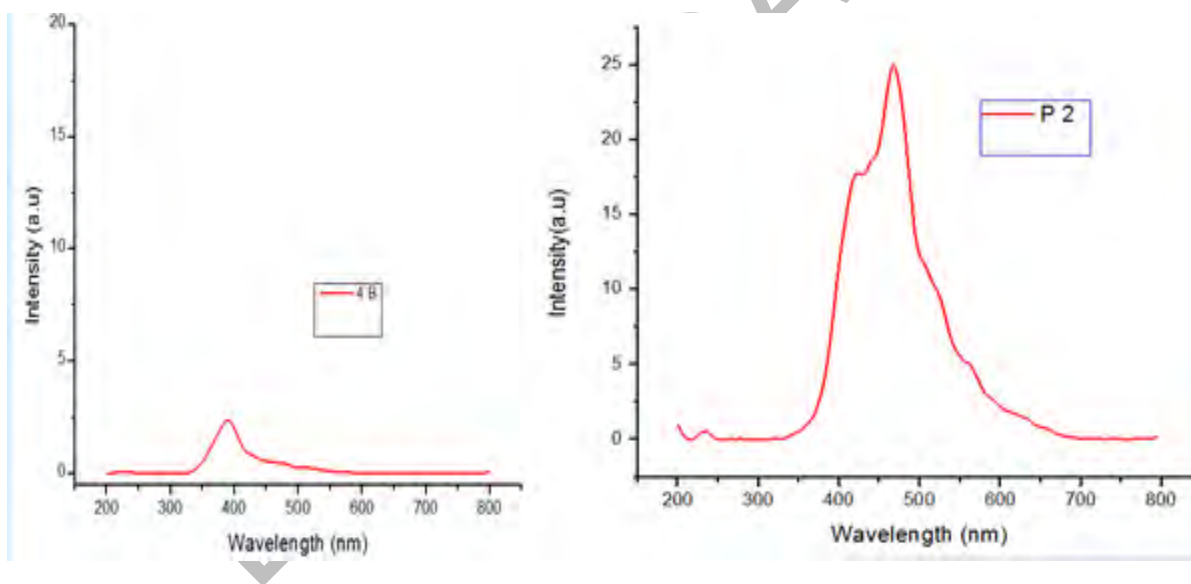


Figure 3.15 (a) PL spectrum of monomer 4B

(b) PL spectrum of polymer P2

3.2.2.4 XRD Analysis of Polymer P2

XRD analysis of P2 was also performed by using Xpert PRO device. The recording angle for XRD was $2\theta=20-80^\circ$. Analysis of microstructure and morphology of P2 polythiophene also showed no crystalline peak in the region from $2\theta=19.9^\circ$ to 90° , hence concluded that synthesized polythiophenes P2 is amorphous in nature.

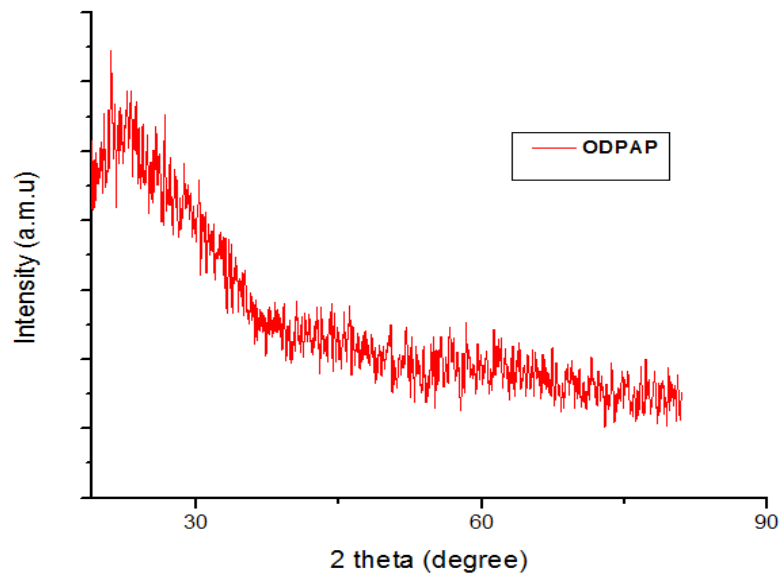


Figure 3.16 XRD plot of polymer P2

DRSML QX

Conclusions

The present work has led to following conclusions:

Novel ester and amide functionalized thiophene monomer and polymer were successfully synthesized and characterized by GC-MS, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral analysis. Negishi mediated coupling polymerization was successfully employed for the first time to synthesize polythiophenes (P1 and P2). Synthesized polymers (P1 and P2) were found to be highly soluble in common organic solvents like CHCl_3 , DMSO, MeOH and THF. Synthesized compounds showed excellent fluorescence as shown by emission spectrum so, these compounds can be good candidate for organic photovoltaics.

The presence of chromophores and conjugation in the polymers was confirmed by UV-visible spectroscopy which showed strong absorption in visible region.

UV-vis data displayed low E_g (2.5-2.9 eV) values meaning that these polymers can be easily oxidized and might be good candidate for optoelectronics properties.

The XRD analysis of synthesized polymers suggested their amorphous nature.

Future Plans

The future plans for the present study are synthesis of amide functionalized polythiophene having different chain lengths and its effect on electronic properties.

Remaining characterization including CV, TGA and GPC of the synthesized compounds.

DRSML QAU

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