CHAPTER 2
Synthesis and characterization of ester substituted polythiophenes
Chapter 2: Synthesis and characterization of ester substituted polythiophenes

2.1 Introduction

Conjugated polymers exhibit unique electronic and optical properties due to their $\pi$-conjugation and special chemical structure [1-11]. The creative design and development strategies for conjugated polymers have led to new materials and enhanced performance. In determining the physical properties of conjugated polymers, more research has been focused on the structure and function of these materials. The synthesis can help to achieve the magnitude of $\pi$ overlap along the backbone and enhanced solubility. In light emitting diode (LED) application, 3-substituted polythiophene have stimulated much interest due to their solubility, environmental stability, fusibility, better processibility and tuneability of colour from UV to IR by changing the substituents [12-18].

Substituted polythiophenes have been prepared by electrochemical and chemical polymerization techniques [19-20]. Electrochemical polymerization fails to produce large scale and soluble polymers. Therefore, chemical polymerization methods have attained popularity for synthesizing the large scale and soluble polymers. The chemical polymerization methods include oxidative coupling, Yamamoto coupling, McCullough method, Grignard Metathesis (GRIM) method, Reike method, Suzuki and Stille method [15, 20-24]. FeCl$_3$ oxidative coupling is a straightforward, simple, versatile and the least expensive method among other chemical polymerization techniques. 3-substituted polythiophenes with alkyl, fluoroalkyl, phenyl, alkoxy, ester groups in side chain have been synthesized by FeCl$_3$ oxidative coupling [25-40]. Ester substituted polythiophenes have been prepared using either a FeCl$_3$ suspension in CHCl$_3$ or FeCl$_3$ precipitated in-situ by a solvent / nonsolvent mixture (CH$_3$NO$_2$ / CCl$_4$) [41-54]. The later method gives higher monomer conversions and polymer yields.

A considerable effort has been made to the synthesis of polymers with special emphasis on the improved solubility. Introduction of side chains on conjugated backbone not only provide solubility, but also they have a major influence on the characteristics of polymers. We have combined the alkyl group with the chain length from C$_6$ to C$_{12}$, 3-pentadecyl phenyl, 3-pentadecyl cyclohexyl and quinoline moiety as a side chain in polythiophene ester backbone.

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This chapter describes the synthesis and characterization of monomers and polymers and their thermal properties. We have synthesized the following 3-ester substituted thiophene.

i) Hexyl 2-(thiophene-3-yl) acetate (HTA)
ii) Octyl 2-(thiophene-3-yl) acetate (OTA)
iii) Decyl 2-(thiophene-3-yl) acetate (DTA)
iv) Dodecyl 2-(thiophene-3-yl) acetate (DDTA)
v) 3-pentadecylphenyl 2-(thiophene-3-yl) acetate (PDPTA)
vi) 3-pentadecylcyclohexyl 2-(thiophene-3-yl) acetate (PDCHTA)
vii) Quinoline -8-yl 2-(thiophene-3-yl) acetate (QTA)

The monomers were synthesized by esterification reaction of 3-thiophene acetic acid and corresponding alcohols and characterized by $^1$H NMR, FTIR and UV-Vis analysis. The polymerization was accomplished by oxidative coupling in the presence of FeCl₃. The synthesized polymers were characterized by $^1$H NMR, FTIR, UV-Vis, XRD and GPC analysis. Thermal properties of polymers were studied by TGA and DSC technique.

2.2 Materials

3- thiophene acetic acid (Aldrich), 1- hexanol (Aldrich), 1- octanol (Aldrich), 1-decanol (Aldrich), 1- dodecanol(Aldrich), 8- hydroxyl quinoline (Fluka), FeCl₃ (Aldrich) were used as received. 3- pentadecyl phenol, 3-pentadecylcyclo hexanol and dimethylamino pyridine (DMAP) were recrystallized from ethanol. All the solvent were distilled before use and the reactions were performed under nitrogen atmosphere.

2.3 Instrumentation

2.3.1 UV- Visible spectrophotometer

UV-Visible (UV-Vis) spectrophotometer provides information about structure and stability of the materials in solution. Various kinds of electronic excitation may occur in organic molecules by absorbing the energies available in the UV-Vis region. The spectrophotometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of
absorbance versus wavelength. The intensity of the absorption is proportional to the number, type and location of colour absorbing structures (chromophores) in the molecule. UV-Visible spectra were recorded on a Shimadzu UV-2550 UV-VIS Spectrophotometer using tetrahydrofuran (THF) solvent.

2.3.2 Fourier transform infrared spectrophotometer (FTIR)

FTIR is a useful method for the characterization of monomer and polymers. It is primarily used for the detection of functional groups, but analysis of spectra in the lower frequency fingerprint region can give evidence of degree of polymerization and the effect of substituents on the electronic properties of the polymer backbone. FTIR spectra were recorded on a Nicolet, Impact 410 by using KBr pallet.

2.3.3 Nuclear magnetic resonance spectrometer (^1H NMR)

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules. Structure of compound can be determined by studying the peaks of NMR spectra. It is a very selective technique, distinguishing among many atoms within a molecules or collection of molecules of the same type but which differ only in terms of their local chemical environment. In proton NMR spectroscopy, structure of molecules is ascertained with respect to hydrogen nuclei within the molecule of a substance. ^1H NMR spectra were obtained on a Bruker AMX 400MHz with deuterated CHCl₃ having TMS as internal standard.

2.3.4 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) is used to determine the relative molecular weight of polymer samples as well as the distribution of molecular weights. Generally, GPC measures the molecular volume and shape function as defined by the intrinsic viscosity of polymer sample. Molecular weights of polymers were measured by gel permeation chromatography (410 Waters differential refractometer) (Water, USA). Flow rate is 1ml/min. Polymers were dissolved in THF solvent. Molecular weights were determined on the basis of polystyrene standards.
2.3.5 X-ray diffraction

X-ray diffraction technique gives the information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. X-ray diffraction technique is based on the elastic scattering of X-rays from structures that have long range order. X-ray diffraction data for the polymer were collected at room temperature on a Rigaku Minislex X-ray diffractometer Cu Kα radiation (λ=0.15418nm) at 30kV and 15mAmp.

2.3.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) reveals the thermal characteristics of polymers including degradation temperature, absorbed moisture content the level of oligomer in polymer etc. It determines the weight loss with respect to temperature. Thermogravimetric analysis (TGA) was conducted on a Shimadzu TG 50 thermogravimetric analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. Analysis was performed at 0- 650 °C temperature ranges.

2.3.7 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is used widely for polymers. It evaluates glass transition temperature (T_g), melting temperature (T_m), purity of polymers. The result of a DSC experiment is a curve of heat flux versus temperature or versus time. Differential scanning calorimetry (DSC) of the polymers was accomplished on DSC-60 (Shimadzu) with a heating rate of 10°C/ min under a nitrogen atmosphere. Analysis was performed at 0- 300 °C temperature ranges.

2.4 Experiment

2.4.1 Monomers synthesis

2.4.1.1 Hexyl2 -(thiophene-3-yl) acetate (HTA)

3-thiophene acetic acid (0.0137 moles) in 20ml dichloroethane (DCE) and thionyl chloride (0.0137 moles) were taken in a round bottom flask and refluxed for 6h. The excess thionyl chloride was removed under vacuum. Then hexanol (0.0137mole) in 15ml DCE and 3ml of
pyridine were added to the flask drop wise through an additional funnel and the mixture was refluxed for 6h. After refluxing, the reaction mixture was washed with 1N HCl (3 × 50ml), then saturated NaHCO₃ (3×50ml), and dried over K₂CO₃. The solvent was removed with a rotary evaporator and crude product was obtained. The crude product was purified by silica gel column chromatography using petroleum ether / ethyl acetate (20:1) mixture as the eluent.

The product was yellow - orange liquid.
Yield: 79%
UV- Vis (THF): \( \lambda_{\text{max}} \) 255 nm
FTIR (KBr): \( \nu \) 3105, 2934, 2861, 1735, 1460, 1257, 1147, 765 cm\(^{-1}\).
\( ^1 \)H NMR (400MHz) (CDCl₃): \( \delta \) 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88 ppm

2.4.1.2 Octyl 2 - (thiophene-3-yl) acetate (OTA)

Synthetic procedure of monomer (OTA) is same as monomer (HTA).

The product was yellow- orange liquid.
Yield: 71%
UV- Vis (THF): \( \lambda_{\text{max}} \) 254 nm
FTIR (KBr): \( \nu \) 2925, 2860, 1730, 1460, 1250, 1140, 765 cm\(^{-1}\).
\( ^1 \)H NMR (400MHz) (CDCl₃): \( \delta \) 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88 ppm

2.4.1.3 Decyl 2 - (thiophene-3-yl) acetate (DTA)

Synthetic procedure of monomer (DTA) is same as monomer (HTA).

The product was yellow orange liquid.
Yield: 73%
UV- Vis (THF): \( \lambda_{\text{max}} \) 254 nm
FTIR (KBr): \( \nu \) 2923, 2857, 1732, 1459, 1245, 1140, 760 cm\(^{-1}\).
\( ^1 \)H NMR (400MHz) (CDCl₃): \( \delta \) 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88 ppm

2.4.1.4 Dodecyl 2 - (thiophene-3-yl) acetate (DDTA)

Synthetic procedure of monomer (DDTA) is same as monomer (HTA).
The product was orange liquid.
Yield: 69%
UV-Vis (THF): $\lambda_{\text{max}}$ 254 nm
FTIR (KBr): $\nu$ 2923, 2856, 1734, 1459, 1261, 1145, 763 cm$^{-1}$.
$^1$H NMR (400MHz) (CDCl$_3$): $\delta$ 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88 ppm

2.4.1.5 3- pentadecylphenyl 2- (thiophene-3-yl) acetate (PDPTA)

3-thiophene acetic acid (0.005 moles) in 20ml dichloroethane (DCE) and thionyl chloride (0.005 moles) were taken in a round bottom flask and refluxed for 6h. The excess thionyl chloride was removed under vacuum. Then 3-pentadecyl phenol (0.005mole) and dimethylamino pyridine (DMAP) (0.005moles) in 15ml DCE were added to the flask drop wise through an additional funnel and the mixture was refluxed for 6h. After refluxing, the reaction mixture was washed with 1N HCl (3x 50ml), then saturated NaHCO$_3$ (3x50ml), and dried over K$_2$CO$_3$. The solvent was removed with a rotary evaporator and crude product was obtained. The crude product was purified by silica gel column chromatography using petroleum ether / ethyl acetate (20:1) mixture as the eluent.

The product was viscous orange-red liquid.
Yield: 62%
UV-Vis (THF): $\lambda_{\text{max}}$ 272 nm
FTIR (KBr): $\nu$ 2919, 2848, 1738, 1469, 1252, 1147, 764 cm$^{-1}$.
$^1$H NMR (400MHz) (CDCl$_3$): $\delta$ 7.27-7.00, 3.65, 2.54, 1.6 -0.88 ppm

2.4.1.6 3-pentadecylocyclohexyl 2- (thiophene-3-yl) acetate (PDCHTA)

Synthetic procedure of monomer (f) was same as (e).

The product was viscous orange-red liquid.
Yield: 64.49%
UV-Vis (THF): $\lambda_{\text{max}}$ 253 nm
FTIR (KBr): $\nu$ 2921, 2848, 1731, 1462, 1251, 1142, 756 cm$^{-1}$.
$^1$H NMR (400MHz) (CDCl$_3$): $\delta$ 7.27, 7.15, 7.03, 4.00, 3.67, 1.98-0.88 ppm
2.4.1.7 Quinolin-8-yI 2 – (thiophene-3-yl) acetate (QTA)

Synthetic procedure of monomer (QTA) was same as monomer (HTA).

The product was solid.

Yield: 61%,  
M.P: 128°C

UV- Vis (THF): \( \lambda_{\text{max}} \) 256 nm

FTIR (KBr): \( \nu \) 3092, 3041, 1755, 1591, 1496, 1467, 1339, 1237, 1138, 805, 755 cm\(^{-1}\).

\(^1\)HNMR (400MHz)(CDCl\(_3\)): \( \delta \) 7.43-8.92, 7.25, 7.15, 7.02, 3.65 ppm.

2.4.2 Polymer Synthesis

General procedure of polymerization

The general procedure of synthesizing the polymers is shown in Scheme 2.1. Monomers in 30ml carbon tetrachloride were taken in a three-necked flask equipped with a condenser, a pressure equalizing funnel, and a nitrogen gas inlet tube and stirring was done by a magnetic stirrer. Ferric chloride (four times of monomer) in 10ml nitromethane was added dropwise to a stirred solution of monomer at 0°C with the continuous flow of nitrogen and the reaction was continued for 24 h. The reaction mixture was poured into stirred methanol (500ml) and precipitate was obtained. The precipitate was dried in vacuum. The product was dissolved in THF and reprecipitated in methanol. Thus polymer was purified by reprecipitation method.

2.4.2.1 Poly (hexyl-2-(thiophene-3-yl) acetate) (PHTA)

0.005 mole of hexyl-2(thiophene-3-yl) acetate monomer and 0.02mole of ferric chloride were used for polymerization reaction.

Yield: 66%

UV- Vis (THF): \( \lambda_{\text{max}} \) 370nm

FTIR (KBr): \( \nu \) 2928, 2860, 1735, 1460, 1257, 1173 cm\(^{-1}\).

\(^1\)H NMR (400MHz) (CDCl\(_3\)): \( \delta \) 7.04, 4.09, 3.64, 1.63-0.88ppm
2.4.2.2 Poly (octyl-2-(thiophene-3-yl) acetate) (POTA)

0.0025 mole of octyl-2(thiophene-3-yl) acetate monomer and 0.01 mole of ferric chloride were used for polymerization reaction.

Yield: 63%
UV-Vis (THF): \( \lambda_{\text{max}} \) 363 nm
FTIR (KBr): \( \nu \) 2934, 2860, 1730, 1440, 1250, 1180 cm\(^{-1}\).
\(^1\)H NMR (400MHz) (CDCl\(_3\)): \( \delta \) 7.04, 4.09, 3.64, 1.63-0.88 ppm.

2.4.2.3 Poly (decyl-2-(thiophene-3-yl) acetate) (PDTA)

0.0037 mole of decyl-2(thiophene-3-yl) acetate monomer and 0.015 mole of ferric chloride were used for polymerization reaction.

Yield: 62.8%
UV-Vis (THF): \( \lambda_{\text{max}} \) 363 nm
FTIR (KBr): \( \nu \) 2922, 2852, 1732, 1459, 1245, 1141 cm\(^{-1}\).
\(^1\)H NMR (400MHz) (CDCl\(_3\)): \( \delta \) 7.04, 4.09, 3.64, 1.63-0.88 ppm.

2.4.2.4 Poly (dodecyl-2-(thiophene-3-yl) acetate) (PDDTA)

0.004 mole of dodecyl-2(thiophene-3-yl) acetate monomer and 0.016 mole of ferric chloride were used for polymerization reaction.

Yield: 61%
UV-Vis (THF): \( \lambda_{\text{max}} \) 359
FTIR (KBr): \( \nu \) 2924, 2853, 1737, 1459, 1261, 1145 cm\(^{-1}\).
\(^1\)H NMR (400MHz) (CDCl\(_3\)): \( \delta \) 7.04, 4.09, 3.64, 1.63-0.88 ppm.

2.4.2.5 Poly (3-pentadecylphenyl-2-(thiophene-3-yl) acetate) (PPDPTA)

0.0034 mole of 3-pentadecylphenyl-2(thiophene-3-yl) acetate monomer and 0.014 mole of ferric chloride were used for polymerization reaction.

Yield: 56%
UV-Vis (THF): \( \lambda_{\text{max}} \) 315 nm
FTIR (KBr): \( \nu \) 2922, 2852, 1740, 1469, 1252, 1152 cm\(^{-1}\).
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2.4.2.6 Poly (3-pentadecylcyclohexyl-2-(thiophene-3-yl) acetate) (PPDCHTA)

0.0036 mole 3-pentadecylcyclohexyl-2(thiophene-3-yl) acetate monomer and 0.0143 mole of ferric chloride were used for polymerization reaction.

Yield: 54.7%

UV-Vis (THF): \( \lambda_{\text{max}} \) 307 nm

FTIR (KBr): \( \nu \) 2923, 2854, 1732, 1462, 1251, 1142 cm\(^{-1}\).

\(^1\)H NMR (400MHz) (CDCl\(_3\)): \( \delta \) 7.15-7.00, 3.65, 2.54, 1.6 -0.88 ppm.

2.4.2.7 Poly (quinoline 8-yl-2-(thiophene-3-yl) acetate) (PQTA)

0.011 mole of quinoline 8-yl-2(thiophene-3-yl) acetate monomer and 0.044 mole of ferric chloride were used for polymerization reaction.

Yield: 42.3%

UV-Vis (THF): \( \lambda_{\text{max}} \) 392nm

FTIR (KBr): 3085, 3045, 1731, 1531, 1586, 1464, 1432, 1322, 1222, 1149 cm\(^{-1}\).

\(^1\)H NMR (400MHz) (CDCl\(_3\)): \( \delta \) 7.5-8.7, 6.98, 3.65 ppm.

2.5 Results and discussions

2.5.1 Characterization of monomers

The monomers were prepared by esterification [54-58] of 3-thiophene acetic acid and corresponding alcohols (hexanol, octanol, decanol, dodecanol, 3-pentadecyl pheno, 3-pentadecyl cyclohexanol, and 8- hydroxyl quinoline) (Scheme 2.1). 3-thiophene acetic acid was first converted to 3-thiophenacetyl chloride using thionyl chloride as a chlorinating agent and subsequently reacted with alcohols in the presence of pyridine (for monomers HTA, OTA, DTA, DDTA, QTA) and dimethyl amino pyridine (DMAP) (for monomers PDPTA, PDCHTA) as acid acceptor. The yield of the monomers is 60-80%. The formation of monomers was confirmed by FTIR, \(^1\)H NMR spectroscopy. The \( \text{C}_\beta-\text{H} \) stretching frequency (Fig2.1 -2.7.) in thiophene ring and alkyl chain on 3000 -2840 cm\(^{-1}\) was observed. The
formation of ester linkage was confirmed by the presence of $\text{C=O}$ stretching vibration at 1720-1735 cm$^{-1}$ and C-O-C stretching vibrations at 1250-1235 and 1145-1135 cm$^{-1}$. The C-H bending vibrations of alkyl group appeared at 1460 cm$^{-1}$. The C-H out of plane bending vibration of thiophene ring on 805-815, 760-750 cm$^{-1}$ was observed.
Figure 2.1: FTIR spectra of monomer HTA

Figure 2.2: FTIR spectra of monomer OTA
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Figure 2.3: FTIR spectra of monomer DTA

Figure 2.4: FTIR spectra of monomer DDTA
Figure 2.5: FTIR spectra of monomer PDPTA

Figure 2.6: FTIR spectra of monomer PDCHTA
Figure 2.7: FTIR spectra of monomer QTA

In $^1$H NMR spectra of the monomers, the signals at $\delta$ 7.05-7.03, 7.15 - 7.13, 7.27-7.25 ppm are assigned to the protons at 4, 5 and 2 position of the thiophene ring (Figure 2.8 - 2.14.). The signal at $\delta$ 3.67 - 3.64 ppm is related to the methylene group protons linked to thiophene ring. The signal at $\delta$ 4.00-4.09 ppm is related to methylene group proton linked to oxygen atom. The broad signal at $\delta$1.63-0.88 ppm is associated with alkyl protons. The signals in the range of $\delta$ 7.43-8.92 ppm are assigned to the aromatic quinolinyl protons. The broad signal at $\delta$ 7.27-7.00 is related to aromatic phenyl protons. The numbers of protons estimated from the integration of peaks are in good agreement with the proposed structure of monomers.
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Figure 2.8: Proton NMR spectra of monomer HTA

Figure 2.9: Proton NMR spectra of monomer OTA
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Figure 2.10: Proton NMR spectra of monomer DTA

Figure 2.11: Proton NMR spectra of monomer DDTA
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Figure 2.12: Proton NMR spectra of monomer PDPTA

Figure 2.13: Proton NMR spectra of monomer PDCHTA
2.5.2 Characterization of polymers

The polymers were prepared by oxidative polymerization using ferric chloride [41-54]. The polymerization process is slow and yields 42-66% polymer. The polymers showed good solubility in chloroform and THF.

The formation of polymers was further confirmed by FTIR and $^1$H NMR spectroscopy. In polymers, the C-H stretching frequency in thiophene ring and alkyl chain at 3000 - 2800 cm$^{-1}$ were observed (Figure 2.15 - 2.21). The bands at 1720 - 1735, 1250-1235 and 1145-1135 cm$^{-1}$ which is due to the $>$C=O and C-O-C stretching vibration of ester group. The C-H bending vibrations of alkyl group appeared at 1460 cm$^{-1}$. The absence of sharp band at 805 - 755 cm$^{-1}$ confirms the polymerization, since these absorptions are characteristic of the C-H$_a$ out of plane deformation in mono substituted thiophene ring.

Figure 2.14: Proton NMR spectra of monomer QTA
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Figure 2.15: FTIR spectra of polymer PHTA

Figure 2.16: FTIR spectra of polymer POTA
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Figure 2.17: FTIR spectra of polymer PDTA

Figure 2.18: FTIR spectra of polymer PDDTA
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Figure 2.19: FTIR spectra of polymer PPDPTA

Figure 2.20: FTIR spectra of polymer PPDCHTA
In the $^1$H NMR spectra of the polymers, the signals in the range of $\delta$ 7.5-8.7 ppm are assigned to the aromatic quinolinyl protons. The signal at $\delta$ 7.04-7.00 ppm is assigned to the proton at four position of the thiophene ring (Figure 2.22 - 2.28). The broad signal at $\delta$ 7.27-7.00 is related to aromatic phenyl protons. The signal at $\delta$ 3.67-3.64 ppm is related to the methylene group protons linked to thiophene ring. The broad signal at $\delta$ 1.63-0.88 ppm is associated with alkyl protons. The absence of the signals at $\delta$ 7.27 & 7.15 ppm related to the hydrogen at 2 and 5 position of the thiophene ring confirmed the polymerization.
Figure 2.22: Proton NMR spectra of polymer PHTA

Figure 2.23: Proton NMR spectra of polymer POTA
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Figure 2.24: Proton NMR spectra of polymer PDDTA

Figure 2.25: Proton NMR spectra of polymer PDDTA
Figure 2.26: Proton NMR spectra of polymer PPDPTA

Figure 2.27: Proton NMR spectra of polymer PPDCHTA
2.5.2.1 Molecular weight of polymers

Molecular weight of polymers has been measured by gel permeation chromatography (GPC) in THF solution using polystyrene standard. Molecular weights of the polymers in THF are shown in Table 2.1. GPC curve of the polymers is depicted in Figure 2.29 - 2.35. The number-average molecular weights of the resulting polymers are in the range of 3154–22260 g/mol with polydispersity indexes in the range of 1.67–3.34. The weight average molecular weights of polymers have been found in the range 6097 – 74566 g/mol. The results show that the soluble part of polymers in THF solvent is of low molecular weight.

Table 2.1 Molecular weight of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w$ (g/mol)</th>
<th>$\bar{M}_w/\bar{M}_n$ (PDI)</th>
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<tbody>
<tr>
<td>PHTA</td>
<td>5372</td>
<td>14698</td>
<td>2.73</td>
</tr>
<tr>
<td>POTA</td>
<td>3338</td>
<td>6097</td>
<td>1.82</td>
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<td>PDTA</td>
<td>3589</td>
<td>13213</td>
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<td>PDDTA</td>
<td>8418</td>
<td>21411</td>
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</tr>
<tr>
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<td>11492</td>
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<tr>
<td>PQTA</td>
<td>22260</td>
<td>74566</td>
<td>3.34</td>
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Figure 2.29: GPC curve of polymer PHTA

Figure 2.30: GPC curve of polymer POTA

Figure 2.31: GPC curve of polymer PDTA
Figure 2.32: GPC curve of polymer PDDTA

Figure 2.33: GPC curve of polymer PPDPTA

Figure 2.34: GPC curve of polymer PPDCHTA
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Figure 2.35: GPC curve of polymer PQTA

2.5.2.1.1 Solubility and degree of polymerization of polymers

The solubility is not only an important criterion to assess conjugated polymers for their possible commercial use but equally important also from characterization point of view. The polymers are soluble in CHCl₃, THF, DMF, DMAc and DMSO. The solubility and degree of polymerization (DP) of the polymers in THF are shown in Table 2.2. The fraction of polymers soluble in THF is 15-90 %. It is observed that solubility decreases with increasing degree of polymerization. The effective conjugation length as well as delocalization of electron depends on degree of polymerization. The delocalization of electrons requires a conjugated chain structure which in turn brings insolubility to the polymers.

Table 2.2 Degree of polymerization and solubility of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molar mass of Monomer unit (g/mol)</th>
<th>Degree of polymerization (DP)</th>
<th>Fraction of polymer soluble in THF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>5372</td>
<td>226</td>
<td>24</td>
</tr>
<tr>
<td>POTTA</td>
<td>3338</td>
<td>254</td>
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<td>PDTA</td>
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<td>13</td>
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<td>PDDTA</td>
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<td>310</td>
<td>27</td>
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<td>PQTA</td>
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</tr>
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</table>
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2.5.2.2 UV- Vis spectra

2.5.2.2.1 UV –Vis spectra of monomers and polymers

The UV-Vis spectra of monomers and polymers are shown in Figure 2.36 - 2.42. The maximum absorption (\(\lambda_{\text{max}}\)) of monomers and polymer and their shifting are demonstrated in Table 2.3. Polymers possess intensive and broad absorption bands in the UV-Visible region, indicating an extensive \(\pi\)-conjugation in the thienylene backbone. The \(\lambda_{\text{max}}\) depends on the effective \(\pi\)-conjugation of the polymer chain and the aggregation state of the polymer. Higher the \(\pi\)-conjugation length, a red shifted \(\lambda_{\text{max}}\) is observed. \(\lambda_{\text{max}}\) of polymers in THF solution are found to be in the range of 307 to 392 nm. A red shifted \(\lambda_{\text{max}}\) in solution is observed for polymer in comparison to their respective monomer. This is due to the \(\pi\)-conjugation of polymer chain. Polymers possessing alkyl side chain with different carbon length ranging from six to twelve have found similar red shifting absorption (105-115 nm) with respect to their monomer. This indicates that alkyl containing polymers have akin \(\pi\)-conjugation length irrespective of their carbon chain length. Polymers containing 3-pentadecyl phenyl and 3- pentadecyl cyclohexyl side chains have experienced 43 and 54 nm red shifting absorption compared with their monomer. This low value of red shifting absorption for polymer PPDTA and PPDCHTA compared to other polymers may be due to the aggregation of polymer side chain [59]. A red shifted \(\lambda_{\text{max}}\) is observed for polymer PQTA having quinoline side chain with reference to monomer unit. The red shifting is higher for polymer PQTA than other ester substituted polymers. The results show that \(\pi\) conjugation length is highest for polymer PQTA. This observation is attributed to an increase in coplanarity of the thienylene backbone [60-61].
Table 2.3 Absorption of monomers and polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Maximum absorption of monomer in THF (nm)</th>
<th>Maximum absorption of polymer in THF (nm)</th>
<th>Red shifting absorption from monomer to polymer (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>255</td>
<td>370</td>
<td>115</td>
</tr>
<tr>
<td>POTA</td>
<td>254</td>
<td>363</td>
<td>109</td>
</tr>
<tr>
<td>PDTA</td>
<td>254</td>
<td>363</td>
<td>109</td>
</tr>
<tr>
<td>PDDTA</td>
<td>254</td>
<td>359</td>
<td>105</td>
</tr>
<tr>
<td>PPDTA</td>
<td>272</td>
<td>315</td>
<td>43</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>253</td>
<td>307</td>
<td>54</td>
</tr>
<tr>
<td>PQTA</td>
<td>256</td>
<td>392</td>
<td>136</td>
</tr>
</tbody>
</table>

Figure 2.36: UV-Vis Spectra of monomer HTA and polymer PHTA
Chapter 2: Synthesis and characterization of ester substituted polythiophenes

Figure 2.37: UV-Vis Spectra of monomer OTA and polymer POTA

Figure 2.38: UV-Vis Spectra of monomer DTA and polymer PDTA
Figure 2.39: UV-Vis Spectra of monomer DDTA and polymer PDDTA

Figure 2.40: UV-Vis Spectra of monomer PDPTA and polymer PPDPCTA
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Figure 2.41: UV-Vis Spectra of monomer PDCHTA and polymer PPDCHTA

Figure 2.42: UV-Vis Spectra of monomer QTA and polymer PQTA
2.5.2.2 Optical band gap

Optical absorption in conjugated polymers which are mostly amorphous or semicrystalline may due to the transition of charge carriers, through a forbidden energy gap, called optical band gap. Attempts have been made to determine the optical band gap using the equation 2.2 [62].

\[
E_{\text{opt}}^g (eV) = \frac{1240}{\lambda_{\text{edge}} (\text{nm})} \tag{2.2}
\]

Where \(E_{\text{opt}}^g\) is the optical band gap of polymers and \(\lambda_{\text{edge}}\) is the absorption edge. The absorption edge (\(\lambda_{\text{edge}}\)) and optical band gap (\(E_{\text{opt}}^g\)) of polymers are listed in Table 2.4. The band gap of polymers is found to be 2.1-2.47 eV. The results show that aromatic containing moieties polymer have higher band gap. We have compared the optical band gap data with electrochemical band gap. Comparison and trend of electrochemical and optical band gap were discussed in next chapter.

Table 2.4 Absorption edge and optical bandgap of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Side chain moiety (R)</th>
<th>Absorption edge of polymer (nm)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>-C(<em>6)H(</em>{13})</td>
<td>524</td>
<td>2.36</td>
</tr>
<tr>
<td>POTA</td>
<td>-C(<em>8)H(</em>{17})</td>
<td>525</td>
<td>2.36</td>
</tr>
<tr>
<td>PDTA</td>
<td>-C(<em>{10})H(</em>{21})</td>
<td>540</td>
<td>2.29</td>
</tr>
<tr>
<td>PDDTA</td>
<td>-C(<em>{12})H(</em>{25})</td>
<td>520</td>
<td>2.38</td>
</tr>
<tr>
<td>PPDPTA</td>
<td></td>
<td>506</td>
<td>2.45</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td></td>
<td>535</td>
<td>2.31</td>
</tr>
<tr>
<td>PQTA</td>
<td></td>
<td>502</td>
<td>2.47</td>
</tr>
</tbody>
</table>
2.5.2.3 XRD analysis

XRD analysis has been performed by preparing the polymer film on the glass substrate. X-ray diffractograms of the polymers are shown in Figure 2.43. XRD analysis reveals a broad peak at $2\theta = 20 - 25^\circ$ with weak intensities for polymers. No diffraction peak is observed for polymers at low angles. Polymers are amorphous in nature. Amorphous morphology prevents light scattering and crystallization-induced degradation [63]. This is generally useful in light emitting diode application.

![Figure 2.43: X-ray diffractograms of polymers](image-url)
2.5.3 Thermal properties of polymers

2.5.3.1 Thermogravimetric analysis

The thermal properties of the polymers have been investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. The TGA curve of polymers is shown in Figure 2.44 - 2.50 and weight losses at different temperature are shown in Table 2.5. PDTA and PPDPTA polymers show 5-10% weight loss at 260° and 125 °C respectively. PHTA, POTA, PPDPTA and PPDCHTA exhibit 10-30 % weight loss at 170°, 150°, 358° and 307°C, respectively. The initial weight loss is due to the presence of oligomer compound in polymers. It is found that these polymers possess good thermal stability with the onset degradation temperature around 300-350 °C under nitrogen atmosphere and 40-60 % weight loss occurred at the temperature of 400-450 °C. The thermal stability of polymers follows the order PQTA > PDTA > PDDTA > PHTA = POTA > PPDCHTA = PPDPTA. PQTA and PDTA have found good thermal stability compared to other polymers. In case of PQTA, this is possibly due to the presence of bulky N-containing quinoline moiety attached to the thiophene backbone for high thermal stability. However, the proper explanation is not found for high thermal stability of PDTA polymer. The thermal stability increases with increasing the molecular weight of polymers.

Table 2.5 Weight loss of polymers at different temperature

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp° at (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-10 % Wt. loss</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>PHTA</td>
<td>-</td>
</tr>
<tr>
<td>POTA</td>
<td>-</td>
</tr>
<tr>
<td>PDTA</td>
<td>260</td>
</tr>
<tr>
<td>PDDTA</td>
<td>-</td>
</tr>
<tr>
<td>PPDPTA</td>
<td>125</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>-</td>
</tr>
<tr>
<td>PQTA</td>
<td>-</td>
</tr>
</tbody>
</table>
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Figure 2.44: TGA curve of polymer PHTA

Figure 2.45: TGA curve of polymer POTA
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Figure 2.46: TGA curve of polymer PDTA

Figure 2.47: TGA curve of polymer PDDTA
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Figure 2.48: TGA curve of polymer PPDPTA

Figure 2.49: TGA curve of polymer PPDCHTA
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2.5.3.2 Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) of polymers under nitrogen atmosphere is shown in Figure 2.51-2.57. The polymers exhibit a glass transition temperature ($T_g$) in the range of 66-154°C (Table 2.6). It is observed that $T_g$ of alkyl containing ester substituted polythiophenes decrease with increasing side chain length. Further, $T_g$ decreases with flexible pentadecyl phenyl and pentadecyl cyclohexyl side chain attached to ester polythiophenes. PPDPTA shows the lower $T_g$ (66°C) and PQTA shows the higher $T_g$ (166°C). Long flexible pentadecyl chain on meta position of phenyl ring serves the internal plasticizer of polymer which lowers the $T_g$ of PPDPTA polymer. The higher $T_g$ of PQTA polymer is due to the presence of bulky and rigid quinoline moiety. A broad peak at 105-122°C for POTA, PDTA, PDDTA, PPDPTA and PPDCHTA polymers is assigned to the melting of side chain having alkyl side chain longer than hexyl group. Similar observation has been made for polyalkylthiophenes possessing C_8 or longer alkyl side chains by other researchers [64-66]. It seems that the rigid backbone exerts strong influence on the side chain crystallization. $T_g$ of the polymers decreases with increasing side chain length. High glass transition temperatures
(T_g) and thermal stability are required to withstand inevitable Joule heating encountered during LED operation, especially at higher electric fields and current densities [63].

Figure 2.51: DSC curve of polymer PHTA

Figure 2.52: DSC curve of polymer POTA
Figure 2.53: DSC curve of polymer PDTA

Figure 2.54: DSC curve of polymer PDDTA
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Figure 2.55: DSC curve of polymer PPDP TA

Figure 2.56: DSC curve of polymer PPDCHTA
Figure 2.57: DSC curve of polymer PQTA

Table 2.6: Tg and Tm of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Side chain moiety (R)</th>
<th>Glass transition temperature (Tg) (°C)</th>
<th>Melting temperature (Tm) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTA</td>
<td>-C₆H₁₃</td>
<td>94</td>
<td>-</td>
</tr>
<tr>
<td>POTA</td>
<td>-C₈H₁₇</td>
<td>-</td>
<td>120</td>
</tr>
<tr>
<td>PDTA</td>
<td>-C₁₀H₂₁</td>
<td>70</td>
<td>119</td>
</tr>
<tr>
<td>PDDTA</td>
<td>-C₁₂H₂₅</td>
<td>69</td>
<td>122</td>
</tr>
<tr>
<td>PPDPTA</td>
<td></td>
<td>63</td>
<td>105</td>
</tr>
<tr>
<td>PPDCHTA</td>
<td>-C₁₅H₃₀</td>
<td>67</td>
<td>107</td>
</tr>
<tr>
<td>PQTA</td>
<td></td>
<td>154</td>
<td>-</td>
</tr>
</tbody>
</table>
2.6 Conclusion

A series of ester substituted thiophene monomers has been synthesized by esterification reaction. The yield of the monomers is 60-80%. The formation of monomers was confirmed by FTIR, $^1$H NMR spectroscopy. The polymers have been prepared by the oxidative polymerization using ferric chloride. The polymerization process is slow and yield of the polymer is 42-66%. The polymers show good solubility in THF, CHCl$_3$, DMF, DMAc, and DMSO. The number average molecular weights of polymers are in the range of 3154 to 22260 g / mole. The soluble part of the polymers is found to be oligomer. The absorption maximum in UV-Vis spectra of the polymers is in the range of 307-392 nm. All the polymers show red shift of absorption maximum with respect to their monomers. Optical band gap of the polymers is found to be in the range of 2.1-2.47 eV. XRD analysis reveals that polymers are amorphous in nature. Polymers possess good thermal stability with the onset decomposition temperature around 300-350 °C under nitrogen atmosphere. Thermal stability increases with the increase in molecular weight of polymers. The polymers exhibit a glass transition temperature (T$_g$) in the range of 63-154°C. It is observed that T$_g$ of the polymers decreases with the increase in length of the side chain.
References