Chapter 4

SYNTHESIS OF POLYMERS AND THEIR CHARACTERISATION

4.1 Introduction
4.2 Result and Discussion
4.3 Experimental part
4.4 Conclusion

This chapter discusses about the synthesis of designed polymers by means of Suzuki and Direct arylation polymerisation reactions. The synthesised polymers were characterised by UV-Vis, $^1$H NMR, PL Spectroscopic techniques, TG/DTG and Cyclic Voltammetry techniques. Detailed synthetic procedures and characterisation data are presented in this chapter. The frontier orbital energy levels and band gap were experimentally determined using cyclic Voltammetric studies and optical measurement. The theoretically calculated values are in good agreement with the experimental results.
Chapter 4

4.1 Introduction

Conducting polymers represent new advanced materials that play a key role in the development of new devices and structures offering combination of various properties required for advanced applications. When key structural requirements are met, conjugated polymers exhibit properties such as solution processability, low band gap, high conductivity, large charge transporting capabilities, and broad optical absorption. As a result, conjugated polymers can be utilized for the fabrication of organic electronic and photonic devices. Zero band gap and intrinsic conductivity have been a major goal for the band gap control of π-conjugated polymers. Although materials with optimal band gap values can be synthesised using known synthetic tools, the difficulty lies in the need to incorporate optimal light-harvesting properties, a rather-low HOMO level and a high hole mobility. Different strategies are used for band-gap control, but roughly divided into two main routes. The first approach involves the planarization, rigidification and quinoidization of the conjugated system which results in a reduction of BLA (Bond Length Alteration). This method leads to a large increase in the photoluminescence efficiency, decrease the reorganization energy and thus to improve the charge mobility. A major drawback of this approach is that, it requires long and complex synthetic work. The second route lies in the association of donor and acceptor units leading to the possibility of intramolecular charge-transfer. This can lead to very low band gaps and is now the most preferred one for the synthesis of polymers for optoelectronic applications.¹⁻⁶

The D-A approach still poses several fundamental problems related to the effects of the mode of connection and relative strengths of the D and A
units in the \( \pi \)-conjugated system. These structural parameters control the width of the band gap as well as the electronic distribution in the conjugated system and hence the charge-transport properties of the material.

\( \pi \)-conjugated systems designed as active materials for electronic and photonic devices must combine processability and high environmental and photochemical stability. These materials will have to be produced by means of cost-effective, simple and straightforward synthetic procedures taking into account of environmental constraints: atom economy, minimal use of organic solvents and toxic metal catalysts, and use of renewable starting materials.

![Catalytic cycle for Pd catalysed reaction](image)

**Fig. 4.1: Catalytic cycle for Pd catalysed reaction**

Although these complex problems represent major challenges for the chemistry of functional \( \pi \)-conjugated systems, their solutions will determine,
the future applications of \( \pi \)-conjugated systems in electronic and photonic devices.\(^{(a)}\) Here we discuss the synthesis of donor-acceptor conjugated polymers by means of Pd catalysed cross-coupling reactions. Most palladium catalysed reactions are believed to follow a similar catalytic cycle and is shown in figure 4.1.\(^{(b)}\)

4.1.1 Pd catalysed polymerisations

In the present work, either Suzuki or Direct arylation polycondensation has been employed to synthesize the conjugated donor-acceptor polymers. Both the Suzuki and Direct arylation are palladium catalysed intermolecular cross-coupling reactions. Suzuki polymerisation, a common cross-coupling reaction involves several advantages that, it is highly tolerant to different functional groups, and boron containing by-products are easily removed by a simple alkali work-up. Although the most commonly used method for the formation of aryl-aryl bonds, the Suzuki reaction is just as effective for the synthesis of highly substituted products.\(^{(c)}\)

D. Muenmart et al reported a range of stable emulsions of spherical and rod-like conjugated polymer nanoparticles (CPN) via Suzuki–Miyaura cross-coupling reactions of 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester with a number of different dibromoarene monomers in xylene, stabilized in water by the nonionic surfactant, Triton X-102. High molar mass poly (9,9-dioctylfluorene) (PF8), poly (9,9-dioctylfluorene-alt-benzothiadiazole) (PF8BT), poly (9,9-dioctylfluorene-alt-4-sec-butyl phenyl diphenylamine) (PF8TAA) and poly (9,9-dioctylfluorene-alt-bithiophene) (PF8T2) emulsions were obtained\(^{8}\) (Scheme 1).
E Lim reported a series of carbazole-benzothiadiazole-triazole based copolymers, poly \(((N-9'\text{-heptadecanyl-2,7-carbazole})\text{-co-}(5,5-(4',7'-\text{di-2-thienyl-2',1',3'-benzothiadiazole}))\text{-co-}((4-(4-butylphenyl)-3,5-diphenyl-4H-1,2,4\text{-triazole}))\) (PCz3TBTz) by Suzuki coupling polymerization \(^9\) (Scheme 2).
Direct (hetero) arylation is an advantageous tool for the synthesis of regioregular polymers as well as alternating copolymers. This methodology has several advantages (1) it reduces the number of steps (2) utilizes monomers with long-term stability that can be easily manipulated (3) produces only acid as a byproduct (4) can give rise to polymeric material with higher molecular weights than those obtained by other methods. High functional group tolerance has been displayed. This method enables more effective preparation of highly efficient known polymers and provide entry into novel and promising materials. According to some recent reports, materials prepared by this method has been successfully incorporated into organic electronic devices such as OTFTs, OLEDs and BHJ-SCs.

X. Wang et al reported the synthesis of thiophene-flanked benzothiadiazole derivatives (DTBTs) via direct arylation coupling. DTBTs were further polymerized with fluorene dibromide via direct arylation polycondensation to give well-defined alternating copolymers (Scheme 3).

Scheme 3: Synthesis of fluorene-thiophene copolymers
Recently, T. Kanbara and co-authors have focused on the Ru-catalyzed direct arylation of pyrrole derivatives bearing a directing group. This resulted in cross-coupling reaction at the $\alpha$-position of the pyrrole monomer without protecting the $\beta$-position. In particular, they successfully proved the directed site-selective polycondensation of 1-(2-pyrimidinyl) pyrrole with 2,7-dibromo-9,9-dioctylfluorene with the 2-pyrimidinyl substituent as directing group\textsuperscript{16} (Scheme 4).

\begin{center}
\textbf{Scheme 4: Synthesis of polymer consisting of pyrrole and fluorine units}
\end{center}

4.2 Polymer Synthesis

4.2.1 Synthesis of fluorene-quinoxaline polymers

The three theoretically designed fluorene-quinoxaline polymers were synthesised by Suzuki cross-coupling reaction using Pd(PPh\textsubscript{3})\textsubscript{4} as the catalyst. The dibromoquinoxaline derivatives was reacted with the dioxaborolane derivative of fluorene in the presence of the catalyst, Pd(PPh\textsubscript{3})\textsubscript{4} to form the corresponding polymers. The crude polymers were purified by precipitating from methanol followed by soxhlet extraction using methanol and hexane. The polymers were soluble in common organic solvents such as chloroform, chlorobenzene and THF. The synthetic route towards the Fluorene-Quinoxaline polymer is depicted in Scheme 5.
The three polymers were characterized using $^1$H NMR, UV-Visible spectroscopy, GPC, Cyclic voltammetry, TGA etc. The molecular weights of the polymers were obtained from gel permeation chromatography in THF referring to polystyrene standards. Among the three polymers, P(FQ-A) showed high molecular weight. The copolymer exhibited number average molecular weight ($M_n$) of 12228 and weight average molecular weight ($M_w$) of 18384 with polydispersity index (PDI) of 1.50. Table 1 summarizes the molecular weight and polydispersity index (PDI) of the copolymers. $M_p$ is the peak molecular weight. Here $M_p$ is the mode of molecular weight.
distribution. It is the molecular weight of the highest peak. The polymers P(FQ-A), P(FQ-B) and P(FQ-P) show peak molecular weight of 14270, 14683 and 10575 respectively.

**Table 4.1: Results of the polymerisation reaction**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_p$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FQ-A)</td>
<td>12228</td>
<td>18384</td>
<td>14270</td>
<td>1.50</td>
</tr>
<tr>
<td>P(FQ-B)</td>
<td>11753</td>
<td>16240</td>
<td>14683</td>
<td>1.38</td>
</tr>
<tr>
<td>P(FQ-C)</td>
<td>8332</td>
<td>11195</td>
<td>10575</td>
<td>1.34</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectra of the polymers (a) P(FQ-A), (b) P(FQ-B) and (c) P(FQ-P) are shown in figure 4.2. The $^1$H NMR spectrum of P(FQ-A) showed multiplets at $\delta$ 0.85-2.1 due to aliphatic protons. It also showed multiplets at $\delta$ 7.5-8.5 due to aromatic protons present in the copolymer. Likewise, P(FQ-B) and P(FQ-P) also showed multiplets in the aliphatic and aromatic region.

![Fig.4.2: $^1$H NMR spectrum of a) (FQ-A), (b) P(FQ-B) and (c) P(FQ-P) (a) P(FQ-A) (b) P(FQ-B) (c) P(FQ-P)](image-url)
4.2.1.1 Optical and photoluminescence properties

Figure 4.3 shows the absorption spectra of the polymers. The optical properties of the polymers, P(FQ-A) and P(FQ-B) were investigated in chloroform and P(FQ-P) with the help of UV-Vis-DRS method. The polymers, P(FQ-A), P(FQ-B) and P(FQ-P) showed absorption maximum around 321 nm, 310 nm and 330 nm respectively. In the absorption spectrum, the band with absorption maximum below 350 nm is due to $\pi$-$\pi$ transition of the backbone and the peak at longest wave length (400 nm- 700 nm) is due to the intermolecular charge transfer (ICT) band. The absorption onset of P(FQ-A), P(FQ-B) and P(FQ-P) occurs at 473 nm, 471 nm, and 505 nm respectively. The optical band gap calculated was found to be 2.62 eV, 2.63 eV and 2.32 eV respectively. From quantum chemical calculations, band gaps obtained were 2.57 eV, 2.60 eV and 2.43 eV respectively. The band gaps calculated from optical methods are in good agreement with the theoretical values.

![Absorption spectra](image)

Fig 4.3: UV-Vis spectra of the polymer: (a) P(FQ-A) and (b) P(FQ-B) in 2mg/10mL chloroform and UV-Vis-DRS of (c) P(FQ-P)
Fig 4.4 shows the emission spectra of P(FQ-A), P(FQ-B) and P(FQ-P) in chloroform. The maximum emission shown by the three polymers are at 516 nm, 520 nm and 557 nm respectively. As expected, the emission spectrum of the polymer P(FQ-P) was redshifted when compared to the other two polymers.

Fig. 4.4: PL Spectra of the polymers: (a) P(FQ-A), (b) P(FQ-B) and (c) P(FQ-P) in 2mg/10mL chloroform (Excitation wavelength 365 nm)
4.2.1.2 Thermal properties

The thermal characteristics of the polymers were investigated by TG-DTG studies. From the TG traces, it is clear that the first two polymers follow single degradation pattern while the third shows step wise degradation. The moisture content present in the polymer was lost below 100°C. In P(FQ-A), DTG traces showed onset of degradation around 380°C and degradation at temperature 450°C, around 18 % weight loss as the onset loss point. In P(FQ-B), the onset of degradation is around 400°C and the degradation temperature is at 450°C. Here only 5 % weight loss took place at the onset loss point. P (FQ-B) is more stable compared to P (FQ-A). Among the three polymers, P(FQ-P) is the least stable one where degradation starts around 300°C. TG-DTG traces of the polymers are shown in the figure 4.5.

Fig.4.5: TG, DTG traces of the polymers: (a) P(FQ-A), (b) P(FQ-B) and (c) P(FQ-P)
4.2.1.3 Electrochemical studies

Cyclic voltammetric studies were carried out to determine the HOMO, LUMO levels and band gap of the polymers. CV studies were performed in a solution of Bu₄NPF₆ (0.1 M) in dry acetonitrile at 100 mV/s under nitrogen atmosphere. The set up consists of a Ag/Ag+ reference electrode, a platinum button electrode (0.08 cm²) coated with thin copolymer as the working electrode, and a platinum wire as the counter electrode. From the onset of oxidation, the HOMO levels of P(FQ-A), P(FQ-B) and P(FQ-P) were calculated to be -5.74 eV, -5.50 eV and -5.48 eV respectively by using the equation, HOMO = -( 4.4 + Eox onset). The LUMO energy levels (from the onset of reduction potentials) of P(FQ-A), P(FQ-B) and P(FQ-P) were calculated to be -2.77 eV, -1.73 eV and -1.078 eV respectively. The HOMO and LUMO energies were lowered on copolymerisation which indicated the enhanced electron accepting / transporting properties in conjugated polymers. Even though some deviations are there, the results are in good agreement with the values obtained from optical and theoretical methods. This is because, the predicted band gaps are for the isolated gas phase chains and also, the solid state effects such as polarisation effects and intermolecular packing forces are neglected. Band gap calculated by means of theoretical, electrochemical and optical methods are depicted in Table 2.

Table 4.2: Band gaps calculated by means of theoretical, electrochemical and optical methods

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Eg (theoretical) eV</th>
<th>Eg (Electrochemical) eV</th>
<th>Eg (Optical) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FQ-A)</td>
<td>2.57</td>
<td>2.9</td>
<td>2.62</td>
</tr>
<tr>
<td>P(FQ-B)</td>
<td>2.60</td>
<td>2.66</td>
<td>2.63</td>
</tr>
<tr>
<td>P(FQ-P)</td>
<td>2.43</td>
<td>2.2</td>
<td>2.32</td>
</tr>
</tbody>
</table>
4.2.2 Synthesis of fluorene-thiophene copolymer

Fluorene-thiophene copolymers were synthesised through the direct arylation polymerisation method. The synthesis of the polymers is shown in Scheme 6. Thiophene based monomers containing active hydrogen atoms were coupled with dibromo derivative of fluorene in the presence of Pd catalyst and phase transfer catalyst to form the corresponding polymers. The resulting polymers were purified by precipitating from methanol followed by soxhlet extraction using methanol and hexane. The polymers are soluble in common organic solvents such as chloroform, chlorobenzene and THF.

![Scheme 6: Synthesis of P(FMT) and P(EF)](image)

The polymers were characterized using $^1$H NMR, UV-Visible spectroscopy, GPC, Cyclic voltammetry, TGA etc. The molecular weights of the polymers were obtained from gel permeation chromatography in THF referring to polystyrene standards. P(FMT) shows number average molecular weight ($M_n$) of 14801 and weight average molecular weight ($M_w$) of 33144 with polydispersity index (PDI) of 2.24. The peak molecular
weight ($M_p$) of the polymer is 24136. P(EF) shows number average molecular weight ($M_n$) of 10873 and weight average molecular weight ($M_w$) of 18270 with polydispersity index (PDI) of 1.68. The peak molecular weight ($M_p$) of the polymer is 12158. GPC results were given in the table 4.3.

Table 4.3: Results of the polymerisation reaction of (a) P(FMT) and (b) P(EF)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_p$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FMT)</td>
<td>14801</td>
<td>33144</td>
<td>24136</td>
<td>2.24</td>
</tr>
<tr>
<td>P(EF)</td>
<td>10873</td>
<td>18270</td>
<td>12158</td>
<td>1.68</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectra of the polymers P(FMT) and P(EF) are shown in figure 4.6. The two polymers showed multiplets in the aliphatic and aromatic regions. In addition to that for P(FMT), it showed a singlet at $\delta$ 4.0 due to methoxy hydrogens. In the case of P(EF) an extra multiplet at $\delta$ 4.0 due to -CH$_2$O- was observed.

Fig.4.6: $^1$H NMR spectra of the polymers : (a) P(FMT) and (b) P(EF)
4.2.2.1 Optical and photoluminescence properties

Figure 4.7 shows the absorption spectra of the polymers. The optical properties of the polymers, P(FMT) and P(EF) were investigated in chloroform. P(FMT) and P(EF) showed absorption maximum around 476 nm and 450 nm respectively which are due to the intramolecular charge transfer (ICT) band. The absorption onset of P(FMT) and P(EF) occurs at 588 nm and 540 nm respectively. The optical band gap calculated was found to be 2.11 eV and 2.63 eV respectively. The band gaps calculated from optical methods are in good agreement with the theoretical values. From quantum chemical calculations, band gap obtained are 2.42 eV and 2.36 eV respectively.

Fig.4.7: UV-Vis Spectra of the polymers: (a) P(FMT) and (b) P(EF) in chloroform (2mg/10mL)

Fig 4.8 shows the emission spectra of P(FMT) and P(EF) in chloroform. The maximum emission shown by the polymers are 554 nm and 548 nm respectively.
Fig.4.8: PL spectra of the polymers: (a) P(FMT) and (b) P(EF) in 2mg/10mL chloroform solution (Excitation wavelength 365 nm)

4.2.2.2 Thermogravimetric studies

The thermal characteristics of the polymers were investigated by TG-DTG studies. From figure 4.9 it is clear that the P(FMT) follow multiple degradation pattern while P(EF) shows single degradation pattern. In P(FMT), DTG traces showed that the major onset of degradation was around 300°C and degradation temperature was around 400°C, losing around 25 % weight at the onset loss point. In P(EF), the onset of degradation is around 350°C and the degradation temperature is at 430°C. Here only 5% weight loss took place at the onset loss point. As shown by the TG-DTG curve, it is clear that the polymer P(EF) shows good thermal stability. The polyfluorene backbone becomes more rigid on the incorporation of EDOT units.¹⁹ This is due to the fact that EDOT units encourage stronger interchain Vander Waals bonding.
4.2.2.3 Electrochemical studies

Cyclic voltammetric studies were carried out to determine the HOMO, LUMO levels and band gap of the polymers. From the onset of oxidation, the HOMO levels of P(FMT) and P(EF) were calculated to be 5.91 eV and -5.19 eV respectively by using the equation, \( \text{HOMO} = -(4.4 + \text{Eox}_{\text{onset}}). \) The LUMO energy levels (from the onset of reduction potentials) of P(FMT) were calculated to be -3.71 eV and for P(EF) LUMO level (-2.9 eV) was estimated using optical band gap. In conclusion, the incorporation of the donor units effectively increases the HOMO level and reduces the LUMO level of the polymers. Band gap calculated by means of theoretical, electrochemical and optical methods are depicted in Table 4.4.

Table 4.4: Band gap calculated by means of theoretical, electrochemical and optical methods

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \text{Eg (theoretical)} ) eV</th>
<th>( \text{Eg (Electrochemical)} ) eV</th>
<th>( \text{Eg (Optical)} ) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(FMT)</td>
<td>2.42</td>
<td>2.2</td>
<td>2.11</td>
</tr>
<tr>
<td>P(EF)</td>
<td>2.36</td>
<td>2.63</td>
<td>2.63</td>
</tr>
</tbody>
</table>
4.2.3 Synthesis of EDOT based polymers

Usually EDOT based polymers are synthesised by electropolymerisation technique. Here we have synthesised two EDOT based polymers, P(EHT) and P(EC) by means of direct arylation polymerisation and is shown in Scheme 7. EDOT based monomers were coupled with dibromo derivative of thiophene and carbazole in the presence of Pd catalyst and phase transfer catalyst to form the corresponding polymers. The polymers were purified by precipitating from methanol followed by soxhlet extraction using methanol and hexane. The polymers are soluble in common organic solvents such as chloroform, chlorobenzene and THF.

![Scheme 7: Synthesis of P(EHT) and P(EC)](image)

The polymers were characterized using $^1$H NMR, UV-Visible spectroscopy, GPC, Cyclic voltammetry, TGA etc. The molecular weights of the polymers were obtained from gel permeation chromatography in THF referring to polystyrene standards. P(EHT) shows number average molecular...
weight ($M_n$) of 12592 and weight average molecular weight ($M_w$) of 20248 with polydispersity index (PDI) of 1.61. The peak molecular weight ($M_p$) of the polymer is 12805. P(EC) shows number average molecular weight ($M_n$) of 2328 and weight average molecular weight ($M_w$) of 3021 with polydispersity index (PDI) of 1.30. The peak molecular weight ($M_p$) of the polymer is 2306. GPC results are presented in Table 4.5.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_p$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EHT)</td>
<td>12592</td>
<td>20248</td>
<td>12805</td>
<td>1.61</td>
</tr>
<tr>
<td>P(EC)</td>
<td>2328</td>
<td>3021</td>
<td>2306</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectra of the polymers P(EHT) and P(EC) are shown in figure 4.10. The $^1$H NMR spectrum of P(EHT) showed multiplets at $\delta$ 0.9-8.5 due to aliphatic protons. It also showed a multiplet at $\delta$ 4.0 due to -CH$_2$-O- in EDOT unit. In the case of P(EC), it showed both aliphatic and aromatic protons.

Fig. 4.10: $^1$H NMR of the polymers: (a) P(EHT) and (b) P(EC)
4.2.3.1 Optical and photoluminescence properties

Figure 4.11 shows the absorption spectra of the polymers. The optical properties of the polymers, P (EHT) and P(EC) were investigated in chloroform. The polymers, P (EHT) and P(EC) showed absorption maximum around 440 nm and 382 nm respectively. The absorption onset of P (EHT) and P(EC) occurs at 583 nm and 571 nm respectively. The optical band gap calculated was found to be 2.12 eV and 2.16 eV respectively. The band gaps calculated from optical methods are in good agreement with the theoretical values. From quantum chemical calculations, band gap obtained are 2.2 eV and 2.86 eV respectively.

![Absorption Spectra](image)

**Fig.4.11:** UV-Vis spectra of the polymers: (a) P (EHT) and (b) P(EC) in 2mg/10mL chloroform

Fig 4.12 shows the emission spectra of P (EHT) and P(EC) in chloroform. The maximum emission shown by the polymers are at 568 nm and 546 nm respectively. The emission and absorption spectrum of P (EHT) is red shifted than that of P(EC).
4.2.3.2 Thermal properties

The thermal characteristics of the polymers were investigated by TG-DTG studies. In P(EHT), DTG traces showed onset of degradation around 300°C and degradation temperature at 400°C, losing around 5% weight at the onset loss point. P(EC) shows multiple degradation pattern, the onset of degradation is around 200°C. Here, about 15% weight loss took place at the onset loss point. From the plot it is clear that P(EHT) is thermally more stable compared to P(EC). TG-DTG traces of the polymers are shown in the fig 4.13.
4.2.3.4 Electrochemical studies

From the Cyclic voltammetric studies carried out, the HOMO levels (the onset of oxidation) of P(EHT) and P(EC) were calculated to be -5.76 eV and -5.58 eV respectively by using the equation, $\text{HOMO} = - (4.4 + \text{Eox}_{\text{onset}})$. The LUMO energy levels (from the onset of reduction potentials) of P(EHT) and P(EC) were calculated to be -3.24 eV and -3.33 eV. The band gaps calculated for P(EHT) and P(EC) are 2.5 eV and 2.25 eV respectively. In conclusion, after copolymerisation HOMO levels were elevated and LUMO levels of the polymers were lowered. Band gap calculated by means of theoretical, electrochemical and optical methods are depicted in Table 4.6.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_g$ (theoretical) eV</th>
<th>$E_g$ (Electrochemical) eV</th>
<th>$E_g$ (Optical) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(EHT)</td>
<td>2.2</td>
<td>2.5</td>
<td>2.12</td>
</tr>
<tr>
<td>P(EC)</td>
<td>2.86</td>
<td>2.25</td>
<td>2.16</td>
</tr>
</tbody>
</table>

4.2.4 Synthesis of cyanovinylene based polymers

The three theoretically designed cyanovinylene based polymers (P(CN1), P(CN2) and P(CN3)) were synthesised by Suzuki cross-coupling reaction using Pd(PPh₃)₄ as the catalyst. The dibromocyanovinylene derivatives were reacted with the dioxaborolane derivative of fluorene in the presence of the catalyst Pd(PPh₃)₄ to form the corresponding polymers. The crude polymers were purified by precipitating from methanol followed by soxhlet extraction using methanol and hexane. The polymers P(CN1) and P(CN2) are soluble in common organic solvents such as chloroform, chlorobenzene and
THF while P(CN3) is only sparingly soluble in these solvents. The synthetic route towards the copolymers is depicted in Scheme 8.

Scheme 8: Synthesis of P(CN1), P(CN2) and P(CN3)
The three polymers were characterized using $^1$H NMR, UV-Visible spectroscopy, GPC, Cyclic voltammetry, TGA etc. The molecular weights of the polymers were obtained from gel permeation chromatography in THF referring to polystyrene standards. Among the three polymers, P(CN3) showed high molecular weight. The copolymer exhibited number average molecular weight ($M_n$) of 14398 and weight average molecular weight ($M_w$) of 16379 with polydispersity index (PDI) of 1.14. Table 4.7 summarizes the molecular weight and polydispersity index (PDI) of the copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_p$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CN1)</td>
<td>7803</td>
<td>12820</td>
<td>8975</td>
<td>1.64</td>
</tr>
<tr>
<td>P(CN2)</td>
<td>7321</td>
<td>11061</td>
<td>7835</td>
<td>1.51</td>
</tr>
<tr>
<td>P(CN3)</td>
<td>14398</td>
<td>16379</td>
<td>11845</td>
<td>1.14</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectra of the polymers P(CN1) and P(CN2) are shown in figure 4.14. Here, the two polymers showed peaks in the aliphatic and aromatic regions. Peaks in the δ 7.0- 8.0 are due to protons of the fluorene, thiophene and phenyl rings and one hydrogen substituted to vinyl group. Because of the poor solubility we could not obtained the $^1$H NMR spectrum of the polymer P(CN3).
4.2.4.1 Optical and photoluminescence properties

Figure 4.15 shows the absorption spectra of the polymers. The optical properties of the polymers, P(CN1) and P(CN2) were investigated in chloroform and P(CN3) with the help of UV-Vis-DRS method. The polymers, P(CN1), P(CN2) and P(CN3) showed absorption maximum around 393 nm, 431 nm and 375 nm respectively. The absorption onset of P(CN1), P(CN2) and P(CN3) occurs at 456 nm, 543 nm, and 575 nm respectively. The optical band gap calculated was found to be 2.71 eV, 2.28 eV and 1.97 eV respectively. The band gaps calculated from optical methods are in good agreement with the theoretical values. From Quantum chemical calculations, band gap obtained are 2.62 eV, 2.25 eV and 2.15 eV respectively.
Figure 4.16 shows the emission spectra of P(CN1) and P(CN2) in chloroform. The maximum emission shown by the two polymers are 494 nm and 547 nm respectively. Here the emission spectrum of the polymer P(CN2) is red shifted when compared to the other polymer due to extensive conjugation present in the polymer.
4.2.4.2 Thermal properties of polymers

From thermogravimetric studies, it is clear that the first two polymers, P(CN1) and P(CN2) follow single degradation pattern and shows degradation temperature around 430°C, while the third shows step wise degradation. In P(CN3), degradation starts around 200°C. In the first two polymers around 15% weight loss took place at the onset loss point. TG-DTG traces of the polymers are shown in figure 4.17.

![TG-DTG traces of the polymers: P(CN1), P(CN2) and P(CN3)](image)

Fig 4.17: TG and DTG traces of the polymers: P(CN1), P(CN2) and P(CN3)
4.2.4.3 Electrochemical studies

From the cyclic voltammetric studies carried out, the HOMO levels (the onset of oxidation) of P(CN2) and P(CN3) were calculated to be -5.9 eV and -5.76 eV respectively by using the equation, HOMO = - (4.4 + Eox\textsuperscript{onset}). The LUMO energy levels (from the onset of reduction potentials) of P(CN2) and P(CN3) were calculated to be -3.21 eV and -3.6 eV. The band gap calculated for P(CN1), P(CN2) and P(CN3) are 2.71 eV, 2.70 eV and 2.0 eV respectively. Band gap calculated by means of theoretical, electrochemical and optical methods are depicted in the Table 4.8.

Table 4.8: Band gap calculated by means of theoretical, electrochemical and optical methods

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Eg (theoretical) eV</th>
<th>Eg (Electrochemical) eV</th>
<th>Eg (Optical) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CN1)</td>
<td>2.62</td>
<td>2.71</td>
<td>2.71</td>
</tr>
<tr>
<td>P(CN2)</td>
<td>2.25</td>
<td>2.70</td>
<td>2.28</td>
</tr>
<tr>
<td>P(CN3)</td>
<td>2.15</td>
<td>2.0</td>
<td>1.97</td>
</tr>
</tbody>
</table>

4.2.5 Synthesis of phenylene based polymers

Phenylene based polymers, P(PDO), P(POF) and P(PF) were synthesised by Suzuki cross-coupling reaction using Pd(PPh\textsubscript{3})\textsubscript{4} as the catalyst. The dibromo derivatives of benzoxadiazole, fluorene and fluorenone were reacted with the benzene 1,4-diboronic acid in the presence of the catalyst Pd(PPh\textsubscript{3})\textsubscript{4} to form the corresponding polymers. The crude polymers were purified by precipitating from methanol followed by soxhlet extraction using methanol and hexane. The polymer P(PDO), P(POF) and P(PF) are only sparingly soluble in common organic solvents such as chloroform, chlorobenzene and THF. The synthetic route towards the copolymers is depicted in Scheme 9.
The polymers were characterized using $^1$H NMR, UV-Visible spectroscopy, GPC, Cyclic voltammetry, TGA etc. Among the polymers, P(PDO) shows high molecular weight. It shows number average molecular weight of 11359 and weight average molecular weight ($M_w$) of 12603 with polydispersity index (PDI) of 1.11. The molecular weight data of the polymers are summarized in Table 4.9.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_p$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PDO)</td>
<td>11359</td>
<td>12603</td>
<td>12419</td>
<td>1.11</td>
</tr>
<tr>
<td>P(POF)</td>
<td>2645</td>
<td>2804</td>
<td>2754</td>
<td>1.06</td>
</tr>
<tr>
<td>P(PF)</td>
<td>5666</td>
<td>8144</td>
<td>8992</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Scheme 9: Synthesis of P(PDO), P(POF) and P(PF)
The $^1$H NMR spectra of the polymers P(PDO), P(POF) and P(PF) are shown in figure 4.18. P(PDO) showed multiplets at $\delta$ 0.8 -2 due to aliphatic protons. It showed multiplets at $\delta$4.0 due to -CH$_2$-O-. It also showed multiplets in the aromatic region. In the case of P(POF), it showed multiplets in both aliphatic and aromatic regions whereas, in P(PF), it showed multiplets only in the aromatic region.

**Fig 4.18: $^1$H NMR of the polymers: a) P(PDO), b) P(POF) and c) P(PF)**
4.2.5.2 Optical and photoluminescence properties

Figure 4.19 shows the absorption spectra of the polymers. The optical properties of the polymers, P(PDO) and P(PF) were investigated by UV-Vis-DRS. P(PDO) and P(PF) showed absorption maximum around 360 nm and 380 nm respectively. The absorption onset of P(PDO) and P(PF) occur at 462 nm and 581 nm respectively. The optical band gap calculated was found to be 2.68 eV and 2.0 eV respectively. The band gaps calculated from optical methods are in agreement with the theoretical values. From quantum chemical calculations band gap obtained are 2.86 eV and 2.68 eV respectively.

Fig 4.19: UV-Vis-DRS of the polymers: (a) P(PDO), (b) P(POF) and (c) P(PF)
Figure 4.20 shows the emission spectra of P(PDO) and P(PF) in chloroform. The maximum emission shown by the two polymers are at 496 nm and 541 nm respectively. Here the emission spectrum of the polymer P(PF) is red shifted when compared to the other polymer due to strong electron withdrawing carbonyl group in the polymer.

4.2.5.3 Thermal and electrochemical studies

The thermal characteristics of the polymers were investigated by TG-DTG studies and are shown in figure 4.21. The polymers showed multiple degradation peaks. In the polymers, P(PDO), P(POF) and P(PF) degradation starts around 200°C. Cyclic voltammetric studies were carried out to determine the HOMO, LUMO levels and band gap of the polymers. From CV studies, the band gap value calculated for the polymers, P(PDO), P(POF) and P(PF) are 2.68 eV, 2.8 eV, and 2.2 eV respectively. Band gap calculated by means of theoretical, electrochemical and optical methods are depicted in Table 4.10.
4.3 Experimental part

4.3.1 Synthesis of fluorene-quinoxaline polymers

Synthesis of P(FQ-A)

Under nitrogen atmosphere, 5,8-dibromoacenaphthyl quinoxaline (0.25 g, 0.60 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.39 g, 0.60 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene. Degassed solution (15 min) of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the reaction mixture. The mixture was stirred vigorously at 80-90°C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate
the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield : 40 %

UV-Vis (CHCl₃) λmax : 321 nm

¹H NMR (400 MHz, CDCl₃) : δ 0.8 (6 H, m), 1.3 (4H, m), 1.6 (20 H, s), 2.1 (4 H, m), 7.5-8.5 (12 H, m)

**Synthesis of P(FQ-B)**

Under nitrogen atmosphere, 5,8-dibromo-2,3-diphenyl quinoxaline (0.16 g, 0.36 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.24 g, 0.36 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90°C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield : 45 %

UV-Vis (CHCl₃) λmax : 310 nm

¹H NMR (400 MHz, CDCl₃) : δ 0.9 (6 H, m), 1.2 (20H, s), 1.6 (4 H, m), 2.3 (4 H, m), 7 - 8 (18 H, m)
Synthesis of P(FQ-P)

Under nitrogen atmosphere, 10,13-dibromodibenzo[a,c]phenazine (0.27 g, 0.61 mmol), 2,7-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.40 g, 0.61 mmol) were mixed together with 10 mol % of Pd(PPh3)4 and aliquat 336 in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90 °C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield : 35 %
UV-Vis (CHCl3) λmax : 330 nm
1H NMR (400 MHz, CDCl3) : δ 0.9 (6 H, m), 1.2 (4H, m), 1.6 (20 H, s), 2.1 (4 H, m), 6.8 – 8.5 (16 H, m)

4.3.2 Synthesis of fluorene-thiophene copolymer

Synthesis of P(FMT)

To a stirred solution of 3,4-dimethoxythiophene (0.05 g, 0.36 mmol) in DMF (10 mL) was added tetrabutylammonium bromide (0.11 g, 0.36 mmol) and sodium acetate (0.12 g, 1.46 mmol) and stirred at room temperature for 15 min followed by the addition of 2,7-dibromo-9,9-dioctyl-9H-fluorene (0.20 g, 0.36 mmol) and palladium acetate (10 mol%). The reaction mixture was stirred at 90 °C for 48 h. The mixture was cooled...
and poured in to cold methanol. The precipitate was filtered and purified by soxhlet extraction using methanol and hexane as solvent. The polymer was dissolved in minimum amount of chloroform and precipitated by adding methanol. The precipitate was filtered and dried under vacuum for 24 h.

Yield : 40 %
UV-Vis (CHCl₃) λmax : 476 nm
¹H NMR (400 MHz, CDCl₃) : δ 0.8 (6 H, m), 1.2 (20H, s), 1.6 (4 H, m), 2.1 (4 H, m), 4(6H, s), 7.8 (5 H, m)

**Synthesis of P(EF)**

EDOT(0.26 g, 1.8 mmol), tetrabutylammonium bromide (0.60 g, 1.8 mmol) and sodium acetate (0.61 g, 7.5 mmol) in DMF (10 mL) were stirred at room temperature for 30 min followed by the addition of 2,7-dibromo-9,9-dioctyl-9H-fluorene (1.03 g, 1.8 mmol) and palladium acetate (10 mol%). The reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was cooled and poured in to cold methanol. The precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol and hexane as solvent. The polymer was dissolved in minimum amount of chloroform and precipitated by adding methanol. The precipitate was filtered and dried under vacuum for 24 h.

Yield : 55 %
UV-Vis (CHCl₃) λmax : 450 nm
¹H NMR (400 MHz, CDCl₃) : δ 0.8 (6 H, m), 1.2 (4H, m), 1.7 (20 H, s), 2 (4 H, m), 4 (4H, m), 7-8 (6H, m)
4.3.3 Synthesis of thiophene and carbazole based polymers

Synthesis of P(EHT)

EDOT (0.05 g, 0.36 mmol), tetrabutylammonium bromide (0.117 g, 0.36 mmol), sodium acetate (0.12 g, 1.4 mmol) in DMF (10 mL) were stirred at room temperature for 15 min followed by the addition of 3,4-dihexyl-2,5-dibromothiophene (0.15 g, 0.36 mmol) and palladium acetate (10 mol%). The reaction mixture was stirred at 90°C for 48 h. The reaction mixture was cooled and poured in to cold methanol. The precipitate was filtered. The polymer was purified by soxhlet extraction using methanol and hexane as solvent. The polymer was dissolved in minimum amount of chloroform and precipitated by adding methanol. The precipitate was filtered and dried under vacuum for 24 h.

Yield : 50%

UV-Vis (CHCl₃) λ\text{max} : 440 nm

\textsuperscript{1}H NMR (400 MHz, CDCl₃):

\[ \delta \ 0.9 \ (6 \ H, \ m), \ 1.2 \ (16 \ H, \ m), \ 1.4 \ (4 \ H, \ m), \ 2.5 \ (4 \ H, \ m), \ 4 \ (4 \ H, \ m) \]

Synthesis of P(EC)

EDOT (0.27 g, 1.89 mmol), tetrabutylammonium bromide (0.55 g, 1.89 mmol) and sodium acetate (0.66 g, 8 mmol) in DMF (10 mL) were stirred at room temperature for 15 min followed by the addition of 3,6-dibromo-N-(2-ethylhexyl) carbazole (0.83 g, 1.89 mmol) and palladium acetate (10 mol%). The reaction mixture was stirred at 90°C for 48 h. The reaction mixture was cooled and poured in to cold methanol. The precipitate was filtered. The polymer was purified by soxhlet extraction using methanol and hexane as solvent. The polymer was dissolved in minimum amount of
chloroform and precipitated by adding methanol. The precipitate was filtered and dried under vacuum for 24 h.

Yield : 55 %

UV-Vis (CHCl₃) \( \lambda_{\text{max}} \) : 382 nm

\(^1\)H NMR (400 MHz, CDCl₃) : \( \delta \) 0.9(6 H, m), 1.3(6H,m), 1.5 (2 H, m), 2.1 (2 H, m) , 4 (1H, m), 4.5 (4H,m), 7- 8.5 (6 H, m)

4.3.4. Synthesis of cyanovinyline based polymers

**Synthesis of P(CN1)**

Under nitrogen atmosphere, (E)-2,3-bis (4-bromophenyl) acrylonitrile (0.15 g, 0.41 mmol), 2,7-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.23 g, 0.41 mmol) were mixed together with 10 mol % of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90°C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and hexane for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield : 35%

UV/Vis (CHCl₃) \( \lambda_{\text{max}} \) : 393 nm

\(^1\)H NMR (400 MHz, CDCl₃) : \( \delta \) 0.8 (6 H, m), 1.2 (4H, m), 1.8 (20 H, s), 2.1 (4 H, m), 7- 8.3 (14H (Aromatic), 1H (vinyl), m)
Synthesis of P(CN2)

Under nitrogen atmosphere, (Z)-3-(4-bromophenyl)-2-(5-bromothiophen-2-yl) acrylonitrile (0.15 g, 0.4 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.22 g, 0.4 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90°C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield: 40%

UV/Vis (CHCl₃) λmax: 431 nm

^1^H NMR (400 MHz, CDCl₃): δ 0.9 (6 H, m), 1.2 (4H, m), 1.7 (20 H, s), 2.1 (4 H, m), 7- 8.5 ( 12 H (Aromatic), 1H (vinyl), m)

Synthesis of P(CN3)

Under nitrogen atmosphere, (2E,2’E)-2,2’-(thiophene-2,5-diy)-bis-(3-(4-bromophenyl)acrylonitrile) (0.32 g, 0.65mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3, 2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.36 g, 0.65 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene.
Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90 °C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield : 50 %

UV/Vis (CHCl₃) λmax : 385 nm

4.3.5. Synthesis of Phenylene based polymers

Synthesis of P(POD)

Under nitrogen atmosphere, 4,7-dibromo-5,6-bis(decyloxy)benzo[c][1,2,5]oxadiazole (0.32 g, 0.54 mmol), benzene 1,4-diboronic acid (0.08 g, 0.54 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90 °C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into stirring methanol to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and hexane for 2 days in a Soxhlet extractor.
to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

**Yield** : 55 %

**UV/Vis (CHCl₃) λmax** : 404 nm

**1H NMR (400 MHz, CDCl₃)** : δ 0.8 (6 H, m), 1.2 (4H, m), 1.6 (24 H, s), 2 (4 H, m), 4 (4H,m), 8 (4H, m)

**Synthesis of P(POF)**

Under nitrogen atmosphere, 2,7-dibromo-9,9-dioctyl-9H-fluorene (0.4 g, 0.72 mmol), benzene 1,4-diboronic acid (0.12 g, 0.72 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90 °C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

**Yield** : 40 %

**UV/Vis (CHCl₃) λmax** : 350 nm

**¹H NMR (400 MHz, CDCl₃)** : δ 0.9 (6 H, m), 1.2 (20 H, s), 1.6 (4 H, m), 2.2 (4 H, m), 7.2- 8 (10H, m)
Synthesis of P(PF)

Under nitrogen atmosphere 2,7-dibromofluorenone (0.5 g, 1.4 mmol), benzene 1,4-diboronic acid (0.24 g, 1.4 mmol) were mixed together with 10 mol% of Pd(PPh₃)₄ and aliquat 336 in 20 mL of toluene. Degassed (15 min) aqueous solution of 2.0 M potassium carbonate (10 mL) and toluene (20 mL) were added to the flask. The mixture was stirred vigorously at 80-90°C for 72 h under nitrogen atmosphere. The resulting solution was added drop wise into methanol with stirring to precipitate the polymer. The solid was collected by filtration and washed with methanol and water. The product was washed continuously with methanol and acetone for 2 days in a Soxhlet extractor to remove the oligomers and catalyst residues. The product was dried under reduced pressure.

Yield : 50 %

UV/Vis (CHCl₃) λmax : 296 nm

¹H NMR (400 MHz, CDCl₃) : δ 7 – 8. (1 H, m),

4.4 Conclusion

Thirteen theoretically designed polymers were synthesised by means of Suzuki and Direct arylation reactions. All the polymers were characterized using ¹H NMR, UV-Visible spectroscopy, GPC, Cyclic voltammetry, TGA etc. HOMO level, LUMO level and band gap values for all the polymers were calculated by Optical and Electrochemical methods. It was found that experimental results were in good agreement with the theoretical results.
Chapter 4

References

(c) M. Baumann, I. R. Baxendale, Beilstein. J. Org. Chem., 2013, 9, 2265
Synthesis of Polymers and their Characterisation


