Chapter 2

Synthesis and characterization of soluble π-conjugated polymers
Chapter 2: Synthesis and characterization of soluble π-conjugated polymers

2.1 Introduction

Conjugated polymers are receiving great research interest due to their unique electronic and optical properties and they offer many possibilities in terms of their potential applications in light emitting diodes (LED), sensors, photovoltaic devices, electrochromic devices etc.\textsuperscript{1-23} 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 different synthetic approaches can help to achieve the magnitude of π overlap along the backbone and choice of suitable side chains influences the properties like band gap, ionic conductivity, morphology and miscibility with other substances.\textsuperscript{1,3,14,24} Chemical architecture to receive improved property and performance of conjugated polymer is hence being carried out in research with high impetus.

Generally, functional conjugated polymers are prepared through electrochemical and chemical methods.\textsuperscript{3,4,24-27} The limitation in producing large amount of polymers by electrochemical process has restricted its utility. Therefore, chemical polymerization methods have attained popularity for synthesizing the large scale and soluble polymer. The chemical polymerization methods include oxidative coupling, Yamamoto coupling, McCullough method, Grignard Metathesis (GRIM) method, Reike method, Suzuki and Still method.\textsuperscript{28-33} FeCl\textsubscript{3} oxidative coupling is a straightforward, simple, versatile, and least expensive method among other chemical polymerization techniques. 3- substituted polythiophenes with alkyl, fluoroalkyl, alkoxy, ester groups in side chain have been synthesized by FeCl\textsubscript{3} based oxidative coupling.\textsuperscript{34-42} Moreover, solution condensation polymerization to form polyazomethines, polyurethanes (PUs) etc. is also employed extensively.\textsuperscript{43-46}

In this chapter, an effort has been made to synthesize conjugated polymers with special emphasis on the solubility and tailor made band gap for application in photovoltaic devices. 1,1'-bis-2-naphthol based polyurethanes, side chain and main chain azomethinic linkage containing polythiophens and polycarbazole derivatives have been synthesized with improved solubility using condensation and oxidative coupling methods.
This chapter describes the synthesis and characterization of monomers and polymers and thermal properties of polymers. We have synthesized the following polymers.

1) Poly [N,N-bis-(2-thienylmethylene)-o-dianisidine] (PBTD)
2) Poly [(3-phenyl azomethine ethyl) thiophene] (PPAET)
3) Poly [(3-phenyl azomethine butyl) thiophene] (PPABT)
4) Poly[(9-dodecylcarbazole)] (PDDC)
5) Poly[(9-dodecylcarbazole)-co-thiophene] (PDDCT)
6) Poly(tolyl-1,1'-binaphthyl carbamate) (PU₁)
7) Poly(hexamethylene-1,1'-binaphthyl carbamate) (PU₂)

The synthetic procedures of monomers and polymers are discussed below. The monomers were characterized by FTIR, $^1$H NMR and CHN analyzer. The synthesized polymers were also thoroughly characterized by FTIR, $^1$H NMR, UV-Vis and GPC analyses. Thermal properties of the polymers were studied using TGA and DSC techniques.

2.2 Materials

2-Thiophenecarboxyldehyde (Aldrich), o-dianisidine (Aldrich), 3-thiophene carboxyldehyde (Aldrich), 4-ethyl aniline (Merck), 4-butyl aniline (Merck), p-toluene sulphonic acid (PTSA) (Aldrich), Carbazole (Aldrich), 3-thiophene carboxyldehyde (Aldrich), thiophene (Aldrich), do-decyl bromide (Merck), 2,4-Toluenediisocyanate (TDI) (Merck), Hexamethylenediamine (HMDI) (Merck), Iron(III) chloride (Aldrich) were highly pure commercial product and used as received. 2-Naphthol (Merck Ltd., Mumbai) was recrystallized from methanol. All the solvents were distilled before use and the reactions were performed under nitrogen atmosphere.
2.3. Instrumentations

2.3.1. 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.

2.3.2. Nuclear Magnetic Resonance Spectrometer (\(^1H\) NMR)

NMR spectroscopy is one of the principal techniques used to obtain 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 400 MHz with deuterated CHCl\(_3\) (d\(_3\)), and DMSO (d\(_6\)) solvents having TMS as internal standard.

2.3.3. Elemental Analysis

Elemental analysis of the samples gives % composition of constituent elements viz, C, H, N, O, S indicating structural identification of the same. Elemental analysis was carried out in Perkin Elmer-2400 Series-II CHNS/O analyzer.

2.3.4. Inherent Viscosity Measurements

Viscosity is an important characteristic for all materials, especially polymers. Inherent viscosity for polymer is defined as the flow time of a polymer solution through a narrow capillary relative to the flow time of the pure solvent through the capillary. It gives an idea of the extent of polymerization and molecular weight. The inherent viscosity (\(\eta_{in}\)) was determined using an Ubbelohde viscometer in N,N'-dimethylacetamide (DMAc) at 30 ± 0.1 °C with 0.5 g/dl polymer solution.
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2.3.5. 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 Model). Flow rate is maintained at 1ml/min. Polymers were dissolved in THF solvent. Molecular weights were determined on the basis of polystyrene standards.

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 TG50 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) and 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- 500 °C temperature ranges.

2.4. Experimental

2.4.1. Monomer Synthesis

2.4.1.1. N,N'-bis -(2-thienylmethylene)-o-dianisidine (BTD)

In a 100 ml three necked round bottom flask equipped with a nitrogen inlet, a condenser and a Dean-Stark trap, 1.82 g (16.1 mmol) thiophene-2-carboxyldehyde and
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1.95 g (8.0 mmol) o-dianisidine were introduced in 30 ml of methanol. P-toluenesulphonic acid was used as the catalyst. Nitrogen gas was purged into the flask and the reaction mixture was allowed to reflux for six hours under stirring. The yellow precipitate obtained after completion of the reaction was filtered out and washed with ethanol and hot water repeatedly and dried in vacuum. The monomer thus obtained was purified by recrystallization in acetone.

Yield 79\%, mp: 207\(^\circ\)C.

\text{FTIR (KBr): 1250, 1443, 1617, 2821, 2964 cm}^{-1}.

\text{\( ^1\)H NMR (400 MHz, CDCl}_3\text{) \( \delta \) (ppm): 3.73, 7.08, 7.23, 7.34-7.82, 8.76}

Elemental analysis: Cal: C, 66.66\%, H, 4.63\%, N, 6.48\%, O, 7.40\%, S, 14.81\%

Found: C, 66.21\%, H, 4.93\%, N, 6.16\%, O, 7.63\%, S, 14.27\% 

2.4.1.2. 3-Phenyl azomethine ethylthiophene (PAET)

In a 100 ml three necked round bottom flask equipped with a nitrogen inlet, a condenser and a Dean-Stark trap, 1.82 g (16.1 mmol) thiophene-3-carboxyldehyde and 1.95 g (16.1 mmol) 4-ethyl aniline was introduced in 30 ml of methanol. P-toluenesulphonic acid was used as the catalyst. Nitrogen gas was purged into the flask and the reaction mixture was allowed to reflux for six hours under stirring. The yellow precipitate obtained after completion of the reaction was filtered out and washed with ethanol and hot water repeatedly and dried in vacuum. The monomer thus obtained was purified by recrystallization in acetone.

Yield 73\%, m.p. 87 \(^\circ\)C.

\text{FTIR (KBr): 1250, 1443, 1607, 2821, 2964, 3021 cm}^{-1};

\text{\( ^1\)H NMR (400 MHz, CDCl}_3\text{) \( \delta \) (ppm): 1.26-2.61, 7.08, 7.19 -7.38, 7.51, 8.27}

Elemental analysis: Cal: C, 72.55\%, H, 6.04\%, N, 6.51\%, S, 14.88\%

Found: C, 72.14\%, H, 6.26\%, N, 6.63\%, S, 14.69\%
2.4.1.3. 3-phenyl azomethine butylthiophene (PABT)

The 3-phenyl azomethine butyl thiophene was synthesized employing the same procedure that for monomer PAET with 1.82 g (16.1 mmol) of thiophene-3-carboxydehyde and 2.40 g (16.1 mmol) of 4-butyl aniline.

Yield 76%, m.p. 83 °C

FTIR (KBr): 1258, 1441, 1605, 2832, 2951, 3029 cm⁻¹;

¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.92-2.72, 7.06, 7.20, 7.34-7.48, 8.23

Elemental analysis: Cal: C, 74.07%, H, 6.99%, N, 5.76%, S, 13.17%
Found: C, 74.18%, H, 7.06%, N, 5.63%, S, 13.04%

2.4.1.4. 9-Dodecyl carbazole (DDC)

To a 250 ml round bottom flask, flushed with nitrogen and equipped with a condenser and magnetic stirrer, carbazole (8 g, 4.8 mmol) dissolved in 50 ml of DMF and dodecyl bromide (11.96 g, 4.8 mmol) were added. Then, K₂CO₃ (8.29 g, 6 mmol) was added to this mixture and allowed to proceed the reaction for 15 hours at 150 °C under continuous stirring. After completion of the reaction, the mixture was cooled to room temperature followed by precipitation of the product in 500 ml of cold water. The precipitate was filtered and washed with a dilute solution of KOH and water. Finally product was dried over anhydrous magnesium sulphate and it was purified by column chromatography using 1:9 ethyl acetate/hexane as the eluent.

Yield 71%, m.p. 68 °C.

FTIR (KBr): 1261, 1446, 2845, 2911, 3021 cm⁻¹;

¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.93-2.87 (dodecyl protons), 7.06-7.81 (Ar-H)

Elemental analysis: Cal: C, 85.97%, H, 9.85%, N, 4.17%
Found: C, 85.34%, H, 10.17%, N, 4.38%
2.4.1.5. 1,1'-bis-2-naphthol (BINOL)

In a 500 ml three necked round bottom flask, provided with a dropping funnel, a sealed stirrer and a reflux condenser, 3 g (0.02 mol) of 2-naphthol was taken in 200 ml of water and heated to the boiling point. To the boiling liquid containing liquid 2-naphthol, 15 ml aqueous solution of 4.5 g of FeCl₃ (0.02 mol) was added slowly. Soon the oily drops of 2-naphthol disappeared and the product separated out in flakes. The mixture is boiled for 1 hour and hot suspension was filtered and washed with hot water. The product was dried in vacuum and recrystallised from toluene. Yield 89%, m.p. 218°C.

FTIR (KBr): \( \nu = 3426, 2935 \text{ cm}^{-1} \)

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) (ppm): 5.03, 7.38, 7.86-7.96

Elemental analysis: Cal: C, 82.81%, H, 5.38%, O, 12.82%.

Found: C, 82.67%, H, 5.43%, O, 12.80%.

2.4.2. Synthesis of polymers

2.4.2.1. Poly [N,N'-bis-(2-thienylmethylene)-o-dianisidine] (PBTD)

The polymer was synthesized by following the standard procedure, FeCl₃ oxidative coupling method. In a 100 ml round bottom flask equipped with a condenser, and a nitrogen gas inlet, 2 g (4.62 mmol) of monomer (BTD) and 10 ml chloroform were introduced. 3.25 g (20 mmol) of anhydrous FeCl₃ was added in small proportions over a period of 1 hour. The reaction was carried out at room temperature with continuous stirring for 24 hours. The product was precipitated in methanol containing small amount of HCl followed by washing with methanol for several times. The collected polymer powder was dissolved in DMAc and reprecipitated in methanol with small amount of ammonia repeatedly to ensure its purification.

Yield 51%.

FTIR (KBr): 3364, 3089, 2959, 1621, 1212 cm\(^{-1}\)

\(^1\)H NMR (400 MHz, DMSO) \( \delta \) (ppm): 3.80, 7.06, 7.18, 7.54-7.71, 8.81
2.4.2.2. Poly [3-phenyl azomethine ethylthiophene] (PPAET)

In a 100 ml round bottom flask equipped with a condenser and a nitrogen gas inlet, 2 g (9.24 mmol) of monomer (PAET) and 10 ml chloroform were introduced. 6.5 g (40 mmol) of anhydrous FeCl₃ was added in small proportions over a period of approximately 1 hour. The reaction was carried out at room temperature with continuous stirring for 24 hours. The product was precipitated in methanol containing small amount of HCl followed by washing with methanol for several times. The collected polymer powder was dissolved in DMAc and reprecipitated in methanol, repeatedly, with small amount of ammonia to ensure its purification.

Yield 59%
FTIR (KBr): 1257, 1608, 2819, 2936, 3034 cm⁻¹;
¹H-NMR (400 MHz, DMSO) δ (ppm): 1.28-2.63, 7.1, 7.56, 7.79, 8.31

2.4.2.3. Poly [3-phenyl azomethine butylthiophene] (PPABT)

Synthetic procedure of PPABT is same as used for PPAET using the monomer PABT (2 g, 5.6 mmol) and FeCl₃ (4.1 g, 30 mmol).
Yield 53%
FTIR (KBr): 1254, 1612, 2856, 2923, 3096 cm⁻¹.
¹H-NMR (400 MHz, DMSO) δ (ppm): 0.96-2.75, 6.78-7.72, 8.26

2.4.2.4. Poly (9-dodecyl carbazole) (PDDC)

9-dodecyl carbazole was dissolved in 50 ml of dry dichloromethane followed by the addition of anhydrous FeCl₃ (4.5 g, 5 mol eq. pre-dissolved in 30 ml dry acetonitrile). The colour of the solution was changed from white to dark green. It was allowed to stir under nitrogen for 24 hours at 0-5 °C. The solution was poured into 100 ml of methanol, and stirred vigorously for 1 hour. The resulting precipitate was collected and washed with methanol and 30% ammonium hydroxide. The collected polymer powder was dissolved in THF and reprecipitated in methanol repeatedly to ensure its purification.
Yield 53%
FTIR (KBr): 1456, 1576, 2855, 2934, 3047 cm⁻¹
¹H NMR (400MHz, DMSO) δ (ppm): 0.94-3.18(N-alkyl), 6.61 -7.09 (Ar-H)
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2.4.4.5. Poly(9-dodecylcarbazole)-co-thiophene (PDDCT)

Synthetic procedure is same as employed in the case of PDDC with the monomer composition of 50% of 9-dodecyl carbazole (2 g, 5.9 mmol) and 50% of thiophene (0.5 g, 5.9 mmol) and 9.57 g (59 mmol) of FeCl₃.
Yield 59%
FTIR (KBr): 1496, 1579, 2867, 2918, 3018, 3049 cm⁻¹
¹H NMR (400MHz) (DMSO): δ 0.96-3.68 (N-alkyl), 7.04, 7.22 (Thiophene-H), 7.37-7.65 ppm

2.4.4.6. Poly(tolyl-l,l'-binaphthyl carbamate) (PU₁)

1 g (3.4 mmol) of 1,1'-bis-2-naphthol, 0.60 g (3.4 mmol) of 2,4-toluenediisocyanate and dried THF (20 ml) were charged in a three-necked flask equipped with nitrogen inlet, reflux condenser and a dropping funnel. The reaction mixture was stirred for 6 h at 70 °C under nitrogen. After completion of the reaction, the polymer was precipitated by drop wise addition of the viscous reaction mixture into methanol. The collected polymer powder was dissolved in DMAc and reprecipitated in methanol repeatedly to ensure its purification.
Yield 86%
IR (KBr): ν = 2967, 1714, 3376, 1207 cm⁻¹.
¹H NMR (400 MHz, DMSO) δ (ppm): 2.41, 7.04-7.46, 7.78, 8.0

2.4.4.7. Poly(hexamethylene-l,l'-binaphthyl carbamate) (PU₂)

Another polyurethane compound (PU₂) was prepared using hexamethylene diisocyanate (HMDI) and 1,1'-bis-2-naphthol by employing same procedure as used in preparation of PU₁.
Yield 84%
IR (KBr): ν = 3089, 2959, 1721, 3364, 1212 cm⁻¹.
¹H NMR (400 MHz, DMSO) δ (ppm): 1.34-2.31, 7.21-7.83, 8.0
2.5. Results and discussion

2.5.1. Characterization of monomers

The monomer (BTD) containing thiophene ring and azomethine linkage within the chain with full conjugated structure has been synthesized by condensation reaction between o-dianisidine and thiophene-2-carboxyldehyde in 1:2 ratio. The reaction scheme for preparation of BTD is shown in Scheme 2.1. The monomer was obtained in good yield. The IR peak at 1617 cm\(^{-1}\) indicates the formation of azomethine linkage. \(^1\)H NMR peaks (Figure 2.1) at 3.73 ppm and 8.76 ppm infer the presence of methoxy and azomethine proton in the monomer.

![Figure 2.1: \(^1\)H NMR spectrum of BTD](image)

The monomers (PAET and PABT) containing thiophene ring and azomethine linkages within the chain with full conjugated structure have been synthesized by condensation reaction between \(p\)-alkylaniline and thiophene-3-carboxyldehyde in 1:1 ratio and reaction scheme is shown in scheme 2.2. The disappearance of carbonyl vibration peak at 1720 cm\(^{-1}\) and appearance of new absorption peak at ~1605 cm\(^{-1}\) in IR spectrum and \(^1\)H NMR singlet peak (Figure 2.2-2.3) at 8.23-8.27 ppm confirm the presence of azomethine proton. Moreover, aliphatic C-H vibrations are observed near
2950 and 2830 cm\(^{-1}\) and NMR peaks in the range of 0.92-2.61 are attributed to extended alkyl chain attached to phenyl rings.\(^{24,26}\) Elemental analyses also strongly suggest the proposed structure of monomer.

**Figure 2.2:** \(^1\)H NMR spectrum of PAET

**Figure 2.3:** \(^1\)H NMR spectrum of PABT
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The monomer, 9-dodecylcarbazole (DDC) was synthesized by alkylation of carbazole in DMF solution using n-dodecylbromide in the presence of anhydrous K$_2$CO$_3$. The reaction scheme is displayed in Scheme 2.3. In FT-IR spectrum of 9-dodecylcarbazole derivative, aliphatic C-H vibrations are observed at 2911 and 2845 cm$^{-1}$. Furthermore, characteristic N-H vibration at 3412 cm$^{-1}$ for secondary amines has disappeared due to substitution of alkyl group. Elemental analyses also suggest the proposed structures of monomers. The $^1$H NMR peak at 0.93 ppm is attributed to N-substituted alkyl -CH$_3$ group and multiplet peaks in the range of 1.31–2.87 ppm indicates the –CH$_2$- group of long dodecyl chain$^{27}$ (Figure 2.4).

![Figure 2.4: $^1$H NMR spectrum of DDC](image)

The monomer (BINOL) was prepared by oxidative coupling of 2-naphthol using FeCl$_3$ as oxidant and the reaction scheme is shown in Scheme 2.4. The characteristics hydroxyl (O-H stretching) and aromatic C-H stretching band at 3426 cm$^{-1}$ and 2935 cm$^{-1}$ are observed for 1,1'-bis-2-naphthol in FTIR spectra. $^1$H NMR spectra (Figure 2.5) also elucidate the structure with the chemical shift (δ) value at 5.03 ppm with a strong peak for two hydroxyl (O-H) protons along with the other aromatic C-H protons within 7-8 ppm of δ-value.$^{28}$
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Figure 2.5: $^1$H NMR spectrum of BINOL

2.5.2. Characterization of polymers

Chemical oxidative polymerization method is employed to synthesize the polymer PBTD using anhydrous FeCl$_3$ as oxidant. The reaction scheme for preparation of PBTD is shown in scheme 2.1. The IR spectrum of the polymer gives important information as strong absorption peak at 1621 cm$^{-1}$ can be assigned to the $\text{–CH=N–}$ stretching. Moreover, the intensity of the peak at 727 cm$^{-1}$ got diminished in the polymer spectrum due to the disappearance of 2-thiophene substituted ring and appearance of the 2,5-disubstituted thiophene rings. The $^1$H NMR spectra (Figure 2.6) of the polymer, PBTD distinctly shows a singlet at 8.81 ppm attributed to the azomethine proton. The NMR singlet at 3.8 ppm and multiple peaks in the range of 7.0-8.0 ppm indicates the presence of methoxy and aromatic protons.$^{49}$
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Scheme 2.1: Reaction scheme for synthesis of BTD and PBTD

**Scheme 2.1**: Reaction scheme for synthesis of BTD and PBTD
The polymers, PPAET and PPABT are also synthesized by chemical oxidative polymerization. The reaction scheme for synthesis of PAET, PABT and PPAET, PPABT is shown in Scheme 2.2. A strong absorption peak at 1608-1612 cm\(^{-1}\) observed in FTIR spectrum can be assigned to the -CH=N- stretching. Moreover, the intensity of stretching frequency as seen in the case of PBTD at 723-728 cm\(^{-1}\) got diminished in the polymer spectrum due to the disappearance of 2-thiophene substituted ring and appearance of the 2,5-disubstituted thiophene rings. The \(^1\)H NMR spectra of the polymers (Figure 2.7-2.8) distinctly show a singlet at 8.26-8.31 ppm attributed to the azomethine proton. The NMR multiplet peaks in the range of 6.7-8.0 ppm indicates the presence of aromatic protons. The side chain alkyl protons attached to the phenyl rings also give NMR peaks in the range of 0.92-2.75. Broadening and slight shifting of the NMR peaks compared to monomers indicates successful polymerization of the monomers.\(^{52}\)
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Scheme 2.2: Reaction scheme for synthesis of PAET, PABT and PPAET, PPABT

Figure 2.7: $^1$H NMR spectrum of PPAET
Scheme 2.3 shows the synthetic procedure of DDC and PDDC as well as PDDCT. The IR spectrum of the polymers (PDDC and PDDCT) gives important information regarding structure of the polymers. The intensity of the absorption peak at 725 cm\(^{-1}\) like other polymers, got diminished in the polymer spectrum due to the disappearance of 3,6-positions of carbazole in case of poly(9-dodecylcarbazole) and poly(9-dodecylcarbazole)-co-thiophene. The \(^1\)H NMR peaks (Figure 2.9-2.10) at 7.18 ppm and 7.24 ppm can be attributed to aromatic protons of 3,4-positions of thiophene in the poly(9-dodecylcarbazole)-co-thiophene copolymer. NMR peaks ranging from 0.94-3.65 ppm are attributed to alkyl proton in PDDC and PDDCT. Moreover, slight shifting and broadening of all the \(^1\)H NMR peaks compared to that of monomer implies polymer formation.\(^{52}\) The copolymer composition in PDDCT has been determined from the integration height in \(^1\)H NMR spectrum and it is found that % molar compositions of thiophene and 9-dodecylcarbazole are 55% and 45%, respectively.\(^{34}\)
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Scheme 2.3: Reaction scheme for synthesis of DDC and polymers PDDC, PDDCT
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Figure 2.9: $^1$H NMR spectrum of PDDC

Figure 2.10: $^1$H NMR spectrum of PDDCT
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The incorporation of binaphthol into the polar polyurethane was achieved by condensation of the corresponding monomer with commercially available TDI and HMDI in dried THF to give PU$_1$ and PU$_2$, respectively. The reaction scheme for synthesis of PU$_1$ and PU$_2$ is shown in Scheme 2.4. The formation of the polyurethanes PU$_1$ and PU$_2$ have been confirmed by the disappearance of O-H stretching frequency peaks at 3426 cm$^{-1}$. Instead sharp peaks at 3376 cm$^{-1}$ and 3364 cm$^{-1}$ are observed for N-H stretching frequency in FTIR. The carbonyl frequency at 1714 cm$^{-1}$ and 1721 cm$^{-1}$ also establish the fact. In $^1$H NMR spectra (Figure 2.11-2.12), no characteristic peaks around δ 5.0 are seen which indicate the reaction of –OH groups in the formation of polyurethanes. Further, Peaks at δ 8.0 for secondary –NH of the polymers confirmed the polyurethane formation.\(^{46}\)

Scheme 2.4: Reaction scheme for synthesis of BINOL and PU$_1$, PU$_2$
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Figure 2.11: $^1$H NMR spectrum of PU$_1$

Figure 2.12: $^1$H NMR spectrum of PU$_2$
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Unlike other conventional conjugated polymers, the interesting feature of all the synthesized polymers is their good solubility in some organic solvents like DMF, DMAc, DMSO, THF and NMP. The presence of alkyl or alkoxy groups as the side chain in the polymer or incorporation of non-conjugated groups in the main chain as seen in case of PU_1 and PU_2 have contributed in imparting solubility to them. The inherent viscosities of the polymers (Table 2.1) are also measured using suspended level Ubbelohde viscometer and found to have in the range of 0.18-0.27. Low values of inherent viscosities indicate oligomeric nature of the synthesized polymers.

### Table 2.1: Physical properties of polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Yield (%)</th>
<th>η_inh (dLg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD</td>
<td>51</td>
<td>0.21</td>
</tr>
<tr>
<td>PPAET</td>
<td>54</td>
<td>0.19</td>
</tr>
<tr>
<td>PPABT</td>
<td>57</td>
<td>0.23</td>
</tr>
<tr>
<td>PDDC</td>
<td>53</td>
<td>0.18</td>
</tr>
<tr>
<td>PDDCT</td>
<td>59</td>
<td>0.22</td>
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<tr>
<td>PU_1</td>
<td>86</td>
<td>0.24</td>
</tr>
<tr>
<td>PU_2</td>
<td>84</td>
<td>0.26</td>
</tr>
</tbody>
</table>

2.5.3. 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 2.2. The number-average molecular weights of the resulting polymers are in the range of 3829–17,647 g/mol with polydispersity indexes (PDI) in the range of 1.05–2.14. Except PU_1 and PU_2, the other synthesized polymers exhibit low molecular weight indicating their oligomeric nature. The weight average molecular weights of polymers have been found in the range 4307-37,891 g/mol. Degree of polymerization of the polymers were also calculated which gives information of effective conjugation length and delocalization of electrons. The polymers synthesized using oxidating coupling methods (i.e. PBTD, PPAET, PPABT, PDDC and PDDCT), show narrow molecular weight distributions (PDI ranging from 1.05-1.40). This might be
resulted from controlled reactions using slow addition of FeCl₃ to the reaction mixture from time to time. However, PDDC and PDDCT show comparatively higher PDI and molecular weights to other oxidative coupled polymers which could be attributed to the poor radical stability after oxidation of the carbazole derivatives causing coupling of the species more feasible.⁵³ On the other hand, condensation polymerization of highly reactive diol (BINOL) and diisocyanates (TDI or HMDI) gives PU₁ and PU₂ with higher PDI. Random intermolecular reaction between molecules in a bifunctional system would lead to linear chain polymers whose chain lengths show wide variation.⁵¹

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Mₙ (g/mol)</th>
<th>Mₘ (g/mol)</th>
<th>Mₘ/Mₙ (PDI)</th>
<th>Degree of polymerization (DP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD</td>
<td>3857</td>
<td>4307</td>
<td>1.12</td>
<td>9</td>
</tr>
<tr>
<td>PPAET</td>
<td>4256</td>
<td>4591</td>
<td>1.10</td>
<td>20</td>
</tr>
<tr>
<td>PPABT</td>
<td>4821</td>
<td>5074</td>
<td>1.05</td>
<td>20</td>
</tr>
<tr>
<td>PDDC</td>
<td>4193</td>
<td>5846</td>
<td>1.40</td>
<td>12</td>
</tr>
<tr>
<td>PDDCT</td>
<td>3829</td>
<td>6413</td>
<td>1.67</td>
<td>9</td>
</tr>
<tr>
<td>PU₁</td>
<td>14,563</td>
<td>32,798</td>
<td>2.25</td>
<td>33</td>
</tr>
<tr>
<td>PU₂</td>
<td>17,647</td>
<td>37,891</td>
<td>2.14</td>
<td>39</td>
</tr>
</tbody>
</table>

2.5.4. Thermal behaviour of polymers

2.5.4.1 Thermogravimetric analysis (TGA)

The thermal properties of polymers were investigated by thermogravimetric analysis under nitrogen atmosphere at the heating rate of 10 °C per minute. All the polymers showed 2-7% weight loss at the temperature range of 80-120 °C which corresponds to loss of moisture and volatilization of solvent. The onset degradation temperatures of the polymers are found to be in the range of 234-305 °C.
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The polymer, PBTD is found to be thermally stable up to 305 °C (Figure 2.13). The first 1.5 % of weight loss step in the TG analysis curves around 80-120 °C corresponds to the loss of moisture and volatilization of the solvent. The second step of 66% of weight loss in the TGA curves between 305-360 °C is due to degradation of polymers. About 10% of residue was finally left when heated to 600 °C.

![Figure 2.13: TGA curve of polymer PBTD](image)

The polymers, PPAET and PPABT show gratifying thermal stability to the range of 300-380 °C (Figure 2.14). 60-70% weight loss in the TGA curves between 300-450 °C is attributed to degradation of polymers. The onset degradation temperature of PPAET \( (T_d, 305 \, ^{\circ}C) \) is found to be higher in comparison to that of PPABT \( (T_d, 285 \, ^{\circ}C) \) due to variation in alkyl chain length as the side group. Nearly, 25% of residue was left when the polymers are heated to 600 °C.
Figure 2.14: TGA curves of (a) PPAET (b) PPABT

The polymers, PDDC and PDDCT are found to have thermal stability upto 350°C (Figure 2.15). The first weight loss step i.e. 5% weight loss in the TGA curves around 80-120°C corresponds to the loss of moisture and volatilization of the solvent. The second step in the TGA curves by loss of 40-50% weight loss between 350-450°C is due to degradation of polymers. The onset decomposition temperature of PDDCT is found a little higher (ca.300°C) than that of PDDC which may be attributed to the attached rigid thiophene ring along the main chain.
Both the conjugated-nonconjugated chain containing polymers, PU₁ and PU₂ shows similar thermal decomposition pattern (Figure 2.16). These polymers are found to have thermal stability up to 250 °C. The degradation of polymers are found in the temperature range of 250-420 °C. Hexamethylene group present in PU₂ results in lowering the degradation temperature in comparison to PU₁. Summary of thermal behavior of all the polymers is given in Table 2.3.
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Figure 2.16: TGA curves of PU1 and PU2

Generally, PU1, PU2 and long side chain alkyl group containing polymers i.e. PDDC and PPABT have shown comparatively lower onset degradation temperature. Whereas, PDDCT copolymer have shown improved thermal stability due to annexed thiophene unit with 9-dodecyl carbazole unit. The degradation range of the polymers witnessed from TG analyses was found within 230-355 °C attributed to final degradation of products by evaluation of CO2 and nitrogenous gases.

2.5.4.2. Differential scanning calorimetry (DSC) analysis

Differential scanning calorimetry (DSC) analyses of polymers have been carried under nitrogen atmosphere at the heating rate of 10 °C/min. All the thermal data of the polymers are listed in Table 2.3. DSC curves (Figure 2.17-2.20) of polymers reveal that the glass transition temperature (Tg) of the polymers are in the range of 51-84 °C. PBTD exhibits the highest Tg compared to others attributed fully conjugated structure with methoxy group side chain on anisidine unit only. The presence of long dodecyl group in the polycarbazole derivatives, PDDC and PDDCT results low Tg. Tg of polymers
synthesized by oxidative coupling reactions is in order of PDDC<PDDCT<PU₂<PPABT<PPAET. Long flexible alkyl groups in the polymer side chain serve as internal plasticizer which lowers T_g of polymers. The response in the thermogram due to glass transition of polymers is quite low as these polymers are of low molecular weight.

The broad endothermic peaks at 160-170°C and 145-152°C for PDDC and PDDCT, respectively, are assigned to the melting of the polymers. On the other hand, a broad endothermic peak in the range of 140-165°C indicates the melting range for PU₂. No distinct melting region was observed for PBTD, PPAET, PPABT and PU₁. It is observed that T_g of the polymers and melting range decreases with increase in side chain length.25,54,55 The thermal stability of the polymers are found to be sufficient for photovoltaic device performance since nonradiative decay i.e. heat dissipation during undesired exciton recombination may lead to produce high heat during the device function.

**Table 2.3: Thermal characteristics of the polymers**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Degradation onset (T_d onset) (°C)</th>
<th>Weight residue (% at 600°C)</th>
<th>Glass transition temperature (T_g) (°C)</th>
<th>Melting temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTD</td>
<td>285</td>
<td>14</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>PPAET</td>
<td>305</td>
<td>25</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>PPABT</td>
<td>280</td>
<td>22</td>
<td>72</td>
<td>-</td>
</tr>
<tr>
<td>PDDC</td>
<td>273</td>
<td>37</td>
<td>51</td>
<td>150</td>
</tr>
<tr>
<td>PDDCT</td>
<td>300</td>
<td>45</td>
<td>59</td>
<td>168</td>
</tr>
<tr>
<td>PU₁</td>
<td>210</td>
<td>9</td>
<td>-</td>
<td>148</td>
</tr>
<tr>
<td>PU₂</td>
<td>214</td>
<td>5</td>
<td>66</td>
<td>-</td>
</tr>
</tbody>
</table>
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Figure 2.17: DSC thermogram of PBTD

Figure 2.18: DSC thermograms of (a) PPAET (b) PPABT
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**Figure 2.19**: DSC thermogram of (a) PDDC (b) PDDCT

**Figure 2.20**: DSC thermogram of (a) \( \text{PU}_1 \) (b) \( \text{PU}_2 \).
2.6. Conclusion

- A series of azomethinic, N-alkyl substituted carbazole derivatives and diol monomers have been synthesised with the yield ranging from 71% to 89%. The formation of monomers was confirmed by FTIR and $^1$H NMR spectroscopy, and CHN analyses.

- The polymers have been prepared by oxidative polymerization using FeCl$_3$ and polyurethanes, PU$_1$ and PU$_2$ have been prepared by condensation reaction. The polymerization process is slow for oxidative coupling reactions and yields are 51-59%.

- The polymers, PBTD, PPAET, PPABT, PDDC and PDDCT show good solubility in THF, DMF, DMAc, DMSO and NMP due to the presence of alkyl and alkoxy groups as side chain. The reason of good solubility for PU$_1$ and PU$_2$ is presence of non-conjugated spacer between the binaphthyl chromophoric groups in the polymer chain.

- The number average molecular weights of polymers are in the range of 3857 to 17647 g/mol. This indicate the prepared polymers are oligomeric in nature.

- Polymers possess good thermal stability with the onset decomposition temperature around 240-305 °C under nitrogen atmosphere, 30-68% weight loss at the temperature of 300-380 °C.

- The polymers exhibit a glass transition temperature (T$_g$) in the range of 51-84°C. T$_g$ of the polymers is established to be side chain dependent. All the polymers possess the suitable thermal properties to receive its applications in photovoltaic devices.
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References


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