

# Direct Arylation Polymerization Toward a D-A Type Copolymer Based on Carbazole and Benzothiadiazole Units - an Analogue of PCDTBT

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Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) is an attractive material for optoelectronic devices, and has been prevalently prepared by traditional couplings. Despite robust and effective, the traditional methods generally involve the use of toxic organometallic reagents. Direct arylation polymerization (DAP), as a simple, green, and cost-effective alternative to traditional coupling, has been utilized in this work to prepare an analogue of PCDTBT, namely poly[(9-hexadecyl-2,7-carbazole)-alt-(4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole)] (**P1**). The copolymer was obtained in 44% yield and satisfactorily characterized by Fourier-transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance (NMR). UV-Vis absorption spectra showed the presence of inter-chain interaction and aggregation in the solid state. The optical bandgap of the copolymer was found to be in the range of 1.77 - 1.81 eV, which is slightly lower than that of PCDTBT (1.88 eV).

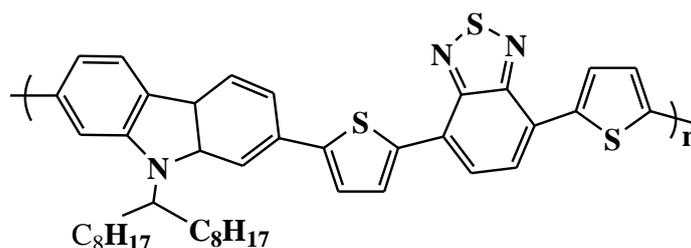
**Key words:** Direct arylation polymerization; carbazole; benzothiadiazole; PCDTBT

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Since the first discovery of conductive polymers in the 1970s, a large library of conjugated polymers has been synthesized and investigated. The excellent optical and electrical properties of conjugated polymers make them potential operative materials in various fields, such as photovoltaics, field-effect transistors, light-emitting diodes, and sensors [1] [2]. Conjugated polymers with Donor-Acceptor (D-A) arrangement are particularly attractive as they possess low bandgaps and broad absorption bands, resulting from their planar configurations [3]. The use of D-A copolymers in Bulk-Heterojunction (BHJ)-based polymer solar cells have shown promising device performances [4] [5].

One of the most widely used D-A type copolymers in BHJ solar cells is poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-

di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), as shown in **Figure 1**, which gives an impressive Power Conversion Efficiency (PCE) of 7.9% when blended with a fullerene acceptor [6] [7]. The deep Highest-Occupied Molecular Orbital (HOMO) energy level of PCDTBT also renders advanced stability and high open-circuit voltages ( $V_{oc} = 0.90$  V) in the solar cells. The synthesis of carbazole-based copolymers is prevalently done by Suzuki couplings. Despite efficient and robust, Suzuki cross-coupling, like other conventional polycondensations, requires costly organometallic reagents to functionalize the monomers before coupling. The low stability of the organometallic reagents (organoboron compounds) involved and the difficulty in the purification of the metalated monomers further discourage the use of this method [8].



**Figure 1.** The chemical structure of poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT)

Direct arylation polymerization (DAP), which involves direct carbon-hydrogen (C-H) metalation, has emerged as a reliable alternative to the traditional polycondensations. It allows direct couplings of aryl halides with nonpreactivated arenes, thereby reduces the synthesis steps and, most importantly, avoids the use of costly toxic organometallic reagents. DAP, thus, does not produce metal-containing toxic waste. Also, the purification step becomes easier as difficult-to-remove byproducts have been minimized [9] [10]. Another notable advantage is that DAP can produce comparable or higher yields and molecular weights as compared to conventional couplings [11]. DAP, hence, can potentially be applied to prepare a wide-range of conjugated polymers.

In 2014, Lombeck and co-workers simplified the synthesis of PCDTBT and its derivatives by combining Direct Arylation with Suzuki coupling [12]. Direct arylation was used for monomer syntheses, while the polymers were prepared by Suzuki polycondensation. PCDTBT derivatives, however, have not been solely prepared by direct arylation. Therefore, this work aimed at synthesizing both monomers and polymers of PCDTBT derivatives via direct arylation method.

In this work, PCDTBT was modified by replacing the branched alkyl chain in the carbazole unit with a linear side chain. The side chains are as important as the conjugated backbones because side chains not only impart sufficient solubility to the resulting polymers but can also affect the optoelectronic properties of the polymers [13] [14]. Linear alkyl chains usually promote intermolecular interactions and crystallinity of polymers, thereby improve the absorption and charge carrier mobility of polymers [15] [16].

## EXPERIMENTAL SECTION

### Materials

Chemicals were purchased from commercial sources (Sigma-Aldrich, Merck, Nacalai Tesque, and Fisher Scientific) and used without purification, unless stated otherwise. 2,7-dibromo-9H-carbazole and 4,7-dibromo-2,1,3-benzothiadiazole were synthesized according to procedures in the literatures [17] [18]. All reactions were carried out under N<sub>2</sub> atmosphere.

### Characterization

The melting point of a product was recorded from the melting point apparatus (Mel-Temp) as a range (the difference between the temperature at which it begins to liquefy and the temperature at which it is completely liquid). FTIR spectra were obtained with PerkinElmer Spectrum 100, which utilized attenuated total reflection (ATR) sampling technique. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on JEOL ECA 600 (600 MHz) spectrometer at 22°C with deuterated chloroform solution (CDCl<sub>3</sub>) as solvent and

tetramethylsilane (TMS) as reference for chemical shifts (δ). UV-Vis absorption spectra were obtained using Agilent Cary 60 UV-Vis spectrophotometer.

### Synthesis Procedures

The synthesis routes of the monomers and polymers are shown in **Scheme 1**.

#### 2,7-Dibromo-9-hexadecyl-9H-carbazole (M1)

The synthesis of 2,7-dibromo-9-hexadecyl-9H-carbazole (**M1**) was performed according to a procedure modified from published papers [19] [20] [21]. 50% aq. NaOH (0.55 g, 13.8 mmol, 15 equiv.) and a catalytic amount of tetrabutylammonium bromide (TBAB) (74 mg, 0.2 mmol) were added to a stirred solution of toluene (5 mL) with dissolved 2,7-dibromocarbazole (0.3 g, 0.9 mmol). The flask was degassed for 10 minutes. 1-bromohexadecane (0.7 g, 2.3 mmol, 2.5 equiv.) was then added and the reaction mixture was heated at 70°C under N<sub>2</sub> atmosphere for 12 hours. The reaction mixture was cooled to room temperature before extracted with CHCl<sub>3</sub>. The organic layer was washed with water, brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* and the crude product was purified via silica gel column chromatography with 0.1% ethyl acetate in hexane as the eluent to give the desired alkylated product (**M1**). The product was eventually recrystallized from hexane, giving 0.40 g (78.43%) of 2,7-dibromo-9-hexadecylcarbazole (**M1**) of white crystals. **TLC:** R<sub>f</sub> = 0.95 in 5:1 hexane/ethyl acetate. **Melting point:** 78-80°C. **FTIR (ATR):** ν (cm<sup>-1</sup>) 2951, 2916, 1588, 1486, 1464, 1327, 722. **<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):** δ (ppm) 7.87 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 1.2 Hz, 2H), 7.33 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.8 Hz, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.82 (m, 2H), 1.33 (m, 2H), 1.23 (m, 24H), 0.86 (t, *J* = 6.6 Hz, 3H). **<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):** δ (ppm) 141.44, 122.58, 121.57, 121.34, 119.76, 112.09, 43.44, 32.02, 29.78, 28.86, 27.26, 22.79, 14.23.

#### 4,7-Di(2-thienyl)-2,1,3-benzothiadiazole (M2)

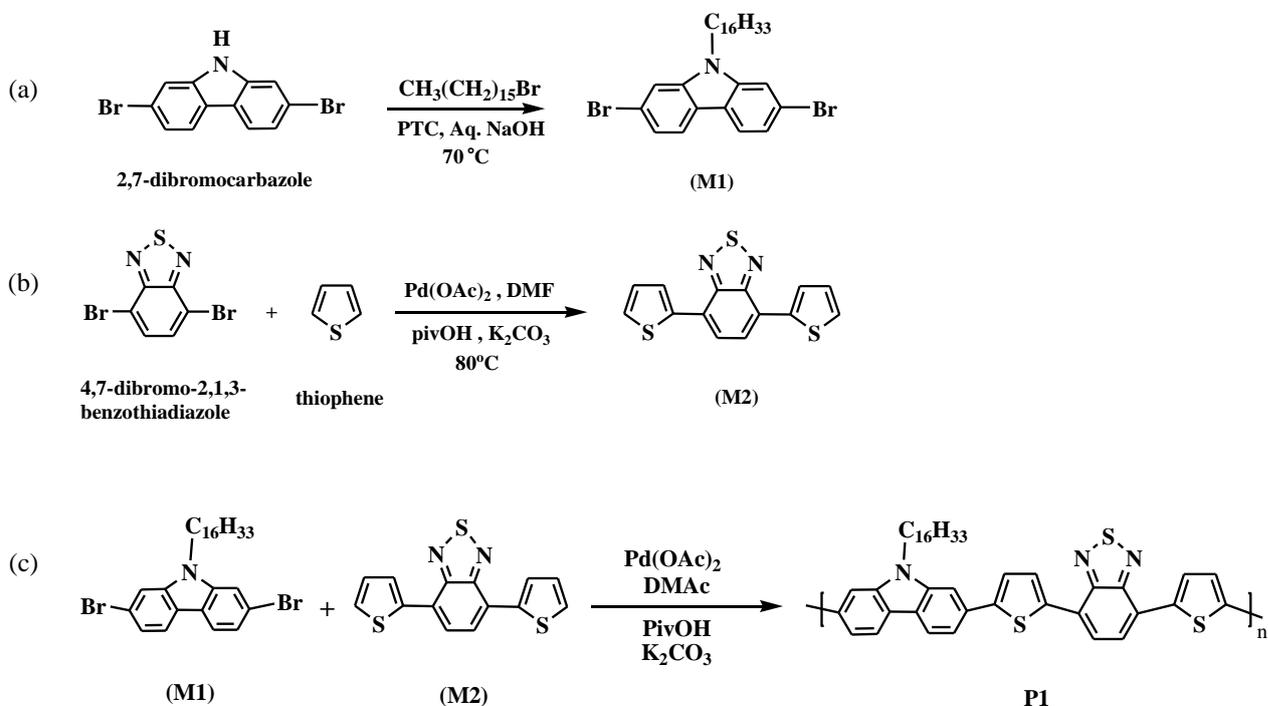
The preparation of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (**M2**) was performed by referring to published procedures [22] [23]. 4,7-dibromo-2,1,3-benzothiadiazole (70 mg, 0.24 mmol) was placed in a dry two-neck round bottom flask filled with 20 mL of DMF. An excess of thiophene (20 equiv., 0.38 mL, 4.76 mmol) was then added, and the mixture solution was purged with nitrogen gas for 15 minutes before the addition of palladium(II) acetate Pd(OAc)<sub>2</sub> (27 mg, 0.12 mmol), pivalic acid (30 mg, 0.36 mmol), and potassium carbonate K<sub>2</sub>CO<sub>3</sub> (170 mg, 1.2 mmol). The reaction mixture was stirred and heated at 80°C under nitrogen atmosphere for 24 hours. After being cooled to room temperature, the reaction mixture was diluted with chloroform. The insoluble species were removed by vacuum filtration. The filtrate was subsequently washed with distilled water and brine, before dried

over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was then evaporated and the crude orange product was purified by column chromatography with 2% ethyl acetate/hexane as eluent. Recrystallization from hexane yielded 0.048 g (66.67%) of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (**M2**) as bright orange needle-like crystals. **TLC**:  $R_f = 0.82$  in 7:1 hexane/ethyl acetate. **Melting point**: 120-122°C. **FTIR (ATR)**:  $\nu$  ( $\text{cm}^{-1}$ ) 3094, 1661, 1579, 1481, 1422, 1215, 1073, 709.  **$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )**:  $\delta$  (ppm) 8.12 (d,  $J = 2.4$  Hz, 2H), 7.87 (s, 2H), 7.46 (d,  $J = 4.2$  Hz, 2H), 7.21 (dd,  $J_1 = 5.4$  Hz,  $J_2 = 4.2$  Hz, 2H).  **$^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ )**:  $\delta$  (ppm) 152.75, 139.44, 128.11, 127.60, 126.92, 126.11, 125.91.

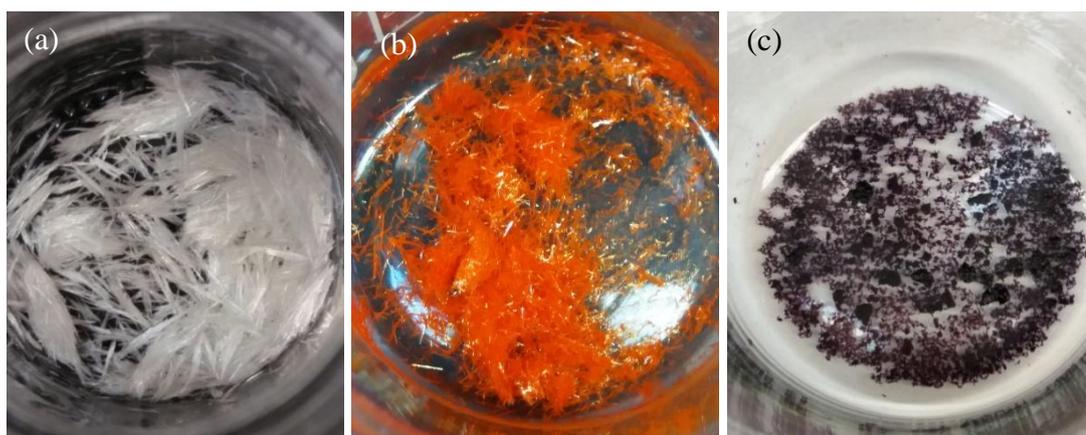
**Poly[(9-hexadecyl-2,7-carbazole)-alt-(4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole)] (P1)**

The designed polymer was synthesized by direct arylation polymerization, referring to published procedures [24-26]. Monomers 2,7-dibromo-9-hexadecylcarbazole (**M1**) (137.3 mg, 0.25 mmol) and 4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole (**M2**) (75.6 mg, 0.25 mmol) were dissolved in 3 mL of dimethylacetamide (DMAc). After that, 0.3 equiv. of PivOH (7.66 mg, 0.075 mmol) and 1.5 equiv. of  $\text{K}_2\text{CO}_3$  (52 mg, 0.375 mmol) were added to the reaction mixture. The solution was degassed for 10 minutes with nitrogen flow.  $\text{Pd}(\text{OAc})_2$  (2.2 mg, 0.01

mmol) was then added and the reaction mixture was further degassed for 20 minutes before immersed into a pre-heated oil bath at 110°C. The reaction was run for 72 hours under nitrogen atmosphere. After being cooled to room temperature, thiophene (1 mL) was added and the reaction mixture was heated at 110°C for another 3 hours. The mixture was cooled and diluted with  $\text{CHCl}_3$ . An ammonium hydroxide solution was subsequently added and the mixture was refluxed overnight. The organic layer was removed and washed three times with water ( $3 \times 150$  mL). It was concentrated to approximately 50 mL and added dropwise into 300 mL of methanol/water mixture (10:1 v/v). The resulting mixture was stirred overnight and filtered through a Soxhlet thimble before subjected to Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform sequentially. The toluene and chloroform fractions were concentrated and precipitated into 250 mL of methanol. The resulting mixtures were left undisturbed overnight. The precipitates were collected by filtration and dried under vacuum before further characterization. Both fractions give dark purple powder, with 33 mg (19.08%) from toluene and 43 mg (24.86%) from chloroform extraction. **Melting point**: >360°C. **FTIR (ATR)**:  $\nu$  ( $\text{cm}^{-1}$ ) 2920, 2851, 1597, 1510, 1457, 1243, 1184, 1055, 835, 722.  **$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )**:  $\delta$  (ppm) 7.96 (s, 2H), 7.42 (s, 2H), 7.35 (s, 2H), 7.30 (s, 2H), 7.20 (s, 2H), 7.01 (s, 2H), 4.31 (brs, 2H), 1.65 (s, 2H), 1.52 (s, 2H), 1.22 (m, 24H), 0.84 (m, 3H).



**Scheme 1.** Syntheses of monomers and polymer. Syntheses of (a) 2,7-dibromo-9-hexadecyl-9H-carbazole (**M1**); (b) 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (**M2**); and (c) poly[(9-hexadecyl-2,7-carbazole)-alt-(4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole)] (**P1**)



**Figure 2.** (a) Needle-like crystals of 2,7-dibromo-9-hexadecylcarbazole (**M1**). (b) The color of (**M2**) recrystallized from hexane. (c) Dark purple precipitate of polymer (**P1**).

**Table 1.** Physical properties of 2,7-dibromo-9-hexadecylcarbazole (**M1**) and 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (**M2**)

Physical Properties	2,7-Dibromo-9-hexadecylcarbazole ( <b>M1</b> )	4,7-Di(2-thienyl)-2,1,3-benzothiadiazole ( <b>M2</b> )
Percent Yield (%)	78.43	66.67
Physical State	Solid	Solid
Appearance	White	Orange
Melting Point (°C)	78-80	120-122
Molecular Formula	C <sub>28</sub> H <sub>39</sub> Br <sub>2</sub> N	C <sub>14</sub> H <sub>8</sub> S <sub>3</sub> N <sub>2</sub>
Molecular Weight (g/mol)	549.34	300.42

## RESULTS & DISCUSSION

### Synthesis and Characterization

The general synthesis routes of the monomers and copolymer are outlined in **Scheme 1**. The alkylated carbazole (**M1**) was obtained as needle-like white crystals with 78.43% yield from the reaction of 2,7-dibromocarbazole with 1-bromohexadecane, in the presence of TBAB as the phase transfer catalyst, NaOH solution as the base, and toluene as the solvent. The crude product was purified via column chromatography on silica gel with 0.1% ethyl acetate/hexane as eluent. **Table 1** summarizes the properties of the monomers. Recrystallization from hexane gave white needle-like crystals, as shown in **Figure 2**. The melting point of the product laid in the range of 78-80°C.

Direct arylation approach was used to prepare the thiophene-flanked benzothiadiazole (**M2**), whereby an excess of thiophene moiety was reacted with 4,7-dibromo-2,1,3-benzothiadiazole, giving 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (**M2**), as bright orange needle crystals at 66.67% yield. Recrystallization from hexane gave bright orange needle-like crystals, as shown in **Figure 3**. The melting point of the product laid in the range of 120-122°C.

The targeted D-A copolymer, **P1** was synthesized by direct arylation polycondensation of **M1** and **M2** under ligand-free conditions with Pd(OAc)<sub>2</sub> as the catalyst, pivalic acid as the additive, and K<sub>2</sub>CO<sub>3</sub> as the base. The polymerization was carried out for 3 days at 110°C in degassed DMAc. Thiophene was added at the end of the reaction, as a capping agent, to terminate the growth of polymer chains. After that, chloroform was added to solubilize the polymers. The acidity of the reaction mixture was neutralized with the addition of NH<sub>4</sub>OH. The isolation of the polymers was achieved through precipitation and Soxhlet extraction.

A Soxhlet thimble with crude sample in it was placed in the extraction chamber and 200 mL of extraction solvent was heated to reflux. The solvent evaporated and condensed in the chamber, bathing the thimble in boiling solvent which improved the efficiency of the extraction. When the solvent reached an overflow level, it carried the extracted analytes back into the flask. This cycle continued repeated until the solvent in chamber turned colorless, marking the completion of the extraction.

During the Soxhlet extraction, different solvents (methanol, acetone, hexane, toluene, and chloroform) were used sequentially to extract

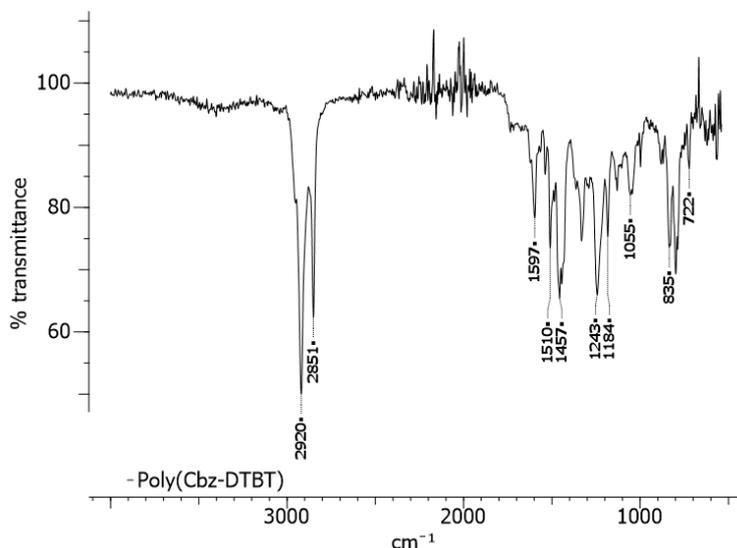
unreacted monomers, catalyst residues, short oligomers, and eventually polymers from the crude product. Toluene and chloroform fractions were collected, concentrated, and purified via precipitation. The purified polymer was obtained at 43.9% yield as dark purple solids. The chemical structures of the polymer were evaluated by FTIR and NMR spectroscopy.

### Infrared Spectroscopic Studies of Polymer (P1)

Functional groups present in Poly[(9-hexadecyl-9H-carbazole)-alt-(4,7-di(thiophen-2-yl) benzo[c][1,2,5]thiadiazole)] (PCbz-DTBT) were determined by FTIR. **Figure 3** shows the infrared spectrum of (PCbz-DTBT).

The alkyl chain showed C-H stretching band at

around  $2851\text{ cm}^{-1}$  for the  $\text{sp}^3$  carbon atoms. Also observed was a rocking band that appeared at  $722\text{ cm}^{-1}$  for long-chain alkanes of four or more carbons. The band at about  $2920\text{ cm}^{-1}$  was assigned to the unsaturated C-H stretching vibration. The discrepancy of  $\text{sp}^2$  CH stretch between the observed value and the typical vibrational frequency ( $> 3000\text{ cm}^{-1}$ ) was probably due to the adjacent aromatic units which reduced the double-bond character through electron delocalization. The C=C stretching bands for aromatic rings appeared at  $1597$  and  $1510\text{ cm}^{-1}$ . The 5-membered ring stretching vibration for thiophene occurred at  $1457\text{ cm}^{-1}$ . The presence of a strong band at  $1243\text{ cm}^{-1}$  was attributed to the C-N stretching vibrations in the alkylated carbazole [27]. **Table 2** lists the functional groups present along with their absorption frequencies.



**Figure 3.** FTIR spectrum of poly[(9-hexadecyl-9H-carbazole)-alt-(4,7-di(thiophen-2-yl) benzo[c][1,2,5]thiadiazole)] (**P1**)

**Table 2.** The vibrational frequencies of poly[(9-hexadecyl-9H-carbazole)-alt-(4,7-di(2-thienyl)-2,1,3-benzothiadiazole)] (**P1**)

Functional Groups	Absorption bands ( $\text{cm}^{-1}$ )		Remarks
	Poly(Cbz-DTBT) ( <b>P1</b> )		
$\text{Sp}^3$ C-H stretch	2851		Alkyl Chain
$\text{CH}_2$ bend (long chain)	722		
C-N stretch	1243		Tertiary amine
$\text{Sp}^2$ C-H stretch	2920		Aromatic
C=C ring stretch	1597, 1510		Thiophene
5-membered ring	1457		
In-plane C-H bend	1055		
Out-of-plane C-H	835		Thiadiazole
Aromatic C-N stretch	1184		

## Nuclear Magnetic Resonance (NMR) Studies of Polymer

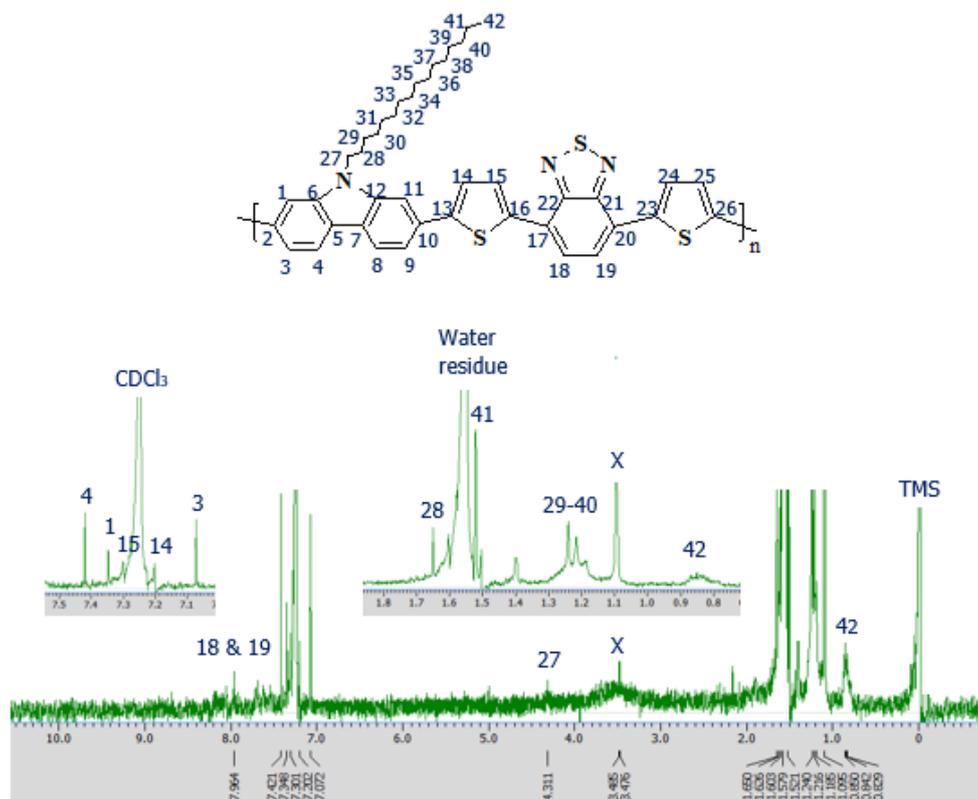
The chemical structures of the polymer were evaluated by NMR spectroscopy. Only  $^1\text{H}$ -NMR spectrum is presented in this context because the amount of polymer sample that could be solubilized by the deuterated chloroform was not sufficient for  $^{13}\text{C}$ -NMR analysis.

**Figure 4** shows the  $^1\text{H}$  spectrum of poly[(9-hexadecyl-9H-carbazole)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PCbz-DTBT). It was notable that considerable line broadening was observed in the spectrum. This problem most probably arose from the high molecular weight (larger mass) of the polymer sample, which slowed down the molecular tumbling (rotation) and gave long relaxation times. Besides, physical entanglements or crosslinks might be present in the polymer sample, which led to polymer swelling, thereby restricted the mobility of the sample and resulted in line-broadening [28]. Discernible spin-spin couplings can be hardly seen in the spectrum. Apparently, the broadening of resonances had obscured some chemical shift information.

Peaks in the 7.0-8.0 ppm region were assigned to aromatic ring hydrogens. The diamagnetic circulation of valence electrons deshielded the aryl protons, causing a downfield shift. Hydrogens on

benzene ring carbons ( $\text{C}_{18}$  and  $\text{C}_{19}$ ) of benzothiadiazole had the largest chemical shifts (7.9 ppm). Apart from the diamagnetic anisotropy effect of rings, the protons were also affected by the neighbouring  $p$  electrons and electronegative nitrogen atoms.

The region from 0.8 ppm to 1.7 ppm was a characteristic area for the alkyl chain hydrogens. Hydrogens in a methyl group ( $\text{C}_{42}$ ) were found at the lowest chemical shift (~0.84 ppm) as an unresolvable group, while the chemical shift of the methylene hydrogens appeared at around 1.2-1.5 ppm, showing a smaller shielding effect. Hydrogens on the carbon ( $\text{C}_{27}$ ) next to the nitrogen atom were de-shielded by the electronegativity of the attached nitrogen and appeared at about 4.3 ppm. An expected peak broadening was observed for this absorption owing to the spin-active nature of nitrogen ( $I > 1/2$ ). Elements that have  $I > 1/2$  possess quadrupole moments arising from the non-spherical distribution of nuclear charge. This electric quadrupole moment interacts with the electric field gradient, leading to a mechanical torque on the nucleus. Relaxation results from a fluctuation in this interaction is very efficient, explaining the broadening of NH absorption [29]. Quadrupole broadening decreases signal-to-noise ratio and obscures any coupling to the NH. Signals marked with 'X' and appeared at about 1.09 ppm and 3.42 ppm were residual methanol left after precipitation of the polymer [30].

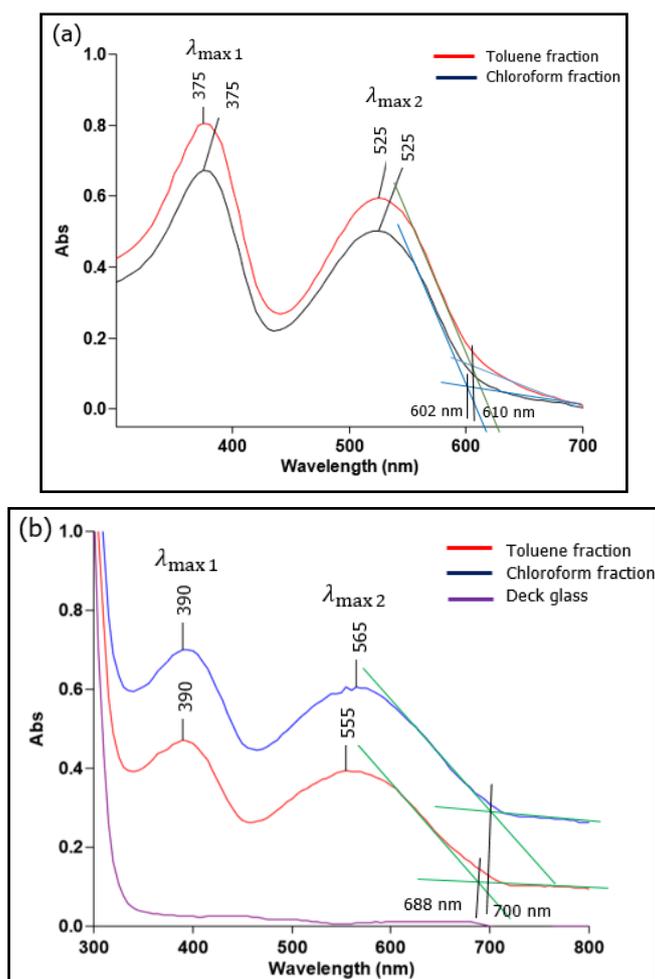


**Figure 4.**  $^1\text{H}$ -NMR spectrum of poly[(9-hexadecyl-9H-carbazole)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)]. Peaks marked with X are the residual methanol left after precipitation.

## Optical Properties

The UV-Vis absorption spectra of the copolymer were obtained from chloroform solutions (**Figure 5a**) and drop-casted films (**Figure 5b**). Both the solution and solid states showed two absorption bands, one at the shorter wavelength (375-390 nm) and the other one at the longer wavelength (525-565 nm). Significant bathochromic shifts were observed for the absorption peaks of the films as compared with that of the solutions, reflecting the increase of inter-chain

interactions and  $\pi - \pi$  stacking in the solid state. The optical bandgaps ( $E_g^{opt}$ ) of the polymer were calculated from the absorption edges ( $\lambda_{edge}$ ) using the equation  $E = h*c/\lambda$ ; where,  $h$  is the Planks constant,  $c$  is the speed of light, and  $\lambda$  is the absorption edge. With absorption edges at around 688 to 700 nm, the polymer films had an optical bandgap lying in the range of 1.77 – 1.81 eV, which is lower than the optical bandgap value (1.88 eV) of the classical PCDTBT [31]. **Table 3** summarizes the optical properties of the polymer.



**Figure 5.** UV-Vis absorption spectra of copolymer in (a) chloroform solution, and (b) drop-casted film

**Table 3.** Optical properties of polymer

Polymer (P1)	States	$\lambda_{max1}$ (nm)	$\lambda_{max2}$ (nm)	$\lambda_{edge}$ (nm)	$E_g^{opt}$ (eV)
Toluene fraction	Solution state (0.2 mg/mL)	375	525	610	2.04
	Film state (dropcast)	390	555	688	1.81
Chloroform fraction	Solution state (0.2 mg/mL)	375	525	602	2.06
	Film state (dropcast)	390	565	700	1.77

## CONCLUSION

In conclusion, an alternating D-A copolymer based on carbazole and benzothiadiazole moieties has been successfully synthesized by direct arylation polymerization. The resulting copolymer, poly[(9-hexadecylcarbazole)-alt-(4,7-di(2-thienyl)-benzo[c][1,2,5]thiadiazole)] (**P1**), was satisfactorily characterized by FTIR and NMR analysis. The incorporation of hexadecyl side chain rendered the resulting copolymer good solubility in common organic solvents such as toluene and chloroform. The optical bandgap of the copolymer was determined from the absorption edges and found to be in the range of 1.77-1.81 eV, which is slightly lower than that of PCDTBT (1.88 eV). This finding suggests **P1** might perform better than PCDTBT in a photovoltaic device, since a reduction of bandgap can extend the absorption bands which increase the amounts of light harvested from the solar spectrum, thereby improves the efficiency of solar cells.

## ACKNOWLEDGEMENTS

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