

# SYNTHESES OF AZOMETHINE-THIOPHENE MONOMERS FOR POTENTIAL APPLICATION IN ENERGY STORAGE DEVICES

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## Abstract

Newly design thiophene monomers containing azomethine base moieties for the preparation of side chain liquid crystalline polymers were successfully synthesized. The proposed monomers are conducting in nature, making it as potential material for energy storage devices. The compounds were characterized by Fourier transform infrared (FT-IR), <sup>1</sup>H nuclear magnetic resonance (NMR) and thermal gravimetric analysis (TGA). The presence of azomethine groups found at 1617 cm<sup>-1</sup> in FTIR, NMR confirms singlet peaks at δ~9.5 ppm and TGA data shows thermal cleavage occurred at 166.6 - 269.93°C. The n-type properties combined with the inherently weak emission and high thermal stability thus make the polythiophenoazomethine suitable candidates for hole and electron transporting materials.

## 1 Introduction

Discovery on conducting polymer by Hideki Shirakawa have terminated the original concept of polymer is an insulator. Conducting polymer is an organic polymer that possessed electrical conductivity behaviour via electrons movement that responsible for carrying charges along its polymeric backbone. Conducting polymer is well known by its flexibility as its structure can be tuned according to suitability. Doping process is essential method used for conducting polymer to generate the charges movement by either removing or adding negative charges along the structure (p-doping and n-doping respectively). Based on a review by Kausar [1], beside remarkable properties such as stability, processability and inexpensive, combination of conducting polymer such as polyaniline, polypyrrole and polythiophene with composite resulting in fast electronic and ionic transfer channels, as well as free space advantages of high

capacity and stable electrochemical cycling. Consequently it has been used in large number of specific application including energy storage and energy conversion such as supercapacitors and batteries (Figure 1) [2].

Polythiophene has been widely studied for its respectable conductivity, thermal stability, third order non-linear (NLO) behavior and facile functionalization. The latter property authorizes to overcome its inherent difficulty to dissolve in any solvents by introducing alkylic chains in the 3-position of the thiophenic ring, thus resulting a solvable and process able materials. The functionalization of the alkylic chain emerges a new material which integrate the common physical properties of the poly-conjugated based with those of the implanted functional group [3]. Recently, new approach has been established to combine side chains onto polythiophenes, in specific the macro-monomer technique (Figure 2). This synthetic methodology use reactive oligomers or polymers bearing a polymerizable functional group at the chain ends [4].

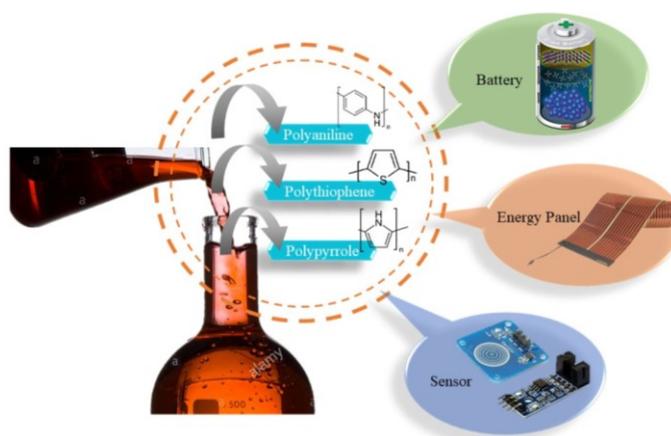


Figure 1: Application and structure of common conducting polymer

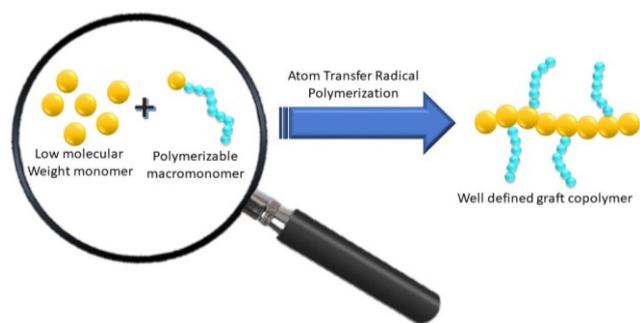


Figure 2: Macro-monomer technique

The synthesized material will result in enhanced mechanical, self-assemble, and physical properties as well as a capability to integrate with metal as composite with referred to the homopolymeric conjugated polymers [5]. The electronic and electrochemical properties of the polythiophenic are scarcely depend on side chain functionalization as long as that the functional group is bearing an aromatic ring. Polyalkylthiophene emerged as one of an outstanding conjugated polymer due to its noteworthy properties. To date, syntheses pathways on the modification of polythiophene have been developed widely [6-10]. It has been found that polythiophene exhibit inimitable properties and efficiency in terms of chemical stability, conjugation and flexibility to be functionalized. Introducing liquid crystalline (LC) as side-chain helps to align conjugated polymer. Alignment of conjugated polymers is important to enhance of the electrical conductivity as well as to develop of the inherent anisotropy. The advantages of having liquid crystal along the conjugated polythiophene are easily soluble in organic solvents, fusible, simultaneously aligned by means of electric and magnetic field applied [11-13]. Thiophene based liquid crystals merged with polythiophene backbones will arise a unique properties that enhance the capabilities in terms of thermal and conductivity. Azomethine act as good ligand which can control the alignment and orientation of metal complexes in their mesophases and able to develop liquid crystalline structures and properties [14]. Isoelectronic character of azomethines ( $-N=C-$ ) made it appealing as an alternatives to conjugated materials. The simplicity of synthesis without the use of intricate reactions conditions or any metal catalyst.

In this study, we presented the syntheses and characterization of 2,5-dibromo-3-(6-(4-((thiophen-2-yl)methyleneamino)hexyl)thiophene) and 2,5-dibromo-3-(6-(4-(phenylimino)methyl)phenyl thiophene-2-carboxylate)-hexyl)thiophene) which could be further polymerize to form side chain liquid crystalline polymers (SCLPs).

## 2 Experimental Section

### 2.1 Materials

4-hydroxybenzaldehyde (Merck, Belgium, 97%), thiophene carbonyl chloride (Aldrich, Germany, 98%), 4-aminophenol (Merck, Belgium, 97%), pyridine (Fisher Scientific, UK, 99%), benzene (Merck, Belgium, 98%), thiophene carboxaldehyde (Aldrich, Germany, 98%), 3-bromothiophene

(Merck, Belgium, 98%), 1,6-dibromohexane (Merck, Belgium, 98%), n-butyllithium (Aldrich, Germany 98%), N-bromosuccinamide (Merck, Belgium, 98%), acetic acid (Merck, Belgium, 98%), sodium hydrogen bicarbonate (Merck, Belgium, 98%), magnesium sulphate anhydrous (Friedemann Schmidt Chemical, 98%), ethanol denatured (John Kollin Corporation, 99%), potassium iodide (Merck, Belgium, 98%), potassium carbonate (Merck, Belgium, 98%), acetone (Fisher Scientific, UK, 99%), dimethyl sulfoxide- $D_6$  (DMSO- $D_6$ ) (Acros Organics, UK, 99.8%) silica gel 60 (Merck, Belgium). The materials are used as received. Tetrahydrofuran (Merck, Belgium, 98%) and hexane (Friedemann Schmidt Chemical, 99.8%) were dried and degassed by freeze and thaw cycles over  $CaH_2$  (Acros Organic, 99%).

### 2.2 Preparation of Mesogen

#### 2.2.1 Synthesis of 4-((thiophen-2-yl)methyleneamino)phenol (TMAP)

4-hydroxybenzaldehyde (122mg, 10 mmol) was added to (112 mg, 10 mmol) 2-aminobenzenethiol in 50 mL ethanol. The mixture was refluxed for 3 hours. Yellow crystal was obtained after recrystallized with ethanol (Figure 3). Yield: 95%, m.p: 203.8-205.5°C.  $^1H$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 6.7 (2H-Ar), 7.5 (2H-Ar), 7.2 (2H-Ar), 7.8 (H-Ar-S), 8.9 (H-C=N), 9.7 (OH).  $^{13}C$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 116.18 (2C-Ar), 156.73 (C-OH), 128.55 (2C-Ar), 142.49 (C-N), 150.98 (C=N), 143.54 (C-C-S), 132.83 (C-Ar), 132.85 (C-Ar), 130.56 (C-S). FT-IR ( $cm^{-1}$ ): 1609 (C=N), 1588 & 1504 (C=C aromatic), 749 (C-S), 3411 (OH).

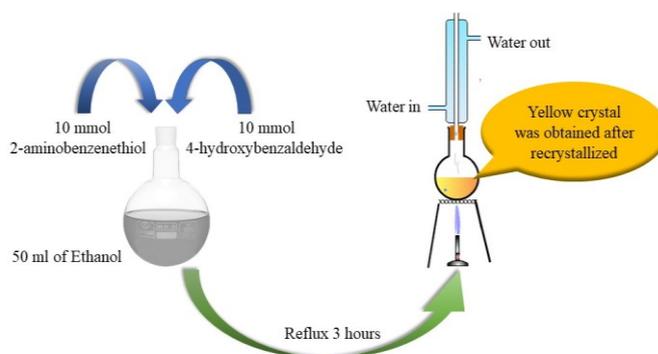


Figure 3: Synthesis of 4-((thiophen-2-yl)methyleneamino)phenol (TMAP)

#### 2.2.2 Synthesis of 4-((4-hydroxyphenylimino)methyl)phenyl thiophene-2-carboxylate (HPMTC)

4-hydroxybenzaldehyde (61 mg, 5mmol) and thiophene carbonyl chloride (73 mg, 5 mmol) were dissolved in 30 mL benzene. 10 mL pyridine was added drop wise into the solution. The solution was refluxed for 2 hours at 60°C. The product then was filtered and the residue was collected and evaporated. (116 mg, 5 mmol) of the intermediate was further mixed with (56 mg, 5 mmol) 4-aminophenol and refluxed for 3 hours. Brown crystal was obtained after recrystallized with ethanol (Figure 4). Yield: 68%, m.p: 201-201.6°C.  $^1H$  NMR

(400 MHz, DMSO- $D_6$ )  $\delta$  (ppm):  $^{13}C$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): FT-IR ( $cm^{-1}$ ): 1609 (C=N), 1588 & 1504 (C=C aromatic), 1738 (C=O), 749 (C-S), 3411 (OH).

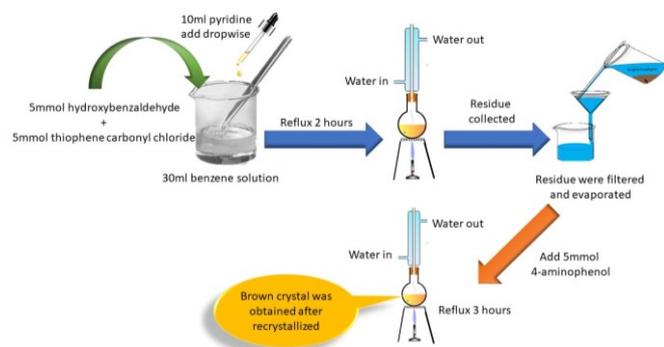


Figure 4: Synthesis of 4-((4-hydroxyphenylimino)methyl)phenyl thiophene-2-carboxylate (HPMTC)

## 2.3 Preparation of monomers

### 2.3.1 Synthesis of 3-(6-bromohexylthiophene) (BHT)

3-bromothiophene (2 mL, 21.3 mmol) was added to the dry, degassed hexane (50 mL). The reaction started by cooling the flask at  $-78^{\circ}C$ . *n*-butyllithium in hexane (2.0 M, 10.16 mL) was poured into the reaction flask and stirred for 10 minutes. THF (5 mL) was injected drop wise for 15 minutes and continuously stirred for 1 hours which produced white precipitate and clear supernatant liquid. The supernatant liquid was removed and changed with hexane/THF (10:1 v/v, 55 mL). 1,6-dibromohexanes (32.7 mL, 213 mmol) was added and stirred for 2 hours. The reaction was stopped with addition of saturated  $NaHCO_3$  (50 mL), diluted diethyl (100 mL). The organic layer was washed with water (100 mL), brine (100 mL), dried with magnesium sulfate anhydrous, treated with decolorizing charcoal, filtered and concentrated in vacuum to give orange oil. Removed excess 1,6-dibromohexane via vacuum distillation (0.04 torr,  $55^{\circ}C$ ) and purified silica gel column chromatography (ethyl acetate/hexane, 1/99 to 5/95 v/v) to obtain oily product. Yield: 52%. b.p:  $303.619^{\circ}C$ .  $^1H$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 1.38-1.46 (4H, m), 1.62 (2H, m), 2.59 (2H, t), 3.35 (2H, t), 6.86 (2H, m), 7.15-7.17 (1H, m).  $^{13}C$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 27.83, 28.5, 30.3, 30.5, 32.7, 35.4, 120.6, 126.04, 128.71, and 142.93. FT-IR ( $cm^{-1}$ ): 3005.47, 2959.71, 2933.71, 2857.26, 1551.4, 1459.60, 1437.01, 1420, 1246.85, 1216, 1031.13, 859.61, 773.32, 643.35 and 559.77.

### 2.3.2 Synthesis of 2,5-dibromo-3-(6-bromohexylthiophene) (BHT2):

3-(6-bromohexylthiophene) (1.93mL, 1.10mmol) was added to the 150 ml two neck flask under nitrogen flow. THF (25 mL) and acetic acid (25 mL) were injected together to flask. *N*-bromosuccinamide (3.8 g, 2.12 mmol) was added and the reaction was stirred for 2 hours at room temperature. The reaction was quenched via  $NaHCO_3$  (50 mL), diluted diethyl (100 mL). The organic layer was washed with water (100

mL), brine (100 mL), dried with magnesium sulfate anhydrous, treated with decolorizing charcoal, filtered and concentrated in vacuum to give orange oil. Purification was done by silica gel column chromatography (ethyl acetate/hexane, 1/10 v/v). Yield 60%.  $^1H$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 1.39-1.41 (4H, m), 1.79 (2H, m), 2.57 (2H, t), 3.5 (2H, t), 7.14 (1H, s).  $^{13}C$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 143.59, 132.29, 110.42, 107.96, 27.68-32.51. FT-IR ( $cm^{-1}$ ): 3005.47, 2959.71, 2933.71, 2857.26, 1551.4, 1459.60, 1437.01, 1420, 1246.85, 1216, 1031.13, 859.61, 773.32.

### 2.3.3 Synthesis of 2,5-dibromo-3-(6-(4-((thiophen-2-yl)methyleneamino)-hexyl)thiophene) (M1)

Mixture of TMAP (313 mg, 15.4 mmol), potassium carbonate (319 mg, 23.1 mmol), potassium iodide (90 mg) and acetone (300 mL) was refluxed with stirring for 2 h at  $80^{\circ}C$  followed by addition of 2,5-dibromo-3-(6-bromohexyl)thiophene (624 mg, 15.4 mmol) and further refluxed for 24 h at  $80^{\circ}C$ . The reaction mixture was filtered under hot condition and the solvent dried under reduced pressure. 100 mL petroleum ether ( $40-60^{\circ}C$ ) was added to the concentrated mixture and it was kept overnight in refrigerator. The solid was filtered off and hot filtration was carried out using ethanol chloroform (2:1) mixture then recrystallized three times with ethanol chloroform mixture. The product was filtered, washed with cold ethanol and dried at  $40^{\circ}C$  in vacuum oven. Yield 61%.  $^1H$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 9.60 ( $-CH_2=N-$ ), 8.28 ( $CH_m=C$  thiophene), 8.13-8.02 (Ar-Ha), 7.75-7.60 (Ar-H), 7.26 (Ar-Hc), 7.19 (Ar-H), 6.80 (Ar-H), 3.97 ( $-O-CH$ ), 1.74-1.41 (Hexyl).  $^{13}C$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm): 157.82, 152.00, 143.80, 143.25, 142.48, 133.29, 132.91, 130.60, 128.64, 128.59, 122.90, 116.49, 116.22, 115.88, 115.45, 35.60-25.11 FT-IR ( $cm^{-1}$ ): 2938.38, 1617, 1499.9, 1426.71, 1239.71, 1018.26, 709.24.

### 2.3.4 Synthesis of 2,5-dibromo-3-(6-(4-(phenylimino)methyl)phenyl thiophene-2-carboxylate)-hexyl)thiophene) (M2)

HPMPTC (497 mg, 15.4 mmol) of potassium carbonate (319 mg, 23.1 mmol), potassium iodide (90 mg) and acetone (300 mL) were refluxed with stirring for 2 h at  $80^{\circ}C$  followed by addition of 2,5-dibromo-3-(6-bromohexyl)thiophene (624 mg, 15.4 mmol) and was further refluxed for 24 h at  $80^{\circ}C$ . The reaction mixture was filtered under hot condition and dried under reduced pressure. 100 mL petroleum ether ( $40-60^{\circ}C$ ) was added to the obtain concentrated mixture and kept overnight in refrigerator. The solid was filtered off and hot filtration was carried out using ethanol chloroform (2:1) mixture then recrystallized three times with ethanol chloroform mixture. The product was filtered, washed with cold ethanol and dried at  $40^{\circ}C$  in vacuum oven. Yield 61%.  $^1H$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm) : 6.61 - 6.63 (1H, d), 1.04 - 4.09 (2H, t), 6.91 - 6.89 (2H, d), 7.11 - 7.13 (2H, d), 9.86 (1H, s), 7.85 - 7.87 (2H, d), 7.29 - 7.46 (3H, d,t), 8.0 (1H, d), 8.03 (1H, d).  $^{13}C$  NMR (400 MHz, DMSO- $D_6$ )  $\delta$  (ppm) : 114.85, 115.38, 129.10 - 132.78, 18.96 - 68.41,

161.21, 191.81, 146.73, 164.15 FT-IR ( $\text{cm}^{-1}$ ): 1220.73, 1603.61, 1724.66, 2859.89- 2935.39.

### 3 Result and discussion

FT-IR spectra in Figure 5 shown -OH stretching at  $3442.90 \text{ cm}^{-1}$  have disappeared resulting from the successful Williamson etherification reaction. Sharp and intense absorption peak at  $1239.71 \text{ cm}^{-1}$  for M1 and  $1220.73 \text{ cm}^{-1}$  for M2 indicated that the stretching of C-O ether presence in both macromonomers. The presences of C=N stretching at  $1617 \text{ cm}^{-1}$  for M1 and  $1603.61 \text{ cm}^{-1}$  for M2 have shown that there were no distraction on the C=N bonds after the reactions have been completed. In addition, due to the existence of ester on the M2 monomer, it was found that there was a presence of C=O stretching absorption peak at  $1724.66 \text{ cm}^{-1}$ . Lastly, the stretching of -CH aliphatic absorption peaks can be seen around  $2858.13 - 2930.79 \text{ cm}^{-1}$  at M1 and M2 spectra showing the formation of spacer groups.

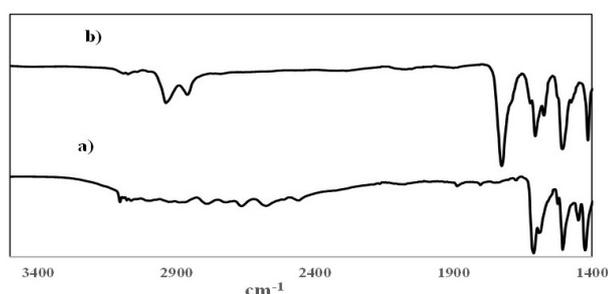


Figure 5: FT-IR spectrum of, a) M2, b) M1

From the proton NMR elemental analysis, the etherification of TMAP and BHT2 was yielded ether product at signals 3.97 ppm for M1 and M2 at 4.09 ppm as shown in Figure 6. The singlet peak is found at 9.60 ppm attributed to the present of proton of CH=N in the M1 and 9.86 ppm for M2. The signals were shifted to the lower field due to the bond attached to the conjugated system.

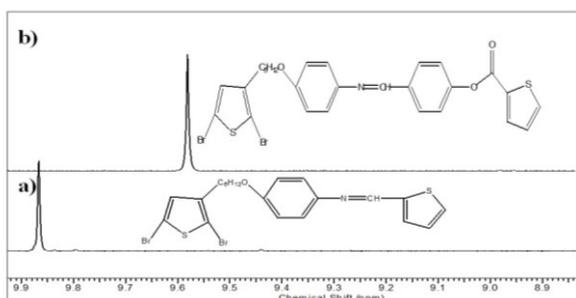


Figure 6: Azomethine peaks a) M2, b) M1

Thermal gravimetric analysis was carried out to give more insight to the structures of the synthesized compounds. Three-staged decompositions have been observed for both compounds. The first decompositions of the prepared compounds have started around  $166.6 - 269.93^\circ\text{C}$  which attributed to the thermal cleavage of the azomethine groups. The first decompositions of M1 with 14.64 % and M2 with

27.742% weight loss were caused by thermal cleavage of the azomethine groups as the bond between carbon and nitrogen is weak. The second decompositions were resulted from the degradation of monomers occurred in the range of  $269.93-503.33^\circ\text{C}$  and  $312 -502^\circ\text{C}$  for M1 and M2 respectively. Third stage decompositions are at  $502^\circ\text{C}$  and above for both monomers due to the breakage of the bromothiophene groups. Table 1 is tabulated to show the range of temperatures for M1 ( $269.93^\circ\text{C}-503.33^\circ\text{C}$ ) which was degraded is slightly longer to compare with M2 ( $312^\circ\text{C}-502^\circ\text{C}$ ) in response to the presence of azomethine and ester group in M2. This was due to the ester group, O=C-O-C which was degraded at lower temperature.

	1 <sup>st</sup> decomposition		2 <sup>nd</sup> decomposition		3 <sup>rd</sup> decomposition	
	Temp ( $^\circ\text{C}$ )	Wt, loss (%)	Temp ( $^\circ\text{C}$ )	Wt, loss (%)	Temp ( $^\circ\text{C}$ )	Wt, loss (%)
M1	166.60	14.64	269.93	37.168	503.33	44.984
	-		-			
	269.93		503.33			
M2	158-312	27.742	312-502	39.514	502	21.389

Table 1: Table 1: Thermal analysis for compounds M1 and M2

### 4 Conclusion

We have successfully synthesized polymerizable thiophene compounds performing 2,5-dibromo-3-(6-(4-((thiophen-2-yl)methyleneamino)-hexyl)thiophene) and 2,5-dibromo-3-(6-(4-(phenylimino)methyl)phenyl thiophene-2-carboxylate)-hexyl)thiophene) by incorporating intramolecularly a mesogenic thiophene azomethine as a side chain linked to thiophene monomer. Polythiophene-based polymers have been extensively applied in various electronic devices such as such as in field-effect transistors, memory devices, organic light-emitting diodes, solar cells, biosensor, hydrogen storage, and batteries. This is because of their capability in controlling their properties by using simple modification technique. The n- type properties combined with high thermal stability thus make the polythiophenoazomethine suitable for use as hole and electron transporting materials. Furthermore, access to these synthetically simple compounds will ultimately yield new materials suitable for functional devices with new operating properties. As such, this material do have significant potential to be fully integrated into a wide range of next generation electronic devices. However, due to limitations, synthetic and structural properties of  $\pi$ -conjugated oligomers or polymers are still not fully investigated. The key parameter in achieving good transporter properties is through its morphology in thin films thus, the polymeric structure should be further explored to enhance the desired properties. Also, intrepreting thiophene monomer with even stronger donor should be taken into account to produce longer-lived charge-separated state. Materials that absorb light in a wider range of the visible spectra in combination with the above

requirements remain a challenge to achieve good monochromatic efficiencies and also better overall light conversion efficiencies.

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