Supporting Information

An efficient method to prepare a new class of regioregular graft copolymer via a click chemistry approach

Shivshankar R. Mane,[a] Santu Sarkar,[a] Vijayakameswara Rao N.,[a] Ashlin Sathyan[a] and Raja Shunmugam*[a]

[a]Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata (IISER-K), India.

Experimental Section:

Materials:

All chemicals were purchased from Sigma Aldrich and used without further purification. Dimethyl formamide (DMF) and dichloromethane **(**DCM) were dried with calcium hydride (CaH_2) and calcium chloride ($CaCl_2$) respectively and then distilled prior to use. All deturated solvents, DMSO-d_6, $CDCl_3$ was purchased from Chembridge Isotope Laboratories. All other solvents and reagents of synthesis and analytical grade were used as received unless otherwise mentioned.

Methods:

Nuclear Magnetic Resonance (NMR). The ^{1}H NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using DMSO-d_6 and $CDCl_3$ as a solvent. ^{1}H NMR spectra of solutions in DMSO-d_6, and $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δH 0.00).

Fourier Transform Infra Red (FT-IR). FT-IR spectra were obtained on FT-IR Perkin-Elmer spectrometer at a nominal resolution of 2 cm^{-1}.

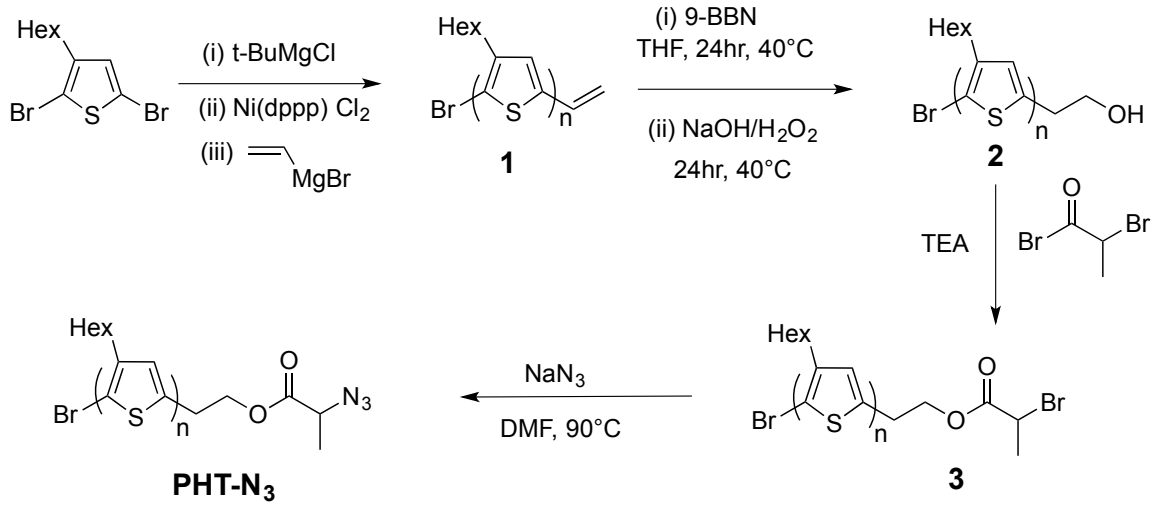
Gel Permeation Chromatography (GPC). Molecular weights and poly dispercity index (PDI) were measured by Waters gel permeation chromatography in THF relative to polystyrene standards on systems equipped with Waters Model 515 HPLC pump and Waters Model 2414 Refractive Index Detector at 35 ^oC with a flow rate of 1 mL/min.

Ultra Violet (UV) Spectroscopy. UV-visible absorption measurements were carried out on U-4100 spectrophotometer HITACHI UV-vis spectrometer, with a scan rate of 500 nm/min.

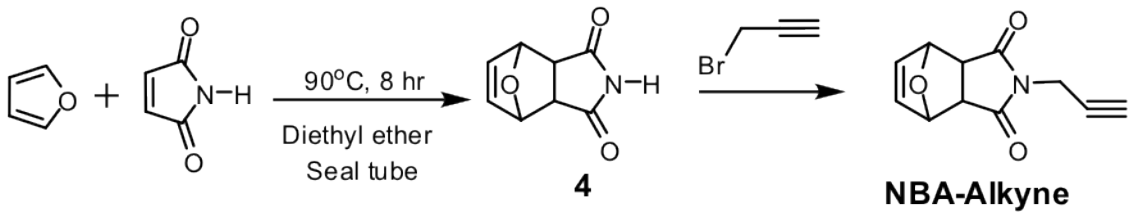
Atomic Force Microscopy (AFM). The polymer morphology was investigated from NT-MDT micro-40 AFM instrument using a semicontact mode at a scan rate of 1 Hz**.**

Scanning Electron Microscopy (SEM). High resolution SEM was performed on a Zeiss microscope; SUPRA 55VP-Field Emission Scanning Electron Microscope. High performance variable pressure FE-SEM with patented GEMINI column technology. Schottky type field emitter system, single condenser with crossover-free beam path. Resolution: 1.0 nm at 15 kV; 1.6 nm at 1 kV high vacuum mode. 2.0 nm at 30 kV at variable pressure mode.

Scheme:



Scheme S1: Synthesis of **PHT-N_3**.



Scheme S2: Synthesis of **NBA-Alkyne**.

Experimental section:

Synthesis of Molecule 1:

Molecule **1** was prepared with modified procedure as reported.[1]

A dry 100 mL three-neck flask was flushed with N_2 and 2,5-dibromo-3-hexylthiophene (0.49 g, 1.5 mmol) and anhydrous THF (15 mL) was added, then to this 2 M solution of butyl magnesium chloride (0.75 mL, 1.5 mmol) in diethyl ether (Et_2O) was added via syringe, and the reaction mixture was refluxed for 90 min. The reaction mixture was cooled down to room temperature, at this time Ni(dppp)Cl_2 (0.015 g, 0.027 mmol) was added. The polymerization was allowed to proceed for 15 min at room temperature followed by 1 M solution of vinyl magnesium bromide (0.3 mL, 0.3 mmol) solution was added. The reaction mixture was stirred for another 5 min before quenching in methanol. The obtained polymer was purified by soxhlet extraction with different solvents as methanol, hexane and chloroform. Finally the product was isolated from the chloroform solution (Yield = 38%; M_n =5200, PDI=1.03). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (s, 1H), 6.81 (t, 1H), 5.71 (d, 2H), 2.82 (t, 2H), 1.28-1.75 (m, 8H), 0.93 (t, 3H).

Synthesis of Molecule 2:

Molecule **2** was prepared with modified procedure as reported.[1-3] A Vinyl terminated PHT molecule **1** (0.2 g, 0.02 mmol) was dissolved in anhydrous THF (10 mL) in N_2 atmosphere. To this flask, 0.5 M solution of 9-BBN (0.4 mL, 0.2 mmol) in anhydrous THF was added via syringe. The reaction mixture was stirred for 24 hr at 40 °C, at this point a 6 M solution of NaOH (0.2 mL) was added. The reaction mixture was stirred for another 15 min. Then the reaction mixture was allowed to cool down to room temperature at this point 33% aqueous solution of hydrogen peroxide (0.2 mL) was added, and the reaction was allowed to proceed for additional 24 hr at 40 °C. Finally the hydroxy terminated PHT was isolated by precipitation in a methanol–water mixture followed by filtration and purified by soxhlet extraction method using methanol solvent (Yield = 68%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.65 (s, 1H), 4.07 (t, 1H), 3.18 (t, 2H), 2.63 (t, 2H), 2.23 (t, 2H), 1.15-1.31 (m, 8H), 0.81 (t, 3H).

Synthesis of Molecule 3:

A molecule **3** was prepared with modified procedure as reported.[1-3] In a round bottomed flask, hydroxy terminated PHT (molecule **2**) (0.1 g, 0.01 mmol) was dissolved in anhydrous THF (100 mL) under N_2. The reaction mixture was stirred for 15 min at 40 °C. Triethylamine (0.9 mL, 6.6 mmol) was added to the reaction flask, followed by drop-wise addition of 2-bromopropionyl bromide (0.75 mL, 6 mmol). Again the reaction mixture was stirred for 24 hr at 40 °C. Finally the PHT macroinitiator was precipitated in methanol and purified by soxhlet extraction method by using solvent methanol (Yield = 63%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.51 (s, 1H), 4.53 (t, 1H), 3.82 (t, 2H), 3.17 (t, 2H), 2.83 (t, 2H), 1.82 (d, 3H), 1.01-1.11 (m, 8H), 0.81 (t, 3H).

Synthesis of PHT-N_3 macroinitiator:

Molecule **3** (50 mg) was dissolved in 10 mL of dry DMF under the N_2 atmosphere. To this solution 50 mg of sodium azide (NaN_3) was added. This reaction mixture was stirred for 24 hr at 90 °C. The product was isolated by precipitation in water (Yield = 72%; M_n =5500, PDI=1.09). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.63 (s, 1H), 3.75 (t, 2H), 3.17 (t, 2H), 2.81 (t, 2H), 2.36 (t, 1H) 1.01-1.91 (m, 10H), 0.78 (t, 3H).

Synthesis of Molecule 4:

In a dry sealed tube, 2 gm (0.02 mol) of maleimide was dissolved in diethyl ether and 3 mL (0.04 mol) of furan was added. The reaction mixture was heated at 95°C for 8 hr. The reaction mixture was washed with diethyl ether several times and the product was collected as white precipitate and dried over night under vacuum (Yield = 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.53 (s, 2H), 5.21 (s, 2H), 2.91 (s, 2H), 11.02 (s, 1H).

Synthesis of NBA-Alkyne:

In a two neck round-bottomed flask, 878 mg (6.36 mmol) of potassium carbonate and 700 mg (4.24 mmol) of molecule **4** was dissolved in dry DMF. The reaction mixture was stirred at 50^0C for 1 hr. The reaction mixture was degassed. At this point, 0.4 mL (4.45 mmol) of propargyl bromide was added to the reaction mixture and stirred for 24 hr at 50°C. After completion of reaction, the crude product was dissolved in ethyl acetate and washed several times with water. The organic layer was evaporated under reduced

pressure. Pure needle shaped white crystals collected after the purification by column ethyl acetate-hexane as eluent (Yield = 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.55 (s, 2H), 5.32 (s, 2H), 4.25 (s, 2H), 2.90 (s, 2H), 2.19 (s, 1H).

Synthesis of macromonomer (MM 1):

The 20 mg of **PHT-N_3** was dissolved in 10 mL of THF-Water (1:1). 20 mg of **NBA-Alkyne** was added, followed by 22 mg of copper sulphate and 18.4 mg of sodium ascorbate was added. The reaction mixture was stirred for 24 hr at room temperature. The product was isolated by precipitation in methanol (Yield = 93%; M_n =5700, PDI=1.12). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.76 (s, 1H), 6.91 (s, 1H), 6.76-6.84 (s, 2H), 5.21 (s, 2H), 4.76 (s, 2H), 4.45 (t, 2H), 3.91 (t, 2H), 3.85 (t, 1H), 2.95 (s, 2H), 2.81 (t, 2H), 2.36 (t, 1H) 1.01-1.91 (m, 10H), 0.84 (t, 3H).

Synthesis of PNBA-*g*-PHT copolymer:

The 10 mg of macromonomer (**MM 1**) was dissolved in 1.5 mL of dry DCM: Methanol (9:1) under N_2. To this solution (1.2 mg) Grubbs' catalyst second generation (G2) was added. The reaction mixture was stirred for 12 hr at room temperature. The polymerization quenched by the addition of vinyl ethyl ether. The product was isolated by precipitation in pentane (Yield = 64%; M_n =20300, PDI=1.14). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.91 (s, -HC=C azide ring), 6.79 (s, -HC=C thiophene ring), 5.34 (s, 2H for polymeric proton), 4.76 (s, -OCH_2), 4.20 (t, -OCH_2-CH_2), 3.91 (t, -CH), 1.01-1.51 (m, -CH aliphatic), 0.67 (t, -CH_3 terminal).

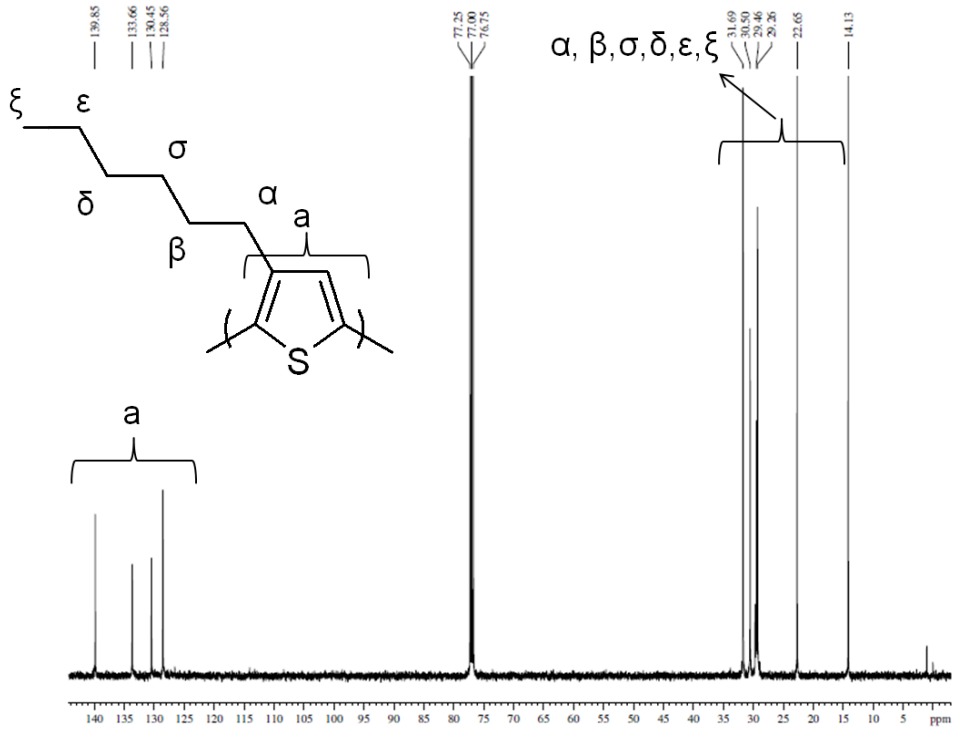


Figure S1. ^{13}C NMR spectra of Poly (3-hexyl thiophene) **1**.

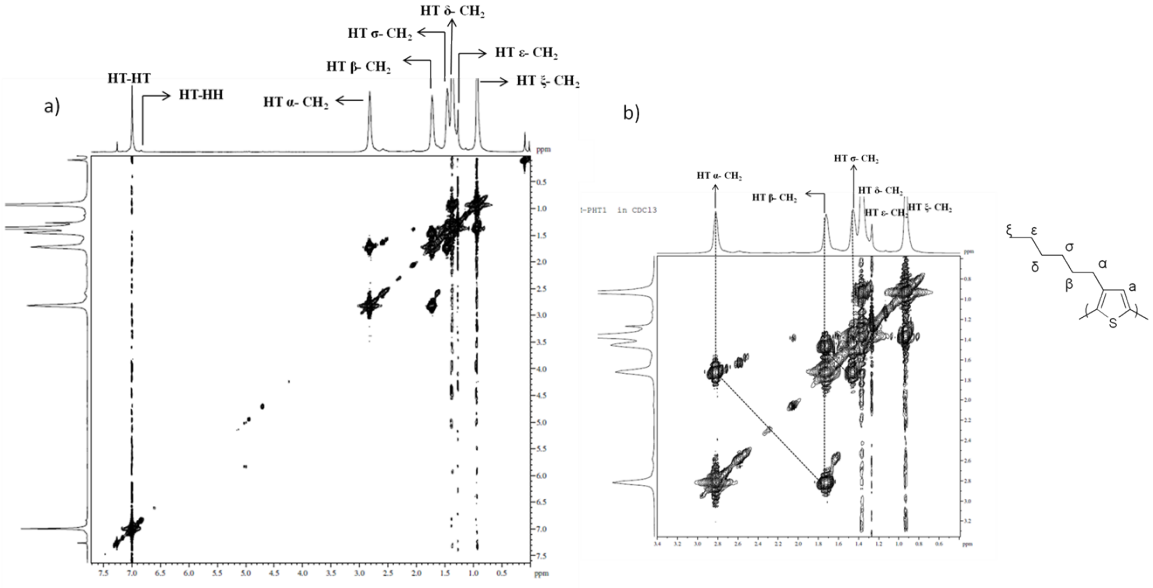


Figure S2. COSY NMR of Poly (3-hexyl thiophene) **1,** (a) Full spectra, (b) expanded.

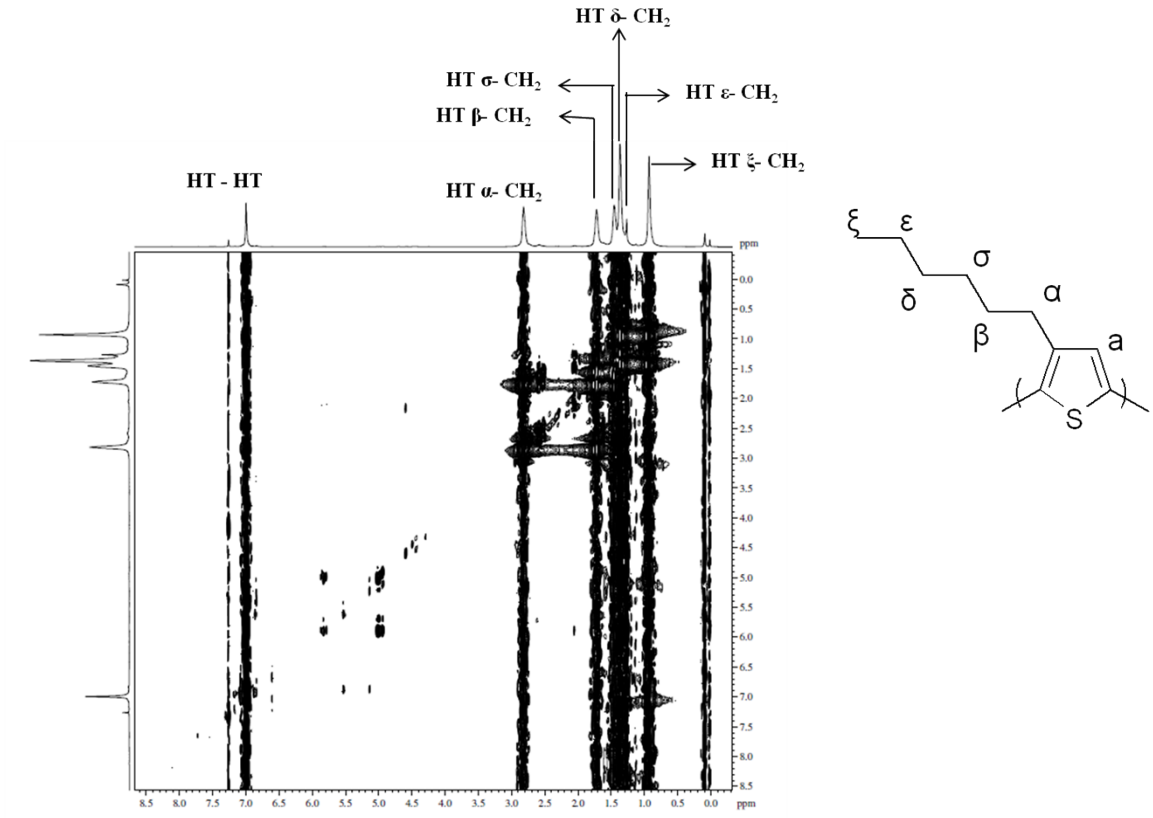


Figure S3. Double Quantum Filtered COSY NMR of Poly (3-hexyl thiophene) **1**.

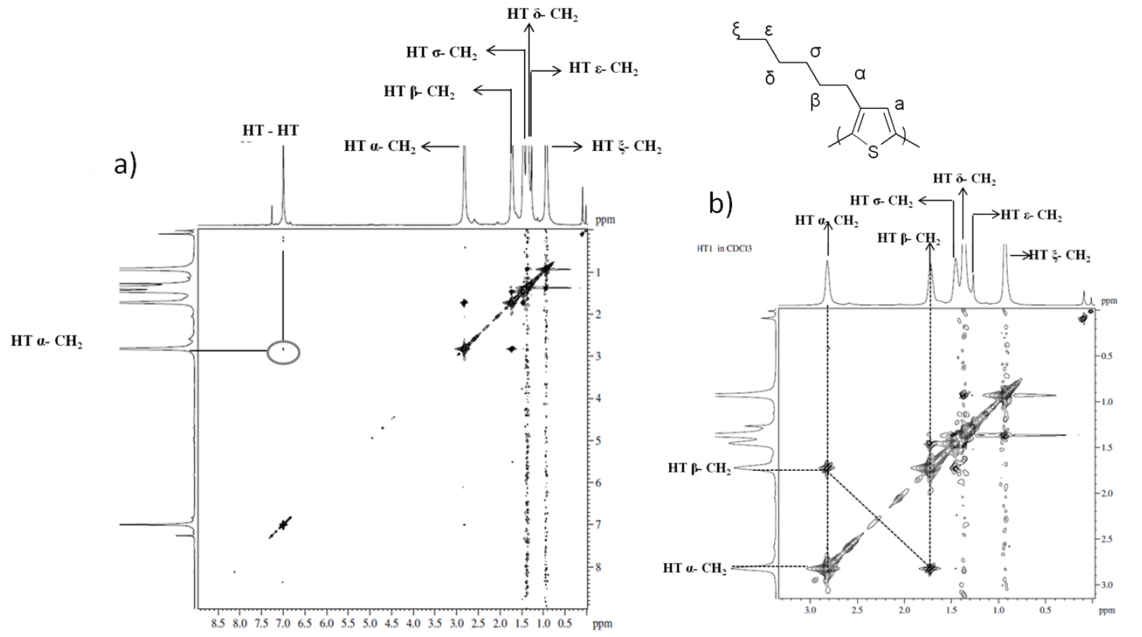


Figure S4. NOESY NMR of Poly (3-hexyl thiophene) **1,** (a) full spectra, (b) expanded spectra.

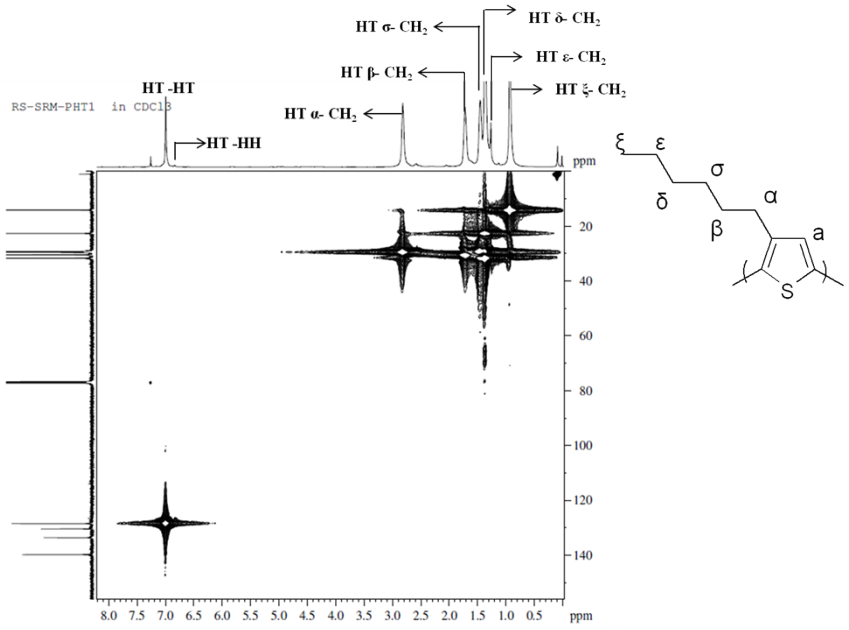


Figure S5. HMQC NMR for Poly (3-hexyl thiophene) **1**.

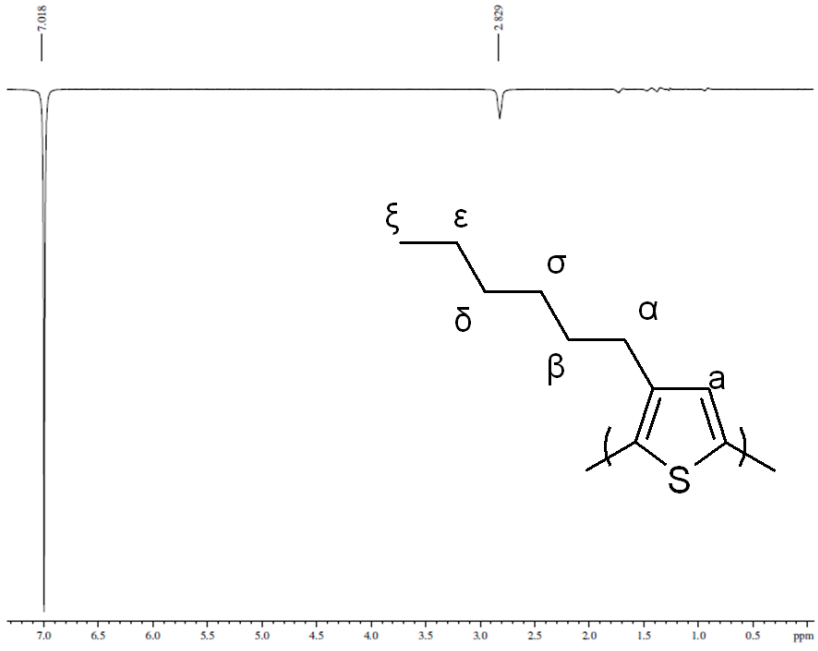


Figure S6. [1]D NOE NMR of Poly (3-hexyl thiophene)**1**.

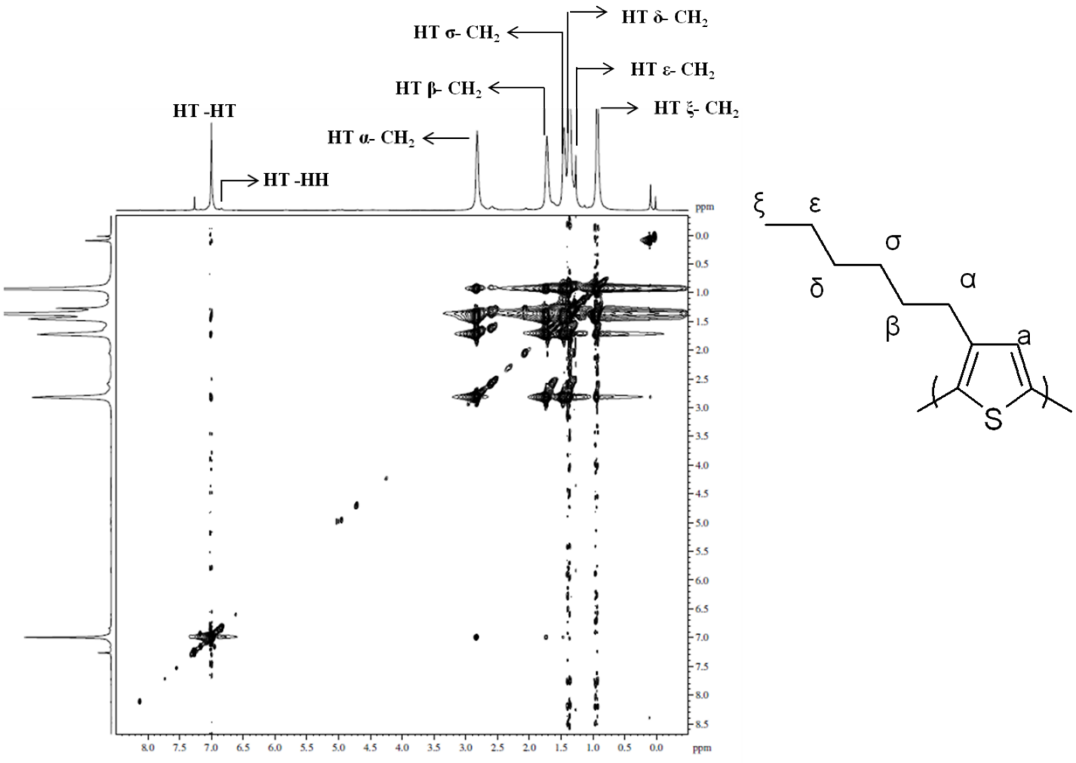


Figure S7. TOCSY NMR of Poly (3-hexyl thiophene) **1 (**Full Spectra).

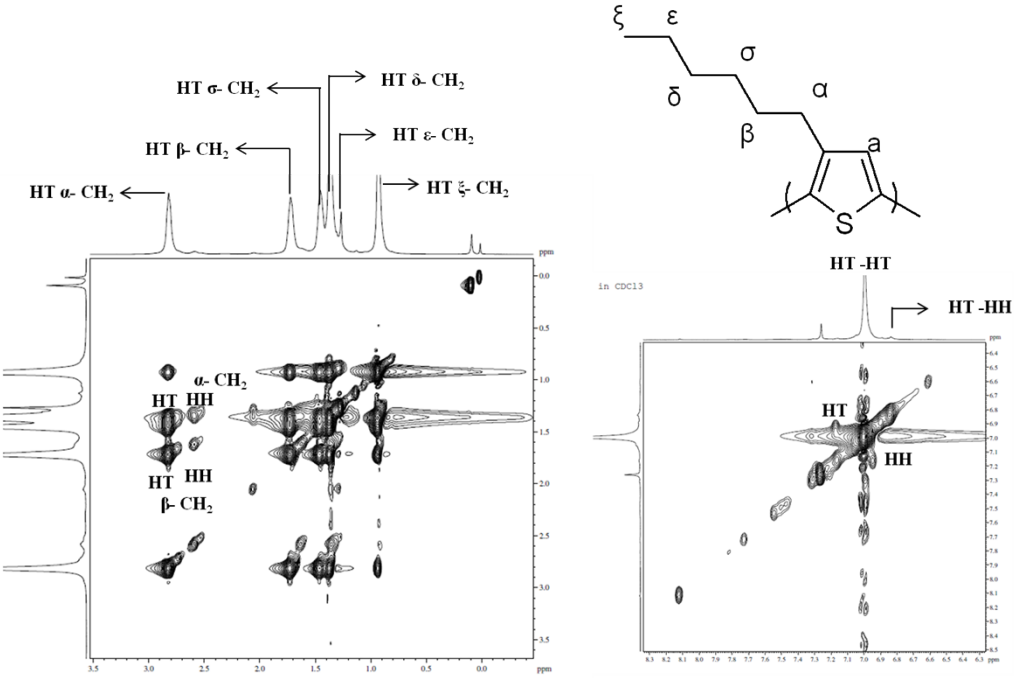


Figure S8. TOCSY NMR Spectra of Poly (3-hexyl thiophene) **1** (Expanded).

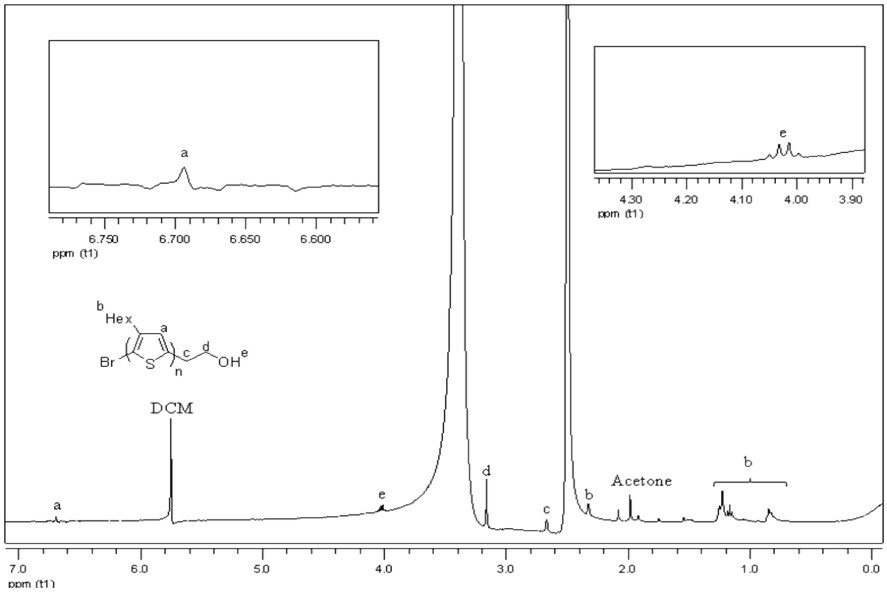


Figure S9. ^{1}H NMR spectra for Molecule **2**.

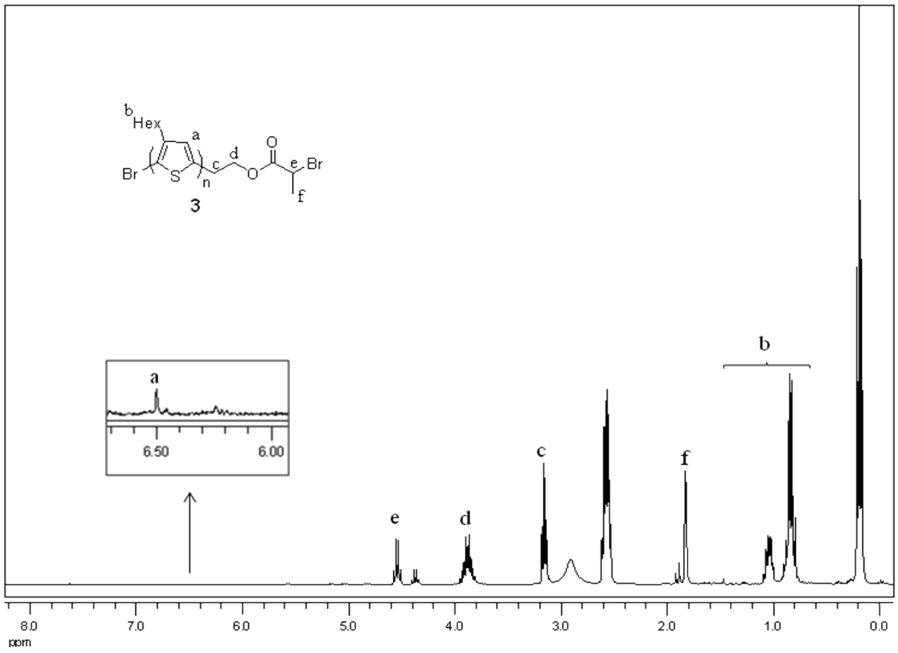


Figure S10. ^{1}H NMR spectra of Molecule **3** in DMSO-d_6.

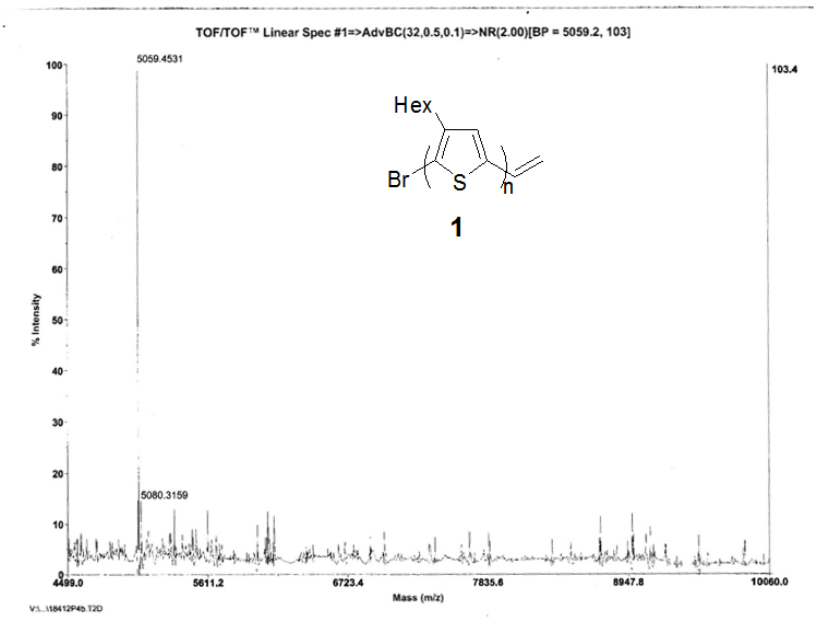


Figure S**11**. MALDI analysis of Molecule **1**.

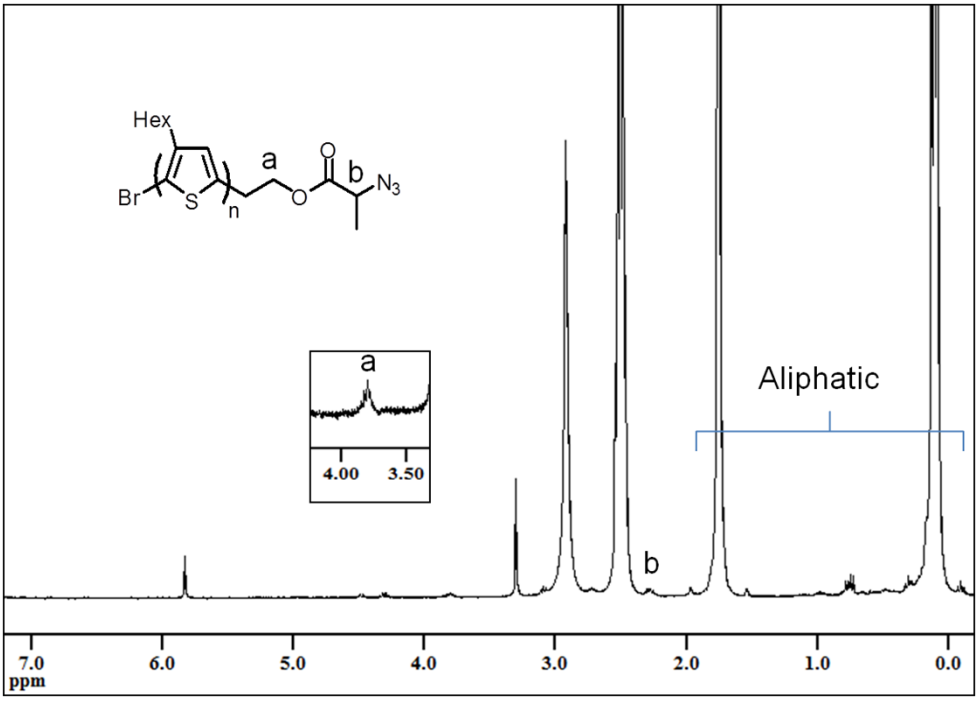


Figure S12. ^{1}H NMR spectra for **PHT-N_3** in DMSO-d_6.

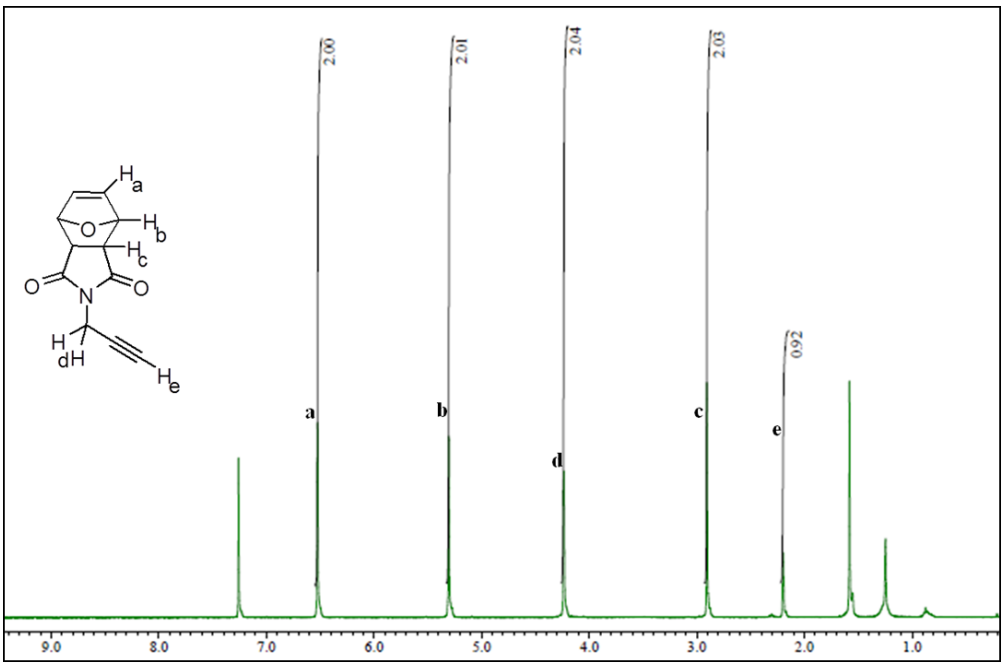


Figure S13. ^{1}H NMR spectra for **NBA-Alkyne** in $CDCl_3$.

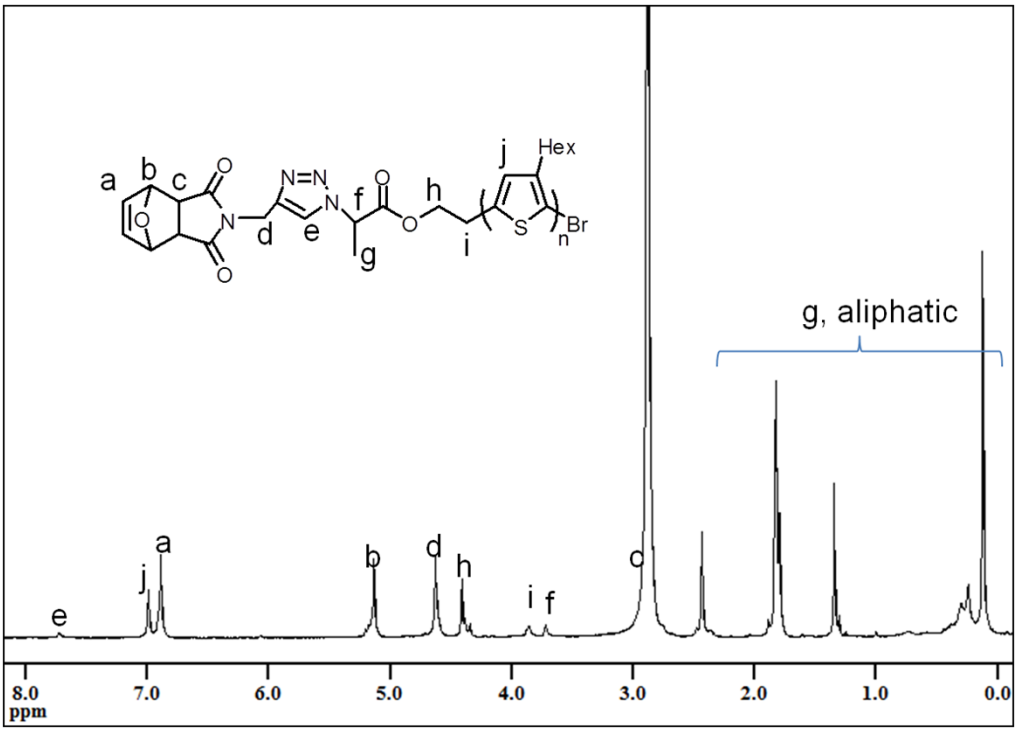


Figure S14. ^{1}H NMR spectra for macromonomer **MM 1** in DMSO-d_6.

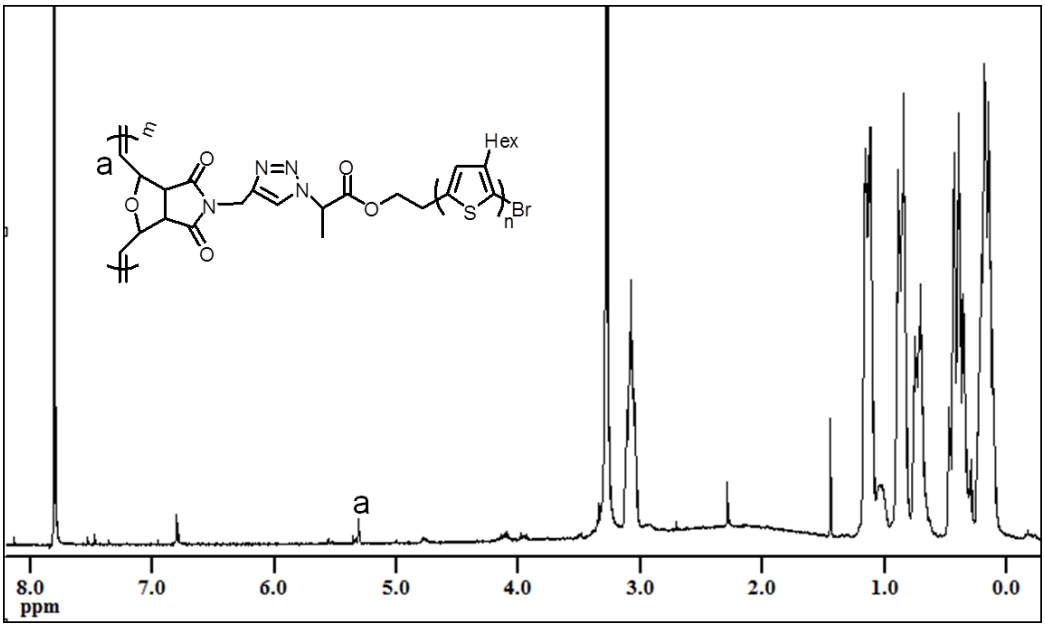


Figure S15. ^{1}H NMR spectra for **PNBA-*g*-PHT** in DMSO-d_6.

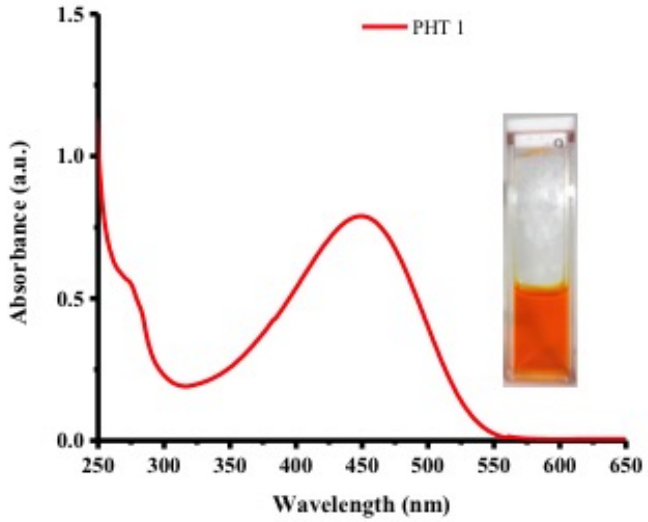


Figure S16. UV spectra of Poly (3-hexyl thiophene) **1.**

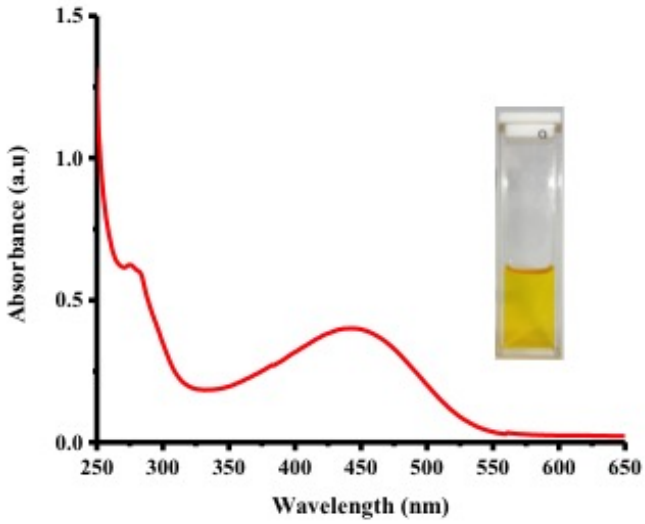


Figure S17. UV spectra of **PNBA-*g*-PHT** copolymer.

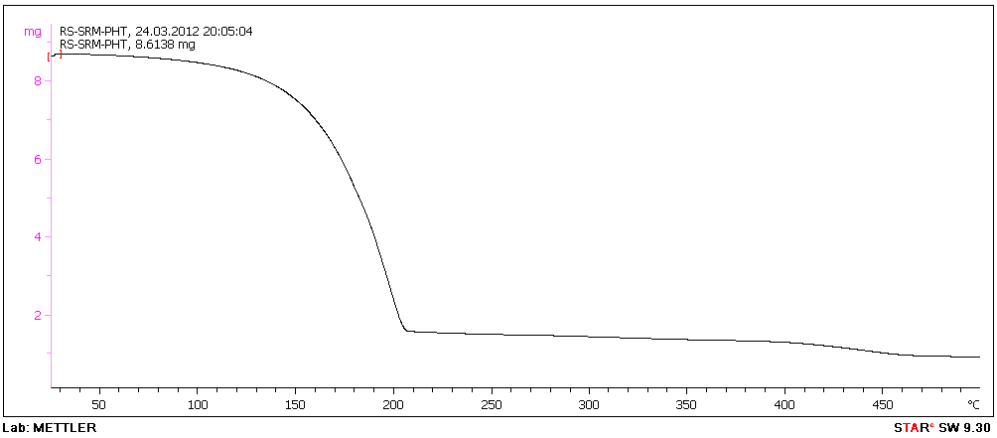


Figure S18. TGA analysis Poly (3-hexyl thiophene) **1**.

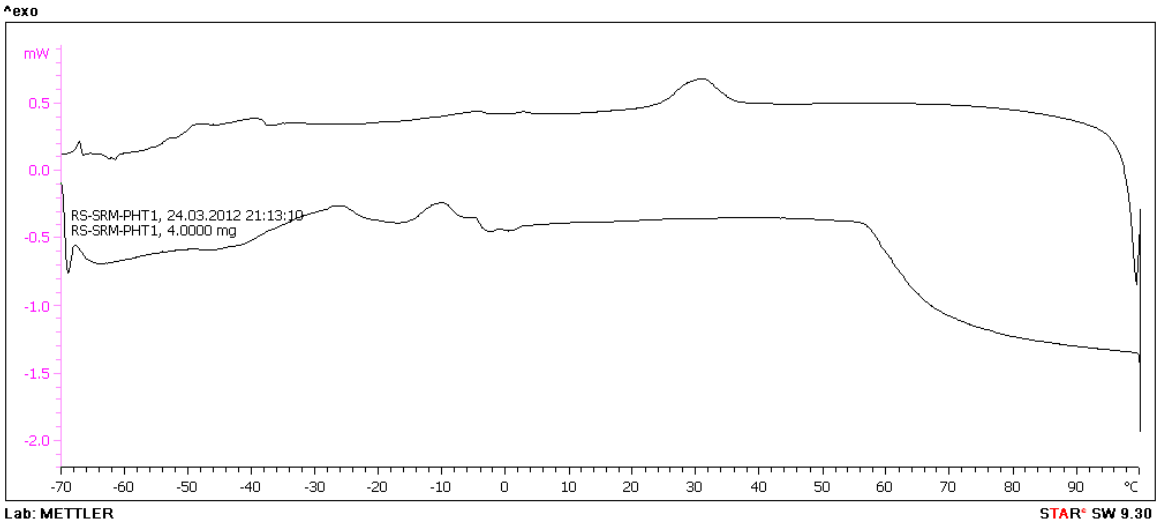


Figure S19. DSC analysis Poly (3-hexyl thiophene) **1.**

References:

1) Mihaela C. Iovu, Malika Jeffries-EL, Elena E. Sheina, Jessica R. Cooper, Richard D. McCullough, *Polymer* **2005,** 46 ,8582–8586.

2) Toshiaki Murai, Kazuki Ui, and Narengerile, *J. Org. Chem*. **2009**, 74, 5703–5706.

3) Kumaranand Palaniappan, Nadia Hundt, Prakash Sista, Hien Nguyen, Jing Hao, Mahesh P. Bhatt , Yun-Yue Han, Elizabeth A. Schmiedel, Elena E. Sheina, Michael C. Biewer, Mihaela C. Stefan, *Journal of Polymer Science Part A: Polymer Chemistry*, **2011**,49,1802-1808.