Investigations into the preparation of donor/acceptor-substituted polyacetylenes by alkyne polymerization

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by

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We, the thesis committee for the above candidate for the

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Abstract of the Thesis

Investigations into the preparation of donor/acceptor-substituted polyacetylenes by alkyne polymerization

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The polymerization of 2-ethynyl-5-hexylthiophene (2E5HT), 2-hexyl-5-((perfluorophenyl)ethynyl)thiophene (HT≡FPh), 2-hexyl-5-(3,3,3-trifluoroprop-1-yn-1-yl)thiophene (HT≡CF_3), 1-ethynyl-2,3,5,6-tetrafluoro-4-methoxybenzene (1ETFMB), 1-ethynyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (PFPA), and ethynylbenzene with transition metal catalysts (tantalum (V) chloride, molybdenum (VI) tetrachloride oxide, and 2nd Generation Grubbs Catalyst) was investigated. The targeted polymers and copolymers were designed to have both electron-donating and electron-withdrawing groups conjugated to the polyacetylene backbone to tune the electronic and optical properties for potential application in organic photovoltaic solar cells. The optical properties of the resulting oligomers and polymers were analyzed by UV-Vis absorption spectroscopy.

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Acknowledgements

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I. INTRODUCTION

i. Organic Photovoltaic (OPV) Cells:

Organic photovoltaic (OPV) cells are devices that convert solar energy to electrical energy. Typical OPV cells have more than one material layer sandwiched by a cathode and an anode. The energy conversion mechanism of OPV cells has four steps: **(1) Light Absorption:** the donor polymer absorbs sunlight and generates excitons; **(2) Exciton Diffusion:** excitons diffuse to the interface of donor and acceptor materials; **(3) Charge Separation:** Excitons are split into an excited electron and a hole; **(4) Charge Extraction:** The excited electron diffuses out of active layer through the anode through the conduction band of the electron-transporting material and the hole diffuses to the cathode through the valence band of hole-transporting material, **Figure** 1. Therefore, the band-gap of the donor material determines the minimum light energy required to generate excitons and defines the ranges of wavelengths that can be absorbed by the cell.

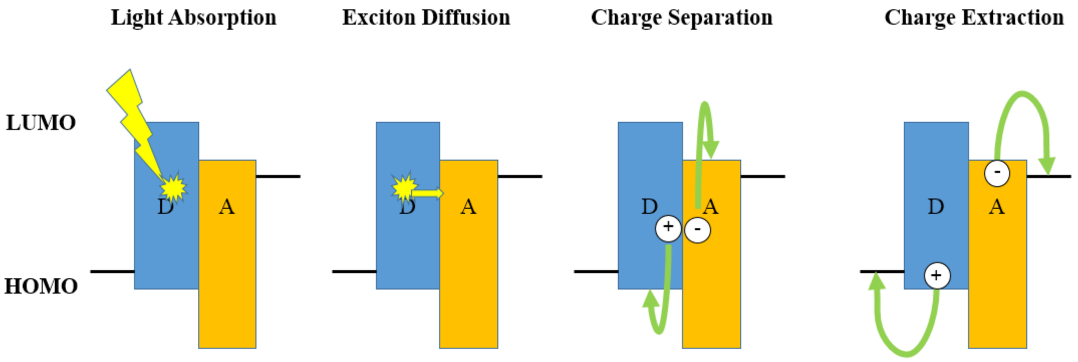


Figure 1. Mechanism of Bulk Heterojunction (BHJ) Organic Photovoltaic Solar Cell.[1]

The sunlight emission spectrum, **Figure 2**, shows the distribution of sunlight energy at the surface of the earth. From the spectrum, we can realize that lowering the band-gap of the absorbing material would result in the absorption of more photons and the generation of more mobile electrons. However, there is a trade-off between electron generation and electronic potential. When the band-gap of polymer decreases, the number of absorbed photons (current) would increase but the electron potential (voltage) would be reduced due to the smaller energy difference between the HOMO of the electron donor and the LUMO of the electron acceptor. Extreme low or high band-gaps both result in reduced device efficiency. Because device efficiency is proportional to the product of current and voltage, the ideal band-gap that does not sacrifice too much current or voltage is around 1.5-1.7 eV.

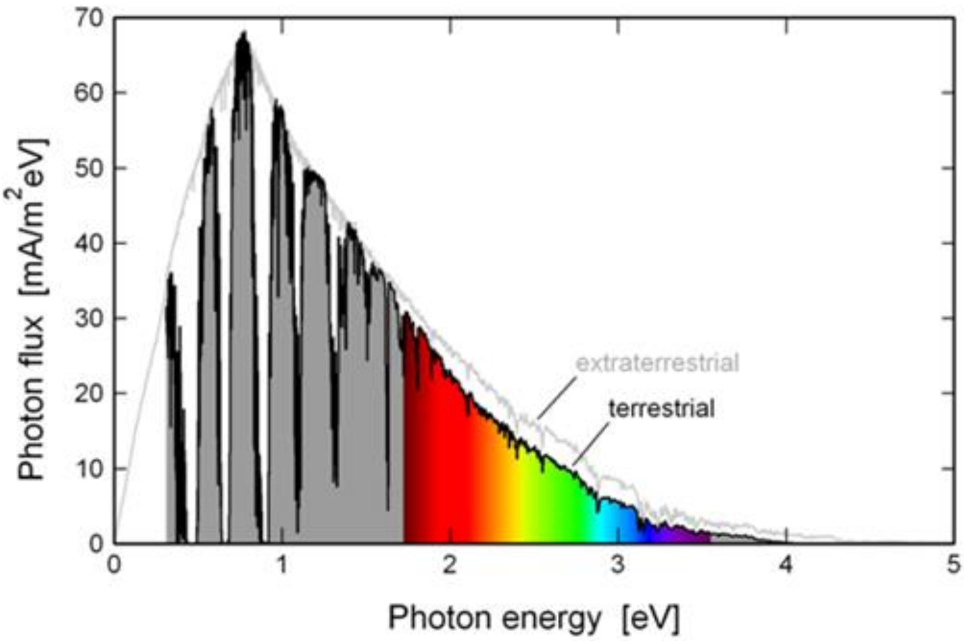


Figure 2. Solar Emission Spectra.[2]

ii. Molecular Design and Synthesis:

Thiophene-based conjugated polymer are widely used as organic semiconductors in organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic (OPVs).[3] One of the classic thiophene-based polymers, poly(3-hexylthiophene) (P3HT) shows outstanding charge transport properties in blends with fullerene-based acceptor materials.[1, 4] The application of P3HT in OPVs is limited by the relatively large bandgap (E_g= ~1.9 eV) and high HOMO level (~5.1 eV). Therefore, modifying the electronic properties of thiophene-based polymers is critical to improving OPV devices. Of the methods used to tune the band gap, the most widely investigated one is to add alternating donor/acceptor groups on the backbone of conjugated polymer. These approaches typically use a step growth polymerization method,[5] which provides poor control over the molecular weight and the molecular weight distribution. The alkyne polymerization in this research is an additional polymerization method, which can potentially be done with better control over molecular weight and polydispersity.

In this research, we chose polyacetylene, a simple conjugated polymer, as the conjugated backbone to study the influence of substituents on properties of polymers. The simple conjugated backbone can easily reflect the effect of substituents on the properties of polymer. In designing the polymers, we utilized the concept of donor-acceptor systems, **Figure 3**, which can effectively reduce the bandgap of conjugated polymers and widen the range of absorbance. All polymers in this research have hexylthiophene groups as electron donors and fluorinecontaining groups as electron acceptors. The hexyl group on thiophene may improve the polymer solubility, miscibility with fullerene, and fullerene diffusion rate in blends for device fabrication.[4b]

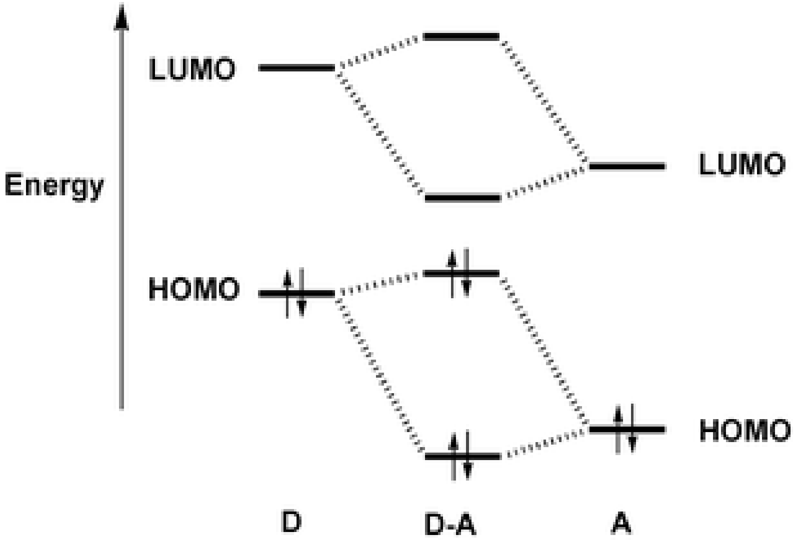


Figure 3. Donor-Acceptor System.[6]

In previous research, the effect of aromatic substituents on the bandgap of polyacetylenes prepared from disubstituted alkynes with two aromatic substituents was examined.[7] Theoretically, the aromatic rings can enlarge the conjugated system of the di-substituted polyacetylene and lower the bandgap, but the previous results have shown that bulky substituents on polyacetylenes reduce overall conjugation length and do not significantly reduce band gap.[7a,8] One aim of this research was to explore the steric constraints determining how small an electron-donating or withdrawing substituent can be before significant de-planarization of the polyacetylene backbone results.

Besides polymers with less bulky substitutes, we have also designed new copolymers with two mono-substituted alkyne monomers: one with an electron-withdrawing substituent and one with an electron-donating substituent. In this case, the new copolymers have the potential to show a longer effective conjugation length due to the larger distance between substituents and the resulting decrease in steric hindrance. Alternation between electron-withdrawing and electron-donating monomers may also improve the optical properties of the resulting polymers.

iii. Polymerization:

Transition metal catalysts are commonly used in the polymerization of substituted acetylenes and are usually paired with some type of cocatalyst to increase the rate of propagation and the molecular weight of the polymer. The mechanism of the polymerization involves metallacyclobutene intermediates, **Figure 4**, and the polymerization has been shown to be living with certain metal catalysts. Of these transition metal catalysts, tungsten, tantalum, and molybdenum are the most widely reported.[9] The three different metal catalysts are used with different substituted acetylenes based on the properties of transition metal and substituents.[9a, 10] In this research, we decided to use $TaCl_5$/*n*-Bu_4Sn and $MoOCl_4/Et_3Al$ as catalysts for the specific polymerization of substituted acetylenes.

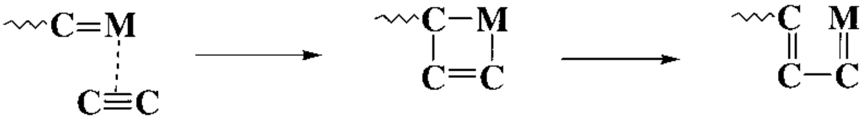


Figure 4. Mechanism of alkyne polymerization.[11]

The $TaCl_5$/*n*-Bu_4Sn catalyst system was chosen for the polymerization of disubstituted acetylenes (**Figure 5**) as it has been shown to result in high molecular weights and low polydispersity indices in the polymerization of disubstituted acetylenes.[10a 9b, 10b] The function of the cocatalyst (*n*-Bu_4Sn) is to accelerate the polymerization and prolong the lifetime of growing polymer chains by preventing secondary metathesis reactions in which double bonds in the polymer backbone undergo further metathesis reactions.[12]

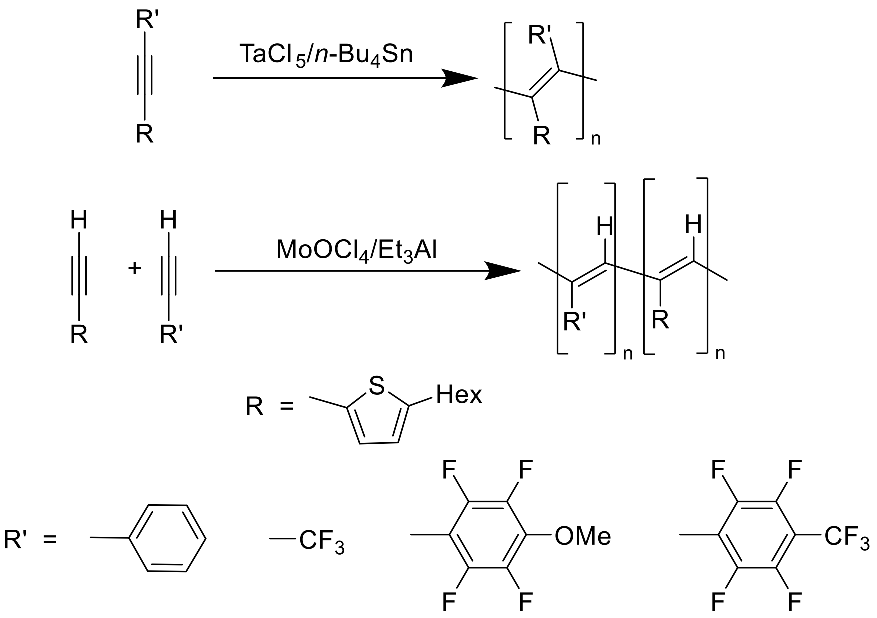


Figure 5. General scheme for alkyne polymerization and copolymerization

A previously reported catalyst system ($MoOCl_4/Et_3Al/EtOH$)[13] was used in the copolymerization of mono-substituted alkynes. In this system, Et_3Al works as a cocatalyst to activate $MoOCl_4$ and ethanol is used to quench the by-products from the activation of $MoCl_4/Et_3Al$, and living copolymerization has been reported.[11] In our research, we used this catalyst system to copolymerize monosubstituted alkynes with electron-withdrawing groups and monosubstituted alkynes with electron-donating groups. This type of copolymerization has been reported by Masuda and co-workers[13] and results in polymers with high molecular weights and narrow molecular weight distributions.

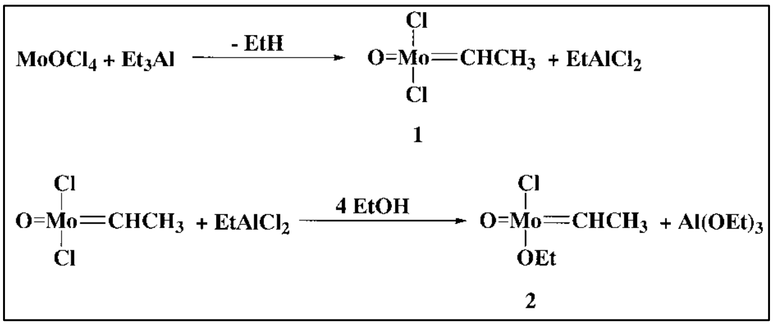


Figure 6. Activation of MoOCl4 with triethylaluminum to generate active catalyst for alkyne polymerization.[11]

In the report from Masuda's group, monomers in **Figure 7**, were polymerized.[13] The highest molecular weights (M_w=24.9 k (g/mol) and $Đ$=1.2) were reported for the polymer prepared by polymerization of monomers ClOc and *p*-BuF4PA with $MoOCl_4$/*n*-BuLi. Copolymerizations of other monomers generally proceeded to moderate molecular weights (M_w=10 kg/mol) and narrow molecular weight distributions ($Đ$=1.07-1.3).[13]

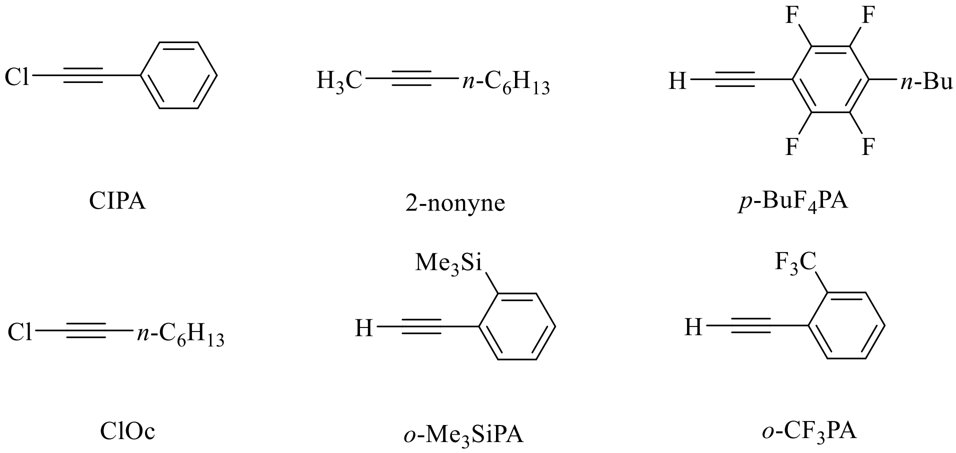


Figure 7. Alkyne monomers reported in polyacetylene copolymers by Masuda's group.[13]

II. Experimental Section

Material

2-Bromo-5-hexylthiophene, tetra-*n*-butyltin (95%), bis(triphenylphosphine)palladium(II) dichloride (>98%), and 2,2,2-trifluoroacetophenone were purchased from Tokyo Chemical Industry Co. triethylsilylacetylene (97%), tantalum chloride (99.8%), pentafluoroiodobenzene (99%), ethynylbenzene (98+%) and trimethylsilylacetylene (97 %) were purchased from Alfa Aesar. Triethylaluminum (93%) was purchased from Strem Chemical Inc. Molybdenum (VI) tetrachloride oxide (97%), tantalum chloride (99.8%), copper (II) trifluoro-methanesulfonate (98%), 1, 10-phenanthroline (99%), and lithium *tert*-butoxide (97%) were purchased from Sigma Alderich Inc.

NMR Spectroscopy

^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on Bruker Fourier 400 NMR Spectrometer at 25 °C and chloroform-*d* or /dichloromethane-d_2 were used as solvents.

GPC Measurement

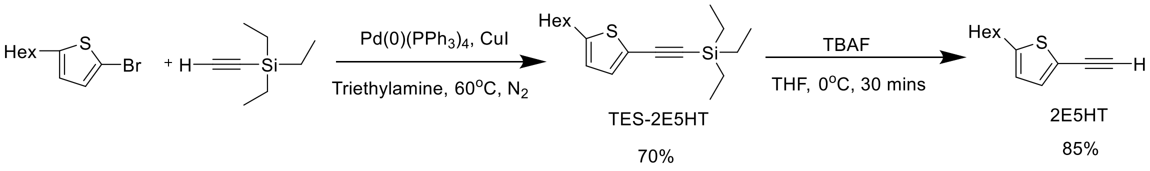
All GPC data were acquired at 40 °C with THF (HPLC grade, J.T. Baker) as the eluent at a flow rate of 1.0 mL/minute. The GPC consisted of a K-501 pump (Knauer), a K-3800 Basic Autosampler (Marathon), 2 × PLgel 5 μm Mixed-D columns (300 × 7.5 mm, rated for linear separations at polymer molecular weights from 200 to 400,000 g/mol, Polymer Laboratories), a CH-30 Column Heater (Eppendorf), a PL-ELS 1000 Evaporative Light Scattering Detector (Polymer Laboratories), and a PL Datastream unit (Polymer Laboratories). Narrow polydispersity polystyrene standards with molecular weights from 580-377,400 g/mol (EasiCal PS-2, Polymer Laboratories) were used to construct a calibration curve for data analysis.

UV-Vis Absorption Measurement

UV/Vis absorption spectra were measured on a Lambda 25 UV/Vis System (PerkinElmer) in chloroform or dichloromethane at the Center for Functional Nanomaterials at Brookhaven National Laboratory.

Synthesis of Monomers

a. Synthesis of 2-ethynyl-5-hexylthiophene (2E5HT)



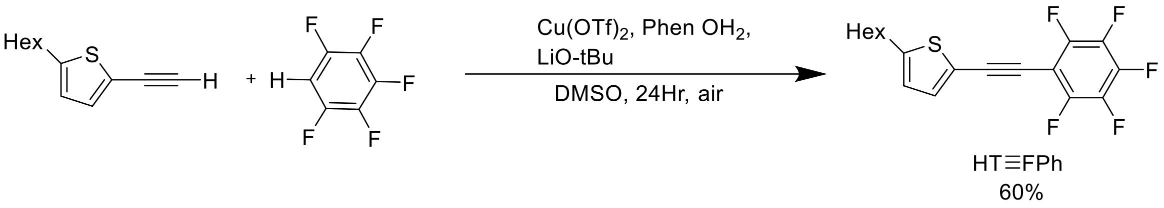
((5-Hexylthiophen-2-yl)ethynyl)triethylsilane (TES-2E5HT)**:** The Sonogashira Coupling reaction was adapted from an experimental procedure in the literature.[14] Copper (I) iodide (586 mg, 1.6 mmol), and tetrakis(triphenylphosphine)palladium(0) (223 mg, 0.4 mmol) were placed in a 50 ml Schlenk tube equipped with a magnetic stir bar. The system was evacuated and refilled with argon three times. After triethylamine (25 ml) was added into the Schlenk tube by cannula, 2-bromo-5-hexylthiophene (984 mg, 0.8 ml, 4 mmol) and triethylsilylacetylene (982 mg, 1.26 ml, 7 mmol) were injected by syringe. The mixture was heated to 60 °C for 48 hours under an argon atmosphere. The solution was added to a separatory funnel with ammonium chloride solution (10%, 20 ml) and the resulting crude product mixture was extracted with chloroform (20 ml) three times. The combined organic layers were washed with ammonium chloride (10%, 20 ml) and dried over sodium sulfate. After filtration, the solvent was evaporated, and the residue was purified by chromatography with hexanes over silica gel to afford TES-2E5HT as a yellow liquid (yield 70%, 860 mg).

^{1}H NMR (400MHz, $CDCl_3$): δ 7.07-7.06 (d, *J*=3.7 Hz, thiophene 3-*H*, 1H), 6.63-6.62 (d, *J*=3.7 Hz, thiophene 4-*H*, 1H), 2.80-2.76 (t, *J*=7.6 Hz, ArCH_2 –, 2H), 1.68-1.64 (quin, –CH_2-C_4H_9, 2H), 1.39-1.29 (m, —$CH_2CH_2CH_2$—, 6H), 1.08-1.04 (t, $Si(CH_2CH_3)_3$, 9H), 0.93-0.89 (t, –CH_3, 3H), 0.72-0.66 (q, SiCH_2-, 6H).

***<u>2-Ethynyl-5-hexylthiophene (2E5HT)</u>*:**[15] The desilylation was adapted from a reported experimental procedure.[16] To a cooled (0 °C) solution of TES-2E5HT (0.86 g, 2.8 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride (3.43 mL, 3.43 mmol, 1M solution in THF). The resulting mixture was stirred at 0 °C for 20 min, concentrated under vacuum, and purified by column chromatography with hexanes to afford the product 2-ethynyl-5-hexylthiophene (yield 85%, 460 mg).

^{1}H NMR (400MHz, $CDCl_3$, δ): 7.11-7.10 (d, *J*=3.5 Hz, thiophene 3-*H*, 1H), 6.65-6.64 (d, *J*=3.5 Hz, thiophene 4-*H*, 1H), 3.3 (s, CH, 1H), 2.80-2.76 (t, *J*=7.7 Hz, Ar CH_2 –, 2H), 1.70-1.63 (m , –CH_2 C_4H_9, 2H), 1.39-1.29 (m, –$CH_2CH_2CH_2$–, 6H) , 0.93-0.89 (t, *J*=6.8 Hz, –CH_3, 3H).

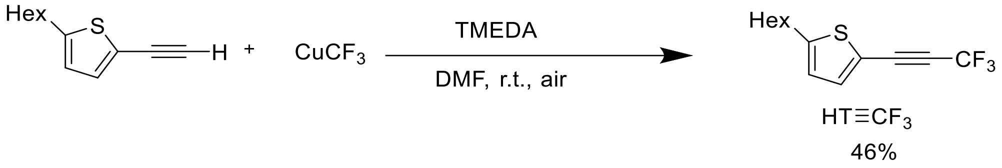
b. Synthesis of 2-hexyl-5-((perfluorophenyl)ethynyl)thiophene) (HT≡FPh)



***2-hexyl-5-((perfluorophenyl)ethynyl)thiophene (HT≡FPh)*:** The alkynylation of pentafluorobenzene with a terminal alkyne was adapted from a reported procedure.[17] Copper (II) trifluoromethane-sulfonate (81 mg, 0.224 mmol), 1,10-phenanthroline (81 mg, 0.448 mmol), lithium *tert*-butoxide (89.6 mg, 1.12 mmol), and DMSO (3 mL) were added to a round-bottom flask. The resulting mixture was stirred for 5 min at room temperature. Solutions of pentafluorobenzene (1.12 ml, 3.36 mmol, 3M in DMSO) and 2E5HT (1.12 ml, 1.12 mmol, 1M in DMSO) were added sequentially. The reaction was stirred at room temperature under air for 24 hr. Water (20 mL) was added and the resulting mixture was extracted with dichloromethane (40 ml) three times. The organic layer was dried over sodium sulfate, then concentrated in vacuo and purified by silica gel chromatography (neat hexanes) to afford red crystals (yield 60%, 243 mg).

^{1}H NMR (400MHz, $CDCl_3$, δ): 7.17-7.16 (d, *J*=3.7 Hz, thiophene 3-*H*, 1H), 6.67-6.66 d, *J*=3.7 Hz, thiophene 4-*H*, 1H), 2.81-2.77 (t, *J*=7.6 Hz, Ar CH_2 –, 2H), 1.69-1.65 (m, –CH_2 C_4H_9, 2H), 1.38-1.26 (m, –$CH_2CH_2CH_2$–, 6H), 0.91-0.88 (t, *J*=6.8 Hz,–CH_3, 3H).

c. Synthesis of 2-hexyl-5-(3,3,3-trifluoroprop-1-yn-1-yl)thiophene (HT≡CF_3)

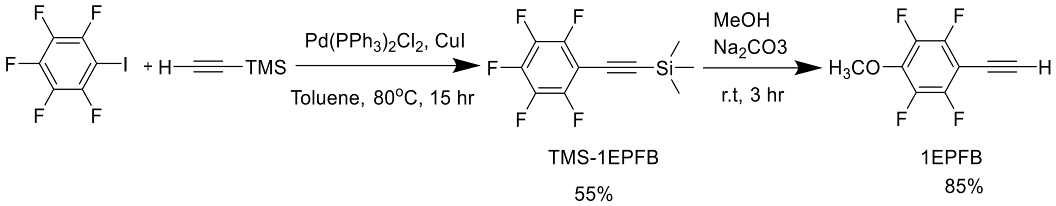


***2-hexyl-5-(3,3,3-trifluoroprop-1-yn-1-yl)thiophene (HT≡CF_3)*:** The trifluoromethylation of terminal alkyne was adapted from a reported procedure.[18] Copper chloride (455 mg, 4.6 mmol), potassium *tert*-butoxide (1032 mg, 9.2 mmol), and dry DMF (9.2 mL) were added to a round bottom flask and stirred for 1 hr under nitrogen atmosphere at room temperature. 2,2,2-Trifluoroacetophenone (0.63 ml, 801 mg, 4.6 mmol) was added dropwise into the solution and the solution was stirred for 30 min under nitrogen to form $CuCF_3$. Trimethylamine hydrochloride (633 mg, 4.6 mmol) and TMEDA (0.69 ml, 535 mg, 4.6 mmol) were then added to the solution of $CuCF_3$. A solution of 2-ethynyl-5-hexylthiophene in DMF (442 mg, 2.3 mmol, 1M in DMF) was added into $CuCF_3$ solution with syringe pump over 1-2 hr under air atmosphere. After addition of the 2E5HT solution was complete, the resulting solution was stirred for an additional 15 min. Aqueous HCl (2M, 2.3 ml) was added and the mixture was extracted with ether (30 ml) three times. The organic layer was washed with saturated brine (20 ml) three times and the product was purified by flash chromatography with neat hexanes over silica gel to afford HT≡CF_3 as a red liquid (yield 46%, 275 mg).

^{1}H NMR (400MHz, $CDCl_3$, δ): 7.29-7.28 (d, *J*=3.7 Hz, thiophene 3-*H*, 1H), 6.74-6.72 (d, *J*=3.7 Hz, thiophene 4-*H*, 1H), 2.84-2.80 (t, *J*=7.7 Hz, Ar CH_2 –, 2H), 1.70-1.66 (m, –CH_2

C_4H_9, 2H), 1.35-1.27 (m, $–CH_2CH_2CH_2–$, 6H), 0.92-0.87 (t, *J*=7.4 Hz, $–CH_3$, 3H). ^{19}F NMR (400MHz, $CDCl_3$, δ): 49.61 (s, $–CF_3$, 3F).

d. Synthesis of 1-ethynyl-2,3,5,6-tetrafluoro-4-methoxybenzene (4F1MPhA)



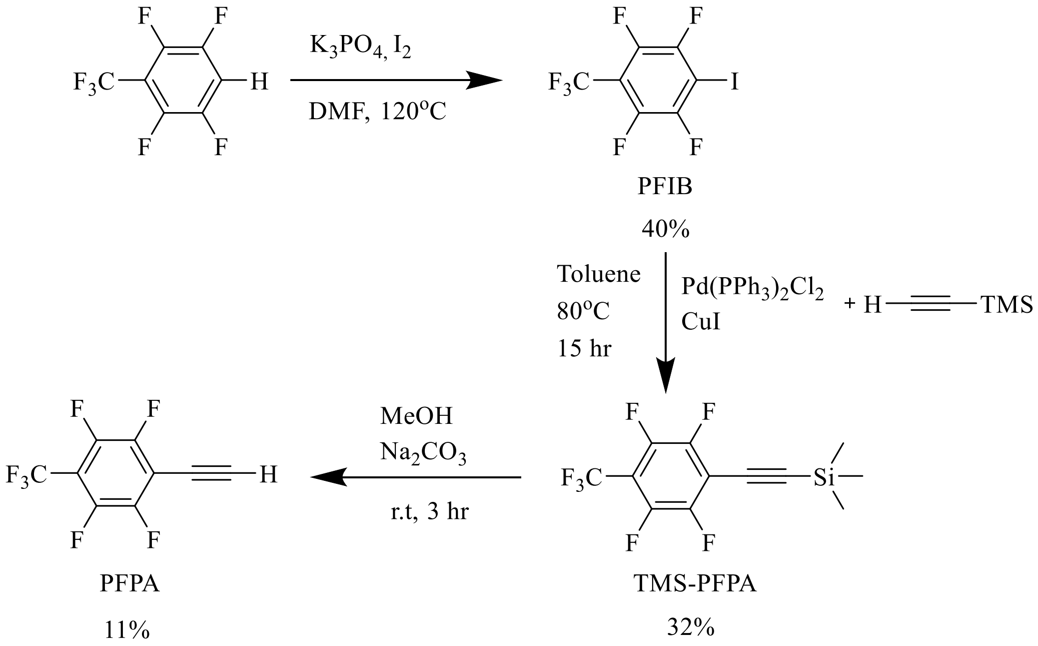
***Trimethyl((perfluorophenyl)ethynyl)silane (TMS-1EPFB)*:**[19] Copper (I) iodide (350.9 mg, 1 mmol), and bis(triphenylphosphine)palladium(II) dichloride (350.9 mg, 0.5 mmol) were placed in a 100 ml two-necked flask equipped with a magnetic stir bar. The system was evacuated and refilled with argon three times. After dry toluene (40 ml) and trimethylamine (3 ml) were added into the flask by cannula, pentafluoroiodobenzene (2939 mg, 1.34 ml, 10 mmol) and trimethylsilylacetylene (1080 mg, 1.55 ml, 11 mmol) were injected by syringes. The mixture was heated to 80 ℃ for 15 hours under a nitrogen atmosphere. The reaction solution was added to a separatory funnel with ammonium chloride solution (10%, 20 ml) and the resulting crude product mixture was extracted with chloroform (20 ml) three times. The combined organic layers were washed with ammonium chloride (10%, 20 ml) and dried over sodium sulfate. After filtration, the solvent was evaporated, and the residue was purified by chromatography with hexanes over silica gel to afford trimethyl((perfluorophenyl)ethynyl)silane as yellowish crystals (yield 55%, 1.44 g).

^{1}H NMR (400MHz, $CDCl_3$, δ): 0.30 (s, $–Si(CH_3)_3$, 9H). ^{19}F NMR (400MHz, $CDCl_3$, δ): -135.9--135.8 (m, Ar F, 1F), -152.5(t, *J*=21 Hz Ar F, 2F), -162--161.9 (m, Ar F, 2F).

***1-Ethynyl-2,3,5,6-tetrafluoro-4-methoxybenzene (4F1MPhA)*:** The reaction followed the reported procedure,[19] the resulting solid was reasonable derivative. Sodium carbonate (0.954 g, 9 mmol) and methanol (20 ml) were added to a round-bottom flask under nitrogen with a stir bar. TMS-1EPFB (1.2 g, 4.5 mmol) was added by syringe and the resulting mixture was stirred under nitrogen for 3 hrs. Water (100 ml) was added and the mixture was extracted with hexanes (50 mL) five times. The organic fraction was concentrated, dried by Sodium sulfate, and purified by flash chromatography over silica gel with hexanes to afford 1-ethynyl-2,3,5,6-tetrafluoro-4-methoxybenzene as white crystals (yield 43%, 400 mg).

^{1}H NMR (400MHz, $CDCl_3$, δ): 4.14 (s, $–OCH_3$, 3H), 3.56 (s, CH, 1H). ^{19}F NMR (400MHz, $CDCl_3$, δ): -137.16 (m, Ar F, 2F), -161.56 (m, Ar F, 2F).

e. Synthesis of 1-ethynyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (PFPA)



***1,2,4,5-Tetrafluoro-3-iodo-6-(trifluoromethyl)benzene (PFIB)*:**[20] 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene (6.6 g, 30 mmol), I_2 (5.08 g, 20 mmol), and K_3PO_4 (8.5 g, 40 mmol) were added to a 50 ml RBF equipped with magnetic stir bar and a reflux condenser. The flask was evacuated and refilled with nitrogen three times. DMF (20 ml) was added and the reaction mixture was stirred at 120 °C for 3 hr. The reaction mixture was allowed to cool and washed with $NaHSO_{4(aq)}$ (1M, 50 ml) twice and the combined aqueous layers were extracted with diethyl ether (30 ml) three times. The combined organic fractions were dried over Na_2SO_4, filtered, and concentrated in vacuum. Flash chromatography on silica (neat Hexane) afforded 1,2,4,5-tetrafluoro-3-iodo-6-(trifluoromethyl)benzene (PFIB) as transparent crystals (yield 40.3%, 4.2 g). ^{19}F-NMR (400MHz, $CDCl_3$, δ): -56.6 (t, *J*=19 Hz, $–CF_3$, 3F), -117.5 (m, Ar F, 1F), -138.8 (m, Ar F, 1F)

***Trimethyl((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethynyl)silane (TMS-PFPA)*:**[20] Copper (I) iodide (228 mg, 1.2 mmol) and bis(triphenylphosphine)palladium(II) dichloride (420 mg, 0.6 mmol) were placed in a 100 ml two-necked flask equipped with a magnetic stir bar. The system was evacuated and refilled with nitrogen three times. After dry THF (30 ml) and trimethylamine (3 ml) were added into the flask by cannula, 1,2,4,5-tetrafluoro-3-iodo-6-(trifluoromethyl)benzene (4.2 mg, 1.34 ml, 12 mmol) and (trimethylsilyl)acetylene (1300 mg, 1.87 ml, 13.2 mmol) were added sequentially by syringe. The reaction mixture was heated to 80 °C for 24 hours under nitrogen. The reaction mixture was added to a separatory funnel with ammonium chloride solution (10%, 20 ml) and the resulting crude product mixture was extracted with chloroform (20 ml) three times. The combined organic layers were washed with ammonium chloride (10%, 20 ml) and dried over sodium sulfate. After filtration, the solvent was evaporated, and the residue was purified by flash chromatography with hexanes over silica gel to afford trimethyl((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethynyl)silane (PFPATMS) as yellowish crystals (yield 32%,1.2 g).

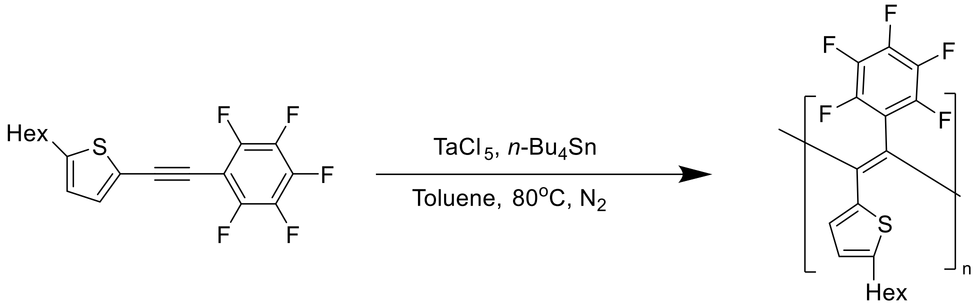
^{19}F-NMR (400MHz, $CDCl_3$, δ): -56.3 (t, *J*=21 Hz, $–CF_3$, 3F), -134.4 (m, Ar F, 1F), -140, (m, Ar F, 1F). ^{1}H-NMR (400MHz, $CDCl_3$, δ): 0.21 (s, $–Si(CH_3)_3$, 9H).

***1-Ethynyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (PFPA)*:**[20] Sodium carbonate (0.5 g, 4.7 mmol) and methanol (10 ml) were added to a round-bottom flask with a stir bar under nitrogen. Trimethyl((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethynyl) silane (1.2 g, 3.82 mmol) was added to the RBF by syringe and the resulting mixture was stirred for 3 hrs. Water (50 ml) was then added and the resulting mixture was extracted with hexanes (50 mL) three times. The organic fraction was dried over sodium sulfate, filtered, concentrated in vacuum, and purified by flash chromatography on silica gel with hexanes to afford 1-ethynyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (PFPA) as a yellowish liquid (yield 11%,100 mg).

^{19}F-NMR (400MHz, $CDCl_3$, δ): -57 (t, *J*=21 Hz, –CF_3, 3F), -136 (m, Ar F, 2F), δ -139 (m, Ar F, 2F). ^{1}H-NMR (400MHz, $CDCl_3$): 0.38 (s, CH, 1H).

Polymerization:

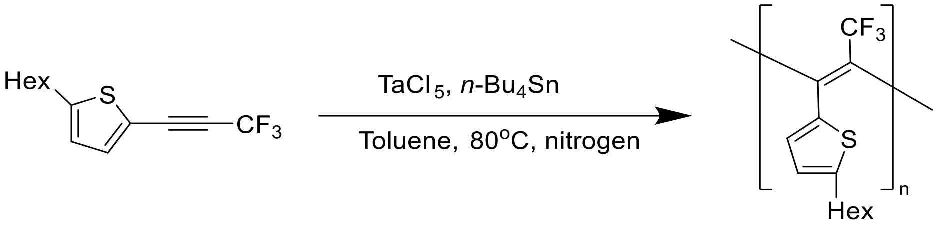
f. Polymerization of *HT≡FPh*



***Poly(HT≡FPh)*:** The polymerization followed the reported procecudure.[10a] Tantalum (V) chloride (18 mg, 0.05 mmol) and tetra-*n*-butyltin (0.066 ml, 69.8 mg, 0.2 mmol) were dissolved in toluene (0.1 ml) in round bottom flask under nitrogen. The resulting solution was stirred at 80 °C under nitrogen for 10 min. HT≡FPh (120 mg, 0.34 mmol) was added to the solution and the solution was stirred for an additional 24 h at 80 °C. The reaction was allowed to cool and diluted with dichloromethane (2 ml). The solution was filtered through a plug of cotton and added dropwise to methanol (50 mL). After 1 h of centrifugation the supernatant was decanted and the isolated solid was washed with methanol to afford the polymer as a dark sticky solid in trace yield.

^{1}H NMR (400MHz, $CDCl_3$, δ): 7.82-6.17 (m, thiophene 3,4-*H*, 2H), 3.16-2.25 (m, Ar CH_2, 2H), 2.81-2.77 (m, $–CH_2–$), 1.95-0.55 (m, $–CH_2CH_2CH_2CH_3$, 9H).

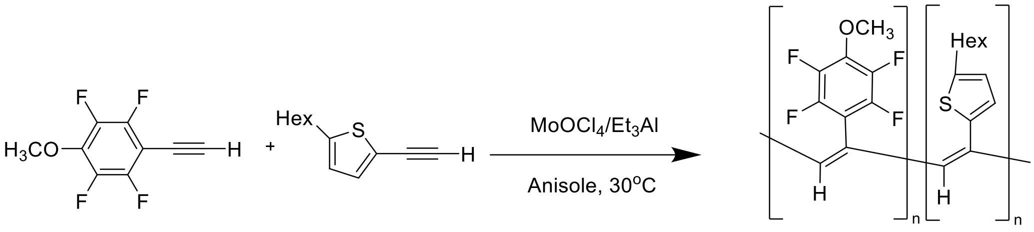
g. Polymerization of *HT≡CF₃*



***Poly(HT≡CF₃)*:** The polymerization followed the reported procecudure.[10a] Tantalum (V) chloride (11mg, 0.03 mmol) and tetra-*n*-butyltin (0.04 ml, 42.3 mg, 0.12 mmol) were dissolved in toluene (0.6 ml) in round bottom flask under nitrogen. The resulting solution was stirred under nitrogen atmosphere for 10 min at 80 °C. HT≡CF_3 (200 mg, 0.77 mmol) was added into the solution and the solution was stirred for an additional 24 hr at 80 °C. The reaction was allowed to cool down and diluted in dichloromethane (2 ml). The solution was filtered through a plug of cotton and added dropwise to methanol (50 mL). After 1 h of centrifugation the supernatant was decanted and the isolated solid was washed with methanol to afford the polymer to afford the polymer as dark sticky solid (2 mg, 1%).

^{1}H NMR (400MHz, CD_2Cl_2, δ):7.61-6.42 (m, thiophene 3,4-*H*, 2H), 3.10-2.56 (m, Ar CH_2–, 2H), 2.50-1.80 (m, –CH_2–), 1.84-0.98 (m, –$CH_2CH_2CH_2$–, 6H), 0.98-0.54(m, –CH_3, 3H). ^{19}F NMR (400MHz, CD_2Cl_2, δ): -63.76 (m, –CF_3, 3F).

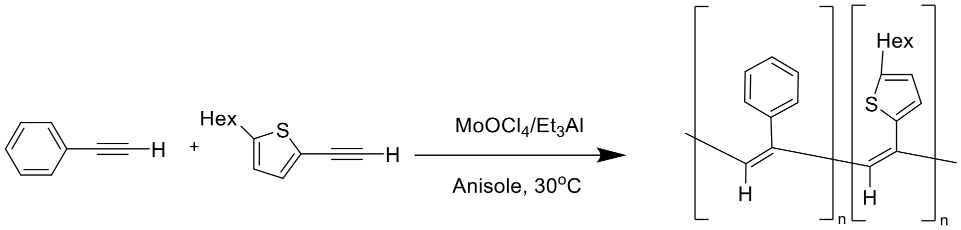
h. Copolymerization of *2E5HT* and *1EPFB*



***Poly(2E5HT/1EPFB)*:** The polymerization followed the reported procecudure.[13] In a nitrogen-filled glove box, molybdenum tetrachloride oxide (40 mg, 0.156 mmol), triethylaluminum (0.832 ml, 0.156 mmol), ethanol (0.789 ml, 0.468 mmol), and anisole (10 ml) were added to a round-bottom flask. The resulting mixture was heated at 30 °C with stirring for 15 mins. Pack solution 1-ethynyl-2,3,5,6-tetrafluoro-4-methoxybenzene (160 mg, 0.78 mmol) with Anisole (3.12 ml) and solution 2-ethynyl-5-hexylthiophene (300 mg, 1.56 mmol) with Anisole (3.12ml) in nitrogen-filled glove box. A solution of 2-ethynyl-5-hexylthiophene (300 mg, 1.56 mmol) in anisole (3.12 mL) was added to the reaction mixture by syringe. Then, a solution of 1-ethynyl-2,3,5,6-tetrafluoro-4-methoxybenzene (160 mg, 0.78 mmol) in anisole (3.12 mL) was added to the reaction mixture by syringe. The resulting mixture was stirred at 30 °C for 24 h. Methanol (1 mL) was then added to the reaction mixture and it was precipitated into water (50 ml). The resulting solid was isolated by filtration and washed with methanol to afford Poly(2E5HT/1EPFB) as a black sticky solid (12 mg, 3%).

^{1}H NMR (400MHz, $CDCl_3$, δ): 6.89 (m, thiophene 3-*H*, 1H), 6.6 (m, thiophene 4-*H*, 1H), 4.17 (m, $–OCH_3$, 3H), 2.79 (m, $–CH_2–$, 2H), 1.67 (m), 1.31 (m), 0.93 (m).

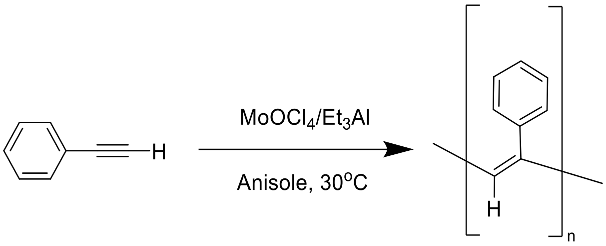
i. Copolymerization of *2E5HT* and *Ethynylbenzene*



***Poly(2E5HT/Ethynylbenzene)*:** The polymerization followed the reported procecudure.[13] In a nitrogen-filled glove box, molybdenum tetrachloride oxide (40 mg, 0.156 mmol), triethylaluminum (0.832 ml, 0.156 mmol), ethanol (0.789 ml, 0.468 mmol) and, anisole (10 ml) were added to a round-bottom flask. The resulting mixture was stirred for 15 mins at 30 °C. A solution of 2-ethynyl-5-hexylthiophene (300 mg, 1.56 mmol) in anisole (3.12 ml) was added into the reaction mixture with syringe. Then, a solution of ethynylbenzene (160 mg, 1.56 mmol) in anisole (3.12 ml) was added into the mixture with syringe. The resulting mixture was stirred at 30 °C for 24 hr. Methanol (2 mL) was then added to the reaction mixture and the polymer was precipitated in water (50 ml). The resulting solid was isolated by filtration and washed with methanol to afford Poly(*2E5HT/*ethynylbenzene) as an orange solid (32 mg, 7%)

^{1}H NMR (400MHz, $CDCl_3$, δ): 7.5-6.4 (m, Ar, H), 6.18-5.8 (d, C=CH, 1H), 2.79 (t, Ar CH_2, 2H), 1.65 (m, $–CH_2–$, 2H), 1.34 (m, $–CH_2CH_2CH_2–$, 6H), 0.93 (m, $–CH_3$, 3H).

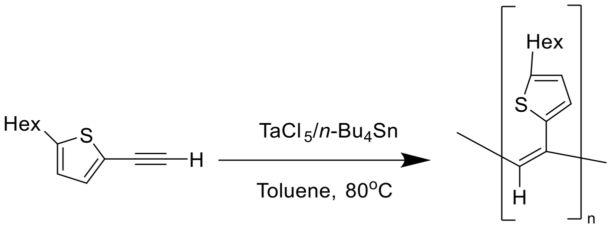
j. Polymerization of *Ethynylbenzene*



Poly(ethynylbenzene)**:** The polymerization followed the reported procecudure.[13] Molybdenum tetrachloride oxide (40 mg, 0.156 mmol), triethylaluminum (0.832 ml, 0.156 mmol), ethanol (0.789 ml, 0.468 mmol), and anisole (10 ml) were added to a round-bottom flask in a nitrogen-filled glove box. The resulting mixture was stirred for 15 mins at 30 °C. A solution of ethynylbenzene (320 mg, 3.12 mmol) in anisole (6.24 ml) was added into the reaction mixture with syringe. The resulting mixture was stirred for 24 hr at 30 °C. Methanol (2 mL) was then added to the reaction mixture and the polymer was precipitated in water (50 ml). The resulting solid was isolated by filtration and washed by methanol to afford poly(ethynylbenzene) as an orange solid (18 mg, 5 %).

^{1}H NMR (400MHz, $CDCl_3$, δ): 7.5-6.4 (m, Ar H, 5H), 6.2-5.8 (m, C=C-H, 1H).

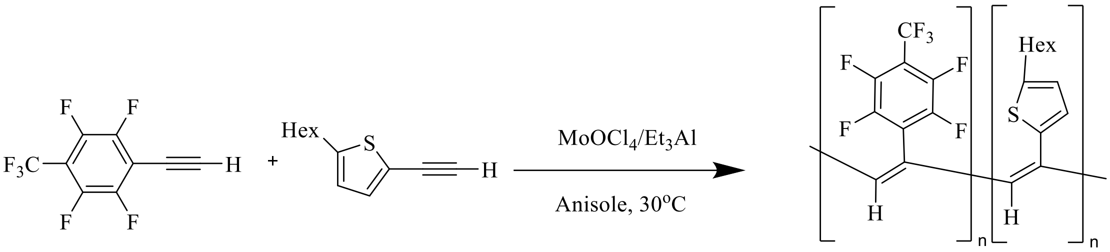
k. Polymerization of *2E5HT*



Poly(2E5HT)*:** The polymerization followed the reported procecudure.[10a] Tantalum (V) chloride (22.35 mg, 0.063 mmol) and tetra-*n*-butyltin (0.0819 ml, 0.25 mmol) were dissolved in toluene (0.12 ml) in a round bottom flask under nitrogen. The resulting mixture was stirred at 80 °C for 10 min under nitrogen. ***2E5HT (300 mg, 1.56 mmol) was added to the mixture and the resulting mixture was stirred at 80 °C for 24 hr. The reaction mixture was allowed to cool down and diluted with dichloromethane (2 ml). The solution was filtered through a plug of cotton and added dropwise to methanol (50 mL). After 1 h of centrifugation the supernatant was decanted and the isolated solid was washed with methanol to afford the polymer as dark sticky solid in trace yield.

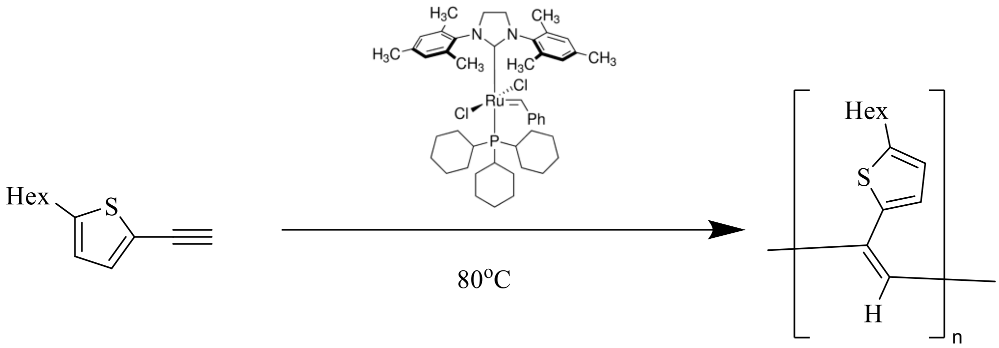
^{1}H NMR (400MHz, CD_2Cl_2, δ): 6.9-6.8 (d, thiophene 3-*H*, 1H), 6.60-6.59 (d, thiophene 4-*H*, 1H), 5.48-5.38(m, C=C-H, 1H), 2.78 (t, Ar CH_2, 2H), 1.66 (m, –CH_2–, 2H), 1.35 (m, –$CH_2CH_2CH_2$–, 6H), 0.92 (m, –CH_3, 3H).

l. Copolymerization of *2E5HT* and *PFPA*

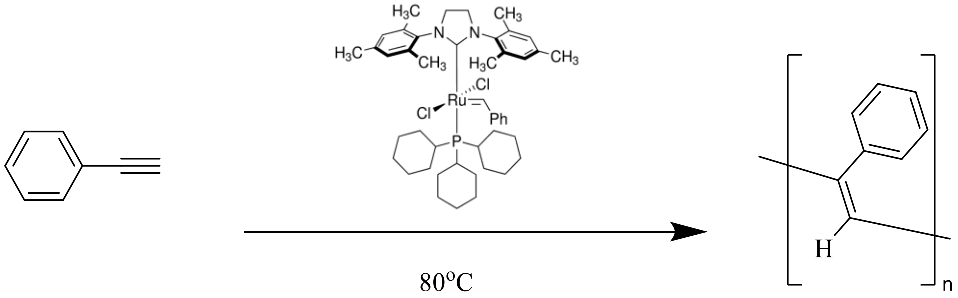


Poly(2E5HT/ PFPA): The polymerization followed the reported procecudure.[13] In a nitrogen-filled glove box, molybdenum tetrachloride oxide (10 mg, 0.04 mmol), triethylaluminum (9.13 mg, 0.04 mmol), ethanol (5.53 ml, 0.12 mmol, and anisole (4 ml) were added to a round-bottom flask. The resulting mixture was stirred for 15 min at 30 ℃. Solution of 2-ethynyl-5-hexylthiophene (0.08g, 0.4 mmol) in anisole (1 ml) was added into the mixture with a syringe. Then, a solution of PFPA (0.1 g, 0.4 mmol) in anisole (1 ml) was added into the mixture with a syringe. The resulting mixture was stirred for 24 hr at 30 ℃. A solution of methanol (20 mL) in anisole (20 mL) was then added to the reaction mixture, but no polymer was observed to precipitate. The resulting solution was extracted with chloroform (20 ml), dried over sodium sulfate, concentrated, and dried under vacuum for 12 hrs. The isolated solid was examined by ^{1}H-NMR spectroscopy, which showed no evidence of polymer formation.

m. Polymerization of *Ethynylbenzene* and *2E5HT* with 2nd Generation Grubbs catalyst



Poly(2E5HT): The polymerization followed the reported procecudure.[21] Monomer 2E5HT (198 mg, 1.03 mmol) and 2nd Generation Grubbs' Catalyst (8.7 mg, 0.01 mmol) were placed in a RBF. The mixture was stirred at 80 °C for 24 hr. The reaction was allowed to cool down and precipitated in methanol. The solid was isolated by filtration and wash with methanol to afford poly(2E5HT) as a black sticky solid, in trace yield. The molecular weight was measured by GPC (M_n=766, $Đ$=1.51).



Poly(ethynylbenzene):[21] Ethynylbenzene (187 mg, 183 mmol) and 2nd Generation Grubbs' Catalyst (13.2 mg, 0.016 mmol) were placed in a RBF. The resulting solution was stirred at 80 °C for 24 hr. The reaction was allowed to cool down and precipitated into methanol. The solid was isolated by filtration and washed with methanol to afford poly(ethynylbenzene) as a yellow powder in traced yield. The molecular weight was measured by GPC (M_n=476, $Đ$=1.6).

III. Results and Discussion

A series of homopolymers and copolymers were prepared by polymerization of HT≡FPh, HT≡CF_3, 2E5HT, 1EPFB, and ethynylbenzene with three different catalyst systems: $TaCl_5$/*n*-Bu_4Sn, $MoOCl_4/Et_3Al$, or the 2nd generation Grubbs catalyst.[21-22] A detailed discussion of each polymerization and the properties of the resulting polymers appears below:

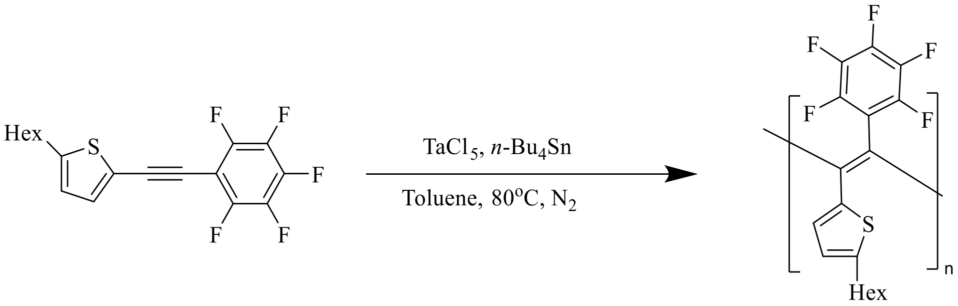
Table 1. Polymerization Information.

Entry	**Polymer**	**Monomers**	**M_n[c]**	**Đ[c]**	**Yield[d]**	**Abs On-set (nm/eV)f**
1[a]	Poly(HT≡FPh)	HT≡FPh	1.2	2.0	Trace	N/A
2[a]	Poly(HT≡CF_3)	HT≡CF_3	1.1	1.6	1%	688/1.8
3[b]	Poly(2E5HT/1EPFB)	2E5HT 1EPFB	0.6	1.8	3%	725/1.7
4[b]	Poly(2E5HT/Ethynylbenzene)	2E5HT Ethynylbenzene	3.8	2.7	7%	532/2.3
5[b]	Poly(Ethynylbenzene)	Ethynylbenzene	12.4	1.2	5%	532/2.3
6[a]	Poly(2E5HT)	2E5HT	1.5	1.6	trace	587/2.1
7[b]	Poly(2E5HT/PFPA)	2E5HT PFPA	N/A	N/A	N/A	N/A
8[e]	Poly(Ethynylbenzene)	Ethynylbenzene	0.5	1.6	trace	N/A
9[e]	Poly(2E5HT)	2E5HT	0.8	1.5	trace	N/A

(a) Polymerized with $TaCl_5$/*n*-Bu_4Sn (20 mM/80 mM) in toluene at 80℃ for 24 hr; (b) Polymerized with $MoOCl_4/Et_3Al/EtOH$ (10mM/10mM/30mM) in Anisole at 30 ℃ for 24 hr; (c) Measured by GPC using polystyrene calibration in THF solution (kg/mol); (d) Determined gravimetrically after precipitation into methanol. (e) Bulk polymerization with 2nd Generation Grubbs' Catalyst. (f) Measured by UV-Vis spectroscopy in chloroform solution (0.05 mg/ml).

1. Homopolymerizations

a. Poly(HT≡FPh)



Poly(HT≡FPh) was prepared by polymerization of monomer HT≡FPh with a tantalum(V) chloride/tetra-*n*-butyltin catalyst system, which has previously been shown to be effective for the polymerization of disubstituted alkynes to a high degree of polymerization with a narrow molecular weight distribution.[10a, 23] The polymerization was run for 24 hr, as longer reaction times may lead to secondary polymerization which may reduce the molecular weight and increase the polydispersity.[12] The color of product was dark brown sticky solid and the monomer was red liquid. The changes of state (from liquid to solid) can be explained by the formation of polymer. In addition to the observed change in color, the polymerization of monomer HT≡FPh can be proved by the appearance of broader peaks in the ^{1}H NMR spectrum, **Figure 9**, corresponding to the two protons on thiophene (δ 7.2-6.2 ppm), the first methylene group (δ 2.5-3.2 ppm), second to fifth methylene groups (δ 1.0-2.0 ppm), and the hexyl methyl group (δ 0.6-1.0 ppm). The molecular weight of polymer was measured by GPC (M_n=1.20 kg/mol, $Đ$=2.03). The polymer was sticky solid stuck to the bottom of RBF and the recovered mass was low. The low yield (only trace amounts were recovered) may result from undesired interaction of the thienyl group with tantalum catalyst.[24]

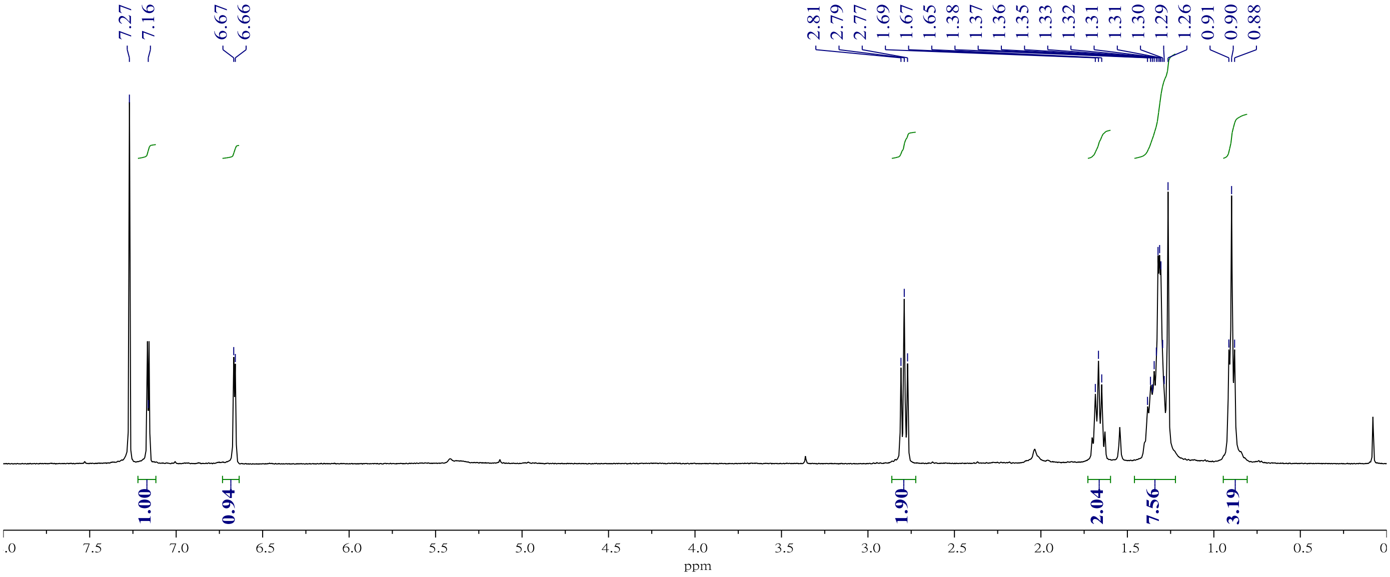


Figure 8. ^{1}**H-NMR of monomer HT≡FPh in CDCl**$_3$.

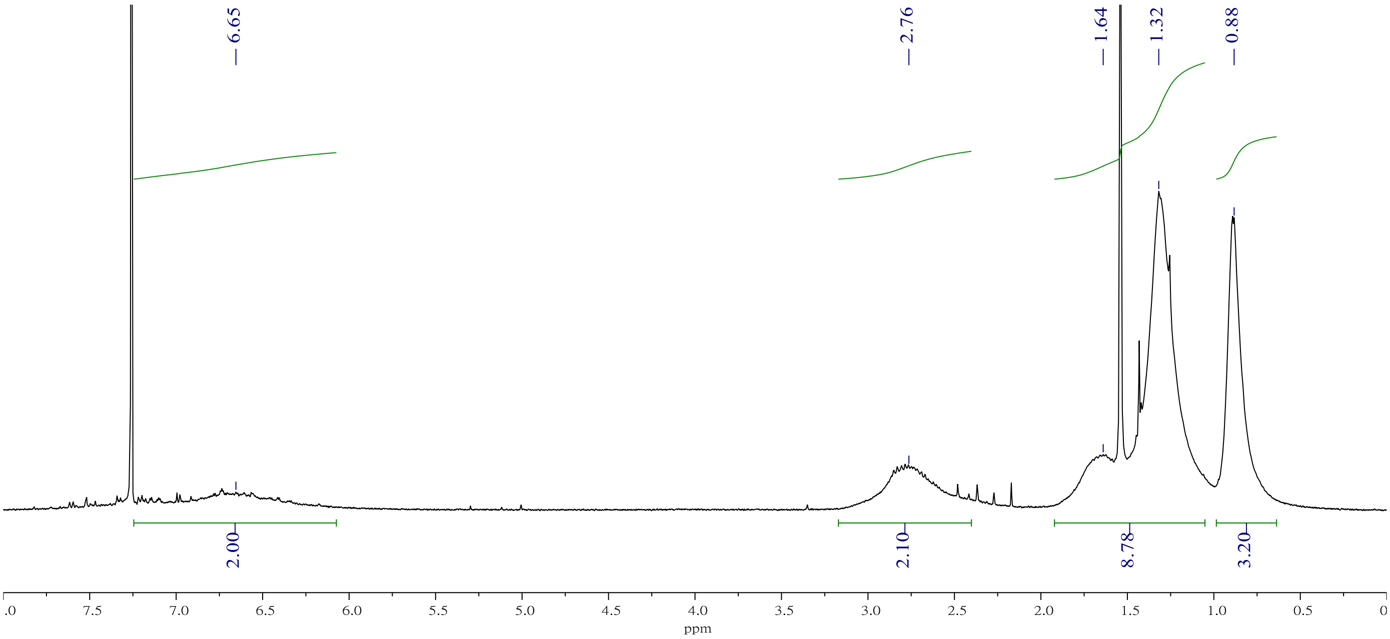
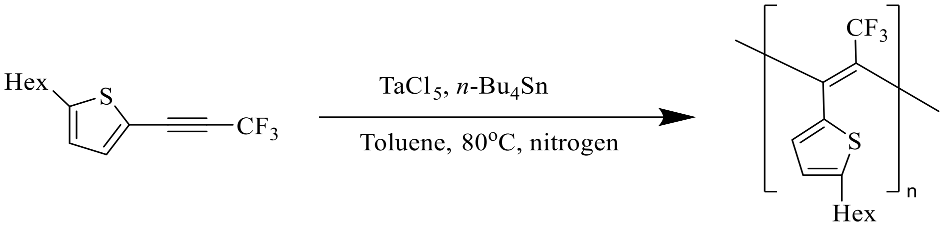


Figure 9, ^{1}**H-NMR of Poly(HT≡FPh) in CDCl**$_3$.

b. **Poly(HT≡CF3)**



After preparing poly(HT≡FPh), two potential problems with the polymerization were identified and used to design the next polymer structure. The first problem was steric hindrance between the bulky substituents along the polyacetylene backbone. It has been reported that steric effects resulting from the presence of substituents on every carbon of the backbone[7] may twist the backbone of polymer and break the conjugated system, resulting in the band-gap not effectively being reduced by the designed Donor/Acceptor system. Therefore, in our case, we try to use less bulky trifluoromethyl as electrophile group instead of aromatic rings as substitute on acetylene to avoid the steric hindrance issue while sustaining the potential reducing effect of alternating donor-acceptor groups on the band gap of the polymer. In this polymer, the pentafluorophenyl group in Poly(HT≡FPh) was replaced by trifluoromethyl group as a smaller electron-withdrawing group.

Poly(HT≡CF3) was prepared by polymerization of monomer HT≡CF3 with $TaCl_5$/*n*-Bu_4Sn as catalyst. The low yield (only trace amounts were recovered) may result from undesired interaction of the thienyl group with tantalum catalyst.[24] The product was isolated as a black sticky solid and the monomer was red liquid. The change of states suggests the formation of polymer. The polymerization of monomer HT≡FPh is consistent with the appearance of broader peaks for the thiophene protons (δ 7.5-6.5, **Figure 11**) in the ^{1}H NMR spectrum, corresponding to the two aromatic thiophene protons. The molecular weight of polymer was measured by GPC (M_n=1.1 kg/mol, $Đ$=1.62).

The low yield (1%) of polymerization mostly possibly resulted from the undesired interaction of tantalum catalyst with thienyl group which affected the course of polymerization.[24]

The result of this polymerization supports the idea that interaction of the tantalum catalyst with the alkyne group in the di-substituted (the thienyl and trifluoromethyl substituents) monomers affects the course of polymerization. Therefore, the results could not clearly determine the effect of steric hindrance on the polymerization. But since some literature suggests the existence of steric hindrance in di-substituted polyacetylenes,[8] we next focused on copolymerization of mono-substituted alkynes to avoid the potentially negative effect steric hindrance on optoelectronic properties of substituted polyacetylenes.

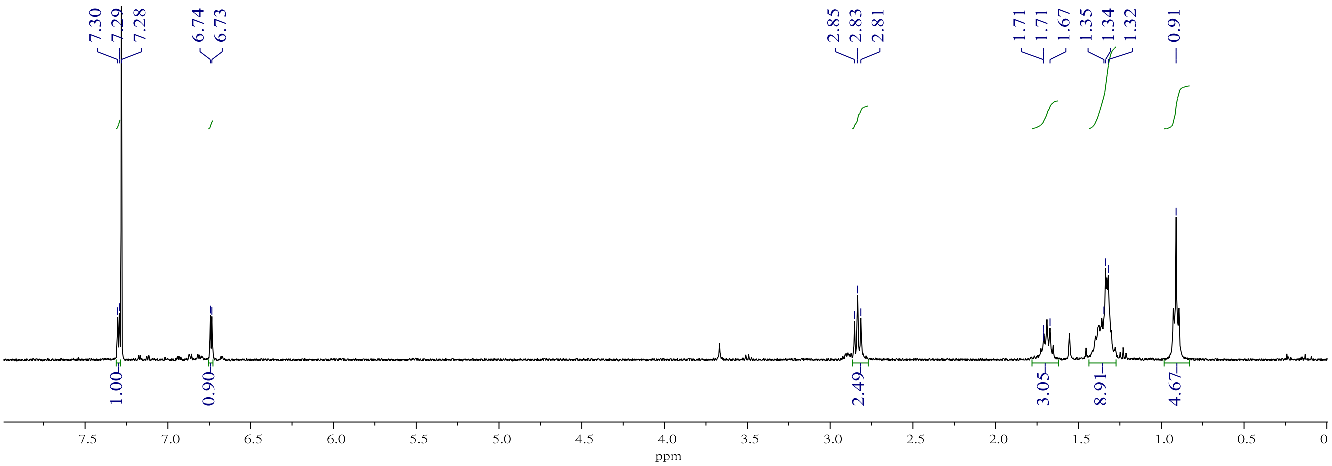


Figure 10. ^{1}H-NMR of Monomer HT≡CF$_3$ in CDCl$_3$

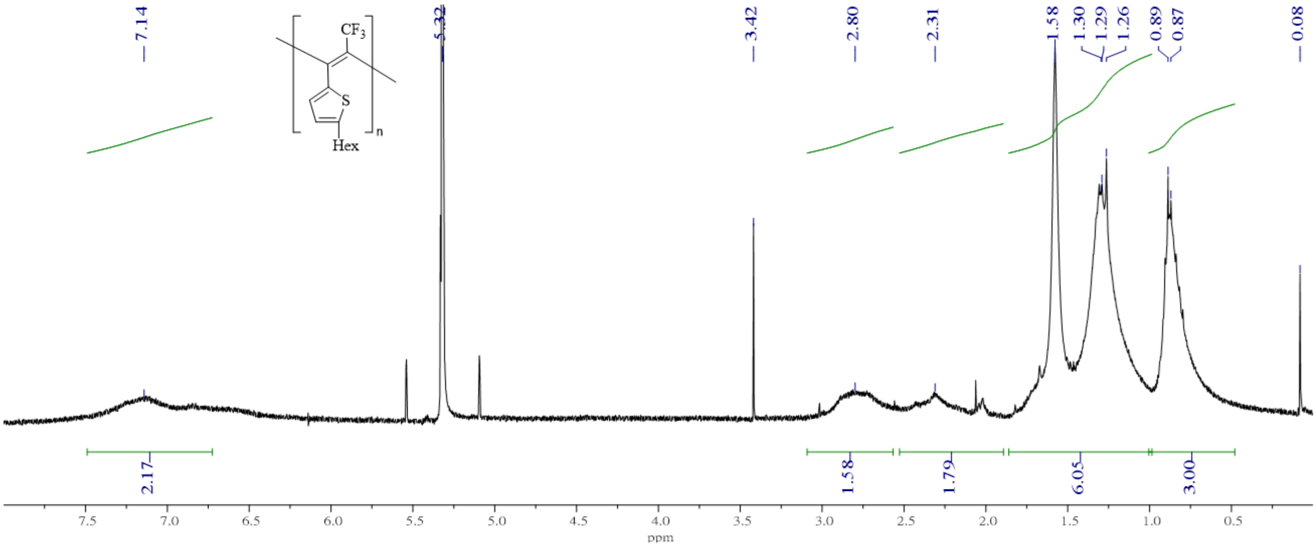
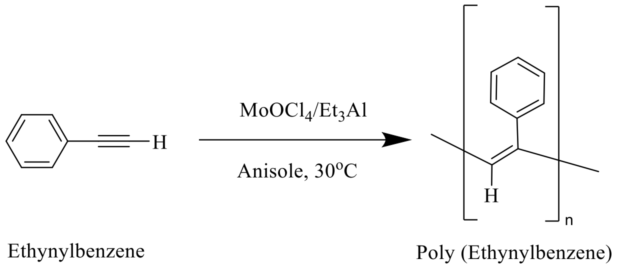


Figure 11. ^{1}H-NMR of Poly(HT≡CF$_3$) in CD$_2$Cl$_2$.

c. **Poly(ethynylbenzene)**



Poly(ethynylbenzene) was prepared by polymerization of ethynylbenzene with molybdenum(VI) tetrachloride oxide/triethylaluminum in anisole at 30 °C for 24 hr.[11, 25] To avoid potential problems with steric effects in the polymerization of disubstituted alkynes, an alternative approach to statistical donor-acceptor-substituted polymers was explored. Commercially available ethynylbenzene was used as monomer to test the steric effects in the polymerization with a previously reported catalyst system, molybdenum (VI) tetrachloride oxide/triethylaluminum. The product was a red powder and the monomer was a yellowish transparent liquid. The change of state from liquid to solid suggests the formation of polymer. The polymerization can be followed by ^1H NMR by observing the disappearance of the monomer alkyne proton peak (δ 3.15,

Figure 12) and the appearance of the polymer alkene proton peak (δ 5.89,

Figure 13). The molecular weight of polymer was measured by GPC (M_n=12.4 kg/mol, *Đ*=1.2).

Poly(ethynylbenzene) was the polymer with highest molecular weight and lowest polydispersity in this series, but the yield was still low (5%). The possible way to improve the polymerization is to use a different catalyst/cocatalyst system. Tetraphenyltin was suggested in the polymerization of acetylene substituted with heteroaromatic rings, instead of organoaluminum.[26]

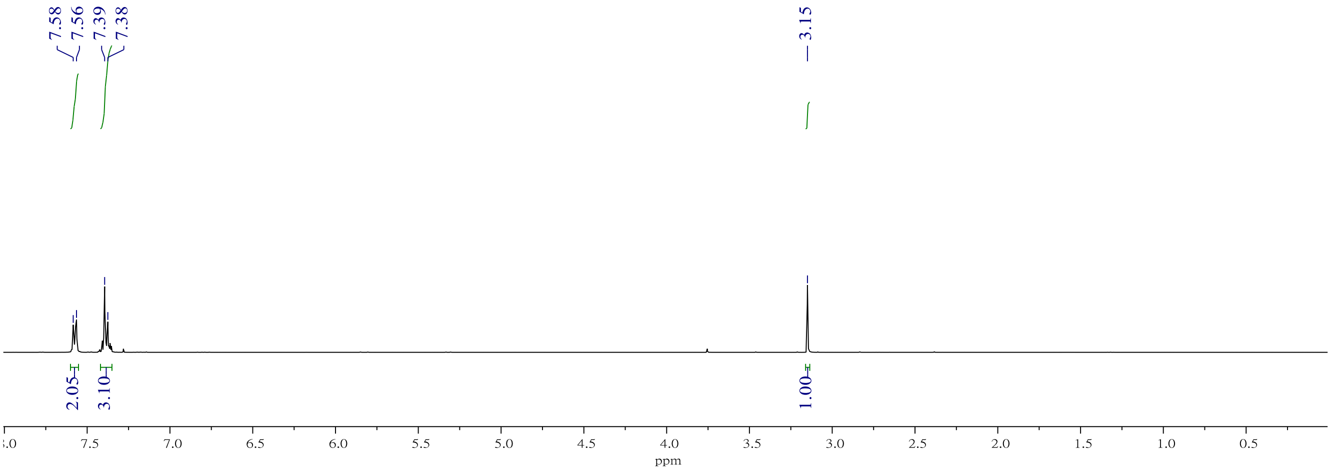


Figure 12. ^{1}H-NMR of Ethynylbenzene in $CDCl_3$.

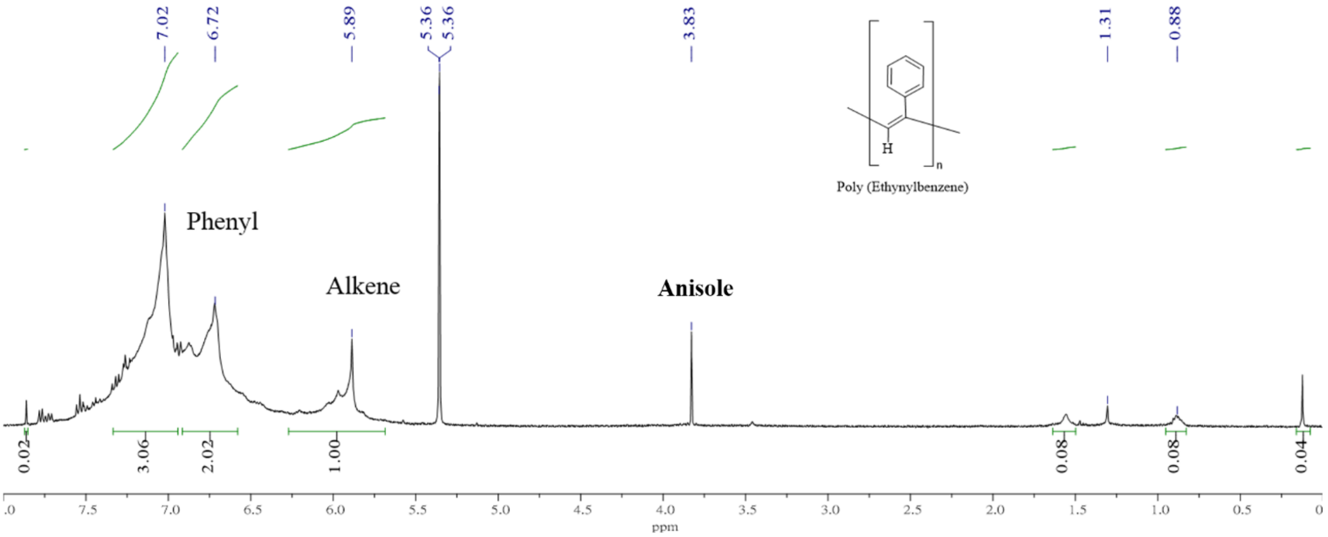
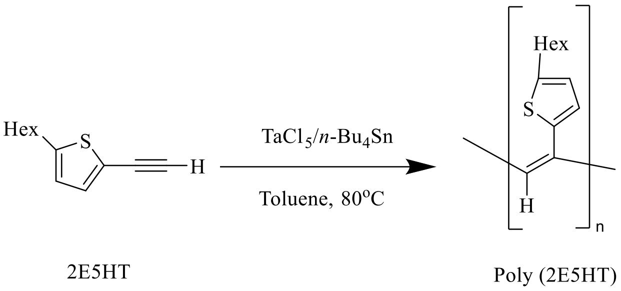


Figure 13. ^{1}H-NMR of Poly(ethynylbenzene) in CD_2Cl_2.

d. Poly(2E5HT)



Poly(2E5HT) was prepared by the polymerization of 2E5HT with tantalum(V) chloride/tetra-*n*-butyltin in toluene at 80℃ for 24 hr. After examining of the problem of polymerization of steric hindrance with phenylacetylene, the monomer monosubstituted with hexylthiophene was examined again in this polymerization with $TaCl_5$/*n*-Bu_4Sn. The polymer was black and sticky, similar to other reported thiophene substituted polyacetylenes,[4a, 27] and the monomer was an orange liquid. The disappearance of the alkyne peak (δ 3.29, **Figure 14**) and the appearance of the alkene peak (δ 5.46, **Figure 15**) were consistent with the formation of polymer. Also the molecular weight of polymer was measured by GPC (Mn= 0.7 kg/mol, *Đ* =1.86).

A possible reason for the large polydispersity and low yield (only trace amounts of polymer were isolated) was the undesired interaction between the tantalum catalyst and the thienyl group, which interrupted the course of polymerization[24] to a greater degree than other transition metal catalysts (W and Mo).[26, 28] Some unassigned peaks (δ 7.5-7.0, **Figure 15**) may belong to the substituted phenyl core of the cyclic trimer.[29] The comparison of molecular weights between poly(2E5HT) and poly(ethynylbenzene) suggested that the high electron density of the thienyl substituent negatively affected the polymerization.[9c]

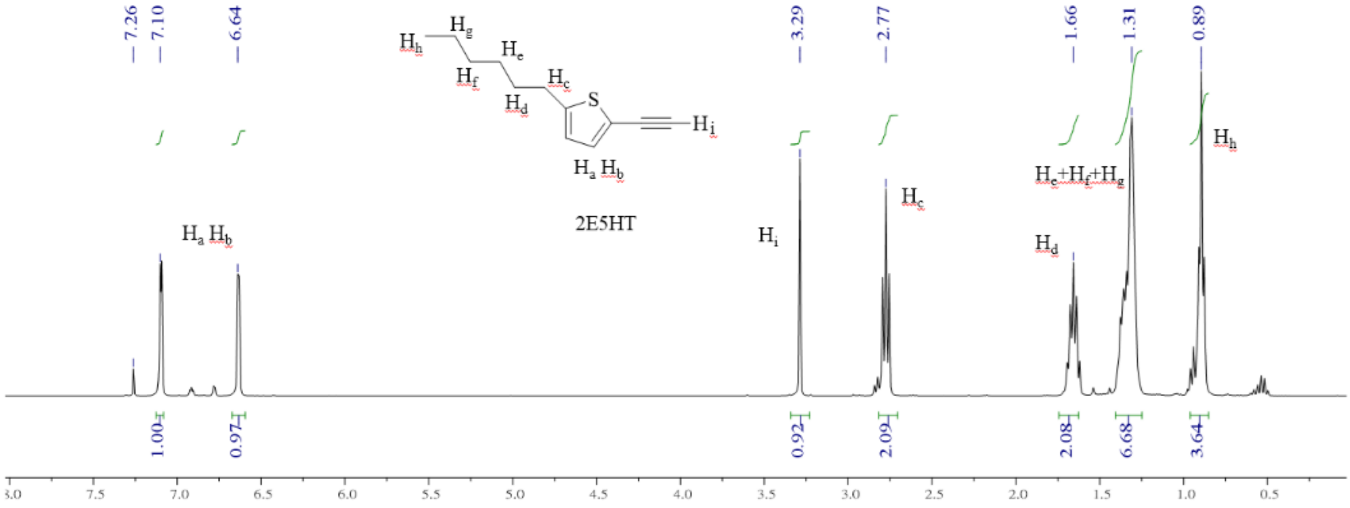


Figure 14. ^{1}H-NMR of Monomer 2E5HT in $CDCl_3$

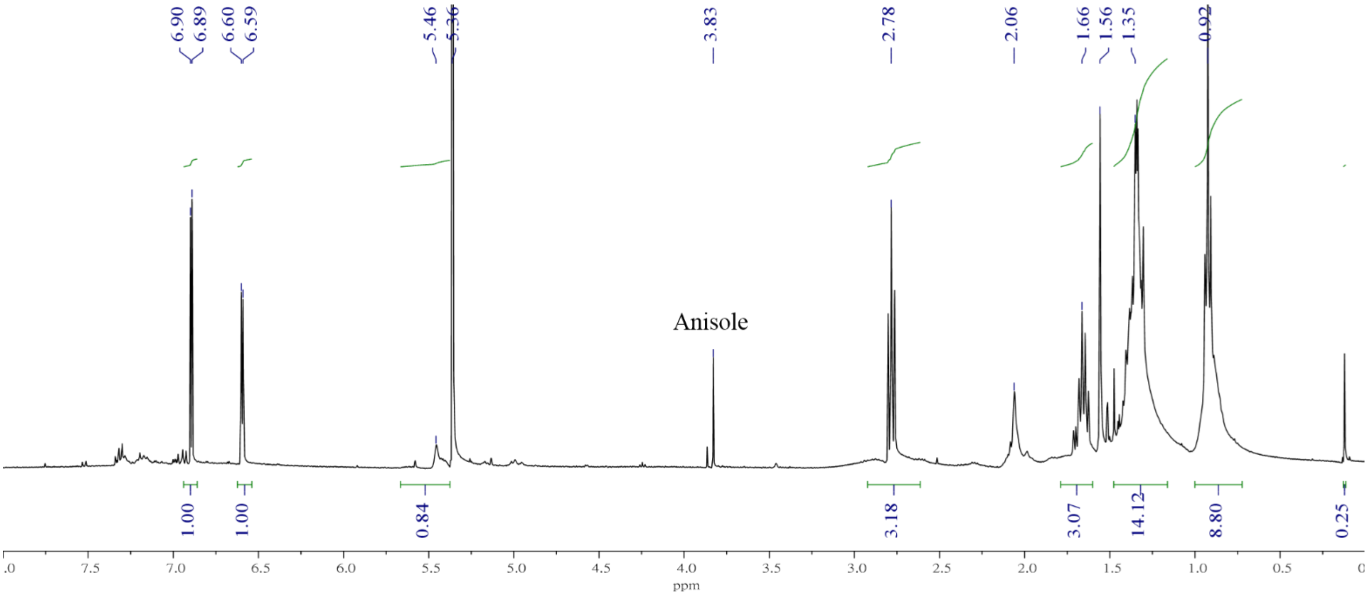
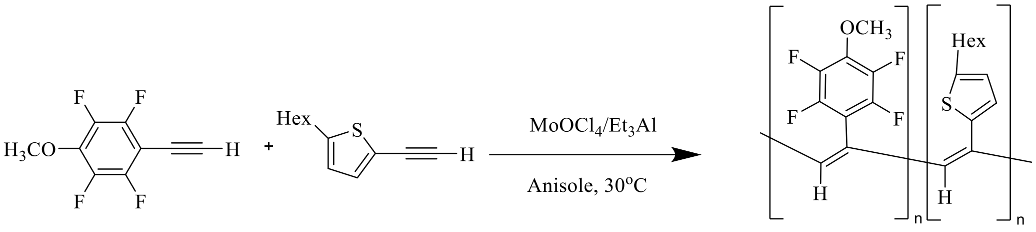


Figure 15. ^{1}H-NMR of Poly(2E5HT) in CD_2Cl_2

2. Copolymerizations

e. Poly(2E5HT/1EPFB)



1EPFB 2E5HT Poly (2E5HT/1EPFB)

Poly(2E5HT/1EPFB) was prepared by the polymerization of monomers 2E5HT and 1EPFB with molybdenum(VI) tetrachloride oxide/triethylaluminum in anisole at 30℃ for 24 hr.[11, 13, 25] In this copolymerization, the properties of polymers with statistically distributed donor and acceptor (electron-rich and electron-deficient alkyne) groups along the backbone were to be investigated. The reaction condition followed the reported copolymerization of mono-substituted alkynes with the $MoOCl_4/Et_3Al/EtOH$ catalyst system, which has been reported to give a high degree of copolymerization of two mono-substituted acetylenes (**Figure 7**)[13] and lower dispersities than the $MoOCl_4$/ *n*-BuLi system. Successful copolymerization of an electron-rich alkyne (*n*-Bu-F_4Ph-Alkyne) and an electron-deficient alkyne (*o*-Me_3SiPh-Alkyne) was reported with this catalyst system. The temperature (30 ℃) and $MoOCl_4/Et_3Al//EtOH$ ratio (1:1:4) was used by E. Iwawaki et al[25a] and the polymerization was reported to give low polydispersity and 100% conversion. The change was that the ethynylthiophene was not used in any of these literature reports.

The product was a black sticky solid while the monomers 2E5HT/1EPFB were white crystal/orange liquid. A modestly higher molecular weight was measured by GPC (M_n=0.7

kg/mol, *Đ* =1.77) and some degree of polymerization or oligomerization was suggested by the appearance of broader peaks in the ^{1}H-NMR spectrum of the product and the disappearance of the alkyne peaks of ethynylthiophene (δ 3.56, **Figure 14**) and 1EPFB (δ 3.29,

Figure 16). but the absence of alkene peaks suggests that chain growth did not proceed as expected.

The disappearance of NMR peaks for alkyne protons without the appearance of alkene peaks could result from Mo-catalyzed side reactions of the alkyne groups. As discussed earlier, the thienyl group in ethynylthiophene may interact with the Mo catalyst without the occurrence of polymerization. Mo catalysts may also result in undesired alkyne metathesis or dimerization side reactions.[30]

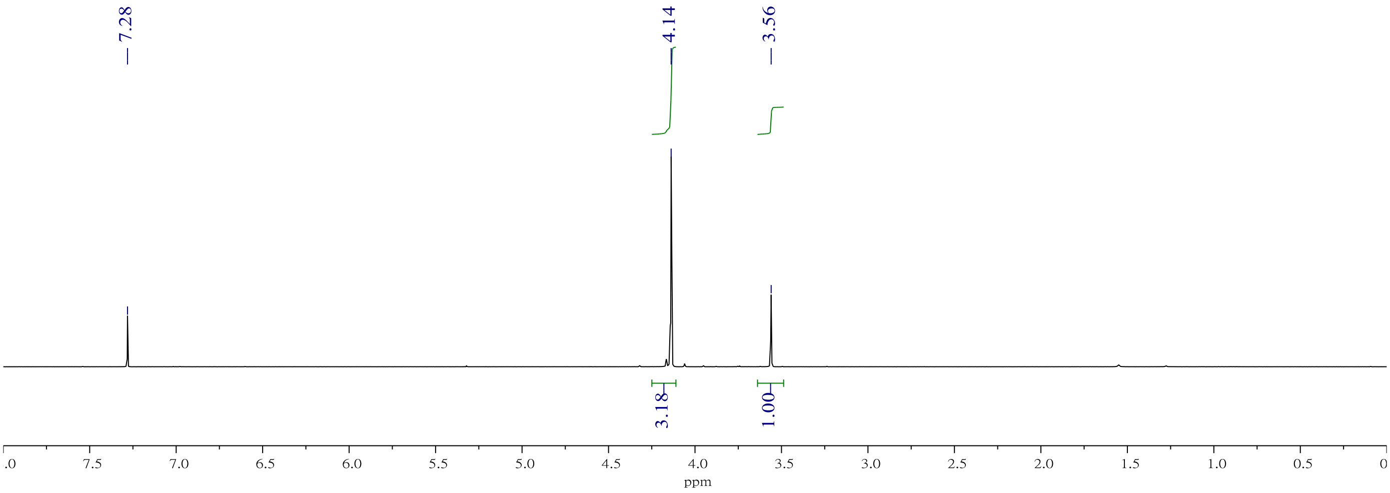


Figure 16. ^{1}H-NMR of Monomer 1EPFB in $CDCl_3$

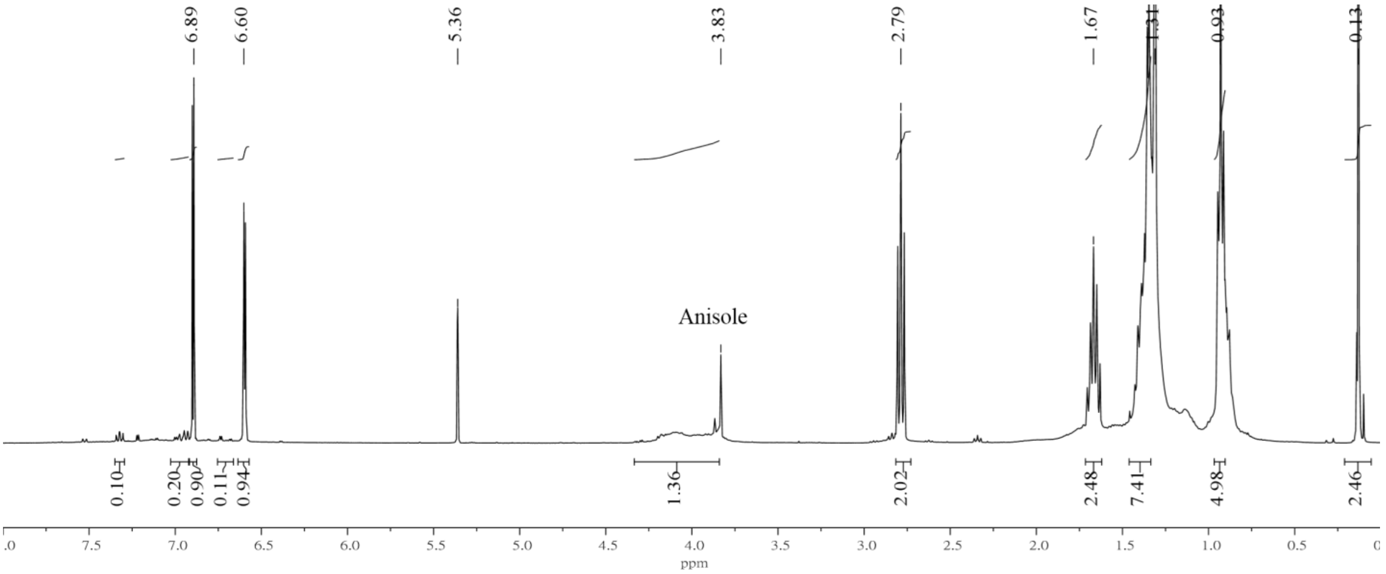
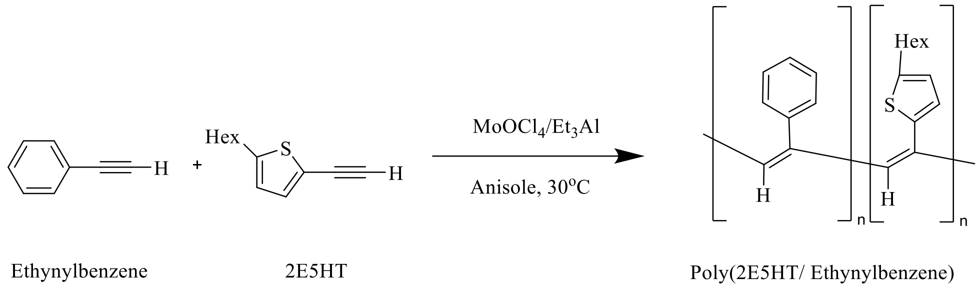


Figure 17. ^{1}H-NMR of Poly(2E5HT/1EPFB) in CD_2Cl_2.

f. Poly(2E5HT/ Ethynylbenzene)



Poly(2E5HT/ethynylbenzene) was prepared by the polymerization of monomer 2E5HT and ethynylbenzene with $MoOCl_4/Et_3Al$ in anisole at 30 °C for 24 hr.[13] In this polymerization, the reactivities of ethynylthiophene and ethynylbenzene in polymerization with $MoOCl_4$ were examined. The product of the polymerization was an orange powder and the monomers 2E5HT/ethynylbenzene are orange/yellow liquids. The change of color and physical property supports the formation of polymer. The polymerization was confirmed by the appearance of peaks in ^{1}H-NMR (δ 5.89, **Figure 18**), which correspond to the backbone alkene proton, and by GPC (M_n = 3.8 kg/mol, *Đ* = 2.7).

^{1}H-NMR spectroscopy of the resulting polymer suggested that the molar ratio of 2E5HT and ethynylbenzene repeating units in the polymer was 7:93 (the feed ratio at the start of the polymerization was 1:1). The resulting ratio may be explained by the lower reactivity of thiophene-substituted acetylene than ethynylbenzene. The molecular weight of polymer poly(2E5HT/ethynylbenzene) (M_n = 3.8 kg/mol) was higher than that found for poly(2E5HT) (M_n = 0.7 kg/mol) under similar polymerization conditions, which may also suggest the polymerization was affected by the higher reactivity of ethynylbenzene. These results are consistent with previous literature showing that phenylacetylene forms polymers of higher molecular weight than thienylacetylene under similar transitional metal-catalyzed polymerization conditions.[26] The high polydispersity and low yield (7%) may have again resulted from interference of the thienyl group of 2E5HT with the catalyst.

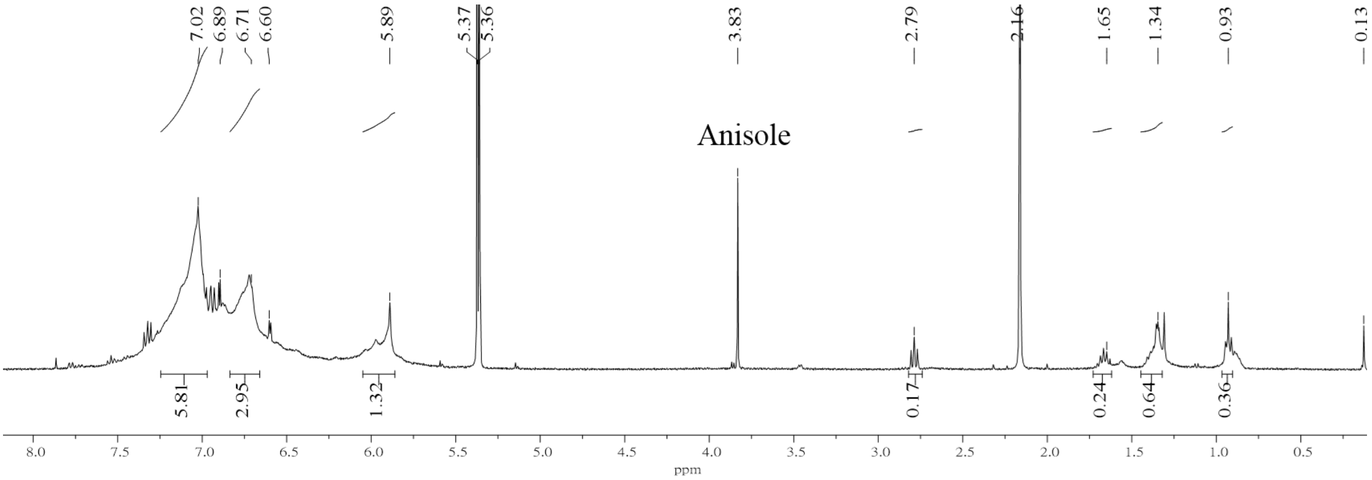
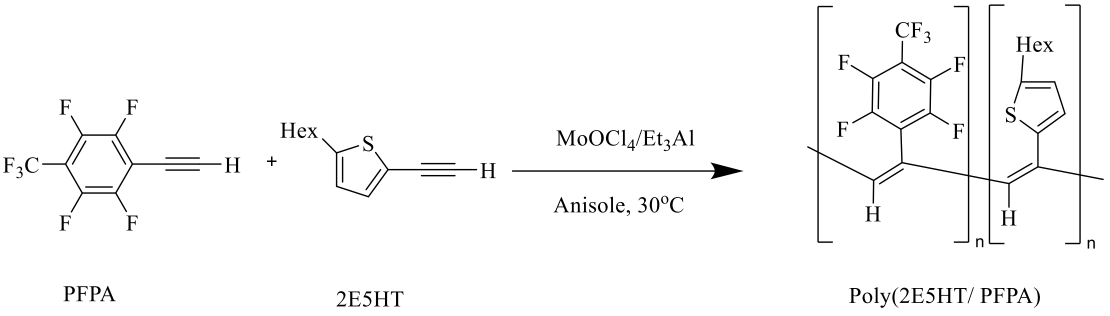


Figure 18. ^{1}H-NMR of Poly(2E5HT/ethynylbenzene) in CD_2Cl_2

g. **Poly(2E5HT/ PFPA)**



Poly(2E5HT/PFPA) was prepared by the polymerization of monomers 2E5HT and PFPA with molybdenum(VI) tetrachloride oxide/triethylaluminum in anisole. The copolymer was designed to allow us to understand if a statistical distribution of electron-donating and electron-withdrawing groups along a polyacetylene backbone would narrow the band gap of the parent polyacetylene, therefore, one electron-donating monomer (ethynylthiophene) and one electron-deficient monomer (PFPA) were used in the copolymerization. The polymerization was conducted under reaction conditions reported for copolymerization of *o*-Me_3SiPA and *p*-BuF_4PA (**Figure 7**) with $MoOCl_4/Et_3Al$ which was reported to result in polymers of high molecular weight (M_w = 25.7 kg/mol) and low dispersity ($Đ$ =1.06).[13]

A trace amount of solid was isolated from the reaction mixture. The isolated solid appeared to only contain monomer as evidenced by the absence of alkene protons in the ^1H NMR spectrum (δ 6.5-5.5, **Figure 19**) However, the alkyne peak (δ 3.29, **Figure 14**) from 2E5HT disappeared from the NMR spectrum, which may suggested something else may have occurred to the proton on alkyne. Two potential factors were considered: (1) the thiophene-substituted monomer interacts with the catalyst system and prevents polymerization; (2) the fluorinated monomer interacts with the catalyst system. According the ^{1}H NMR spectrum of the isolated solid, **Figure 19**, there was not any new peak (δ 6.86 and 6.55 belongs to the thiophene peaks) in the range of aromatic rings (δ 7.5-5.5), therefore, the possibility of exclusive trimer formation was excluded. The possible explanation of disappearance of alkyne and alkene peaks was some side-reaction, alkyne metathesis or dimerization, occurred in the presence of Mo catalyst.[30]

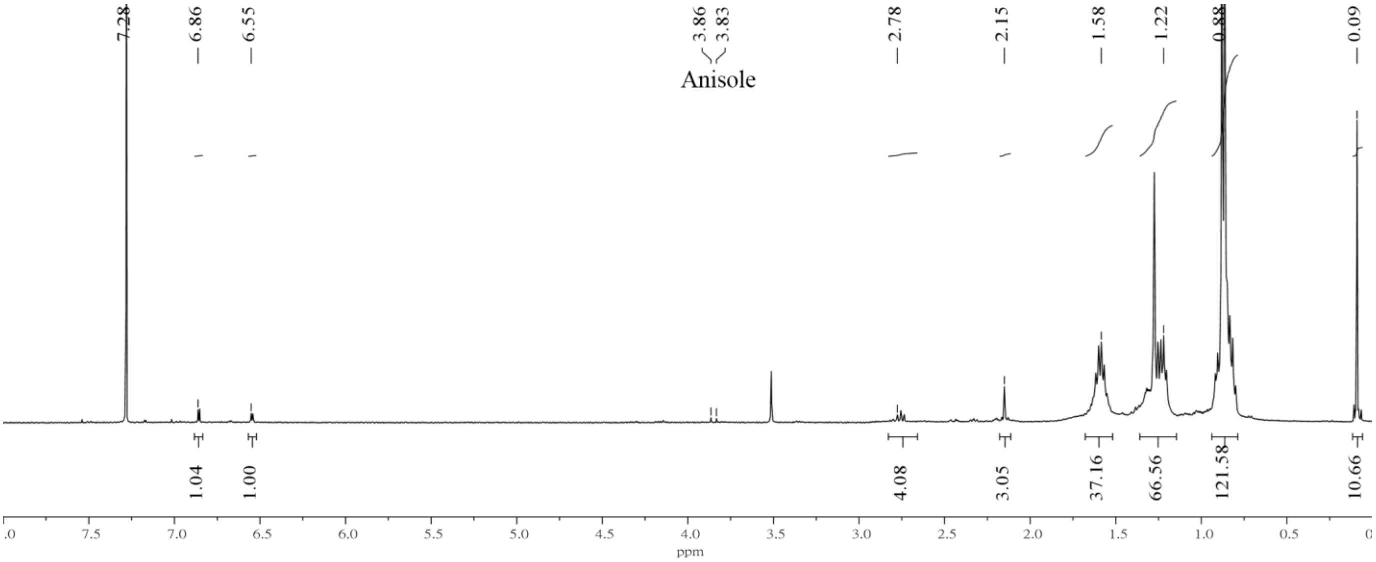
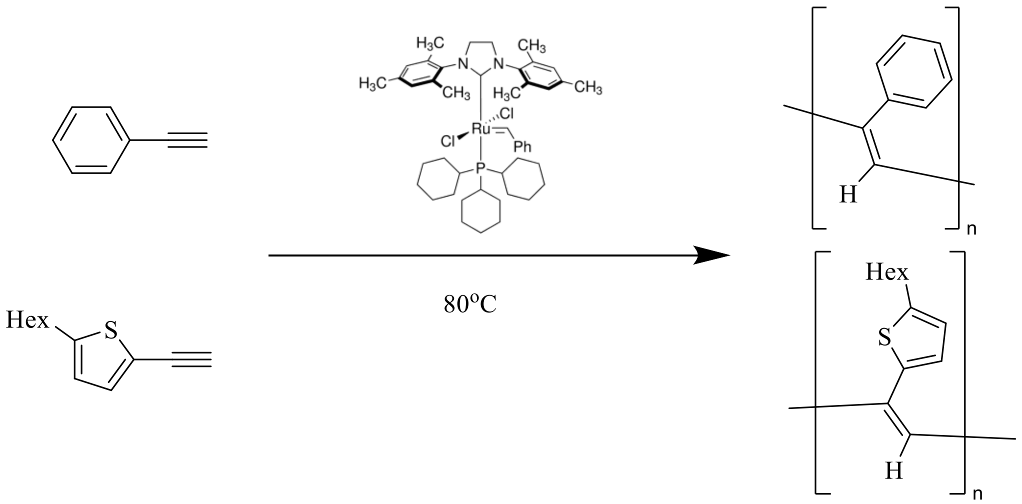


Figure 19. ^{1}H NMR of product in $CDCl_3$.

h. Polymerization of Ethynylbenzene and 2E5HT with 2nd Generation Grubbs' catalyst:



Ruthenium alkylidene catalysts have been reported for alkyne polymerization.[21-22] The homopolymerization of ethynylbenzene and the copolymerization of ethynylbenzene with 2E5HT were investigated as alternative routes to substituted polyacetylenes.

Poly(ethynylbenzene) was prepared by bulk polymerization of ethynylbenzene with 2nd Generation Grubbs' catalyst at 80 °C for 24 hr. 2nd Generation Grubbs' Catalyst was reported for successful polymerization of gaseous acetylene in solution[31] and reacts with diphenylacetylene, suggesting its utility for the polymerization of diphenylacetylene.[21] Therefore, the polymerization of phenylacetylene was examined by following the reported reaction condition. Theoretically, the mono-substituted alkyne should polymerize more easily than the disubstituted alkyne because of the lower steric hindrance present. However, the reaction only afforded a small amount of yellow powder which was examined by GPC (M_n = 0.8 kg/mol, $Đ$ = 1.6).

Poly(2E5HT) was also prepared under the same reaction conditions.[21] The reaction afforded only a trace amount of sticky solid which was also examined by GPC (M_n = 1.2 kg/mol, $Đ$ = 1.5). Poly(2E5HT) resulting from the 2nd generation Grubbs catalyst showed a higher molecular weight than that resulting from the $TaCl_5$/$n$$Bu_4Sn$ system, which may suggest less undesired interaction between ethynylthiophene and ruthenium than with tantalum. Some literature also suggests that different transition metal catalysts (Ta, Mo, W) can give large differences in molecular weight of the resulting polymers.[9c, 32]

The polymerization only afforded oligomers which suggested that the polymerization was interrupted for some reason. According the literature,[21] 2nd Generation Grubbs' catalyst was inclined to form stable complexes with electron-rich alkynes. The formation of a stable intermediate could be the reason that polymerization was interrupted.

Grubbs–Hoveyda ruthenium carbene complex has also been reported for successful polymerization of mono- and disubstituted alkynes.[22a] Therefore, some electron-deficient alkyne will be studied in future experiments to see if the catalyst can be applied in the polymerization of different alkynes. Grubbs-Hoveyda catalyst will also be examined for electron-rich alkynes (ex: ethynylthiophene) and copolymerizations in the future.

i. Characterization

1. Optical Properties

Conjugated polymers substituted with donor and acceptor groups are expected to have narrower band gaps than the polymers without D/A groups.[6, 33] The effective conjugation length of the polymer backbone also affects the band gap. However, once the polymer backbone is longer than the effective conjugation length (ECL), the effect of further increases in backbone length on band gap will significantly decrease.[6, 34]

The polymer with a smaller band gap has a higher absorption onset wavelength, the lowest energy at which the polymer absorbs photons, in its absorption spectrum. Generally, the optical band gaps of similar polymers can be compared by comparing the absorption onset wavelengths under similar conditions.

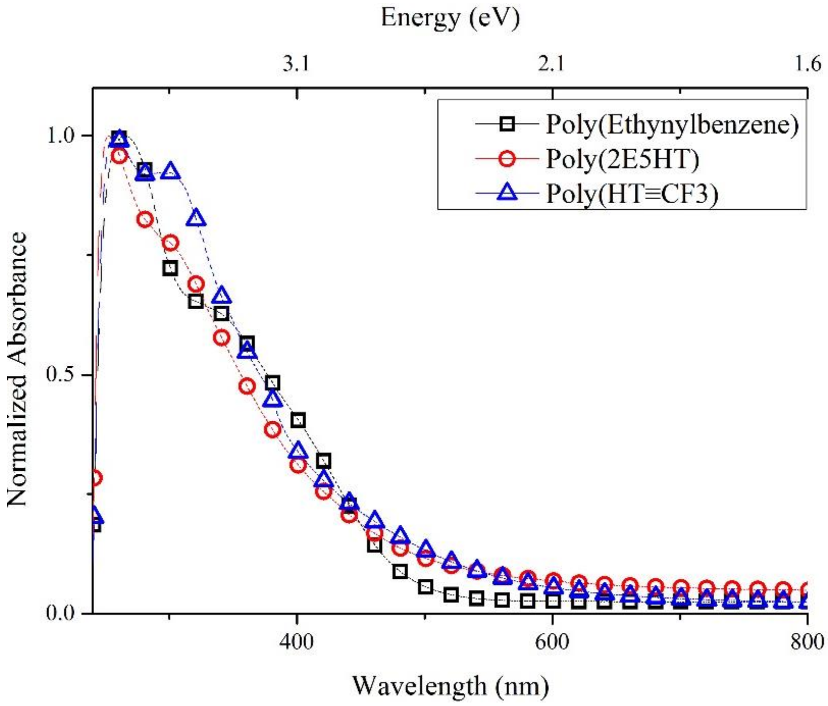


Figure 20. UV-Vis Absorption Spectrum of Homopolymers

(1). Poly(Ethynylbenzene) (-□-); (2). Poly(2E5HT) (-○-); (3). Poly(HT≡CF_3) (-△-) in chloroform solution (0.05 mg/ml).

In **Figure 20**, the band gaps of poly(2E5HT) and poly(HT≡CF_3) are similar and they are smaller than the band gap of poly(ethynylbenzene).[35] Because poly(HT≡CF_3) was designed to have alternating electron-donating and electron-accepting groups, the band gap was expected to be lowest one. However, the lack of planarity induced by steric effects in the disubstituted backbone may significantly weaken the D-A effect. Poly(2E5HT) was substituted with hexylthiophene. Thiophene is electron-rich and an electron-donating group which may enhance the conjugation of the polymer backbone to a greater degree than a phenyl substituent,[36] but it is unclear if this is the specific reason resulting in the smaller measured band gap for the poly(ethynylthiophene) than for poly(ethynylbenzene).

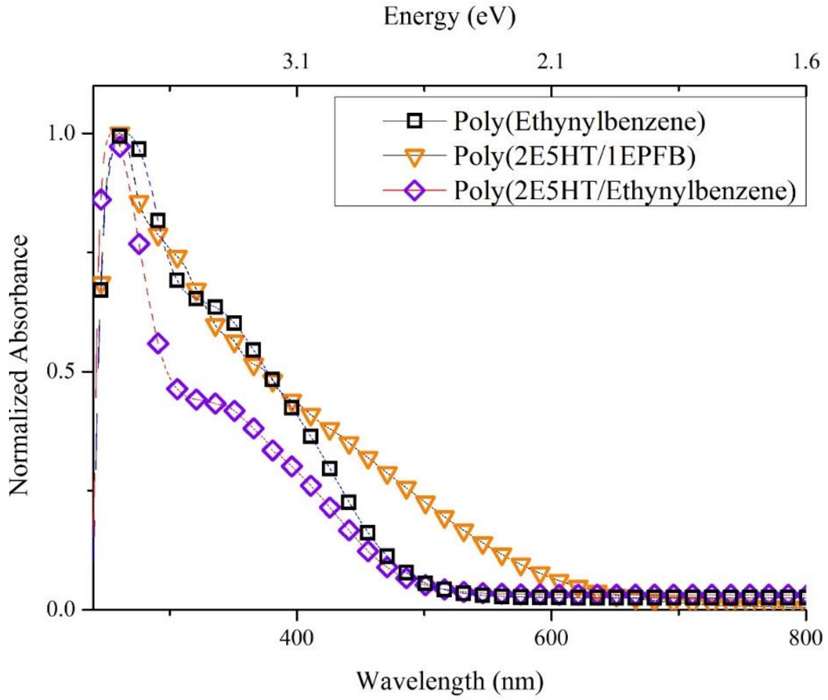


Figure 21. UV-Vis Spectra of Copolymers and Poly(ethynylbenzene).
(1). Poly(ethynylbenzene) (-□-); (2). Poly(2E5HT/1EPFB) (-▽-); (3) Poly(2E5HT/Ethynylbenzene) (-◇-). All absorption spectra were measured in chloroform solution (0.05 mg/ml).

Even though the donor and acceptor groups in poly(2E5HT/1EPFB) are not strictly alternating along the backbone, the band gap appears to be reduced (**Figure 21**). However, poly(2E5HT/ethynylbenzene) does not show a significant change in band gap from poly(ethynylbenzene), most likely due to the smaller electron-withdrawing effect of ethynylbenzene when compared to the *p*-methoxytetrafluorophenyl substituents of 1EPFB and relatively small amount (6.5% of ethynylthiophene and 93.5 % of ethynylbenzene) of ethynylthiophene incorporated in the polymer.

The UV-Vis spectroscopy studies show the importance of planarity of the conjugated backbone and suggest that a statistical distribution of donor and acceptor groups along a conjugated polymer backbone can lead to a reduction in the band gap, but the reliable evidence required more extensive studies. In the substituted polyacetylene system, the repulsion and steric hindrance between substituents should be avoided to maintain the planarity of the conjugated backbone, which is a difficult task because substituted polyacetylene only has two functionalizable positions for each monomer. Therefore, finding appropriate electron-donating and electron-withdrawing substituents with less steric bulk or synthesizing a monomer with more widely spaced functional groups, like 1,2- or 1,3-disubstituted butadiene, and polymerizing anionically with subsequent oxidation to the polyacetylene backbone[37] would be an alternative method to solve this task.

2. Gel-Permeation Chromatography

With di-substituted acetylenes (Table 1, Entries (1) and (2)), the $TaCl_5$/n-Bu_4Sn catalyst system was used due to the higher degree of polymerization reported for di-substituted acetylenes with these systems.[10, 38] With mono-substituted acetylenes (Table 1, entries (3), (4), (5), and (6)), the $MoOCl_4$/Et_3Al/EtOH catalyst system was used, as high degrees of polymerization and narrow molecular weight distributions have been reported for these systems with mono-substituted acetylenes and also with copolymerization of multiple mono-substituted acetylenes.[11, 13, 25]

However, previous work with these two catalysts systems did not include polymerization of acetylenes substituted with thiophene rings but only with phenyl or alkyl groups. Therefore, we attempted a series of polymerizations with various thiophene-substituted acetylenes.

Polymerizations involving ethynylbenzene resulted in higher molecular weights and yields than polymerizations involving mono- or di- substituted acetylenes (entry (1), (2), (4) and (6)). The result implies that the molybdenum and tantalum catalysts are not efficient catalysts for polymerization of thiophene-substituted acetylenes.

For the polymerizations of ethynylbenzene and 2E5HT with 2nd Generation Grubbs' catalyst (entry (8) and (9)), the reactions each afforded only a small amount of solid with low molecular weights and yields suggesting problems in the polymerization. 2nd Generation Grubbs' catalyst has been reported to form complexes with electron-rich disubstituted acetylene,[21] which may explained the results of polymerization. Grubbs-Hoveyda catalyst was reported for better alkyne polymerization results than the 2nd Generation Grubbs' catalyst.[22] Therefore, Grubbs-Hoveyda catalyst will be examined in the following polymerization in the future and the homopolymerization of electron-deficient monomers will be investigated to avoid the undesired interaction of electron-rich monomer with catalyst and to explore the potential for preparation of *n*-type semiconducting polyacetylenes.

For polymerization of mono-substituted acetylenes containing heteroaromatic rings, rhodium complexes may be efficient catalysts except for their unpleasant price. But for disubstituted alkynes bearing a thienyl group, efficient catalysts have still not been discovered.

IV. CONCLUSION

Polymerization of alkynes bearing different electron-donating and electron-withdrawing groups was explored with two different transition metal catalyst systems, but the degree of polymerization was limited in each case. Even with different thiophene-substituted alkynes, the polymerization only appeared to work well when ethynylbenzene was used as a comonomer. This phenomenon may suggested that the tantalum and molybdenum are not appropriate catalysts for these monomer systems.

This research was designed to focus on the optoelectronic properties of the substituted polyacetylene as a new OPV polymer system, but the polymerization could only give us oligomers, which made us switch the focus to the synthesis in an attempt to improve polymerizability of these functionalized alkyne monomers.

In the future, there are two directions for modification. First, change the application of the project to polymer light emitting devices (PLED)[39] or organic thin film transistor,[40] therefore, the thiophene-substituted monomer will not be necessary anymore, but the project can still focus on tuning band gap by bigger variety of moieties. Much research has focused on of the light-emitting properties of substituted polyacetylenes.[35, 38b, 39c]

The second direction is to continue studying thiophene-substituted polyacetylenes, but with different method of polymerizations, like rhodium catalysts,[27, 40] which was reported for polymerization of thiophene-acetylene, or anionic method,[37, 41] which may require complicated monomer synthesis.

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VI. APPENDIX

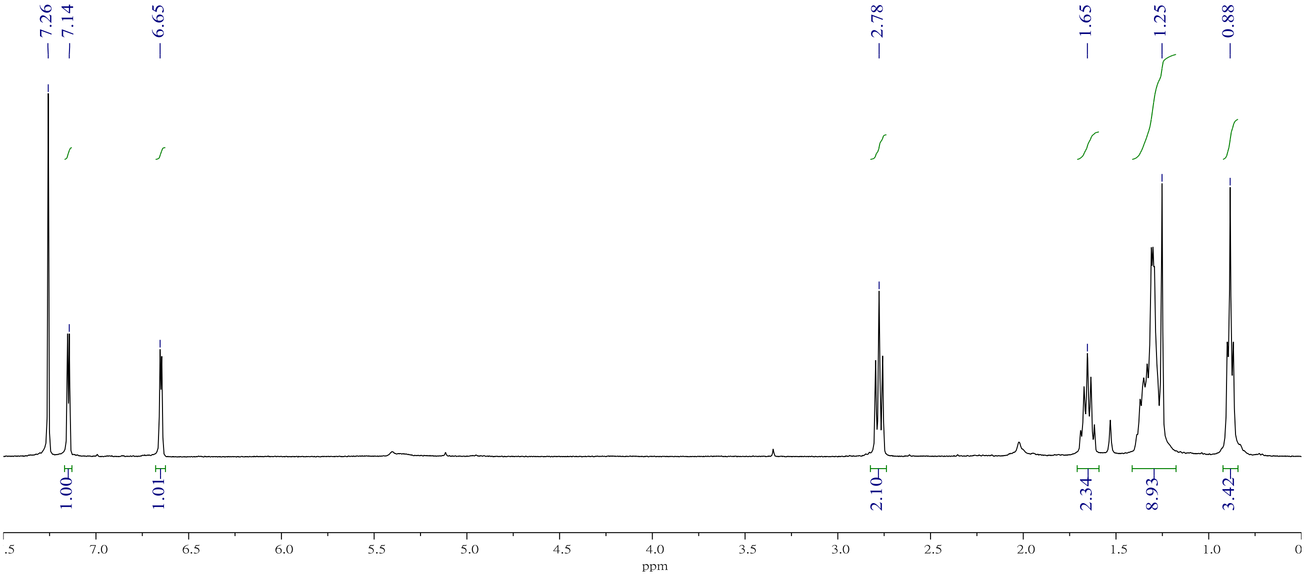

Figure A 1. ^{1}H-NMR of TMS-2E5HT in $CDCl_3$.

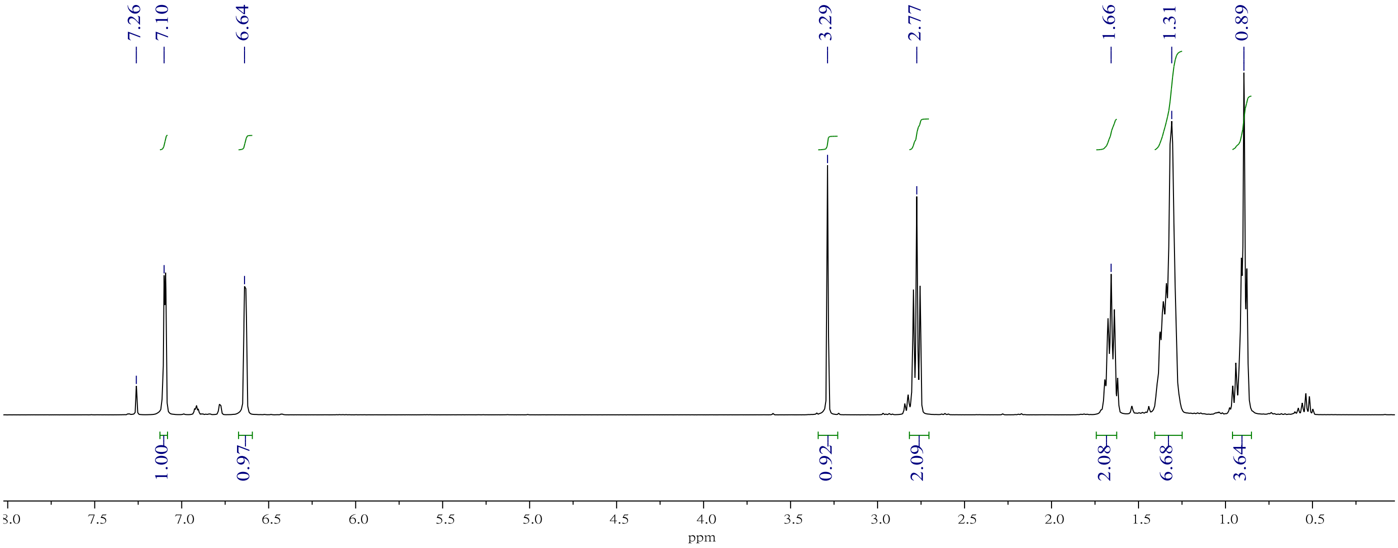

Figure A 2. ^{1}H-NMR of 2E5HT in $CDCl_3$.

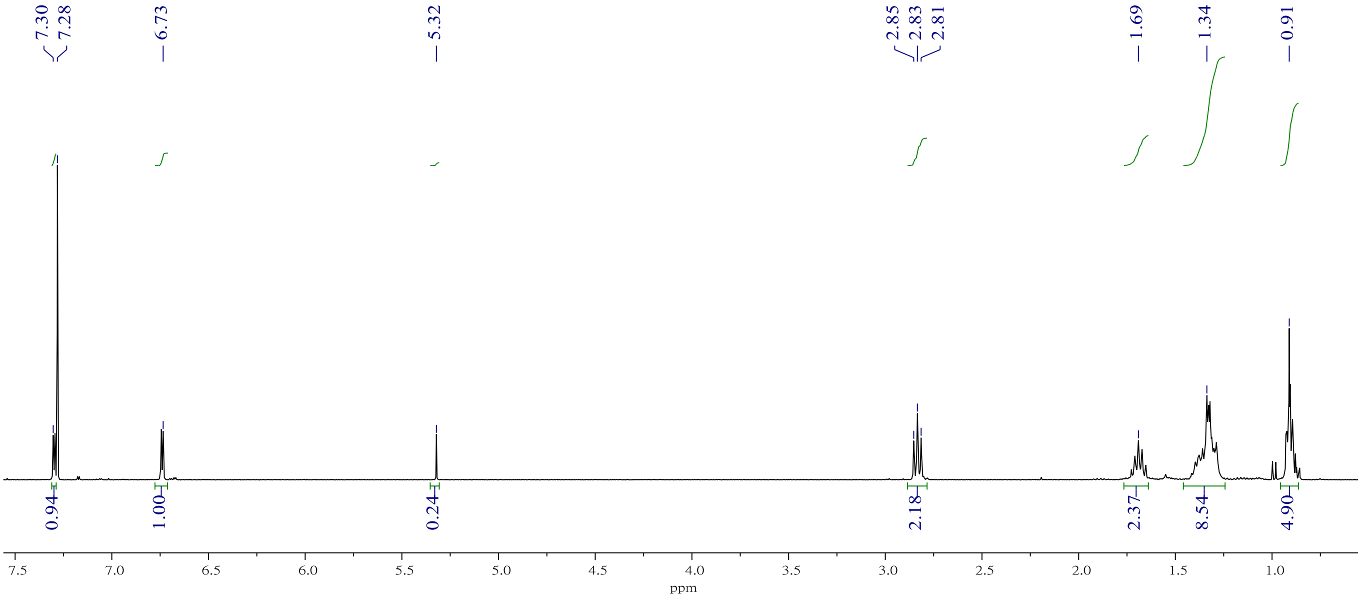

Figure A 3. ^{1}H-NMR of HT≡CF_3 in $CDCl_3$.

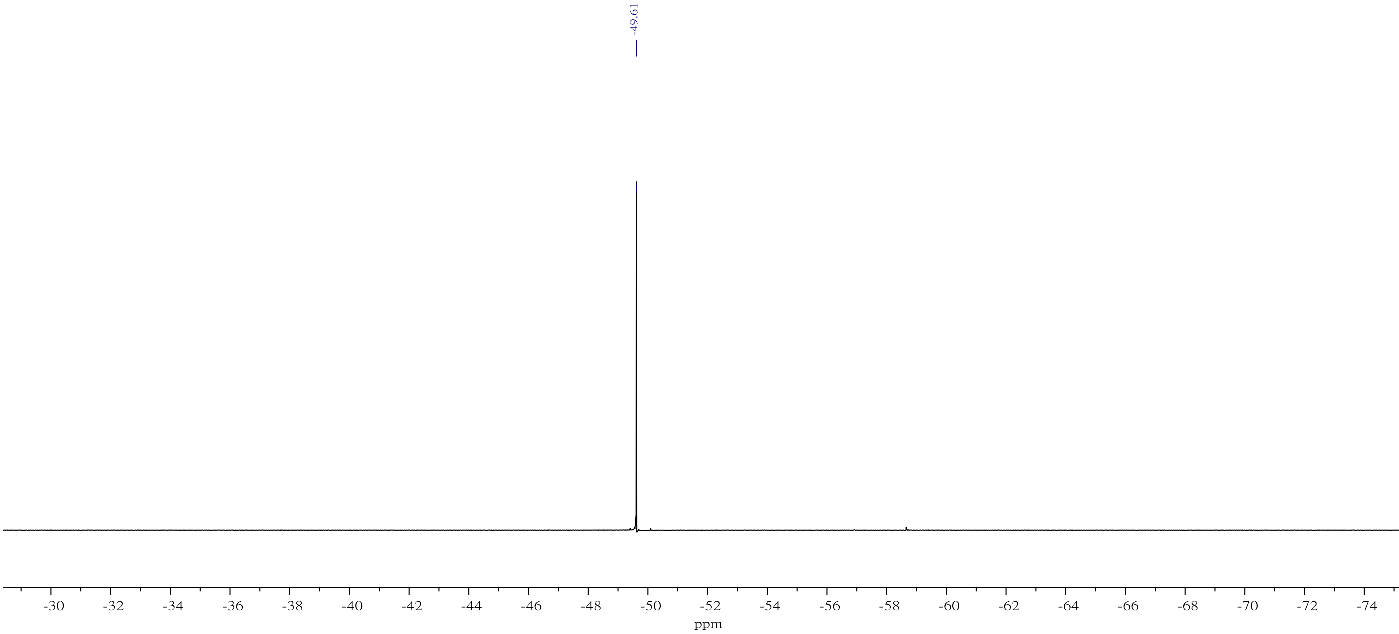

Figure A 4. ^{19}F-NMR of HT≡CF_3 in $CDCl_3$.

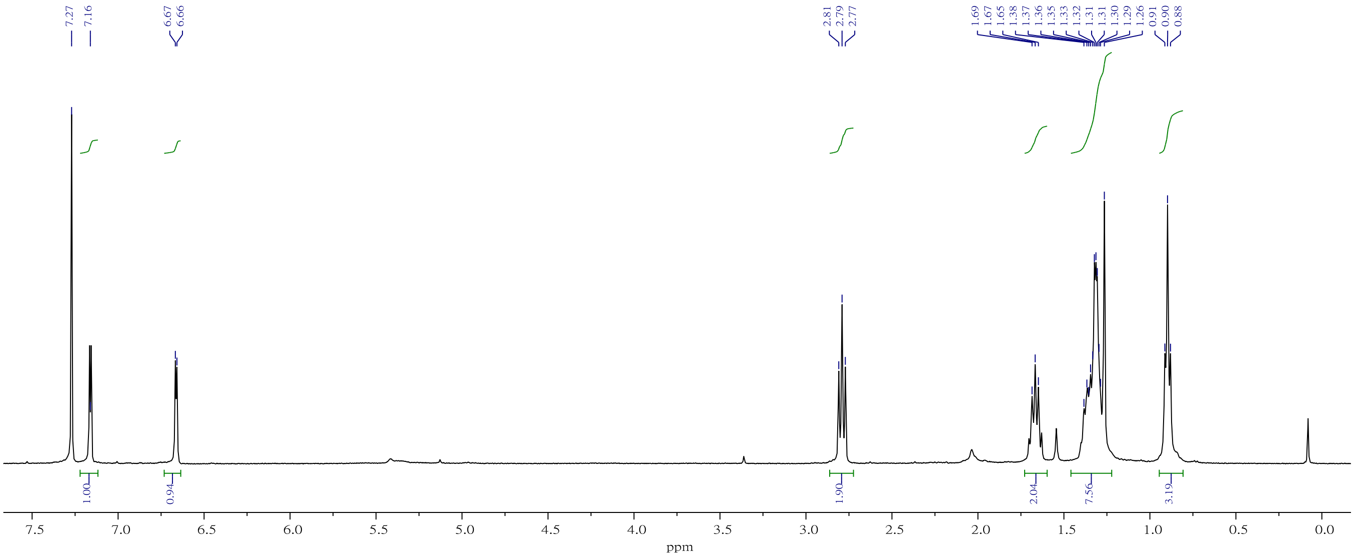

Figure A 5. ^{1}H-NMR of HT≡FPh in $CDCl_3$.

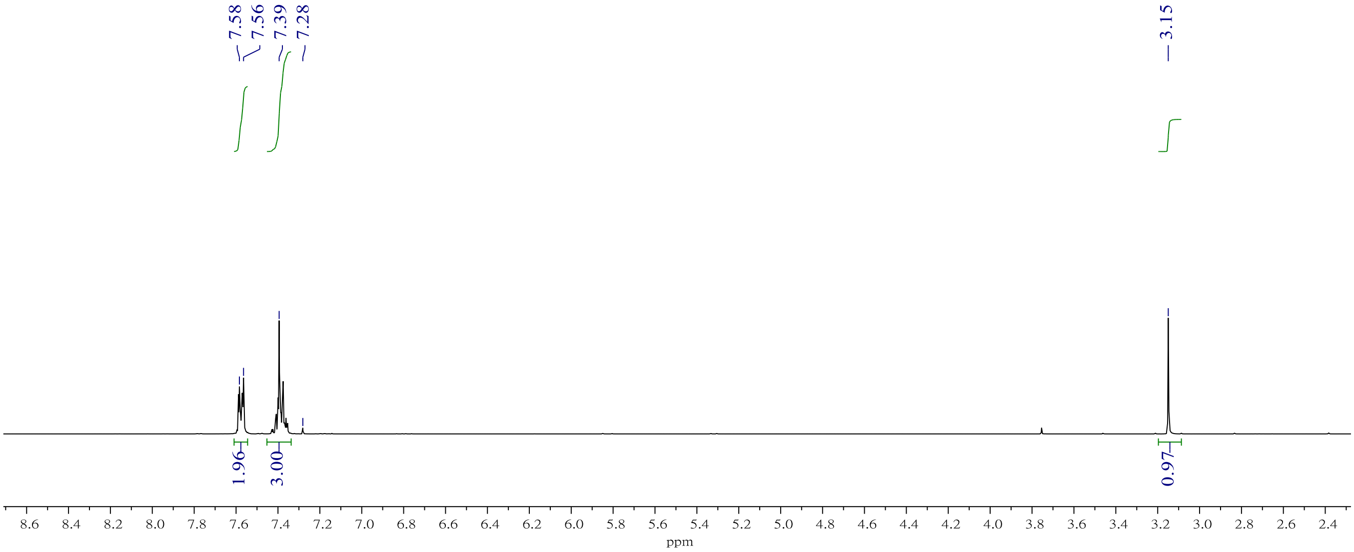

Figure A 6. ^{1}H-NMR of Ethynylbenzene in $CDCl_3$.

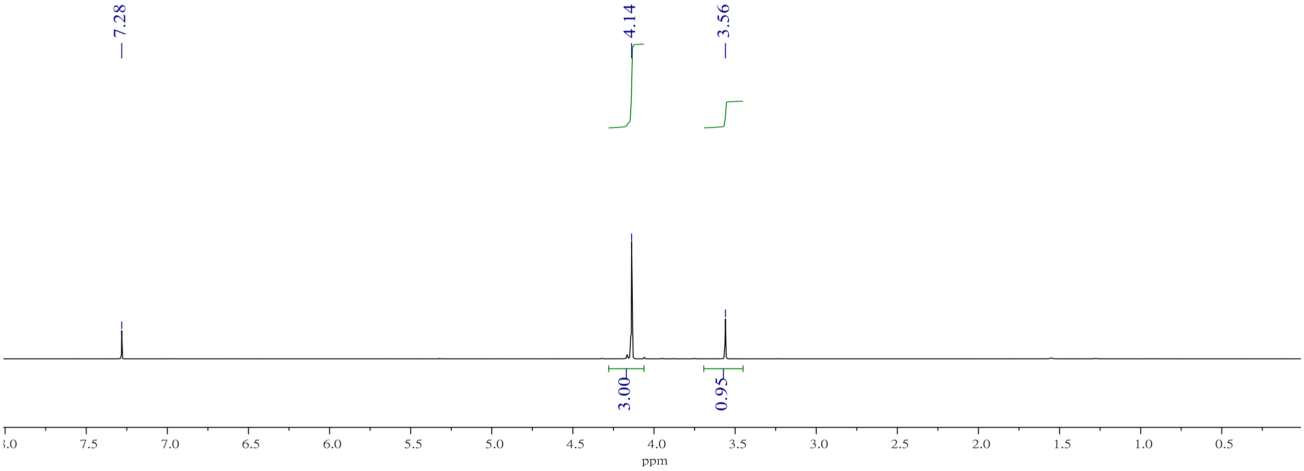

Figure A 7. ^{1}H-NMR of 1ETFMB in $CDCl_3$.

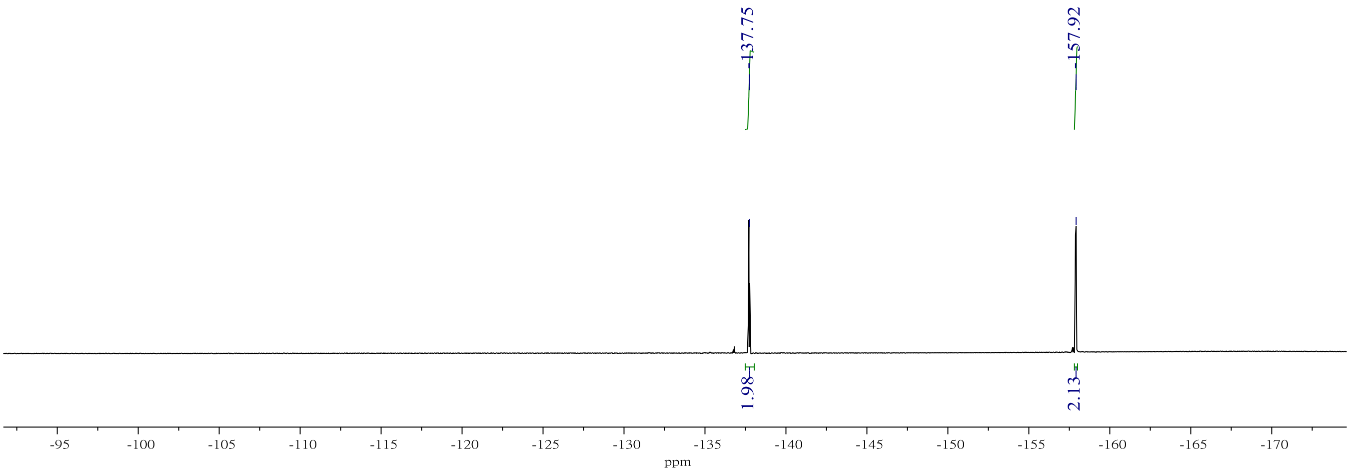

Figure A 8. ^{19}F-NMR of 1ETFMB in CDCl$_3$.

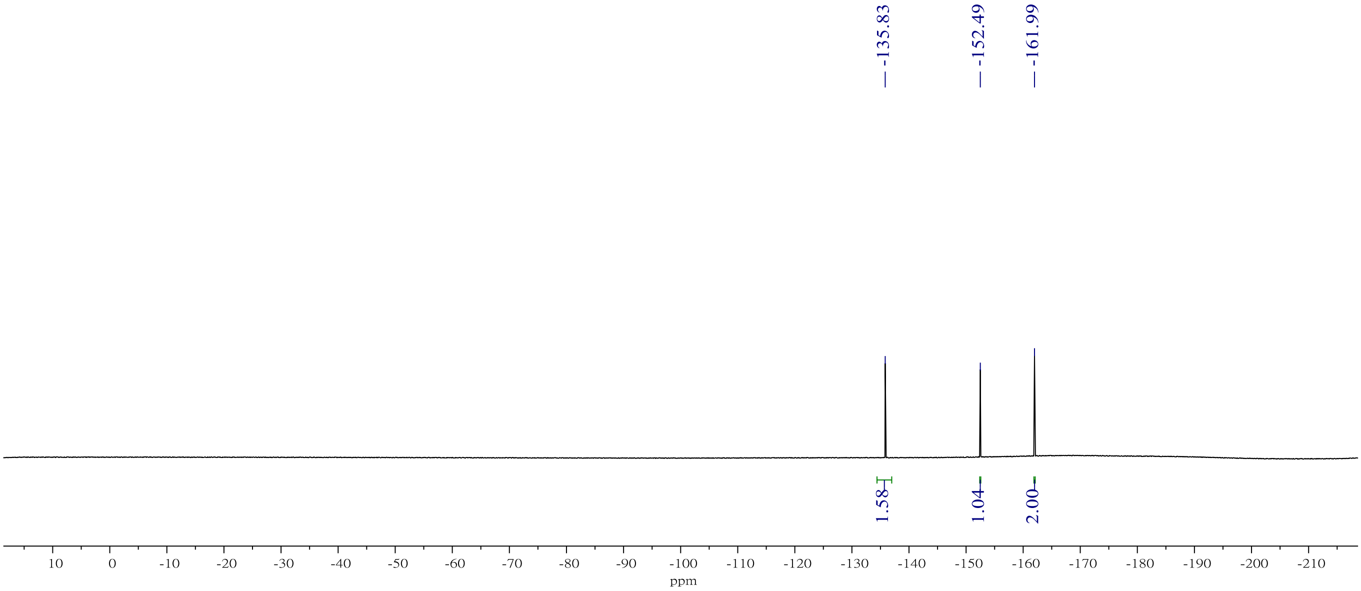

Figure A 9. ^{19}F-NMR of TMS-1EPFB in CDCl$_3$.

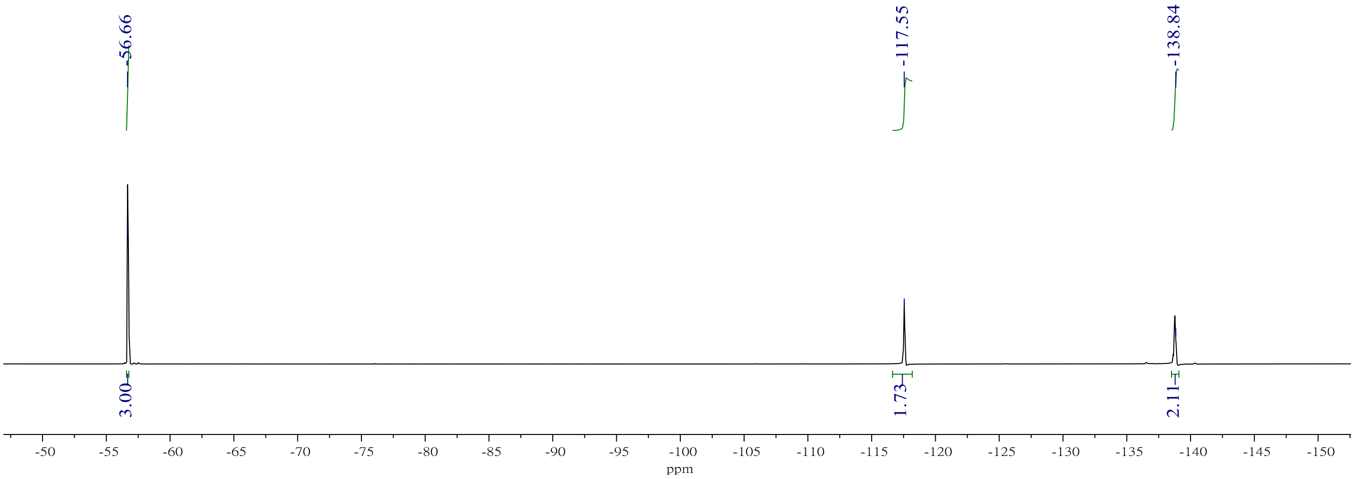

Figure A 10. ^{19}F-NMR of PFIB in CDCl$_3$.

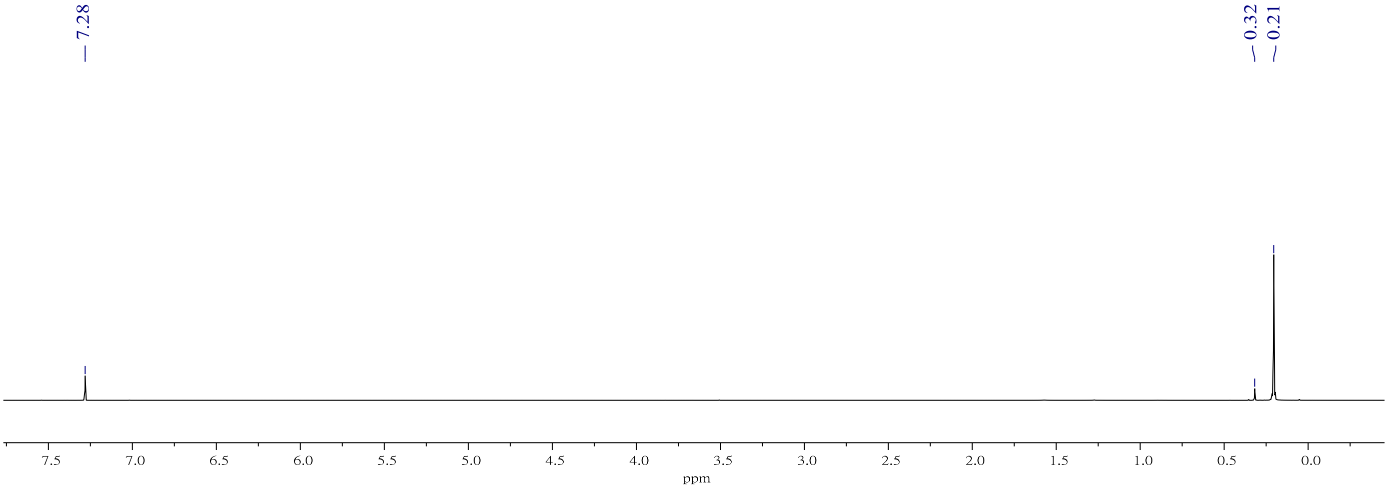

Figure A 11. ^{1}H-NMR of TMS-PFPA in $CDCl_3$.

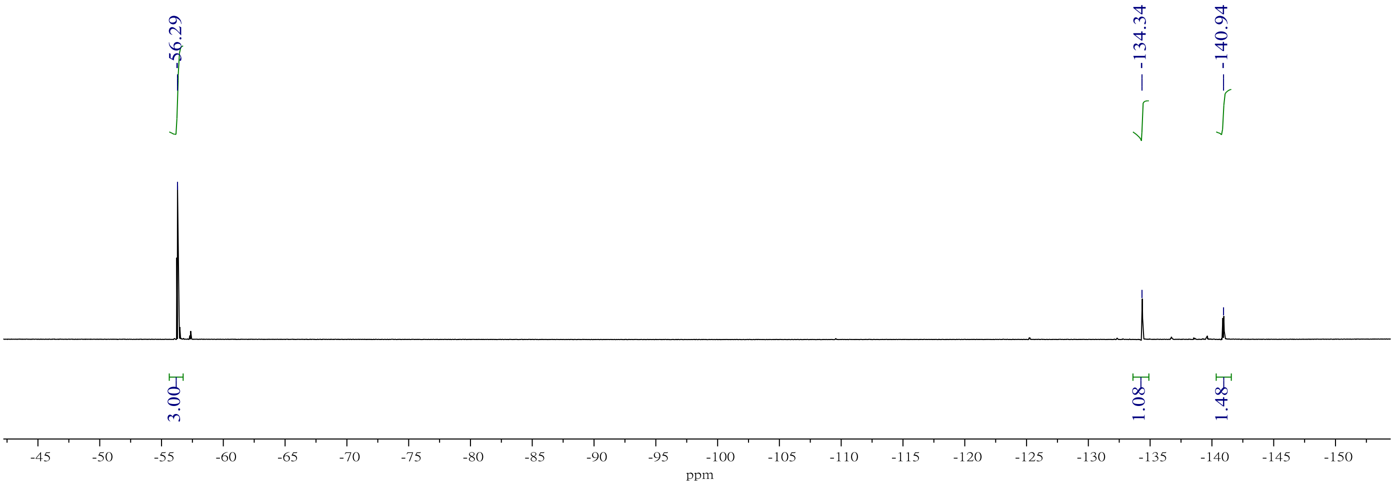

Figure A 12. ^{19}F-NMR of TMS-PFPA in $CDCl_3$.

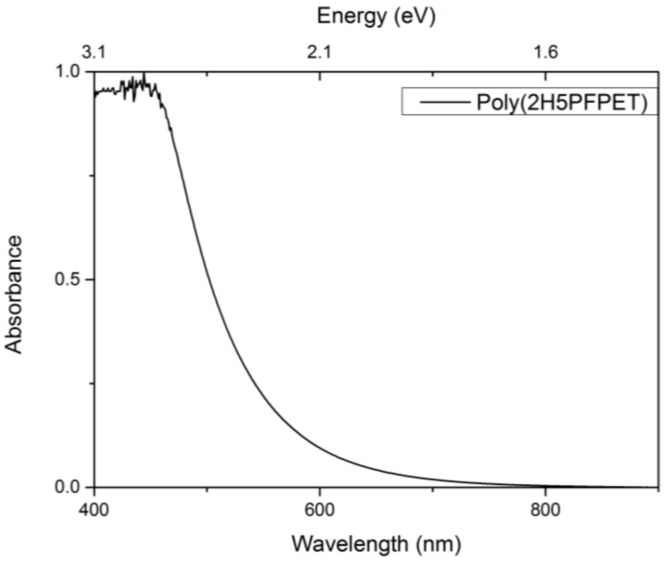

Figure A 13. UV-Vis Spectra of Poly(HT≡FPh) in chloroform (concentration was unknown).