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Synthetic Approach towards P3EHT-b-PSS Conjugated and Ionic Block Copolymer

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SYNTHETIC APPROACH TOWARDS P3EHT-b-PSS
CONJUGATED AND IONIC BLOCK COPOLYMER

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Chemistry

by
Zhaoyuan Liu
BS, Peking University, 2008
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List of Acronyms and Abbreviations

ATRP	Atom transfer radical polymerization
BCP	Block copolymer
bipy	2,2'-Bipyridine
cod	Cyclooctadiene
CuAAC	Cu-catalyzed azide-alkyne cycloaddition
DAD	Diode-array detector
DCM	Dichloromethane
DIPEA	N,N-Diisopropylethylamine
DMF	Dimethylformamide
DP	Degree of polymerization
dppe	1,3-Bis(diphenylphosphino)ethane
dppp	1,3-Bis(diphenylphosphino)propane
DSC	Differential scanning calorimetry
eq.	Equivalent
LED	Light-emitting diode
MALDI-TOF MS	Matrix assisted light desorption ionization time of flight mass spectroscopy
M_n	Number average molecular weight
MW	Molecular Weight
NBS	N-bromosuccinimide

NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance spectroscopy
OFET	Organic field-effect transistor
P3AT	Poly(3-alkylthiophene)
P3EHT	Poly(3-(2-ethylhexyl)thiophene)
P3HT	Poly(3-hexylthiophene)
PA	Polyacetylene
PDI	Polydispersity index
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Poly(ethylene glycol)
PESS	Poly(ethyl p-styrenesulfonate)
PMDETA	N,N,N',N'',N''-Pentamethyldiethylenetriamine
PNSS	Poly(neopentyl p-styrenesulfonate)
PPP	Polyparaphenylene
PPV	Polyparaphenylene vinylene
PPy	Polypyrrole
PS	Polystyrene
PSS	Polystyrene sulfonate
PSSNa	Poly(sodium 4-styrenesulfonate)
PT	Polythiophene
RAFT	Reversible addition-fragmentation chain-transfer

ROMP	Ring-opening metathesis polymerization
SEC	Size exclusion chromatography
SSNa	Sodium 4-styrenesulfonate
TBAF	Tetrabutylammonium fluoride
THF	Tetrahydrofuran
WAXS	Wide-angle X-ray scattering

Abstract

This work is focused on the design, synthesis and characterization of block copolymers (BCPs) containing both conjugated and polyelectrolyte blocks. This type of rod-coil BCP is considered to have microphase separation which is different compared to coil-coil BCPs. The conjugated block used for studies is regioregular poly(3-alkylthiophene) (P3AT), which can be synthesized by Grignard metathesis (GRIM) polymerization. The polyelectrolyte block used is polystyrene sulfonate with well-defined structure, which can be synthesized by atom transfer radical polymerization (ATRP).

Chapter II is focused on evaluation of synthetic routes for P3EHT-*b*-PSS, including using bifunctional initiator to synthesize both blocks, and separately synthesizing end-functionalized polymer blocks for Cu-Catalyzed Azide-Alkyne Cycloaddition (CuAAC). The advantages and disadvantages of these synthetic routes were summarized to find the best to synthesize P3EHT-*b*-PSS.

Chapter III is focus on the detailed synthesis of propynyl-terminated P3EHT and azido-terminated PNSS, which are the two blocks used for CuAAC to synthesize P3EHT-*b*-PNSS. The optimum conditions for synthesizing both blocks were found. This synthetic route can achieve better MW, PDI and end-group control compared to other reported synthetic attempts for similar end-group functionalities. CuAAC was also tried to synthesize P3EHT-*b*-PNSS by using previously mentioned polymer blocks.

Chapter I. Introduction

1.1 Introduction to self-assembly of block copolymers (BCPs)

Self-assembly is a term used to describe spontaneous processes where nanoscale entities pack into regular arrangements to attain minimum free energy through minimizing repulsive molecular interactions and maximizing attractive molecular interactions.¹ In chemistry field, self-assembly was studied from nanoscale such as the assembly of molecules even to microscale such as the assembly of spherical particles.² In polymer field, the studies were confined to the self-assembly or self-organization of polymers. Self-assembly refers to systems that are driven to equilibrium via physical interactions between entities (to minimize free energy). Self-organization is generally used for a dynamic process where the organized structure is in a kinetically stable state.¹ The difference between these two terms is difficult to differentiate in chemistry, and these terms are used interchangeably.³ As polymers are relatively large molecules in dimension, it is hard to determine whether it reaches an equilibrium or is still in a dynamic process in the system, so the term self-assembly is generally used as a generic term.⁴ Differed from homopolymers with chemically identical components, block copolymers with chemically distinct blocks exhibit the preference of microphase separation to form various nanostructures in the solid phase.⁴ Compared to polymer blends, the advantage of BCPs by using a single macromolecule is that the macroscopic phase separation in mixtures cannot occur.⁴ As the high preference of forming well-defined self-assembled structures, the morphology of BCPs is of high interest. The morphology of BCPs is influenced by

factors such as the chemical composition of each block, and the volume ratio of blocks, etc., which could be tuned by synthetic chemistry. Since the size, shape, and arrangement of these nanoscopic structures are tunable through synthetic chemistry of the constituent molecules, well-defined nanostructures can be targeted for specific uses in nanotechnologies.

Researchers studied the phase diagram of BCPs, which demonstrated the relationship between the identity of polymer blocks to the phase of the resulting BCPs. A theoretical phase diagram of coil-coil BCPs in bulk (Figure 1.1) has previously been reported by Bates et al.⁵ The phase structures of lamellar, cylindrical or spherical are determined by the volume fraction of individual block (f) and χN , where χ is the Flory–Huggins interaction parameter and N is the total degree of polymerization.⁶

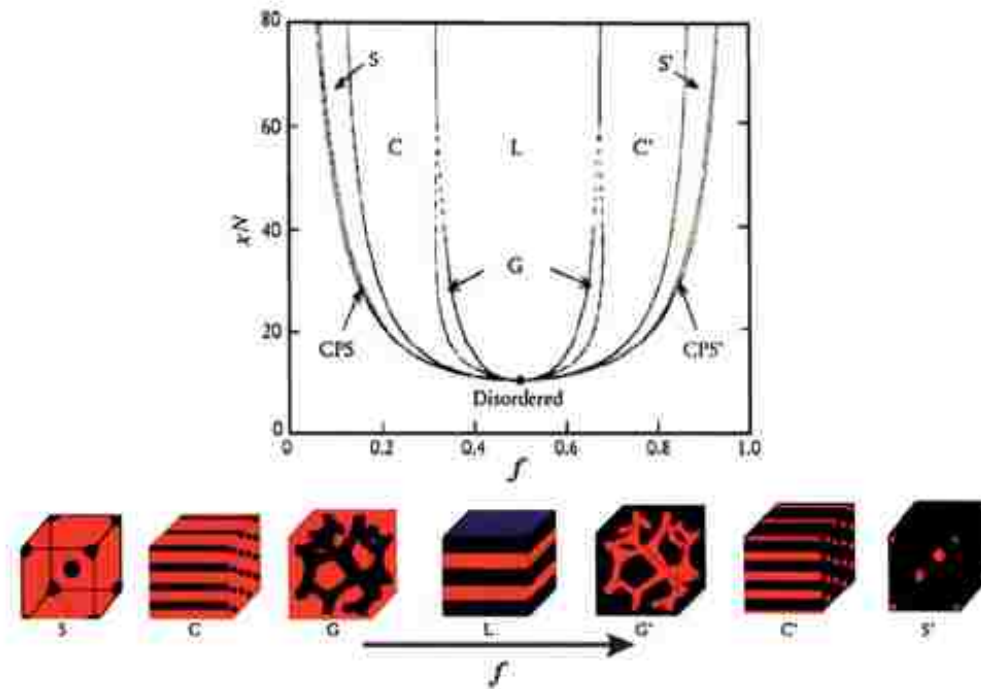


Figure 1.1. Theoretical phase diagram of coil-coil diblock copolymers in bulk⁵

In BCP films, when heating around their glass transition temperature, microphase separation will be effected and changes in film structure will occur to minimize surface energies and maximize bonding interactions with the surface. The phase structures are mainly determined by the factors mentioned previously in bulk condition, but the difference of substrates used to process the polymer films may determine the orientation of structures. To minimize the interface energy between the polymer films and substrates, the orientation could be vertical or horizontal respect to the surface.⁴

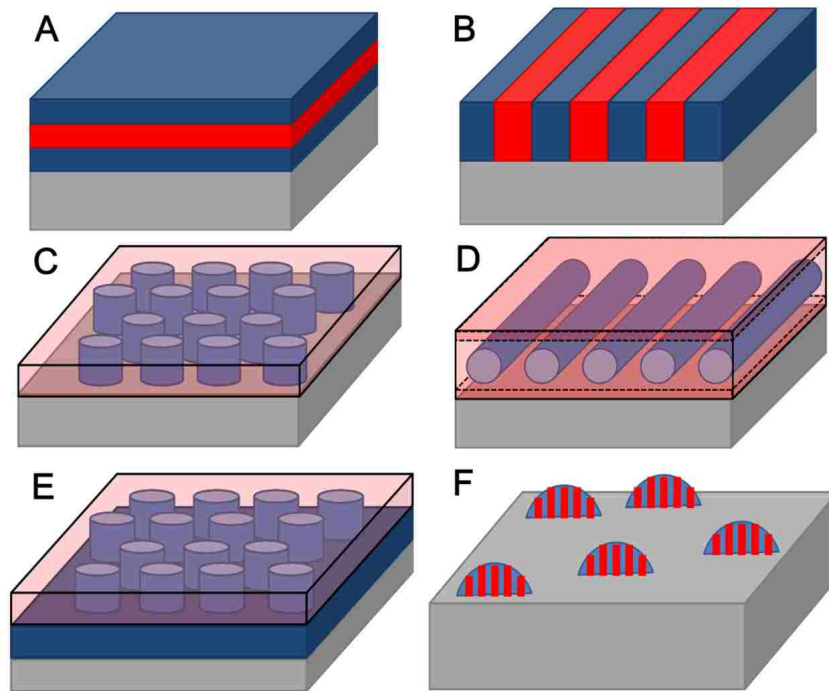


Figure 1.2. Orientational effects in BCP thin films on self-assembly⁴

Compared to coil–coil BCPs, which were studied more thoroughly on fundamental theories, rod–coil and rod–rod systems are more complicated and additional parameters such as ratio of the characteristic coil-to-rod dimensions influence the microphase separation as well.⁷ The nanostructured BCPs often do not have long range orientational

order. Control over the macroscopic orientation and alignment of microdomains can be obtained through chemical and physical manipulation.⁸ But in general, the self-assembly of rod-coil BCPs needs to be further investigated to construct a widely accessible theory for the guidance of precise control over microstructures. For BCPs with coil blocks as ionic polymers, the morphologies still need to be put into more attention, so this subfield is worth being carefully investigated.

1.2 Introduction to conjugated polymers

Conjugated polymers are organic macromolecules characterized by a backbone with alternating double and single bonds. Their system of delocalized π -electrons which created by overlapping p-orbitals results in interesting and useful optical and electronic properties. Certain conjugated polymers behave as electrical semiconductors, and sometimes are called conductive polymers. Conjugated polymers having extended electron delocalization are promising for materials for electronic and optical devices such as polymer light-emitting diodes (LEDs) and organic field-effect transistors (OFETs).⁹

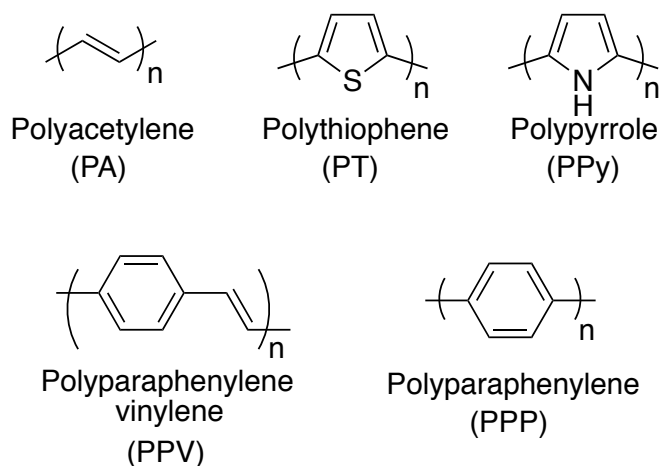
1.2.1 Typical conjugated polymers

The most well-known conjugated polymer is polyacetylene. The discovery of the conductivity of doped polyacetylene started a new era of conductive polymers. In 1977, Heeger, MacDiarmid, and Shirakawa reported the discovery of conductive properties of doped polyacetylene¹⁰, and these three scientists were awarded the Nobel Prize in Chemistry for this significant discovery in 2000. Polyacetylene has the structure of repeat unit C_2H_2 in either all cis or all trans configuration, and cannot be dissolved in organic solvents. When

doped with iodine, bromine, boron trifluoride, or arsenic trifluoride, the conductivity of polyacetylene approaches that of metals.¹¹

Since the discovery of polyacetylene, polymer chemists developed various categories of conjugated polymers. The most common unsaturated units are mono(poly)cyclic aromatic hydrocarbons, heterocycles, benzofused systems, and simple olefinic and acetylinic groups. Several common conjugated polymers are listed in Scheme 1.1. Besides polyacetylene (PA), polythiophene (PT), polypyrrole (PPy), Polyparaphenylene vinylene (PPV), polyparaphenylene (PPP) and other kinds of conjugated polymers and their derivatives were synthesized.¹²

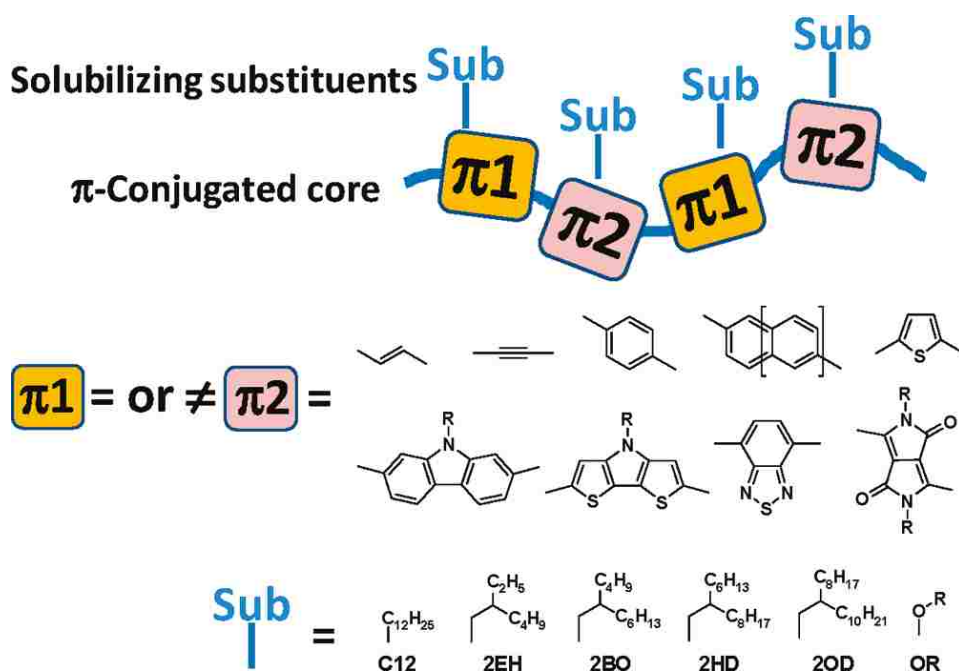
Scheme 1.1. Examples of conjugated polymers



Similar to polyacetylene, other types of conjugated polymer also have solubility issue. In order to process polymer films and other types of materials, solubility in common organic solvent is necessary. Introducing alkyl or alkoxy side groups to the polymer is the common method to promote the solubility in organic solvents. (Scheme 1.2)¹³ Because the improved solubility, the characterization of conjugated polymers becomes possible using

solution-based analytical techniques, and these modified polymers with side chains are widely studied.

Scheme 1.2. Conjugated polymers with alkyl or alkoxy side chains¹³

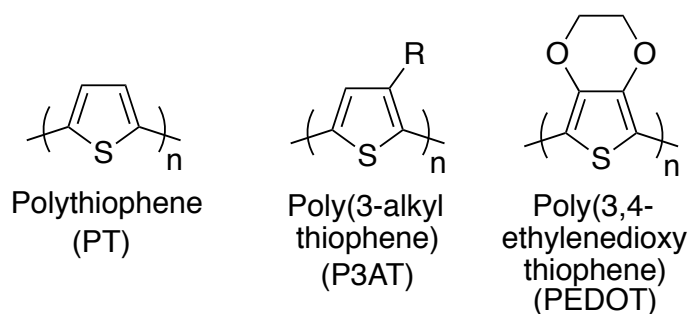


1.2.2 Polythiophenes and its derivatives

Polythiophene is one of the most important representative class of conjugated polymers. The category of polythiophene usually includes thiophene units linked either in 2,4- or 2,5- position, but the most wellknown polythiophene is the type with 2,5- position linkages. Polythiophene and its derivatives are relatively environmentally and thermally stable, and can be used as electrical conductors, nonlinear optical devices, polymer LEDs, sensors, batteries, electromagnetic shielding materials, solar cells, electrodes, nanoswitches, optical modulators and valves, and transistors, etc..⁹ Scheme 1.3 showed some of the examples of polythiophene and its derivatives, including poly(3-alkylpolythiophene) (P3AT) and Poly(3,4-ethylenedioxythiophene) (PEDOT), which are

the most commonly studied polythiophene derivatives. Because of introducing the side chains, which improved the solubility, these polymers can be processed in solution for materials applications. The development in synthesis of these polymers also brings higher performance of materials.

Scheme 1.3. Polythiophene and its derivatives



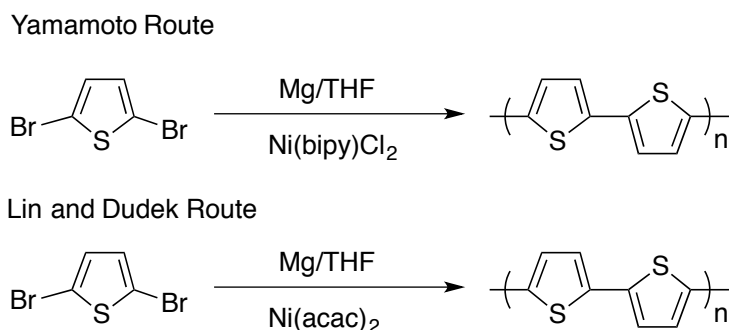
1.2.3 Synthetic methods towards polythiophene

Synthetic methods towards polythiophene and its derivatives includes electrochemical polymerization, chemical oxidative polymerization and metal-catalyzed cross-coupling polymerization. Sugimoto reported the synthesis of PT by treating thiophene with ferric chloride for oxidative cationic polymerization.¹⁴ Kaneto synthesized polythiophene perchlorate electrochemically in an electrolyte of 0.5 M silver perchlorate and 0.2 M thiophene in acetonitrile.¹⁵ Waltman polymerized thiophene monomer electrochemically with 0.1 M electrolyte in acetonitrile with platinum electrode.¹⁶ Kim used chemical oxidative polymerization with ferric chloride / hydrogen peroxide system to synthesize polythiophene particles in water.¹⁷ Although polythiophene can be synthesized via both electrochemical polymerization and chemical oxidative polymerization, the development

of metal-catalyzed coupling reactions is more rapidly due to its advantage in simpler reaction system and higher purity of resulting product.

Now metal-catalyzed cross-coupling polymerization is the most widely used synthetic method to produce polythiophene. The first catalytic chemical preparation of unsubstituted polythiophene was reported in 1980. Yamamoto treated 2,5-dibromothiophene with Mg in THF, and polymerize in the presence of Ni(bipy)Cl₂ as catalyst.¹⁸ Lin and Dudek found similar results using Pd, Ni, Co, or Fe catalytic systems.¹⁹ The resulting PT polymers in these studies is not soluble for MW higher than 3000, which limited the applications. Other synthetic routes with changes including using different kinds of catalysts were also developed, but have similar limitations.⁹

Scheme 1.4. Synthetic routes for unsubstituted polythiophene



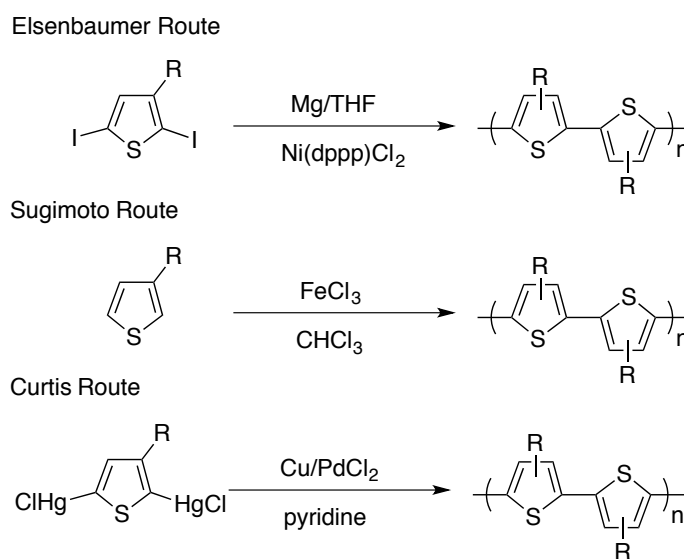
1.2.4 Synthetic methods towards poly(3-alkylpolythiophene)

Compared to unsubstituted polythiophene, its derivatives with substituent groups achieved better solubility in organic solvents. One of the most deeply studied polythiophene derivatives is poly(3-alkylpolythiophene) (P3AT).

The first chemical preparation of P3AT was done by Elsenbaumer using Kumada cross-coupling.²⁰ Equal equivalent of 2,5-diiodo-3-alkylthiophene and magnesium reacted in THF to generate a mixture of Grignard species. Catalytic amount of Ni(dppp)Cl₂ was added and polymer was generated by coupling reaction. P3AT can also be synthesized from 2,5-diiodo-3-alkylthiophene and zero-valent nickel catalyst.²¹

Besides metal-catalyzed cross-coupling polymerization, oxidative polymerization using FeCl₃ was first reported in 1986 by Sugimoto.²² 3-alkylthiophene monomer reacts with FeCl₃ and generates HCl gas. Curtis developed another method to polymerize 2,5-bis(chloromercurio)-3-alkylthiophenes using Cu power and catalytic amount of PdCl₂ in pyridine.²³

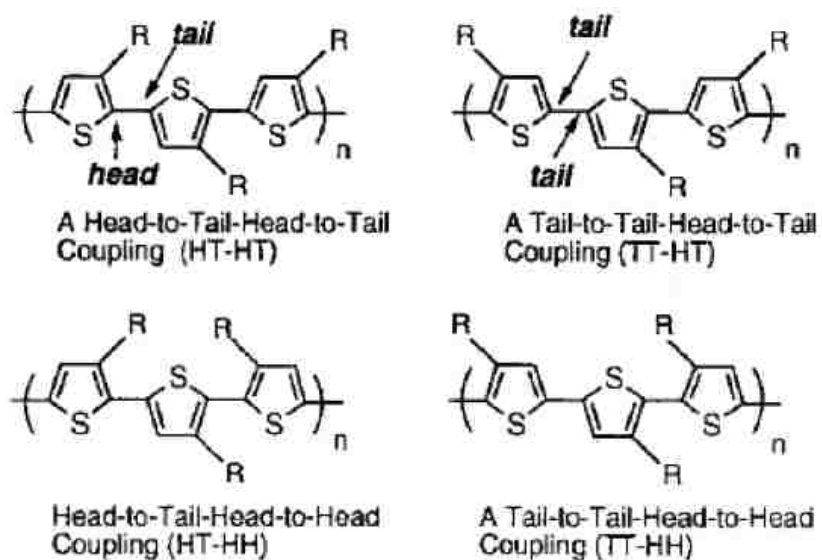
Scheme 1.5. Synthetic routes for substituted polythiophene



These methods can yield polymers in high molecular weight, but PDI of resulting polymer is broad (around 2), which showed the polymerization is more like a step-growth polymerization, and the control is even worse in some cases (higher than 2). Another issue

is by introducing alkyl side chains, the asymmetry of 3-alkylthiophene brings regiochemical control into account for P3ATs. There are three relative orientations when two thiophene rings are coupled between 2- and 5- positions: 2,5'- or head-to-tail coupling (HT), 2,2'- or head-to-head coupling (HH), 5,5' or tail-to-tail coupling (TT). This leads to four chemically distinct triad regioisomers when three monomer units linked together. (Shown in Scheme 1.6) The chemical shifts of aromatic protons in different conformations showed in $^1\text{H-NMR}$ are HT-HT (6.98), TT-HT (7.00), HT-HH (7.03), TT-HH (7.05) for P3HT, which could be used to determine the regioregularity of polymers synthesized.²⁴

Scheme 1.6. Regiochemical coupling possibilities in P3ATs⁹



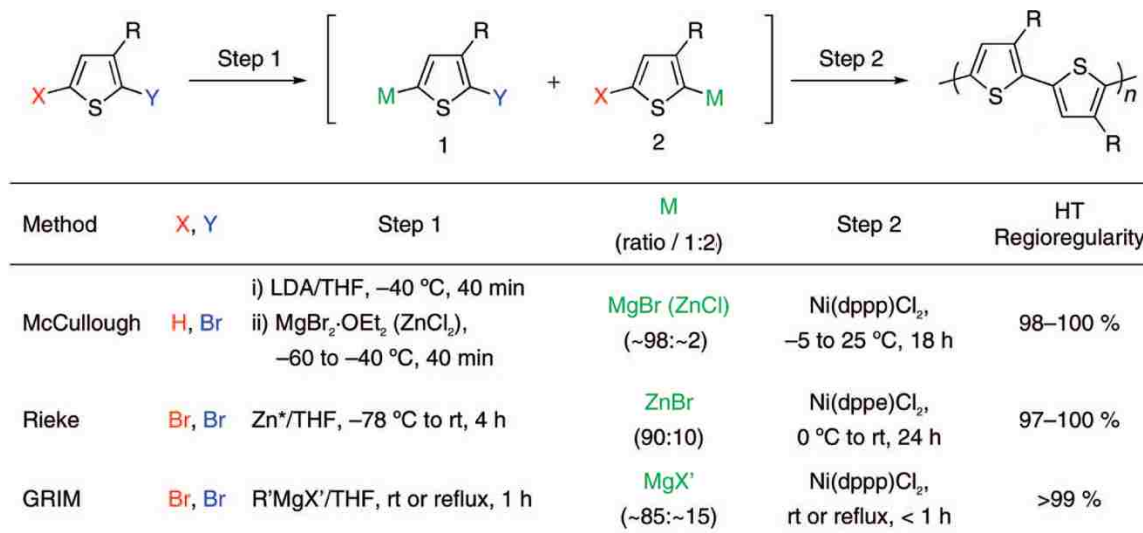
The structural irregularity of side groups introduced by insufficient regioselectivity in coupling results in loss of conjugation. Because the alkyl groups in HH conformation can twist the thiophene rings by steric hindrance effect, the desired properties of conjugated polymers such as conductivity decreases.⁹ The demand of synthesizing regioregular HT P3AT with highly conjugated polymer chain is high.

1.2.5 Synthetic methods towards regioregular P3ATs

Although there are three possible conformations for two adjacent substituted thiophene units, in order to get higher conjugation, the desired polymer conformation is only 100% HT. The synthetic strategies towards this kind of P3ATs utilize asymmetric coupling of asymmetric monomers in order to achieve regioregular HT-coupled structures of polythiophene derivatives.⁹

The first synthesis of regioregular HT P3AT was reported by McCullough in 1992.²⁵ This synthetic method uses 2-bromo-3-alkylthiophene treated with lithiation and transmetallation with MgBr_2 to regiospecifically generate 2-bromo-5-(bromomagnesio)-3-alkylthiophene, which is polymerized with catalytic amounts of $\text{Ni}(\text{dppp})\text{Cl}_2$ using Kumada cross-coupling to give P3ATs with 98-100% HT-HT couplings. Rieke treated 2,5-dibromo-3-alkylthiophene with activated Rieke zinc to generate the organozinc derivatives of 3-alkylthiophene, and then further polymerized with $\text{Ni}(\text{dppp})\text{Cl}_2$ as catalyst to generate regioregular poly(3-alkylthiophene).²⁶ This method can also achieve similar regioregularity compared to McCullough method. Although P3ATs with high regioselectivity can be synthesized via these two synthetic routes, it requires low temperature in metal halogen exchange step. The improvement of regioselectivity in these two methods broadened the application of P3ATs for enhanced electrical and optical properties. But the strict reaction condition limits the wide utilization of the polymerization method.

Scheme 1.7. Synthetic methods for regioregular P3ATs²⁷



Grignard metathesis (GRIM) polymerization was developed by McCullough in 1999, which allows the preparation of P3ATs in large scale at room temperature.²⁸ In this method, 2,5-dibromo-3-alkylthiophene is treated with one equivalent of Grignard reagent to form a mixture of regioisomers 1 and 2 (in Scheme 1.7) in a ratio of 85:15 to 75:25.²⁹ This ratio appears to be independent to the reaction time, temperature, and the influence of using different Grignard reagents appears to be small. Although the ratio of the desirable to undesirable isomers is lower in this method compared with the McCullough and Rieke methods, this method still affords HT P3ATs with high regioregularity of over 99%. This method can be used to synthesize P3ATs with well-defined MW and narrow PDI. Yokozawa's group also reported nickel catalyzed cross-coupling polymerization of using 2-bromo-5-iodo-3-hexylthiophene as monomer precursor.³⁰ GRIM polymerization is also referred to as Kumada catalyst-transfer polycondensation (KCTP) as proposed by Kiriy.³¹

As the general mechanism of transition-metal-catalyzed cross coupling reactions, GRIM polymerization involves a catalytic cycle of three consecutive steps: oxidative addition, transmetalation, and reductive elimination. Since nickel-catalyzed polymerization is formally a polycondensation reaction, it was generally supposed proceeding via a step-growth mechanism when this method was first reported. Yokozawa³⁰ and McCullough³² investigated the polymerization system and found it to be a chain-growth and living system. The evidences include the degree of polymerization increasing with monomer conversion, molecular weight predictable by loading ratio, end-group changeability by addition of various Grignard reagents at the end of polymerization, and ability of chain extension. According to these features, a mechanism was proposed as showed in Scheme 1.8. The first step of the reaction is 2 equivalent of monomer react with Ni(dppp)Cl₂, and form an associated pair of 2,2'-dibromo-3,3'-dialkyl-5,5'-bithiophene (a TT coupling product) and Ni(0) through reductive elimination. Then it undergoes fast oxidative addition to the nickel center and generates a new organonickel compound. Transmetalation further occurs and the polymer chain propagates by the insertion of one monomer at a time as shown in the reaction cycle through oxidative addition, transmetalation, and reductive elimination. The mechanism proposed showed the reason for the living feature of GRIM polymerization. Because the Ni catalyst formed associated pair with the polymer chain, and then moved to polymer chain end and insert by oxidative addition, one catalytic nickel center always associate with one polymer chain, which is the key feature to achieve a living polymerization.

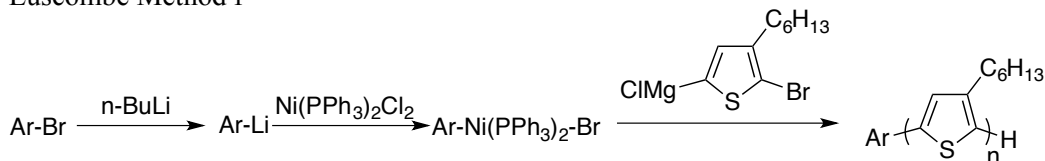
The first external initiator was synthesized by Kiriy in 2008.^{33,31} $\text{Ni}(\text{PPh}_3)_4$ undergoes oxidative addition with various aryl halides such as bromobenzene or orthobromotoluene, to give adducts $\text{Ar-Ni}(\text{PPh}_3)_2\text{-Br}$. When applied to GRIM polymerization system, although there are two types of isomers generated in situ, the reactivity of these two isomers are quite different, and only “regular” monomer 1 can be polymerized in the presence of “reversed” monomer 2. (Structures showed in Scheme 1.7) The polymer synthesized has low PDI and high regioregularity, which are comparable to in situ initiation systems. Almost 100% of the initiator Ar group was incorporated into the polymer for DP smaller than 30, but for DP above 30, reinitiation occurred resulting in a significant fraction of poly(3-hexylthiophene) (P3HT) with no initiator group. Luscombe used air-stable $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ precursor and n-butyllithium to react with aryl halides carrying different substituents to prepare $\text{Ar-Ni}(\text{PPh}_3)_2\text{-Br}$ initiators.³⁴ Further study using Nickel cyclooctadiene ($\text{Ni}(\text{cod})_2$) reacted with aryl halides followed by addition of two equivalent of monodentate ligand PPh_3 also showed end group controllability.³⁵ All the attempts mentioned above (Scheme 1.9) used monodentate ligands PPh_3 , although the end-group control is reasonable, limitations still exist for broader MW distribution and portions of polymer without desired end groups. These disadvantages are due to less interaction between polymer chain and Ni catalyst by the larger steric hindrance introduced by using monodentate ligands, which increases the chance for chain transfer to another polymer chain or monomer.

Scheme 1.9. Synthetic methods for P3HT via Ni initiator with monodentate ligands

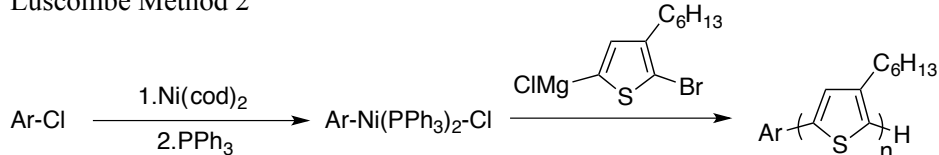
Kiriy Method



Luscombe Method 1



Luscombe Method 2

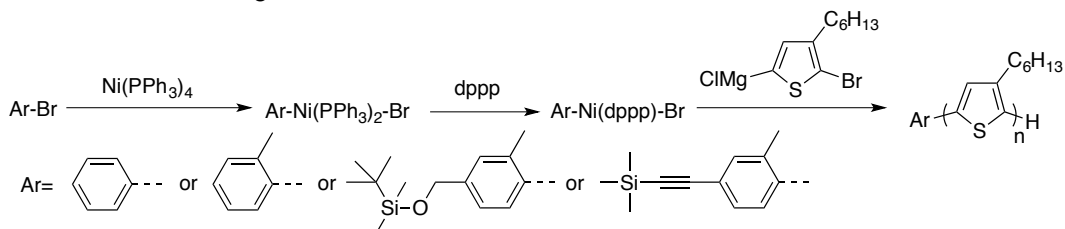


Generally the performance of Ni complex formed with bidentate ligands such as dppp or dppe showed much better control in polymerization compared to monodentate ligands PPh_3 .³⁶ To improve control of end group structure and reaction efficiency, initiators with bidentate ligands were synthesized. (Shown in Scheme 1.10) Luscombe further treated $\text{Ar-Ni(PPh}_3)_2\text{-Br}$ initiator with bidentate ligand dppp to generate Ar-Ni(dppp)-Br in situ.³⁷ Koeckelberghs synthesized series of initiators with different substituent groups on the aromatic ring of the initiator.³⁸ Senkovskyy, Sommer and Kiriy developed a synthetic route involving reaction of Ni(dppp)Cl_2 with sterically crowded Grignard reagents.³⁹ Another synthetic approach was also developed by Kiriy.^{40,41} Aryl halide reacts with $\text{Et}_2\text{Ni(bipy)}$, and the intermediate complex is further converted via ligand exchange. Nesterov developed a method via direct oxidative addition of Ni(dppp)_2 to aryl halides to synthesize Ni

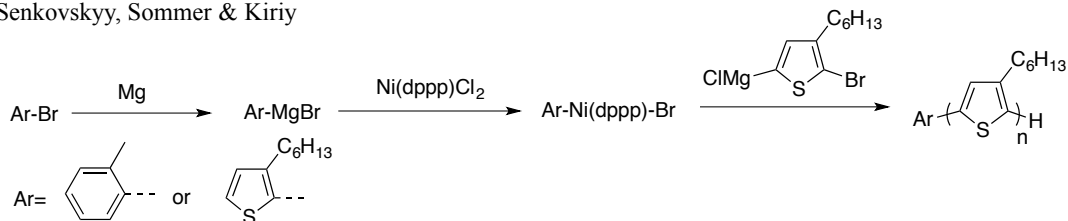
initiator.⁴² For all these methods, controlled molecular weight, low PDI and almost complete transfer of the initiator group were observed. Studies also showed the stability of these initiators is relatively low compared to traditional commercialized Ni(dppp)Cl₂, and aryl-aryl homocoupling may occur for several cases.^{39,42} Due to these disadvantages, initiators with bidentate ligands have to be synthesized by ligand exchange reactions in situ. The relatively complicated synthetic procedure still limits the wide application of these initiators.

Scheme 1.10. Synthetic methods for P3HT via Ni initiator with bidentate ligands

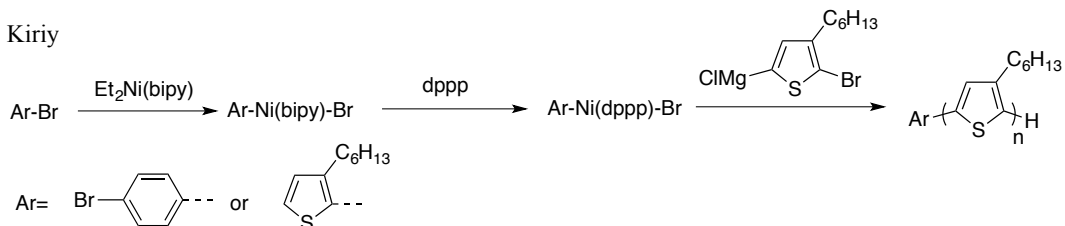
Luscombe & Koeckelberghs



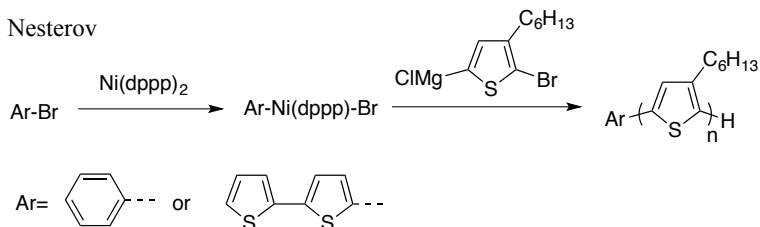
Senkovskyy, Sommer & Kiriy



Kiriy



Nesterov



1.2.7 In situ end-capping for GRIM polymerization

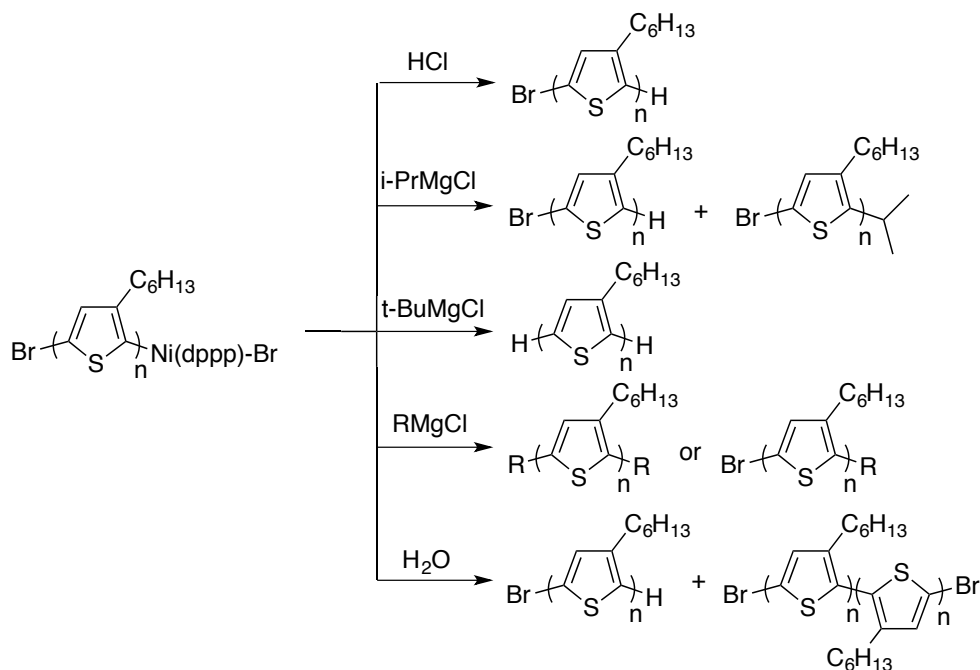
Modification of end-groups of polymers is attractive for its potential use in synthesizing block copolymers. For P3ATs, besides the attempts of introducing functional end-group onto P3ATs by using specially designed Ni complex bearing the functional group as external initiators, another considerable way of end-group modification is post-polymerization modification of the chain end. Regular methods for end-group modification involves several steps, but the living feature makes the in situ end-capping of GRIM polymerization possible.

The termination in GRIM polymerization was studied by Yokozawa first in 2004.³⁰ The termination by using water have part of product generated through disproportionation. But when treated reaction solution with 5 M HCl, there is no disproportionation and end-groups are more restricted to Br/H. Yokozawa further investigated the influence of the amount of Grignard reagent used for the conversion of 2-bromo-3-hexyl-5-iodothiophene into the active monomer to the end-groups of P3HTs.⁴³ When using 0.80 or 1.20 eq. *i*-Pr-MgCl for the preparation of the active monomer, the MW distribution became broad. When using 0.95-1.05 eq. *i*-Pr-MgCl, polymer with low PDI and controlled MW was obtained. However, 1.05 eq. of *i*-Pr-MgCl resulted in a fraction of *i*-Pr-terminated P3HT. This study showed that excess *i*-Pr-MgCl may compete with the active monomer and result in chain termination. When using *t*-Bu-MgCl as the Grignard reagent for reaction, there was no *t*-Bu-terminated P3HT observed. These results suggest that if there is excess Grignard

reagent present in the reaction system, end-groups of polymer could be changed. The type of Grignard reagent also plays a role in determining end-group structures.

Intentional end-capping by using an excess of a Grignard reagent was first reported by McCullough.^{44,45} By in situ addition of Grignard reagent after polymerization step either mono-capped or di-capped P3HTs can be synthesized based on the structure of Grignard reagents used. When the end group is allyl, ethynyl, or vinyl group, the nickel catalyst is proposed to be bound to the end group through a nickel- π complex, and mono-capped P3HT is observed. When the end group is aryl, di-capped product is observed. This in situ end-capping method became a popular route toward the preparation of P3HT macroinitiators, and was used for synthesizing rod-coil block copolymers. The synthetic routes for P3HTs with different end groups are listed in Scheme 1.11.

Scheme 1.11. Synthesis of P3HTs with various end-groups by termination



1.2.8 Influence of the alkyl group of P3ATs on main chain interaction

For P3ATs, the backbone of the polymer is polythiophene, which has high tendency for aggregation by rod-rod interaction. This was proved by the study of properties of unsubstituted polythiophene. The substituted alkyl side chains, not only can be used to solubilize the polymer into organic solvents but also influence the polymer aggregation behavior. McCullough synthesized P3ATs with alkyl group as *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl groups via GRIM polymerization.²⁹ Causin systematically studied the crystallization and melting behavior of these polymers via DSC and WAXS, and found that the shorter the alkyl side chains, the less flexible is the polymer, and higher is the melting temperature of polymer.⁴⁶ Segalman synthesized P3AT with branched side chain, namely 2-ethylhexyl.⁴⁷ This P3EHT is a semicrystalline polymer similar to P3HT, but has much lower melting transitions compared to P3ATs with straight side chains. The rod-rod interaction is reduced by introducing the asymmetric branching on the side chain, which leads to higher order microstructural control. Koeckelberghs synthesized P3ATs with an increasing degree of bulkiness of the alkyl side chain.⁴⁸ When the bulkiness of the polymers' side chain increases, the aggregation diminishes. These studies point out a direction for further studies to design and tune the phase behavior of P3ATs and their block copolymers.

1.3 Introduction to polyelectrolytes

Polyelectrolytes are polymers carrying either positively or negatively charged ionizable groups in each repeating unit.⁴⁹ Based on the charge on the polyelectrolytes, the two main categories are polyanions and polycations. Electrostatic interactions between

charges lead to different behavior either in solution state or solid state compare to those of uncharged polymers (e.g., ion conducting properties). Examples of polyelectrolytes include polystyrene sulfonate, polyacrylic and polymethacrylic acids and their salts, DNA and other polyacids and polybases.

1.3.1 Synthetic methods towards polystyrene sulfonates

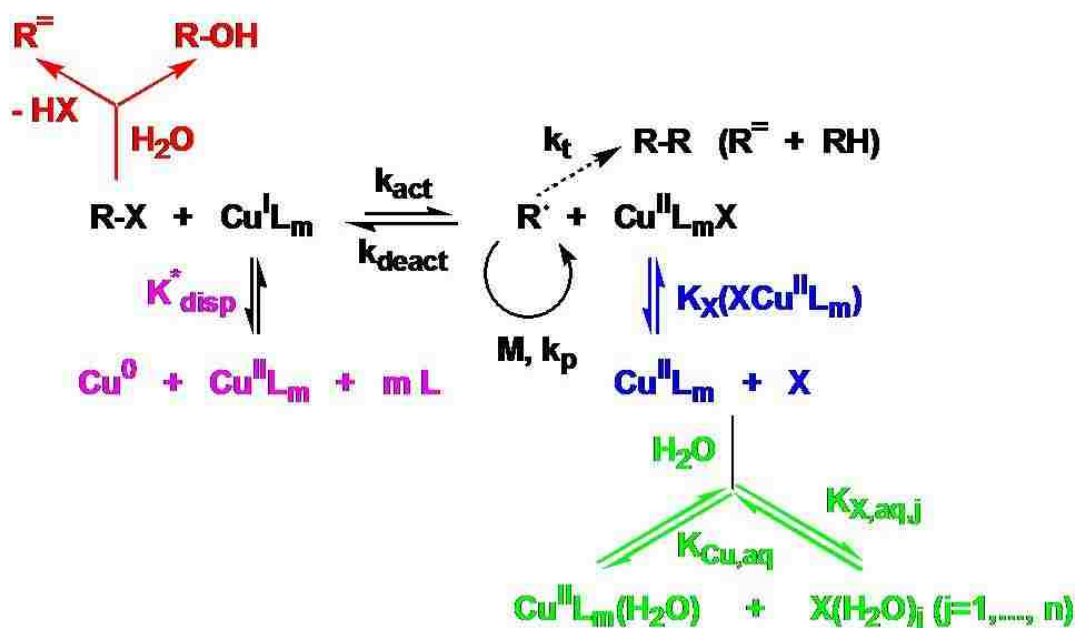
Polystyrene sulfonate (PSS) is a polyelectrolyte widely used in concrete additives, ionexchange resins, membranes, medicines, polymeric stabilizers for emulsion polymerization, and polymeric dopant for conducting polymers.^{50,51} The traditional synthetic method of PSS is typically carried out via sulfonation of polystyrene (PS) using concentrated sulfuric acid, acetyl sulfate or sulfur trioxide.⁵¹ Although Coughlin tried to improve the sulfonation to synthesize PSS with no crosslinking and 100% sulfonation, which cannot be achieved in traditional synthetic methods, the PSS still contains about 6% with meta substitution, which made to polymer still not regular.⁵⁰ PSS with all para substitution still cannot be synthesized through traditional sulfonation method.

Synthesis of PSS was also achieved by polymerization of sodium 4-styrenesulfonate in protic media via controlled polymerization techniques. These attempts successfully synthesized PSS with controlled MW and low PDI. Keoshkerian used nitroxide-mediated polymerization (NMP) in mixture solvent of ethylene glycol/water.⁵² Rizzardo used reversible addition-fragmentation chain transfer (RAFT) polymerization in water.⁵³ Kim⁵⁴ and Armes⁵⁵ synthesized PSS via atom transfer radical polymerization (ATRP) in water or

a mixture solvent of methanol/water. These attempts showed promising results in achieving PSS with all sulfonate groups at para position.

Above mentioned controlled polymerizations in protic media still have limitation in yielding PSS with high MW. The control of polymerization is also not as good as that in non-protic media. Such as in ATRP, this phenomenon is contributed to several complex equilibria competitions including disproportionation of the Cu^{I} complex (K_{disp}), reduction in the concentration of the copper^{II} based deactivator via dissociation of the halide ligand (K_X), complexation of the dissociated complex or ligand with the solvent and/or the polar monomers ($K_{\text{Cu,aq}}$ or $K_{\text{X,aq,j}}$), disproportionation or hydrolysis of the initiator or dormant chain end for termination. These factors influence the efficiency of ATRP.⁵⁶ The deactivation and termination reactions in this complex system prohibit the elongation of polymer chains and promote the increase in PDI.

Scheme 1.12. Equilibria competition in protic media for ATRP⁵⁶



1.3.2 Synthesis of PSS derivatives by controlled polymerizations

Another approach to synthesize PSS is to firstly synthesize PSS derivatives, namely polystyrene sulfonate esters, and use consecutive hydrolysis or thermolysis for deprotection. The styrene sulfonate ester monomer can be polymerized via various living radical polymerization techniques, such as NMP by Okamura⁵⁷, ATRP by Wegner⁵⁸, and RAFT by Topham⁵¹. These controlled polymerization techniques resulted in high MW and low PDI polymers with well-defined structures, which cannot be obtained by traditional methods. The living feature of these synthetic methods also is useful for making block copolymers. For ATRP and RAFT, another advantage is that the end-groups of polymers can be controlled, and may be used for further chemical treatments for synthesizing block copolymers. Among these methods, ATRP is of interest for its simplicity in synthesis of polymers with various functional end-groups, such as azido group.⁵⁹

Chapter II. Design of synthetic route for P3EHT-*b*-PSS

2.1 Objectives

BCP containing both conjugated polymer block and polyelectrolyte block - P3EHT-*b*-PSS is of interest to access nanostructured polymers with tunable morphologies resulted from microphase separation. For this typical rod-coil BCP, by using P3EHT instead of P3HT, the liquid crystalline interaction between conjugated polymer segments can be reduced, which can enable access to morphology commonly observed for coil-coil BCPs. The morphology of the BCPs can be tuned by controlling relative volume fraction of constituent blocks, the total MW of polymers, processing condition and interfacial energy (in thin film configuration). The polymer thin films with lamellar morphology that parallels the substrate have potential uses of making Faraday effect sensor for its extraordinary high Verdet constant compared to common inorganic materials.^{60,61} The BCP thin films with macroscopically aligned hexagonal morphology will also have potential uses as artificial photosynthesis membrane where both electrical and ion conductivity is required.⁶² This study mainly focuses on the synthesis of P3EHT-*b*-PSS, while the characterization of the materials properties will be pursued in future. Synthetic strategies towards BCPs containing P3AT block will be investigated to enable convenient and efficient access of this material.

2.2 Review on synthetic routes for BCPs containing P3AT block

Conjugated polymers are rod-like polymers, which is quite different from traditional coil-like polymers. The development of GRIM polymerization made the synthesis of

P3ATs with high regioregularity and low PDI possible, which results in much more well-defined structure of conjugated polymers.

BCPs containing P3AT block can be classified in two categories, all-conjugated BCPs and partially conjugated BCPs. The synthesis of all-conjugated BCPs is conducted by sequential addition of two or more types of monomers into the reaction system in a one-pot process. The most common initiator used is the traditional Ni(dppp)Cl₂ or Ni(dppe)Cl₂. Usually the P3AT block is synthesized first (normally P3HT), and a second monomer which can be polymerized by Ni catalyst was added consecutively to yield desired polymer. The second block is not limited to P3AT with different alkyl group, such as dodecyl³², 2-ethylhexyl⁶³, octyl⁶⁴, and cyclohexyl⁶⁵, but also can be other monomers such as 3-hexylselenophene⁶⁶, and *n*-decyl 4-isocyanobenzoate⁶⁷.

Compared to all-conjugated BCPs, the phase behavior of partial-conjugated BCPs is more complicated. Based on the monomer used for synthesizing the non-conjugated block, the block could be either rigid like a rod (such as PBLG)⁶⁸ or flexible like a coil (such as PS).⁶⁹ Several groups have attempted the successful synthesis of BCPs containing P3AT block with different coil blocks.

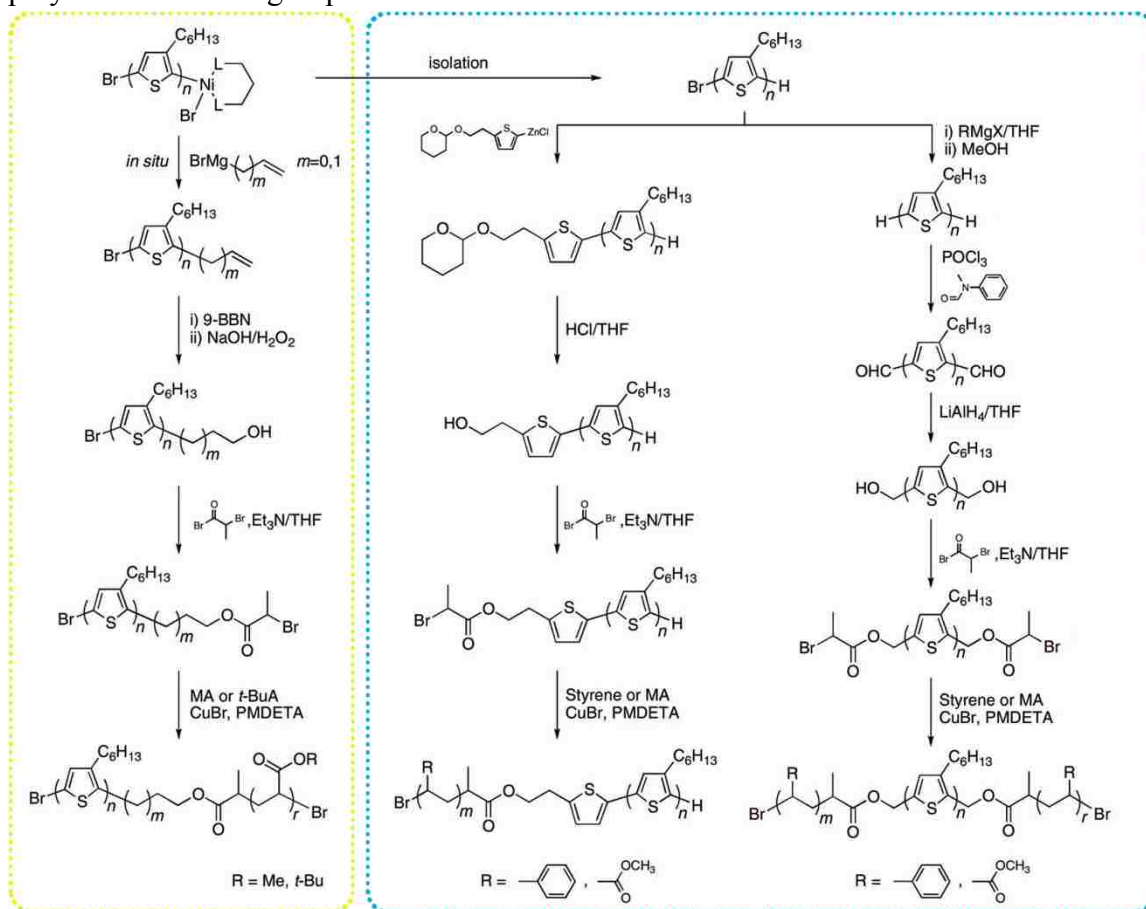
The synthetic routes for P3AT BCPs can be divided into three categories. The first synthetic route mainly uses two consecutive steps to synthesize two or three blocks of polymers. In this method, several steps of post-polymerization treatments are usually required to convert end-groups of P3ATs to appropriate initiation sites in order to grow the second block. The first synthesis of diblock and triblock copolymers containing P3HT

block was reported by McCullough⁷⁰. P3HT block was synthesized by McCullough method, then several post-polymerization reaction steps was used to convert end-groups for synthesizing the second block of polystyrene or poly(methyl acrylate) by ATRP.

The development of in situ end-capping strategy has also simplified the BCP synthesis because end groups of P3ATs can be modified by simple addition of different Grignard reagents. The end-groups of P3ATs can be changed to much more reactive groups other than H and Br from regular GRIM polymerization to simplify the end-group modification process. P3ATs with vinyl or allyl group were synthesized and can be directly used for synthesizing block copolymer by ring-opening metathesis polymerization (ROMP).⁷¹ The allyl group can be modified to hydroxypropyl group, and further changed into other initiation moieties for controlled radical polymerization such as NMP, ATRP or RAFT. BCPs with a P3AT block and a coil block such as polystyrene⁷², polyisoprene⁷², poly(methyl acrylate)⁷³, poly(t-butyl acrylate)⁷³, poly(methyl methacrylate)⁷⁴, poly(t-butyl methacrylate)⁷⁴, poly(isobornyl methacrylate)⁷⁴, poly(acrylic acid)⁷⁵, poly(2-(dimethylamino)ethyl methacrylate)⁷⁶, poly(fluorooctyl methacrylate)⁷⁷, and poly(4-vinylpyridine)⁷⁸ were synthesized through this pathway. Several other attempts by modifying end-groups for anionic polymerization or cationic ring-opening polymerization including synthesis of BCPs containing poly(2-vinylpyridine)⁷⁹, poly(tetrahydrofuran)⁸⁰, poly(2-ethyl-2-oxazoline)⁸¹ This synthetic method involves several reactions to convert end-groups of P3AT. Although the conversion for each step can be high, the complexity of multi-step synthesis still limits the application, especially the polymerization for the

second block need to be accomplished in a suitable solvent which can dissolve P3AT block and also can be used for polymerization of the second block. This can pose a problem sometimes due to the poor solubility of P3HT in common solvents and solvent restrictions for polymerization to produce the other block.

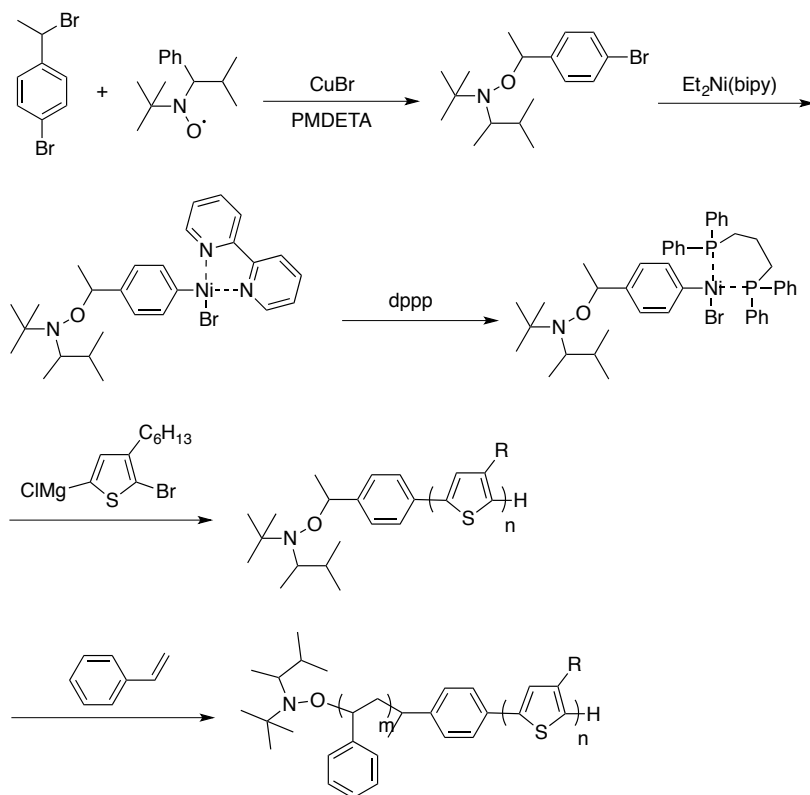
Scheme 2.1. Examples of synthesis of P3AT containing BCPs via in situ and post-polymerization end-group functionalization²⁷



The second synthetic route is using a bifunctional initiator to polymerize both blocks consecutively. Kiriy synthesized P3HT- b -PS by consecutive GRIM polymerization and NMP using a bifunctional initiator TIPNO-Ph-Ni(dppp)-Br (TIPNO = 2,2,5-trimethyl-4-

phenyl-3-azahexane-3-nitroxide).⁸² This method is not well developed yet, because this initiator must be freshly made in situ because of its instability.

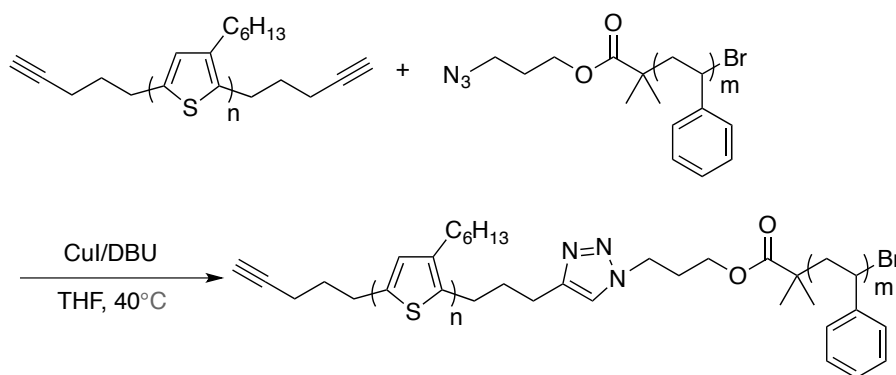
Scheme 2.2. Synthetic route using bifunctional initiator for P3HT-*b*-PS



The third synthetic route mainly synthesizes two separate polymer blocks with designed end-groups first, and then uses click chemistry to connect two blocks together. The end-groups of P3AT block can be modified by consecutive in situ addition of Grignard reagent after polymerization as mentioned above. McCullough used allyl terminated P3HT and living poly(styryl)lithium by coupling reaction to generate P3HT-*b*-PS.⁸³ The most widely used synthetic method to couple two polymer blocks is Cu-Catalyzed Azide-Alkyne Cycloaddition (CuAAC). Several P3AT containing BCPs were synthesized by CuAAC, such as P3HT-*b*-PS⁸⁴, P3AT-*b*-PEG⁸⁵, poly(3-dodecylthiophene)-*b*-poly(methyl

methacrylate)⁸⁶. The advantage of this synthetic route is that both blocks can be synthesized separately and then connected together, which is quite useful in tuning the length of each block in BCPs. The potential problem of this route is the need of finding a proper solvent to solubilize both polymer blocks for CuAAC. But THF is a good solvent for P3ATs and most of conventional polymer and can be used for CuAAC reaction.

Scheme 2.3. Synthetic route using CuAAC for P3HT-*b*-PS⁸⁴



2.3 Results and discussion

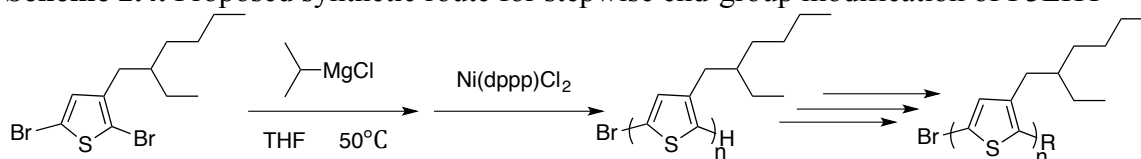
2.3.1 General synthetic route selection

Targeted BCP P3EHT-*b*-PSS has similar structure compared to P3HT-*b*-PS. Both P3EHT and P3HT are P3ATs, where the only difference is the alkyl group. PSS is a derivative of PS, which has a sulfonate group at the para position of styrene. Because of the similarity in structure, synthetic methods for P3EHT-*b*-PSS also can be divided to three directions.

In the first synthetic method, P3EHT block is synthesized first and then consecutive polymerization for PSS block will be conducted after the end-group modification of P3EHT. This method needs several steps to convert end-group to an initiator moiety.

(Scheme 2.4) No matter post-polymerization or in situ treatment used, the end-group of polymer obtained after polymerization cannot be directly used for polymerization of the PSS block, so multistep synthesis is still required. The complexity of reactions and purifications limits the efficiency of synthesis, which is not an optimum route for synthesizing P3EHT-*b*-PSS.

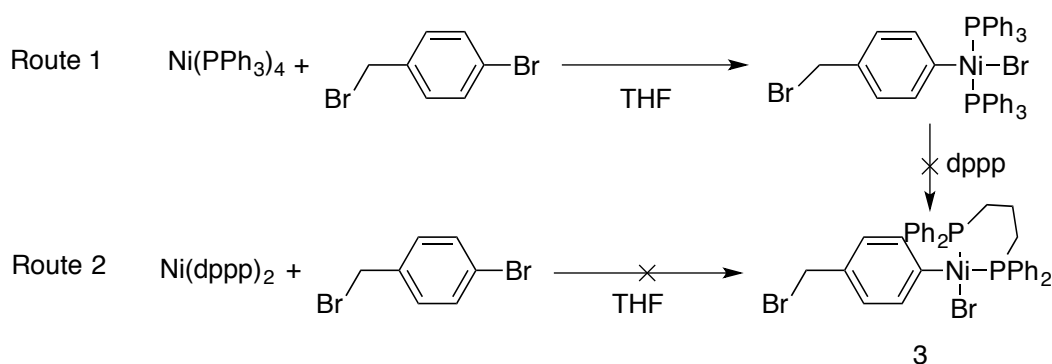
Scheme 2.4. Proposed synthetic route for stepwise end-group modification of P3EHT



The second synthetic method uses a bifunctional initiator to consecutively synthesize two polymer blocks. A bifunctional nickel initiators **3** with chelating dppp ligand are designed. (Shown in Scheme 2.5) The synthetic approaches of synthesizing **3** including two pathways using Ni (0) compound and 4-bromobenzyl bromide as starting materials. For route 1, when mixing both reagents in THF, precipitate formed in 15min, indicating the decomposition of product. After reducing the reaction time to 5 minutes in each step, the solution was directly used for initiating the polymerization of P3EHT, but polymer is not obtained after reaction. The instability of Ni complex prohibited the successful synthesis. For route 2, although ^{31}P NMR indicated formation of a new Ni complex, when using this in situ generated compound to initiate the polymerization for P3EHT, polymer can be synthesized, but the end group structures were not what expected from initiation by species **3** (Scheme 2.5). The exact end group structures presently remain unclear, but the disappearance of bromo end-group prohibited the synthesis of PSS block. One possibility

is that the Ni complex formed at the benzyl position instead of phenyl position, and previous study by Jamison also supported the possibility of forming a η^3 -Ni complex.⁸⁷ To further pursue the bifunctional initiator route to access P3EHT-*b*-PSS, synthesis and a complete characterization of a Nickel complex bearing bifunctional ligand with a different structural design are required

Scheme 2.5. Synthetic approaches towards bifunctional initiator



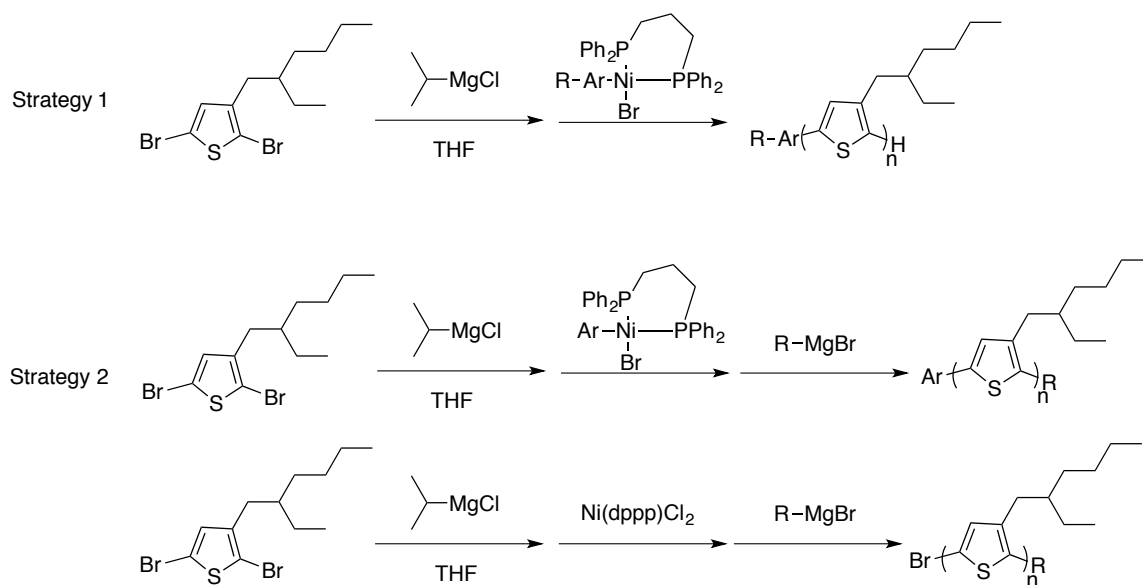
The third synthetic method separately synthesizes two polymer blocks with functional end-groups, and uses click chemistry to combine into a block copolymer. By reviewing previous published works for synthesizing BCPs containing P3AT block, P3EHT with terminal alkyne and PSS with azido end-group are designed for synthesizing BCP by CuAAC.

2.3.2 Synthetic strategy selection for P3EHT block with terminal alkyne

For synthesizing P3EHT block with terminal alkyne moiety, there are mainly two categories of synthetic strategies can be chosen from. The first strategy is polymerization using in situ generated external Ar-Ni(dppp)-X initiators which have alkyne moieties. The second strategy is introducing end-group with terminal alkyne moiety by in situ addition

of a Grignard reagent after polymerization. The initiator used could be either external Ar-Ni(dppp)-X initiators or traditional Ni(dppp)Cl₂. External Ar-Ni(dppp)-X initiators are first investigated because more accurate control of end-groups are expected.³⁹

Scheme 2.6. Synthetic strategies for P3EHT block with terminal alkyne moiety



R represents group with alkyne moiety

For synthesizing external Ar-Ni(dppp)-X initiators, by reviewing published synthetic methods, the method developed by Nesterov and coworkers was chosen to be further investigated for its simplicity in synthesis.⁴² Several aryl halides (listed in Scheme 2.7) were used to react with premade Ni(dppp)₂ to in situ generate Ar-Ni(dppp)-X. The first two trials used aryl halides with alkyne moieties, but the latter three used aryl halides without alkyne moieties, and end-capping by consecutive addition of Grignard reagent containing alkyne moiety is needed. For all trials, after reacted at room temperature or 50 °C in THF for 72h, the resulting solutions were checked by ³¹P NMR. Results showed that only reaction using 5-bromo-2,2'-bithiophene gave reasonable conversion. The

conversion of Ni(dppp)₂ monitored by ³¹P NMR was in the range of 22-37% when using 1:1 ratio of 5-bromo-2,2'-bithiophene/Ni(dppp)₂. By changing loading ratio to 2:1, the conversion of Ni(dppp)₂ reached 40-89%. But the reproducibility of this reaction still cannot meet the expectation. Although unreacted 5-bromo-2,2'-bithiophene and Ni(dppp)₂ cannot react with monomer during polymerization, homocoupling through disproportionation between two molecules of Ni initiator still may happen during the in situ preparation of Ni initiator, and generate Ni(dppp)Br₂, which can also act as an initiator for polymerization.⁴² This side reaction can reduce the controllability of end-groups. For this reason, to end-groups of P3HTs synthesized by this method were investigated, and polymers with H/Br were observed, indicating the formation of Ni(dppp)Br₂ side product in the preparation of Ni initiator.

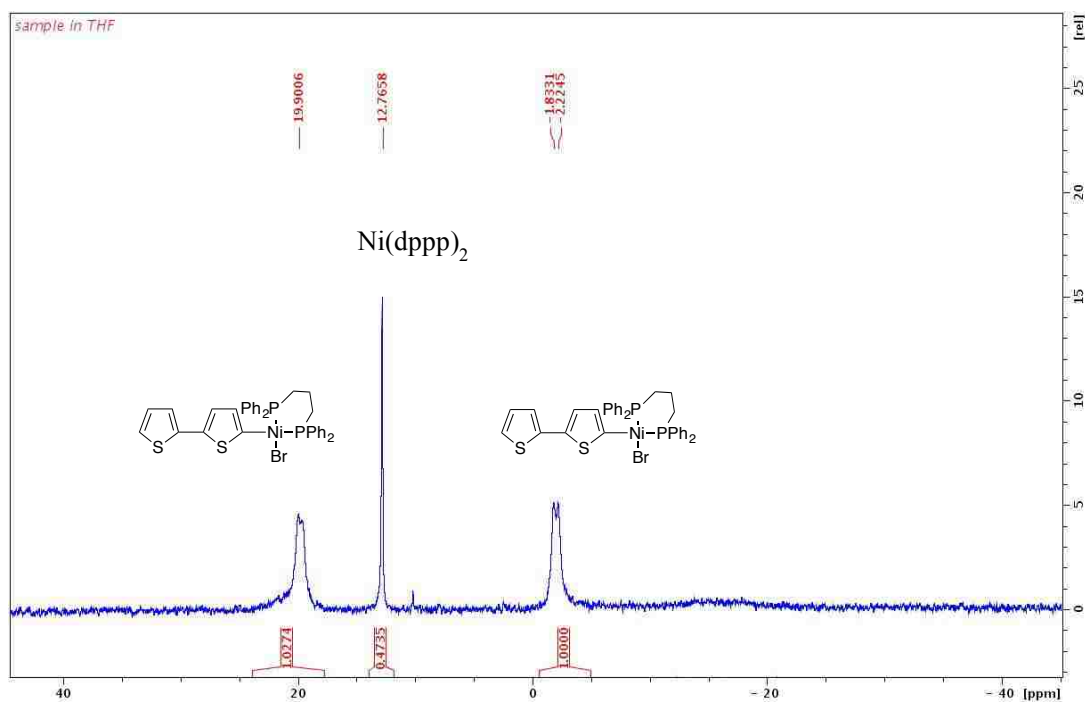
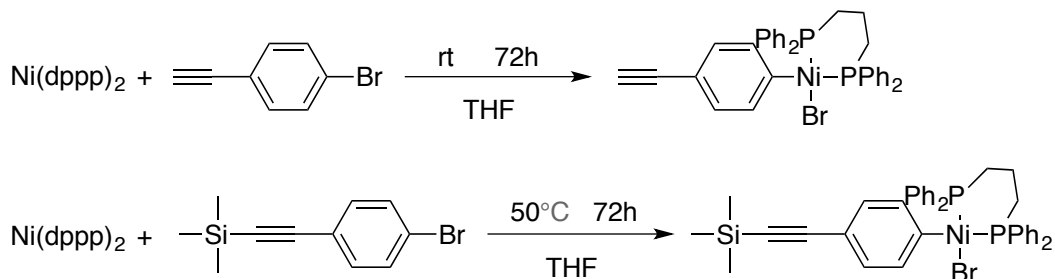


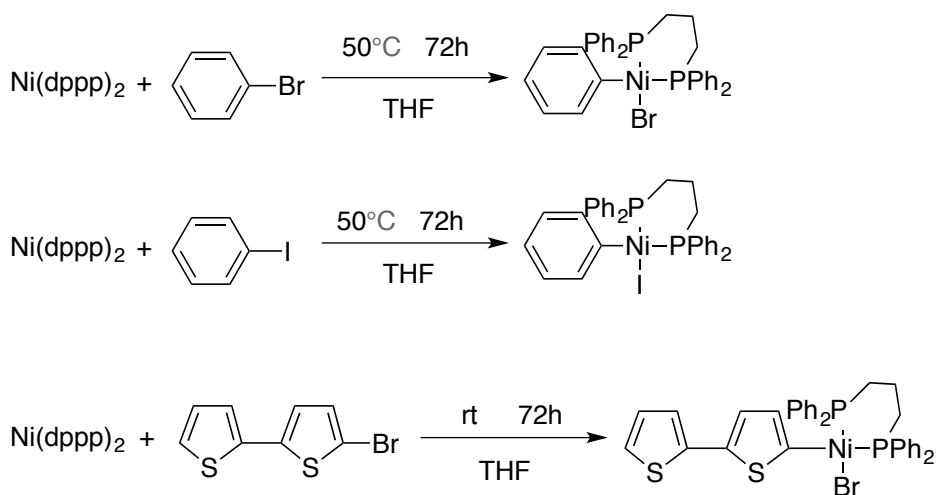
Figure 2.1. ³¹P NMR spectrum of Ni complex external initiator collected in THF-d₈. (5-bromo-2,2'-bithiophene/Ni(dppp)₂=2:1)

Scheme 2.7. Synthetic approaches towards external initiators

Initiators with alkyne moiety



Initiators without alkyne moiety



Polymerizations using bithiophene- Ni(dppp)-Br and Ni(dppp)Cl_2 initiators were conducted for comparison. Instead of using 2,5-dibromo-3-(2-ethylhexyl)thiophene as monomer, much more easily accessible 2,5-dibromo-3-hexylthiophene was used for studies of polymerization based on similar behavior in GRIM polymerization.⁴⁷ The results of polymerizations using bithiophene- Ni(dppp)-Br and Ni(dppp)Cl_2 initiators are summarized in Table 2.1. Under the same condition, the MW and PDI control of bithiophene- Ni(dppp)-Br initiator is worse compared to Ni(dppp)Cl_2 . Attempts of isolating bithiophene- Ni(dppp)-Br solid was not successful as well, so the initiator must be made

freshly, which limits the reproducibility. All above-mentioned drawbacks limit the application of this pathway.

Table 2.1. Molecular weight analysis of P3HT obtained by GRIM polymerization using bithiophene-Ni(dppp)-Br and Ni(dppp)Cl₂ initiators at varying [M]₀: [I]₀ ratio ^{a,b}

Initiator	[M] ₀ : [I] ₀	<i>M_n</i> (theo.) (kg·mol ⁻¹) ^c	<i>M_n</i> (SEC) (kg·mol ⁻¹) ^d	PDI ^d
bithiophene-Ni(dppp)-Br	45:1	7.6	8.7	1.90
bithiophene-Ni(dppp)-Br	90:1	15.1	10.8	2.10
bithiophene-Ni(dppp)-Br	180:1	30.1	11.4	2.40
Ni(dppp)Cl ₂	45:1	7.5	9.4	1.64
Ni(dppp)Cl ₂	90:1	15.0	15.8	1.44
Ni(dppp)Cl ₂	180:1	29.9	26.8	1.59

^{a.} All polymerizations were conducted at [M]₀=1.0 M in THF at room temperature for 2 h;

^{b.} The Grignard monomers used for polymerization were prepared by reacting 1 eq. of *i*-PrMgCl with 1 eq. of 2,5-dibromo-3-hexylthiophene ^{c.} theoretical molecular weights were calculated from the [M]₀: [I]₀ ratio; ^{d.} polymer molecular weights and the molecular weight distribution were determined by SEC relative to polystyrene standards.

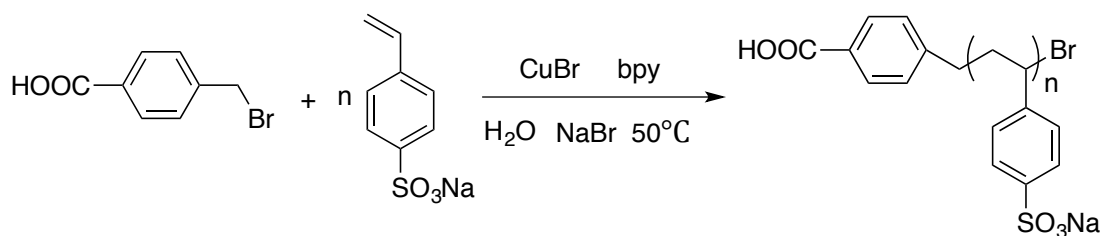
According to studies mentioned above, Ni(dppp)Cl₂ is selected as the initiator for synthesizing P3EHT block. All the detailed experimental studies of synthesizing P3EHT with terminal alkyne moiety will be discussed in Chapter III.

2.3.3 Synthetic strategy selection for PSS block with terminal azido group

Among all the synthetic methods for PSS mentioned in Chapter I, ATRP was selected for this particular project of synthesizing PSS block with terminal azido group. The advantages of ATRP include good control over MW and PDI, and easier accessibility of initiators and catalysts.

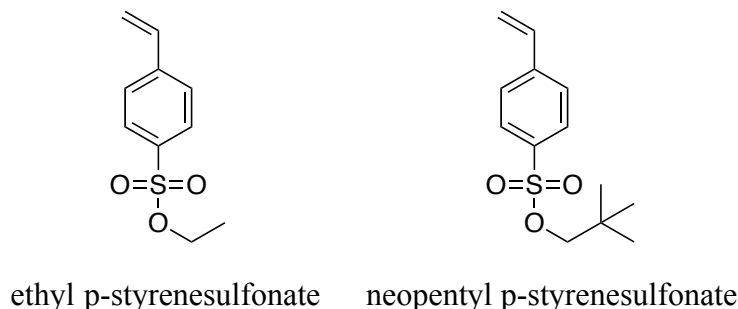
There are two routes for synthesizing PSS block. The first route is synthesizing PSS directly by polymerization of sodium 4-styrenesulfonate (SSNa) in protic media. 1 eq. NaBr compared to SSNa was added to keep excess sodium cation in solution, and 2 eq. of CuBr/bipy catalyst compared to initiator were used as well. The excess reagent is used to minimize the influence of interaction between Cu and sulfonate group, and maintain the concentration of active catalytic center. The conversion of reaction can reach 80%, but the Cu cannot be easily removed from the system by dialysis or ion exchange. The charges of polyelectrolyte prohibit the ion separation. The extra reagents also lower the atom economy of this reaction. These disadvantages limit the use of this synthetic route.

Scheme 2.8. Synthetic approaches towards PSSNa



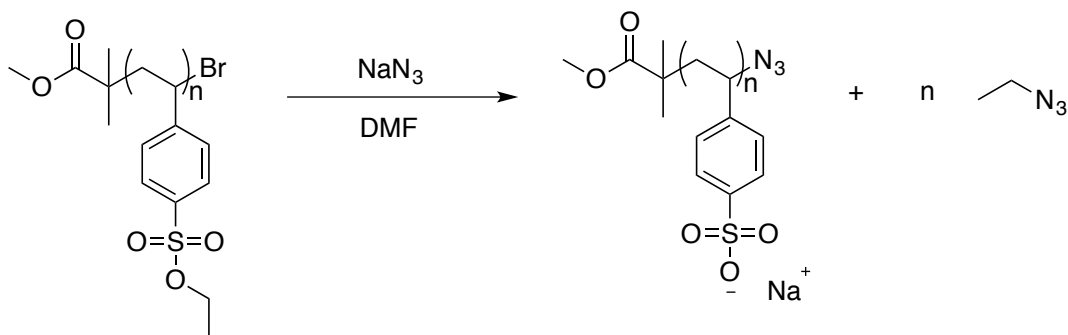
The second route is to synthesize PSS derivatives by ATRP first and use consecutive hydrolysis or thermolysis for deprotection. Styrene sulfonate ester monomers are used for polymerization because its stability under ATRP conditions and good control over MW and PDI. Ethyl p-styrenesulfonate monomer was investigated first, but because the monomer has a low melting point (is a liquid at room temperature), self-polymerization happened even stored at -30 °C in inert atmosphere after several weeks. The choice of monomer then switched to neopentyl p-styrenesulfonate, which is a solid at room temperature and stable under storage.

Scheme 2.9. Structure of styrene sulfonate ester monomers



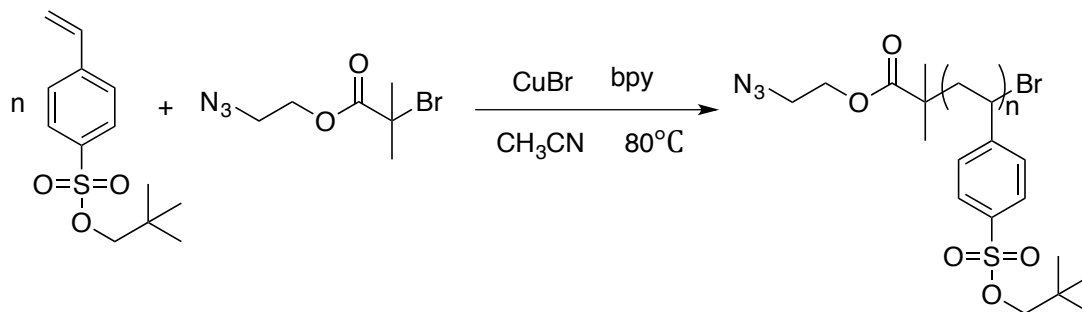
To incorporate azido end-group to PSS block, there are two major approaches. The first approach is chain end modification. In ATRP, nearly every chain should contain a halogen atom at chain end. This halogen atom can be replaced through a variety of reactions leading to chain end functionalities.⁸⁸ Nucleophilic displacement can be carried out by reacting with NaN_3 in DMF.⁸⁹ When trying to apply this end group functionalization method after synthesis of poly(ethyl p-styrenesulfonate) (PESS), the ethyl group was missing after stirring with NaN_3 . The possible reason for this phenomenon is that nucleophilic substitution can also occur at the polymer side chain other than polymer chain end. Styrenesulfonate which has the similar structure as tosylate, is a good leaving group in nucleophilic substitution reactions. With the presence of azide which behaves as a nucleophile in the azidation, the styrene sulfonate can also be taken off. In this reaction, not only the end-group of PESS was changed, but also the polymer was change to poly(sodium 4-styrenesulfonate) (PSSNa). The side product of this reaction is ethyl azide, which is explosive and highly toxic. Another disadvantage is that as the polymer is changed to polyelectrolyte, the CuAAC reaction in next step to connect both blocks still may have the problem of removing Cu from polymer.

Scheme 2.10. Reaction of PESS with sodium azide



The second approach is using of functional ATRP initiators containing azido group. The azido group can be incorporated to the polymer chain end directly by selecting a proper initiator, and all the other moieties in monomer will not be influenced under the reaction condition. Compared to the first approach, this method is convenient in handling because no further treatment is needed to acquire the desired end-group, and the reaction can be done in a single step. The most commonly used initiator is 2-azidoethyl 2-bromoisobutyrate⁸⁴, which is commercially available. Although the price of this reagent is relatively high, it is still acceptable because only limited amount is needed in reaction. Also, this method does not need to use sodium azide, which is not environmentally friendly. This method was selected for synthesizing PSS with azido moiety for above-mentioned advantages. The detailed synthesis of PNSS with functional ATRP initiators containing azido group will be discussed in Chapter III.

Scheme 2.11. Synthesis of PNSS with functional ATRP initiators containing azido group



2.4 Conclusions

Various synthetic strategies to synthesize P3EHT-*b*-PSS were evaluated. A bifunctional initiator was designed, but the Ni complex did not form as predicted, and the resulting P3EHT did not have the desired end-group structure. Several attempts for synthesizing P3EHT block with clickable alkyne moiety have been made. Among these trials, multiple Ni complex initiators were found to be unstable under the synthetic conditions. The only working Ni complex initiator with bithiophene moiety has its limitation in produce polymer with good control over MW and PDI. The best choice found is using $\text{Ni}(\text{dppp})\text{Cl}_2$ as initiator for synthesis of P3EHT block. For synthesizing PSS block with clickable azido moiety, direct polymerization of sodium 4-styrenesulfonate in protic media using ATRP has to use NaBr additive to maintain good control, but removing Cu from the system is challenging because the interaction between polymer chains and Cu cations. Using ATRP to synthesizing PSS derivatives – PESS or PNSS was found to be successful in producing PSS with controlled MW and PDI. 2-Azidoethyl 2-bromoisobutyrate was chosen as a functional initiator to incorporate azido moiety to the polymer. The final designed synthetic route for P3EHT-*b*-PSS is to independently

synthesize P3EHT block by using Ni(dppp)Cl₂ initiator and consecutive in situ end-capping for alkyne moiety, PNSS block with azido moiety by using 2-azidoethyl 2-bromoisobutyrate as initiator using ATRP method, and CuAAC for connecting these two blocks.

2.5 Experimental

2.5.1 Materials and instrumentation

All chemicals were used as received unless noted otherwise. ¹H NMR spectra were recorded on a Bruker AVIII-400. Chemical shifts were determined in reference to the protio impurities of deuterated solvents CDCl₃, D₂O or THF-d₈. Anhydrous deuterated tetrahydrofuran (THF-d₈) was obtained by stirring THF-d₈ (Sigma-Aldrich) over CaH₂ overnight followed by vacuum transfer. ³¹P NMR spectra were recorded on a Bruker AVIII-400. Chemical shifts were determined in reference to the external 85% H₃PO₄. Size exclusion chromatography (SEC) data were collected on an Agilent 1100 SEC with a set of two PLgel 5 μm MIXED-C and one PLgel 5 μm 1000 Å columns and a refractive index detector or UV-Vis detector. THF at 40 °C was used as the mobile phase at a flow rate of 0.7 mL/min. The instrument was calibrated with polystyrene (PS) standards (Polymer Laboratories). The MALDI-TOF MS experiments were carried out on a Bruker ultrafleXtreme tandem time-of-flight (TOF) mass spectrometer equipped with a smartbeam-IITM 1000 Hz laser (Bruker Daltonics, Billerica, MA). Prior to the measurement of each sample, the instrument was calibrated with Peptide Calibration Standard II consisting of a mixture of standard peptides Angiotensin I, Angiotensin II, Substance P,

Bombesin, ACTH clip 1-17, ACTH clip 18-39, and Somatostatin 28 (Bruker Daltonics, Billerica, MA). Samples were measured in positive reflector mode. 30 mg/mL trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in chloroform was used as the matrix in all measurements. Polymer samples were dissolved in THF at 1 mg/mL. The matrix and polymer samples were combined (v/v, 50/50). Samples (1 μ L) were deposited onto a 384-well ground-steel sample plate using the dry droplet method. Data analysis was conducted with flexAnalysis software.

2.5.2 Synthetic approaches towards end-functionalized P3EHT

Synthesis of Ni(dppp)₂. Ni(dppp)₂ was synthesized from a known procedure reported by Nesterov.⁴² In the glovebox, Ni(COD)₂ (550 mg, 2.0 mmol) and dppp (1.65 g, 4.0 mmol) was dissolved in ether (10 mL) and stirred at ambient temperature under a nitrogen atmosphere for 4 h. Resulting solid was filtered and rinsed with 60 mL ether. Orange solid was obtained and dried under vacuum. (1.31 g, 74.0%)

Synthesis of 3-(2-ethylhexyl)thiophene. The synthesis of 3-(2-ethylhexyl)thiophene was done by slightly modification of reported procedure.⁴⁷ The solution of 0.407 M 2-ethylhexyl magnesium bromide in diethyl ether (48.7 mL, 19.8 mmol) was added dropwise to the solution of Ni(dppp)Cl₂ (0.10 g, 0.019 mmol) and 3-bromothiophene (3.10 g, 18.9 mmol) in dry THF (20mL) at 0 °C by cannula under inert atmosphere. The solution was stirred at room temperature for 16 h and terminated by adding 25 mL 1 M HCl solution. 25 mL saturated NaHCO₃ was added to the solution, and the solution was extracted with 50 mL chloroform. The aqueous phase was washed with 25 mL chloroform for three times.

The organic solutions were combined and washed with 25 mL brine for two times. Solution was dried over MgSO_4 and concentrated by rotary evaporation and purified by column chromatography (eluent hexanes). (3.23g, 87.1%)

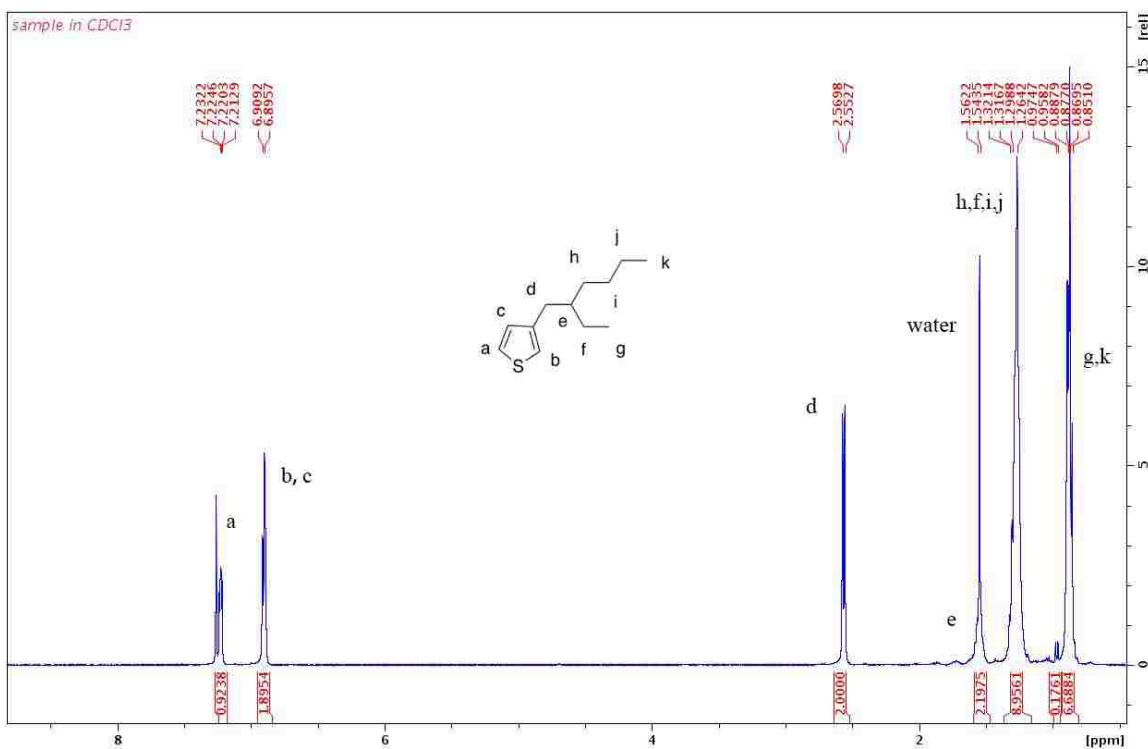


Figure 2.2. ^1H NMR spectrum of 3-(2-ethylhexyl)thiophene collected in CDCl_3

Synthesis of 2,5-dibromo-3-(2-ethylhexyl)thiophene. The synthesis of 2,5-dibromo-3-(2-ethylhexyl)thiophene was done by slightly modification of reported procedure.⁴⁷ N-bromosuccinimide (NBS) (8.55 g, 48.0 mmol) was added to 3-(2-ethylhexyl)thiophene (3.15 g, 16.0 mmol) in THF (150 mL) and stirred at room temperature for 4 h. The reaction was quenched by addition of 75 mL water and then the solution was extracted with 150 mL ether. The organic phase was washed with 10 wt.% aqueous sodium thiosulfate (150 mL), 10 wt.% aqueous potassium hydroxide (150 mL), and 1:1 brine/water (150 mL), and

was dried over MgSO_4 . Solution was concentrated by rotary evaporation and purified by column chromatography (eluent hexanes) to obtain colorless liquid. (5.11g, 90.0%)

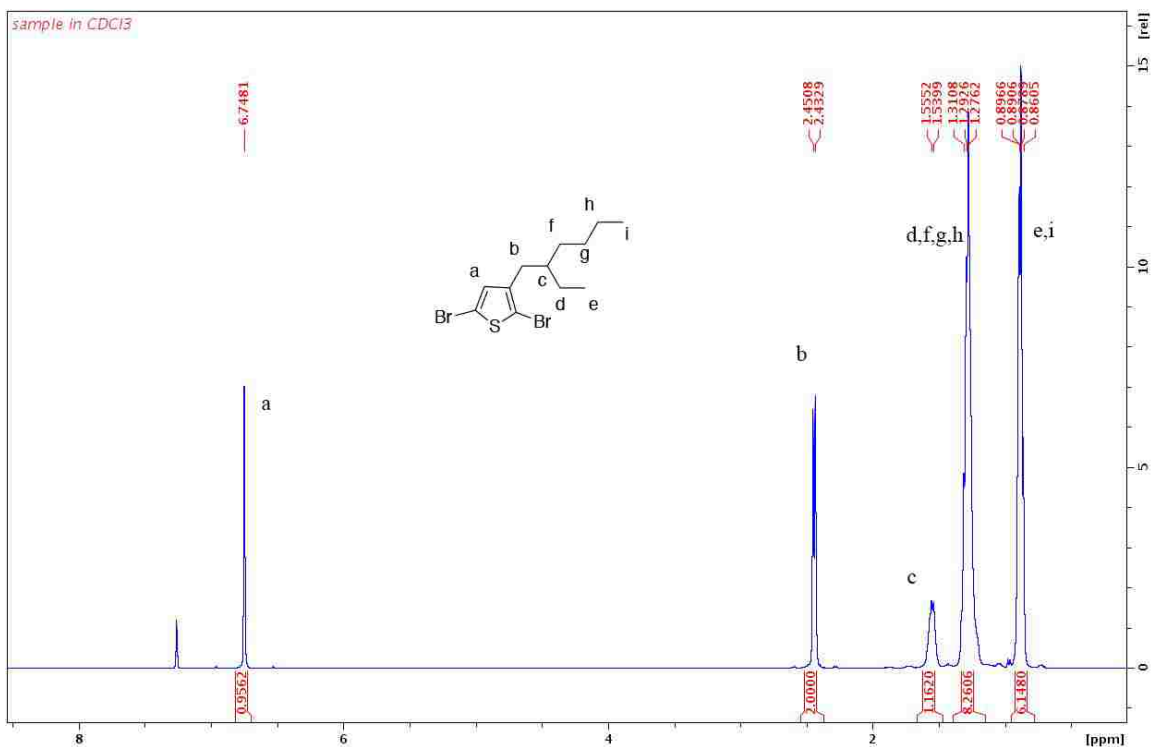


Figure 2.3. ^1H NMR spectrum of 3-(2-ethylhexyl)thiophene collected in CDCl_3

Synthetic approach towards Ni complex bifunctional initiator. In the glovebox, $\text{Ni}(\text{dppp})_2$ (18 mg, 0.020 mmol) and 4-bromobenzyl bromide (5.0 mg, 0.020 mmol) was dissolved in THF (2.0 mL) and stirred at ambient temperature under a nitrogen atmosphere for 2 h. Several drops of THF-d_8 was added to the solution and ^{31}P NMR was tested. Conversion was found 78.9% with unreacted $\text{Ni}(\text{dppp})_2$ left.

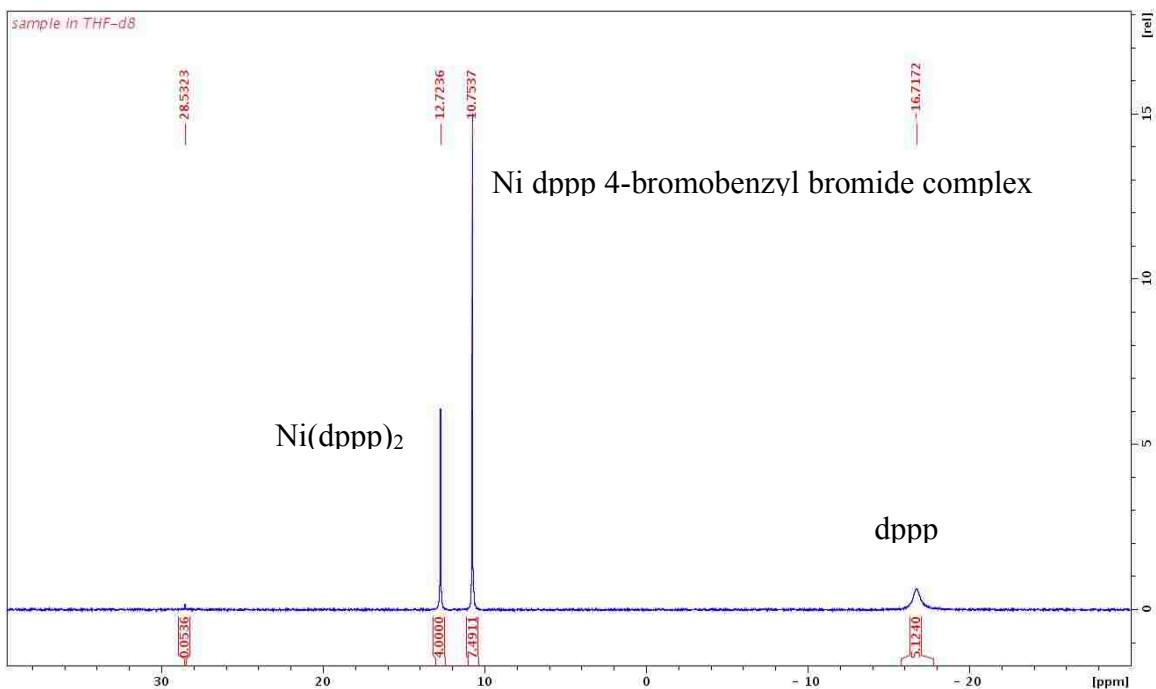


Figure 2.4. ^{31}P NMR spectrum of Ni complex bifunctional initiator collected in THF- d_8

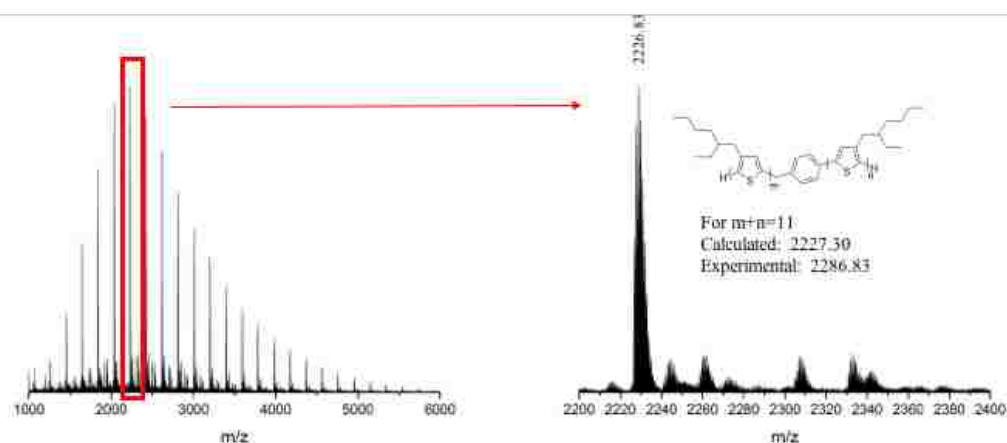


Figure 2.5. MALDI-TOF MS spectra of P3EHT obtained using Ni complex initiator ($[\text{M}]_0:[\text{I}]_0=25:1$, $[\text{M}]_0=0.1\text{ M}$, $50\text{ }^\circ\text{C}$, THF).

Subsequent polymerization for P3EHT using synthesized Ni complex. 2,5-dibromo-3-(2-ethylhexyl)thiophene (177 mg, 0.50 mmol) and 2.0 M isopropyl magnesium chloride (0.250 mL, 0.50 mmol) was mixed in THF (5.0 mL) and stirred at $50\text{ }^\circ\text{C}$ for 2 h. The in situ generated Ni complex solution (2.0 mL, 0.020 mmol) was added to the solution and stirred

at room temperature for another 2 h. Solution was added into 10 mL methanol and centrifuged. Solid was dissolved in 2 mL chloroform and added solution into 10 mL methanol and centrifuged to obtain red solid. (10 mg, 10.3%) MALDI-TOF MS result did not suggest desired end groups.

Representative synthesis of Ni complex external initiators. In the glovebox, Ni(dppp)₂ (88 mg, 0.10 mmol) and 5-bromo-2,2'-bithiophene (50 mg, 0.020 mmol) was dissolved in THF (5.0 mL) and stirred at room temperature under inert atmosphere for 72 h. Several drops of THF-d₈ was added to the solution and ³¹P NMR was tested. Conversion was found 89.5% with unreacted Ni(dppp)₂ left.

Subsequent polymerization for P3HT using Ni complex external initiator. 2,5-dibromo-3-hexylthiophene (163mg, 0.50 mmol) and 1.649 M isopropyl magnesiumchloride (0.288 mL, 0.475mmol) was mixed in THF (5.0 mL) and stirred at room temperature for 2 h. 0.50 mL solution was taken and 0.03 mL water was added to the aliquot for conversion check by ¹H NMR (conversion 93.2%). The in situ generated Ni complex solution (0.50 mL, 0.010 mmol) was added to rest of the solution and stirred at room temperature for another 1 h. Reaction was terminated by addition of 0.5 mL 5 M HCl. Solution was added into 10 mL methanol and centrifuged. Solid was dissolved in 2 mL chloroform and added solution into 10 mL methanol, centrifuged and dried to obtain red solid. (48.4 mg, 64.8%) MALDI-TOF MS spectra showed major product with end-group of bithiophene/Br, and minor products with bithiophene/H and Br/Br.

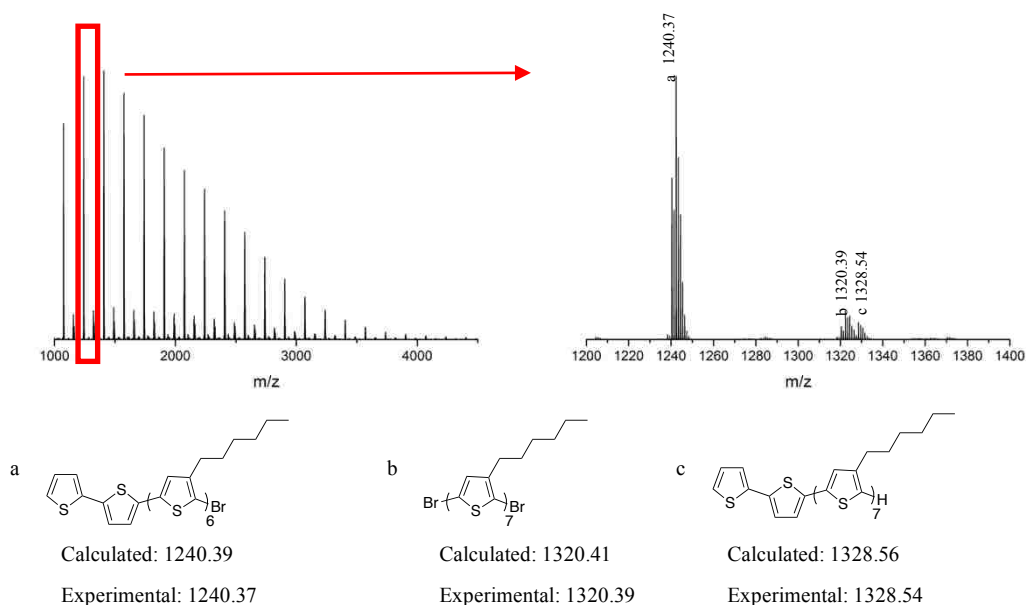


Figure 2.6. MALDI-TOF MS spectra of P3HT obtained using Ni complex external initiator ($[M]_0:[I]_0=50:1$, $[M]_0=0.1$ M, rt, THF).

2.5.3 Synthetic approaches towards PSS block with terminal azido group

Synthesis of PSS using ATRP in protic media. Sodium 4-styrenesulfonate (1.03 g, 5.0 mmol) and NaBr (522 mg, 5.0 mmol) were dissolved in water (20 mL) in an air-free flask. Solution was degassed for 3 cycles. Then 4-(bromomethyl)benzoic acid (11 mg, 0.050 mmol), CuBr (14 mg, 0.10 mmol), and bipyridine (32 mg, 0.20 mmol) was added into the flask under N_2 flow. Solution was stirred at 30 °C for 5 h. 1H NMR was used to check conversion by taking aliquot. (conversion 74.1%) Resulting solution was dialyzed against Ethylenediaminetetraacetic acid disodium salt (EDTA) solution in distilled water for 5 days (MWCO=1000 Da) with the water being changed once daily, but the solution is still blue, indicating presence of Cu.

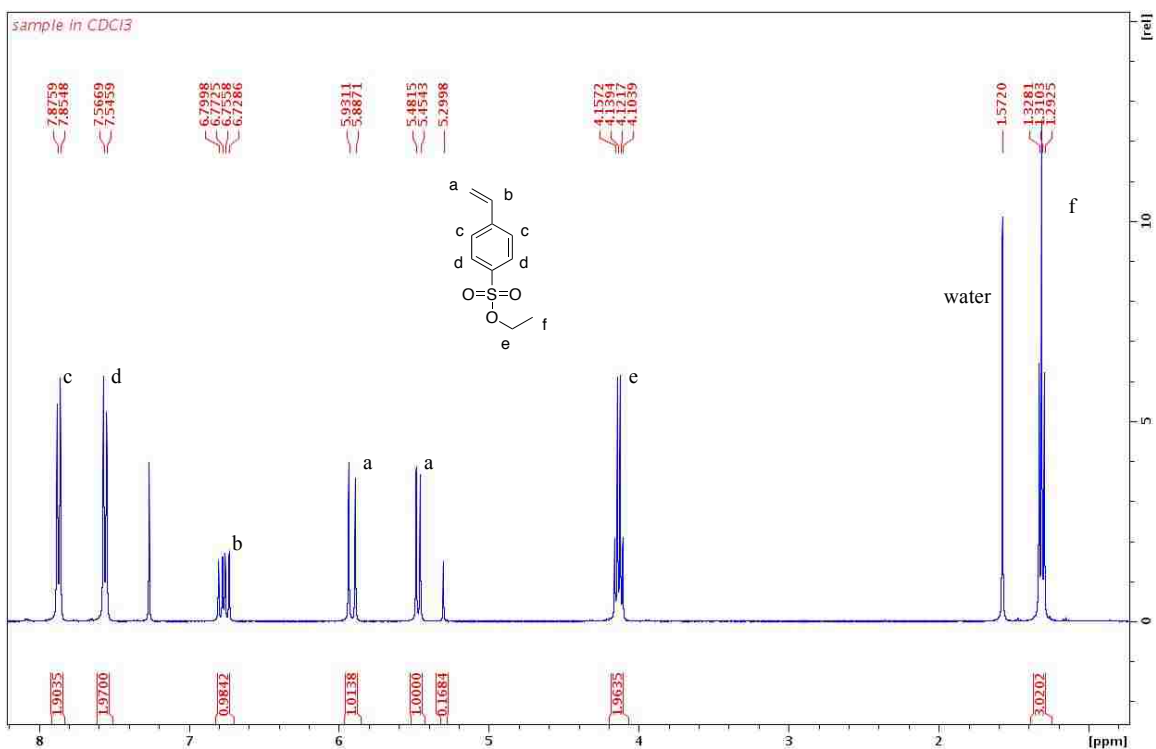


Figure 2.7. ¹H NMR spectrum of ethyl p-styrenesulfonate collected in CDCl₃

Synthesis of ethyl p-styrenesulfonate. The synthesis of ethyl p-styrenesulfonate was done by slightly modification of reported procedure.⁵⁸ The solution of AgNO₃ (9.32 g, 55 mmol) in 25 mL water was added dropwise into the solution of sodium 4-styrenesulfonate (10.32 g, 50 mmol) in 75mL water at 0 °C. The mixture was stirred for 3 h avoiding light exposure. Solid formed was filtered, and was rinsed three times by water and three times by ether. The solid was dissolved in 250mL acetonitrile and filtered to remove insoluble impurities. The filtrate was added into a flask and bromoethane (10 mL) was introduced. Solution was heated at 70 °C for 16 h. The yellow solid formed is filtered and the filtrate was condensed by rotary evaporation. The product was further purified by passing through a short Al₂O₃ column to obtain colorless liquid. (5.96 g, 56%)

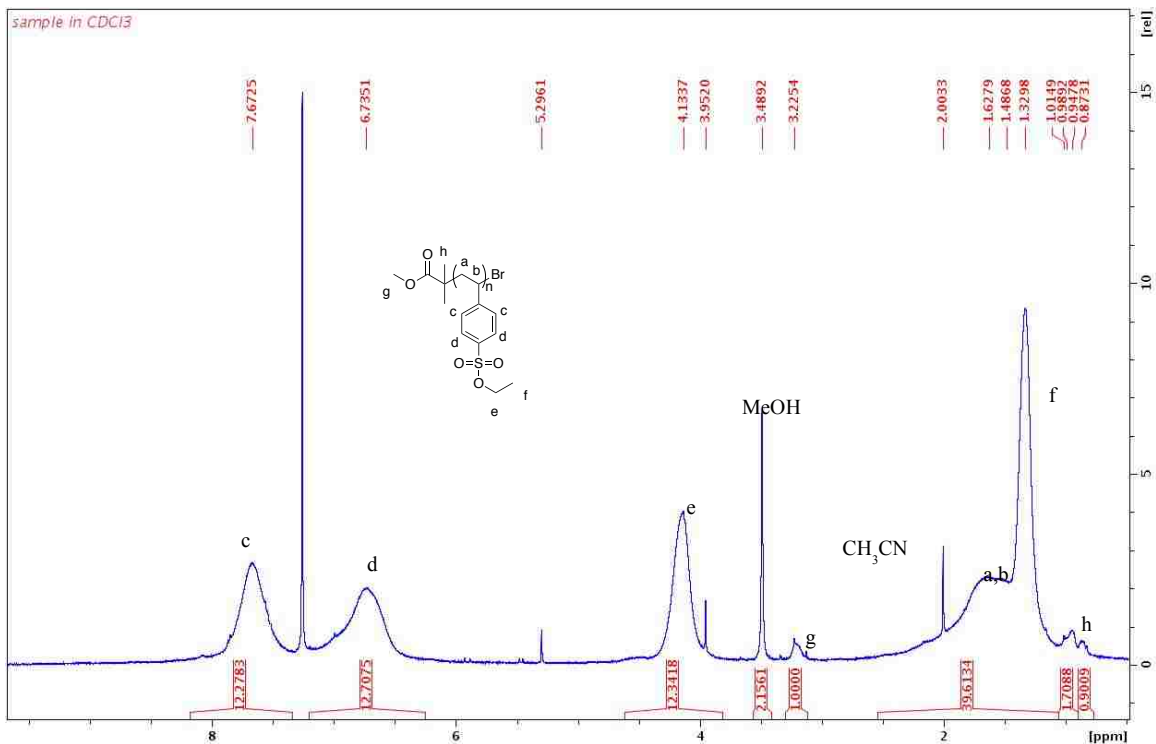


Figure 2.8. ¹H NMR spectrum of PESS collected in CDCl₃

Synthesis of PESS using ATRP. In the glovebox, ethyl p-styrenesulfonate (265 mg, 1.25 mmol), methyl 2-bromo-2-methylpropionate (9.1 mg, 0.050 mmol), CuBr (7.2 mg, 0.050 mmol), and bipyridine (16 mg, 0.10 mmol) were dissolved in acetonitrile (1.0 mL). Solution was heated at 80 °C for 2 h. Conversion was checked by ¹H NMR. (63.8%). Then solution was added into 10 mL methanol and centrifuged. Solid was dried under vacuum. (116 mg, 66.3%, calculated DP=18)

Synthesis of p-styrenesulfonyl chloride. The synthesis of p-styrenesulfonyl chloride was done by slightly modification of reported procedure.⁵⁷ Sodium 4-styrenesulfonate (20.62 g, 100 mmol) was added in portions into the solution of thionyl chloride (50 mL) in DMF (60 mL) at 0 °C and stirred for 2 h. Reaction was quenched by adding into 300 mL ice water. Solution was extracted by 100 mL DCM twice, and then washed with 200 mL water

three times, 200 mL saturated NaHCO₃ twice. Solution was dried over MgSO₄ and concentrated to obtain yellow liquid. (16.63 g, 82.1%)

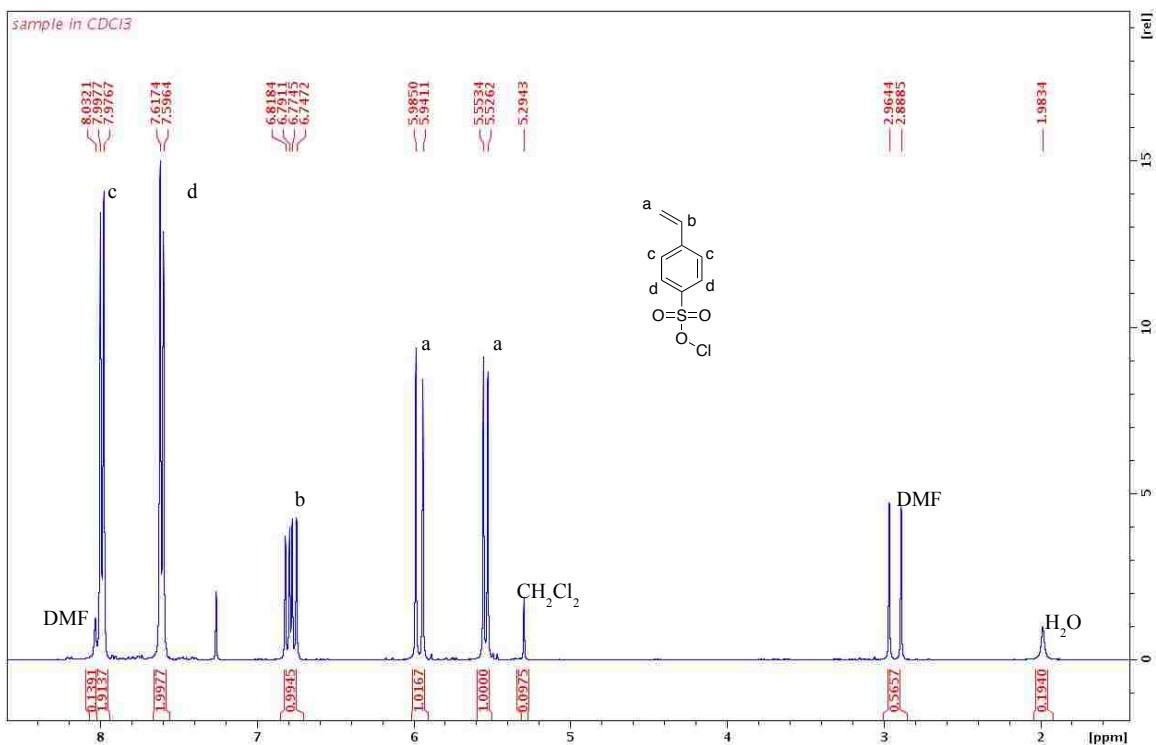


Figure 2.9. ¹H NMR spectrum of p-styrenesulfonyl chloride collected in CDCl₃

Synthesis of neopentyl p-styrenesulfonate. The synthesis of neopentyl p-styrenesulfonate was done by slightly modification of reported procedure.⁵⁷ p-Styrenesulfonyl chloride (8.11 g, 40 mmol) was added slowly into the solution of 2,2-dimethyl-1-propanol (3.70 g, 42 mmol) in pyridine (10 mL) at 0 °C and stirred for 2 h. 1 M HCl was used to adjust solution to weak acidic. Solution was extracted with 100 mL ethyl acetate. Organic phase was washed with water (100 mL) for three times and then saturated NaHCO₃ for three times. Solution was dried over MgSO₄ and concentrated by rotary evaporation, and then purified by column chromatography (eluent 1:4 ethyl acetate/hexanes) to obtain white solid. (6.13g, 60.2%)

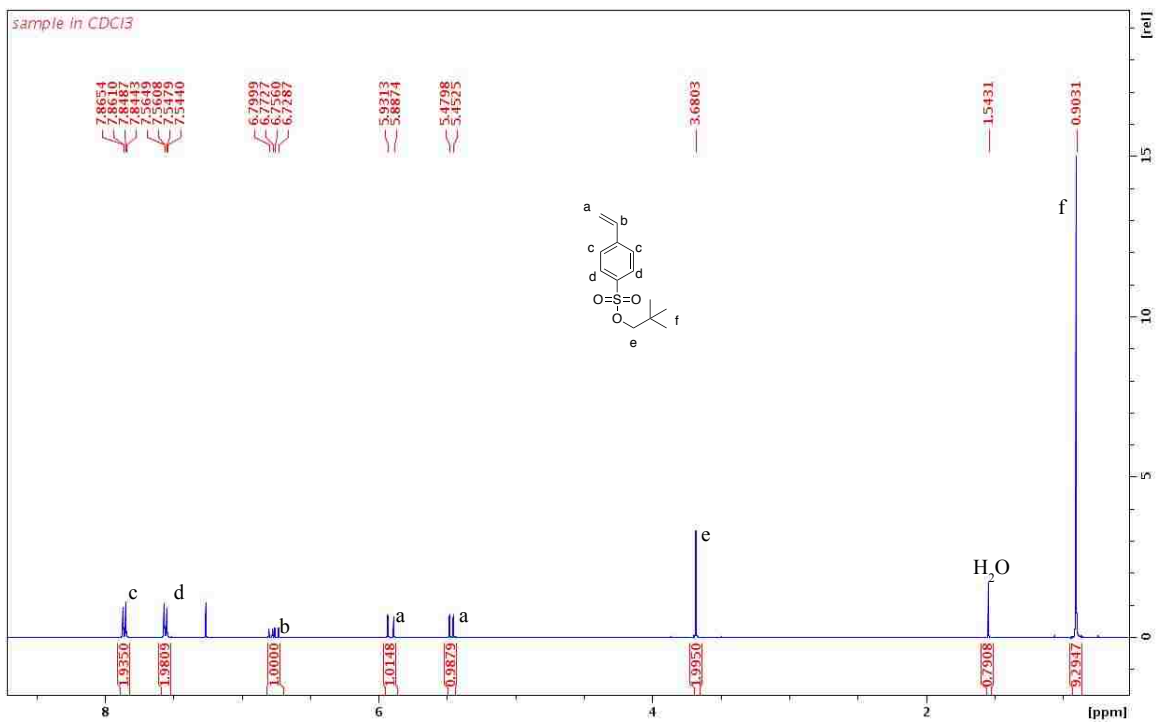


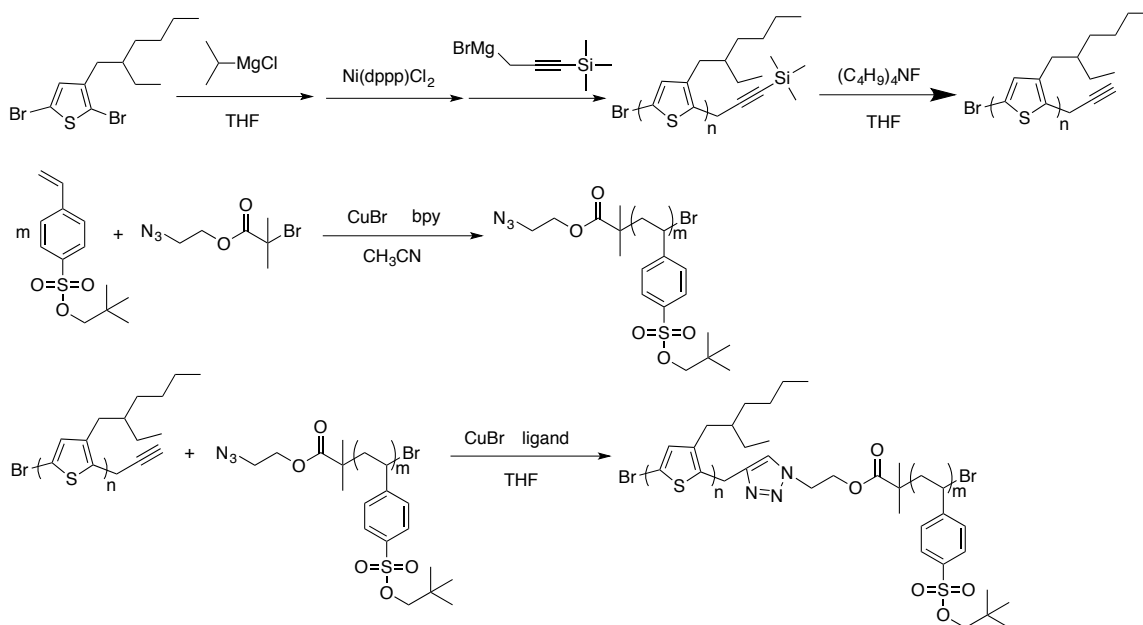
Figure 2.10. ¹H NMR spectrum of neopentyl p-styrenesulfonate collected in CDCl₃

Chapter III. Synthesis of end functionalized P3EHT and PNSS and P3EHT-*b*-PSS

3.1 Objectives

In Chapter II, multiple synthetic routes towards P3EHT-*b*-PSS were evaluated, and attempts were made to determine the most efficient synthetic route. The final synthetic route I chose to pursue further is to independently synthesize P3EHT block using Ni(dppp)Cl₂ initiator and subsequent in situ end-capping for alkyne moiety, PNSS using 2-azidoethyl 2-bromoisobutyrate initiator by the ATRP method, and connect these two blocks by CuAAC chemistry (showed in Scheme 3.1). The polymerization conditions to produce the respective block have been optimized and will be discussed in details.

Scheme 3.1. Designed synthetic route for P3EHT-*b*-PSS



3.2 Results and discussion

3.2.1 Synthesis of P3EHT block

3.2.1.1 Influence of 2,5-dibromo-3-alkylthiophene/Grignard reagent ratio

GRIM polymerization uses 2,5-dibromo-3-alkylthiophene as monomer precursor. When Grignard reagent is added, 2-bromo-5-(bromomagnesio)-3-alkylthiophene is generated in situ, which can be further polymerized using Ni catalyst. Previous studies showed that the ratio between 2,5-dibromo-3-alkylthiophene and Grignard reagent can influence the MW control. Yokozawa reported that the best ratio to control the reaction between *i*-Pr-MgCl and 2-bromo-3-hexyl-5-iodothiophene is 0.95-1.05.⁴³ Nesterov and coworker reported that the best ratio is 1.1 for *i*-Pr-MgCl and 2,5-dibromo-3-hexylthiophene.⁴² The optimum ratio appears to be sensitive to the specific monomer precursors. In my study, it was found that when using Ni(dppp)Cl₂ as initiator to synthesize P3HT, the optimum ratio between 2,5-dibromo-3-hexylthiophene and *i*-Pr-MgCl was found to be 1:0.95. Under this condition, 5% 2,5-dibromo-3-hexylthiophene is left unreacted and it does not react in the polymerization step. For higher ratio such as 1:1, *i*-Pr-terminated polymer was observed, and M_n of polymer became lower, indicating chain termination during polymerization. Theoretically, the optimum ratio is 1:1, because the magnesium-halogen exchange reaction is quite efficient to achieve full conversion. In practice even when the conversion to active monomers was 98% as determined by ¹H NMR analysis, the termination still existed during polymerization. By contrast, when conversion to the active monomer is around 95%, polymerization termination was reduced

significantly. As a result, a 1:0.95 ratio of 2,5-dibromo-3-hexylthiophene and *i*-Pr-MgCl is required for the formation of active monomer in order to achieve precise control over end-groups during the subsequent polymerization.

Table 3.1. Molecular weight analysis of P3HT obtained by GRIM polymerization using Ni(dppp)Cl₂ initiators at varying 2,5-dibromo-3-hexylthiophene/*i*-Pr-MgCl ratio ^{a,b}

2,5-dibromo-3-hexylthiophene/ <i>i</i> -Pr-MgCl	M_n (theo.) (kg·mol ⁻¹) ^c	M_n (SEC) (kg·mol ⁻¹) ^d	PDI ^d
1:0.95	7.5	6.8	1.55
1:1	7.5	5.2	1.49

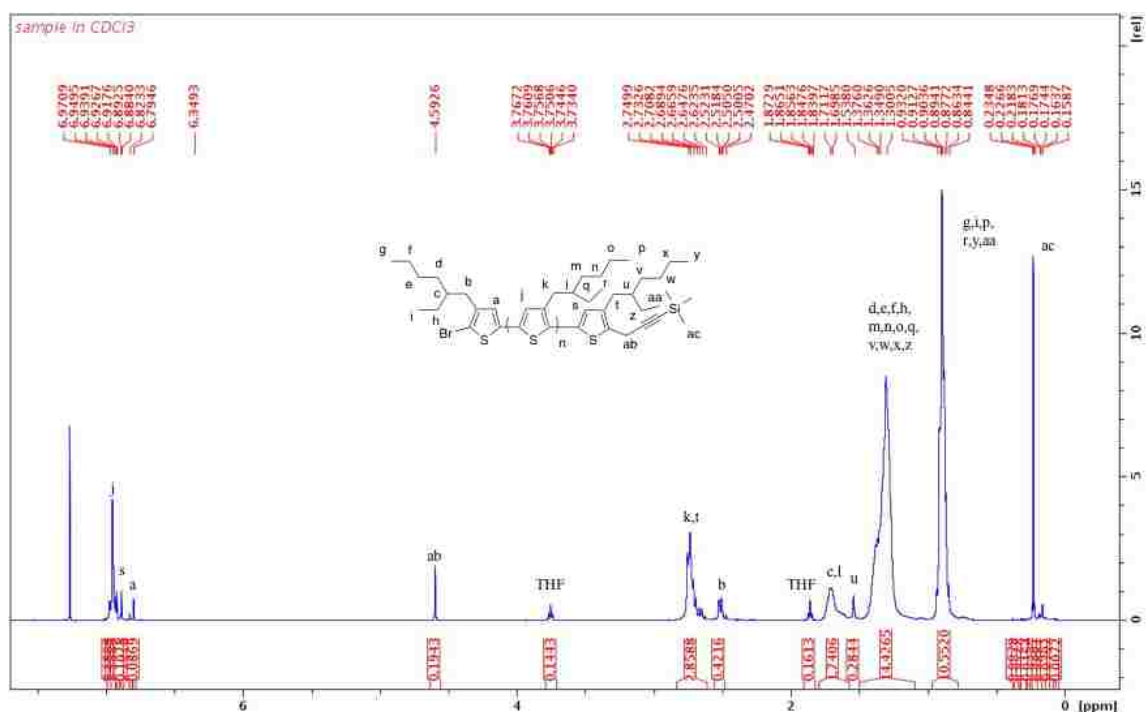
^a. All polymerizations were conducted at [M]₀=1.0 M in THF at room temperature for 2 h;

^b. [M]₀: [I]₀ ratio used for polymerization is 50:1^c; ^c theoretical molecular weights were calculated from the [M]₀: [I]₀ ratio; ^d polymer molecular weights and the molecular weight distribution were determined by SEC relative to polystyrene standards.

3.2.1.2 Selection of end-capping reagent for conjugated block

To incorporate alkyne moiety into the P3HT, successful attempts including consecutive addition of ethynylmagnesium bromide or (5-chloromagnesio-1-pentynyl)trimethylsilane after polymerization. McCullough used ethynylmagnesium bromide for end-capping, and found resulting P3HT with 85% monocapped species and 15% dicapped species.⁴⁵ Although this method was used to synthesize BCP containing P3HT block⁹⁰, when trying to repeat this work for multiple times, resulting polymer was found without desired end-group in MALDI-TOF MS spectrum. Cloutet and Vignau used (5-chloromagnesio-1-pentynyl)trimethylsilane for end-capping to obtain dicapped P3HT, which was deprotected with tetrabutylammonium fluoride (TBAF) to obtain α,ω -pentynyl-P3HT.⁸⁴

Inspired by these works, (3-bromomagnesio-1-propynyl)trimethylsilane was used as end-capping Grignard reagent to obtain end-capped P3EHT. Both ^1H NMR and MALDI-TOF MS confirmed majority resulting polymer as monocapped species. The percentage of P3EHT with Br/propynyltrimethylsilane end-groups is over 97% by MALDI-TOF MS analysis (Figure 3.2), and only less than 3% is dicapped with propynyltrimethylsilane. Deprotection using TBAF in THF successfully yielded propynyl-terminated P3HT without significant change of polymer molecular weight (Figure 3.5). Based on MALDI-TOF MS analysis (Figure 3.4), the total percentage of P3EHT with Br/propynyl end-groups is over 98%. (3-Bromomagnesio-1-propynyl)trimethylsilane was proved to be a promising reagent used for end-capping to introduce alkyne moiety to P3EHT. The P3EHT synthesized with well-defined end-groups is ideal for uses of synthesizing diblock copolymer.



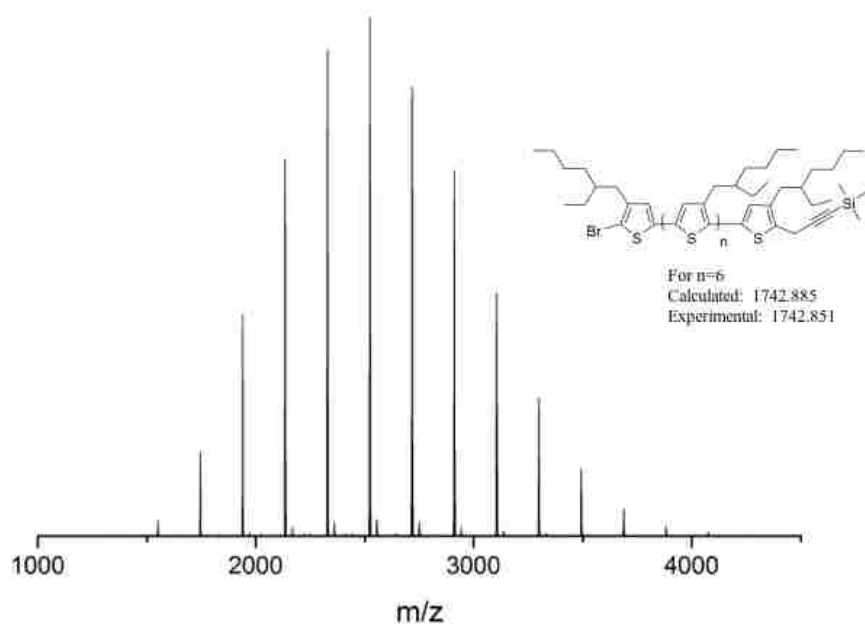


Figure 3.2. MALDI-TOF MS spectrum of propynyltrimethylsilane end-capped P3EHT ([M]₀:[I]₀=25:1)

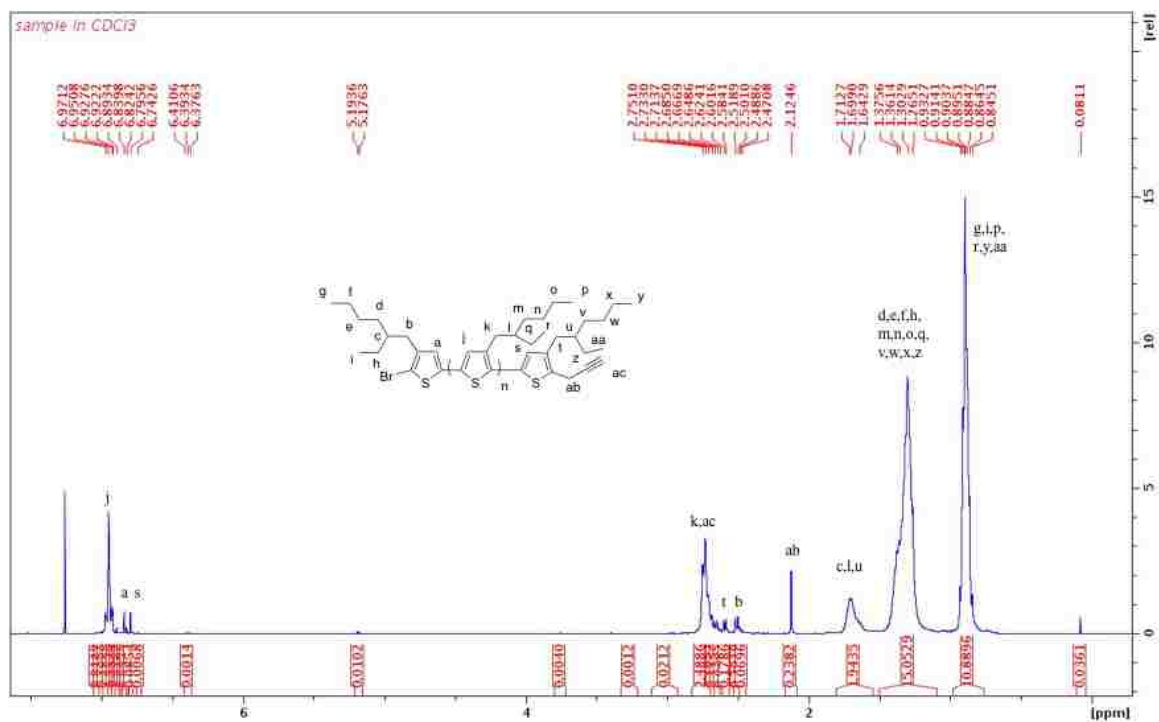


Figure 3.3. ¹H NMR spectrum of propynyl end-capped P3EHT collected in CDCl₃

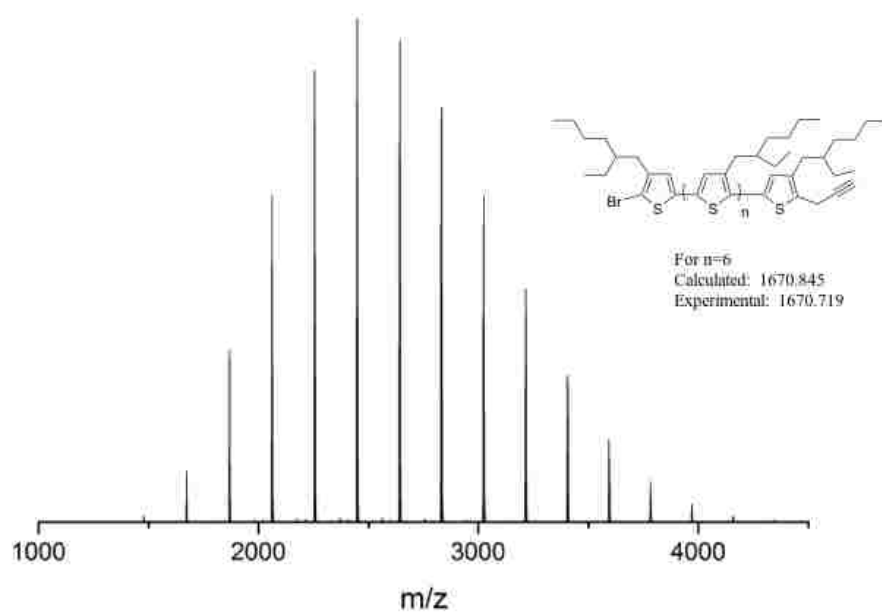


Figure 3.4. MALDI-TOF MS spectrum of propynyl end-capped P3EHT

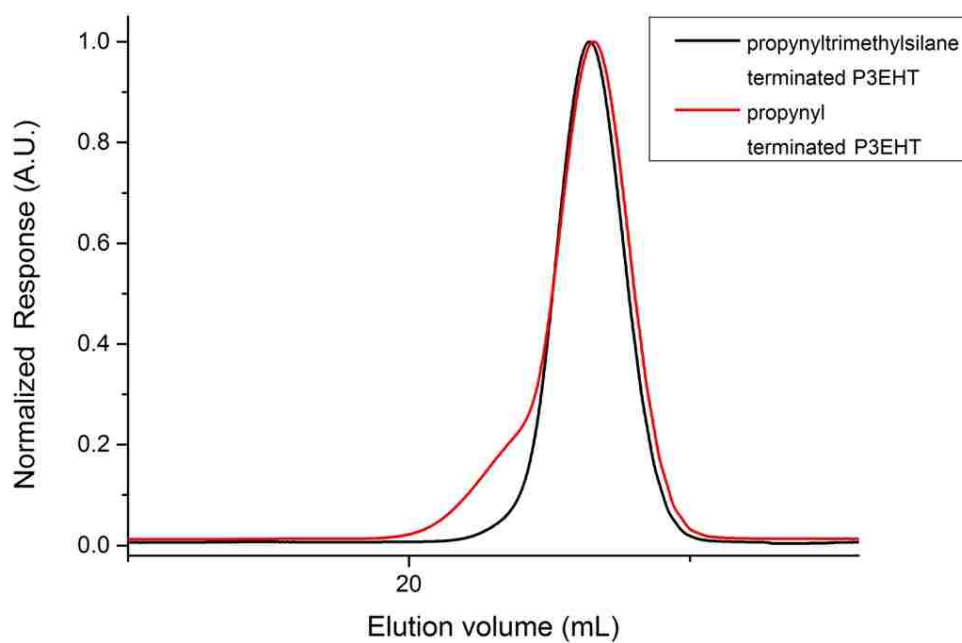


Figure 3.5. SEC-DAD chromatograms of P3EHTs before and after deprotection using TBAF

3.2.1.3 Synthesis of P3EHT with different MW

Using previous mentioned polymerization condition, P3EHTs with variant MW were synthesized. ^1H NMR and SEC were used to determine the MW and PDI of resulting polymer. Results showed good control over MW and PDI for different loading ratios between monomer and initiator. P3EHT synthesized with variant MW can subsequently be used for synthesizing BCPs containing P3EHT block with different volume ratios of building blocks, to intentionally tune the morphology of designed P3EHT-*b*-PSS, either in solution of solid phase.

Table 3.2. Molecular weight analysis of P3EHT obtained by GRIM polymerization using Ni(dppp)Cl₂ initiator and (3-bromomagnesio-1-propynyl)trimethylsilane for end-capping at varying [M]₀:[I]₀ ratio ^{a,b}

[M] ₀ : [I] ₀	<i>M_n</i> (theo.) (kg·mol ⁻¹) ^c	<i>M_n</i> (NMR) (kg·mol ⁻¹) ^d	<i>M_n</i> (SEC) (kg·mol ⁻¹) ^e	PDI ^e
23:1	4.6	3.8	3.4	1.12
45:1	8.9	7.7	7.1	1.08
90:1	17.7	13.7	12.6	1.07

^{a.} All polymerizations were conducted at [M]₀=1.0 M in THF at room temperature for 2 h;

^{b.} The Grignard monomers used for polymerization were prepared by reacting 0.95 eq. of *i*-PrMgCl with 1 eq. of 2,5-dibromo-3-(2-ethylhexyl)thiophene ^{c.} theoretical molecular weights were calculated from the [M]₀: [I]₀ ratio; ^{d.} polymer molecular weights were determined by ^1H NMR integration; ^{e.} polymer molecular weights and the molecular weight distribution were determined by SEC relative to polystyrene standards.

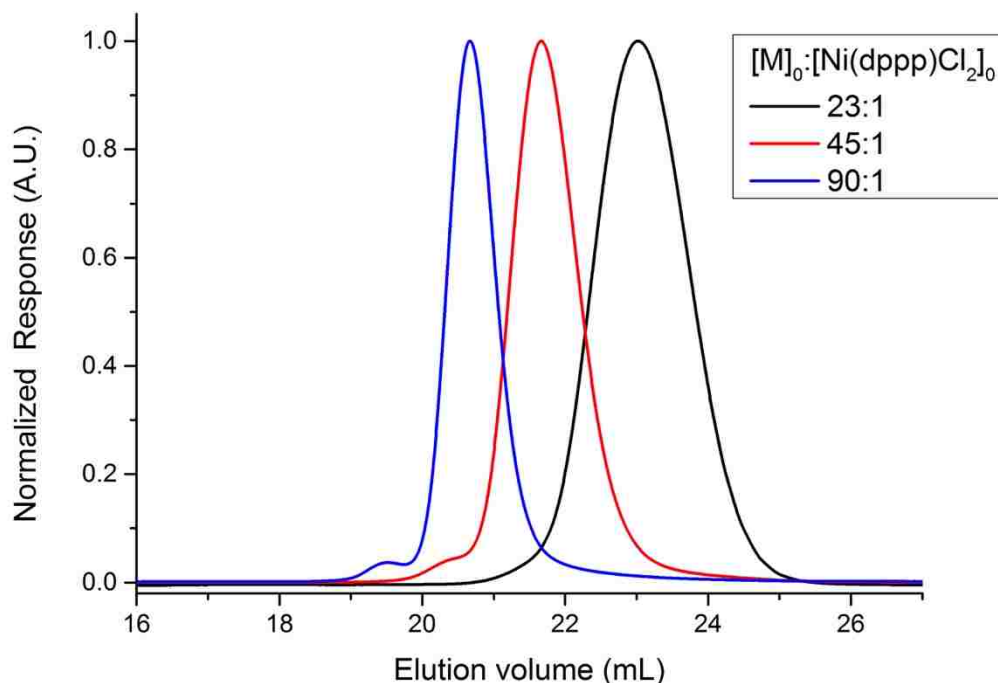


Figure 3.6. SEC-DAD chromatograms of P3EHTs obtained by GRIM polymerization

3.2.2 Synthesis of PNSS block

In Chapter II, both the syntheses of PESS and PNSS were investigated. Since neopentyl *p*-styrenesulfonate monomer is more stable compared to ethyl *p*-styrenesulfonate, it is selected to yield the desired polymers with varying MW by ATRP method. Previous studies only reported the synthesis of low molecular weight PNSS (DP<50) using RAFT and NMP methods.^{57,51} Azido-terminated PNSS with a range of target DPs from 10 to 100 were successfully synthesized by ATRP method in this study (in Table 3.2). This is important for future efforts in tuning the morphology of P3EHT-*b*-PSSNa BCPs by controlling the total MW and block volume ratio. Differed from early studies where THF, toluene and anisole were used as the polymerization solvent,

acetonitrile was selected in my study to give a homogenous solution without any precipitation during polymerization. This change of solvent clearly resulted in enhanced control over MW, allowing access to higher MW polymers.

Table 3.3. Molecular weight analysis of PNSS at varying $[M]_0:[I]_0$ ratio ^{a,b}

$[M]_0:[I]_0$	Time (h)	Conversion (%)	M_n (theo.) (kg·mol ⁻¹) ^c	M_n (NMR) (kg·mol ⁻¹) ^d
10:1	4	95.5	2.7	3.7
25:1	24	96.3	6.4	7.7
50:1	24	91.2	11.8	17.9
100:1	48	93.1	23.9	35.3

^a. All polymerizations were conducted at $[M]_0=2.0$ M in acetonitrile at 80 °C; ^b. CuBr used was 1 eq. compared to initiator, bipy used was 2 eq. compared to initiator. ^c. theoretical molecular weights were calculated from the $[M]_0:[I]_0$ ratio and conversion; ^d. polymer molecular weights were determined by ¹H NMR integration.

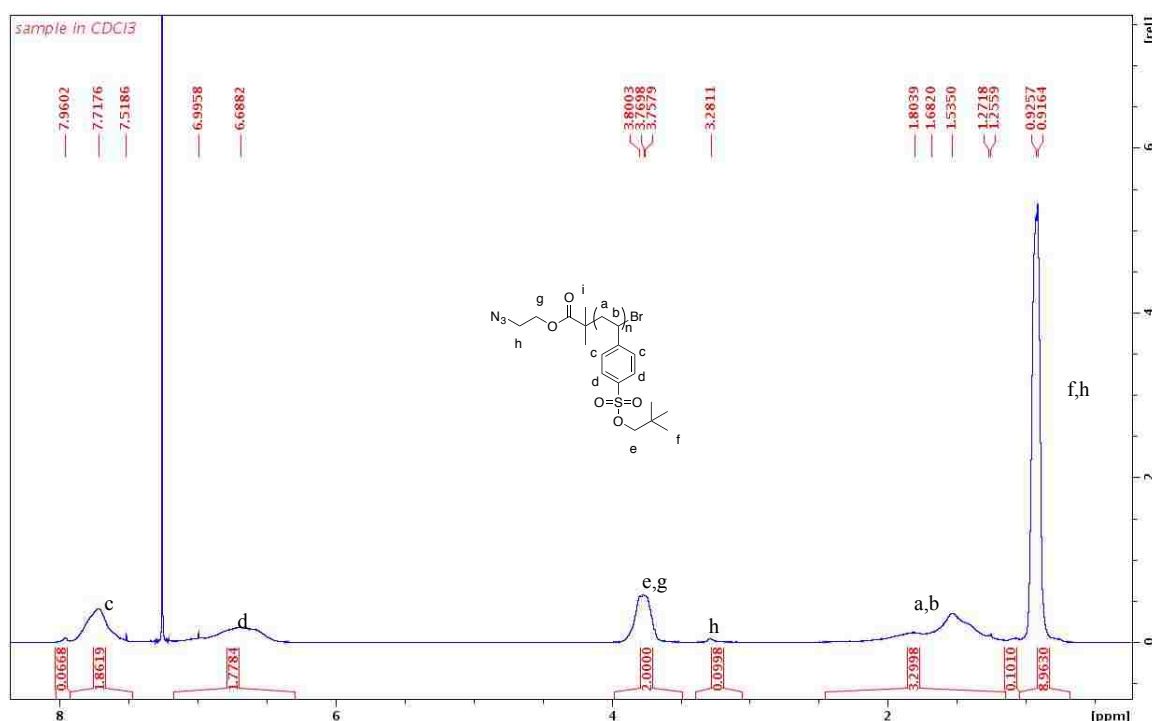


Figure 3.7. Representative ¹H NMR spectrum of PNSS collected in CDCl₃ ($[M]_0:[I]_0=25:1$)

3.2.3 Attempts of CuAAC to synthesize P3EHT-*b*-PNSS

Cloutet and Cramail reported that ethynyl-terminated P3HT and azido-terminated PS cannot be used to synthesize P3HT-*b*-PS through CuAAC by using CuBr/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) or CuI/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst.⁸⁴ Topham reported CuAAC for synthesizing P3HT-*b*-PNSS in THF using CuI/ N,N-diisopropylethylamine (DIPEA) as catalyst.⁹⁰ Since small differences are in both side chain and chain end of P3AT, P3EHT-*b*-PNSS were synthesized by using CuBr/DIPEA or CuBr/PMDETA with propynyl-terminated P3EHT and azido-terminated PNSS. But the bimodal peak in SEC suggested that CuAAC was not successful. When applied similar condition to propynyl-terminated P3EHT and model compound 2-azidoethyl 2-bromoisobutyrate to check the efficiency of CuAAC, MALDI-TOF MS testified the unsuccessful coupling. The condition of CuAAC still need to be further investigated.

3.3 Conclusions

Both propynyl-terminated P3EHT and azido-terminated PNSS were synthesized via controlled polymerization techniques including GRIM polymerization and ATRP. The best ratio of monomer precursor and Grignard reagent used in GRIM polymerization to achieve end-group control was considered to be 1:0.95. By consecutive in situ addition of (3-bromomagnesio-1-propynyl)trimethylsilane, and further treatment with TBAF, propynyl-terminated P3EHTs with DP in range of 15 to 70 were synthesized. The end-group control is much better compared to previous studies for synthesizing monocapped P3AT. Azido-

terminated PNSSs was synthesized by ATRP in acetonitrile for DP in range of 14 to 137. Coupling of the two polymers together by CuAAC have been attempted without much success under current conditions.

3.4 Experimental

3.4.1 Materials and instrumentation

All chemicals were used as received unless noted otherwise. ^1H NMR spectra were recorded on a Bruker AVIII-400. Chemical shifts were determined in reference to the protio impurities of deuterated solvents CDCl_3 or THF-d_8 . Anhydrous deuterated tetrahydrofuran (THF-d_8) was obtained by stirring THF-d_8 (Sigma-Aldrich) over CaH_2 overnight followed by vacuum transfer. ^{31}P NMR spectra were recorded on a Bruker AVIII-400. Chemical shifts were determined in reference to the external 85% H_3PO_4 . Size exclusion chromatography (SEC) data were collected on an Agilent 1100 SEC with a set of two PLgel 5 μm MIXED-C and one PLgel 5 μm 1000 \AA columns and a refractive index detector or diode-array detector (DAD). THF at 40 $^\circ\text{C}$ was used as the mobile phase at a flow rate of 0.7 mL/min. The instrument was calibrated with polystyrene (PS) standards (Polymer Laboratories). The MALDI-TOF MS experiments were carried out on a Bruker ultrafleXtreme tandem time-of-flight (TOF) mass spectrometer equipped with a smartbeam-IITM 1000 Hz laser (Bruker Daltonics, Billerica, MA). Prior to the measurement of each sample, the instrument was calibrated with Peptide Calibration Standard II consisting of a mixture of standard peptides Angiotensin I, Angiotensin II, Substance P, Bombesin, ACTH clip 1-17, ACTH clip 18-39, and Somatotatin 28 (Bruker Daltonics,

Billerica, MA). Samples were measured in positive reflector mode. 30 mg/mL trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in chloroform was used as the matrix in all measurements. Polymer samples were dissolved in THF at 1 mg/mL. The matrix and polymer samples were combined (v/v, 50/50). Samples (1 μ L) were deposited onto a 384-well ground-steel sample plate using the dry droplet method. Data analysis was conducted with flexAnalysis software.

3.4.2 Synthesis of P3EHT block with terminal propynyl group

Synthesis of propynyltrimethylsilane end-functionalized P3EHT. 2,5-dibromo-3-(2-ethylhexyl)thiophene (177 mg, 0.50 mmol) and 1.827 M isopropyl magnesium chloride (0.260 mL, 0.475 mmol) was mixed in THF (5.0 mL) and stirred at room temperature for 1 h. 0.5 mL solution was taken out for conversion test by ^1H NMR. Rest solution was transferred into a vial containing Ni(dppp)Cl₂ (11 mg, 0.020 mmol) and stirred at room temperature for another 2 h. 0.0458M (3-bromomagnesio-1-propynyl)trimethylsilane solution in THF (2.18 mL, 0.10 mmol) was introduced and stirred at room temperature for 1 h. 0.5 mL 5 M HCl was added to solution to terminate reaction. Solution was added into 10 mL methanol and centrifuged. Solid was dissolved in 2 mL THF and added solution into 10 mL methanol and centrifuged to obtain red solid. (51 mg, 62.1%, calculated DP=17.0)

Synthesis of propynyl end-functionalized P3EHT. propynyltrimethylsilane end-functionalized P3EHT (49 mg, 0.014 mmol) was dissolved in THF (2.0 mL). 1.0 M TBAF in THF (140 μ L, 0.14 mmol) was introduced and stirred at room temperature for 2 h.

Solution was added into 20 mL methanol and centrifuged. Solid was dissolved in 2 mL THF and added solution into 20 mL methanol and centrifuged to obtain red solid. (28 mg, 57.2%, calculated DP=15.2)

3.4.3 Synthesis of PNSS block with terminal azido group

Synthesis of neopentyl p-styrenesulfonate. In the glovebox, neopentyl p-styrenesulfonate (511 mg, 2.0 mmol), 2-azidoethyl 2-bromoisobutyrate (19 mg, 0.080 mmol), CuBr (12 mg, 0.080 mmol), and bipyridine (25 mg, 0.16 mmol) were dissolved in acetonitrile (1.0 mL). Solution was heated at 80 °C for 24 h. Conversion was checked by ^1H NMR. (91.3%). Then solution was added into 10 mL methanol and centrifuged. Solid was dissolved in 2 mL chloroform and solution was added into 10 mL methanol and centrifuged. Solid was dried under vacuum. (325 mg, 69.7%, calculated DP=20)

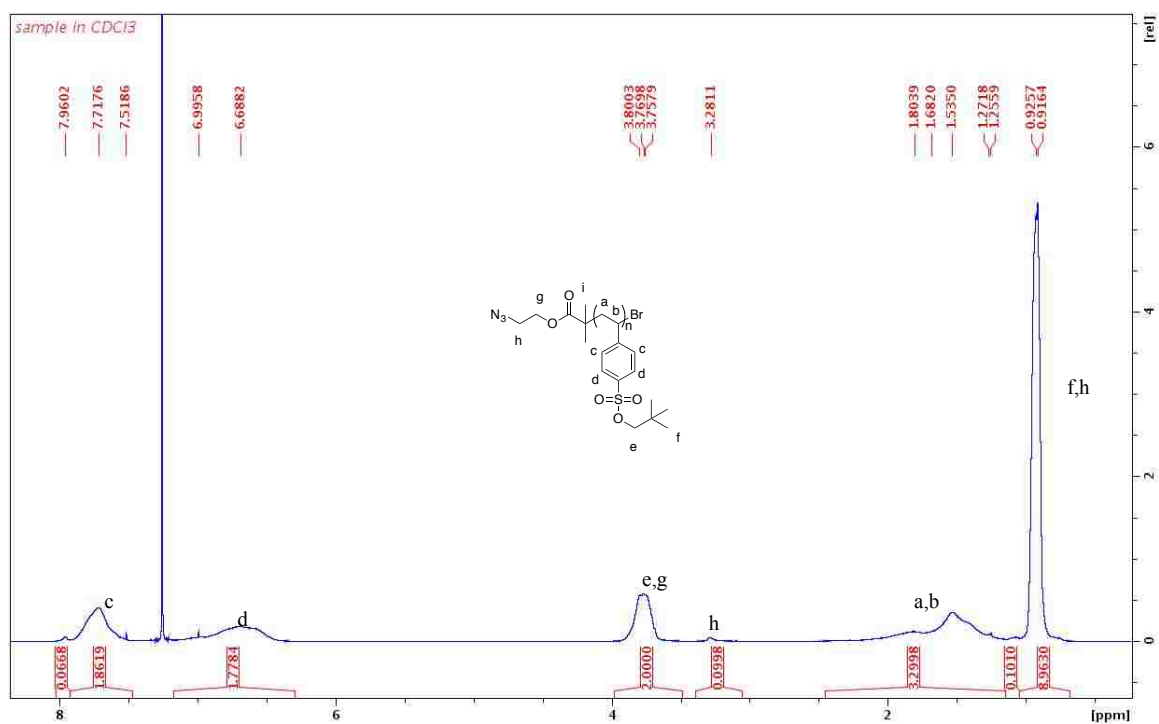


Figure 3.8. ^1H NMR spectrum of PNSS collected in CDCl_3

3.4.4 Synthetic attempts towards P3EHT-*b*-PNSS

“Click” reaction between P3EHT and PNSS. Propynyl end-functionalized P3EHT (8.0 mg, 2.5×10^{-3} mmol), azido end-functionalized PNSS (66 mg, 7.6×10^{-3} mmol), CuBr (7.3 mg, 0.051 mmol) and DIPEA (45 μ L, 0.26 mmol) were dissolved in THF (1.0 mL) in glovebox and stirred at 50 °C for 72 h. Solution was concentrated and separated by column chromatography on Al₂O₃ (eluent 1:9 THF/hexanes and 1:1 THF/hexanes). Portions separated were checked by ¹H NMR, MALDI-TOF MS and SEC. No block copolymer was observed.

“Click” reaction between P3EHT and 2-azidoethyl 2-bromoisobutyrate. Propynyl end-functionalized P3EHT (8.1 mg, 2.6×10^{-3} mmol), 2-azidoethyl 2-bromoisobutyrate (1.5 μ L, 9.0×10^{-3} mmol), CuBr (7.5 mg, 0.052 mmol) and DIPEA (45 μ L, 0.26 mmol) were dissolved in THF (1.0 mL) in glovebox and stirred at 50 °C for 72 h. Solution was concentrated and passed through a short Al₂O₃ column (eluent 1:9 THF/hexanes). ¹H NMR and MALDI-TOF MS showed no expected product observed.

Chapter IV. Conclusions and future work

In this work, a block copolymer P3EHT-*b*-PSS was designed for intentionally tuning microphase separation behavior. Several synthetic methods to obtain P3EHT-*b*-PSS have been evaluated. Among these synthetic methods, attempts were made to synthesize P3EHT block through bifunctional initiator and external Ni initiators bearing functional groups which can be used for further synthesis of block copolymer, but the end-group control of P3EHT was found not ideal since side reactions may happen during preparing Ni initiators. Synthesizing P3EHT by using Ni(dppp)Cl₂, consecutive in situ addition of (3-bromomagnesio-1-propynyl)trimethylsilane, and deprotection with TBAF can result in P3EHT with well-defined end-groups as over 98% Br/propynyl with variant MW. PNSS was selected to be PSS derivative used for synthesizing BCP. ATRP in acetonitrile at 80 °C was found to be a good condition of synthesizing PNSS with different MW.

Although both blocks were synthesized to give well-defined end-groups, which could be used for CuAAC, several attempts made to synthesize BCP were not successful. Even coupling reaction using P3EHT and model compound 2-azidoethyl 2-bromoisobutyrate was found to be unsuccessful. The coupling reaction needs to be further investigated to obtain P3EHT-*b*-PNSS.

In future, P3EHT-*b*-PNSS can be hydrolyzed to obtain P3EHT-*b*-PSS with various counterions such as sodium and potassium. BCP with different block volume ratios can be synthesized, whose microphase separation behavior can be systematically studied. Thin

films made by BCPs with specific microphase structures can be used for devices such as Faraday effect sensor and artificial photosynthesis membrane.

References

1. Whitesides, G. M.; Grzybowski, B., Self-assembly at all scales. *Science* **2002**, *295* (5564), 2418-2421.
2. Winkleman, A.; Gates, B. D.; McCarty, L. S.; Whitesides, G. M., Directed Self-Assembly of Spherical Particles on Patterned Electrodes by an Applied Electric Field. *Advanced Materials* **2005**, *17* (12), 1507-1511.
3. Misteli, T., The concept of self-organization in cellular architecture. *J Cell Biol* **2001**, *155* (2), 181-5.
4. Farrell, R. A.; Fitzgerald, T. G.; Borah, D.; Holmes, J. D.; Morris, M. A., Chemical interactions and their role in the microphase separation of block copolymer thin films. *Int J Mol Sci* **2009**, *10* (9), 3671-712.
5. Bates, F. S.; Fredrickson, G. H., Block Copolymers—Designer Soft Materials. *Physics Today* **1999**, *52* (2), 32.
6. Zhou, F.; Ye, T.; Shi, L.; Xie, C.; Chang, S.; Fan, X.; Shen, Z., Synthesis and Self-Assembly of Rod–Rod Block Copolymers with Different Rod Diameters. *Macromolecules* **2013**, *46* (20), 8253-8263.
7. Matsen, M. W.; Barrett, C., Liquid-crystalline behavior of rod-coil diblock copolymers. *The Journal of Chemical Physics* **1998**, *109* (10), 4108.
8. Darling, S., Directing the self-assembly of block copolymers. *Progress in Polymer Science* **2007**, *32* (10), 1152-1204.
9. McCullough, R. D., The chemistry of conducting polythiophenes. *Advanced Materials* **1998**, *10* (2), 93-116.
10. Chiang, C.; Druy, M.; Gau, S.; Heeger, A.; Louis, E.; MacDiarmid, A. G.; Park, Y.; Shirakawa, H., Synthesis of highly conducting films of derivatives of polyacetylene,(CH)_x. *Journal of the American Chemical Society* **1978**, *100* (3), 1013-1015.

11. Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P., Solitons in conducting polymers. *Reviews of Modern Physics* **1988**, *60* (3), 781-850.
12. Balint, R.; Cassidy, N. J.; Cartmell, S. H., Conductive polymers: Towards a smart biomaterial for tissue engineering. *Acta Biomaterialia* **2014**, *10* (6), 2341-2353.
13. Facchetti, A., Π -conjugated polymers for organic electronics and photovoltaic cell applications†. *Chemistry of Materials* **2010**, *23* (3), 733-758.
14. Katsumi, Y.; Shigenori, H.; Ryu-ichi, S., Preparation and Properties of Conducting Heterocyclic Polymer Films by Chemical Method. *Japanese Journal of Applied Physics* **1984**, *23* (12A), L899.
15. Kaneto, K.; Yoshino, K.; Inuishi, Y., Electrical properties of conducting polymer, poly-thiophene, prepared by electrochemical polymerization. *Japanese Journal of Applied Physics* **1982**, *21* (9A), L567.
16. Waltman, R. J.; Bargon, J.; Diaz, A. F., Electrochemical studies of some conducting polythiophene films. *The Journal of Physical Chemistry* **1983**, *87* (8), 1459-1463.
17. Lee, J. M.; Lee, S. J.; Jung, Y. J.; Kim, J. H., Fabrication of nano-structured polythiophene nanoparticles in aqueous dispersion. *Current Applied Physics* **2008**, *8* (6), 659-663.
18. Yamamoto, T.; Sanechika, K.; Yamamoto, A., Preparation of thermostable and electric-conducting poly (2, 5-thienylene). *Journal of Polymer Science: Polymer Letters Edition* **1980**, *18* (1), 9-12.
19. Lin, J. W. P.; Dudek, L. P., Synthesis and properties of poly (2, 5-thienylene). *Journal of Polymer Science: Polymer Chemistry Edition* **1980**, *18* (9), 2869-2873.
20. Jen, K.-Y.; Miller, G.; Elsenbaumer, R. L., Highly conducting, soluble, and environmentally-stable poly (3-alkylthiophenes). *Journal of the Chemical Society, Chemical Communications* **1986**, (17), 1346-1347.

21. Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z. H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K., Preparation of π -conjugated poly (thiophene-2, 5-diyl), poly (p-phenylene), and related polymers using zerovalent nickel complexes. Linear structure and properties of the π -conjugated polymers. *Macromolecules* **1992**, *25* (4), 1214-1223.
22. Sugimoto, R.-I.; Takeda, S.; Gu, H.; Yoshino, K., Preparation of soluble polythiophene derivatives utilizing transition metal halides as catalysts and their property. *Chem. Express* **1986**, *1* (11), 635-638.
23. McClain, M. D.; Whittington, D. A.; Mitchell, D. J.; Curtis, M. D., Novel Poly (3-alkylthiophene) and Poly (3-alkylthienyl ketone) Syntheses via Organomercurials. *Journal of the American Chemical Society* **1995**, *117* (13), 3887-3888.
24. Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J., Effect of Molecular Weight on Spectroscopic and Spectroelectrochemical Properties of Regioregular Poly(3-hexylthiophene). *Macromolecules* **1998**, *31* (15), 5051-5058.
25. McCullough, R. D.; Lowe, R. D., Enhanced electrical conductivity in regioselectively synthesized poly (3-alkylthiophenes). *J. Chem. Soc., Chem. Commun.* **1992**, (1), 70-72.
26. Chen, T. A.; Rieke, R. D., The first regioregular head-to-tail poly (3-hexylthiophene-2, 5-diyl) and a regiorandom isopolymer: nickel versus palladium catalysis of 2 (5)-bromo-5 (2)-(bromozincio)-3-hexylthiophene polymerization. *Journal of the American Chemical Society* **1992**, *114* (25), 10087-10088.
27. Osaka, I.; McCullough, R. D., Advances in molecular design and synthesis of regioregular polythiophenes. *Accounts of chemical research* **2008**, *41* (9), 1202-1214.
28. Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D., A Simple Method to Prepare Head-to-Tail Coupled, Regioregular Poly (3-alkylthiophenes) Using Grignard Metathesis. *Advanced materials* **1999**, *11* (3), 250-253.
29. Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D., Regioregular, head-to-tail coupled poly (3-alkylthiophenes) made easy by the GRIM method:

investigation of the reaction and the origin of regioselectivity. *Macromolecules* **2001**, *34* (13), 4324-4333.

30. Yokoyama, A.; Miyakoshi, R.; Yokozawa, T., Chain-growth polymerization for poly (3-hexylthiophene) with a defined molecular weight and a low polydispersity. *Macromolecules* **2004**, *37* (4), 1169-1171.

31. Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriya, A., Kumada catalyst-transfer polycondensation of thiophene-based oligomers: robustness of a chain-growth mechanism. *Macromolecules* **2008**, *41* (21), 7817-7823.

32. Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D., Experimental evidence for the quasi-“living” nature of the grignard metathesis method for the synthesis of regioregular poly (3-alkylthiophenes). *Macromolecules* **2005**, *38* (21), 8649-8656.

33. Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Simon, F.; Nitschke, M.; Stamm, M.; Grötzschel, R.; Kiriya, A., Grafting of poly (3-hexylthiophene) from poly (4-bromostyrene) films by Kumada catalyst-transfer polycondensation: revealing of the composite films structure. *Macromolecules* **2008**, *41* (20), 7383-7389.

34. Doubina, N.; Ho, A.; Jen, A. K. Y.; Luscombe, C. K., Effect of Initiators on the Kumada Catalyst-Transfer Polycondensation Reaction. *Macromolecules* **2009**, *42* (20), 7670-7677.

35. Doubina, N.; Stoddard, M.; Bronstein, H. A.; Jen, A. K. Y.; Luscombe, C. K., The Effects of Binding Ligand Variation on the Nickel Catalyzed Externally Initiated Polymerization of 2-Bromo-3-hexyl-5-iodothiophene. *Macromolecular Chemistry and Physics* **2009**, *210* (22), 1966-1972.

36. Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriya, A., Conductive polymer brushes of regioregular head-to-tail poly (3-alkylthiophenes) via catalyst-transfer surface-initiated polycondensation. *Journal of the American Chemical Society* **2007**, *129* (20), 6626-6632.

37. Bronstein, H. A.; Luscombe, C. K., Externally initiated regioregular P3HT with controlled molecular weight and narrow polydispersity. *Journal of the American Chemical Society* **2009**, *131* (36), 12894-12895.
38. Smeets, A.; Van den Bergh, K.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G., Incorporation of Different End Groups in Conjugated Polymers Using Functional Nickel Initiators. *Macromolecules* **2009**, *42* (20), 7638-7641.
39. Senkovskyy, V.; Sommer, M.; Tkachov, R.; Komber, H.; Huck, W. T. S.; Kiriy, A., Convenient Route To Initiate Kumada Catalyst-Transfer Polycondensation Using Ni(dppe)Cl₂ or Ni(dppp)Cl₂ and Sterically Hindered Grignard Compounds. *Macromolecules* **2010**, *43* (23), 10157-10161.
40. Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A., Random catalyst walking along polymerized poly (3-hexylthiophene) chains in Kumada catalyst-transfer polycondensation. *Journal of the American Chemical Society* **2010**, *132* (22), 7803-7810.
41. Kohn, P.; Huettner, S.; Komber, H.; Senkovskyy, V.; Tkachov, R.; Kiriy, A.; Friend, R. H.; Steiner, U.; Huck, W. T.; Sommer, J.-U., On the role of single regiodefects and polydispersity in regioregular poly (3-hexylthiophene): defect distribution, synthesis of defect-free chains, and a simple model for the determination of crystallinity. *Journal of the American Chemical Society* **2012**, *134* (10), 4790-4805.
42. Chavez, C. A.; Choi, J.; Nesterov, E. E., One-Step Simple Preparation of Catalytic Initiators for Catalyst-Transfer Kumada Polymerization: Synthesis of Defect-Free Polythiophenes. *Macromolecules* **2014**, *47* (2), 506-516.
43. Miyakoshi, R.; Yokoyama, A.; Yokozawa, T., Catalyst-transfer polycondensation. Mechanism of Ni-catalyzed chain-growth polymerization leading to well-defined poly (3-hexylthiophene). *Journal of the American Chemical Society* **2005**, *127* (49), 17542-17547.

44. Jeffries-EL, M.; Sauvé, G.; McCullough, R. D., In-Situ End-Group Functionalization of Regioregular Poly (3-alkylthiophene) Using the Grignard Metathesis Polymerization Method. *Advanced materials* **2004**, *16* (12), 1017-1019.
45. Jeffries-El, M.; Sauvé, G.; McCullough, R. D., Facile synthesis of end-functionalized regioregular poly (3-alkylthiophene) s via modified Grignard metathesis reaction. *Macromolecules* **2005**, *38* (25), 10346-10352.
46. Causin, V.; Marega, C.; Marigo, A.; Valentini, L.; Kenny, J. M., Crystallization and melting behavior of poly (3-butylthiophene), poly (3-octylthiophene), and poly (3-dodecylthiophene). *Macromolecules* **2005**, *38* (2), 409-415.
47. Ho, V.; Boudouris, B. W.; Segalman, R. A., Tuning polythiophene crystallization through systematic side chain functionalization. *Macromolecules* **2010**, *43* (19), 7895-7899.
48. Peeters, H.; Jivanescu, M.; Stesmans, A.; Pereira, L. M. C.; Dillemans, L.; Locquet, J.-P.; Van Bael, M. J.; Persoons, A.; Koeckelberghs, G., Influence of the bulkiness of the substituent on the aggregation and magnetic properties of poly(3-alkylthiophene)s. *Journal of Polymer Science Part A: Polymer Chemistry* **2014**, *52* (1), 76-86.
49. Dobrynin, A.; Rubinstein, M., Theory of polyelectrolytes in solutions and at surfaces. *Progress in Polymer Science* **2005**, *30* (11), 1049-1118.
50. Coughlin, J. E.; Reisch, A.; Markarian, M. Z.; Schlenoff, J. B., Sulfonation of polystyrene: Toward the “ideal” polyelectrolyte. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51* (11), 2416-2424.
51. Fraga Domínguez, I.; Kolomanska, J.; Johnston, P.; Rivaton, A.; Topham, P. D., Controlled synthesis of poly(neopentylp-styrene sulfonate) via reversible addition-fragmentation chain transfer polymerisation. *Polymer International* **2015**, *64* (5), 621-630.
52. Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D., Living free-radical aqueous polymerization. *Macromolecules* **1995**, *28* (18), 6381-6382.

53. Chiefari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G., Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. *Macromolecules* **1998**, *31* (16), 5559-5562.
54. Choi, C.-K.; Kim, Y.-B., Atom transfer radical polymerization of styrenesulfonic acid sodium salts (SSNa) in aqueous phase. *Polymer Bulletin* **2003**, *49* (6), 433-439.
55. Iddon, P. D.; Robinson, K. L.; Armes, S. P., Polymerization of sodium 4-styrenesulfonate via atom transfer radical polymerization in protic media. *Polymer* **2004**, *45* (3), 759-768.
56. Matyjaszewski, K., ATRP in Protic Media.
<http://www.cmu.edu/maty/chem/fundamentals-atrp/protic-media.html#clasic%20ATRP>.
57. Okamura, H.; Takatori, Y.; Tsunooka, M.; Shirai, M., Synthesis of random and block copolymers of styrene and styrenesulfonic acid with low polydispersity using nitroxide-mediated living radical polymerization technique. *Polymer* **2002**, *43* (11), 3155-3162.
58. Lienkamp, K.; Ruthard, C.; Lieser, G.; Berger, R.; Groehn, F.; Wegner, G., Polymerization of Styrene Sulfonate Ethyl Ester and Styrene Sulfonate Dodecyl Ester by ATRP: Synthesis and Characterization of Polymer Brushes. *Macromolecular Chemistry and Physics* **2006**, *207* (22), 2050-2065.
59. Matyjaszewski, K., Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives. *Macromolecules* **2012**, *45* (10), 4015-4039.
60. Gangopadhyay, P.; Koeckelberghs, G.; Persoons, A., Magneto-optic Properties of Regioregular Polyalkylthiophenes†. *Chemistry of Materials* **2010**, *23* (3), 516-521.
61. Yamamoto, T., Molecular assembly and properties of polythiophenes. *NPG Asia Materials* **2010**, *2* (2), 54-60.
62. McFarlane, S. L.; Day, B. A.; McEleney, K.; Freund, M. S.; Lewis, N. S., Designing electronic/ionic conducting membranes for artificial photosynthesis. *Energy & Environmental Science* **2011**, *4* (5), 1700.

63. Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K., Synthesis of all-conjugated diblock copolymers by quasi-living polymerization and observation of their microphase separation. *Journal of the American Chemical Society* **2008**, *130* (25), 7812-7813.
64. Wu, P.-T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A., Crystalline diblock conjugated copolymers: Synthesis, self-assembly, and microphase separation of poly (3-butylthiophene)-b-poly (3-octylthiophene). *Macromolecules* **2009**, *42* (7), 2317-2320.
65. Wu, P. T.; Ren, G.; Kim, F. S.; Li, C.; Mezzenga, R.; Jenekhe, S. A., Poly (3-hexylthiophene)-b-poly (3-cyclohexylthiophene): Synthesis, microphase separation, thin film transistors, and photovoltaic applications. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48* (3), 614-626.
66. Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S., Controlling phase separation and optical properties in conjugated polymers through selenophene– thiophene copolymerization. *Journal of the American Chemical Society* **2010**, *132* (25), 8546-8547.
67. Wu, Z.-Q.; Ono, R. J.; Chen, Z.; Bielawski, C. W., Synthesis of poly (3-alkylthiophene)-block-poly (arylisocyanide): Two sequential, mechanistically distinct polymerizations using a single catalyst. *Journal of the American Chemical Society* **2010**, *132* (40), 14000-14001.
68. Hundt, N.; Hoang, Q.; Nguyen, H.; Sista, P.; Hao, J.; Servello, J.; Palaniappan, K.; Alemseghed, M.; Biewer, M. C.; Stefan, M. C., Synthesis and Characterization of a Block Copolymer Containing Regioregular Poly (3-hexylthiophene) and Poly (γ -benzyl-L-glutamate). *Macromolecular Rapid Communications* **2011**, *32* (3), 302-308.
69. Yu, X.; Xiao, K.; Chen, J.; Lavrik, N. V.; Hong, K.; Sumpter, B. G.; Geohegan, D. B., High-performance field-effect transistors based on polystyrene-b-poly (3-hexylthiophene) diblock copolymers. *ACS nano* **2011**, *5* (5), 3559-3567.
70. Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D., Tuning the Electrical Conductivity and Self-Assembly of Regioregular Polythiophene by Block

Copolymerization: Nanowire Morphologies in New Di- and Triblock Copolymers.

Angewandte Chemie International Edition **2002**, *41* (2), 329-332.

71. Radano, C. P.; Scherman, O. A.; Stingelin-Stutzmann, N.; Müller, C.; Breiby, D. W.; Smith, P.; Janssen, R. A.; Meijer, E., Crystalline-crystalline block copolymers of regioregular poly (3-hexylthiophene) and polyethylene by ring-opening metathesis polymerization. *Journal of the American Chemical Society* **2005**, *127* (36), 12502-12503.

72. Iovu, M. C.; Craley, C. R.; Jeffries-El, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D., Conducting regioregular polythiophene block copolymer nanofibrils synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxide mediated polymerization (NMP). *Macromolecules* **2007**, *40* (14), 4733-4735.

73. Iovu, M. C.; Jeffries-El, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D., Regioregular poly (3-alkylthiophene) conducting block copolymers. *Polymer* **2005**, *46* (19), 8582-8586.

74. Iovu, M. C.; Zhang, R.; Cooper, J. R.; Smilgies, D. M.; Javier, A. E.; Sheina, E. E.; Kowalewski, T.; McCullough, R. D., Conducting Block Copolymers of Regioregular Poly (3-hexylthiophene) and Poly (methacrylates): Electronic Materials with Variable Conductivities and Degrees of Interfibrillar Order. *Macromolecular Rapid Communications* **2007**, *28* (17), 1816-1824.

75. Craley, C.; Zhang, R.; Kowalewski, T.; McCullough, R. D.; Stefan, M. C., Regioregular Poly (3-hexylthiophene) in a Novel Conducting Amphiphilic Block Copolymer. *Macromolecular Rapid Communications* **2009**, *30* (1), 11-16.

76. Huang, K. K.; Fang, Y. K.; Hsu, J. C.; Kuo, C. C.; Chang, W. H.; Chen, W. C., Synthesis, micellar structures, and multifunctional sensory properties of poly (3-hexylthiophene)-block-poly (2-(dimethylamino) ethyl methacrylate) rod-coil diblock copolymers. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49* (1), 147-155.

77. Rashid, M.; Seo, M.; Kim, S. Y.; Gal, Y. S.; Park, J. M.; Kim, E. Y.; Lee, W. K.; Lim, K. T., Synthesis and self-assembly of diblock copolymers composed of poly (3-hexylthiophene) and poly (fluorooctyl methacrylate) segments. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49* (21), 4680-4686.
78. Palaniappan, K.; Hundt, N.; Sista, P.; Nguyen, H.; Hao, J.; Bhatt, M. P.; Han, Y. Y.; Schmiedel, E. A.; Sheina, E. E.; Biewer, M. C., Block copolymer containing poly (3-hexylthiophene) and poly (4-vinylpyridine): Synthesis and its interaction with CdSe quantum dots for hybrid organic applications. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49* (8), 1802-1808.
79. Dai, C.-A.; Yen, W.-C.; Lee, Y.-H.; Ho, C.-C.; Su, W.-F., Facile synthesis of well-defined block copolymers containing regioregular poly (3-hexyl thiophene) via anionic macroinitiation method and their self-assembly behavior. *Journal of the American chemical society* **2007**, *129* (36), 11036-11038.
80. Alemseghed, M. G.; Gowrisanker, S.; Servello, J.; Stefan, M. C., Synthesis of Di-block Copolymers Containing Regioregular Poly (3-hexylthiophene) and Poly (tetrahydrofuran) by a Combination of Grignard Metathesis and Cationic Polymerizations. *Macromolecular Chemistry and Physics* **2009**, *210* (23), 2007-2014.
81. Alemseghed, M. G.; Servello, J.; Hundt, N.; Sista, P.; Biewer, M. C.; Stefan, M. C., Amphiphilic Block Copolymers Containing Regioregular Poly (3-hexylthiophene) and Poly (2-ethyl-2-oxazoline). *Macromolecular Chemistry and Physics* **2010**, *211* (12), 1291-1297.
82. Kaul, E.; Senkovskyy, V.; Tkachov, R.; Bocharova, V.; Komber, H.; Stamm, M.; Kiriya, A., Synthesis of a Bifunctional Initiator for Controlled Kumada Catalyst-Transfer Polycondensation/Nitroxide-Mediated Polymerization and Preparation of Poly (3-hexylthiophene)– Polystyrene Block Copolymer Therefrom. *Macromolecules* **2009**, *43* (1), 77-81.

83. Iovu, M. C.; Jeffries-El, M.; Zhang, R.; Kowalewski, T.; McCullough, R. D., Conducting Block Copolymer Nanowires Containing Regioregular Poly (3-Hexylthiophene) and Polystyrene. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* **2006**, *43* (12), 1991-2000.
84. Urien, M.; Erothu, H.; Cloutet, E.; Hiorns, R. C.; Vignau, L.; Cramail, H., Poly (3-hexylthiophene) based block copolymers prepared by “click” chemistry. *Macromolecules* **2008**, *41* (19), 7033-7040.
85. Kempf, C. N.; Smith, K. A.; Pesek, S. L.; Li, X.; Verduzco, R., Amphiphilic poly (alkylthiophene) block copolymers prepared via externally initiated GRIM and click coupling. *Polymer Chemistry* **2013**, *4* (6), 2158-2163.
86. Park, J.; Lee, K. S.; Choi, C.; Kwak, J.; Moon, H. C.; Kim, J. K., Effect of Molecular Weight on Competitive Self-Assembly of Poly (3-dodecylthiophene)-block-poly (methyl methacrylate) Copolymers. *Macromolecules* **2016**, *49* (9), 3647-3653.
87. Matsubara, R.; Gutierrez, A. C.; Jamison, T. F., Nickel-catalyzed Heck-type reactions of benzyl chlorides and simple olefins. *J Am Chem Soc* **2011**, *133* (47), 19020-3.
88. Matyjaszewski, K.; Xia, J., Atom transfer radical polymerization. *Chemical reviews* **2001**, *101* (9), 2921-2990.
89. Coessens, V.; Nakagawa, Y.; Matyjaszewski, K., Synthesis of azido end-functionalized polyacrylates via atom transfer radical polymerization. *Polymer Bulletin* **1998**, *40* (2-3), 135-142.
90. Erothu, H.; Kolomanska, J.; Johnston, P.; Schumann, S.; Deribew, D.; Toolan, D. T. W.; Gregori, A.; Dagron-Lartigau, C.; Portale, G.; Bras, W.; Arnold, T.; Distler, A.; Hiorns, R. C.; Mokarian-Tabari, P.; Collins, T. W.; Howse, J. R.; Topham, P. D., Synthesis, Thermal Processing, and Thin Film Morphology of Poly(3-hexylthiophene)–Poly(styrenesulfonate) Block Copolymers. *Macromolecules* **2015**, *48* (7), 2107-2117.

Vita

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