Development of Hydroarylation and Dehydration Methods for Conjugated Polymers

by

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Author’s Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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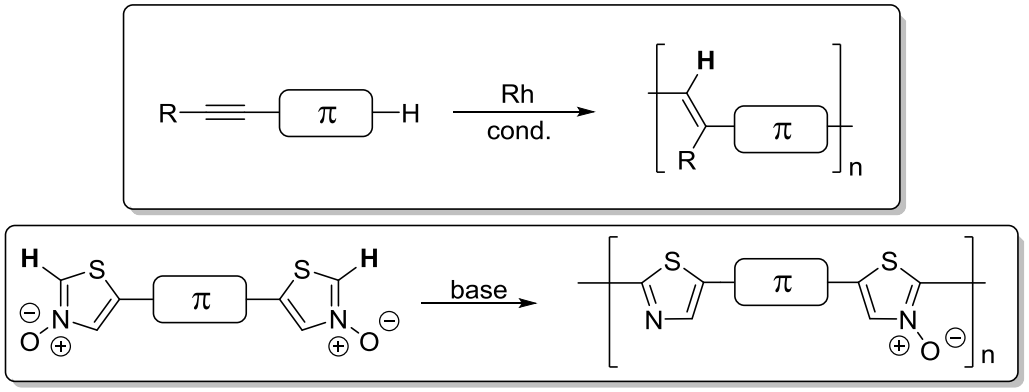
Abstract

Conjugated polymers represent an important next step for solar cell, field effect transistor, and light emitting diode technologies. However, there are several drawbacks to the current syntheses of this class of polymer that limit the field. The current routes to access conjugated polymers suffer from one or more of: synthetic complexity of the monomers, poor heteroaromatic tolerance or toxic by-products. Here we present two new methods to address these issues. First, a hydroarylation reaction to access poly(arylene vinylene)polymers and, second, a dehydration reaction of thiazole *N*-oxides for poly(heteroarene) polymers.



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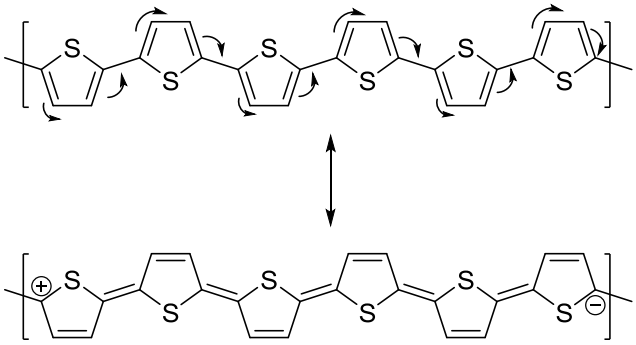
Ar	Aromatic ring
Bu	Butyl
Cp*	Pentamethylcyclopentadiene
DCM	Dichloromethane
DCE	1,2-Dichloroethane
DMA	Dimethyl Acetamide
DMF	Dimethyl Formamide
DPPF	1,1′-Bis(diphenylphosphino)ferrocene
E1cb	Unimolecular conjugate base elimination
E_2	Bimolecular Elimination
E_g	Energy gap or band gap
EH	2-ethylhexyl
Et_2O	Diethyl Ether
GC	Gas chromatography
HMPA	Hexamethylphosphoramide
HRMS	High Resolution Mass Spectrometry
***m*CPBA**	meta-Chloroperbenzoic acid
Me	Methyl
MeCN	Acetonitrile
M_n	Number average molecular weight
M_w	Weight average molecular weight
MS	Mass spectroscopy
NMR	Nuclear magnetic resolution
O/N	Overnight
OFET	Organic field effect transistor
OLED	Organic light emitting diode
OPV	Organic photovoltaic
PAV	Poly(arylenevinylene)
PBDB-T	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b'] dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-thylhexyl)benzo [1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PDI	Polydispersity index
PPV	Poly(phenelynevinylene)
Ph	Phenyl
Pin	Pinacolato
Piv	Pivaloyl
PPV	Poly(*p*-phenylenevinylene)
PT	Poly(thiophene)
SEC	Size exclusion chromatography
SPhos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl
TBB	Tolane-bis-benzyl
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TLC-MS	Thin layer chromatography-Mass Spectrometry
Tol.	Toluene

1.0 Introduction

1.1.0 Conjugated Polymers

The history of modern conjugated polymer research traces its origin to the studies performed in 1977 by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, where it was discovered that polyacetylene possessed atypically high conductivity for a polymer upon doping,[1] and were awarded the Nobel Prize in 2000 for their contributions.[2] Interest in this class of material continues to be driven by their wide variety of applications which take advantage of their unique combination of optoelectronic and polymeric properties. These applications include incorporation into organic photovoltaics (OPVs), light emitting diodes (OLEDs), and field effect transistors (OFETs).[3] Due to the fact that these materials are polymeric, rather than inorganic, several attractive properties become achievable: mechanical flexibility, impact resistance, optical transparency, improved processability to reduce costs, and tunability of the polymers by modification of the repeating units.[3]



Scheme 1. Delocalization of electrons along a conjugated polymer's backbone.

In many applications, it is accepted that polymer-based devices may never be able to outperform traditional electronic devices.[3] However, interest in these materials remains because their unique properties could allow them to be used in scenarios where silicon-based material cannot. Firstly, the deposition of transparent conjugated polymeric thin films on window panes convert them to low-efficiency solar cells, indistinguishable from regular window panes.[4] Their flexibility has allowed them to be implemented into curved displays that have found use in consumer products, as well as artistic and architectural applications.[5] Also, their reduced cost of manufacturing has allowed them to be used in transistor applications where requirements for device performance were not demanding.[6]

Even though these examples show that the potential of these materials has begun to be harnessed, much of it remains unrealized. This is due in large part to limited reactions that provide defect-free polymerization reactions that tolerate a good range of heteroaromatic rings and functional groups. A further drawback to the current syntheses is the synthetic complexity required to access the monomers increases the cost of production. By developing new polymerization strategies that resolve these issues, it would allow for a greater variety of high performing materials to be synthesized and studied at an increased pace.

The synthetic tools available to researchers are of great importance because they allow for control over one of the most important traits of conjugated polymers: their tunability. When designing conjugated polymers, there are several elements that must be considered: the length of the polymer, the electronic properties of the π-systems and substitutions, twist angle between π-groups, and solubility in organic solvents.

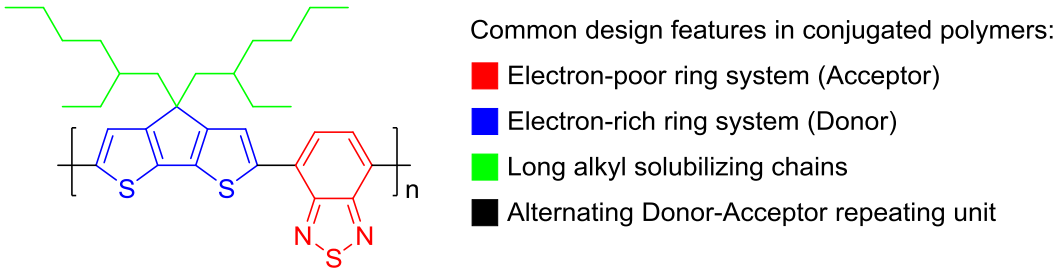


Figure 1. Conjugated polymer incorporating common design features.

To a point, the length of the chains affect the polymer's electronic properties by increasing the number of π-bonds that can be in conjugation where longer chains tend to lower the LUMO of the polymer and increase the charge carrier mobility. However this effect has shown saturation dynamics where there is a maximal effective conjugated length that can be achieved.[7] Above this effective conjugated length, the bandgap energy ceases to be affected by increasing the length of the polymer.

The relevant values for characterizing of the length of a polymer are the number average molecular weight (M_n), the weight average molecular weight (M_w), and the polydispersion index (PDI). In brief, the M_n is the average molecular weight in which the number of chains above and below it are equal. Whereas the M_w is the average molecular weight in which the mass of chains above and below it are equal. Because longer chains have a heavier mass, M_w is always greater than or equal to M_n. Thus the PDI, defined as M_w/M_n, is always greater than or equal to 1. The PDI functions much like a measurement of standard deviation in molecular weights to express the uniformity, or lack thereof, in chain length; the closer the PDI is to 1, the more monodisperse the polymer.[8]

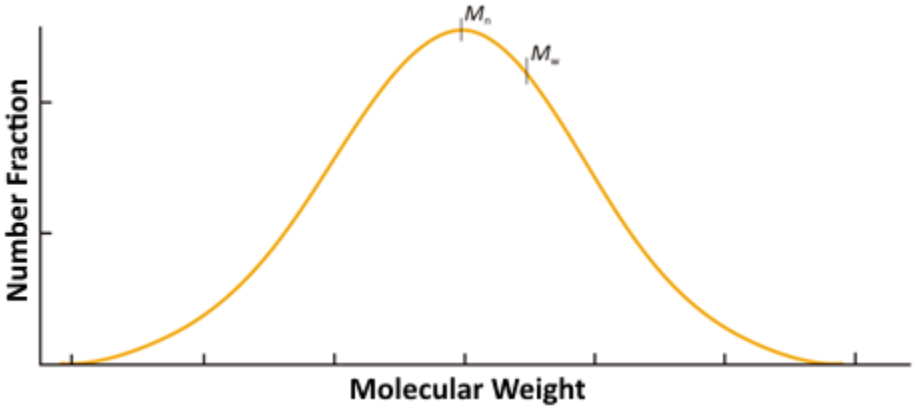


Figure 2. Graph illustrating the distribution of molecular weights amongst polymer chains.

Because there are a large variety of conjugated polymers that are used in wide range of applications, it is difficult to prescribe a precise number on what the desired molecular weight is best for device performance. However, for poly(thiophene), some studies suggest that an M_w of ~25kDa should be achieved to ensure reproducibility and that the effective conjugated length is met.[9]

One of the main advantages of conjugated polymers is their tunability. Even simple substitutions of the side chains of polymers used in LEDs will alter the colours emitted (**Figure 3**)[10] and substitutions of the side chains of polymers used in solar cells will shift the range of light absorbed.[11]

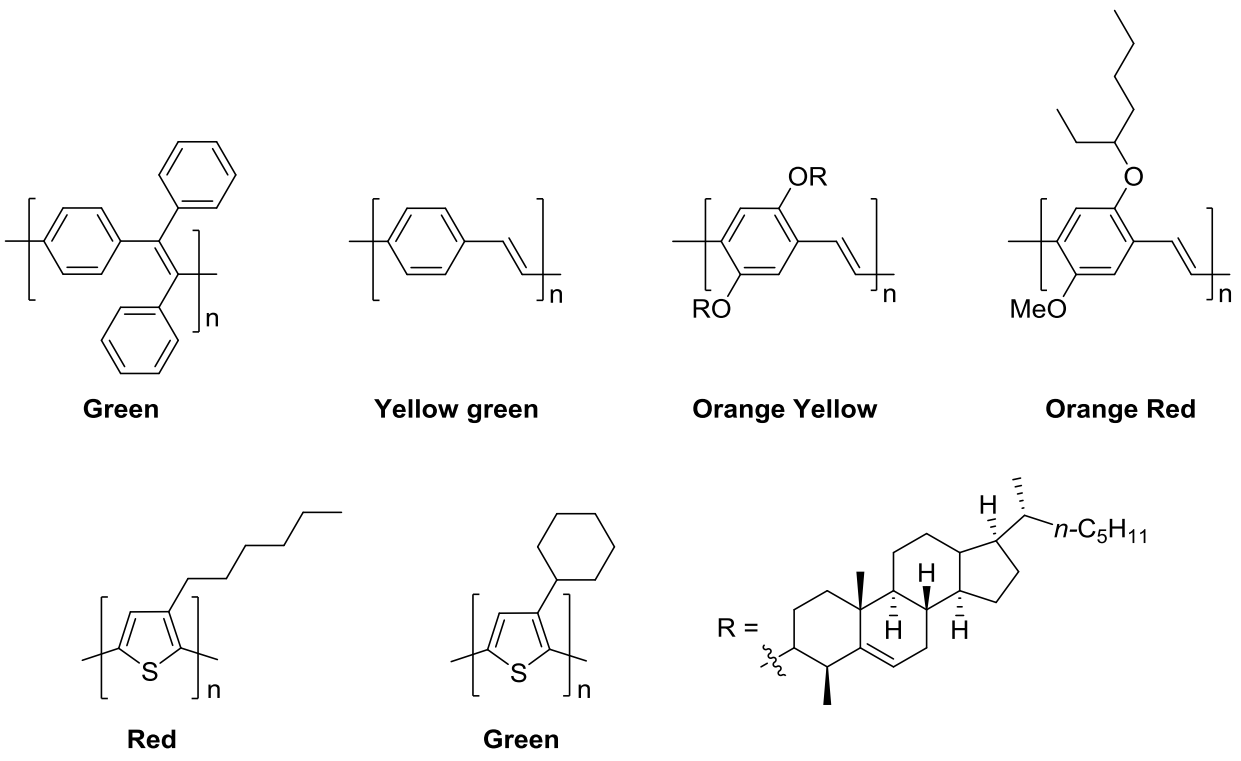


Figure 3. Effect of substitutions to the repeating on the colour of light emitted in polymeric LEDs.

The electronics can be further tuned by the choice of aromatic rings incorporated in the polymer backbone. For example, the polymer poly(thiophene) has a band gap (E_g) of 1.8 to 2.2 eV whereas poly(pyrrole) has an E_g of 2.9 to 3.2 eV.[12] Furthermore, by designing the repeating unit to contain alternating donor (electron rich) and acceptor (electron poor) rings, the HOMO-LUMO gap is significantly reduced.[3]

For the polymer to have conductive properties, there must be little to no twisting in the backbone such that the p-orbitals can overlap and allow delocalization along the chain. Consider poly(*p*-phenylene) (**Figure 4**), which has steric interactions between adjacent rings: the angle between benzene units are ~40˚ and thus the material is insulating (E_g of 4.0 eV).[13] Whereas poly(*p*-phenyl vinylene) has vinyl groups which limits the steric interactions that inhibit coplanarity of the rings and allows for p-orbital overlap.[14] In poly(thiophene), the five-membered rings adopt an orientation that avoid steric interactions of the hydrogens at the 3 and 4 positions to achieve high coplanarity along the chain.[15] Twisting thus depends on steric effects which must be kept to a minimum. This is often in direct competition with solubility (and thus processability) of the polymer because the primary method to increase solubility is to add large alkyl chains to the repeating units.

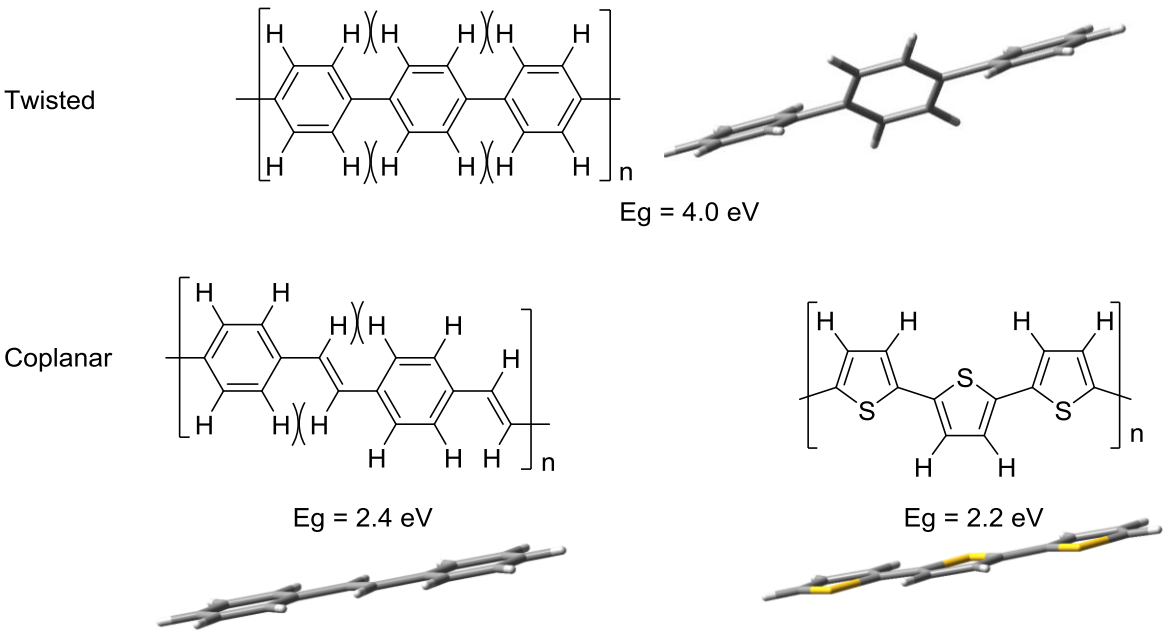


Figure 4. PPP[16] is twisted compared to PPV[17] and PT[12].

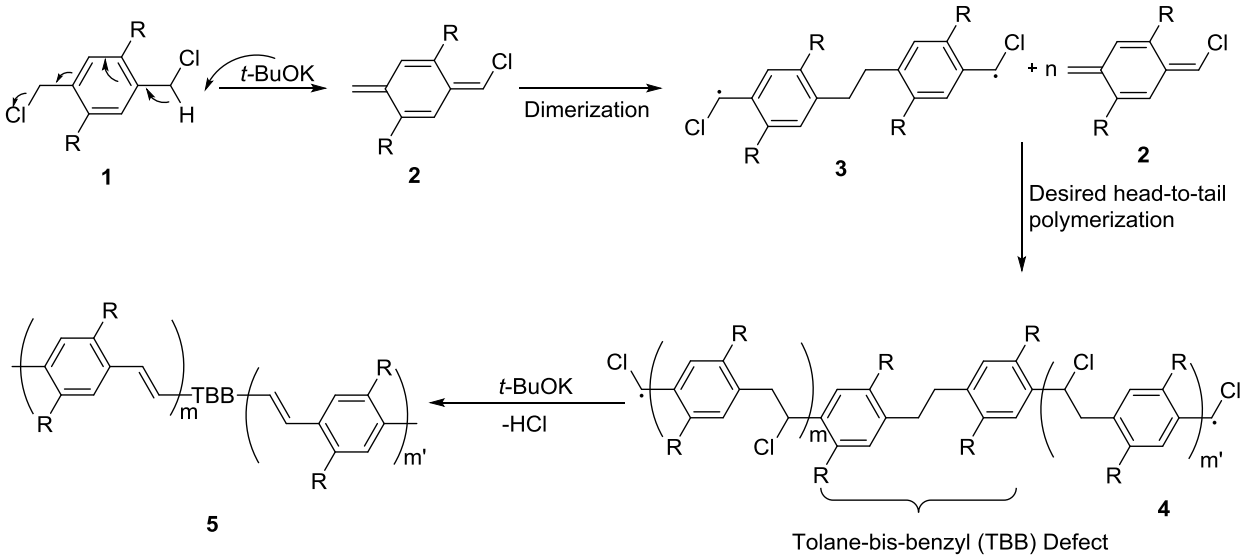
In addition to these properties that, to some degree, can be rationally pursued by design of the repeating unit, performance depends significantly on the solid state packing of the polymer which is very difficult to predict and control.[3] As a result of this, and the previously presented aspects that can be tuned, a large amount of effort must be invested by chemists to synthesize a large number and wide scope of polymers. Thus, advancements in the field greatly rely on developing robust and streamlined synthetic strategies.

1.2.0 Synthesis of Poly (*p*-Phenyl Vinylene)-Type Polymers

Conjugated polymers composed of alternating aromatic and alkene in the repeating units, such as poly(*p*-phenylenevinylene) (PPV) and the more general structure known as poly(arylenevinylene) (PAV) are of particular importance in the field of optoelectronic organic materials.[18] Historically, their importance comes from being the first polymers to exhibit electroluminescence, the phenomenon exploited in light-emitting diodes, in 1990 by Burroughes et al.[19] However, research in this type of polymer has stagnated as compared to other conjugated polymers, in large part due to lack of recent innovation in synthetic methods used for accessing them.

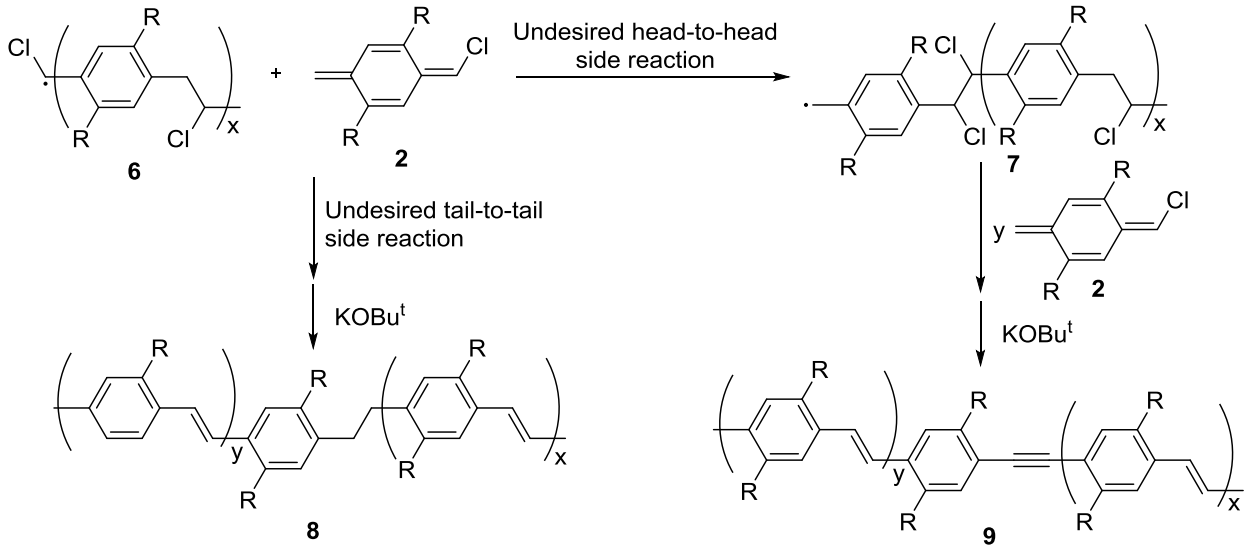
There are currently two general approaches to synthesizing PPV-type polymers: the precursor routes, which proceed through *p*-quinodimethane monomers, and the polycondensation routes, which employ cross-coupling and olefination reactions.[18,20] The precursor routes most widely used today are the Gilch polymerization (**Scheme 2**), which results in many defects (**Scheme 3**), the Wessling polymerization (**Scheme 4**), and the dithiocarbamate polymerization (**Scheme 5**). A variety of cross-coupling and olefination reactions have been investigated, including the Wittig reaction, the Knoevenagel reaction, the Heck, Suzuki, and Stille couplings (**Scheme 6**).[21] Such reactions will be referred to as polycondensations.

The first reported synthesis of a PPV occurred in 1966 when Gilch and Wheelwright showed the polymerization of a symmetrical α,α'-dichloro *p*-xylylene precursor (**1**).[22] This reaction is considered a precursor route because the reactive monomer that is being polymerized (**2**) is generated via a 1,6-E_2 elimination by treating **1** with base.[23] The mechanism is presented in **Scheme 2**. Polymerization initiated by the dimerization of **2** to produce an α,ω-biradical (**3**) which will ultimately result in a tolane-bis-benzyl (TBB) in the chain. Subsequent to initiation, the chain then propagates through radical polymerization to form the PPV-precursor polymer (**4**) which is converted *in situ* to PPV (**5**) (if an excess of base was used) or can be converted in a separate step if not.[24] Conjugated polymers typically have poor solubility in organic solvents. As a result, the R-groups incorporated into the precursor are usually long alkyl chains to increase solubility.



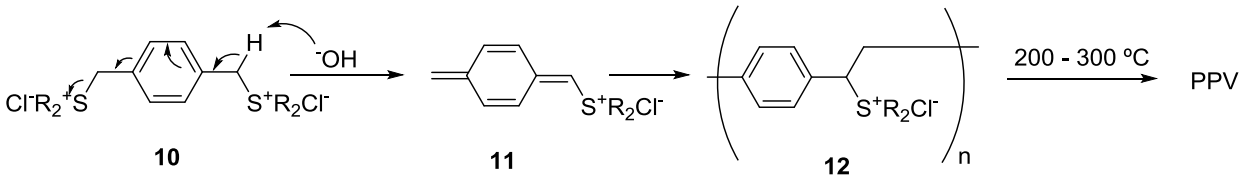
Scheme 2. Gilch approach to PPV.

A major problem with the Gilch route is that the resulting polymer incorporates many defects. The polymer inherently contains a TBB defect due to the initiation mechanism and, furthermore, the undesired head-to-head and tail-to-tail additions lead to TBB (**8**) and alkynyl (**9**) defects, respectively (**Scheme 3**). These structural defects that accumulate in significant amounts severely compromise the Gilch polymerization's synthetic usefulness in electronic devices which require virtually defect-free polymers.[25]



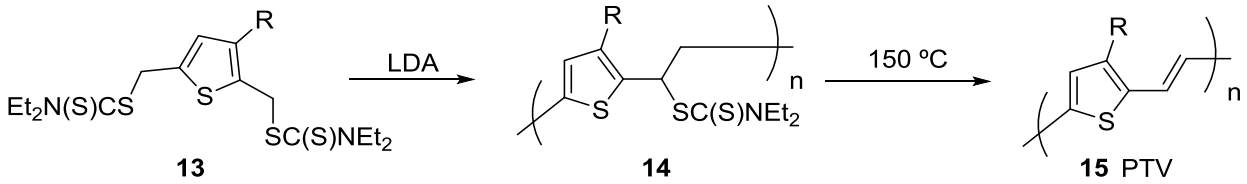
Scheme 3. Defect resulting from head to head polymerization.

Another precursor route is the Wessling polymerization (**Scheme 4**), which was developed in 1968.[26] Again, the precursor is converted to a reactive monomer through an E_2 like 1,6-elimination. However, in this route the precursor is a 1,4-bis-(dialkylsulfoniomethyl)-benzene salt (**10**). The ionic functional groups also serve as hydrophilic solubilizing groups that allow for the polymerization to occur in water and can be removed by treating the polymer with heat.



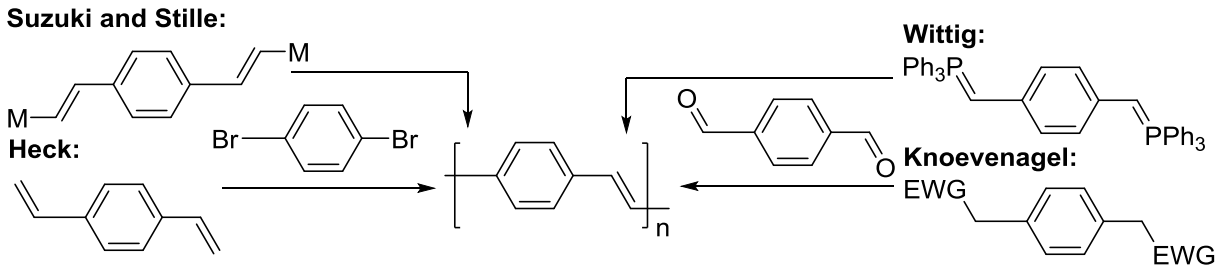
Scheme 4. The Wessling method to synthesize PPV.

The previous two methods discussed, the Gilch and Wessling polymerizations, have another significant drawback: they tolerate heterocyclic aryl rings poorly, which are extremely important in organoelectronic materials.[18] This limitation has been overcome with the development of the dithiocarbamate route (e.g. **Scheme 5**).[27] However, this method still has the structural defect problems of the other precursor routes listed above.[28]



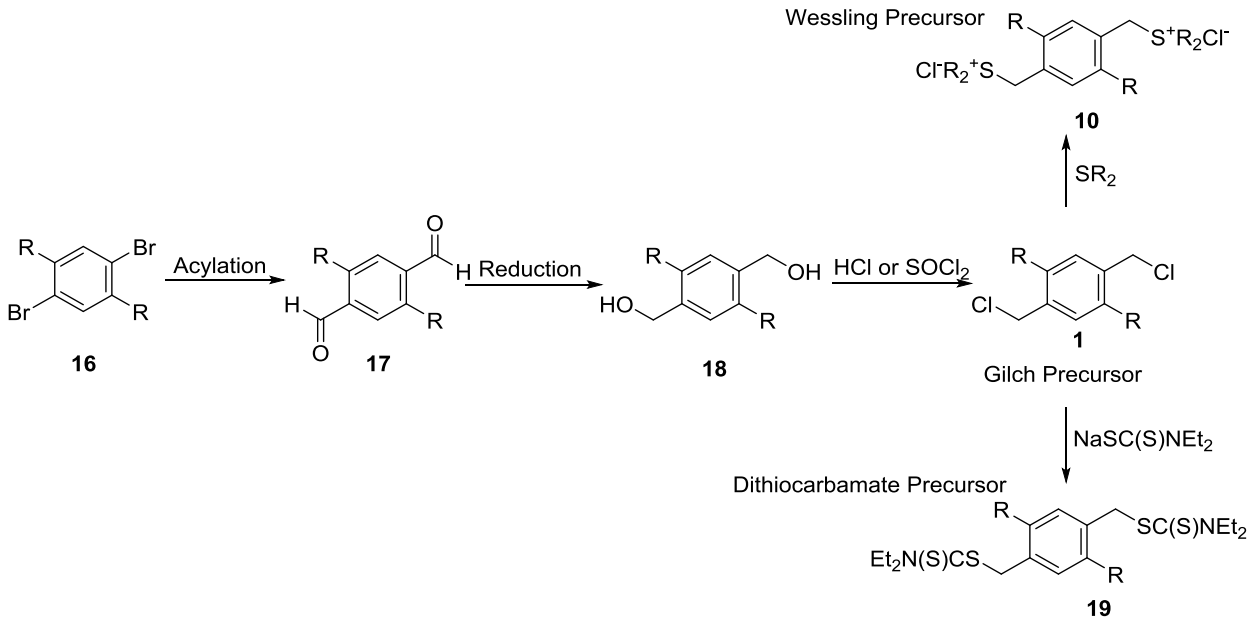
Scheme 5. Synthesis of poly(thienylvinylene) (PTV) via the dithiocarbamate route.

Although these precursor routes offer polymers of relatively high molecular weights (mass average molar mass, M_w, up to 250 kDa) and relatively low molecular weight distribution (polydispersity index, PDI, of 1.4-2.1), they lack the control over design of the polymer that polycondensation reactions (**Scheme 6**) can provide. Due to the step-growth nature of polycondensation reactions, strictly alternating copolymers can be synthesized. In many electronic applications, this becomes vital because alternating donor-acceptor units lead to low band gaps, excellent light-harvesting abilities, and high charge mobility.[29] Unfortunately, PAVs synthesized by polycondensation reactions have low M_w (8 to 25 kDa).[20]



Scheme 6. Access to PPV via polycondensation reactions.

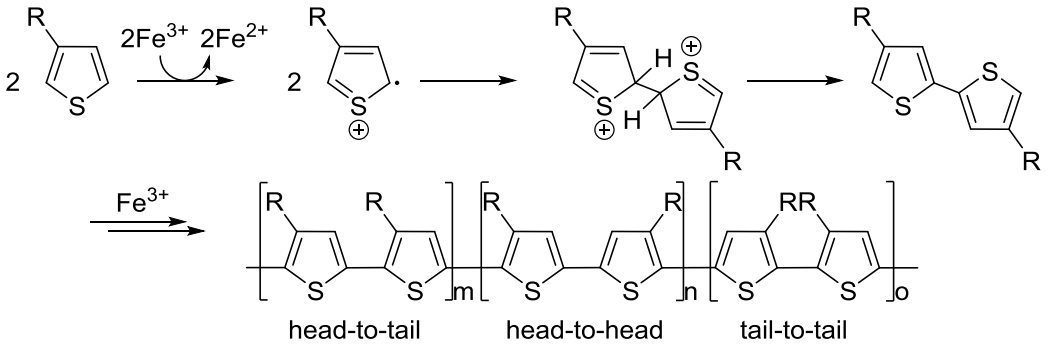
In all of the routes discussed thus far, another disadvantage is the fact that the monomers are highly functionalized and require several steps to produce which adds to the synthetic complexity and decreases the efficiency of the overall synthesis. In **Scheme 7**, it can be seen that the precursor for the Gilch route requires at least three synthetic steps in addition to any steps that are required for installing the solubilizing R groups.[30] Furthermore, the precursors in the Wessling and dithiocarbamate routes require another step to access them. Similarly, in the polycondensation routes, both monomers need to be functionalized to a significant degree to create reactive carbon-heteroatom bonds. Often, these heteroatoms produce stoichiometric waste molecules that may be difficult to separate from the desired polymers.



Scheme 7. General synthetic approach to the various monomers.

1.3.0 Synthesis of Poly(hetero)arene-Type Polymers

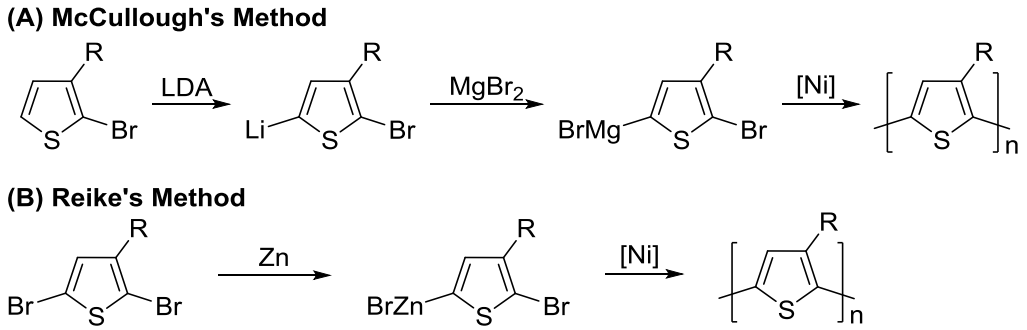
The first syntheses of poly(thiophene)s, one of the most important poly(hetero)arene-type polymers, were achieved through electrochemical and oxidative polymerization techniques.[30] However, completely unmodified poly(thiophene) suffers from poor solubility do its rigid rod morphology. To overcome this, a solubilizing chain is placed on the 3-position of the thiophene units, such as a hexyl group. In these two polymerization techniques, there is little to no regiocontrol and thus many head-to-head and tail-to-tail defects occur instead of the desired head-to-tail repeating unit.[31]



Scheme 8. Oxidative polymerization leads to head-to-head and tail-to-tail defects.

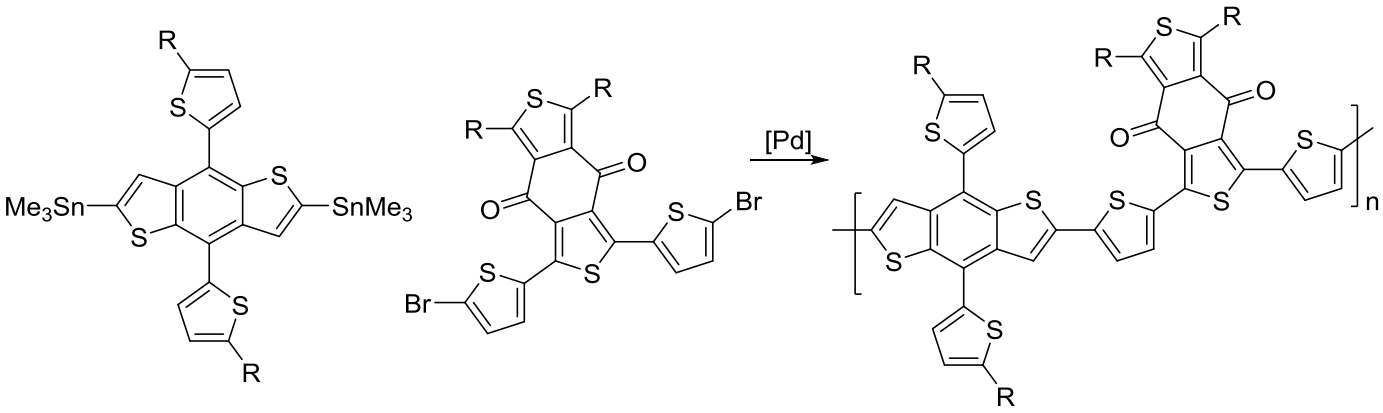
Highly regioregular poly(3-alkylthiophene)s can be achieved by LDA lithiation of 2-bromo-3-alkylthiophene followed by metal-catalyzed Kumada cross-coupling of thiophene Grignard reagents (McCullough's method).[32] Alternatively, selective oxidative addition of zinc followed by a Negishi cross-coupling reaction (Reike's method) can be used.[33] Both methods can afford highly regioselective products, and they are illustrated in **Scheme 9**.

The reason that regioregularity is important is that compared with their regiorandom counterparts, UV-Vis absorption wavelength (λ max) of regioregular poly(3-alkylthiophene)s have red-shifts of 40 to 90 nm. This indicates a reduction of the bandgap compared to the regiorandom polymers, which is important in many applications.[32,33]



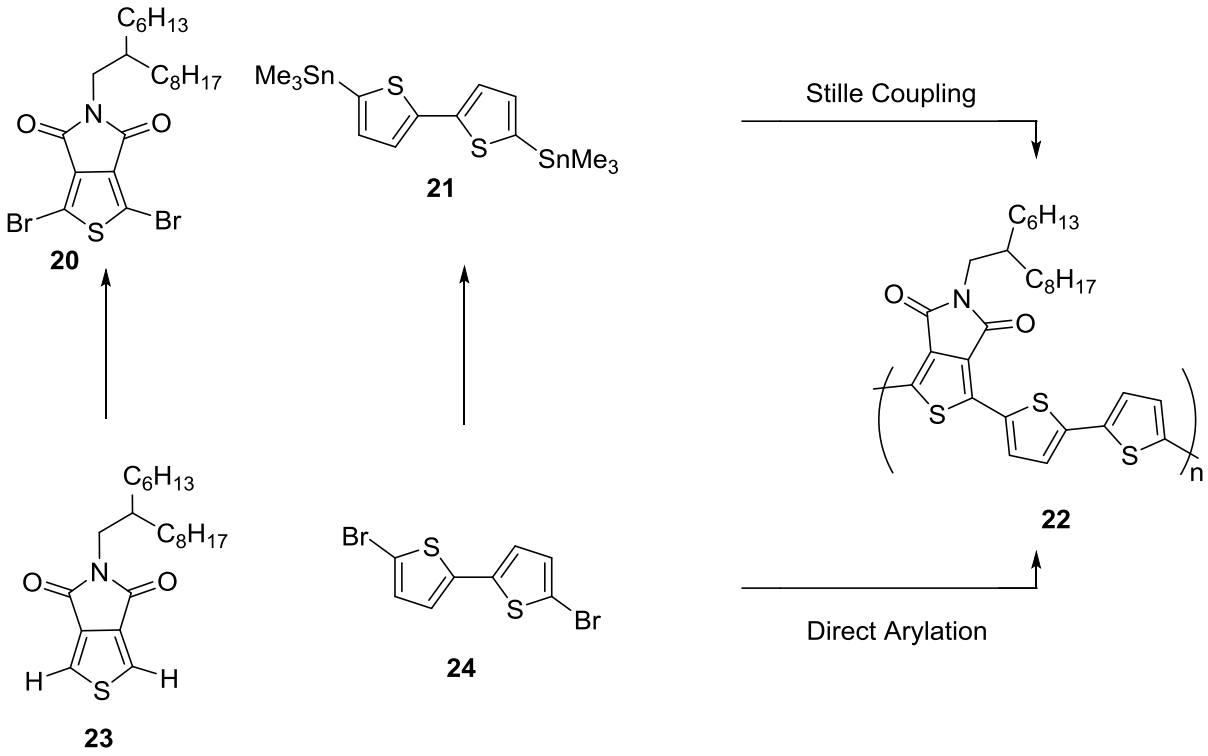
Scheme 9. (A) McCullough's and (B) Reike's method for synthesizing regioregular poly(thiophene).

However, these aforementioned routes do not allow for incorporating the complex heteroaromatic rings typically observed in high performance materials. To access these repeating units, such as the one in PBDB-T (**Scheme 10**), which has the current power-conversion efficiency world record, the Stille route has been extensively used.[34] It has the advantages of working for a large scope of heteroaromatic systems, granting access to alternating donor-acceptor motifs, and can achieve high molecular weights. However, one of the drawbacks is that synthesizing these monomers can be rather laborious, in part due to incorporating the stannyl groups.



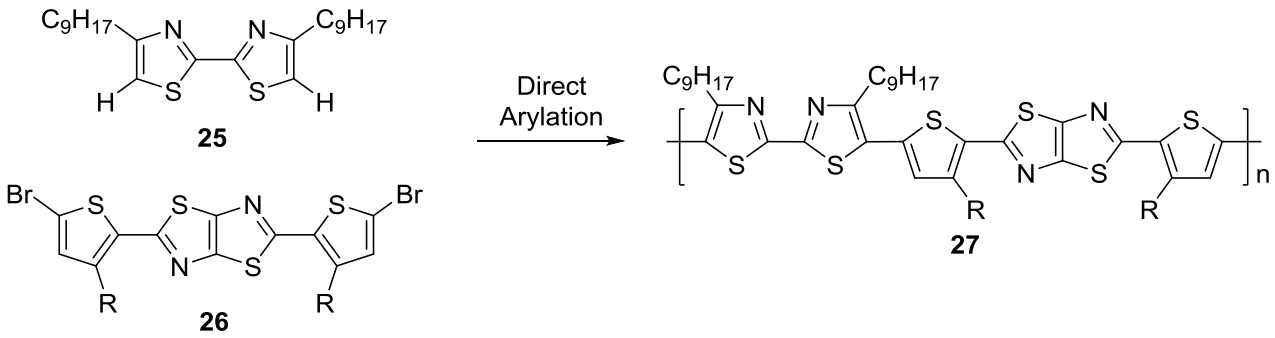
Scheme 10. Development of complex, high-performing conjugated polymer PBDB-T through a Stille strategy.

A recent approach to reduce synthetic complexity is to employ transition metal catalyzed reactions that can directly activate carbon-hydrogen (C-H) bonds. This eliminates steps that convert hydrogens into halides, metals, or other heteroatoms that are typically required for carbon-carbon bond forming reactions. One example of C-H bond activations is the direct arylation transformation presented in **Scheme 11**, which allows for couplings that would normally necessitate an extra synthetic step for the installation of highly toxic alkyltin.[35] It has been shown that direct arylation polymerization has been able to streamline the monomer synthesis while retaining the key strengths of the Stille coupling route. A further benefit of this route is that the tin byproduct of the reaction was eliminated.



Scheme 11. Comparison of the Stille coupling and direct arylation as polymerisation reactions.

The above example, from the Leclerc group at the University of Laval,[35] demonstrated a high performance polymer, **22**, being made both by the Stille and DArP methods. In using the DArP strategy, the monomer synthesis was streamlined due to the fact that both (**23**) and (**24**) were isolated synthetic intermediates towards the monomers (**20**) and (**21**) used in the Stille route.



Scheme 12. Direct arylation example incorporating thiazoles into the polymer.

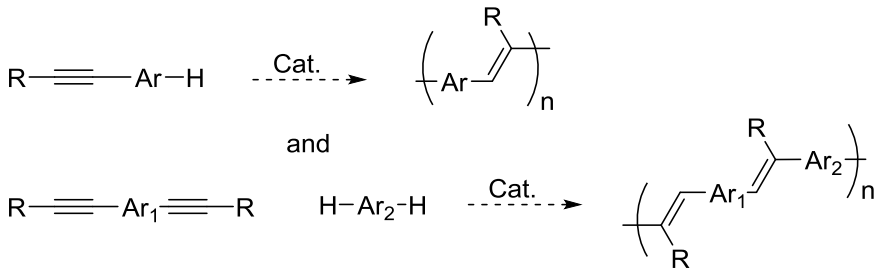
A heteroaromatic ring of great importance in conjugated polymers that has demonstrated high performance in several key properties is thiazole.[36] Incorporation of such heteroaromatic rings would be difficult without the Stille and DArP routes (**Scheme 12**), thus demonstrating that two relatively recent advances in these polymerization methods has been key to advancing organic device performance.

2.0.0 Results and Discussion

2.1.0 Hydroarylation Polymerization

2.1.1 Optimization of the AB Homopolymerization

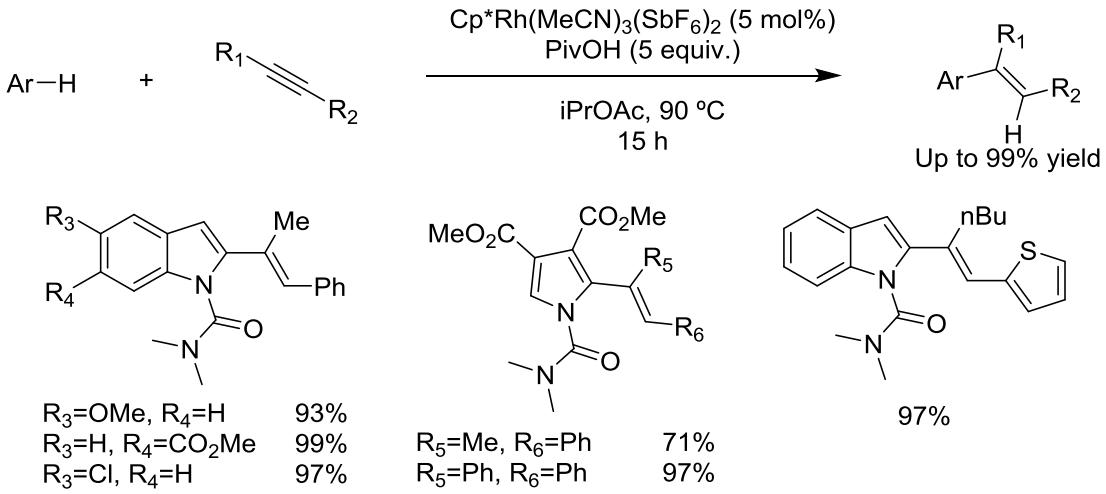
With the desired structural aspects of the repeating units and the desired traits of polymerization reactions outlined, this thesis presents two robust synthetic strategies that reduce synthetic complexity of monomers, incorporate heteroaromatic rings, and limit toxic by-products. First, we present a hydroarylation reaction strategy, the formal addition of an arene C-H bond across an alkyne, for accessing PAVs (**Scheme 13**) as an alternative polymerization. The advantages we were aiming for with this approach over previous routes for PAVs are that it will be atom-efficient, not generate toxic by-products, and have a high tolerance to functional groups and heteroaromatic rings. With the emerging field of conjugated polymers, developing new synthetic tools with such traits will be essential for their continued growth in efficiency.



Scheme 13. Proposed hydroarylation polymerization

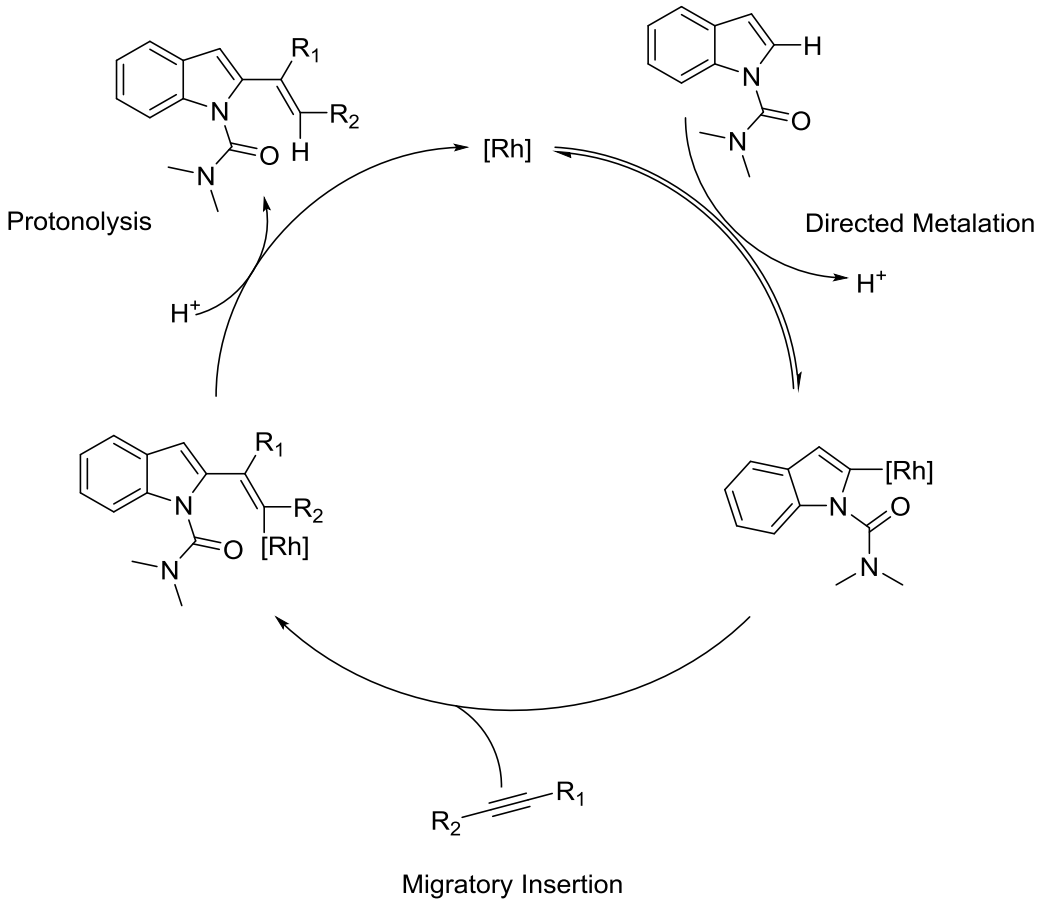
From examining a Fagnou *et al.* hydroarylation paper, we had a clear idea of initial conditions and substrates to investigate for the purpose of polymerization. We imagined that this rhodium catalysed transformation reported for small molecule reactions could be extended to polymerization because many of the compounds undergo hydroarylation in very high yield, which would be vital in synthesizing high molecular weight polymers (**Scheme 14**).[37] Another attractive trait of this small molecule reaction was that it

proceeded in high regioselectivity, with only the regioisomer that resulted in linear π-conjugation being observed.



Scheme 14. Small molecule reaction to be adapted to polymerization reaction with partial scope presented.

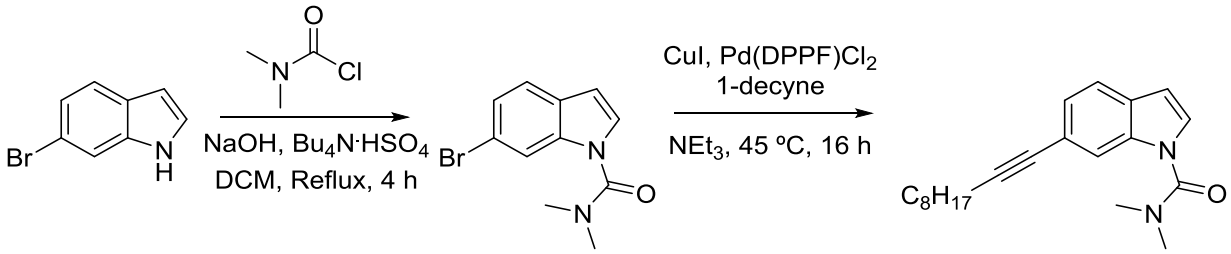
This hydroarylation reaction is proposed to proceed through the mechanism shown in **Scheme 15**.[37] The catalytic cycle begins with the directed metalation 2-position of the indole resulting in C-H bond cleavage by rhodium. It is in this elementary step that the carbomoyl group performs its role; as a directing group it guides the rhodium to the 2-position by interacting with the rhodium to form a 5-membered ring. This is followed by the migratory insertion of the alkyne and finally protonolysis to expel the 2-vinyl indole product and regenerate the rhodium catalyst.



Scheme 15. Mechanism for the hydroarylation reaction. [37]

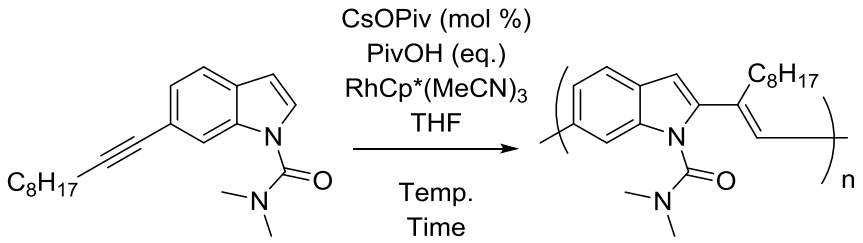
For our purposes of extending this reactivity to a polymerization reaction, the initial monomer investigated for optimization was a 6-alkynyl indole (**30**) because the carbomoyl capped indole showed remarkable reactivity in the literature small molecule reaction and because of its ease of preparation (**Scheme 16**). Another reason for selecting this as our model monomer is that AB polymerization (AB referring to the two functional groups involved in the transformation reaction being on the same monomer) required the synthesis of only one monomer and this assures that the reactive C-H and alkyne are present in an exact one-to-one ratio. The commercially available 6-bromoindole (**29**) had the carbamoyl group installed through previously reported conditions.[37] Subsequently, a

Sonogashira reaction was performed to couple the alkyne at the 6-position to produce **30** in acceptable yield (**Scheme 16**). With **30** in hand, various conditions were then screened and optimized to produce the polymer **31** (**Scheme 17**).



28 **29** 89 % **30** 68 %

Scheme 16. Synthesis of the AB monomer (**30**).



30 **31**

Scheme 17. General polymerization conditions investigated and optimized

Our original attempt to transfer the literature conditions to this AB monomer did not result in anything more than small oligomers that we did not bother to isolate (**Table 1, line 1**). The monomer **30** required the addition of catalytic CsOPiv to produce polymers large enough to be isolated by precipitation in methanol. The rationale for the addition of this CsOPiv was that a base may aid in the C-H bond cleavage taking place in the directed metalation step of the hydroarylation and that specifically CsOPiv would be good due to PivOH already being the acid present for the protonolysis step.[37] Loading of CsOPiv at

5% was found to produce the highest molecular weight polymers (**Table 1, line 2**). Next, a fairly typical screening of the concentration of the monomer in THF took place. There appeared to be a local maximum at 0.25 molar but its effect was not very pronounced (**Table 2**).

Table 1. CsOPiv screening

CsOPiv (mol%)	THF [M]	PivOH (eq.)	Temp (°C)	Time (h)	M_n (kDa)	M_w (kDa)	PDI
0	0.33	5	90	22	NA	NA	NA
5	**0.33**	**5**	**90**	**22**	**6.7**	**12.5**	**1.6**
10	0.33	5	90	22	6.9	11	1.6
20	0.33	5	90	22	NA	NA	NA
50	0.33	5	90	22	NA	NA	NA

Table 2. Solvent concentration screening

CsOPiv (mol%)	THF [M]	PivOH (eq.)	Temp (°C)	Time (h)	M_n (kDa)	M_w (kDa)	PDI
5	0.33	5	90	22	7.6	12.2	1.6
5	**0.25**	**5**	**90**	**22**	**8.6**	**12.8**	**1.5**
5	0.22	5	90	22	7.7	12.5	1.6
5	0.20	5	90	22	7.2	12	1.7

Next the amount of pivalic acid (PivOH) used was screened. This was shown to have a significant effect on the molecular weight. The number average molecular weight (M_n) was found to almost double when changing from the original 5 equivalents to 10 equivalents (**Table 3**).

Table 3. PivOH screening

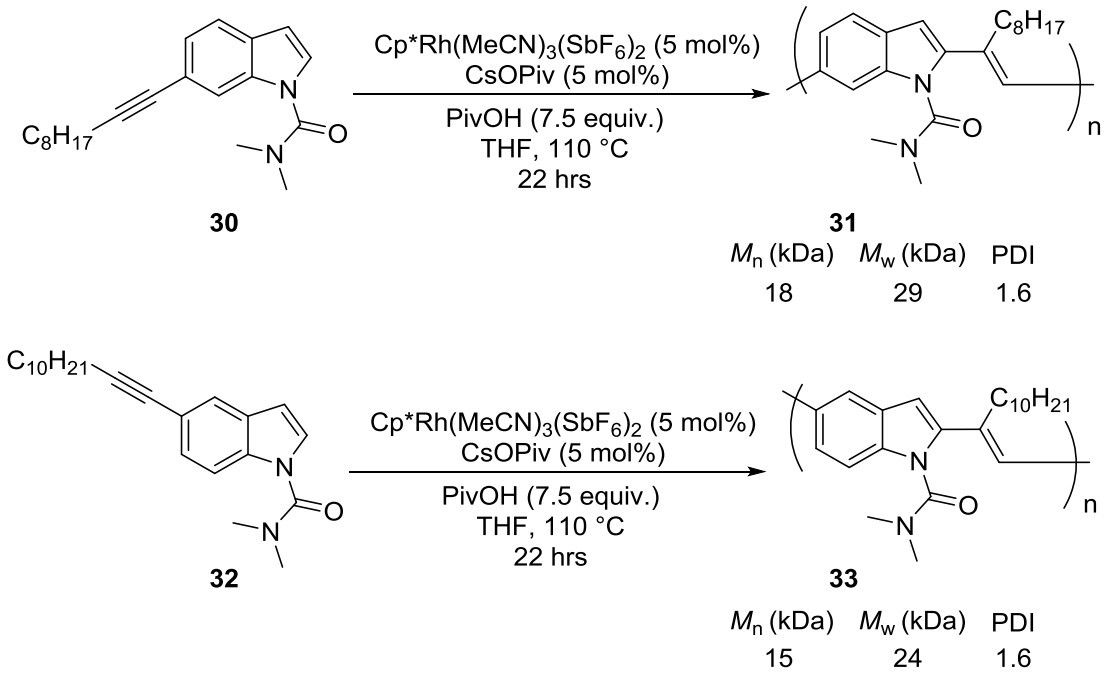
CsOPiv (mol%)	THF [M]	PivOH (eq.)	Temp (°C)	Time (h)	M_n (kDa)	M_w (kDa)	PDI
5	0.25	5.0	90	22	8.6	12.8	1.5
5	0.25	7.5	90	22	9.0	15.3	1.7
5	**0.25**	**10.0**	**90**	**22**	**15.9**	**18.8**	**1.2**
5	0.25	15.0	90	22	10.8	21.2	2.0

Our next investigation into optimizing the reactions was a fairly standard temperature screening. Investigations included determining whether the use of an oil bath for an overnight reaction or running the reactions in a microwave reactor (MW) for 4 hours was more effective. It was found that increasing the temperature to 110 °C in an oil bath resulted in the highest molecular weights (**Table 4**). Above this temperature, the molecular weights achieved diminished.

Table 4. Temperature Screening

CsOPiv (mol%)	THF [M]	PivOH (eq.)	Temp (°C)	Time (h)	M_n (kDa)	M_w (kDa)	PDI
5	0.25	7.5	90 (MW)	4	9.3	13.8	1.5
5	0.25	7.5	100	22	16.5	22.4	1.4
5	0.25	7.5	100 (MW)	4	13.0	20.0	1.5
5	**0.25**	**7.5**	**110**	**22**	**18.4**	**29**	**1.6**
5	0.25	7.5	110 (MW)	4	11.0	18.9	1.7
5	0.25	7.5	120	22	17.1	23.0	1.3
5	0.25	7.5	130 (MW)	4	10.6	19.5	1.8
5	0.25	7.5	150 (MW)	4	9.6	17.6	1.8

The optimal conditions to date for the homopolymerization are presented below in **Scheme 19**. In addition to the 6-alkynylindole that had been investigated for the optimization screenings, a 5-alkynylindole was also polymerized.

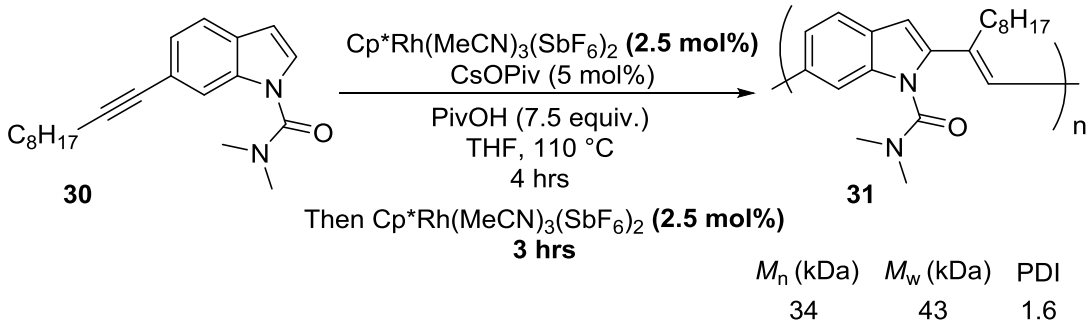


Scheme 18. Optimized homopolymerization conditions using a single addition of the rhodium catalyst.

Our MW reactor in the lab has a robotic arm, which allows for reaction mixtures to be queued. During our screening efforts, we found that samples earlier in the queue routinely resulted higher molecular weights and reactions that were third in queue or later would fail to polymerize. This led us to believe that the deactivation of the rhodium catalyst may be limiting the molecular weights obtained. Following this observation, new conditions were devised to attempt to polymerize monomer **30**. Rather than add all 5% mol of the rhodium catalyst at the beginning of the reaction, 2.5% mol was added at the start of the reaction then an additional 2.5% mol was added after 4 hours. The reasoning behind the choice of 4 hours was that because a reaction that was in the microwave queue for 4 hours failed to react, the catalyst must be deactivated and rendered ineffective by that time when in the reaction medium. The results from this 2 x 2.5% addition experiment were very promising. For the first time, the reaction mixture was pushed to

the point insolubility, a phenomenon that occurs when the polymer reaches sufficiently large molecular weight. Optimizing the reaction time subsequent to the second addition were performed where it was found that the optimal time was found to be 3 hours, with the polymers resulting in molecular weights of M_n of 34 kDa and an M_w of 43 kDa. No further optimization took place after this, because higher molecular weight could not be achieved beyond the molecular weights that are still soluble in THF and, at this time, we did not want to pursue solubilizing chains other than the octyl chain in these screenings (such as the branched 2-ethyl hexyl which may have increased polymer solubility).

This hydroarylation reaction formed C-C bonds through the formal addition of a C-H bond at the 2-position of an indole across an internal alkyne to access PAV polymers. Optimization efforts brought molecular weights of this AB polymer from small oligomeric products to a relatively large molecular weights M_n = 34, M_w= 43 kDa (**Scheme 19**). Solutions to low reactivity under the original conditions inspired by the source literature's small molecule reaction included the addition of catalytic CsOPiv, raising the equivalents of PivOH additive, and doing portionwise additions (two 2.5 mol% loadings) of the rhodium catalyst. With optimized polymerization conditions identified, the scope of the reaction was examined through AA BB polymerization strategies.

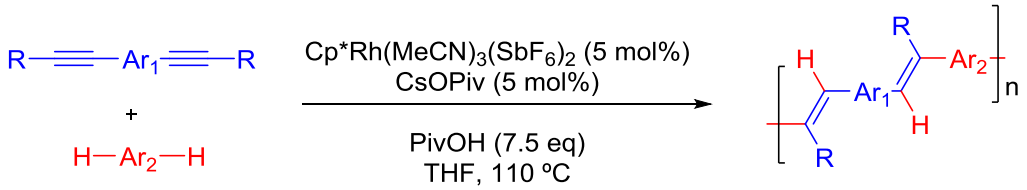


Scheme 19. Optimized polymerization conditions for the 6-position derivative using multiple additions, at reduced molar equivalence, of the rhodium catalyst.

2.1.2 Scoping of the AA BB Homopolymerization

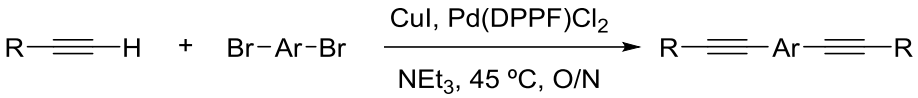
With the optimized reaction conditions for the AB polymerization completed, attention turned to extending reactivity to an AA BB polymerization strategy (**Scheme 20**), where two monomers, one possessing two alkynes, was reacted with another monomer possessing two reactive C-H bonds. To access the dialkyne monomers, Sonogashira reactions were used to couple terminal alkynes to dibromo arenes (**Scheme 21**

A). The terminal alkyne that was chosen was didodecyne because it allowed for the incorporation of a solubilizing chain to the repeating unit. Next, for the monomer containing two reactive C-H bonds, diindole species were designed for their simplicity to synthesize through Suzuki-Miyaura coupling reactions (**Scheme 21B**). The amidated 6-bromoindole (**29**) was converted to the pinacol boronate ester (**34**) and this product was isolated in 96% yield. The motivation for isolating the boronate ester instead of doing a one-pot synthesis of diindole was that the boronate ester could be further used to incorporate arenes that are common in conjugated polymers, such as thiophenes, benzothiodiazoles, and fluorenes.

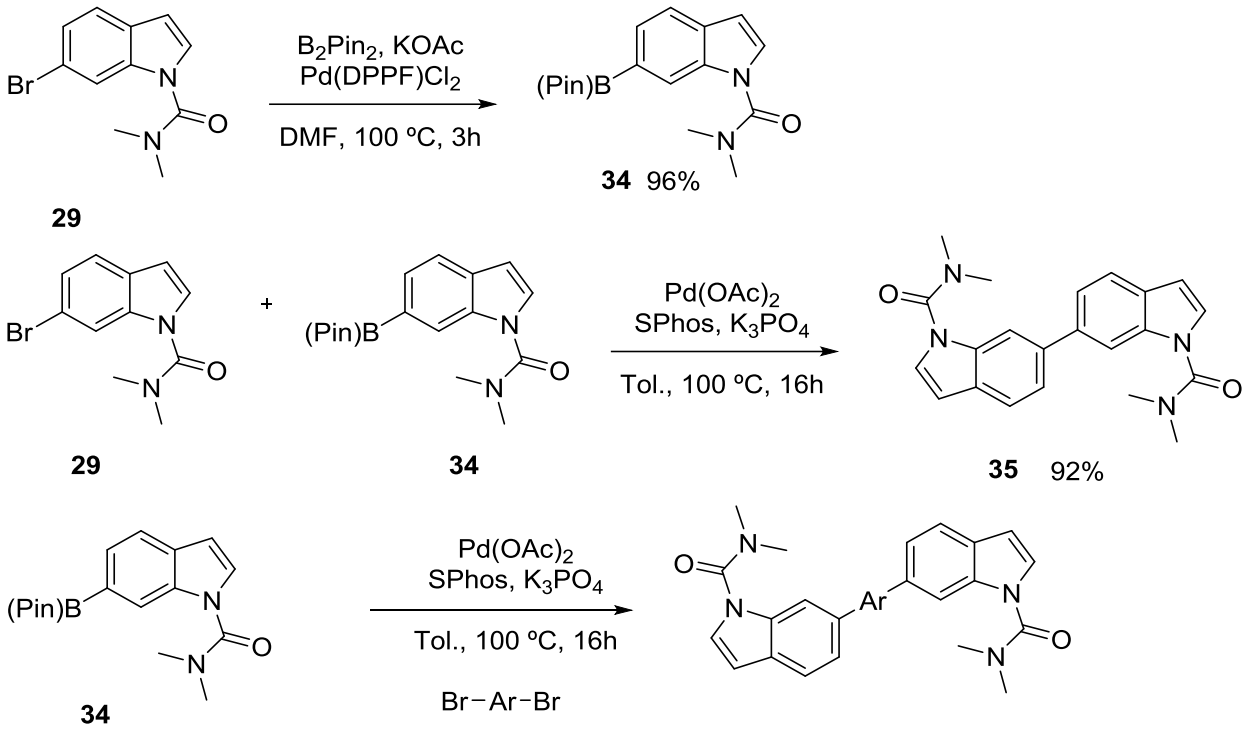


Scheme 20. General reaction equation for an AA BB homopolymerization via the hydroarylation reaction.

(A) Sonogashira Coupling Strategy



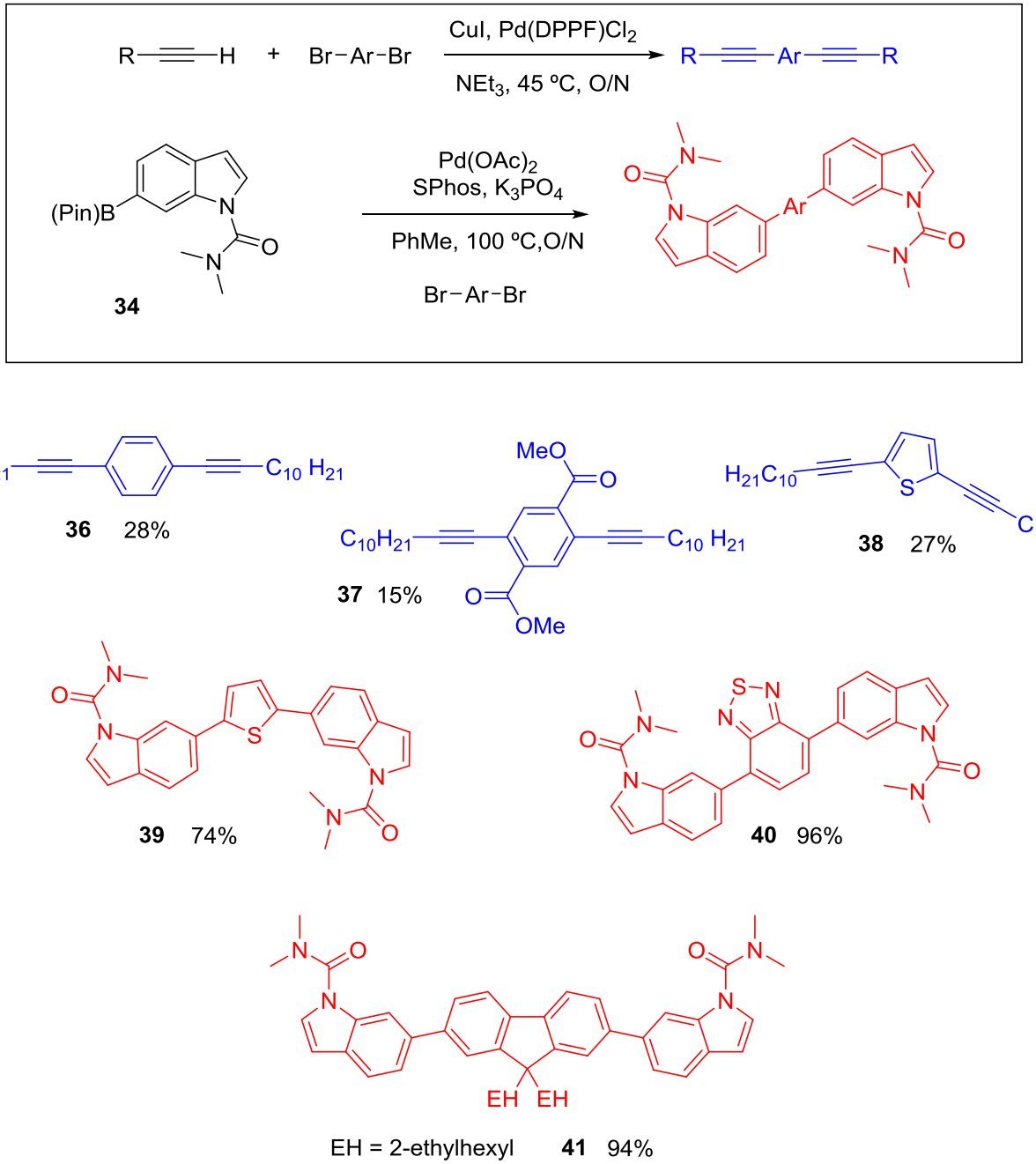
(B) Suzuki-Miyaura Coupling Strategies



Scheme 21. (A) A Sonogashira coupling strategy for dialkyne monomers and (B) Suzuki-Miyaura coupling strategies for diindole monomers.

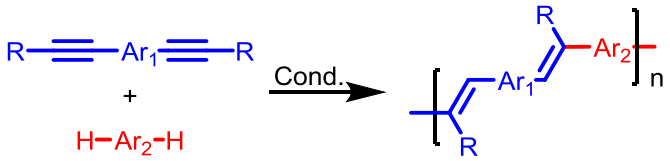
Monomers synthesized through these two strategies are summarized in **Scheme 22**. The arenes included in the scope of the dialkynes investigated were an electron-neutral benzene (**36**), an electron-poor terephthalate ester (**37**), and an electron-rich thiophene (**38**). These strategies proved to be efficient, facile routes to access the monomers upon which we were able to test the scope of the polymerization reaction conditions that were developed. The various dialkynes were then reacted with the various diindoles and the results are summarized in **Table 5**. In addition to the diindoles that were investigated, a pyrrole monomer that possessed carbonyl directing groups on the 3 and 4 positions was also tested for reactivity.

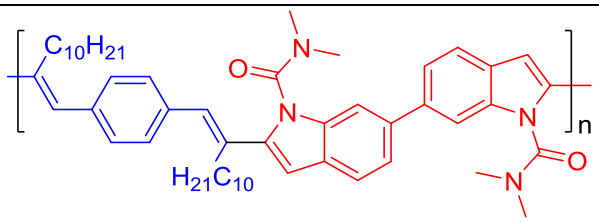
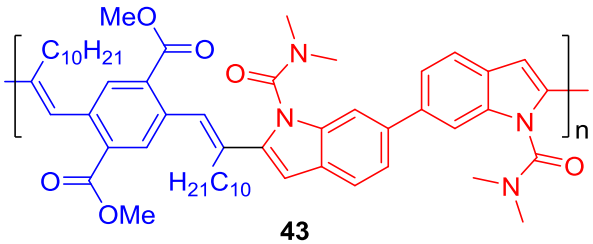
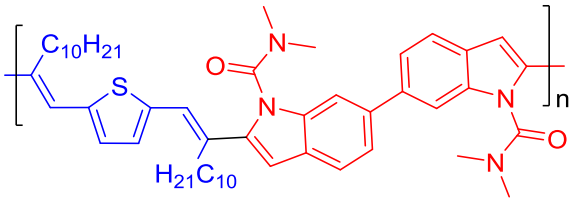
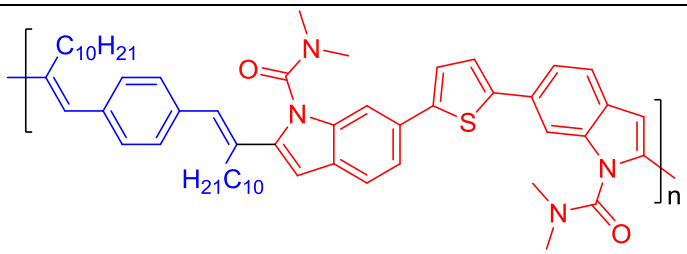
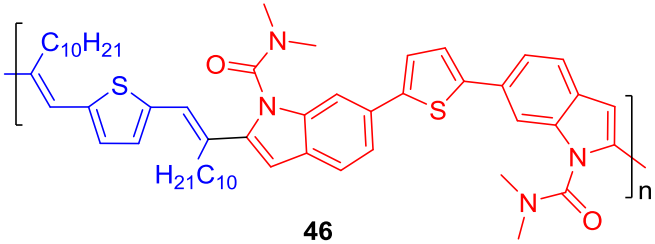
Generally, reactivity transferred well to AA BB polymerizations with M_n's up to 23 kDa. However, the limiting phenomenon of gelation was encountered at much lower molecular weights than in the AB polymerizations due to the larger repeating units. This was especially notable for the monomers with the spacer arene between the diindoles. Other appreciable trends are that the thiophene and the terephthalate dialkynes had decreased reactivity compared to the phenyl species.

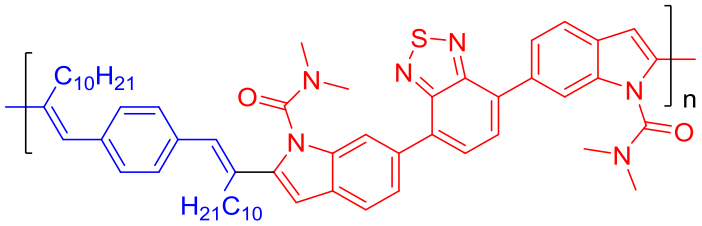
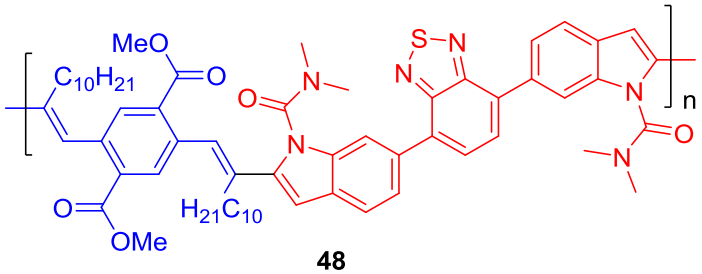
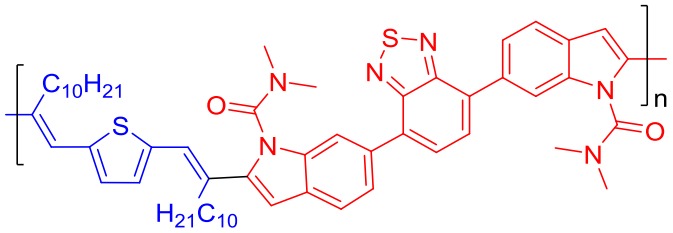
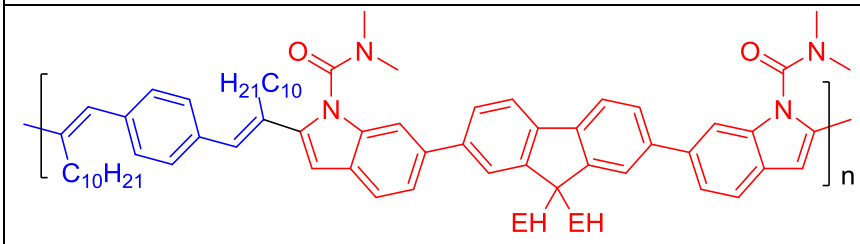
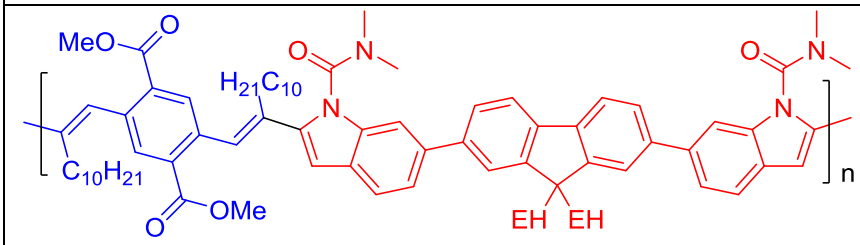


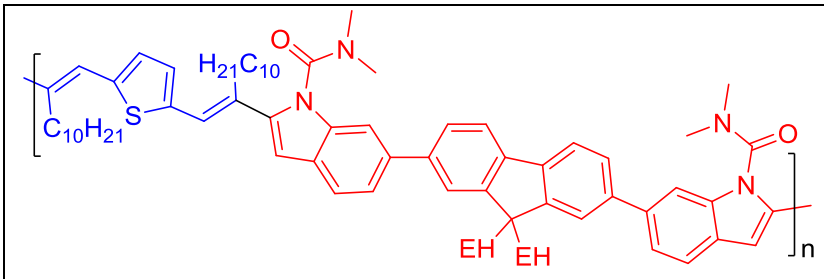
Scheme 22. Monomer synthesis yields for AA BB hydroarylation polymerizations. Dialkynes in blue and diindoles in red.

Table 5. AA BB hydroarylation polymerizations results



Compound	M_n (kDa)	M_w (kDa)	PDI
 **42**	23	37	1.6
 **43**	10	12	1.2
 **44**	10	17	1.7
 **45**	10	19	1.9
 **46**	10	16	1.6

 **47**	8	13	1.6
 **48**	7	11	1.6
 **49**	11	19	1.9
 **50**	10	19	1.9
 **51**	8	12	1.5

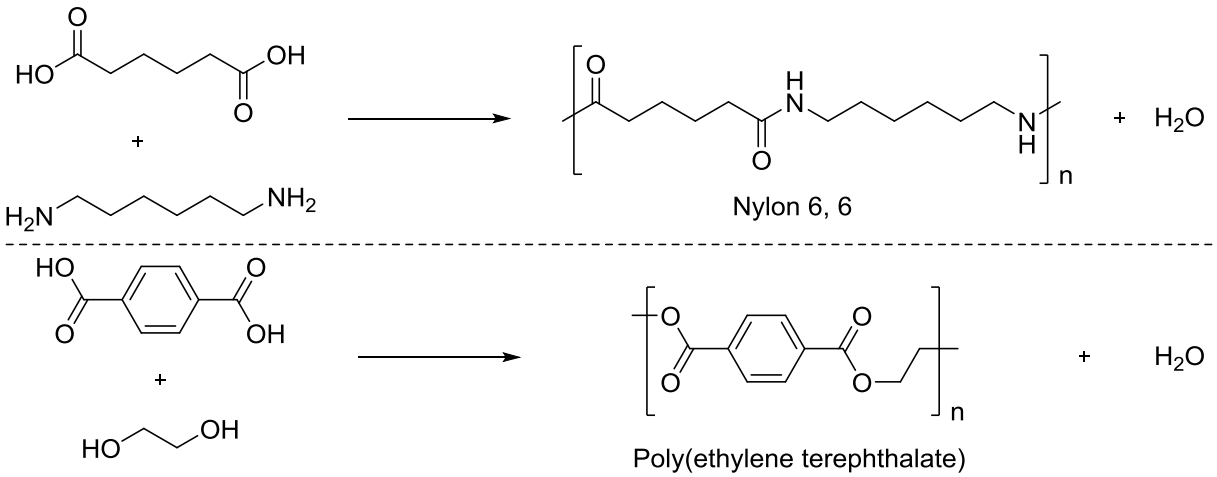
 **52**	11	22	2.0

These examples incorporated heteroaromatic rings such as thiophene and benzothiazole, and other aromatic systems such as fluorenes and terephthalate esters in the repeating unit of the polymer. Advantages of this C-H activation reaction are that it can incorporate a variety heteroaromatic rings, synthesize polymers of relatively high molecular weights, and greatly reduces synthetic complexity towards access of conjugate polymers. However, an area for further improvement to this method is that the lack of diversity in C-H bonds that it can effectively activate. Only the 2-position on indoles were able to be polymerized through our efforts.

2.2.0 Dehydration Polymerization

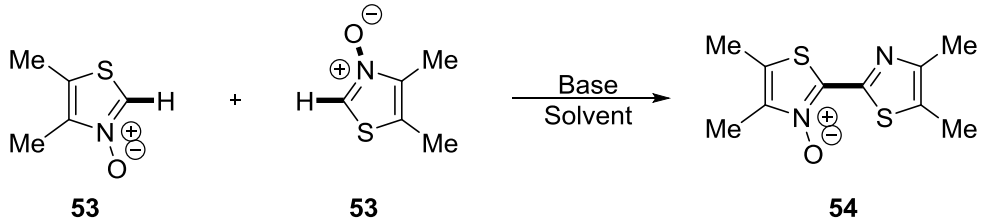
2.2.1 Initial Discovery, Optimization, and Scope

This thesis also presents the first dehydrative technique discovered for the synthesis of conjugated polymers. Two of the most industrially important polymers, nylon 6,6 and poly(ethylene terephthalate), are annually synthesized on megaton scale through dehydration reactions that produce an equivalent of water as their sole bypoduct for each new bond formed in the polymeric backbone (**Scheme 23**).[38] Development of an efficient dehydration reaction for conjugated polymers would represent an important and elusive advance of synthetic tools.

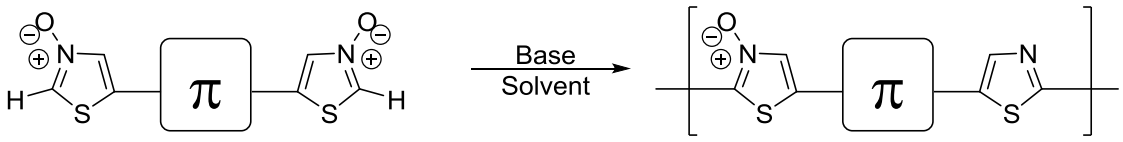


Scheme 23. Examples of industrially important polymers formed by dehydration reactions.

The dehydration reaction described in this thesis (**Scheme 24**) results in the carbon-carbon bond formation from two thiazole *N*-oxides. In this reaction, the two thiazole *N*-oxides react to form a biaryl system through the loss of the hydrogens at the reactants' 2-position and one of the *N*-oxide oxygens, giving a formal loss of one equivalent of water, as catalyzed by base. We also investigated if this dehydration reaction discovered in our group could be extended to a polymerization reaction that could afford conjugated polymers (**Scheme 25**).

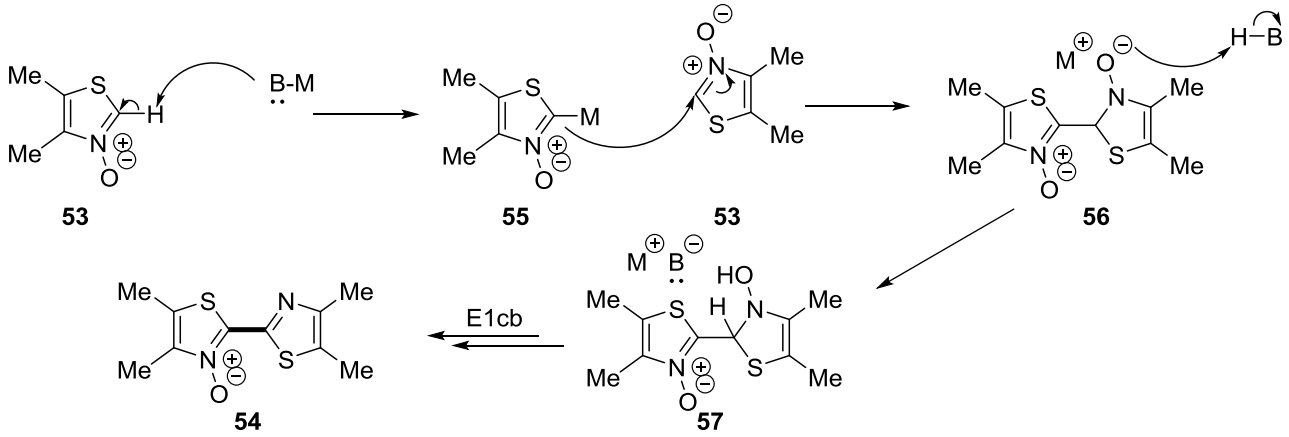


Scheme 24. Dehydration dimerization developed in the Schipper Group



Scheme 25. The dehydration reaction can yield either small molecules or high molecular weight conjugated polymers.

The mechanism that we propose (**Scheme 26**) for this transformation begins with deprotonation at the 2-position the thiazole *N*-oxide (**53**) The resulting metalated thiazole (**55**) performs a nucleophilic attack on the 2-position of the other equivalent of the thiazole *N*-oxide (**53**), this sequence could be considered a directed metalation reaction.. Following this attack, formal loss of H_2O from **57** through an E1cb mechanism is envisioned to obtain **54**.



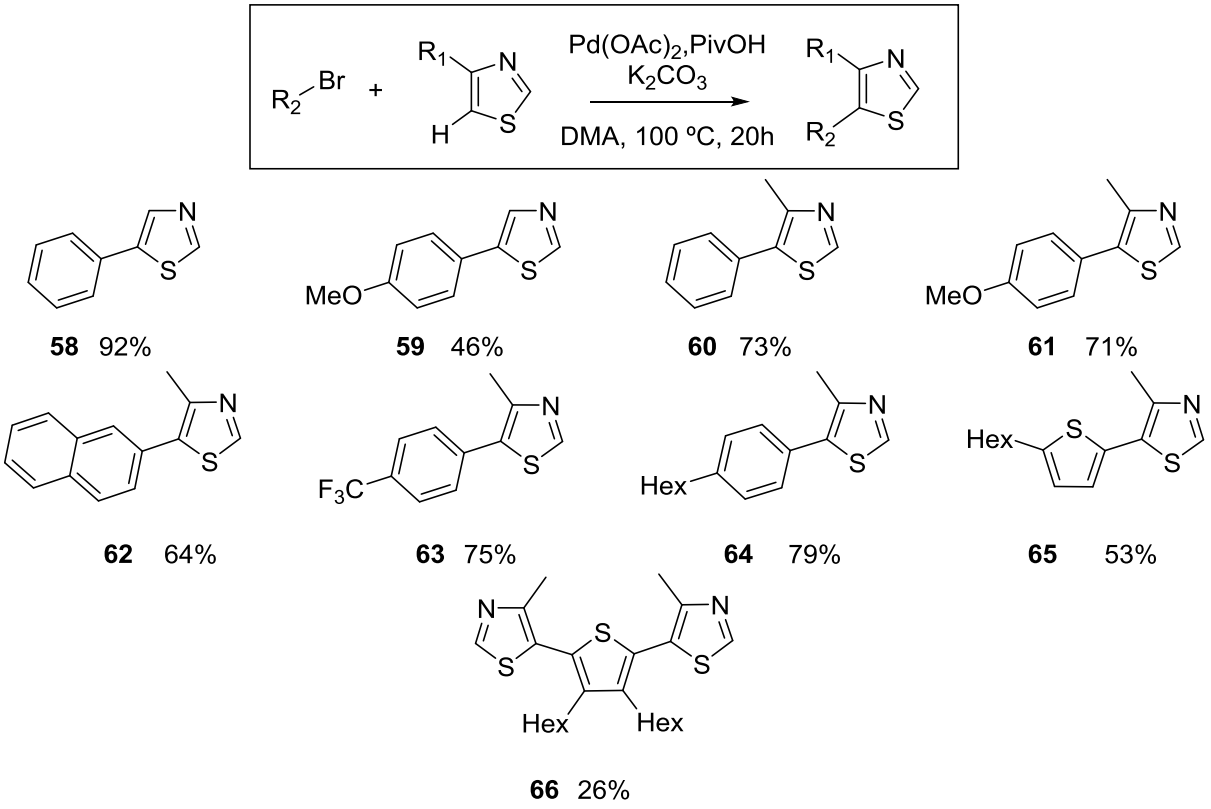
Scheme 26. Proposed mechanism for the dehydration dimerization.

Initial discovery and optimization of the reaction conditions are both summarized in T**able 6**. The reaction was discovered using toluene at 90 ºC with NaO*t*Bu. Lowering the temperature to 50 ºC improved yields but lower than this had diminishing returns when the reaction was performed in toluene. However, switching to an ethereal solvent and lowering the temperature to room temperature significantly increased the yield to 70%. Base screening also revealed that LiO*t*Bu promoted the reaction well. Further optimization found that switching to dropwise addition of LiO*t*Bu in THF at 0 ºC then warming room temperature increased the yield of the reaction yet again.

Table 6. Summary of the optimization of the dehydration reaction.

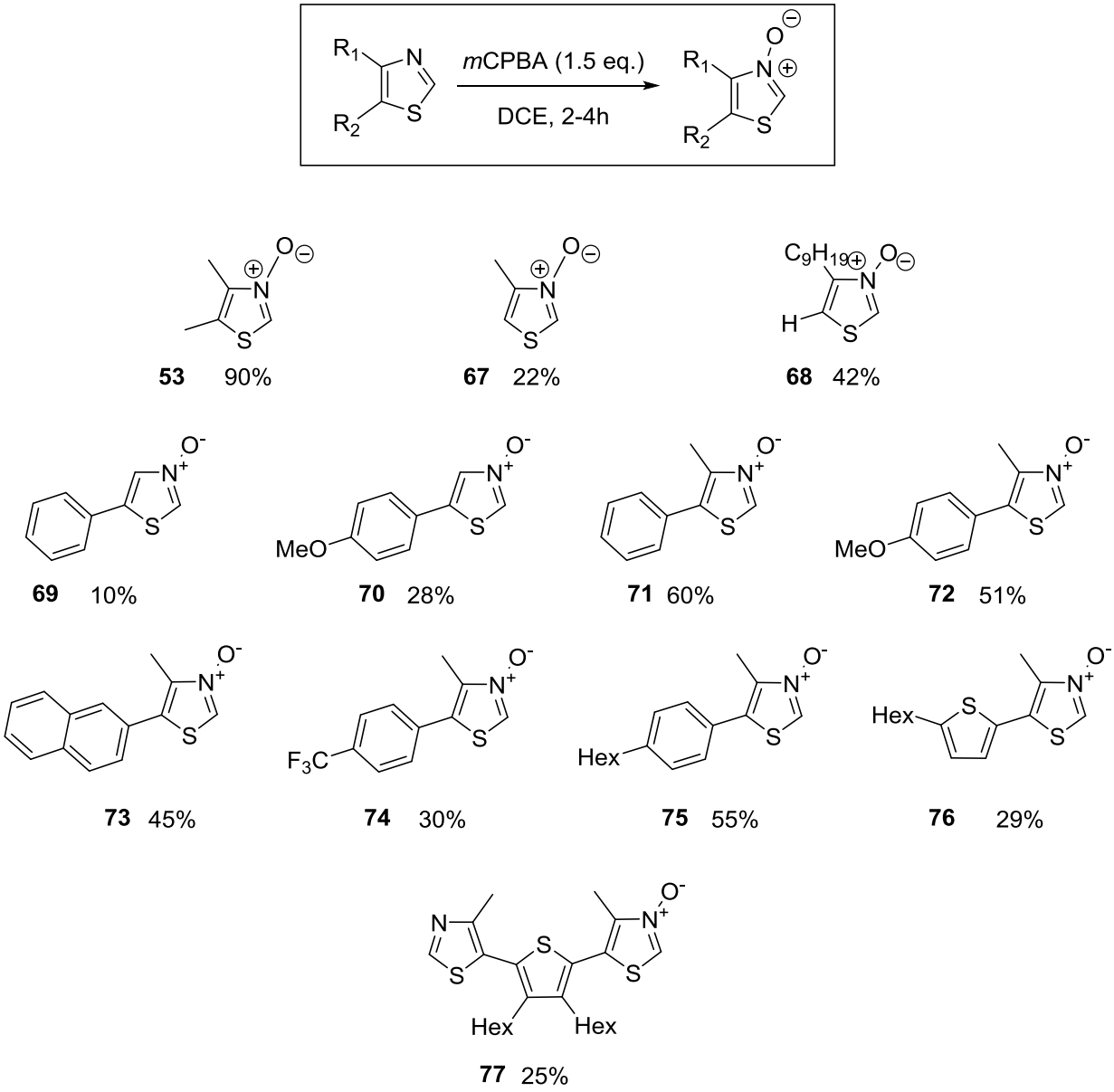
Solvent	Base	Temp. (ºC)	Time (min)	Yield (%)
Tol.	NaO*t*Bu	90	30	25
Tol.	NaO*t*Bu	50	30	63
Tol.	NaO*t*Bu	rt	30	25
Tol.	LiO*t*Bu	90	30	83
Et_2O	NaO*t*Bu	rt	30	70
THF	LiO*t*Bu	0	30	77
THF	**LiO*t*Bu**	**0→rt**	**5**	**88**

To investigate the scope of these dehydration conditions on the small molecule scale, a series of thiazoles had to be synthesized while keeping the 2-position open for the dehydration reaction. Direct arylation reactions for thiazoles is known to be regioselective for the 5-position.[45] This fact was used to design a library of thiazoles to investigate the scope of the reaction by coupling various aryl bromides to thiazole and 4-methyl thiazole, two commercially available compounds (**Scheme 27**).



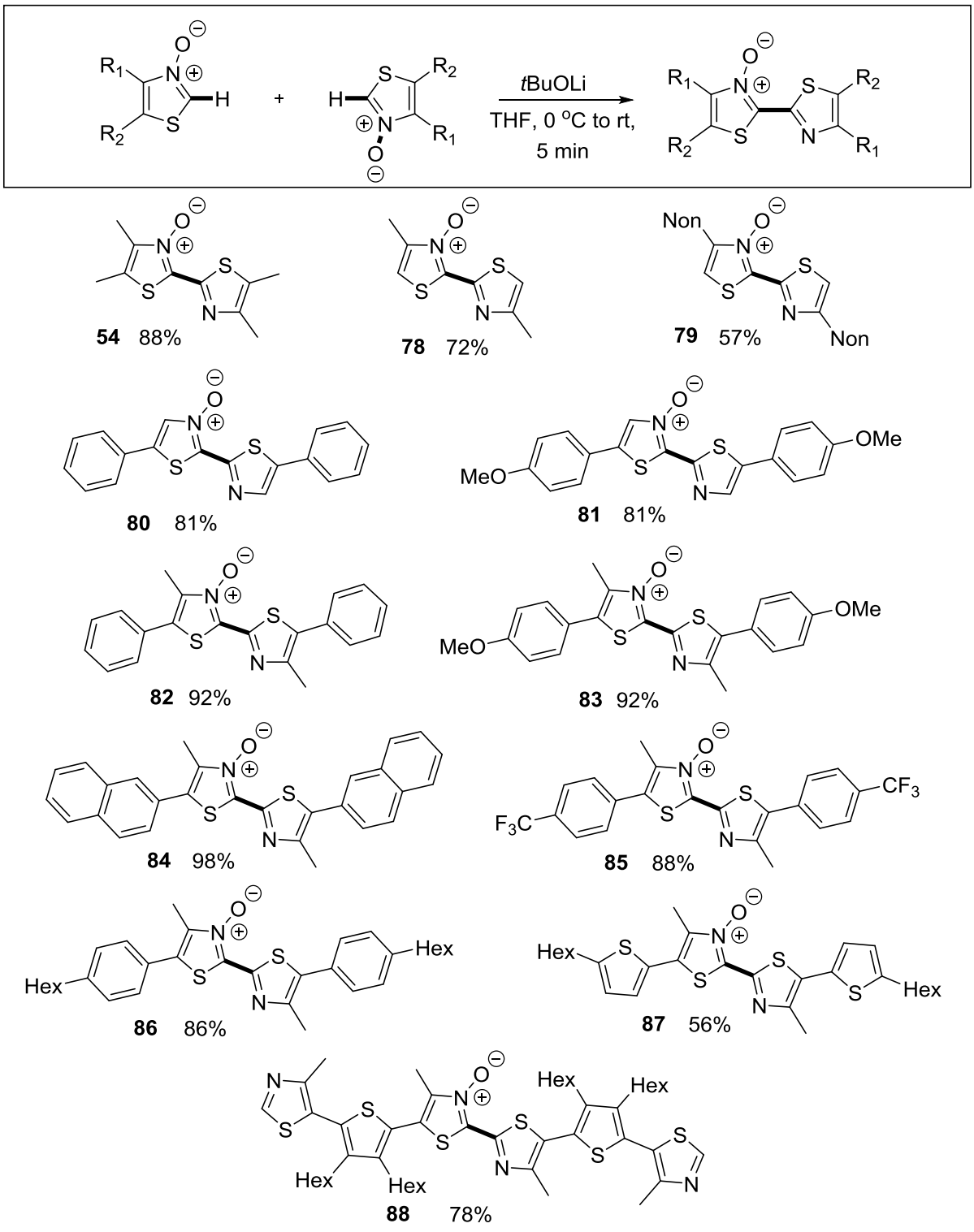
Scheme 27. Synthesis of 5-aryl thiazoles via direct arylation.

With this library of thiazoles in hand, the next step of the project was to oxidize them to form the thiazole *N*-oxides required for the dehydrations. A variety of oxidation conditions were tested, but *m*CPBA proved to be the most viable oxidant. When R_1 at the 4-position was a hydrogen, the oxidation proceeded in prohibitively low yields for most derivatives other than **69** and **70**. However, when R_1 was a methyl group (**71**, **72**), yields significantly improved but were still low for many derivatives (eg **74**, **76**, **77**). Longer alkyl chains at the 4-position, such as the 4-nonyl thiazole (**68**) example did not seem to have lower oxidation yields as compared to 4-methyl thiazole (**68**). Another important trend to note, derivatives where the aryl ring that has been coupled to the thiazole is a thiophene (**76**, **77**), the yield of the oxidation also significantly lower than when it is a phenyl ring.



Scheme 28. Summary of thiazole oxidation results.

With the *N*-oxides that were able to be isolated, dehydrations reaction conditions that were optimized for 4,5-dimethylthiazole were performed on the various *N*-oxide thiazoles (**Scheme 29**). Separate to this thesis, work in the Schipper lab is being performed to provide alternative, higher yielding routes to thiazole *N*-oxides.

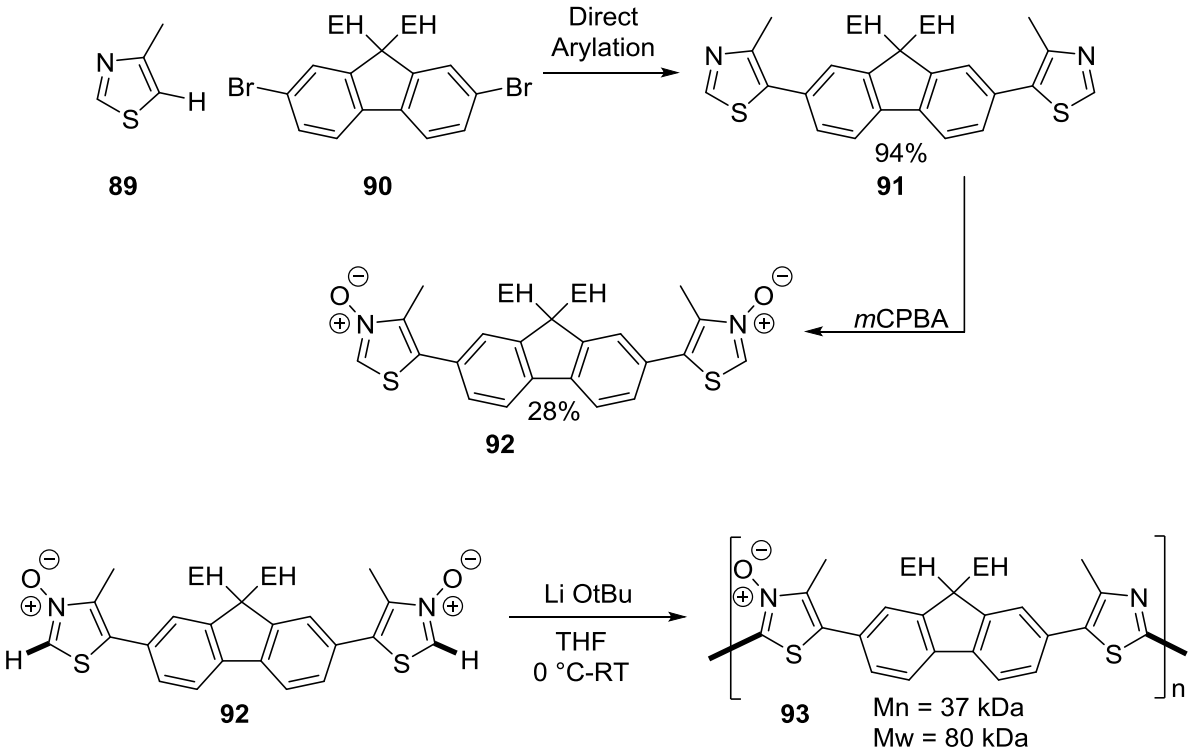


Scheme 29. Summary of thiazole *N*-oxides dehydrative coupling results.

It was shown that a variety of 5-phenylthiazole derivatives (**80**-**86**) were well tolerated in the dehydration reactions with yields of over 80%. Thiazoles coupled to thiophene groups (**87**, **88**) performed worse. The apparent trend amongst the alkyl derivatives (**54**, **78**, **79**) was that the removal of a 5-substitution was detrimental to the reaction, as was increase in chain length at the 4-position.

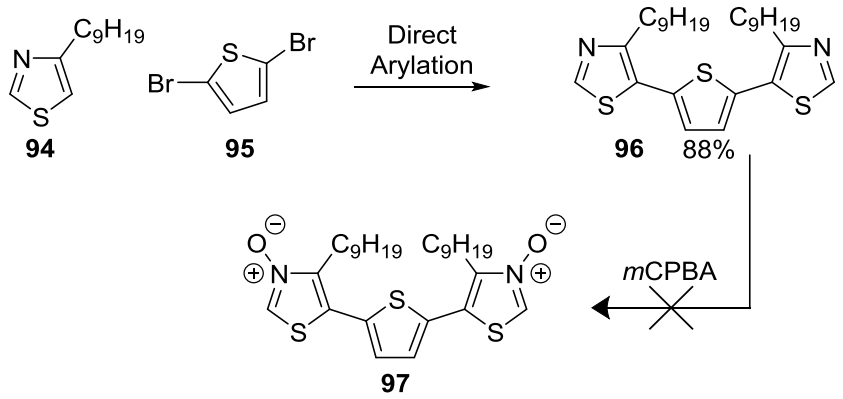
2.2.2 Extending reactivity to a polymerization strategy

The first route to a monomer is described in **Scheme 30a**. With *N*-oxides on either ends of the molecule, the compound should be able to polymerize via the dehydration reaction developed. The branched 2-ethylhexyl groups on the fluorene ring between the thiazoles were selected because they are effective solubilizing chains. The 4-methylthiazole (**89**) and the dibromofluorene (**90**) derivative are both commercially available compounds. A direct arylation with similar conditions as the reactions performed for the small molecules was effective at forming the bisthiazole system present in the monomer. The oxidation reaction proceeded with significant challenges: the yield of the di-*N*-oxide product **92** was very low and it was difficult to isolate due to its high polarity, despite its long, branched solubilizing chains such as the two geminal 2-ethylhexyl groups. Ultimately, a flash column with 20% methanol in ethyl acetate as the mobile phase followed by a celite plug afforded pure **92** in 28% yield. The same conditions used in the small molecule dehydration reactions (with extended reaction time) transferred well and produced a high molecular weight polymer; M_n = 37, M_w = 80 kDa (**Scheme 30b**).



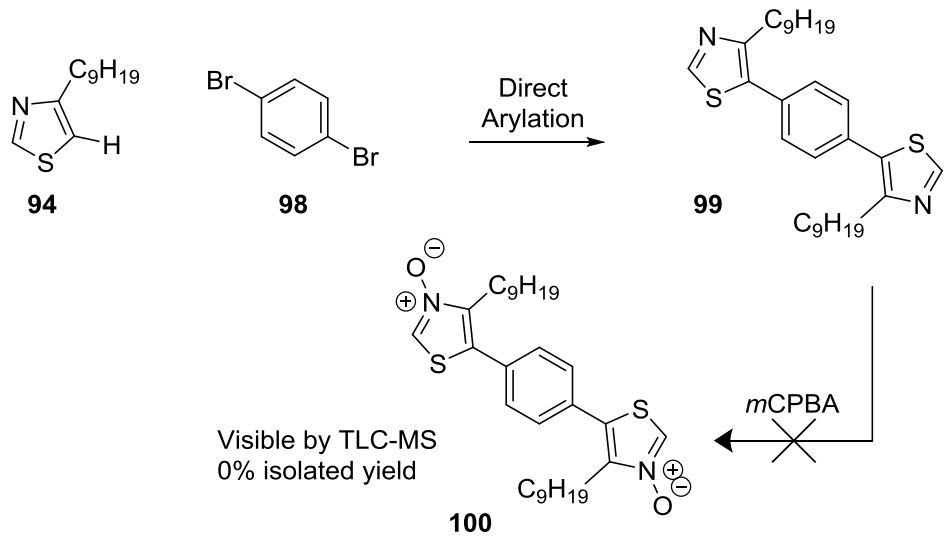
Scheme 30. Route used to access a fluorene-based monomer and its dehydration polymerization conditions.

With this successful route to the first polymer synthesized, attention turned towards further investigating the scope the polymerization. Of particular interest was synthesizing a polymer that had a third heteroaromatic system between the thiazoles. **Scheme 30** represents our first attempt at incorporating a thiophene in the repeating unit of the polymer. For this monomer (**97**), the location of the solubilizing chain was moved from the middle ring system to the thiazoles by using 4-nonylthiazole as our starting material in the direct arylation reaction. This proceeded well, but unfortunately the oxidation did not proceed to the di-*N*-oxide species. The only products isolated were the starting material and the mono-*N*-oxide.



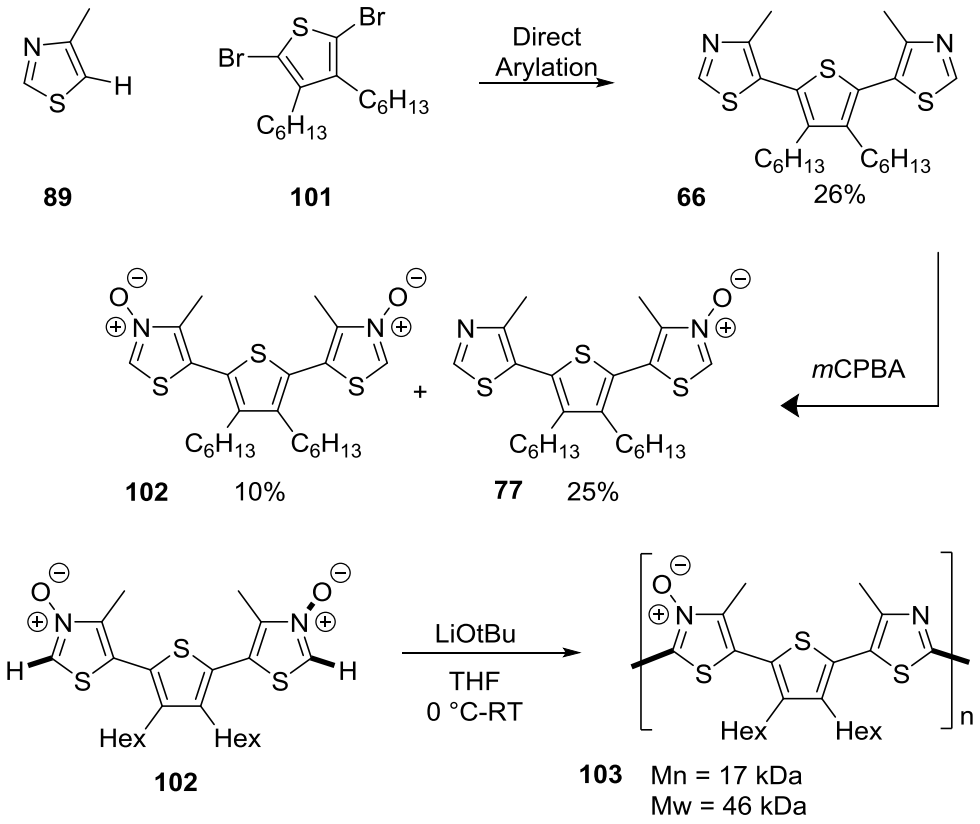
Scheme 31. First attempt at accessing a thiophene-based monomer.

Two theories as to why this oxidation of **96** did not proceed well were conjectured: typically, the oxidation yields for the thiophene-coupled thiazoles were significantly lower than the phenyl-coupled thiazoles (**Scheme 27**) and, additionally, it was hypothesized that the nonyl chains at the 4-position of the thiazoles were hindering the reaction due to steric effects. Thus, our next prospective monomers were designed to avoid either of these potential issues. **Scheme 31** shows our route to a monomer with nonyl chains remaining on the thiazole, but replacing the thiophene with a phenyl ring. **Scheme 32** shows our route to a monomer where the solubilizing chains have been moved to the thiophene ring.



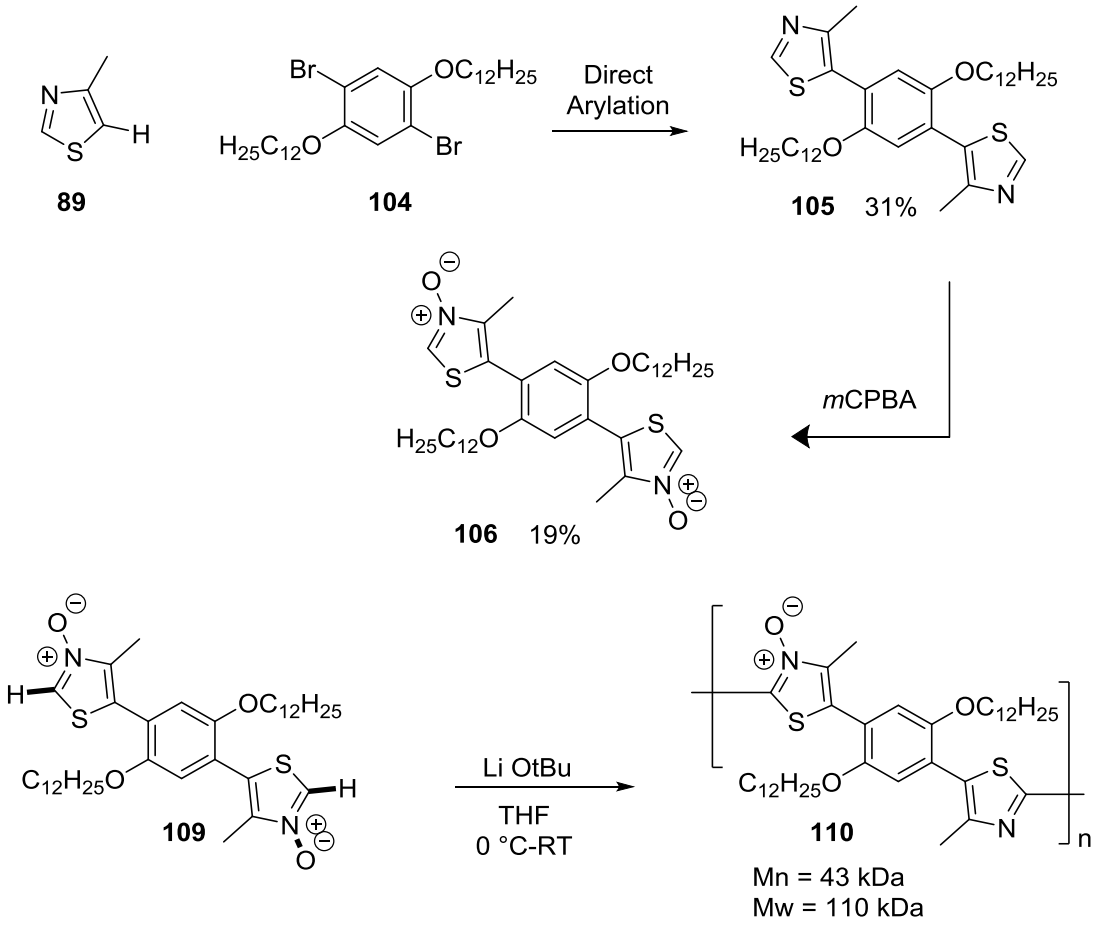
Scheme 32. Attempts to isolate a monomer with solubilizing chains on the 4-position.

Unfortunately, our route to **100** proved unsuccessful, though the desired product could be observed by NMRs of the crude reaction mixture and through TLC-MS analysis, it could not be purified and isolated off a column due to its high polarity. Lyophilisation and reverse-phase chromatography also proved fruitless. Thus, this pursuit of **100** was terminated and attempts to test the polymerization reaction with a monomer bearing solubilizing chains thiazoles were never performed. However, when the solubilizing chains were moved to the thiohphene ring (**Scheme 33**) a small amount of **102** could be isolated from the oxidation reaction. Though the yield of the oxidation was low, it did provide enough di-*N*-oxide to test our polymerization conditions on a thiophene-containing monomer – a commonly seen heterocycle in conjugated polymers. The corresponding polymerization proceeded well with M_n = 17, M_w = 46 kDa.



Scheme 33. Succesful attempts at isolating and polymerizing a thiophene containing monomer.

Our final attempts to successfully synthesize a third monomer was using 4-methylthiazole (**89**) and 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**104**) as the starting materials. Though the direct arylation proceeded in uncharacteristically low yield, enough product (**105**) could be carried through to the oxidation reaction. With the long decyl solubilizing chains, the monomer could be isolated in decent yield from flash chromatography. Attempts to polymerize this monomer (**106**) proceeded well (**Scheme 34**), with an M_n similar to that of the fluorene-incoporated polymer, though the PDI was relatively high.



Scheme 34. Successful attempt at synthesizing and polymerizing a bis(dodecyloxy)benzene monomer.

3.0 Conclusion

The paucity of reactions to synthesize conjugated polymers has been limiting advances for the related applications and devices. The aim of these projects were to develop new synthetics tools for producing conjugated polymers of sufficiently large molecular weight, functional group and heteroaromatic ring tolerance, and reducing toxic by-products. In this thesis, we aimed to develop reactions that would allow access to conjugated polymers in streamlined, efficient manners. To this end, we presented work relating to the optimization and application of a C-H activating hydroarlyation polymerization reaction for the synthesis of 12 PAV-type polymers. This strategy possessed beneficial traits such as readily accessed monomers, incorporation of heteroaromatic rings, and avoiding stoichiometric organometallic by-products. Also in this thesis, we presented the initial discovery and optimization of a thiazole *N*-oxide dehydration reaction, through which 12 small molecules and 3 polymers were synthesized. Reactants for this transformation were accessed through a straightforward 2-step route, neither of which had organometallic by-products.

The first reaction developed was a hydroarylation reaction that formed bounds through the formal addition of a C-H bond at 2-position of several indoles examples across an internal alkyne to access PPV-type polymers. Optimization efforts brought molecular weights of an AB polymer from small oligomeric products to a relatively large M_n = 34, M_w= 43 kDa. Solutions to low reactivity under the original conditions inspired by the source literature's small molecule reaction included the addition of catalytic CsOPiv, raising the equivalence of PivOH additive, and doing two 2.5 mol % loadings of the rhodium catalyst.

With optimized polymerization conditions identified, the scope of the reaction was examined through AA BB polymerization strategies. In total, 11 AA BB polymers were synthesized through this approach. These examples incorporated heteroaromatic rings such as thiophene and benzothiazole, and other aromatic rings such as fluorenes and terephthalate esters in the repeating unit of the polymer. Though the molecular weights of these polymers were lower than the AB polymer, they were still large enough to be seen as a success. Advantages of this C-H activation reaction are that it can incorporate a variety heteroaromatic rings, synthesize polymers of relatively high molecular weights, and greatly reduces synthetic complexity towards access of conjugate polymers. A significant limitation that still remains for to this method is that the lack of diversity in C-H bonds that it can effectively activate. Namely, only the 2-position on indoles has been shown to work for polymerization reactions.

Another approach to simplifying the synthesis of conjugated polymers presented in this thesis was a dehydration reaction that forms C-C bonds between sp^2-hybridized carbons. Initial discovery, optimization, and scoping investigation of a dimerization reaction was presented. The first attempts at extending this reactivity to a polymerization method were successful but were significantly limited by the ability to access the di-*N*-oxide monomers required. Any monomers that we could access readily polymerized in high molecular weights. To substantially increase the impact of this reaction on the field of conjugated polymer synthesis, improvements on the oxidation reaction must be made. To this end, there is ongoing work in the Schipper group to improve oxidation yield and scope through exploring protecting groups on the 2-position of the thiazoles.

The scope of this thesis was limited to the development of the synthetic tools to access these conjugated polymers. With that in mind, this thesis presents significant breakthroughs that provide chemists with two new polymerization reactions to access conjugated polymers of high molecular and heteroaromatic ring tolerance. Both reactions represent major steps forward for each class of conjugated polymers: a C-H activation reaction for poly(*p*-phenyl vinylene)-type polymers and a transition-metal-free reaction for poly(hetero)arene-type polymers.

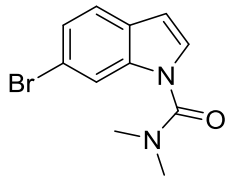
4.0.0 Experimental Procedures

4.1.0 General Methods:

Unless otherwise specified all reactions were run without regard to exclusion of ambient air or moisture. All starting materials were purchased from Aldrich. The *m*CPBA used was ≤ 77% purity and obtained through Sigma-Aldrich™. Dry THF, DCM, Tol, and trimethylamine were obtained from a JC Meyer™ solvent purification system when needed. DMA and DCE were not distilled, and only partially dried by storing over 4A sieves. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AVANCE 300 spectrometer. The chemical shift data are reported in units of δ (ppm) and were reported relative to residual $CHCl_3$ (^{1}H: $CHCl_3$ was reference to 7.26 ppm; ^{13}C: $CHCl_3$ was referenced to 77.0 ppm). Number-average (M_n) and weight-average (M_w) molecular weights are relative to polystyrene standards and were determined by size exclusion chromatography using a Viscotek GPC MAX VE2001 at 35 °C equipped with a VE 3580 RI detector and two PAS-104 Styrene-Divinylbenzene gel columns. The flow rate was fixed at 1.0 mL/min using tetrahydrofuran (THF) as the eluent. All GPC samples were prepared nominally at 2 mg/ml in THF and filtered through a 0.22µM PTFE filter into a 1 mL chromatography vial. High resolution mass spectra (HRMS) were obtained via electrospray ionization (ESI) which were measured on a Thermo Scientific Q Exactive™ Plus Hybrid Quadrupole-Orbitrap™ at the University of Waterloo Mass Spectrometry Facility.

4.2.0 Hydroarylation Project

6-Bromo-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (29)



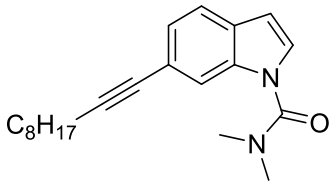
A round bottomed flask was charged with 6-bromoindole (1.47 g, 7.50 mmol, 1.0 eq.), $Bu_4N{\cdot}HSO_4$ (253 mg, 0.75 mmol, 0.1 eq.) and NaOH (747 mg, 18.7 mmol, 2.5 eq.). The flask was then fitted with a reflux condenser and flushed with argon. CH_2Cl_2 (30 mL) and dimethylcarbamylchloride (1.61 g, 15.0 mmol, 2.0 eq.) were added to the flask and the resulting solution was refluxed for 2-3 hours until the reaction was complete as judged by TLC. The reaction was quenched with 30 mL of saturated NH_4Cl solution. The layers were partitioned and the aqueous phase was extracted (2 x 30 mL) with CH_2Cl_2. The organics were combined, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography. This product was obtained in 97% yield, 1.94 g.

^{1}H NMR (300 MHz, $CDCl_3$): 7.87 (d, *J* = 0.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.31 (m, 2H), 6.58 (dd, *J* = 3.5, 0.6 Hz, 1H), 3.11 (s, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 154.6, 136.2, 128.2, 126.7, 125.1, 122.1, 117.2, 116.6, 105.6, 38.4;

HRMS: calculated for $C_{11}H_{12}BrN_2O$ $(M+H)^+$ = 267.0128; found = 267.0128.

6-(Dec-1-yn-1-yl)-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (30)



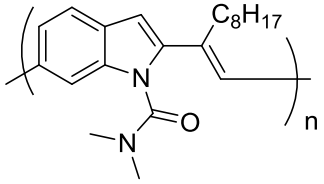
A round bottomed flask was charged with **29** (1.00 g, 3.74 mmol, 1 eq.) and flushed with argon. Next, to the round bottomed flask was added, in this order, degassed triethylamine (37.5 mL), 1-decyne (673 mg, 4.87 mmol, 1.3 eq.), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (152 mg, 0.187 mmol, 0.05 eq.), and copper (I) iodide (71.2 mg, 0.374 mmol, 0.1 eq.). The solution was refluxed for 2-3 hours until the reaction was complete as judged by TLC. The reaction was quenched with 60 mL of saturated NH_4Cl solution. The layers were partitioned and the aqueous phase was extracted (2 x 60 mL) with CH_2Cl_2. The organics were combined, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography. This compound was obtained in 83% yield, 1.01 g.

^{1}H NMR (300 MHz, $CDCl_3$): 7.65 (d, *J* = 1.3 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 3.5 Hz, 1H), 7.21 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H), 6.53 (d, *J* = 3.4 Hz , 1H), 3.05 (s, 6H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.61 (tt, *J* = 7.3, 7.3 Hz, 2H), 1.45 (tt, *J* = 7.3, 7.0 Hz, 2H) 1.29 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 154.8, 135.1, 128.8, 127.1,125.4,120.7, 119.1, 116.6, 105.8, 89.5, 81.4, 38.4, 31.9, 29.2, 29.2, 29.0, 28.9, 22.7, 19.5, 14.1;

HRMS: calculated for $C_{21}H_{29}N_2O$ $(M+H)^+$ = 325.2274; found = 325.2278.

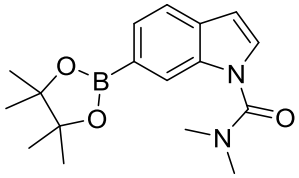
Poly [6-(Dec-1-yn-1-yl)-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide] (31)



To a microwave vial, the indole **30** (64.9 mg, 0.200 mmol, 1 eq.), CsOPiV (2.3 mg, 0.01 mmol, 0.05 eq.), and PivOH (204 mg, 2.00 mmol, 10 eq.) were dissolved in THF (0.8 mL). To the stirred solution, Cp*Rh(MeCN)$_3$ (4.16 mg, 0.005 mmol, 0.025 eq.) was added, the vial was sealed, and the reaction was heated to 110 ºC. After the 4 hours, the reaction was cooled to room temperature, the seal was removed and an additional Cp*Rh(MeCN)$_3$ $(SbF_6)_2$ (4.16 mg, 0.005 mmol, 0.025 eq.) was added. The vial was then sealed again and the reaction was resumed at 110 ºC. After three hours, the polymer was purified by precipitation into methanol and isolated by filtration.

^{1}H NMR (300 MHz, $CDCl_3$): 7.55 (d, *J* = 8.2 Hz, 1H), 7.37 (br, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.85 (br, 1H) 6.67 (br, 1H), 3.40-2.60 (m, 8H), 1.75-1.20 (m, 12H), 0.92 (br, 3H).

_N_,_N_-Dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1_H_-indole-1-carboxamide (34)



A round bottomed flask was charged with **29** (1.00 g, 3.74 mmol, 1 eq.), bis(pinacolato)diboron (1.04 g, 4.11 mmol, 1.1 eq.), KOAc (1.10 g, 11.2 mmol, 3.0 eq.), Pd(dppf)Cl_2·CH_2Cl_2 (91.2 mg, 0.112 mmol, 0.03 eq.). The flask was then fitted with a reflux condenser and flushed with argon. DMF (20 mL) was added to the flask and the resulting solution was stirred at 100 ºC until the reaction was complete (16 hours) as judged by

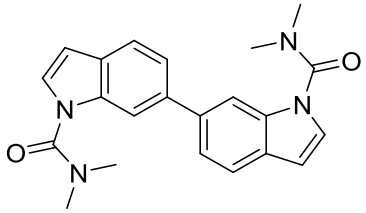
TLC. To the reaction was added 50 mL of EtOAc and 50 mL of saturated NaCl solution. The layers were separated and the aqueous phase was extracted (2 x 50 mL) with EtOAc. The organics were combined, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography. This compound was obtained in 96% yield, 1.13 g.

^{1}H NMR (300 MHz, $CDCl_3$): 8.11 (d, *J* = 0.7 Hz, 1H), 7.65 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.61 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 6.61 (dd, *J* =3.5, 0.7 Hz, 1H), 3.11 (s, 6H), 1.38 (s, 12H);

^{13}C NMR 300 MHz, $CDCl_3$): 154.9, 135.1, 131.9, 127.6, 127.4, 120.3, 119.8, 105.5, 83.6, 38.4, 24.9, one overlapping signal as one peak is missing even with prolonged scans;

HRMS: calculated for $C_{17}H_{24}BN_2O$ $(M+H)^+$ = 315.1874; found = 315.1862.

N^1,*N*^{1},*N*$^{1'}$,*N*$^{1'}$-Tetramethyl-1*H*,1'*H*-[6,6'-biindole]-1,1'-dicarboxamide (35)



A round bottom flask under inert atmosphere was charged with **29** (334 mg, 1.25 mmol, 1.0 eq.), **34** (471 mg, 1.50 mmol, 1.2 eq.), K_3PO_4 (531 mg, 2.50 mmol, 2.0 eq.), and SPhos (10.3 mg, 0.025 mmol, 0.02 eq.). The flask was then flushed with argon and 10:1 toluene:water (5 mL), which was sparged with nitrogen, was added. To the stirred solution, $Pd(OAc)_2$ (2.80 mg, 0.0125 mmol, 0.01 eq.) was added. The reaction was stirred at 100 ºC for 16 hours before 10 mL of EtOAc and 10 mL of saturated aqueous NaCl solution were added. The layers were partioned and the aqueous phase was extracted (2 x 10 mL) with EtOAc. The organics were combined, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography to isolate the pure product. Compound **35** was isolated in 92% yield, 430 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.94 (d, *J* = 0.8 Hz, 2H), 7.66 (dd, *J* = 8.2, 0.5 Hz, 2H), 7.54 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.36 (d, *J* = 3.5 Hz, 2H), 6.64 (dd, *J* = 3.5, 0.7 Hz, 2H), 3.14 (s, 12H);

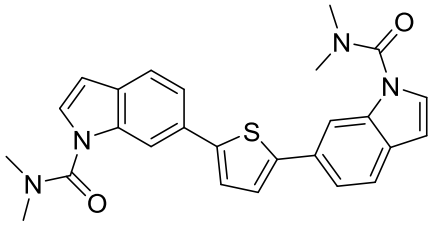
^{13}C NMR (300 MHz, $CDCl_3$): 155.1, 137.9, 136.1, 128.4, 126.6, 122.1, 121.0, 112.3, 105.5, 38.5;

HRMS: calculated for $C_{22}H_{23}N_4O_2$ $(M+H)^+$ = 375.1816; found = 375.1815.

General Diindole Synthesis

A round bottom flask under inert atmosphere was charged with the dibromo arene (1.25 mmol, 1.0 eq.), **34** (943 mg, 3.00 mmol, 2.4 eq.), K_3PO_4 (1.06 g, 5.00 mmol, 4.0 eq.), and SPhos (20.5 mg, 0.05 mmol, 0.04 eq.). The flask was then flushed with argon and 10:1 toluene:water (10 mL), which was sparged with nitrogen, was added. To the stirred solution, $Pd(OAc)_2$ (5.61 mg, 0.025 mmol, 0.02 eq.) was added. The reaction was stirred at 100 ºC for 16 hours before 20 ml of EtOAc and 20 ml of saturated aqueous NaCl solution were added. The layers were partitioned and the aqueous phase was extracted (2 x 20 ml) with EtOAc. The organics were combined, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography to isolate the pure product.

6,6'-(Thiophene-2,5-diyl)bis(*N*,*N*-dimethyl-1*H*-indole-1-carboxamide) (39)



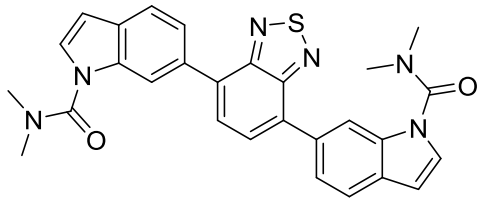
Compound **39** was synthesized through the general diindole synthesis procedure to isolate the product in 74% yield, 422 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.98 (s, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2, 1.6 Hz, 2H), 7.35 (m, 4H), 6.62 (d, *J* = 3.5 Hz, 2H), 3.15 (s, 12 H);

^{13}C NMR 300 MHz, $CDCl_3$): 154.9, 144.1, 136.0, 130.3, 128.9, 126.9, 123.8, 121.3, 120.2, 110.5, 105.7, 38.5;

HRMS: calculated $C_{26}H_{25}N_4O_2S$ $(M+H)^+$ = 457.1693; found = 457.1693.

6,6'-(Benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(N,N-dimethyl-1H-indole-1-carboxamide) (40)



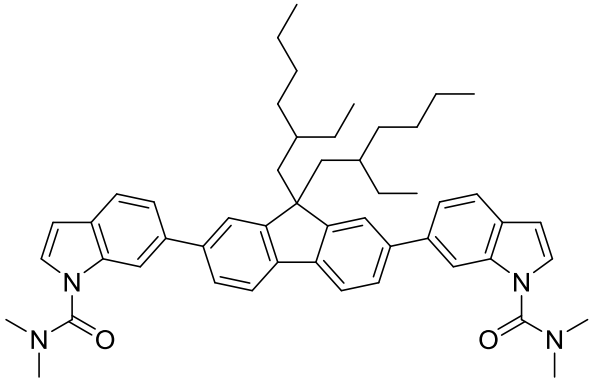
Compound **40** was synthesized through the general diindole synthesis procedure to isolate the product in 96% yield, 610 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.31 (s, 2H), 7.85 (s, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 3.5 Hz, 2H), 6.67, (d, *J* = 3.5 Hz, 2H), 3.16 (s, 12H);

^{13}C NMR (300 MHz, $CDCl_3$): 155.0, 154.4, 135.8, 133.6, 133.0, 129.5, 128.4, 127.3, 123.2, 121.0, 114.6, 105.6, 38.6;

HRMS: calculated for $C_{28}H_{25}N_6O_2S$ $(M+H)^+$ = 509.1754; found = 509.1755.

6,6'-(9,9-Bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(N,N-dimethyl-1H-indole-1-carboxamide) (41)



Compound **41** was synthesized through the general diindole synthesis procedure to isolate the product in 94% yield, 865 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.99 (d, *J* = 4.5 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.71-7.67 (m, 6H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 4.5 Hz, 2H), 6.65 (d, *J* = 4.4 Hz, 2H), 3.11 (s, 12H), 2.15 (br, 4H), 0.91 (m, 18H), 0.65 (m, 12H);

^{13}C NMR 300 MHz, $CDCl_3$): 155.1, 151.2*, 140.1, 140.0, 137.9, 136.1*, 128.5, 126.7*, 126.5, 123.1*, 121.7, 121.1*, 119.8, 111.9, 105.5, 44.6, 38.5, 34.7, 33.9, 28.2*, 27.0*, 24.8, 22.7, 14.0, 10.4*;

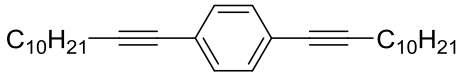
* denotes peaks that appear as multiplets due to the presence of diastereomers;

HRMS: calculated for $C_{51}H_{63}N_4O_2$ $(M+H)^+$ = 763.4946; found = 763.4940.

General Dialkyne Synthesis

In a round bottom flask, the dibromoarene (10.0 mmol, 1.0 eq.) was dissolved in NEt_3 (200 mL). To this, triphenyl phosphine (262 mg, 1.00 mmol, 0.1 eq.), 1-dodecyne (4.92 mL, 23.0 mmol, 2.3 eq.), copper (I) iodide (190 mg, 1.00 mmol, 0.1 eq.), and $Pd(PPh_3)_2Cl_2$ (351 mg, 0.500 mmol, 0.05 eq.) were added, in that order, to the reaction. After 16 hours of stirring at 50 ºC, 200 mL of EtOAc and saturated aqueous 200 mL of NH_4Cl solution were added. The layers were partitioned and the aqueous phase was extracted (2 x 200 mL) with EtOAc. The organics were combined, dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography to isolate the pure product.

1,4-Di(dodec-1-yn-1-yl)benzene (36)



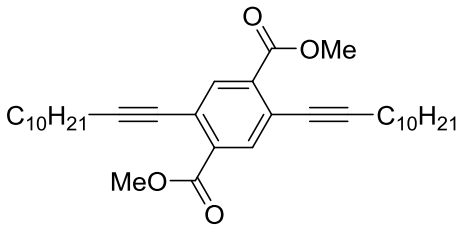
Compound **36** was synthesized through the general dialkyne synthesis procedure to isolate the product in 28% yield, 1.14 g.

^{1}H NMR (300 MHz, $CDCl_3$): 7.25 (s, 4H), 2.38 (t, *J* = 7.2 Hz, 4H), 1.60-1.20 (m, 32H), 0.86 (t, *J* = 7.3 Hz, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 131.3, 123.3, 91.8, 80.5, 32.0, 29.7, 29.6, 29.4, 29.2, 28.9, 28.8, 22.7, 19.5, 14.1;

HRMS: calculated for $C_{30}H_{47}$ $(M+H)^+$ = 407.3672; found = 407.3671.

Dimethyl 2,5-di(dodec-1-yn-1-yl)terephthalate (37)



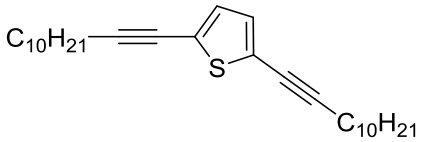
Compound **39** was synthesized through the general dialkyne synthesis procedure to isolate the product in 15% yield, 784 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.96 (s, 2H), 3.90 (s, 6H) 2.45 (t, *J* = 7.0 Hz, 4H), 1.56 (tt, H-7.2, 7.1 Hz, 4H), 1.50-1.15 (m, 28H), 0.86 (t, *J* = 6.9 Hz, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 165.8, 135.9, 134.2, 123.1, 98.4, 78.4, 52.4, 31.9, 29.6, 29.5, 29.3, 29.2, 29.0, 28.6, 22.7, 19.9, 14.1;

HRMS: calculated for $C_{34}H_{51}O_4$ $(M+H)^+$ = 523.3782; found = 523.3779.

2,5-Di(dodec-1-yn-1-yl)thiophene (38)



Compound **40** was synthesized through the general dialkyne synthesis procedure to isolate the product in 27% yield, 1.11 g.

^{1}H NMR (300 MHz, $CDCl_3$): 6.89 (s, 2H), 2.38 (t, *J* = 7.2 Hz, 4H), 1.60-1.20 (m, 32H), 0.86 (t, *J* = 7.3 Hz, 6H);

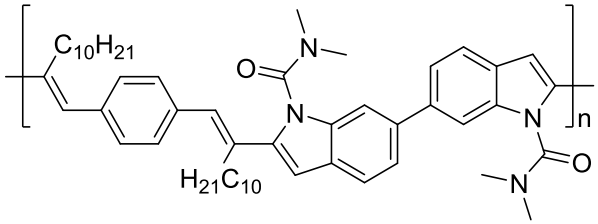
^{13}C NMR (300 MHz, $CDCl_3$): 130.5, 124.4, 94.8, 73.6, 32.0, 29.7, 29.6, 29.4, 29.2, 29.0, 28.6, 22.8, 19.8, 14.2;

HRMS: calculated for $C_{28}H_{45}S$ $(M+H)^+$ = 413.3237; found = 413.3237.

General procedure for AA BB polymerization:

To a microwave vial, the diindole (0.100 mmol, 1 eq.), the diyne (0.100 mmol,1 eq.), CsOPiV (2.34 mg, 0.01 mmol, 0.05 eq.), and PivOH (102 mg, 1.00 mmol, 10 eq.) were dissolved in THF (0.8 mL). To the stirred solution, $Cp^*Rh(MeCN)_3$ $(SbF_6)_2$ (8.32 mg, 0.01 mmol, 0.05 eq.) was added, the vial was sealed, and the reaction was heated to 110 ºC. After the 22 hours or once the solution became too viscous to stir. The polymer was purified by precipitation into methanol and isolated by filtration.

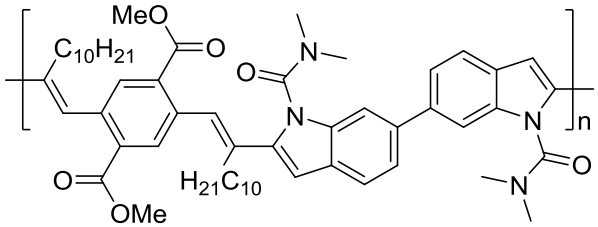
Poly[2-(1-(4-(dodec-1-en-1-yl)phenyl)dodec-1-en-2-yl)-N^1,N^1,$N^{1'}$,$N^{1'}$-tetramethyl-1H,1'H-[6,6'-biindole]-1,1'-dicarboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=23, M_w=37 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.70-7.35 (m), 6.80-6.70 (m), 3.50-2.50 (m), 1.60-1.20 (m), 0.90 (br).

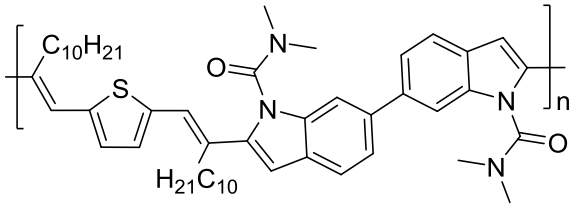
Poly[dimethyl 2-(2-(1,1'-bis(dimethylcarbamoyl)-1H,1'H-[6,6'-biindol]-2-yl)dodec-1-en-1-yl)-5-(dodec-1-en-1-yl)terephthalate]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=10, M_w=12 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 8.01 (br), 7.70-7.35 (m), 6.80-6.70 (m), 3.90 (br), 3.50-2.75 (m), 2.50 (br), 1.60-1.20 (m), 0.90 (br).

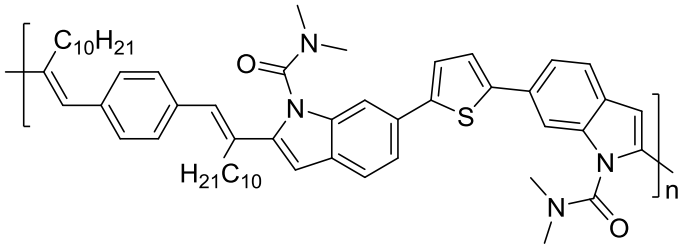
Poly[2-(1-(4-(dodec-1-en-1-yl)thiophenyl)dodec-1-en-2-yl)-N^1,N^1,$N^{1'}$,$N^{1'}$-tetramethyl-1H,1'H-[6,6'-biindole]-1,1'-dicarboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=10, M_w=17 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.70-7.40 (m), 7.00 (br), 6.86 (br), 6.71 (br), 3.50-2.50 (m), 1.60-1.20 (m), 0.90 (br).

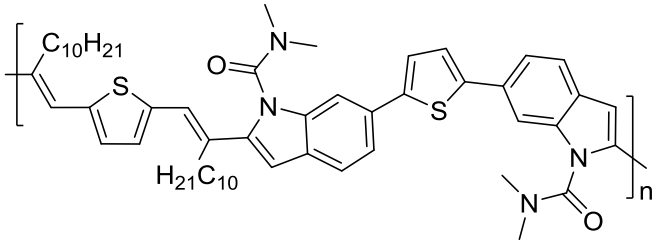
Poly[6-(5-(1-(dimethylcarbamoyl)-2-(1-(4-(2-dodec-1-en-1-yl)phenyl)dodec-1-en-2-yl)-1H-indol-6-yl)thiophen-2-yl)-N,N,2-dimethyl-1H-indole-1-carboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=10, M_w=19 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.70-7.35 (m), 6.75 (br), 6.67 (br), 3.50-2.50 (m), 1.60-1.20 (m), 0.90 (br).

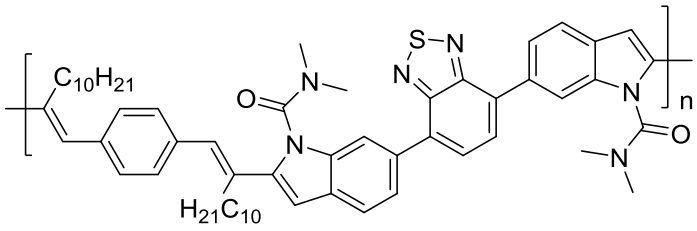
Poly[6-(5-(1-(dimethylcarbamoyl)-2-(1-(4-(2-dodec-1-en-1-yl)thiophenyl)dodec-1-en-2-yl)-1H-indol-6-yl)thiophen-2-yl)-N,N,2-dimethyl-1H-indole-1-carboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=10, M_w=16 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.70-7.35 (m), 7.02 (br), 6.75 (br), 6.67 (br), 3.50-2.50 (m), 1.50-1.20 (m), 0.86 (br).

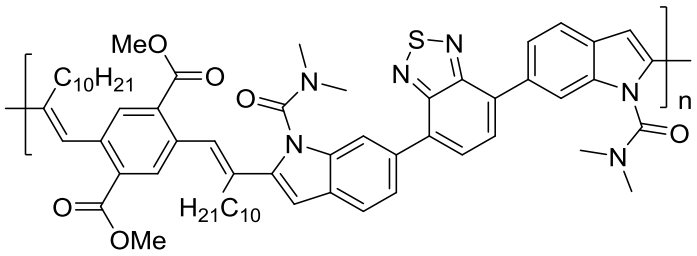
Poly[6-(5-(1-(dimethylcarbamoyl)-2-(1-(4-(2-dodec-1-en-1-yl)phenyl)dodec-1-en-2-yl)-1H-indol-6-yl)benzothiodiazole-2-yl)-N,N,2-dimethyl-1H-indole-1-carboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=8, M_w=13 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 8.00-7.50 (m), 7.36 (br), 6.80-6.70 (m), 3.50-2.50 (m), 1.60-1.20 (m), 0.90 (br).

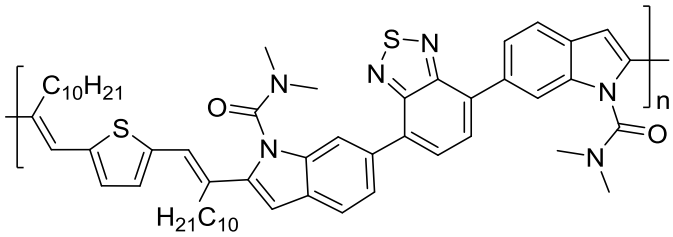
Poly[dimethyl 2-(2-(1-(dimethylcarbamoyl)-6-(7-(1-(dimethylcarbamoyl)-1H-indol-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-1H-indol-2-yl)dodec-1-en-1-yl)-5-(dodec-1-en-1-yl)terephthalate]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=7, M_w=11 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 8.00-7.75 (m), 7.21 (br), 7.36 (br), 6.80-6.70 (m), 3..44 (br) 3.20-3.00 (m), 1.76 (br), 1.40-1.20 (m), 0.84 (br).

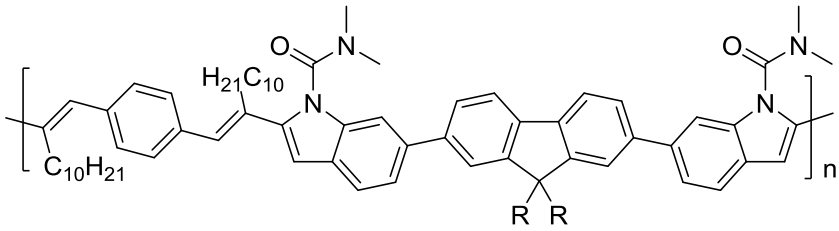
Poly[6-(5-(1-(dimethylcarbamoyl)-2-(1-(4-(2-dodec-1-en-1-yl)thiophenyl)dodec-1-en-2-yl)-1H-indol-6-yl) benzothiodiazole -2-yl)-N,N,2-dimethyl-1H-indole-1-carboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=11, M_w=19 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 8.00-7.50 (m), 7..02 (br), 6.89 (br), 6.76 (br), 3.50-2.50 (m), 1.60-1.20 (m), 0.86 (br).

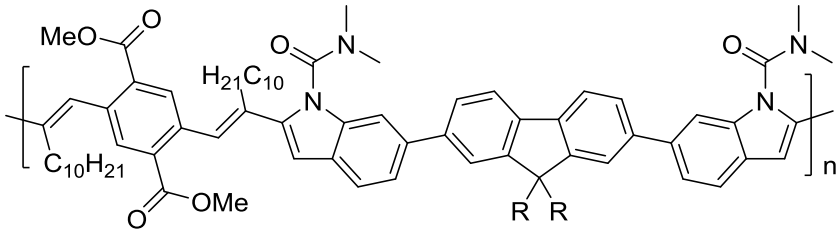
Poly[6-(7-(1-(dimethylcarbamoyl)-2-(-1-(4-(2-methyldodec-1-en-1-yl)phenyl)dodec-1-en-2-yl)-1H-indol-6-yl)-9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-N,N,2-dimethyl-1H-indole-1-carboxamide]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=10, M_w=19 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.70-7.35 (m), 6.80-6.70 (m), 3.50-2.50 (m), 2.00 (br), 1.60-1.20 (m), 0.86 (br), 0.58 (br).

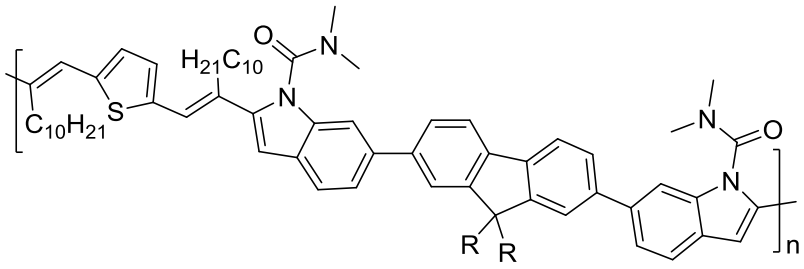
Poly[dimethyl 2-(2-(1-(dimethylcarbamoyl)-6-(7-(1-(dimethylcarbamoyl)-1H-indol-6-yl)-9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-1H-indol-2-yl)dodec-1-en-1-yl)-5-(dodec-1-en-1-yl)terephthalate]



This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=8, M_w=12 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 8.10-7.35 (m), 6.80-6.70 (m), 3.95-3.75 (m), 3.50-2.50 (m), 2.10 (br), 1.60-1.20 (m), 0.86 (br), 0.60 (br).

Poly[6-(7-(1-(dimethylcarbamoyl)-2-(-1-(4-(2-methyldodec-1-en-1-yl)thiophenyl)dodec-1-en-2-yl)-1H-indol-6-yl)-9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-N,N,2-dimethyl-1H-indole-1-carboxamide]

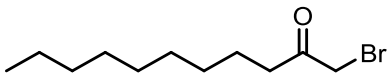


This polymer was synthesized via the general procedure for AA BB polymerization to a molecular weight of M_n=11, M_w=22 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.70-7.45 (m), 7.01 (br), 6.86 (br), 6.73 (br), 3.50-2.50 (m), 2.08 (br), 1.60-1.20 (m), 0.86 (br), 0.58 (br).

4.3.0 Experimental Procedures of the Dehydration Project

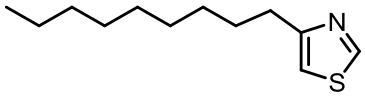
1-Bromoundecan-2-one



1-Bromoundecan-2-one was prepared according to a previously reported procedure.[39]

^{1}H NMR (300 MHz, $CDCl_3$): 3.88 (s, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 1.62 (tt, *J* = 7.3, 7.0 Hz, 2H), 1.26 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H).

4-Nonylthiazole (89)



4-Nonylthiazole was synthesized according to a previously reported procedure.[40]

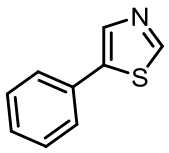
^{1}H NMR (300 MHz, $CDCl_3$): 8.73 (s, 1H), 6.91 (s, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.72 (tt, *J* = 7.6, 7.6 Hz, 2H), 1.40-1.20 (m, 12H) , 0.86 (t, *J* = 7.0 Hz, 3H).

General Direct Arylation Procedure:

The 5-aryl thiazoles were synthesized following literature procedure.[41] K_2CO_3 (4.14 g, 30.0 mmol, 1.5 eq.), $Pd(OAc)_2$ (89.8 mg, 0.400 mmol, 0.02 eq.), $PCy_3 \cdot HBF_4$ (294 mg, 0.800 mmol, 0.04 eq.), and PivOH (612 mg, 6.00 mmol, 0.30 eq.) were weighed to air and placed in a screw-cap vial equipped with a magnetic stir bar. The thiazole (30.0 mmol, 1.5 eq.) and the aryl bromide (20.0 mmol, 1 eq.) were added at this point if solids. The vial was purged with argon, and DMA (65 mL) was added. The thiazole (30.0 mmol, 1.5 eq.) and the aryl bromide (20.0 mmol, 1 eq.) were added at this point if liquids. The reaction mixture was then vigorously stirred at 100 °C for 20 hours. The solution was cooled to room temperature, diluted with 200 mL of EtOAc, washed (3 x 200 mL) with saturated aqueous NH_4Cl, dried over $MgSO_4$, filtered, and evaporated under reduced

pressure. The mixtures were then purified via silica gel column chromatography to afford the corresponding product in 40-95% yield.

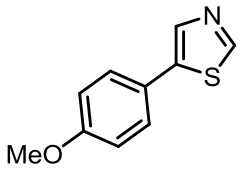
5-Phenylthiazole (58)



5-Phenylthiazole was synthesized according to the general direct arylation procedure to give the product in 92% yield, 2.97 g, and exhibited identical data to previously reported.[42]

^{1}H NMR (300 MHz, $CDCl_3$): 8.76 (s, 1H), 8.09 (s, 1H), 7.59 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.50-7.30 (m, 3H).

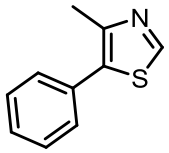
5-(4-Methoxyphenyl)-thiazole (59)



5-(4-Methoxyphenyl)-thiazole was synthesized according to the general direct arylation procedure to give the product in 46% yield, 1.76 g, and exhibited identical data to previously reported.[42]

^{1}H NMR (300 MHz, $CDCl_3$): 8.70 (s, 1H), 7.98 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H).

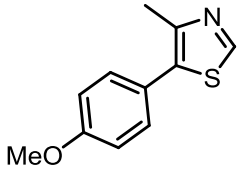
4-Methyl-5-phenylthiazole (60)



4-Methyl-5-phenylthiazole was synthesized according to general direct arylation procedure to give the product in 73% yield, 2.56 g, and exhibited identical data to previously reported.[43]

^{1}H NMR (300 MHz, $CDCl_3$): 8.50 (s, 1H), 7.48-7.23 (m, 5H), 2.49 (s, 3H).

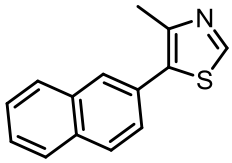
5-(4-Methoxyphenyl)-4-methylthiazole (61)



5-(4-Methoxyphenyl)-4-methylthiazole was synthesized according to the general direct arylation procedure to give the product in 71% yield, 2.91 g, and exhibited identical data to previously reported.[43]

^{1}H NMR (300 MHz, $CDCl_3$): 8.74 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 3H), 2.52 (s, 3H).

4-Methyl-5-(naphthalen-2-yl)thiazole (62)



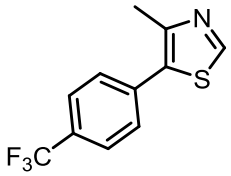
4-Methyl-5-(naphthalen-2-yl)thiazole was synthesized according to the general direct arylation procedure to give the product in 64% yield, 2.88 g.

^{1}H NMR (300 MHz, $CDCl_3$): 8.72 (s, 1H), 7.95-7.79 (m, 4H), 7.60-7.45 (m, 3H), 2.60 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 150.5, 148.9, 133.3, 132.7, 132.1, 129.4, 128.5, 128.4, 128.1, 127.8, 127.2, 126.7, 126.6, 16.3;

HRMS: calculated for $C_{14}H_{12}NS$ $(M+H)^+$ = 225.0685; found = 226.0674.

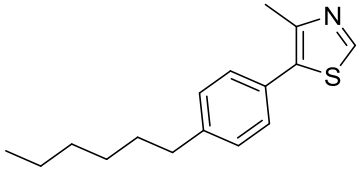
4-Methyl-5-(4-trifluoromethylphenyl)thiazole (63)



4-Methyl-5-(4-trifluoromethylphenyl)thiazole was synthesized according to the general direct arylation procedure to give the product in 75% yield, 3.65 g, and exhibited identical data to previously reported.[44]

^{1}H NMR (300 MHz, $CDCl_3$): 8.65 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.48 (d, 8.0 Hz, 2H), 2.48 (s, 3H).

5-(4-Hexylphenyl)-4-methylthiazole (64)



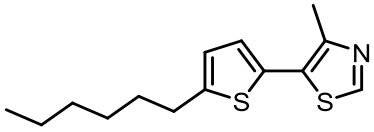
5-(4-Hexylphenyl)-4-methylthiazole was synthesized according to the general direct arylation procedure to give the product in 79% yield, 4.10 g.

^{1}H NMR (300 MHz, $CDCl_3$): 8.63 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.52 (s, 3H), 1.71-1.55 (m, 2H), 1.43-1.23 (m, 6H), 0.88 (t, *J* = 6.3 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 149.8, 148.1, 142.8, 131.9, 129.0, 128.6, 35.6, 31.6, 31.2, 28.9, 22.5, 16.0, 14.0, one overlapping signal as one peak is missing even with prolonged scans;

HRMS: calculated for $C_{16}H_{22}NS$ $(M+H)^+$ 260.1467; found = 260.1460.

5-(5-Hexylthiophen-2-yl)-4-methylthiazole (65)



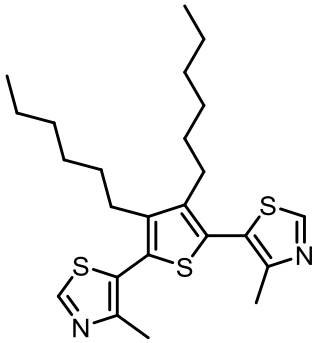
5-(5-Hexylthiophen-2-yl)-4-methylthiazole was synthesized according to the general direct arylation procedure to give the product in 53% yield, 2.81 g.

^{1}H NMR (300 MHz, $CDCl_3$): 8.51 (s, 1H), 6.90 (d, *J* = 3.3 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 1.75-1.56 (m, 2H), 1.44-1.20 (m, 6H), 0.86 (t, *J* = 6.3 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 149.2, 148.2, 147.0, 130.4, 126.7, 126.0, 124.5, 31.4, 30.0, 28.9, 23.6, 22.5, 16.4, 14.0;

HRMS: calculated for$C_{14}H_{20}NS_2$ $(M+H)^+$ 266.1032; found = 266.1033.

5,5'-(3,4-Dihexylthiophene-2,5-diyl)bis(4-methylthiazole) (66)



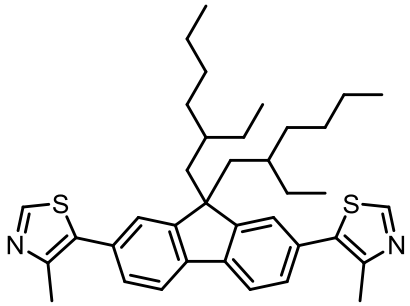
5,5'-(3,4-Dihexylthiophene-2,5-diyl)bis(4-methylthiazole) was synthesized in 26% yield, 1.16 g, according to the general direct arylation procedure with the exception of employing only 0.5 equivalents (10 mmol) of the dibromothiophene instead 1 equivalent of the aryl bromide.

^{1}H NMR (300 MHz, $CDCl_3$): 8.78 (s, 2H), 2.50-2.40 (m, 10H), 1.70-1.20 (m, 16H), 0.85 (t, *J* = 6.8 Hz, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 152.3, 152.2, 143.1, 127.1, 123.5, 31.5, 30.6, 29.5, 28.1, 22.6, 16.1, 14.1;

HRMS: calculated for $C_{24}H_{35}N_2S_3$ $(M+H)^+$ 447.1957; found = 447.1956.

5,5'-(9,9-Bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(4-methylthiazole) (91)



5,5'-(9,9-Bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(4-methylthiazole) was synthesized in 94% yield, 5.50 g, according to the general direct arylation procedure with the exception

of employing only 0.5 equivalents (10 mmol) of the dibromofluorene instead 1 equivalent of the aryl bromide.

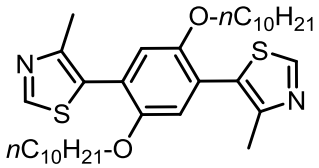
^{1}H NMR (300 MHz, $CDCl_3$): 8.65 (s, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.48-7.32 (m, 4H), 2.54 (s, 6H), 2.11-1.91 (m, 4H), 0.90-0.44 (m, 30H);

^{13}C NMR (300 MHz, $CDCl_3$): 151.0*, 149.9, 148.2*, 140.3, 132.4, 130.2*, 128.2*, 124.9*, 119.8, 55.1, 44.4, 34.6, 33.7*, 28.1*, 26.9*, 22.5, 16.0*, 13.8, 10.2*;

* denotes peaks that appear as multiplets due to the presence of diasteromers;

HRMS: calculated for $C_{37}H_{49}N_2S_2$ $(M+H)^+$ 585.3332; found = 585.3329.

5,5'-(2,5-Bis(decyloxy)-1,4-phenylene)bis(4-methylthiazole) (105)



5,5'-(2,5-bis(decyloxy)-1,4-phenylene)bis(4-methylthiazole) was synthesized in 31% yield, 1.813 g, according to the general direct arylation procedure with the exception of employing only 0.5 equivalents (10 mmol) of dibromobenzene derivative instead 1 equivalent of the aryl bromide.

^{1}H NMR (300 MHz, $CDCl_3$): 8.73 (s, 2H), 6.91 (s, 2H), 3.89 (t, *J* = 6.5 Hz, 4H), 2.47 (s, 6H), 1.68 (tt, *J* = 6.9, 6.7 Hz, 4H), 1.23 (m, 28H), 0.85 (t, *J* = 6.8 Hz, 6H);

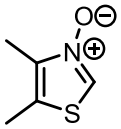
^{13}C NMR (300 MHz, $CDCl_3$): 151.2, 150.2, 150.0, 126.8, 121.7, 116.2, 69.5, 31.8, 29.4, 29.2, 29.1, 29.0, 25.9, 22.6, 16.4, 14.0, one overlapping signal as one peak is missing even with prolonged scans;

HRMS: calculated for $C_{34}H_{53}N_2O_2S_2$ $(M+H)^+$ 585.3554; found = 585.3541.

General Oxidation Procedure:

The thiazole (5.00 mmol, 1 eq.) was dissolved in reagent grade dichloroethane (15 mL). To this solution was added *m*CPBA (1.68 g, 7.50 mmol,1.5 eq.) portion-wise. Once all of the *m*CPBA had been added, the reaction was stirred for 2-4 h. The *N*-oxides were then purified via silica gel column chromatography using a gradient of 0-15% MeOH/EtOAc as the eluent to afford the corresponding product in 10-90% yield.

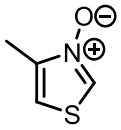
4,5-Dimethylthiazole 3-oxide (53)



4,5-Dimethylthiazole 3-oxide was synthesized according to the general oxidation procedure in 90% yield, 581 mg, and exhibited identical data to previously reported.[45]

^{1}H NMR (300 MHz, $CDCl_3$): 8.06 (s, 1H), 2.39 (s, 3H), 2.30 (s, 3H).

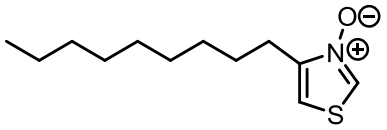
4-Methylthiazole 3-oxide (67)



4-Methylthiazole 3-oxide was synthesized according to the general oxidation procedure in 22% yield, 127 mg, and exhibited identical data to previously reported.[45]

^{1}H NMR (300MHz, $CDCl_3$, 293K): 8.20 (d, *J* = 3.1 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 2.38 (s, 3H).

4-Nonylthiazole 3-oxide (68)



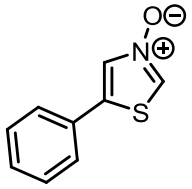
4-Nonylthiazole 3-oxide was synthesized according to the general oxidation procedure in 40% yield, 455 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.24 (d, *J* = 3.1 Hz, 1H), 6.96 (d, *J* = 3.1 Hz, 1H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.64 (tt, *J* = 7.7, 7.3 Hz, 2H), 1.25-1.00 (m, 12H), 0.81 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 149.8, 130.2, 112.5, 31.7, 29.3, 29.2, 29.1, 29.0, 26.5, 22.5, 14.0, one overlapping signal as one peak is missing even with prolonged scans;

HRMS: calculated for $C_{12}H_{22}NOS$ $(M+H)^+$ 228.1422; found = 228.1417.

5-Phenylthiazole 3-oxide (69)



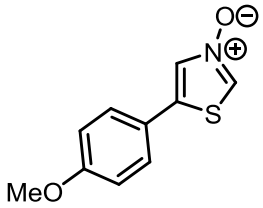
5-Phenylthiazole 3-oxide was synthesized according to the general oxidation procedure in 10% yield, 88.6 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.22 (s, 1H), 7.89 (s, 1H), 7.45 (m, 5H);

^{13}C NMR (300 MHz, $CDCl_3$): 139.2, 134.1, 131.6, 130.8, 129.8, 128.3, 126.4;

HRMS: calculated for C_9H_8NOS $(M+H)^+$ 178.0321; found = 178.0321.

5-(4-Methoxyphenyl)thiazole 3-oxide (70)



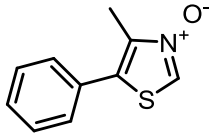
5-(4-Methoxyphenyl)thiazole 3-oxide was synthesized according to the general oxidation procedure in 28% yield, 290 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (s, 1H), 7.80 (s, 1H), 7.35 (d, *J* = 6.5 Hz, 2H), 6.88 (d, *J* = 6.8 Hz, 2H), 3.80 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 161.0, 137.6, 131.4, 129.2, 127.4, 121.2, 114.7, 55.3;

HRMS: calculated for $C_{10}H_{10}NO_2S$ $(M+H)^+$ 208.0427; found = 208.0427.

4-Methyl-5-phenylthiazole 3-oxide (71)



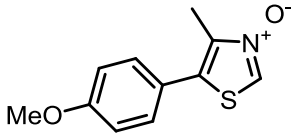
4-Methyl-5-phenylthiazole 3-oxide was synthesized according to the general oxidation procedure in 60% yield, 574 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.24 (s, 1H), 7.54-7.40 (m, 5H), 2.46 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 141.4, 130.9, 130.6, 129.4, 129.2, 128.6, 128.4, 11.8;

HRMS: calculated for $C_{10}H_{10}NOS$ $(M+H)^+$ 192.0478; found = 192.0477.

5-(4-Methoxyphenyl)-4-methylthiazole 3-oxide (72)



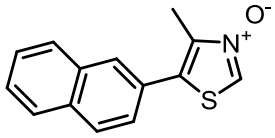
5-(4-Methoxyphenyl)-4-methylthiazole 3-oxide was synthesized according to the general oxidation procedure in 51% yield, 564 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.19 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.42 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 160.5, 140.7, 130.8, 129.9, 127.9, 122.8, 114.6, 55.4, 11.7;

HRMS: calculated for $C_{11}H_{12}NO_2S$ $(M+H)^+$ 222.0583; found = 222.0583.

4-Methyl-5-(naphthalen-2-yl)thiazole 3-oxide (73)



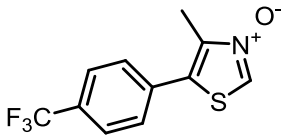
4-Methyl-5-(naphthalen-2-yl)thiazole 3-oxide was synthesized according to the general oxidation procedure in 45% yield, 543 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.29 (s, 1H), 7.99-7.87 (m, 4H), 7.62 (m, 3H), 2.54 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 141.7, 133.3, 133.1, 131.1, 129.2, 129.0, 128.3, 128.2, 127.9, 127.4, 127.2, 125.6, 12.0, one overlapping signal as one peak is missing even with prolonged scans;

HRMS: calculated for $C_{14}H_{12}NOS$ $(M+H)^+$ 242.0634; found = 242.0634.

4-Methyl-5-(4-trifluoromethylphenyl)thiazole 3-oxide (74)



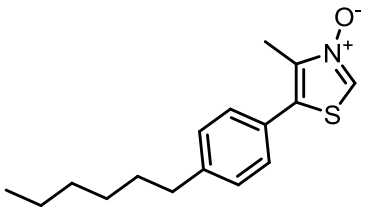
4-Methyl-5-(4-trifluoromethylphenyl)thiazole 3-oxide was synthesized according to the general oxidation procedure in 30% yield, 389 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.27 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 142.5, 134.1, 131.4 (q, *J* = 33.2 Hz), 129.1, 129.0, 128.9, 126.2 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 272.3 Hz), 11.8;

HRMS: calculated for $C_{11}H_9F_3NOS$ $(M+H)^+$ 260.0351; found = 260.0351.

5-(4-Hexylphenyl)-4-methylthiazole-3-oxide (75)



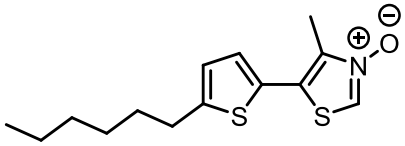
5-(4-Hexylphenyl)-4-methylthiazole-3-oxide was synthesized according to the general oxidation procedure in 55% yield, 760 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 1H), 7.30-7.20 (m, 4H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 1.56 (tt, *J* = 7.6, 7.1 Hz, 2H), 1.24(m, 6H), 0.80 (t, *J* = 6.7 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 150.3, 149.2, 148.0, 143.0, 130.2, 129.2, 128.8, 35.7, 31.7, 31.4, 29.0, 22.6, 16.0, 14.1;

HRMS: calculated for $C_{16}H_{22}NOS$ $(M+H)^+$ 276.1417; found = 276.1406.

5-(5-Hexylthiophen-2-yl)-4-methylthiazole 3-oxide (76)



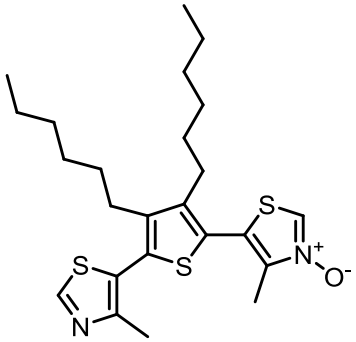
5-(5-Hexylthiophen-2-yl)-4-methylthiazole 3-oxide was synthesized according to the general oxidation procedure in 29% yield, 408 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.21 (s, 1H), 7.04 (d, *J* = 3.6 Hz, 1H), 6.78 (d, *J* = 3.6 Hz, 1H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.513 (s, 3H), 1.68 (tt, *J* = 7.6, 7.1 Hz, 2H), 1.32 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 149.0, 140.4, 128.8, 127.9, 127.3, 125.3, 124.9, 31.4, 30.0, 28.6, 22.4, 13.9, 11.9;

HRMS: calculated for $C_{14}H_{20}NOS_2$ $(M+H)^+$ 282.0981; found = 282.0981.

4-Methyl-5-(5-(4-methylthiazol-5-yl)thiophen-2-yl)thiazole 3-oxide (77)



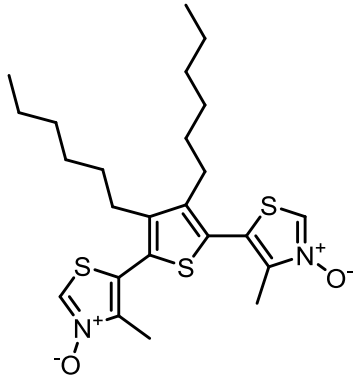
4-Methyl-5-(5-(4-methylthiazol-5-yl)thiophen-2-yl)thiazole 3-oxide was synthesized according to the general oxidation procedure, with the exception of employing 3 equivalents of *m*CPBA. The product was obtained in 25% yield, 578 mg. Note: the di-*N*-oxide (**102**) was also produced and isolated from this reaction.

^{1}H NMR (300 MHz, $CDCl_3$): 8.80 (s, 1H), 8.44 (s, 1H), 2.50-2.40 (m, 7H), 2.35 (s, 3H), 1.50-1.10 (m, 16H), 0.85 (t, *J* = 5.5 Hz, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 152.5, 152.2, 144.1, 143.3, 130.9, 128.7, 127.8, 124.7, 123.1, 122.5, 31.3, 30.6, 30.2, 29.3, 29.2, 28.0, 27.8, 22.4, 15.8, 13.9, 12.0;

HRMS: calculated for $C_{24}H_{35}N_2OS_3$ $(M+H)^+$ 463.1906; found = 463.1906.

5,5'-(3,4-Dihexylthiophene-2,5-diyl)bis(4-methylthiazole 3-oxide)) (102)



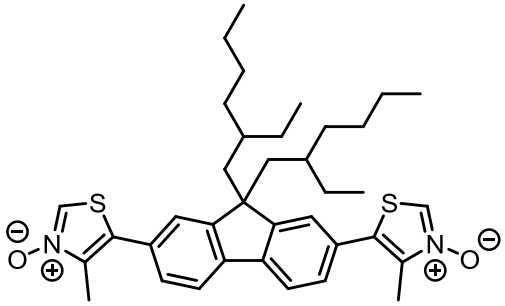
5,5'-(3,4-Dihexylthiophene-2,5-diyl)bis(4-methylthiazole 3-oxide)) (**102**) was synthesized according to the general oxidation procedure, with the exception of employing 3 equivalents of *m*CPBA. The product was obtained in 10% yield, 239 mg. Note the mono-*N*-oxide (**77**) was also produced and isolated from this reaction.

^{1}H NMR (300 MHz, $CDCl_3$): 8.37 (s, 2H), 2.48 (tt, *J* = 8.1, 7.7 Hz, 4H) 2.33 (s, 6H), 1.50-1.10 (m, 16H), 0.84 (t, *J* = 6.7 Hz, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 144.6, 144.5, 130.1, 126.4, 122.3, 31.3, 30.6, 29.3, 27.9, 22.4, 13.9, 12.0;

HRMS: calculated for $C_{24}H_{35}N_2O_2S_3$ $(M+H)^+$ 479.1855; found = 479.1855.

5,5'-(9,9-Bis(2-ethylhexyl)-9H-fluorene-2,7-diyl)bis(4-methylthiazole 3-oxide) (92)



The general oxidation procedure was followed with the following deviations: 3 eq of *m*CPBA was added instead of 1.5 eq. Additionally, after 2 hours of stirring, another 3 eq of *m*CPBA was added to the reaction. The product (**92**) was afforded in 28% yield, 864 mg.

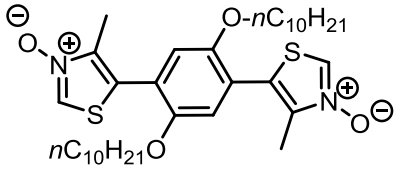
^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 2H), 7.85 (d, *J* = 8.1, 2H), 7.47-7.43 (m, 4H), 2.46 (s, 6H), 2.05 (m, 4H), 0.90-0.40 (m, 30H);

^{13}C NMR (300 MHz, $CDCl_3$): 151.8*, 141.4, 141.3, 131.2, 129.3*, 128.3, 127.8*, 124.3, 120.8*, 55.5, 44.4, 34.8, 33.9*, 28.2*, 27.0*, 22.6, 13.9, 11.8*, 10.2*;

* denotes peaks that appear as multiplets due to the presence of diasteromers;

HRMS: calculated for $C_{37}H_{49}N_2O_2S_2$ $(M+H)^+$ 617.3230; found = 617.3227.

5,5'-(2,5-Bis(decyloxy)-1,4-phenylene)bis(4-methylthiazole 3-oxide) (106)



The general oxidation procedure was followed with the following deviations: 3 eq of *m*CPBA was added instead of 1.5 eq. Additionally, after 2 hours of stirring, another 3 eq of *m*CPBA was added to the reaction. Compound **106** was afforded in 19% yield, 586 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.43 (s, br, 2H), 6.90 (s, 2H), 3.93 (t, *J* = 6.5 Hz, 4H), 2.39 (s, 6H), 1.71 (tt, *J* = 6.9, 6.7 Hz, 4H), 1.23 (m, 28H), 0.85 (t, *J* = 6.8 Hz, 6H);

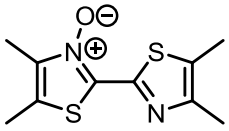
^{13}C NMR (300 MHz, $CDCl_3$): 150.1, 150.1, 126.8, 120.9, 115.4, 69.6, 31.8, 29.6, 29.4, 29.2, 29.1, 29.0, 25.9, 22.6, 14.0, 12.4, one overlapping signal as one peak is missing even with prolonged scans

HRMS: calculated for $C_{34}H_{53}N_2O_4S_2$ $(M+H)^+$ 617.3441; found = 617.3441.

General Dehydration Procedure:

The *N*-oxide (0.1 mmol, 1 eq.) was dissolved in reagent grade THF (0.4 mL) and the solution was cooled in an ice bath. To this cold solution was added 1.0M Li*O*t*Bu* in THF (150 µL, 0.15 mmol, 1.5 eq.) dropwise which usually resulted in a significant color change. After consumption of starting material (5-15 minutes), the mixture was poured into an extraction funnel containing CH_2Cl_2 and saturated NH_4Cl. The aqueous phase is washed with CH_2Cl_2 (2 x 15 mL) and the organics are combined, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The products were generally analytically pure after work up and did not need further purification in 55-98% yield.

4,4',5,5'-Tetramethyl-[2,2'-bithiazole] 3-oxide (54)



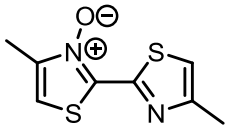
4,4',5,5'-Tetramethyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 88% yield, 10.6 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 2.38 (m, 6H), 2.35 (s, 3H), 2.30 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 149.1, 148.4, 140.9, 137.8, 128.1, 123.5, 14.7, 13.0, 11.2, 10.4;

HRMS: calculated for $C_{10}H_{13}N_2OS_2$ $(M+H)^+$ 241.0464; found = 241.0463.

4,4’-Dimethyl-[2,2'-bithiazole] 3-oxide (78)



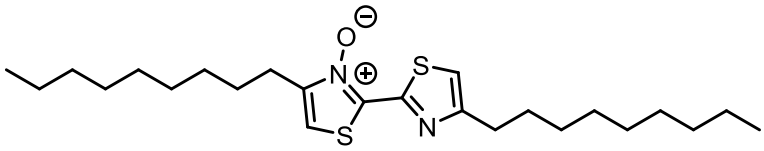
4,4’-Dimethyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 72% yield, 7.54 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.07 (s, 1H), 7.06 (s, 1H), 2.50 (s, 3H), 2.42 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 153.6, 152.7, 145.4, 140.1, 115.8, 111.7, 17.2, 12.7;

HRMS: calculated for $C_8H_9N_2OS_2$ $(M+H)^+$ 213.0151; found = 213.0142.

4,4’-Dinonyl-[2,2'-bithiazole] 3-oxide (79)



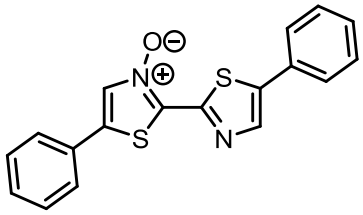
4,4’-Dinonyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 57% yield, 12.4 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.08 (s, 1H), 7.01 (s, 1H), 2.83 (m, 4H), 1.74 (m, 4H), 1.26 (m, 24H), 0.87 (m, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 158.6, 152.5, 149.7, 140.5, 115.0, 111.0, 31.9, 31.9, 31.5, 29.6, 29.5, 29.5, 29.3, 29.3, 29.3, 26.8, 26.6, 22.7, 22.7, 14.1, overlapping signals as multiple peaks are missing even with prolonged scans;

HRMS: calculated for $C_{24}H_{41}N_2OS_2$ $(M+H)^+$ 437.2655; found = 437.2655.

5,5'-Diphenyl-[2,2'-bithiazole] 3-oxide (80)



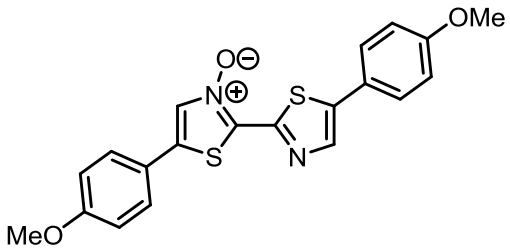
5,5'-Diphenyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure but required flash column chromatography to purify using 40% EtOAc/Hexanes to afford the product in 81% yield, 13.6 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.19 (s, 1H), 8.01 (s, 1H), 7.70-7.3 (m, 10H);

^{13}C NMR (300 MHz, $CDCl_3$): 151.1, 140.6, 139.6, 139.2, 135.7, 131.9, 131.0, 130.4, 129.5, 129.2, 128.7, 128.7, 126.9, 126.0;

HRMS: calculated for $C_{18}H_{13}N_2OS_4$ $(M+H)^+$ 337.0464; found = 337.0463.

5,5'-Bis(4-methoxyphenyl)-[2,2'-bithiazole] 3-oxide (81)



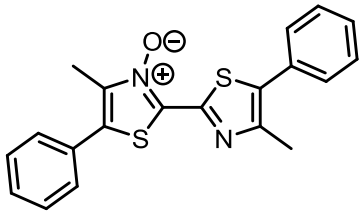
5,5'-Bis(4-methoxyphenyl)-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 81% yield, 16.1 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.08 (s, 1H), 7.91 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 161.4, 160.1, 140.7, 139.15, 138.2, 132.2, 130.9, 128.3, 127.5, 123.7, 121.3, 115.0 114.8, 113.6, 55.5, 55.4;

HRMS: calculated for $C_{20}H_{17}N_2O_3S_2$ $(M+H)^+$ 397.0675; found = 397.0676.

4,4'-Dimethyl-5,5'-diphenyl-[2,2'-bithiazole] 3-oxide (82)



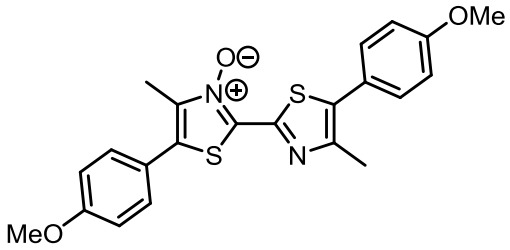
4,4'-Dimethyl-5,5'-diphenyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 92% yield, 16.8 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.60-7.30 (m, 10H), 2.59 (s, 3H), 2.55 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 149.9, 148.8, 140.9, 139.2, 133.8, 131.9, 130.4, 129.5, 129.3, 129.2, 129.1, 128.7, 128.5, 127.9, 16.4, 11.8;

HRMS: calculated for $C_{20}H_{17}N_2OS_2$ $(M+H)^+$ 365.0777; found = 365.0777.

5,5'-Bis(4-methoxyphenyl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide (83)



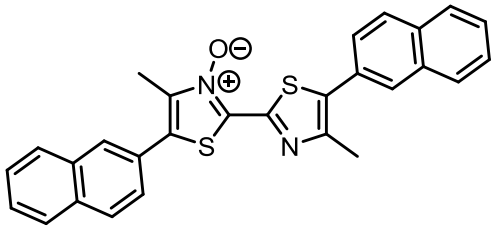
5,5'-Bis(4-methoxyphenyl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 92% yield, 19.5 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.50-7.40 (m, 4H), 7.10-6.95 (m, 4H), 3.88 (s, 3H), 3.87 (s, 3H), 2.58 (s, 3H), 2.53 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 160.7, 159.6, 149.5, 148.3, 140.2, 138.9, 133.7, 130.5, 130.0, 129.1, 124.3, 122.8, 114.9, 114.4, 55.5, 55.4, 16.5, 11.9;

HRMS: calculated for $C_{22}H_{21}N_2O_3S_2$ $(M+H)^+$ 425.0988; found = 425.0986.

4,4'-Dimethyl-5,5'-di(naphthalen-2-yl)-[2,2'-bithiazole] 3-oxide (84)



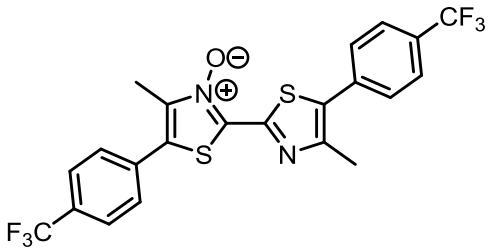
4,4'-Dimethyl-5,5'-di(naphthalen-2-yl)-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 98% yield, 22.8 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.02-7.87 (m, 8H), 7.69-7.52 (m, 6H), 2.70 (s, 3H), 2.66 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 150.3, 149.3, 141.3, 139.5, 134.1, 133.5, 133.4, 133.3, 132.8, 129.5, 129.5, 129.4, 128.7, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.6, 127.4, 127.0, 126.9, 126.7, 125.7, 16.8, 12.2;

HRMS: calculated for $C_{28}H_{21}N_2OS_2$ $(M+H)^+$ 465.1090; found = 465.1090.

4,4'-Dimethyl-5,5'-bis(4-(trifluoromethyl)phenyl)-[2,2'-bithiazole] 3-oxide (85)



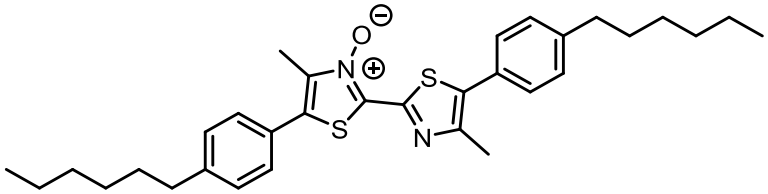
4,4'-Dimethyl-5,5'-bis(4-(trifluoromethyl)phenyl)-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 88% yield, 22.0 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.80 (s, 2H), 7.72 (m, 2H), 7.66 (s, 4H), 2.62 (s, 3H), 2.59 (s, 3H);

^{13}C NMR (300 MHz, $CDCl_3$): 150.5, 150.0, 142.1, 139.6, 135.6, 134.0, 132.3, 131.6 (q, *J* = 32.6 Hz), 130.0 (q, *J* = 33.5 Hz), 129.4, 129.0, 127.8, 126.4 (q, *J* = 3.5 Hz), 125.8 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 272.1 Hz), 123.6 (q, *J* = 272.2 Hz), 16.5, 12.0;

HRMS: calculated for $C_{22}H_{15}F_6N_2OS_2$ $(M+H)^+$ 501.0525; found = 501.0524.

5,5'-Bis(4-hexylphenyl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide (86)



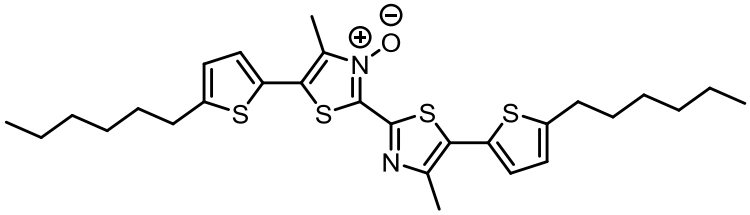
5,5'-Bis(4-hexylphenyl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 86% yield, 22.9 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.50-7.40 (m, 4H), 7.35-7.20 (m, 4H), 2.75-2.40 (m, 10H), 1.66 (m, 4H), 1.34 (m, 12H), 0.90 (m, 6H);

^{13}C NMR (300 MHz, $CDCl_3$): 148.5, 144.8, 143.1, 140.6, 134.0, 129.4, 129.3, 129.2, 129.1, 129.1, 128.9, 128.4, 127.8, 35.8, 35.7, 31.7, 31.7, 31.3, 31.2, 29.0, 29.0, 22.6, 16.5, 14.1, 11.9, overlapping signals as multiple peaks are missing even with prolonged scans;

HRMS: calculated for $C_{32}H_{41}N_2OS_2$ $(M+H)^+$ 533.2655; found = 533.2655.

5,5'-Bis(5-hexylthiophen-2-yl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide (87)



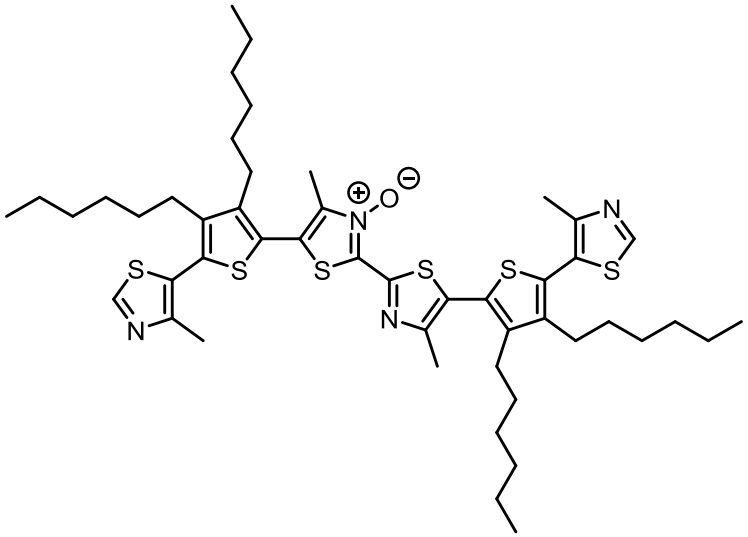
5,5'-Bis(5-hexylthiophen-2-yl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide was synthesized according to the general dehydration procedure in 56% yield, 15.3 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 7.13 (d, *J* = 3.5 Hz, 1H), 7.07 (d, *J* = 3.5 Hz, 1H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 2.84 (m, 4H), 2.66 (s, 3H), 2.62 (s, 3H), 1.71 (m, 4H), 1.45-1.20 (12H, m), 0.90 (6H, m);

^{13}C NMR (300 MHz, $CDCl_3$): 149.4, 148.5, 148.5, 147.7, 139.7, 137.8, 130.9, 129.2, 128.3, 127.4, 126.9, 125.2, 125.0, 123.8, 31.6, 31.5, 30.2, 30.2, 29.7, 28.8, 28.8, 22.7, 22.6, 22.6, 17.0, 14.2, 14.1, 12.1;

HRMS: calculated for $C_{28}H_{37}N_2OS_4$ $(M+H)^+$ 545.1783; found = 545.1782.

5,5'-Bis(3,4-dihexyl-5-(4-methylthiazol-5-yl)thiophen-2-yl)-4,4'-dimethyl-[2,2'-bithiazole] 3-oxide (88)



5,5'-Bis(3,4-dihexyl-5-(4-methylthiazol-5-yl)thiophen-2-yl)-4,4'-dimethyl-[2,2'-bithiazole]

3-oxide was synthesized according to the general dehydration procedure in 78% yield,

36.4 mg.

^{1}H NMR (300 MHz, $CDCl_3$): 8.81-8.75 (m, 2H), 2.65-2.30 (m, 20H), 1.42 (m, 8H), 1.23 (m, 24H), 0.85 (m, 12H);

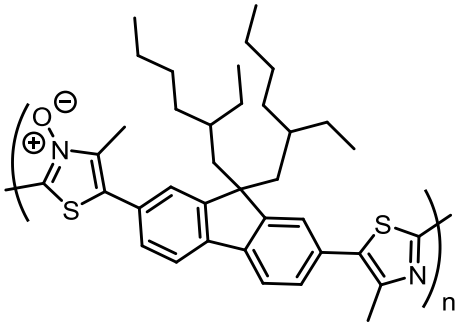
^{13}C NMR (300 MHz, $CDCl_3$): 152.5, 152.1, 151.3, 144.2, 143.6, 143.5, 143.1, 143.0, 140.1, 128.9, 127.3, 127.0, 125.8, 124.7, 121.6, 31.4, 31.3, 31.3, 30.7, 30.4, 30.3, 30.3, 29.3, 29.2, 29.2, 27.9, 27.9, 22.4, 22.4, 16.1, 15.9, 13.9, 12.0, overlapping signals as multiple peaks are missing even with prolonged scans;

HRMS: calculated for $C_{48}H_{67}N_4OS_6$ $(M+H)^+$ 907.3634; found = 907.3623.

General Dehydration Polymerization Procedure:

The di-*N*-oxide (0.20 mmol, 1 eq.) was dissolved in reagent grade THF (0.6 mL) and the solution was placed in an ice bath. To this cold solution was added 1.0M Li*O*t*B*u in THF (300 µL, 0.30 mmol, 1.5 eq.) which usually resulted in a significant color change. The mixture was allowed to warm to room temperature and was stirred for 3 hours. The solution was then concentrated and precipitated in methanol and isolated through filtration.

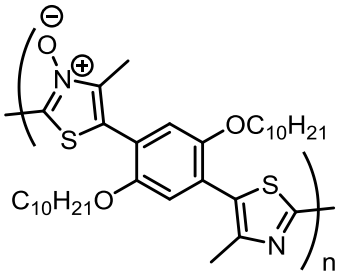
Poly[5-(9,9-bis(2-ethylhexyl)-7-(4-methylthiazol-5-yl)-9H-fluoren-2-yl)-4-methyl-3-(λ^1-oxidaneyl)-3λ^4-thiazole] (95)



95 was synthesized according to the general polymerization procedure in quantitative yield, M_n = 37, M_w = 80 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 7.84 (br, 2H), 7.59 (m, 4H), 2.75-2.50 (m, 6H), 2.20-1.90 (m, 4H), 0.90-0.40 (m, 30H).

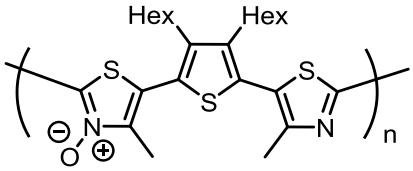
Poly[5-(2,5-bis(decyloxy)-4-(2,4-dimethylthiazol-5-yl)phenyl)-4-methylthiazole 3-oxide] (110)



110 was synthesized according to the general polymerization procedure in quantitative yield, M_n = 43, M_w = 110 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 6.96 (s, 2H), 3.93 (br, 4H), 2.25 (br, 6H), 1.80 (br, 4H), 1.24 (m, 28H), 0.85 (br, 6H).

Poly[5-(3,4-dihexanoyl-5-(4-methylthiazol-5-yl)thiophen-2-yl)-4-methylthiazole 3-oxide] (106)



106 was synthesized according to the general polymerization procedure in quantitative yield, M_n = 17, M_w = 46 kDa.

^{1}H NMR (300 MHz, $CDCl_3$): 2.65-2.30 (br, 10H), 1.50-1.10 (m, 16H), 0.85 (br, 6H).

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