

Direct (Hetero)Arylation: A New Tool for Polymer Chemists

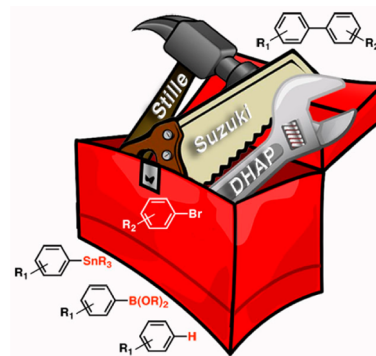
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CONSPECTUS

The coupling of aryl halides with catalytically activated aryl C–H bonds provides a desirable and atom-economical alternative to standard cross-coupling reactions for the construction of new C–C bonds. The reaction, termed direct (hetero)arylation, is believed to follow a base-assisted, concerted metalation-deprotonation (CMD) pathway. During this process, carboxylate or carbonate anions coordinate to the metal center, typically palladium, in situ and assist in the deprotonation transition state. Researchers have employed this methodology with numerous arenes and heteroarenes, including substituted benzenes, perfluorinated benzenes, and thiophenes. Thiophene substrates have demonstrated high reactivity toward C–H bond activation when appropriately substituted with electron-rich and/or electron-deficient groups. Because of the pervasive use of thiophenes in materials for organic electronics, researchers have used this chemistry to modularly prepare conjugated small molecules and, more recently, conjugated polymers. Although optimization of reaction conditions such as solvent system, phosphine ligand, carboxylate additives, temperature, and time is necessary for efficient C–H bond reactivity of each monomer, direct (hetero)arylation polymerization (DHAP) can afford high yielding polymeric materials with elevated molecular weights. The properties of these materials often rival those of polymers prepared by traditional methods. Moreover, DHAP provides a facile means for the synthesis of polymers that were previously inaccessible or difficult to prepare due to the instability of organometallic monomers. The major downfall of direct (hetero)arylation, however, is the lack of C–H bond selectivity, particularly for thiophene substrates, which can result in cross-linked material during polymerization reactions. Further fine-tuning of reaction conditions such as temperature and reaction time may suppress these unwanted side reactions. Alternatively, new monomers can be designed where other reactive bonds are blocked, either sterically or by substitution with unreactive alkyl or halogen groups. In this Account, we illustrate these methods and present examples of DHAP reactions that involve the preparation of common homopolymers used in organic electronics (P3HT, PEDOT, PProDOT), copolymers formed by activation of electron-rich (bithiophene, fused bithiophenes) and electron-deficient monomers (TPD, 1,2,4,5-tetrafluorobenzene, 2,2'-bithiazole). Our group is optimizing these reactions and developing ways to make DHAP a common atom-economical synthetic tool for polymer chemists.

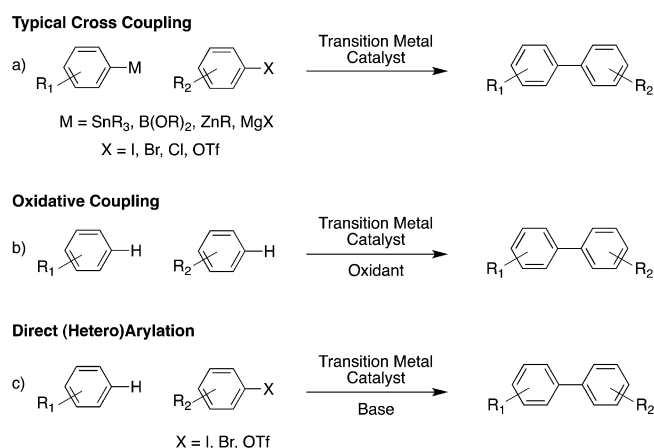


Introduction

Aryl C–C bond formation is a key reaction in the “toolbox” of synthetic chemists and is vital for the preparation of molecules with relevance in many disciplines including biopharmaceuticals, organic electronics, materials science, and so forth. This process can be facilitated by a transition metal catalyst, which couples two aryl groups that are functionalized with preactivated units.^{1,2} Conventionally, one arene is substituted with a leaving group (I, Br, OTf, etc.), while the other contains an organometallic moiety such as $-\text{B}(\text{OR})_2$, $-\text{SnR}_3$, $-\text{ZnR}$, or $-\text{MgX}$ (Scheme 1a). However, installation of these functional groups entails extra

synthetic steps and the compounds are sometimes unstable. Alternatively, two unsubstituted arenes can undergo C–H activation and be joined by an oxidative coupling process (Scheme 1b). This methodology requires a directing group to activate the relatively inert bonds and is unselective.³ A combination of the previous two protocols, termed direct (hetero)arylation, involves coupling of a prefunctionalized arene bearing a leaving group with an arene C–H bond (Scheme 1c).^{3–5} Regioselectivity in these reactions is dependent on the arene systems used. A base is also added to assist in C–H bond activation and neutralizes the stoichiometric amount of acid formed.

SCHEME 1



Direct (hetero)arylation has been applied to the coupling of a number of different arene and heteroarene systems.⁵ Our group was specifically interested in the activation of thiophene C–H bonds, given the ubiquitous occurrence of this building block in materials for organic electronic devices such as light emitting diodes (OLEDs), thin film transistors (OTFTs), and bulk heterojunction solar cells (BHJ-SCs). A large volume of work has shown that direct (hetero)arylation is high yielding for thiophenes and 2,2'-bithiophenes substituted with electron-rich and electron-poor substituents.^{6–8} For 2-substituted thiophenes, C–H activation typically occurs in the 5-position, but can take place at the 3-position depending on the substituents^{9,10} or catalytic system^{11,12} used. Thiophenes substituted in the 3-position undergo activation at the 2-position primarily,⁶ but reactions occur at the 4-¹² and/or 5-positions¹³ as well. This body of work prompted us, and others, to apply direct (hetero)arylation polymerization (DHAP) to the construction of conjugated organic polymers.¹⁴ Due to the relatively limited number of polymerization reactions for conjugated polymers (Stille and Suzuki reactions are conventionally employed), DHAP has already made a strong impact in the field of polymer chemistry. As we will outline in this account, application to monomers other than thiophenes has also been demonstrated. However, C–H bond selectivity during polymerization is difficult to control and for some examples, insoluble cross-linked material is formed. Linear high molecular weight polymers can still be prepared by DHAP when monomers are properly designed and/or selected. This methodology can also provide entry into polymers that were previously inaccessible, or difficult to prepare by traditional methods. This account will present examples of DHAP published to date and discuss the outlook of this promising tool.

Mechanistic Insight

The mechanism by which C–H activation occurs has been studied experimentally and computationally, and possible pathways include electrophilic aromatic substitution, Heck-type coupling and concerted metalation-deprotonation (CMD).^{15,16} Most heterocycles, such as thiophenes and indoles, are believed to follow a base-assisted CMD pathway. Two catalytic cycles for a CMD coupling of bromobenzene and thiophene using a palladium/phosphine catalytic system and cesium carbonate are shown in Figures 1 and 2. Figure 1 depicts a carboxylate-mediated process, while Figure 2 represents the reaction process in the absence of a carboxylate additive.

Under carboxylate-mediated conditions (Figure 1), oxidative addition of the carbon–halogen bond is followed by exchange of the halogen ligand for the carboxylate anion to form complex **1**. With the assistance from the carboxylate ligand, this complex then deprotonates the thiophene substrate while simultaneously forming a metal–carbon bond and goes through transition state **1-TS**.¹⁶ The phosphine ligands, or the solvent, can re-coordinate to the metal center following Pathway 1, or the carboxylate group can remain coordinated throughout the entire process (Pathway 2).¹⁷ Finally, reductive elimination renders the aryl coupled product. In the absence of a carboxylate additive, after oxidative addition of the aryl bromide, the reaction follows one of the two pathways shown in Figure 2. If a bidentate phosphine is employed, C–H activation of thiophene can follow Pathway 1, where deprotonation is assisted intermolecularly (**2-TS**).⁴ When a monodentate phosphine is used, the reaction may follow Pathway 1 or Pathway 2.⁴ The latter mechanism most closely resembles Pathway 2 in Figure 1 where the carbonate coordinates to the metal center to give the zwitterionic species **1'**. From here, deprotonation occurs intramolecularly through transition state **1'-TS**.⁴ Reductive elimination then renders 2-phenylthiophene.

Density functional theory (DFT) calculations (B3LYP//DZVP/TZVP) of the CMD process reveal that the energy required to form transition state **1-TS** can be broken into two components: the energy needed to distort the aryl C–H bond and the energy to be overcome when the distorted aryl fragment interacts with the metal center.¹⁶ The authors have computed the activation energy of a number of C–H bonds for various (hetero)arenes and compared the regioselectivity for those containing more than one reactive site. These arenes were then divided into three classes based on the factors that control the regioselectivity in the CMD reaction: (1) Class I (hetero)arenes depend on the energy required to distort each C–H bond (i.e., benzenes and

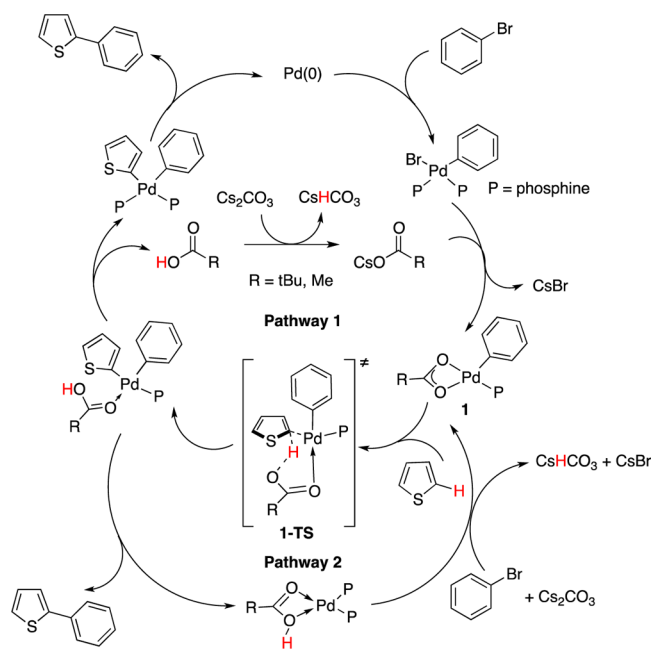


FIGURE 1. Catalytic cycle for cross coupling between thiophene and bromobenzene using a carboxylate additive.

perfluorinated benzenes). (2) Class II (hetero)arenes rely on the interaction energy between the metal center and the distorted aryl fragment (i.e., furans and thiazoles). (3) Class III (hetero)arenes, where the site of reactivity depends on both the distortion and interaction energy (i.e., thiophenes and pyrroles).¹⁶ Interestingly, a small activation energy difference of 4.3 kcal/mol between the 2- and 3-positions in thiophene was calculated according to these criteria.^{16,18} This study also investigated C5-functionalization of thiophenes with electron donating and withdrawing groups in the 2-position. Thiophenes substituted with electron donating groups are good π -nucleophiles and therefore have a strong interaction with the palladium center, which gives a more negative interaction energy, but requires more energy to distort the C–H bond.¹⁶ To the contrary, substitution with electron withdrawing groups on thiophenes decreases the π -nucleophilicity of the system, which imparts a less negative interaction energy. These thiophenes also requires less energy to distort the C–H bond.¹⁶ Both of these components affect reactivity, making it difficult to find trends based on electronic effects of the substituents (i.e., acidity of the proton or π -nucleophilicity of the system). These calculations displayed good correlation with experimental results.¹⁶

The mechanism was examined experimentally by Ozawa and co-workers, who isolated a single crystal of complex **3** suitable for X-ray analysis and studied the catalytic activity toward C–H activation.¹⁹ In solution, this dimeric species disproportionates into two molecules of **4**, which is the active

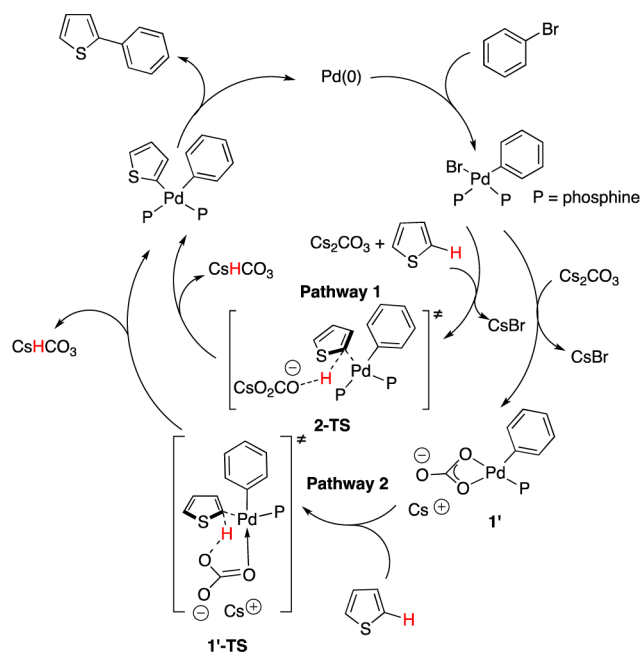


FIGURE 2. Catalytic cycle for cross coupling between thiophene and bromobenzene without a carboxylate additive.

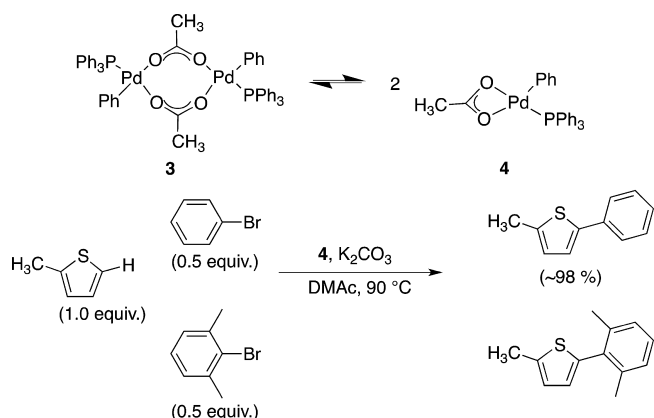
catalytic species. Complex **4** was then utilized as a catalyst in a competition experiment between bromobenzene and 2-bromo-1,3-dimethylbenzene (0.5 equiv each) using 2-methylthiophene as the C–H activation substrate (Scheme 2). They concluded that C–H activation was not the rate limiting step and that oxidative addition of the C–Br bond was most likely slower, since coupling with bromobenzene took place preferentially.¹⁹ However, this was not confirmed by deuterium labeling experiments.

These results, combined with the extensive library of work on small molecule thiophene coupling chemistry, compelled our group and others to apply this synthetic tool to the polymerization of thiophene monomers. The broad scope of this reaction has been demonstrated over the past few years as there have been a growing number of publications utilizing C–H activation. Electron-rich and electron-deficient (hetero)arene monomers undergo activation readily, but as the examples discussed in this Account will expound, this new reaction is not yet without disadvantages.

Electron-Rich Monomers

Direct (hetero)arylation polymerization was first demonstrated with the synthesis of poly(3-hexyl)thiophene (P3HT) since it is the most abundantly employed conjugated polymer for organic electronics. Typically preparation is carried out by chemical (Mg/Zn and Ni, FeCl₃) or electrochemical processes.²⁰ The properties of this polymer are

SCHEME 2



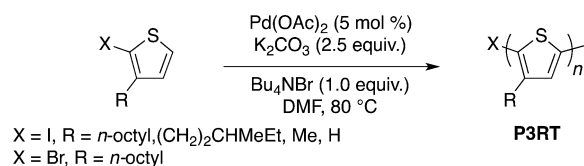
dependent on regioregularity (*rr*), which is the ratio of repeating head-to-tail units, compared to other coupling patterns, and relies heavily on the methods used for preparation. Direct (hetero)arylation of 2-halo-3-alkylthiophenes for the preparation of polymers (**P3RT**) was first published in the late 1990s, and polymerization was carried out with monohalogenated thiophenes (Scheme 3).²¹

Coupling of iodothiophenes or bromothiophenes, with branched and straight alkyl chains, gave polymers with number average molecular weights (M_n) of ~ 3 kDa (PDI = 1–2), which corresponded to 15–16 repeating units.²¹ The polymers had *rr* = 90% (measured by ¹H NMR spectroscopy) and moderate to high yields (78–93%).

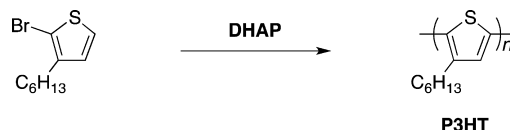
Over 10 years later, Ozawa and co-workers revisited this chemistry and increased the molecular weight (M_n = 30.6 kDa, PDI = 1.6), regioregularity (98%), and yield (99%) of **P3HT**.²² The reactions took place at high temperatures (130 °C), which required the use of the Herrmann–Beller catalyst (*trans*-bis(acetato)bis[*o*-(*di*-*o*-tolylphosphino)benzyl]dipalladium(II)) since it could withstand high reaction temperatures (Scheme 4). Screening of several phosphine ligands revealed that electron-rich bidentate aryl phosphines, such as $P(o\text{-anisole})_3$ and $P(o\text{-NMe}_2(\text{C}_6\text{H}_4))_3$, gave much higher molecular weights than bulky trialkyl phosphines (PCy_3 and PtBu_3).^{22,23}

Thompson and co-workers carried out this transformation using pivalic acid (PivOH) in *N,N*-dimethylacetamide (DMAc) (Scheme 4) and obtained an M_n = 15.5 kDa (PDI = 2.9) in 39% yield with a lower degree of regioregularity (*rr* = 88%).²⁴ The discrepancy between these two methods is perhaps due to the diminished solubility of **P3HT** in DMAc or that higher temperatures are necessary to increase yields, which requires the use of an abiding palladium source. These results reveal that diverse reaction conditions may be employed for DHAP, but that optimization of catalyst,

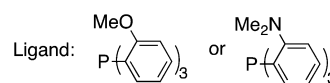
SCHEME 3



SCHEME 4



Ozawa Conditions: Herrmann–Beller Catalyst (2 mol %)
Ligand (4 mol %), Cs_2CO_3 (1.0 equiv.)
THF, 125 °C, 48 h



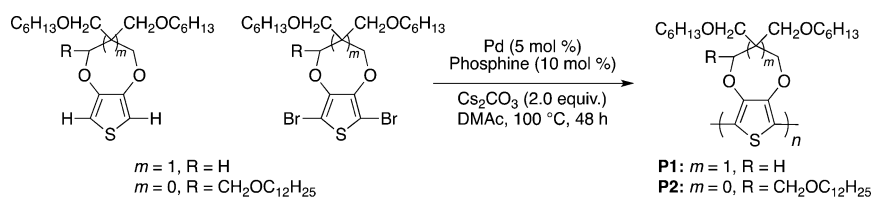
Thompson Conditions: $\text{Pd}(\text{OAc})_2$ (2.0 mol %)
PivOH (30 mol %), K_2CO_3 (1.5 equiv.)
DMAc, 95 °C, 48 h

ligand, solvent, temperature, and so forth is required to achieve high molecular weight materials with desired properties and increased yields.

Two other commonly utilized families of electron-rich thiophene-based homopolymers in organic electronics are poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-propylenedioxythiophene) (PProDOT). Again, typical synthetic routes involve chemical or electrochemical oxidative coupling.²⁵ C–H activation of EDOT monomers and dimers and coupling with aryl bromides to extend conjugation has previously been demonstrated.⁷ More recently, this chemistry was expanded to polymerization reactions (see Scheme 5).^{26,27} Good molecular weights (M_n = 8.4–9.6 kDa, PDI ~ 2.0) and yields (up to 91%) for **P1** were achieved with tetrabutylammonium bromide, or alkyl/aryl phosphine ligands. Both $\text{Pd}(\text{OAc})_2$ and the Herrmann–Beller catalyst were active. For **P2**, the highest molecular weight (M_n = 4.8 kDa, PDI = 1.1) was obtained using conditions similar to those reported by the Ozawa group for the formation of **P3HT** (Herrmann–Beller catalyst and $P(o\text{-anisole})_3$).²⁷

By this methodology, nonregioregular **P2** was synthesized, although polymerization of the monobrominated monomer could give rise to highly regioregular versions of **P2**, as was demonstrated for the synthesis of **P3HT**.^{22,28} DHAP was also used to polymerize EDOT monomers substituted with different functional groups (–OTBDMS, CO_2tBu , NHtBOC), which could be converted into reactive

SCHEME 5



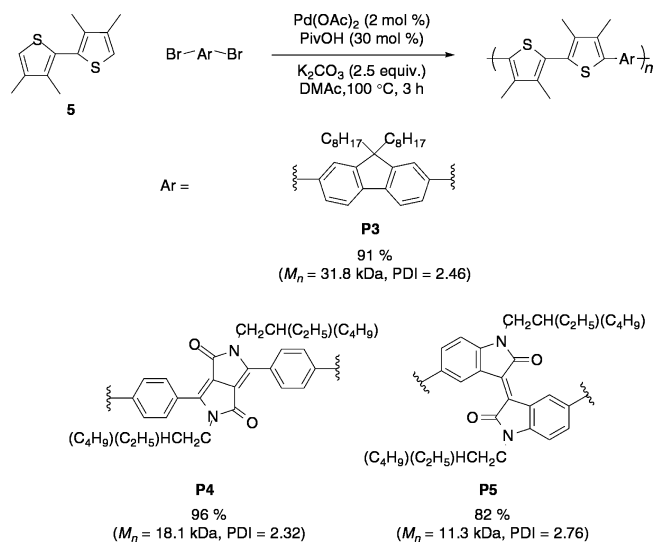
groups (–OH, CO₂H, NH₂) for bioconjugation.²⁷ Interestingly, the functional groups were tolerant to DHAP conditions and the polymers were obtained in relatively moderate molecular weights ($M_n = 3\text{--}4$ kDa).²⁷ DHAP provided entry into ProDOT and PEDOT polymers using several different reaction conditions that were amenable to a number of different functional groups.

Many conjugated copolymers contain 2,2'-bithiophene units, which undergo facile C–H bond activation. Unlike the previous examples, this thiophene-based monomer has more than one type of reactive C–H bond, although reactions typically occur in the 5- and 5'-positions first.⁶ Attempts to copolymerize 2,2'-bithiophene with 2,7-dibromo-9,9-dioctylfluorene rendered materials with low solubility due to cross-linking in the 3,3'- and 4,4'-positions of the bithiophene monomer.^{29,30} To evade these side reactions, other reactive C–H bonds on the thiophene monomers were blocked with methyl groups to give monomer **5**. Copolymerization with several dibrominated monomers provided materials with high molecular weights (Scheme 6).^{29,30}

The absorption onsets of thin films of **P4** and **P5** (520 and 580 nm), measured by UV–vis spectroscopy, were hypsochromically shifted compared to the “unprotected” bithiophene analogues (580 and 701 nm, respectively).³⁰ The methyl groups indeed cause twisting in the polymer backbone and disrupt conjugation.³⁰ Although protection of the 3,3',4,4'-positions of bithiophene circumvented cross-linking on this monomer, the planarity of the copolymers was disrupted and optimal packing properties diminished.

Fused bithiophene monomers are also ubiquitously employed in organic electronics as electron-rich groups. Copolymer **P6** is a low band gap material that has exhibited superior hole mobilities³¹ in organic field effect transistors (OFETs) and high efficiencies³² in bulk heterojunction solar cells (BHJ-SCs). Copolymerization of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (**6**) with **7** to give **P6** via DHAP has been reported by the Scherf group³³ and the Horie group (see Scheme 7).³⁴ Molecular weights as high as 40.3 kDa (PDI = 3.5)³³ and 72 kDa (PDI = 4.52)³⁴ were obtained, respectively, which both surpass those achieved

SCHEME 6



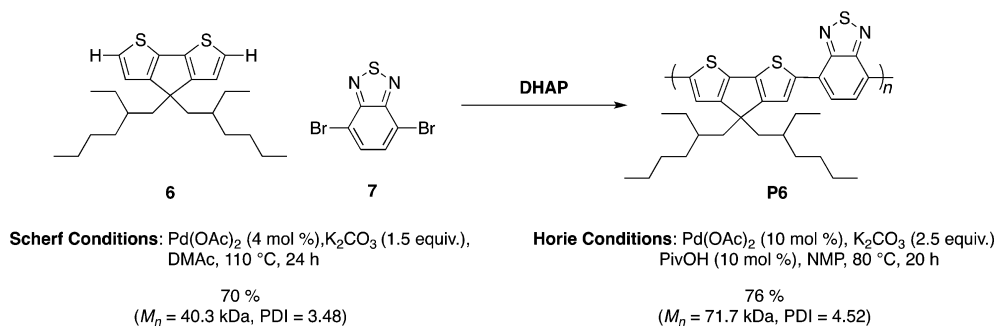
by Stille ($M_n = 28$ kDa, PDI = 1.5)³⁵ or Suzuki ($M_n = 15.3$ kDa, PDI = 2.05)³⁶ polymerization methods.

However, in both reports, branched and cross-linked material formed and was confirmed by ¹H NMR spectroscopy, which showed two small peaks corresponding to 3,6-disubstituted and 2,3,6-trisubstituted **6**,³³ and MALDI-TOF mass spectrometry.³⁴ In DMAc, shorter reaction times gave soluble material³³ and UV–vis maxima of thin films were also slightly blue-shifted (7 nm) compared to those of polymers prepared by Stille coupling ($M_n = 10$ kDa).³³ The absorption maximum of thin films of **P6** prepared by Horie and co-workers was red-shifted (20 nm) compared to that of the polymer prepared by Scherf and co-workers due to the elevated molecular weight.^{33,34} Polymerization of **6** with DHAP is not ideal since a great deal of cross-linking is observed by activation of the α - and β -protons on the thiophene moieties.

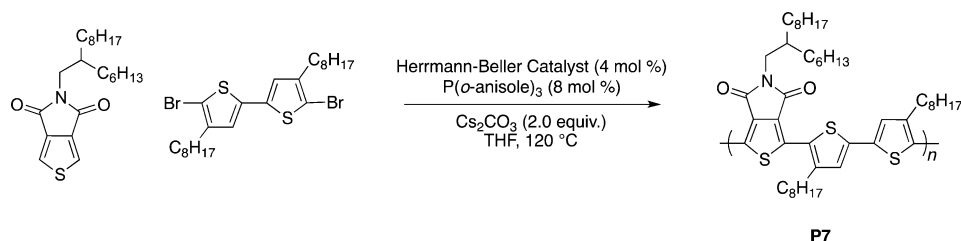
Electron-Deficient Monomers

A number of examples of C–H bond activation of electron-deficient arenes for polymerization strategies have also been reported. Our group has focused on the C–H activation of electron-deficient thiophene-based monomers including thieno[3,4-*c*]pyrrole-4,6-dione (TPD). This monomer has

SCHEME 7



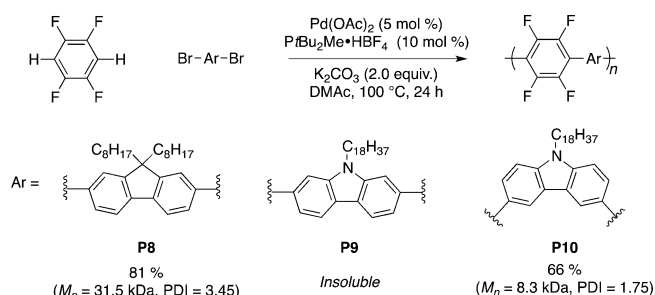
SCHEME 8



been incorporated into many *push*–*pull* copolymers and can be functionalized with different alkyl chains on the imide nitrogen, or by modification of the heteroatom in the thiophene ring (O, Se).³⁷ A polymer similar to **P7** (2-ethylhexyl chain on the TPD unit) was synthesized by Stille methods (*M_n* = 9.7 kDa, PDI = 1.4) and incorporated into BHJ-SCs (donor = PC₇₁BM) to afford optimized power conversion efficiencies (PCEs) of 7.3%.^{38,39} Since PCE has been shown to be proportional to increasing molecular weight,⁴⁰ our group applied DHAP methodology to the synthesis of **P7**⁴¹ with the expectation of further elevating the *M_n*. We envisioned this unit would be amenable to C–H activation since it contains one type of C–H bond, and the imide moiety may not only electronically favor this reaction, but could potentially chelate the palladium center after C–H bond insertion. The same conditions used by the Ozawa group²² were employed (Scheme 8), and indeed a molecular weight of 56 kDa (PDI = 2.6) was achieved in 96% yield.⁴¹ The ¹H NMR spectrum and X-ray diffraction patterns of **P7** are almost identical to that of the same polymer prepared by Stille methods, while the UV–vis absorption spectrum is slightly red-shifted (10 nm) due to the increase in molecular weight.⁴¹ Cross-linking by activation of C–H bonds on the thiophene unit was not observed, most likely due to steric effects.

We have also employed C–H activation of TPD and furo[3,4-*d*]pyrrole-4,6-dione (FPD) monomers for copolymerization with brominated thiophene-based electron-rich

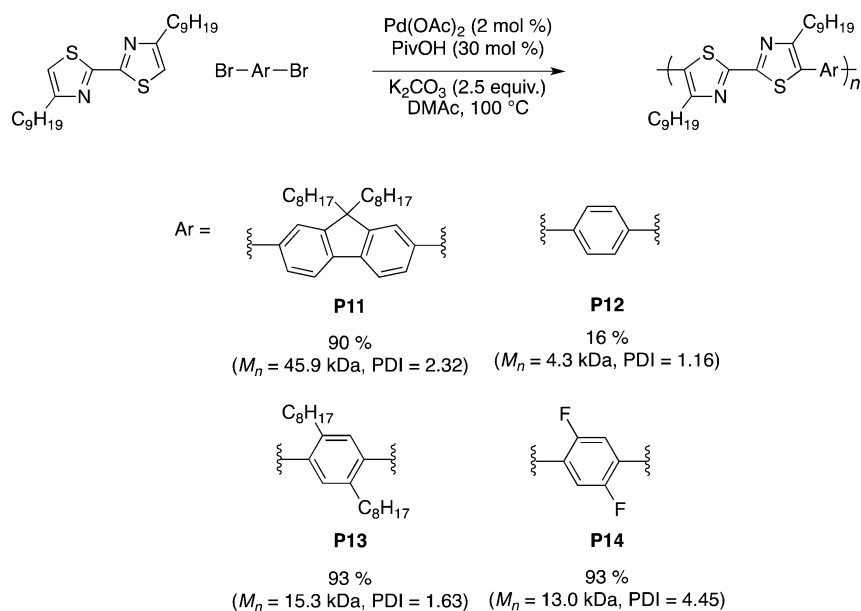
SCHEME 9



monomers such as benzodithiophene,⁴² dithienosilole, and dithienogermole,⁴³ and electron-deficient monomers including diketopyrrolopyrrole⁴⁴ and isoindigo,⁴⁵ as well as for the formation of TPD homopolymers.²⁸ We also prepared copolymers containing thieno[3,4-*d*]thiazole,⁴⁶ another electron-poor thiophene based substrate that is highly reactive toward C–H activation. Reaction conditions were similar to those shown in Scheme 8, but high molecular weight materials were also obtained in toluene using catalytic amounts of PivOH.

Other electron-poor monomers with one type of C–H bond have been investigated for DHAP. Prior to our report, the Kanbara group demonstrated copolymerization of 1,2,4,5-tetrafluorobenzene,^{47,48} and later expanded this methodology to 4,4'-dinonyl-2,2'-bithiazole.⁴⁹ Copolymerization with a number of brominated monomers by direct arylation has given rise to novel copolymers (**P8**–**P14**).^{47,48}

SCHEME 10



These reactions have been carried out using a phosphine ligand (Scheme 9) or with a catalytic amount of acid (Scheme 10).

As was demonstrated with **5**, copolymerization with 2,7-dibromo-9,9-dioctylfluorene gave rise to high molecular weight linear materials for both monomers (**P8**, **P11**). In the case of **P11**, a higher molecular weight was achieved with DHAP than under Suzuki polymerization conditions (69%, $M_n = 18$ kDa, PDI = 2.5).⁵⁰ However, copolymerization with dibrominated carbazoles (**P9**, **P10**) produced cross-linked materials via activation of arene C–H bonds. In the case of **P9**, C–H activation in the 3- and 6-positions of carbazole caused the material to be completely insoluble in common organic solvents. Reactivity of these positions was eliminated using 3,6-dibromocarbazole and the ensuing polymer (**P10**) was soluble in common solvents at elevated temperatures. Copolymerization of 4,4'-dinonyl-2,2'-bithiazole with 1,4-dibromobenzene (**P12**) also afforded insoluble cross-linked material though shorter reaction times (10 min) diminished these side reactions. This showed that coupling with 4,4'-dinonyl-2,2'-bithiazole occurred prior to activation of other C–H bonds on the aryl monomers.⁴⁹ Substitution with alkyl chains (**P13**) or fluorine atoms (**P14**) suppressed side reactions by limiting the number of C–H bonds and sterically blocking reactive sites.⁴⁹ Regioselectivity during C–H activation is a major issue; these examples clearly illustrate that when designing or selecting monomers, all potential activation sites need to be considered. C–H bond activation is quite facile (oxidative addition of the carbon–halogen bond is the rate limiting step)¹⁹ and may occur with

any reactive bond. Undesired reactions can be curbed by blocking C–H bonds with unreactive groups and truncated reaction times.

Outlook for C–H Activation

Direct (hetero)arylation is an advantageous tool for the synthesis of regioregular polymers as well as alternating copolymers. This methodology utilizes monomers with aryl carbon–halogen and C–H bonds to form new C–C bonds and in doing so (1) reduces the number of steps for monomer preparation since organometallic reagents are no longer necessary; (2) utilizes monomers with long-term stability that can be easily manipulated; (3) produces only acid as a byproduct, unlike typical polymerization reactions that give rise to stoichiometric amounts of waste; (4) can give rise to polymeric material with higher molecular weights than those obtained by other methods. However, the reactions are not easily controlled for some monomers and can produce branched and cross-linked polymers, which result from activation of more than one C–H bond. These reactions occur at a faster rate than oxidative addition of C–Br bonds and must be restrained.¹⁹ Protection of other active sites with alkyl chains or fluorine atoms may minimize these side reactions, but can disturb necessary morphological properties.³⁰ Alternatively, diminishing reaction temperature and time may impede higher energy pathways.

Reaction conditions for each monomer, or set of comonomers, are substrate specific and require optimization. High functional group tolerance has been displayed.²⁷ All polymerization examples used palladium catalysts; some have

exploited the highly stable Herrmann–Beller catalyst, while most were carried out with Pd(OAc)₂. A number of examples included catalytic addition of pivalic acid, which aids in C–H activation, while some groups have found that phosphine-free conditions gave high molecular weight materials. Nevertheless, we believe these reactions follow a CMD pathway, which is assisted by a carboxylate or carbonate base, and the polymer chain grows via polycondensation reactions. Polar (DMAc, DMF, NMP, THF) and nonpolar (toluene) solvents are suitable for these reactions and should be selected based on polymer solubility. In our hands, DMAc was not a suitable solvent for polymerization and always gave brown soluble material. Addition of carboxylic acid additives may be beneficial in nonpolar solvents due to the high polarity of the C–H bond transition states. However, C–H bond activations have been accomplished in toluene and xylenes without carboxylic acids.^{7,12}

Direct (hetero)arylation polymerization is a new methodology that can be added to a polymer chemists' toolbox. Application of this reaction from small molecule to polymer synthesis is quite timely, given the ubiquitous use of these materials in organic electronics. It may enable more effective preparation of highly efficient known polymers and provide entry into novel and promising materials. Some recent reports have already demonstrated successful incorporation of materials prepared by these methods into organic electronic devices such as OTFTs,⁴⁵ OLEDs,⁴⁷ and BHJ-SCs.^{51,52} This reaction may be applied to the preparation of novel polymers synthesized from monomers that are unstable as organometallic reagents. It can abridge the synthesis of known polymers if the monomers can be selectively activated; however, careful optimization and control is required. Application of this methodology to polymerization is still in its infancy, but we foresee the number of examples of this methodology to grow in the future and DHAP to become a typical polymerization strategy. However, we caution that proper choice of monomers and conditions are essential to attain well-defined material.

BIOGRAPHICAL INFORMATION

Lauren G. Mercier was born in Calgary, Alberta, Canada. In 2006 she completed a B.Sc. at the University of Waterloo, where she held a research position in the laboratory of Prof. Eric Fillion. She then headed back to Alberta to carry out graduate work at the University of Calgary. She joined the lab of Prof. Warren Piers and studied conjugated organoboron and organosilicon small molecules. Lauren completed her Ph.D. at the end of 2011 and started as a postdoctoral fellow in the laboratory of Prof. Mario Leclerc at Université Laval in 2012. She is currently investigating DHAP

and its application to thiophene-based monomers. She was awarded an Alexander von Humboldt Postdoctoral Fellowship and will commence research in the laboratory of Prof. Dr. Peter Bäuerle at the beginning of 2013. Her research interests are focused on the design and preparation of conjugated organic materials with applications in electronics.

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FOOTNOTES

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The authors declare no competing financial interest.

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