

Direct (Hetero)arylation Polymerization: Trends and Perspectives

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ABSTRACT: Conjugated polymers have attracted much attention in recent years, as they can combine the best features of metals or inorganic semiconducting materials (excellent electrical and optical properties) with those of synthetic polymers (mechanical flexibility, simple processing, and low-cost production), thereby creating altogether new scientific synergies and technological opportunities. In the search for more efficient synthetic methods for the preparation of conjugated polymers, this Perspective reports advances in the field of direct (hetero)arylation polymerization. This recently developed polymerization method encompasses the formation of carbon–carbon bonds between simple (hetero)arenes and (hetero)aryl halides, reducing both the number of synthetic steps and the production of organometallic byproducts. Along these lines, we describe the most general and adaptable reaction conditions for the preparation of high-molecular-weight, defect-free conjugated polymers. We also discuss the bottleneck presented by the utilization of certain brominated thiophene units and propose some potential solutions. It is, however, firmly believed that this polymerization method will become a versatile tool in the field of conjugated polymers by providing a desirable atom-economical alternative to standard cross-coupling polymerization reactions.

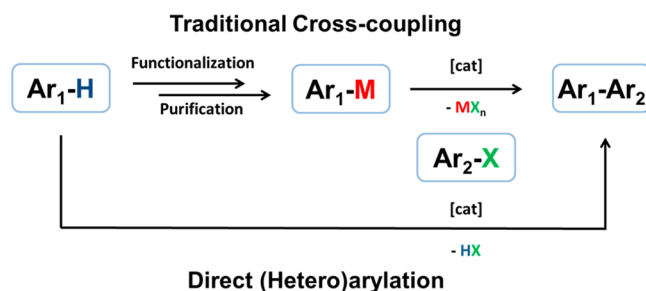
INTRODUCTION

Conjugated polymers combine the electrical and optical features of inorganic semiconductors with the mechanical properties unique to polymers. Because conjugated polymers can often be dissolved in common solvents, processing techniques such as inkjet printing, spin coating, and roll-to-roll printing become readily available, thus rendering possible the fabrication of low-cost printed electronic and photonic devices. Such devices include light-emitting diodes,^{1,2} field-effect transistors,^{3–5} chemical and biochemical sensors,⁶ and photovoltaic cells.^{7,8} The list continues to grow.⁹ However, it must be recognized that the development of so-called plastic electronics has been and still remains highly dependent on the availability of robust coupling methods, such as Ziegler–Natta, Migita–Stille, Kumada, Heck, Miyaura–Suzuki, and Negishi coupling as well as olefin metathesis, in order to afford well-defined, reliable, and reproducible conjugated polymers.^{10–13}

Unfortunately, current synthetic methods generally involve many steps in order to functionalize monomers with costly organometallic reagents. This gives rise to stoichiometric quantities of metallic byproducts, some of which are toxic (i.e., tin). Cheaper, cleaner, and more efficient synthetic procedures would clearly be an important asset for the preparation and

commercialization of conjugated polymers.¹⁴ Along these lines, polymerization by metal-catalyzed direct (hetero)arylation of aromatic compounds has recently been reported and may be the development necessary for many polymers to move beyond the research lab.¹⁴ These cross-coupling reactions, in which C–C bonds are formed as the result of condensation between an aryl C–H bond and an aryl halide (C–Br or C–I), exhibit several key benefits, including fewer reaction steps, simpler purification of monomers, and the generation of only acidic byproducts (H–Br or H–I). This is shown in Scheme 1, which compares the general reaction equation of a traditional aryl–aryl coupling method with that of direct (hetero)arylation.

Scheme 1. Comparison of Traditional Cross-Coupling Reactions with Direct (Hetero)arylation

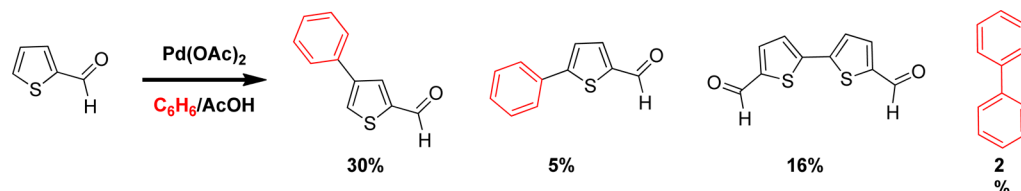


Interestingly, methods for creating C–C bonds between two unsaturated substrates have been studied since the 1960s, beginning with the pioneering work of Fujiwara and Moritani, in which derivatives of stilbene were formed via the arylation of styrene.^{15–20} In the early 1980s, Itahara undertook a number of studies regarding the arylation of various functionalized heterocycles (thiophene, furan, and pyrrole) using a palladium acetate catalytic system with acetic acid as the solvent, an example of which is shown in Scheme 2.^{21,22} These results constitute one of the first examples exploring the issues of homocoupling and activation of multiple C–H bonds, problems that would later become key considerations for a successful polymerization reaction.

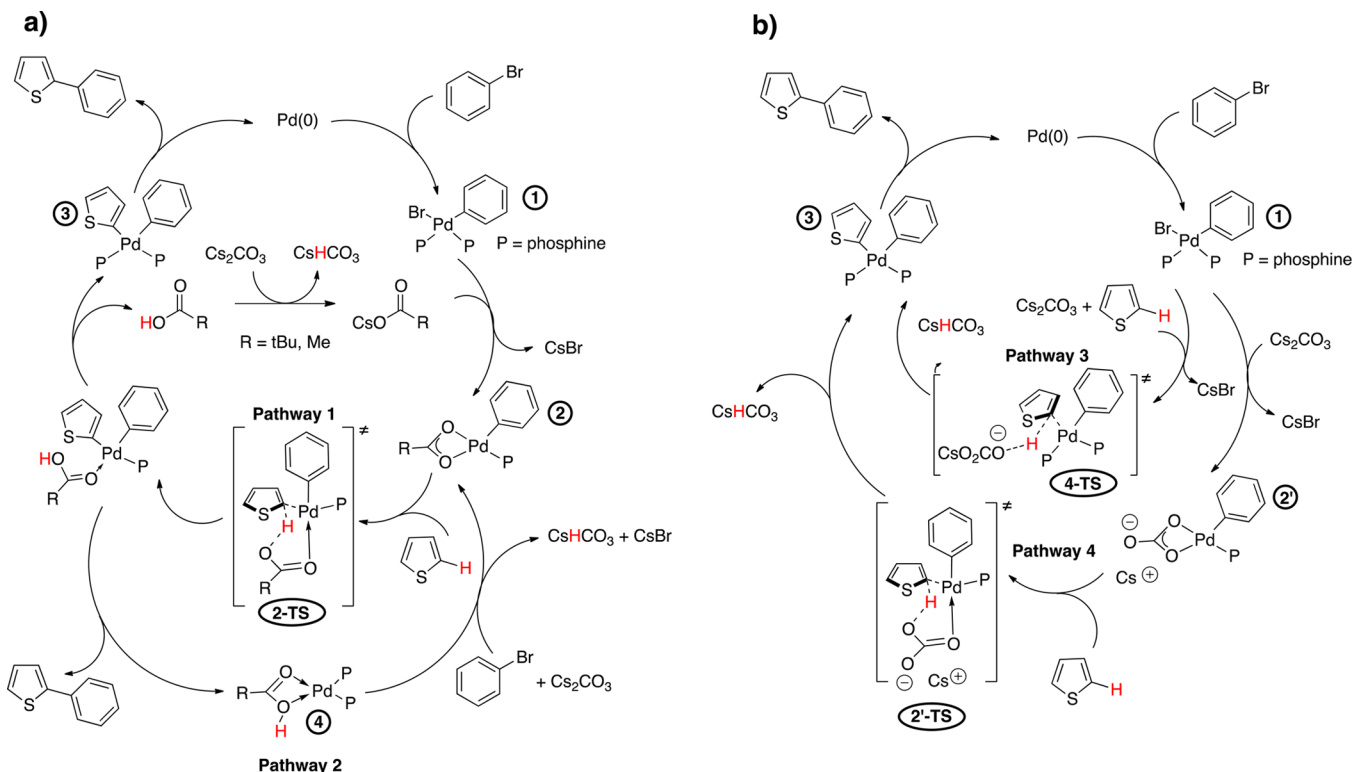
Mechanistic Insight. Following the advent of this class of reactions, many experimental and theoretical studies have been undertaken in order to elucidate the fundamental mechanisms that govern these reactions. As this Perspective focuses on polymerization methods based on the direct (hetero)arylation reaction, the reader is invited to explore the reviews dealing with the application of direct (hetero)arylation in organic synthesis.^{23–29} However, it is important to recall the principal

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Scheme 2. An Example of the Arylation of a Substituted Thiophene As Presented by Itahara²²

Scheme 3. Catalytic Cycles for Direct (Hetero)arylation (a) with and (b) without a Carboxylate Additive



mechanistic elements of this reaction with regard to small molecules, as presented in detail in certain selected studies.

In 2000, Sakaki and colleagues undertook one of the earliest theoretical studies of the C–H bond activation mechanism of benzene and methane with palladium and platinum complexes.³⁰ By an evaluation of the evolution of bond lengths over the course of the reaction, it was determined that with a bisformate complex the C–H bond of benzene undergoes heterolytic cleavage, in which an oxygen atom from one of the formate ligands decoordinates from the metal in order to deprotonate benzene, while at the same time the resulting C_6H_5 aryl group occupies the vacated coordination site on the metal center. This occurs via a series of six-membered transition states. This study served as an early example of palladium-catalyzed C–H activation of an aromatic molecule, elucidating the fundamental role that the base ligand plays in the deprotonation of the arene. Such observations, further elucidated over the next decade by Fagnou,^{31–33} Doucet,³⁴ Echavarren^{35,36} and others, led to the mechanism that will be described below.

In general terms, the mechanism of direct (hetero)arylation comprises oxidative addition of an aryl halide substrate on a palladium catalyst and heterolytic cleavage of the C–H bond of a second aromatic substrate, followed by the formation a new C–C bond via reductive elimination. The reaction is mediated by stoichiometric or excess quantities of carbonate and sometimes

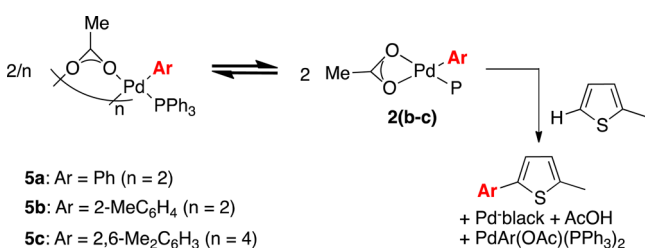
carboxylate ions. Various studies initially indicated that different reaction mechanisms occur depending on the nature of the substrates and the catalytic system used as well as the choice of solvent and additives.^{37–40} This being said, most (hetero)arenes seem to follow the concerted metalation–deprotonation (CMD) process. As a model, two catalytic processes for the coupling of bromobenzene and thiophene using a carboxylate additive^{41–43} and without a carboxylate^{23,44} are described in Scheme 3a,b, respectively. Similarly to many palladium-mediated catalytic systems, the first stage is oxidative addition of the halogenated derivative on Pd^0 to form 1. Exchange of the newly formed halide ligand by the carboxylate anion forms complex 2 (Scheme 3a, pathway 1). In the CMD step, the carboxylate within the coordination sphere of the metal center deprotonates thiophene while at the same time the Pd–carbon bond is formed, hence the name concerted metalation–deprotonation. This occurs via the six-membered transition state 2-TS.^{30,42}

The phosphine or other ligand initially coordinated to the metal center may then re-coordinate, which is the case for pathway 1 (3), or the carboxylate group may remain coordinated throughout the entire process (pathway 2, complex 4).³¹ In both pathways, the final compound is formed by reductive elimination. In the absence of a carboxylate additive, the catalytic system may proceed according to Scheme 3b. In this case, carbonate replaces the carboxylate during the CMD stage (2'-

TS). The latter mechanism (pathway 4) most closely resembles pathway 2 in Scheme 3a, in which the carbonate coordinates to the metal center to give the species 2'. When a bidentate phosphine is used, C–H activation may follow pathway 3, in which case deprotonation of thiophene is intermolecular, meaning that the base may remove the proton without itself being coordinated to the metal center.

Investigations of the Reaction Mechanisms. In 2012, Ozawa and colleagues performed an experimental study of the active species responsible for the C–H activation.⁴⁵ In this study it was shown that the reactivity of the catalytic system depended upon the presence of species 2 in solution (Scheme 4), which is

Scheme 4. Disproportionation of 5 To Generate the Active Species 2⁴⁵

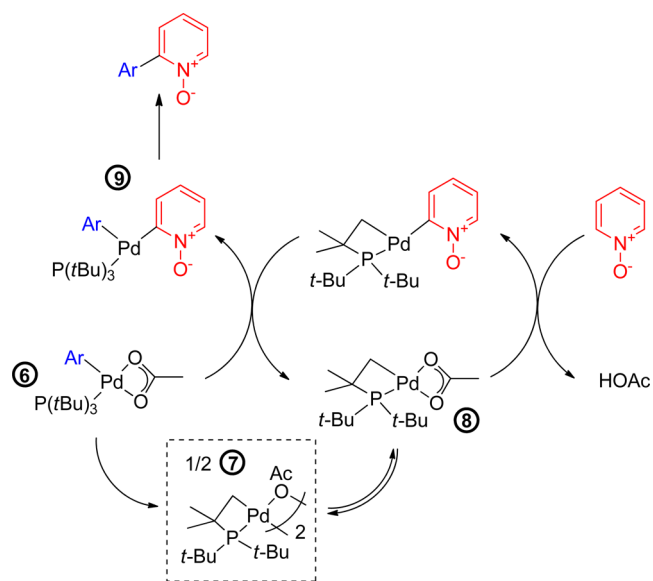


equivalent to species 2 in Scheme 3. The synthesis and characterization of three complexes demonstrated the presence of either a dimeric or tetrameric species in the solid state depending on the bulkiness of the aryl group coordinated to the metal center (5a–c). However, in solution only the structures with more hindered aryl groups (5b and 5c) reached an equilibrium with their corresponding monomeric forms (2b and 2c). From IR spectroscopy studies of the bridging versus bidentate nature of the carboxylate ligand's CO bond, it was determined that the greater the bulkiness of the aryl group, the more the monomeric species was favored in solution. In order to determine the reactivity of the complexes existing in solution, coupling reactions were undertaken with 2-methylthiophene in order to afford 2-phenyl-5-methylthiophene. It was demonstrated that of the above-mentioned species, the one for which the monomeric state was most prevalent in solution led to the greatest reactivity.

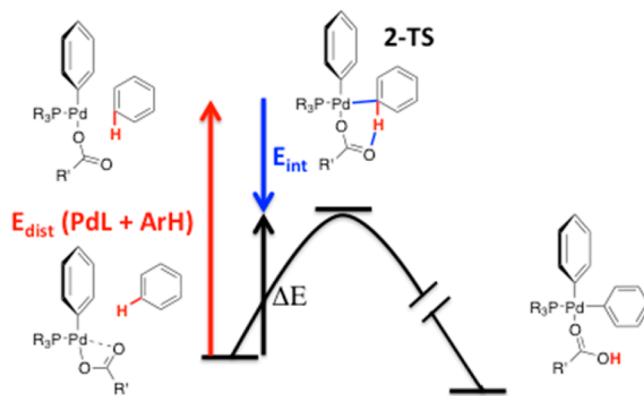
In the same year, Hartwig and collaborators also undertook experimental studies of C–H bond activation of small molecules. The results obtained agree with those of Ozawa but also contributed greater understanding of a possible mechanism that relies on two metal centers (Scheme 5).⁴⁶ According to this model, the monomeric complex 8 is responsible for the C–H cleavage of pyridine *N*-oxide (PyO) by means of protonation of the κ^2 -acetate ligand. The 2-pyridyloxide group is then transferred to 6, forming the diaryl species 9, which then undergoes reductive elimination to generate the 2-arylpyridine oxide product.

Density functional theory calculations on the CMD step illustrate that when the substrate contains multiple C–H bonds, the selectivity is dependent upon the energy necessary to attain transition state 2-TS. This energy can be decomposed into two categories.^{43,47} The first corresponds to the energy necessary to distort the C–H bond (E_{dist}) and the second to the energy necessary to counter the electronic interaction between the distorted substrate and the metal center (E_{int}) (Scheme 6). The substrates that are able to undergo selective C–H activation can be divided into three classes. The first class comprises

Scheme 5. Cooperative Mechanism for the Arylation of Pyridine *N*-Oxide (PyO) Proposed by Hartwig and Collaborators⁴⁶



Scheme 6. Diagram Illustrating the Two Principal Factors (E_{dist} and E_{int}) That Contribute to the Energy Level of the Transition State (ΔE)^{43,47}



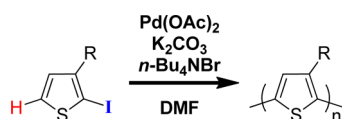
heteroarenes that are dependent on the E_{dist} of the targeted C–H bond (as in the case of benzene and benzothiophene). The second class contains heteroarenes for which the catalyst–arene E_{int} determines the most reactive C–H bonds (e.g., furan and pyridine). The third class contains heteroarenes for which both E_{int} and E_{dist} influence the CMD step, which is the case for thiophene and pyrrole derivatives.

Requirements for Polymerization. The combination of a large number of experimental and theoretical studies has established experimental protocols that through improved coupling selectivity and yield have granted access to a new array of compounds obtainable via direct (hetero)arylation. However, it is imperative to underline the fact that certain factors are especially important with regard to polymerization methods. For instance, the selectivity of cross-coupling reactions represents a major challenge because organic molecules display several C–H bonds with comparable dissociation energies. When one considers polymerization reactions, however, it is important to note that structural defects such as branching, cross-linking, and homocoupling cannot be removed by purification

processes, as these defects are chemically embedded within the polymer chains. These side reactions thereby influence the physical properties of the final polymeric material. Moreover, side reactions can interfere with the initial stoichiometry between monomers. As for any other step-growth polymerization reaction, such variations in stoichiometry limit the degree of polymerization (DP) according to the classical Carothers equation.⁴⁸ This equation assumes an equilibrium polymerization in which the polymer remains fully soluble during the course of polymerization, a well-balanced stoichiometry of highly pure monomers exists, and the reaction conversion (yield) approaches unity. For these reasons, many protocols reported for small molecules cannot be applied directly to the synthesis of high-molecular-weight polymers. For instance, all reactions requiring an excess of one reagent do not conform to these restrictions and must be excluded. Only synthetic methods that combine both high yield (>98%) and high selectivity can be considered for the preparation of well-defined materials with a high degree of polymerization. With the Migita–Stille and Miyaura–Suzuki couplings, in each case more than a decade elapsed before the first polymers were synthesized using these methods.^{49–53} This may be explained by the fact that the protocols used led to yields that were acceptable for coupling but not efficient enough for polymerization reactions.

The first direct (hetero)arylation polymerization (DHAP) reaction was reported by Lemaire and colleagues in 1999 (Scheme 7), in which they attempted to polymerize 2-halo-3-

Scheme 7. Lemaire's Heck-like Conditions for Poly(3-alkyl)thiophenes^{54,55}

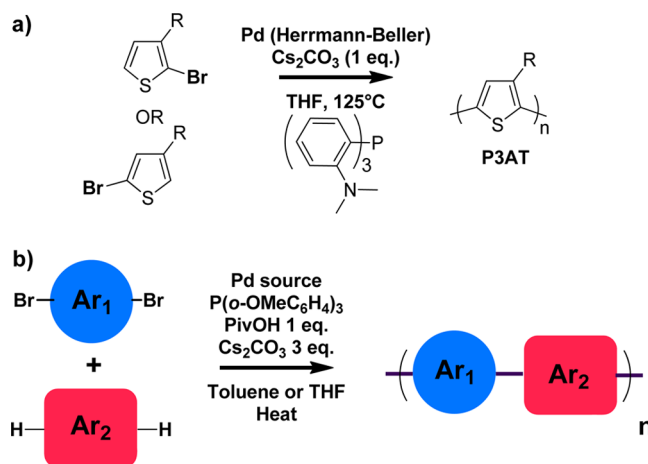


alkylthiophenes in order to obtain the corresponding poly(3-alkylthiophene) (P3AT) products.^{54,55} Under the conditions presented, which consisted of Pd(OAc)₂, K₂CO₃, and *n*-Bu₄NBr in *N,N*-dimethylformamide (DMF), the authors obtained a polymer with a low DP and a regioregularity of 90%. These conditions were directly inspired by Jeffery's conditions for Heck coupling protocols because at the time it was believed that the direct (hetero)arylation reaction consisted of a Heck-like mechanism. Although this method was very innovative, it remained relatively unpopular for a number of years because the results obtained were inferior to those accessible via other methods for the synthesis of P3ATs that were available at the time.^{56,57}

RECENT TRENDS

More than a decade after these first studies were performed by Lemaire and co-workers, two efficient (and relatively similar) polymerization conditions have emerged for a wide range of aromatic monomers (see Scheme 8). With these general protocols, a large number of well-defined conjugated polymers can now be synthesized with properties similar or even superior to those of their counterparts prepared via more traditional methods, such as Miyaura–Suzuki, Migita–Stille, Grignard metathesis (GRIM), and oxidative coupling. The first family includes alkyl-substituted thiophene monomers suitable for homopolymerization to give P3ATs (Scheme 8a). The second and broader class is represented by various bromoarene (Ar₁)

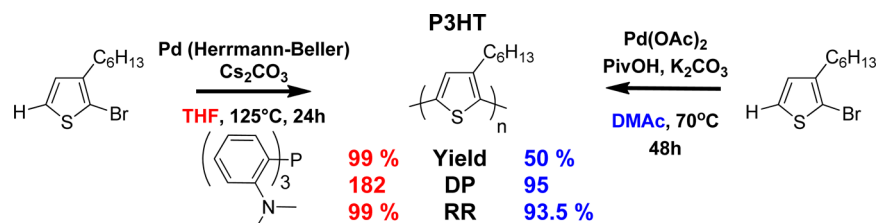
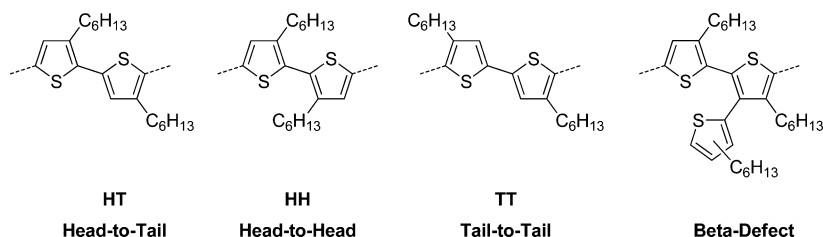
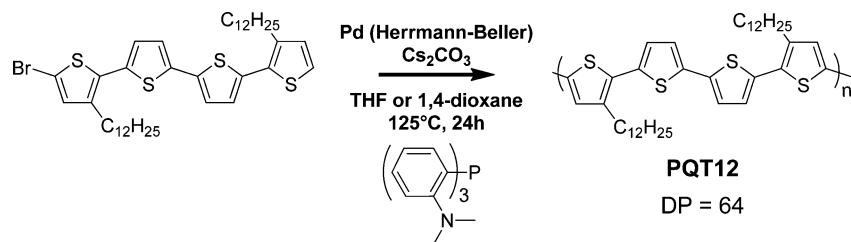
Scheme 8. General Protocols Available To Obtain Regioregular Polymers by DHAP



compounds that can be cross-coupled with many different heterocycles (Ar₂), generating a large range of conjugated copolymers (Scheme 8b).

Influence of the Solvent. In general polymerization methods, the solvent plays multiple roles, such as solubilizing the monomer(s), maintaining the growing polymer chain in solution, and stabilizing the catalytic system. In the beginning, two classes of solvents were investigated: amide-containing polar solvents such as *N,N*-dimethylacetamide (DMAc), DMF, and *N*-methylpyrrolidone (NMP) and less polar solvents such as tetrahydrofuran (THF), toluene, dioxane, and chlorobenzene. The comparison of results obtained during the synthesis of the highly studied poly(3-hexylthiophene) (P3HT) by direct (hetero)arylation of 2-bromo-3-hexylthiophene by these two classes of solvents was undertaken by the Ozawa and Thompson groups, among others. P3HT is one of the most extensively studied conjugated polymers and has become a reference compound for the study of polymer catalytic systems. Ozawa and collaborators published in 2010 the synthesis of this polymer via the direct (hetero)arylation of 2-bromo-3-hexylthiophene in THF.⁵⁸ The reaction takes place at a high temperature (125 °C) and requires the use of the thermally stable Herrmann–Beller catalyst *trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]-dipalladium(II), the phosphine P(*o*-NMe₂(C₆H₄)₃), and the base Cs₂CO₃ (see Scheme 9). For DHAP, the base plays an important role since it is believed to assist in C–H activation as described above and also neutralizes the stoichiometric quantity of acid formed. Cs₂CO₃ is also soluble in THF, which is not the case in the above-mentioned highly polar amide solvents. Under these conditions, a nearly quantitative yield (99%), a high degree of polymerization (DP = 182), and more importantly, a regioregularity (head-to-tail content) greater than 99% were obtained.^{58,59} The remaining head-to-head or tail-to-tail couplings (<1%) can be attributed to homocoupling reactions (Scheme 10). However, the ¹H NMR analyses did not reveal any defects related to β-branching, a side reaction involving couplings at the 4-position of the thiophene ring (Scheme 10).

The second class of solvents includes highly polar coordinating solvents such as DMAc, DMF, and NMP, which are known to improve the reactivity of the catalyst. In fact, the presence of a ligand is not always necessary when these solvents are used. This specificity was rationalized by Tan and Hartwig in 2011.⁶¹ It was shown that when DMAc was used as the solvent, the presence of

Scheme 9. Synthesis of P3HT by DHAP Using Two Different Sets of Conditions^{58–60}Scheme 10. Representation of the Results of Regular (Hetero)arylation Coupling (HT) as well as Homocoupling (HH and TT) and β -Branching in P3HTScheme 11. Synthesis of PQT12 by DHAP⁶⁸

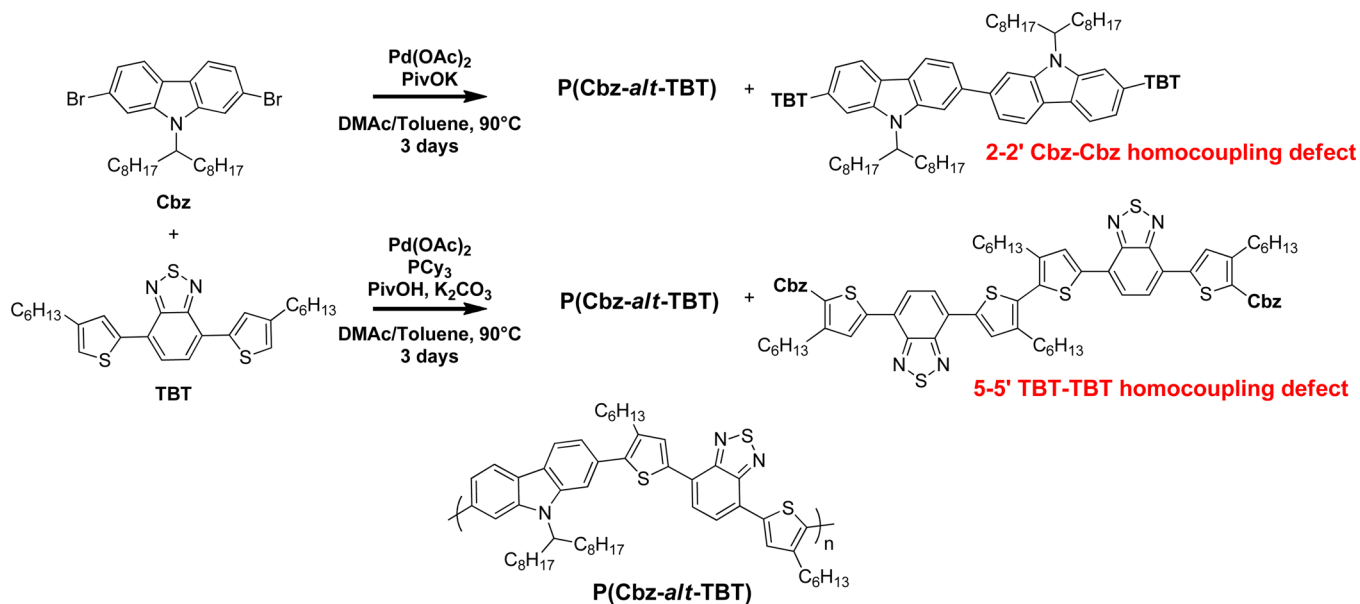
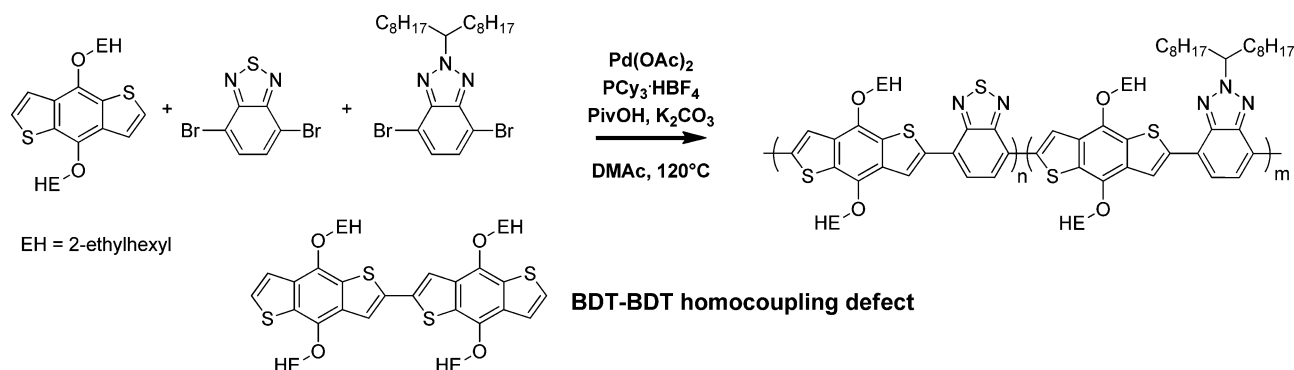
a phosphine ligand in fact partially inhibited the reactivity of the catalyst, whereas in its absence, the reaction time was reduced and the conversion was improved. The increased reactivity of polar solvents vis-à-vis nonpolar ones was recently analyzed by Ozawa and co-workers.⁴⁵ In the study mentioned in the Introduction, it was observed that polar solvents favored the dissociation of **5** to form the active species **2**, thereby increasing the catalyst reactivity, as discussed earlier (Scheme 4).

Along these lines, Thompson and co-workers revisited the preparation of P3HT under conditions that required the use of $\text{Pd}(\text{OAc})_2$, K_2CO_3 , and pivalic acid ($(\text{CH}_3)_3\text{CCOOH}$) in DMAc at 70 °C (Scheme 9).^{60,62–64} The addition of a carboxylic acid, which acts as a proton shuttle, has been shown to assist in the deprotonation process and to decrease the free energy of activation (ΔG^\ddagger) by about 1.3 kcal/mol.³¹ Under these conditions, the authors obtained P3HT with DP values similar to those obtained via Migita–Stille coupling, albeit in an inferior yield. NMR analyses determined that the regioregularity of the DHAP polymer was 88%, compared with 93.5% for the Migita–Stille analogue. According to the authors, this difference in regioregularity is explained by couplings at the β -position of the thiophene due to the high reactivity of the catalytic system used. In another report, the authors studied the influence of the catalyst loading, reaction temperature, and time on the regioregularity and demonstrated that the regioregularity could be controlled by tuning the conditions, albeit with difficulty. When the molar concentration of the catalyst was lowered from 2 to 0.25%, the reaction time was increased from 48 to 72 h, and the reaction was performed at a temperature of 70 °C, P3HT with 93.5% regioregularity could be obtained.

In all cases, and despite lengthy optimization, the results were not as striking as those reported by Ozawa.⁵⁸ However, the authors were able to improve the regioregularity by replacing pivalic acid with neodecanoic acid. This point will be discussed in more detail later.⁶⁴ It is worth noting that Luscombe's group used $\text{Pd}(\text{OAc})_2$ and 2 equiv of KOAc in DMAc at 130 °C in order to exploit usually undesired β -branching side reactions in order to synthesize thiophene-based hyperbranched polymers.⁶⁵

The reaction conditions applied to the preparation of P3HT⁵⁸ were also used for PQT12, another well-known polythiophene derivative studied for its application in organic electronics.^{66,67} As shown in Scheme 11, PQT12 was obtained from the homopolymerization of 5-bromo-3,3'-didodecyl-2,2':5',2''-quaterthiophene in THF or dioxane.⁶⁸ The comparison of ¹H NMR, differential scanning calorimetry (DSC), and UV–vis data in the solid state of this resulting polymer displayed regioregularity as good as that reported for its analogues obtained by Migita–Stille cross-coupling and oxidative polymerization.^{66–68} Thus, these conditions provide high regioregularity when applied to members of the poly-(alkylthiophene) (PAT) family.

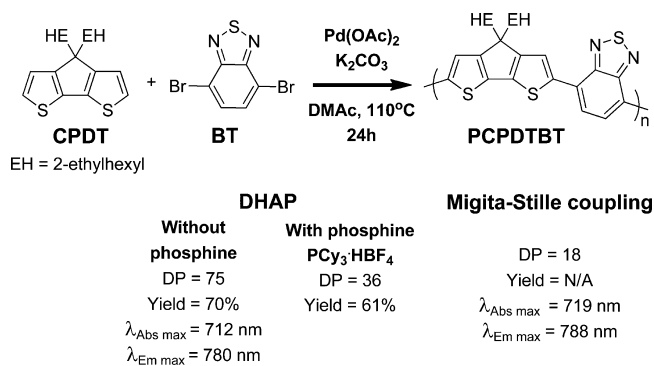
From these first examples, it seems that using polar conditions favors undesired side reactions (homocoupling and β -branching) compared with less polar solvents. These observations can be found in various studies, some of which will now be discussed. For instance, Sommer and co-workers demonstrated that during the synthesis of poly(Cbz-*alt*-TBT) under polar conditions, homocoupling reactions also take place (Scheme 12).⁶⁹ Indeed, for polymerization conditions involving $\text{Pd}(\text{OAc})_2$ and potassium pivalate (PivOK) in a DMAc/toluene blend, ¹H NMR

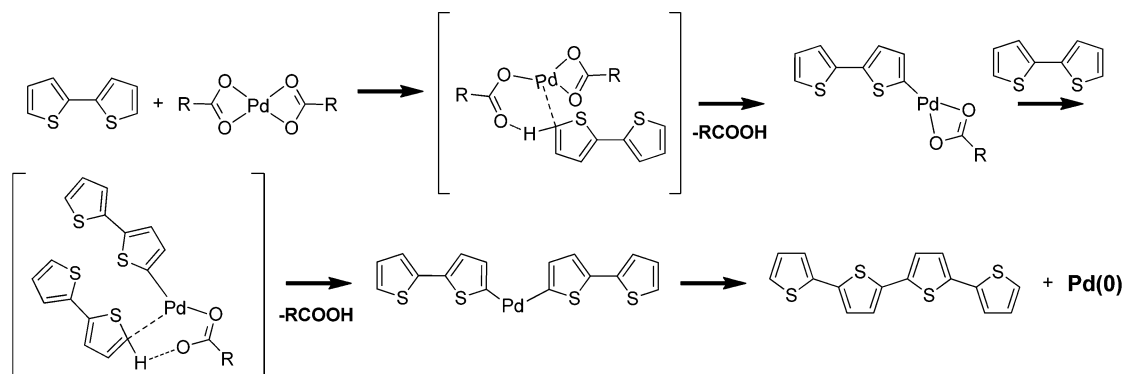
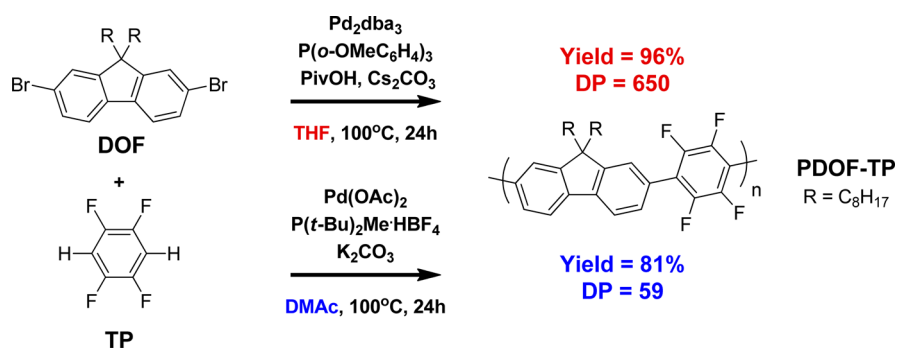
Scheme 12. Preparation of Poly(Cbz-*alt*-TBT) and Reported Homocoupling Defects⁶⁹Scheme 13. Preparation of a Terpolymer via DHAP and a Reported Homocoupling Defect⁷⁰

analyses revealed homocoupling reactions between TBT units (see Scheme 12). The addition of a bulky alkylphosphine (PCy₃) along with an acid/base mixture of pivalic acid (PivOH) and K₂CO₃ to the catalytic system prevented these side reactions. However, these conditions led to homocoupling reactions between carbazole (Cbz) units, with a clear correlation with the temperature of polymerization. Although optimization of the polymerization conditions led to a reduction of the homocoupling side reactions, comparisons of the UV–vis spectra demonstrated systematic hypsochromic shifts for DHAP-synthesized polymers compared with polymers synthesized through Suzuki coupling. This discrepancy is likely attributable to the presence of homocoupling and/or β -branching.

In parallel, Po and collaborators used DHAP to synthesize a terpolymer from dibromobenzotriazole, dibromobenzothiadiazole, and benzodithiophene (BDT) units in DMAC (see Scheme 13).⁷⁰ Comparisons of UV–vis and ¹H NMR spectra of the terpolymers synthesized under highly polar DHAP conditions with those of reference compounds prepared from Migita–Stille coupling also indicated the presence of irregular couplings. For instance, BDT–BDT homocouplings were observed at short polymerization times (Scheme 13). Interestingly, these authors reported that the DHAP-prepared polymer synthesized in THF presented UV–vis spectra similar to those of its Migita–Stille analogue.

Another noteworthy case involves the synthesis of PCPDTBT by Scherf and co-workers via DHAP under polar conditions consisting of Pd(OAc)₂ and K₂CO₃ in DMAC.⁷¹ The reaction was carried out both with and without a phosphine ligand, and the highest DP values were obtained in the latter case (see Scheme 14). It is worthwhile to note that this observation is in agreement with that of Tan and Hartwig regarding increased catalytic activity under phosphine-free conditions.⁶¹ Using these conditions, Scherf and colleagues were able to attain a DP of 75

Scheme 14. Synthesis of PCPDTBT via DHAP^{71,72}

Scheme 15. A Possible Homocoupling Mechanism, As Proposed by Kanbara and Co-workers⁷⁵Scheme 16. Polymerization of PDOF-TP Using Two Synthetic Pathways^{77,78}

without a phosphine, while the Migita–Stille-prepared homologue displayed a DP of only 18. NMR and UV–vis analyses indicated the presence of homocoupling defects.⁷¹ These side reactions could be diminished by the use of a sterically hindered phosphine (PCy_3), although the reaction occurred at a lower rate. This observation had also been made by Sommer and colleagues in the example discussed earlier.⁶⁹ Drawing on the work of Ozawa et al., the authors moved to a catalytic system comprising $\text{PdCl}_2(\text{MeCN})_2$, K_2CO_3 , KOAc, and $\text{P}(o\text{-OMe-C}_6\text{H}_4)_3$ in THF.^{73,74} Under these conditions, no homocoupling side reaction was detected by ^1H NMR spectroscopy, whereas when DMAc was used instead of THF, homocoupling with both units was identified (CPDT–CPDT and BT–BT).

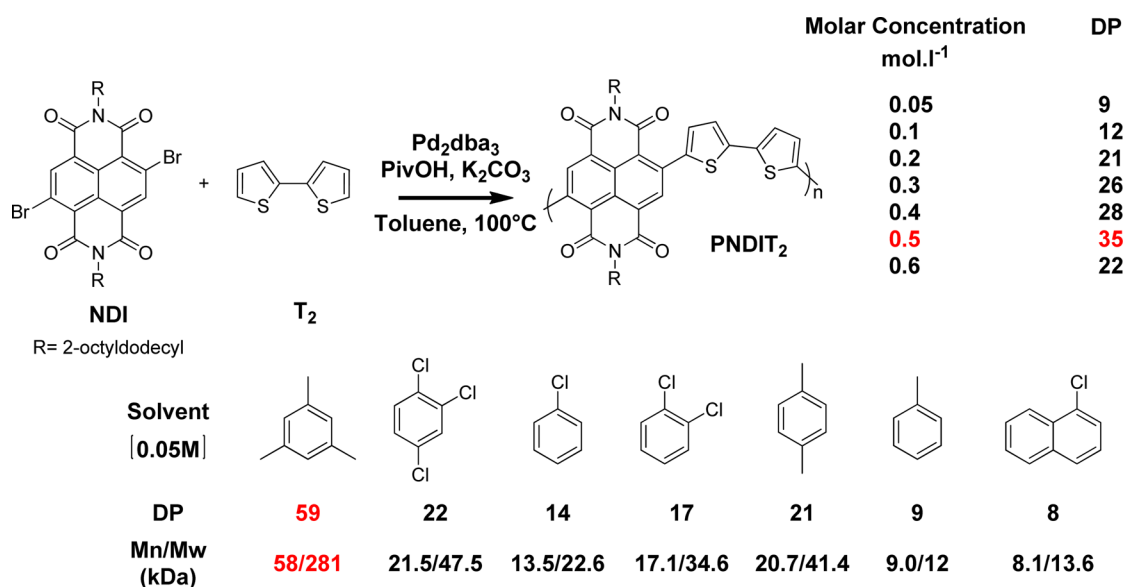
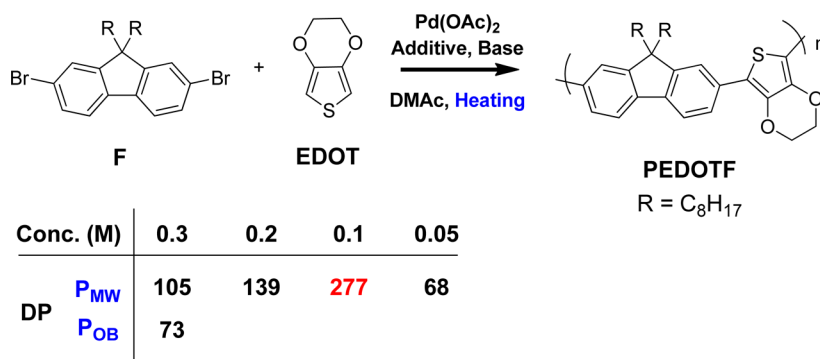
The origin of homocoupling reactions in DMAc without a phosphine was recently investigated by Kanbara and co-workers with bithiophene model compounds.⁷⁵ In the system presented, the reduction of Pd^{II} to Pd^0 proceeds by an oxidative coupling between two bithiophene units, as represented in Scheme 15. The reductive elimination step supplies the corresponding quaterthiophene as well as the Pd^0 species, which either becomes available to react in order to form the desired C–C couplings or in some cases precipitates as carbon black. According to the authors, the outcome is dependent on the stabilizing nature of the carboxylate ligands. Under the same conditions, it was demonstrated that homocoupling reactions between two bromoaryl compounds are possible via a disproportionation mechanism.^{45,61} A reduction in catalyst loading to 1 mol % limited these homocoupling side reactions. This is similar to a report from Itahara and co-workers in which oxidative homocoupling of a thiophene derivative under similar conditions was used to obtain 2,2'-bithiophene and 2,3'-bithiophene.^{22,76} It is interesting to note that the mechanism proposed by Kanbara is reminiscent of that obtained from density functional theory

(DFT) calculations on C–H activation by Sakaki and co-workers.³⁰

Another difference between highly polar and less polar solvents is their solubilizing efficiency. For instance, highly polar solvents such as amides and alcohols are not suited for alkyl-substituted conjugated polymers. The synthesis of PDOF-TP using different solvents (DMAc, THF, and toluene) supports this assertion (see Scheme 16). In DMAc at a concentration of $0.5 \text{ mol}\cdot\text{L}^{-1}$, Kanbara and co-workers obtained a polymer exhibiting a DP of 59 with a yield of 81%.⁷⁷ Ozawa synthesized the same polymer and obtained a much higher DP of 150 in toluene and a surprisingly high DP of 650 in THF with a yield of 96% at the same monomer concentration.⁷⁸

Influence of the Monomer Concentration. Another factor that is somewhat related to the solvent is the monomer concentration. To date, in most cases the best DP values have been obtained with monomer concentrations between 0.1 and 0.5 M. The concentrations used for DHAP are at least 5–10 times higher than those traditionally utilized for Migita–Stille or Miyaura–Suzuki cross-coupling reactions. Furthermore, it is often noticed that the increase in DP follows a linear relationship with the concentration of the reaction medium.^{58,77,79} Although this observation can be used to control the DP, it becomes problematic when one attempts to achieve the highest possible DP for a polymer. Indeed, polymerization at very high monomer concentrations leads to gelification of the reaction medium. This often stops the reaction, limiting the rate of conversion.

This variation of the catalyst reactivity as a function of the monomer concentration was studied by Sommer and colleagues for the synthesis of PNDIT₂ and PNDIT₄T by DHAP.^{80,81} In a first report, an increase in the DP as a function of the monomer concentration was noted.⁸⁰ For instance, the DP increased from 9 to 32 for monomer concentrations varying from 0.05 to 0.5 M

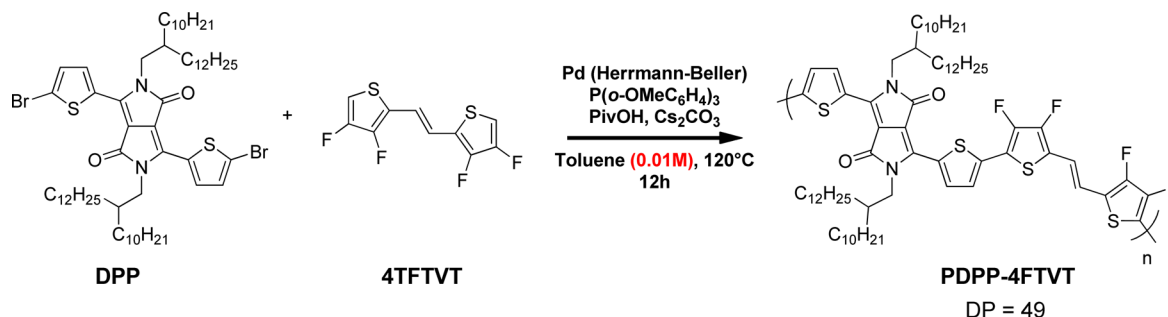
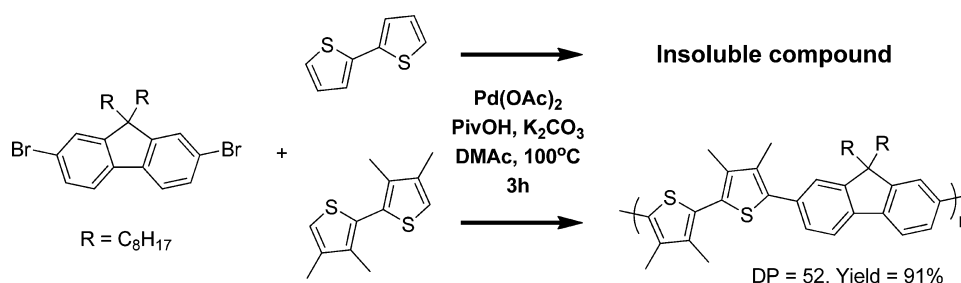
Scheme 17. Effect of the Monomer Concentration and Nature of the Aromatic Solvent on the Degree of Polymerization^{80,81}Scheme 18. Comparison of Oil Bath (P_{OB}) and Microwave (P_{MW}) Heating in the Preparation of PEDOTF^{87,88}

in toluene (Scheme 17). According to the authors, lower DP values at lower monomer concentrations could be associated with end-capping reactions with the solvent. In a second report, the authors studied more in detail the C–H reactivity of seven different substituted aromatic solvents in connection with the rate of end-capping. From these experiments it was observed that the end-capping side reaction can be suppressed by modifying either the nature of the solvent or its concentration. They observed that the most highly substituted solvents were less apt to engage in end-capping reactions, which may be explained by an increase in steric hindrance around the available C–H bonds of the solvent. For example, the use of mesitylene as a solvent led to polymers that possessed higher molecular weights than those prepared with other less substituted solvents and presented optical properties similar to those of their Migita–Stille-prepared analogues (Scheme 17). A similar observation had been reported earlier by Moritani and Fujiwara²⁰ in their first report of the coupling of styrene with various aromatic compounds, in which the most highly functionalized benzene derivative did not react because of steric hindrance.

It was also shown that the nature of the end-capping could vary depending on the polarity of the solvent. For example, non-aromatic polar solvents (DMAc, THF) favored the insertion of a hydroxyl or pivalate group via electrophilic substitution as a chain-terminating reaction.^{80–82} It is also interesting to note that for PNDIT₂, which was tested in n-type organic field-effect

transistors (OFETs), the electron mobility values were consistently higher for polymers prepared using the DHAP protocol than for the Migita–Stille homologues, regardless of the DP.⁸⁰

Obtaining a high DP at lower concentration is possible when microwave heating is used. In fact, it is understood that the localized heating initiated by microwave radiation increases the kinetics (and yield) of reactions in organic synthesis.⁸³ Recently, this technique has been used in the direct (hetero)arylation preparation of both organic compounds^{84–86} and polymers.^{85,87} The advantages of this technique have been demonstrated in the polymerization of PEDOTF by Kanbara and co-workers (Scheme 18). In a first report concerned with optimization of the catalytic conditions, the authors synthesized this polymer using conventional oil bath heating (P_{OB}) and achieved a DP of 73 following a reaction carried out at 100 °C for 6 h at a monomer concentration of 0.3 M.⁸⁸ In a second study, the same reaction was carried out using microwave heating (P_{MW}), and a DP of 105 was reached after only 30 min at 80 °C.⁸⁷ The rapid and uniformly distributed heating of the reaction environment was given as a reason for the efficiency of this method. In a subsequent study of the same polymer, PEDOTF samples prepared by these different heating methods and by the Suzuki coupling were compared in both solar cell and OFET devices. The DP values, hole mobilities, and power conversion

Scheme 19. Synthesis of PDPP-4FTVT by DHAP at a Low Monomer Concentration⁹⁰Scheme 20. Synthesis of Copolymers from β -Protected or Nonprotected 2,2'-Bithiophene and 2,7-Dibromo-9,9-dioctylfluorene⁹²

efficiencies (PCEs) were all found to be superior in the case of the microwave-heated DHAP polymer.⁸⁹

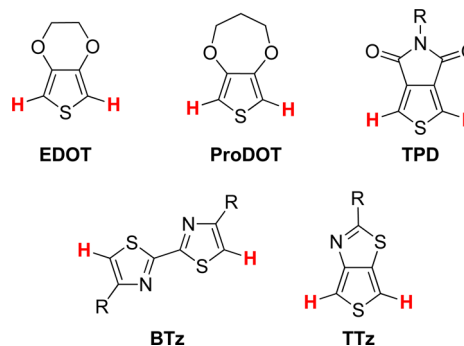
The reactivity of the C–H bond must also be considered. For instance, Wang and co-workers recently synthesized a copolymer (PDPP-4FTVT; see Scheme 19) by DHAP with one of the lowest monomer concentrations reported (0.01 M).⁹⁰ These results may be explained by the highly acidic C–H bond of the monomer, which is induced by the presence of fluorine atoms on the thiophene unit.

A polymerization reaction at relatively low concentration (0.05 M) was also performed by Coughlin and co-workers with dibrominated diketopyrrolopyrrole (DPP) and 3,4-difluorothiophene or 2,5-difluorophenyl units.⁹¹ It is interesting to note that in both of these examples the monomers contain fluorine atoms. These observations allow us to postulate that polymerization reactions exhibiting faster kinetics can be performed at low monomer concentrations, in a similar fashion as those with microwave heating. Thus, a high reactivity of C–H bonds may permit a decrease in the monomer concentration.

Influence of the Nature of the Monomers. As for Migita–Stille or Miyaura–Suzuki coupling, when DHAP is employed, the position of the functional groups involved in the coupling reaction must be taken into consideration. This is particularly true for heterocycles, such as thiophene and furan derivatives, where the aromatic C–H bonds are more reactive than those present in benzene derivatives. An example of this was provided by Kanbara and co-workers in 2012 when their attempts to copolymerize 2,2'-bithiophene with 2,7-dibromo-9,9-dioctylfluorene in polar solvents yielded materials with low solubility (see Scheme 20).⁹² This was most likely due to β -branching at the 3,3'- and 4,4'-positions of the 2,2'-bithiophene monomer. However, because of the low solubility of the resulting polymer, characterization was not possible. To avoid these side reactions, other reactive C–H bonds on the thiophene monomers were blocked or “protected” with methyl groups. Thus, copolymerization with several dibrominated monomers provided processable materials with high molecular weights.⁹³

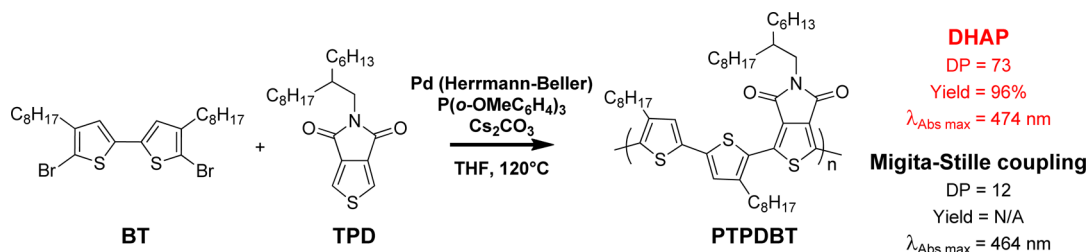
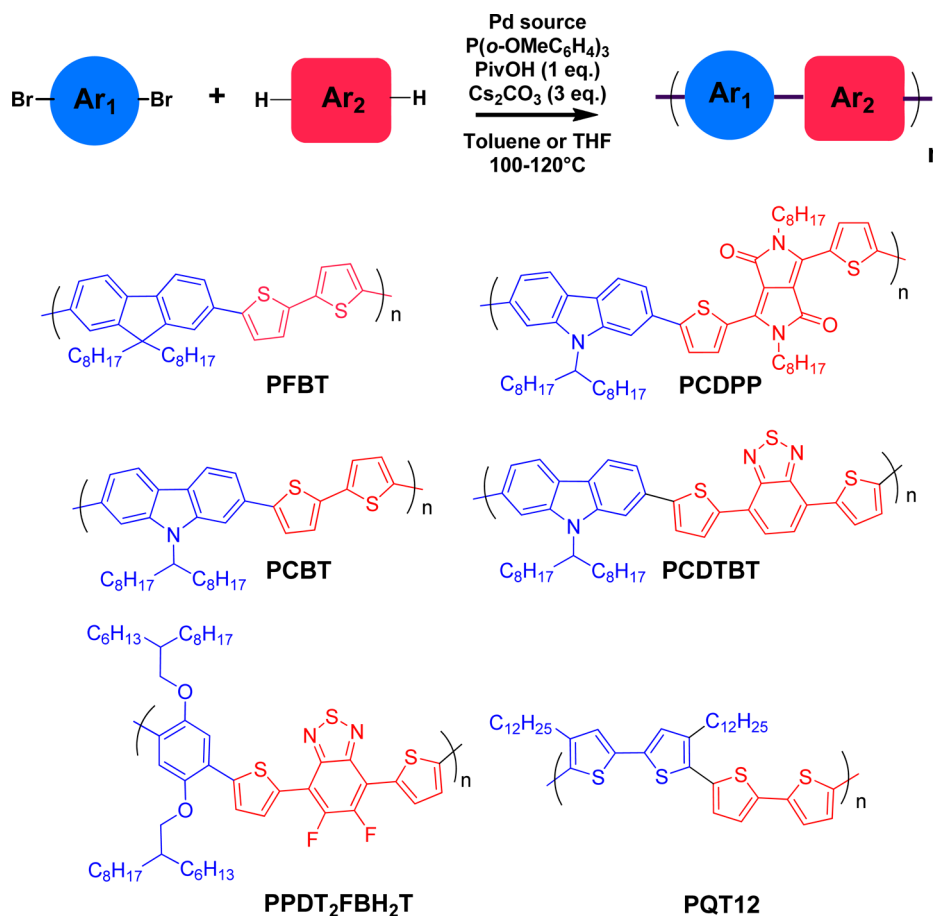
Unfortunately, there are often adverse effects associated with blocking the β -position, with alkyl chains for instance. Indeed, higher band gaps, lower charge-carrier mobilities, and poor packing are often observed and have been attributed to a significant torsion angle between the aromatic units.⁹³ This strategy is therefore limited to few classes of monomers that exhibit low steric hindrance from their side chains and display good performance in organic electronics even with pendant side chains.

In this regard, certain monomers that intrinsically have only one available C–H bond but at the same time possess proven electronic properties can be used as building blocks in DHAP protocols (Scheme 21). Indeed, well-defined copolymers and

Scheme 21. Examples of Monomers without Available C–H Bonds at the β -Position

homopolymers have been prepared using 3,4-ethylenedioxythiophene (EDOT),^{88,94,95} 3,4-propylenedioxythiophene (ProDOT),⁹⁶ thieno[3,4-*c*]pyrrole-4,6-dione (TPD),^{73,95,97–100} 4,4'-dialkyl-2,2'-bithiazole (BTz),^{101–103} thieno[3,4-*d*]thiazole (TTz),¹⁰⁴ and other useful 3,4-disubstituted thiophene derivatives.^{105–109}

A specific example of this is the preparation of an alternating copolymer (PTPDBT) from a thienopyrroledione (TPD)

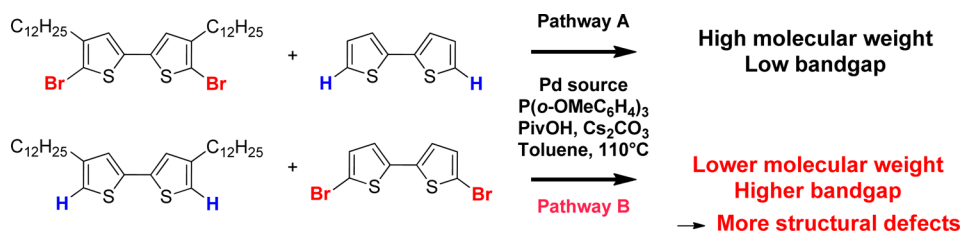
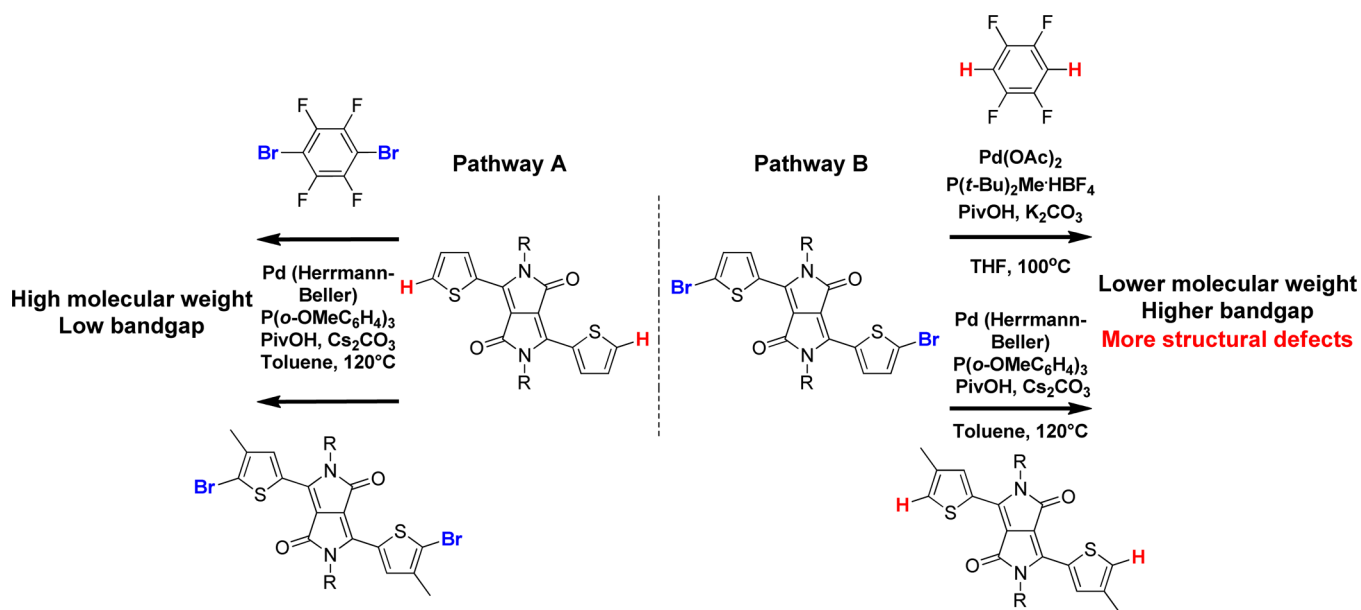
Scheme 22. Synthesis of PTPDBT by DHAP⁹⁷Scheme 23. General Conditions for the Synthesis of Various Conjugated Copolymers¹¹³

derivative and a bithiophene (BT) unit, as shown in Scheme 22.⁹⁷ Analogue compounds that exhibited acceptable properties in organic electronics had already been synthesized by Wei^{110,111} and Marks¹¹² using Migita–Stille coupling. When the conditions described in Scheme 22 were used, a DP of 73 was achieved with a yield of 96% in THF. The ¹H NMR spectrum and X-ray diffraction patterns were found to be almost identical to those reported for the same polymer prepared by the Migita–Stille method (DP = 12), while the UV–vis absorption spectrum was slightly red-shifted by 10 nm because of the increase in molecular weight. Interestingly, cross-linking or branching by activation of C–H bonds on the bithiophene unit was not observed.

Moreover, Leclerc and colleagues presented the synthesis of many different conjugated copolymers in nonpolar solvents following the general conditions described in Schemes 8b and 23.¹¹³ Various bromoarenes, including 2,7-dibromofluorene, 2,7-dibromocarbazole, and 1,4-dibromobenzene, have been efficiently copolymerized with bithiophene (BT), an electron-rich

unit, or electron-poor units such as dithienylbenzothiadiazole (TBT) and diketopyrrolopyrrole (DPP) derivatives. Controlling the reaction time allows the synthesis of processable and well-defined alternating copolymers with high DPs even though many of them, particularly bithiophenes,⁹² can be subject to branching and cross-linking. ¹H NMR and UV–vis absorption analyses have demonstrated that these polymers display structures similar to those of their Migita–Stille- or Miyaura–Suzuki-synthesized analogues. In order to evaluate the quality of the copolymers obtained under these conditions, field-effect transistors were fabricated and tested for PCDPP and PCDTBT and displayed hole mobilities of up to 0.54 cm² V⁻¹ s⁻¹ for PCDPP and 1.7 × 10⁻² cm² V⁻¹ s⁻¹ for PCDTBT. These were both superior to those obtained for the same polymers prepared via Suzuki coupling with comparable DP values (0.27 cm² V⁻¹ s⁻¹ for PCDPP and 5.3 × 10⁻³ cm² V⁻¹ s⁻¹ for PCDTBT).

Systematic comparisons of the physical and spectral properties of polymers prepared by DHAP and Migita–Stille or Miyaura–

Scheme 24. Influence of the Brominated Thiophene Monomer Used in DHAP on the Selectivity¹¹³Scheme 25. Comparison of Brominated Comonomers for DPP-Based Polymers^{118,120}

Suzuki methods demonstrate that a high selectivity can be obtained using the DHAP protocol. This observation can be confirmed with a number of recent studies. For example, Sommer and co-workers were able to synthesize well-defined naphthalenediimide bithiophene-based (PNDIT₂)⁸⁰ and DPP-based polymers,¹¹⁴ both of which possess good electronic properties. This is also the case for indigo- and EDOT-based copolymers prepared in continuous flow¹¹⁵ and phenanthridine-based copolymers.¹¹⁶ From these results it is clear that if the bromoarene is an electron-rich unit and the unit containing the targeted C–H bond is a heterocycle derivative, the corresponding copolymer is well-defined.

Unfortunately, this method cannot be directly applied to all aromatic heterocycles, and the choice of which monomer to brominate seems to be essential. Indeed, on the basis of previous studies it can be asserted that the same copolymer can have different properties depending on the monomer containing the halide function. This trend can be observed in following studies.

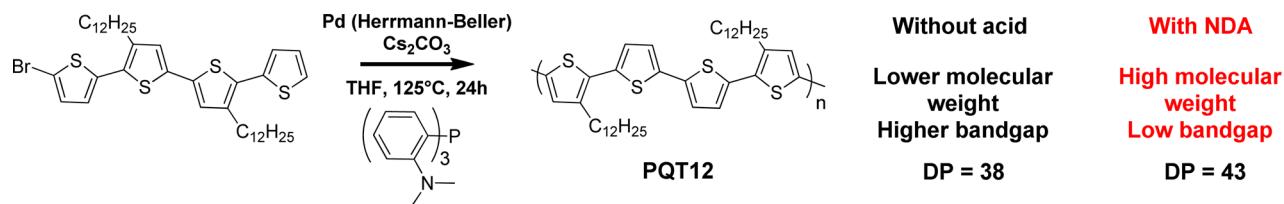
While the synthesis of PQT12 via pathway A (see Scheme 24) generates a quite regioregular polymer, pathway B produces a compound presenting different physical properties attributed to structural defects.¹¹³

Wang and co-workers also observed these structural differences through the application of differing synthetic pathways while synthesizing polymers containing electron-poor thiophene units such as DPP (Scheme 25).¹¹⁷ Indeed, when the polymerization reaction includes dibromotetrafluorobenzene with DPP, the resulting polymers present absorption maxima in agreement with the compound synthesized via Migita–Stille

coupling, which was reported by Jo and co-workers.¹¹⁸ ¹H NMR analysis confirmed a well-defined structure for this polymer. However, the polymerization of tetrafluorobenzene with dibromo-DPP yields a polymer with entirely different properties: the absorption maximum is blue-shifted and displays a pronounced band-edge tail. Recently, Janssen and co-workers demonstrated that the apparition of this high-wavelength absorption band is due to homocoupling between DPP units.¹¹⁹ NMR analyses of a model DPP homopolymer confirmed this. However, NMR analyses did not show any extra peak attributable to β -branching; according to the authors, such signals would be indistinguishable from those generated from homocoupling.

Similar results were obtained by our research group with DPP-based copolymers, where β -protected α -brominated DPP monomers led to more regular copolymers than those obtained from nonprotected α -brominated DPP units (Scheme 25).¹²⁰ β -Branching and dehalogenation reactions seem to occur more easily for these species, whereas β -alkylated bromothiophenes (and bromoarenes) appear less prone to such undesirable side reactions.

From these results it would seem that the use of certain brominated thiophene species is not suitable in order to obtain a well-defined polymer by DHAP. This can be due to the fact that if dehalogenation of a bromothiophene occurs, the resulting thiophene compound can undergo cross-coupling with a still-brominated thiophene. Activation of the β -proton adjacent to the C–Br bond is also possible. Conversely, if dehalogenation of a

Scheme 26. Influence of a Bulky Acid (Neodecanoic Acid, NDA) on the Polymerization of PQT12⁶⁸

bromoarene occurs, the newly formed C–H bond would lead only to chain endings because of its higher activation energy.¹³

Influence of the Acid, Base, Ligand, and Additives. A fourth factor that influences the reactivity and/or selectivity is the acid-to-base ratio. Initially, a 0.3:2.3 molar ratio was often utilized, which was directly transposed from studies on small molecules performed by Lafrance and Fagnou.³¹ First investigations with polymeric compounds employed this ratio with reasonable success.^{28,95,109} In 2013, Ozawa studied the influence of the acid-to-base ratio for the synthesis of PDOF-TP (see Scheme 16) and showed that the use of a 1:3 ratio of pivalic acid and Cs₂CO₃ resulted in very high DP values.⁷⁸ Different carboxylic acids have also been studied, but pivalic acid has systematically provided superior reactivity.

A second study describing the influence of these ratios and the nature of these reagents was published by Wang and Wang in 2014.⁷⁹ The results presented are consistent with the observations made by Ozawa et al. and display optimal efficiency for a 1:3 acid-to-base molar ratio.⁷⁸ The role of the base in the reaction efficiency has also been studied, and the best results were obtained with carbonate and phosphate bases.

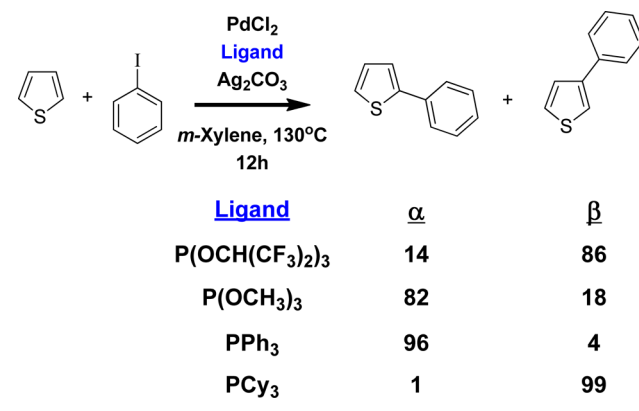
By using P3HT as a model compound, Rudenko and Thompson⁶⁴ recently undertook a study focusing on the carboxylic acid used in the DHAP protocol in an attempt to determine the effect of its structure on the characteristics of the resulting material. Of the numerous aliphatic cyclic and linear acids chosen, the regioregularity remained relatively consistent (93–96%) regardless of the bulkiness of the acid but tended to be highest when α -tertiary acids were used. β -Branching side reactions were avoided altogether only when α -tertiary acids were used. The sole exception to this was pivalic acid, which displayed a β -defect content of 1%. When the ensemble of molecular weight, polydispersity, regioregularity, and branching was considered, neodecanoic acid (NDA) was determined to be the most attractive choice of carboxylic acid.

This effect was also observed by the Leclerc group during the synthesis of PQT12.⁶⁸ Indeed, a well-defined polymer was obtained with the monomer described in Scheme 11, whereas polymerization of the monomer described in Scheme 26 led to PQT12 with some structural defects. For the latter reaction, the addition of NDA limited β -branching side reactions and afforded a well-defined polymer as determined by DSC and solid-state UV–vis measurements. These studies highlight the fact that steric hindrance near the catalytic center enhances the selectivity for α -couplings.

The effect of anionic additives on the polymerization reaction has also been the subject of some investigation. These were influenced by previous optimizations of the Heck reaction. For instance, it has been shown that Heck couplings are greatly enhanced by the addition of tetraalkylammonium halide salts, leading to the so-called Jeffery's conditions.¹²¹ These developments were recently transposed to DHAP by Hayashi and Koizumi.¹²² The authors compared the efficiencies of two

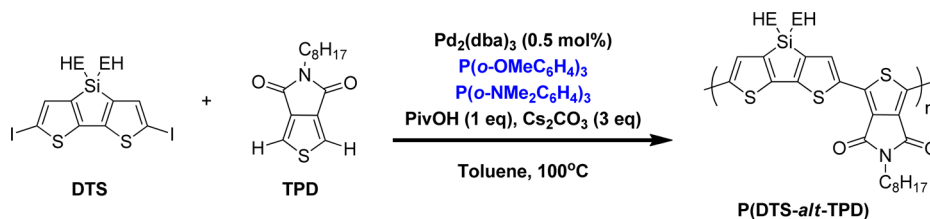
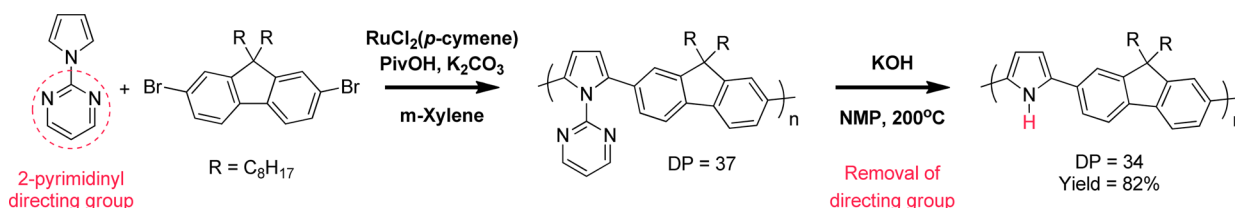
sources of palladium, PdCl₂ and Pd(OAc)₂, and showed that PdCl₂ systematically affords higher DPs. As demonstrated for Jeffery's conditions, this outcome could be related to stabilization of the catalytic system by the presence of halide ions. It is worth noting that the addition of *n*-Bu₄X (X = F, Br) additives in a low-polarity solvent (i.e., *o*-xylene) was tested by Wang and Wang⁷⁹ but failed to be conclusive. This methodology therefore remains to be optimized for DHAP.

Another factor influencing the selectivity and reactivity of the polymerization method is the nature of the ligand, specifically with regard to its steric and electronic characteristics. For instance, Itami and collaborators have demonstrated highly variable α versus β reactivity on thiophene by modifying the nature of the phosphine ligand (Scheme 27).^{38,123,124}

Scheme 27. α versus β Selectivity for the Cross-Coupling of Thiophene and Iodobenzene Using Various Phosphine Ligands^{38,124}

In 2011, Fu's group undertook a DFT study³⁹ in order to elucidate the influence of the phosphine on the coupling selectivity observed by Itami. In that study, the authors demonstrated that the ligand plays a significant role in modulating the activation energy barrier, depending on the reaction mechanism. More recently, Larrosa and co-workers also studied the selectivity of α - versus β -couplings on benzo[*b*]-thiophene and thiophene derivatives.⁴⁰ Under the conditions described above, the authors obtained high yields and high selectivities for the β -position (>99%) with many different functional groups. The combination of kinetic isotope studies and DFT calculations confirmed a Heck-type mechanism, which explains the β -selectivity. It is interesting to note that in the work of both Itami and Larrosa the presence of fluorinated ligands favors reactivity at the β -position.

To the best of our knowledge, the ligand P(*o*-NMe₂(C₆H₄))₃ seems to be restricted to members of the poly(alkylthiophene) family (see Scheme 8a). Indeed, the synthesis of P3HT with diverse ligands displays variable regioregularity (HT content) ranging from 77% with PPh₃ to 96% with P(*o*-OMe(C₆H₄))₃,

Scheme 28. Synthesis of Poly(DTS-*alt*-TPD) Using Two Ligands in Tandem¹²⁸Scheme 29. Synthesis of a Polypyrrole Derivative by DHAP with the Use of a Directing Group¹³⁰

compared with upward of 99% with $P(o\text{-NMe}_2(\text{C}_6\text{H}_4))_3$.^{58,59,125} In contrast, $P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$ presents favorable selectivity and reactivity for copolymers, such as those presented in Scheme 8b. Various phosphine ligands, such as the alkylphosphines $P(t\text{-Bu})_2\text{Me}\cdot\text{HBF}_4$ (in DMAc),⁷⁷ $P(t\text{-Bu})_3\cdot\text{HBF}_4$,¹¹⁵ and $\text{PCy}_3\cdot\text{HBF}_4$,^{95,126} have also displayed acceptable efficiencies, but these examples are relatively scarce in the literature.

The particular properties of the ligand $P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$ were recently studied by Ozawa and colleagues.¹²⁷ As seen before (Scheme 4), the reactivity of the catalytic system depends heavily upon the presence of the monomeric species 2.⁴⁵ In this second study, Ozawa explored the influence of the phosphine on the reactivity of the catalytic system by comparing the phosphines PPh_3 and $P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$. In the presence of the latter, species 2 was observed regardless of the choice of solvent or aryl group. This indicates that this ligand reduces the aggregation of the palladium species in solution, which otherwise would limit its reactivity, thereby favoring the more reactive compound 2.

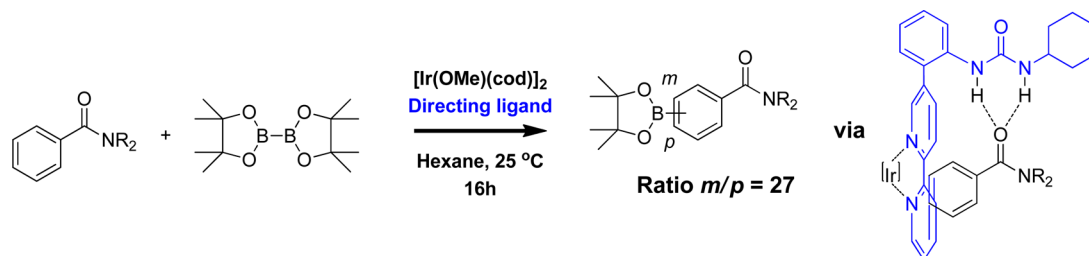
It was observed that in the preparation of the polymers PCPDTBT (Scheme 14) and $P(\text{Cbz}\text{-alt}\text{-TBT})$ (Scheme 12), the use of a highly encumbered phosphine considerably limited homocoupling reactions (the coupling of either two C–X or two C–H bonds) under polar conditions. However, when less polar conditions were used, homocoupling was less pronounced and could also be diminished further by means of the phosphine. Finally, Ozawa and colleagues synthesized poly(DTS-*alt*-TPD) and noted that using two phosphines ($P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$ and $P(o\text{-NMe}_2(\text{C}_6\text{H}_4))_3$) in tandem reduced the rate of homocoupling (see Scheme 28).¹²⁸ NMR analysis of the oligomeric samples obtained after a short polymerization time indicated that the use of $P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$ alone led to both homocoupling and DTS chain-end reduction of DTS-I to DTS-H in the same ratio (2.6%), indicating that the oxidative homocoupling and reductive dehalogenation reactions occur in concert with one another. Homocoupling also favored branching on the DTS unit, leading to an insoluble fraction in the corresponding polymer material and a reduced yield. Used alone, $P(o\text{-NMe}_2(\text{C}_6\text{H}_4))_3$ did not yield any polymeric product. However, when $P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$ and $P(o\text{-NMe}_2(\text{C}_6\text{H}_4))_3$ were combined (2 equiv of each per Pd atom), homocoupling and chain-end reductions were limited to 1.2%, despite a lower degree of polymerization and lower reaction rate.

PERSPECTIVES

Clearly, well-defined high-molecular-weight conjugated polymers can be obtained by DHAP when the monomers as well as the polymerization conditions are chosen carefully (see Scheme 8). However, the reactivity and stability of some bromothiophene derivatives still present some challenges. The principal issues with this class of monomers are homocoupling and β -branching, detrimental side reactions that can hamper the synthesis of defect-free high-molecular-weight polymers. A better understanding of these side reactions could therefore contribute to the development of polymers with enhanced regioregularity. To achieve this goal, future DHAP studies should be combined with systematic comparisons with Migita–Stille, Miyaura–Suzuki, or other traditional polymerization methods. They could even lead to a better understanding of the Migita–Stille and Miyaura–Suzuki polymerization reactions. Indeed, most reported conjugated polymers are tacitly assumed to exhibit a backbone that perfectly fits with the written (theoretical) structure. As previously mentioned, this is clearly not always the case with DHAP, and therefore, similar thorough structural studies for the more classical polymerization methods would also be welcome.

The present Perspective has also mentioned the positive role played by steric protection around the catalytic center in the coupling selectivity. These observations could serve for future studies specifically addressing the influence of the steric hindrance created by the ligands. On the basis of the various examples provided above, it can be noted that to date only a limited number of ligands offer both high reactivity and selectivity. For instance, we observed that the ligand $P(o\text{-NMe}_2(\text{C}_6\text{H}_4))_3$ affords high regioregularity for poly(alkylthiophene)s,^{58,68} and that $P(o\text{-OMe}(\text{C}_6\text{H}_4))_3$ permits good results for the bromoarene family.¹¹³ We therefore believe that the use of ligands specifically designed for a given class of monomers could be a promising approach to obtain well-defined polymers. Indeed, when one considers the development of other homogeneous metal-catalyzed coupling methods, innovation in ligand design has served as the impetus for overcoming synthetic difficulties in virtually every case.¹²⁹

In the case of selectivity problems with new monomers, the utilization of a directing group is another option to achieve well-defined polymeric structures. The directing group may either be incorporated into the compound requiring activation, as shown

Scheme 30. Meta-Borylation via C–H Activation Directed by the Ligand¹³¹

in Scheme 29, or be bound to the catalytic system.¹³⁰ Itahara proposed such an interaction between the catalyst and the N-substituted moiety as a possible factor favoring arylation at the α -position.²² However, this strategy is limited to certain building blocks and increases the number of synthetic steps with regard to the functionalization and then removal of the directing group, thereby going against the assets of DHAP.

Interestingly, Kuninobu et al.¹³¹ recently synthesized a specific ligand for meta-selective C–H borylation directed by a secondary interaction between the ligand and substrate. This ligand enables the positioning of a catalytic center near the C–H bond at the meta position of the aromatic substrate (see Scheme 30). While limited to a few examples, this study demonstrates that the utilization of ligands capable of creating secondary interactions with either the catalyst or the substrate can promote selectivity. This is an approach that could possibly be adapted to DHAP.

Finally, theoretical studies could help in the design of optimized monomers and polymerization systems. To date, however, DFT calculations have essentially focused on the activation energy of monomeric substrates using PMe_3 as a ligand.⁴⁷ A better understanding of the polymerization reactions and the influence of ligands will clearly require in-depth computational analyses of the relevant systems.

CONCLUSION

After just a few years of investigation, direct (hetero)arylation polymerization has already become an important tool in the polymer chemist's arsenal. By drawing on the first studies undertaken with small molecules, this polymerization method is now being thoroughly scrutinized from both experimental and theoretical standpoints. This Perspective has presented the essential features necessary in order to understand the DHAP reaction, notably the mechanisms of catalysis, special considerations with regard to homo- versus copolymerization, and the various defects that may occur as well as their sources. The current scope of monomers that can be polymerized using this method has also been discussed, especially with regard to the availability and reactivity of both intended and undesired aromatic C–H bonds. Certain peculiarities that have not yet been fully elucidated, including the location of the halide on comonomers, the possibility of β -protection, and the influence of the acid, base, ligand, and other additives, have also been laid out. Some of these still present open-ended questions, and indeed, some improvements are still needed to obtain defect-free conjugated polymers with generic and robust protocols. However, we are confident that DHAP, which is inherently efficient and environmentally benign, will soon become the synthetic method of choice in the preparation of many conjugated polymers.

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Notes

The authors declare no competing financial interest.

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