Pairing Suzuki-Miyaura cross-coupling and catalyst transfer polymerization

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Complete List of Authors:	Bautista, Michael; Carnegie Mellon, Chemistry Varni, Anthony; Carnegie Mellon, Chemistry Ayuso-Carrillo, Josue; Carnegie Mellon University, Chemistry Carson, Matthew; Carnegie Mellon, Chemistry Noonan, Kevin; Carnegie Mellon, Chemistry

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Pairing Suzuki-Miyaura cross-coupling and catalyst transfer polymerization

Michael V. Bautista, Anthony J. Varni, Josue Ayuso- Carrillo, Matthew C. Carson, Kevin J.T. Noonan*

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Suzuki-Miyaura catalyst transfer polymerization (SM CTP) is a versatile method to prepare conjugated polymers with control over molecular weight, sequence, and dispersity. This perspective aims to highlight some of the progress in using Suzuki-Miyaura coupling to prepare well-defined conjugated polymers. We describe some of the advantages and challenges of Suzuki-Miyaura coupling to make aromatic polymers from difunctional monomers. The proposed mechanism for transmetalation in Suzuki-Miyaura polymerization is discussed, as it is different than the more typical Kumada coupling. Finally, some of the advances in catalyst design to prepare conjugated polymers using SM CTP are noted.

Introduction

Conjugated polymers are comprised of repeating aromatic rings and have a set of alternating single and double bonds along the backbone. These π-electron frameworks have desirable optical and electronic properties that can be tuned by the choice of aromatic repeat unit(s) along the backbone and by the solid-state organization of the material. Molecular weight and molecular weight distribution in particular,[1-3] are important parameters that can influence packing and charge transport in poly(3-hexylthiophene) (P3HT), a benchmark conjugated polymer.[4-7] These studies were made possible by the advances in P3HT synthesis over the past 30 years.[8]

Given the importance of molecular weight, precise methods to ensure reproducibility and specificity in conjugated polymer synthesis are desirable. Conjugated macromolecules are typically synthesized using step-growth polymerization, and though this method is synthetically simpler, it can be difficult to control molecular weight with this approach.[9-16] Preparing polyaromatics using a chain-growth process (known as catalyst-transfer polymerization or CTP) enables improved control over the molecular weight and molecular weight distribution of the resultant sample. Moreover, controlled polymerization offers the possibility to build backbone compositions that are inaccessible using step-growth techniques (e.g. block copolymers). The chain-growth process relies on catalyst complexation to the growing polymer chain during the reaction, as shown in Fig. 1.[17-24]

To date, the number of aromatic building blocks which can be polymerized via a chain-growth mechanism is limited.[17-24] Herein, we highlight the opportunities and challenges of Suzuki-Miyaura coupling as a method to expand the choice of aromatic repeat units in CTP. Yokozawa reported the first Suzuki-Miyaura CTP (SM CTP) reaction with a 9,9-dialkylfluorene monomer in 2007,[25] not long after the discovery of controlled polymerization of 3-alkylthiophenes using Kumada coupling.[26-30] Since that time, SM CTP has been used to prepare alkyl and ester-functionalized polythiophenes, polyfluorenes, ester-functionalized polyfurans, poly(*para*-phenylenes), poly(*meta*-phenylenes), poly(*ortho*,*para*-alternating-phenylenes) poly (benzo[1,2,3]triazoles), poly(3,6-phenanthrenes) and poly(phenylene-vinylenes).[31-59]

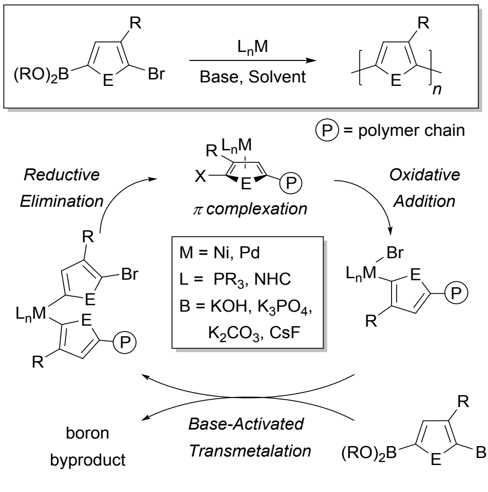

Fig. 1. General mechanism of Suzuki-Miyaura catalyst-transfer polymerization with a 3-substituted heteroarene monomer (where E = element). M refers to metal, L refers to the ancillary ligand bound to the metal centre and B refers to the inorganic base. PR_3 and NHC represent a tricoordinate phosphine and N-heterocyclic carbene, respectively.

In this perspective, we specifically highlight the combination of Suzuki-Miyaura coupling with controlled polymerization to prepare well-defined polyaromatics. To this end, we first compare Suzuki polymerization to direct arylation and Kumada polymerization. We then describe the typical methods used to

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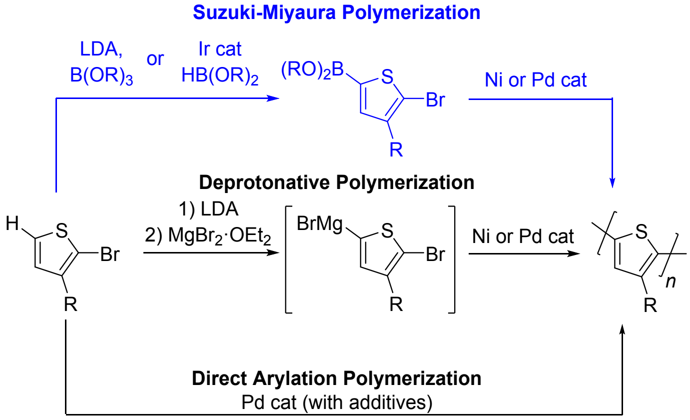
[a] *Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213-2617, USA. E-mail: noonan@andrew.cmu.edu.*

prepare difunctional organoboron monomers for SM CTP. We briefly discuss the mechanism of this reaction, and how transmetalation differs from the more conventional Kumada CTP. Next, we highlight the versatility of the boron coupling partner and discuss the impact of protodeboronation. Finally, we showcase some of the catalysts that have been used in SM CTP to date.

Why use Suzuki-Miyaura Coupling for Chain-Growth Polymerization?

The Suzuki-Miyaura reaction has become ubiquitous in the organic chemist's toolbox. It is used to prepare organic molecules, therapeutics, and advanced materials. It involves cross-coupling of an aryl halide (or pseudo-halide) and an organoboron reagent to form a new C-C bond.[60] The exceptional functional group tolerance, mild reaction conditions, and non-toxic byproducts make this method highly attractive for the polymerization of aromatics.[61]



Suzuki-Miyaura Polymerization	Deprotonative Polymerization	Direct Arylation Polymerization
ADVANTAGES	ADVANTAGES	ADVANTAGES
1. Functional group tolerance 2. Mild rxn conditions 3. Isolable monomer 4. Chain-growth	1. Highly reactive transmetalating group 2. Mild rxn conditions 3. Chain-growth	1. Functional group tolerance 2. Atom economy 3. High M_w
CHALLENGES	CHALLENGES	CHALLENGES
1. Extra synthetic step 2. Requires base 3. Atom economy	1. Functional group tolerance 2. Atom economy	1. Harsh conditions 2. Chain-growth 3. Defects possible

Fig. 2. Typical methods used for poly(3-alkylthiophene) synthesis including advantages and challenges of each method. Lithium diisopropylamide is abbreviated as LDA.

Difunctional monomers (e.g, H-Ar-Br or $(HO)_2B$-Ar-Br) are required for chain-growth polymerization,[17-24] and Fig. 2 highlights advantages and drawbacks of Suzuki-Miyaura coupling as compared to other polymerization approaches for this type of monomer. Deprotonative polymerization via Kumada coupling has been used extensively for the preparation of poly(3-alkylthiophenes).[17-24] The active monomer is formed by deprotonation with lithium diisopropylamide (LDA) followed by magnesiation (Fig. 2),[62, 63] or by activation of a carbon-halogen bond with isopropylmagnesium chloride.[27] The resultant Grignard monomer is polymerized rapidly in excellent yield most often using a Ni catalyst. This method offers precise control over side chain orientation and molecular weight, but the nucleophilicity of the organomagnesium monomer limits the choice of aromatic ring and side group in this reaction.

Suzuki-Miyaura polymerization has the same benefits as the Kumada reaction (controllable side group orientation and rapid reaction rates under basic conditions) but is more functional group tolerant than Kumada coupling. The reduced nucleophilicity of the boron group makes Suzuki-Miyaura coupling an excellent alternative for polymerization of more sensitive substrates (e.g. with ester or amide side groups) though the additional synthetic step adds time and expense relative to the other two methods (Fig. 2). Beyond simply functional group tolerance, the boron group can also be used as a tool to tailor polymerization chemistry. The –OR groups bound to the boron attenuate monomer reactivity and therefore can be used to change polymerization rate. As will be discussed below, masking group strategies can also enable precise feeding of monomers into polymerization to access block copolymers in one-pot. As such, the boron group is unique in that it can be changed to improve polymerization behaviour and access different polymer compositions.

Direct arylation polymerization (DArP), has rapidly become one of the most important methods to construct polyaromatics via coupling of a C-Br and C-H bond. [12-15] This atom economical approach to synthesizing conjugated polymers can be optimized in most instances to afford high molecular weight materials and is compatible with a diverse set of monomers. While this method has many advantages, chain-growth polymerization is difficult due to the harsh reaction conditions required, and backbone defects can arise when multiple C-H sites are present on the monomer.[12-15]

Preparation of Difunctional Monomers For SM CTP

The most common borylation strategies are highlighted in Fig 3. Metalation of a C-H or C-X bond with LDA or *n*-butyllithium (nBuLi) produces a metalated arene that can be quenched with a borate ester to afford a difunctional monomer (Fig. 3, Method A).[64] This strategy is highly effective for the preparation of aryl boronic esters, but the nucleophilicity of the organometallic reagents can limit the choice of arene and R group, similar to Kumada polymerization.

Fortunately, aromatics can also be borylated using transition metals and boron reagents via C-H[65] and C-X[66-68] activation (Fig. 3, Method B). These strategies are operationally simple and highly functional group tolerant making them attractive for monomer synthesis. Our group and others have utilized Ir borylation to prepare Suzuki-type monomers for polymerization.[35, 46, 69] The iridium borylation is highly regioselective and tolerates chloro and bromo substituents on the arene[70] or heteroarene.[71]

Miyaura borylation can also be used to borylate the C-I bond in iodobromoarenes using bis(pinacolato)diboron (B_2pin_2) and potassium acetate (KOAc), (Fig. 3, Method B).[72] Our group has recently expanded on this work with $[Rh(COD)Cl]_2$ as the catalyst rather than Pd(dppf)Cl_2. This is beneficial for the selective borylation of the C-I bond in heteroarenes (e.g. iodobromothiophenes).[73] The chemo- and regioselectivity of these transition metal catalysed borylation reactions is ideal for monomer synthesis.

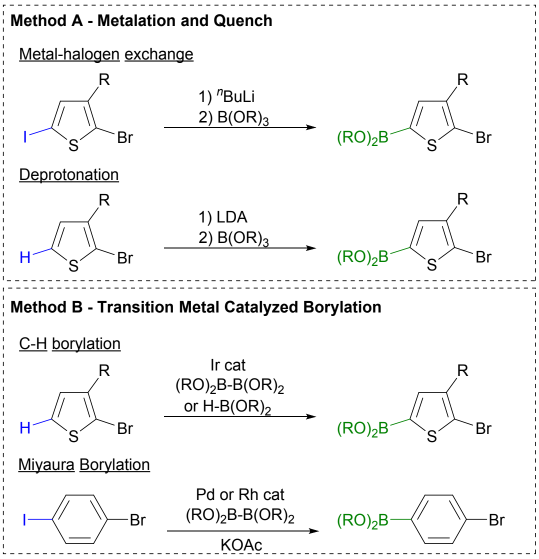


Fig. 3. Common methods used to synthesize halogenated aryl boronic esters. Abbreviations nBuLi = *n*-butyllithium and KOAc = potassium acetate. Generic borate esters are represented as $B(OR)_3$ and diboron reagents as $(RO)_2B$-$B(OR)_2$.

MECHANISTIC CONSIDERATIONS FOR SUZUKI-MIYAURA CTP

A cross-coupling polymerization proceeds via oxidative addition, transmetalation, and reductive elimination to build the polymer chain (Fig. 1). Coordination of the M(0) catalyst to the π-system of the growing chain during polymerization has been proposed as the key intermediate which brings about a controlled polymerization.[26-30] This proposed intermediate is consistent with NMR studies that identify a Ni π-complex as the first irreversible step in Kumada cross-coupling.[74] The metal polymer π-complex, which forms after each reductive elimination event, promotes intramolecular oxidative addition of the halide end-group, such that the catalyst acts effectively as an initiator for the reaction (Fig. 1). Though the π-complex has not been directly observed during polymerization, studies have provided indirect support for this proposed intermediate.[75-77]

CTP has some of the characteristics of a living polymerization including: linear increase of molecular weight with conversion, narrow molecular weight distributions, well defined end-groups, and reactive chain ends that can be used to synthesize block copolymers.[17-24] Dissociation of the catalyst from the growing chain, catalyst disproportionation, or loss of ancillary ligand from the metal will result in deviations from ideal behaviour.[17-24] The active catalyst in these reactions is typically a Ni or Pd complex with an electron-rich ancillary ligand (L) such as a phosphine, diphosphine, or N-heterocyclic carbene (Fig. 1). This metal species must promote efficient cross-coupling and formation of the π-complex to promote a chain-growth mechanism. Computational efforts have helped provide additional insight into the metal polymer π-complex.[78-81] Further efforts with computation are likely to help predict catalyst and monomer pairings for future exploration.

The key difference between Kumada and Suzuki-Miyaura cross-coupling is the transmetalation step. In Kumada coupling, which is used most often in CTP, no additives are needed to transfer the organic group to the metal catalyst. However, Suzuki-Miyaura coupling requires inorganic bases and water to promote effective transfer of the organic group to the metal. In THF with base and water present, the Suzuki-Miyaura reaction is typically biphasic.[82] The aqueous phase acts as a reservoir for the inorganic base, with the coupling reaction proceeding in the organic phase. Importantly, transmetalation is proposed to be the rate-determining step in Suzuki-Miyaura reactions when oxidative addition is fast (e.g. with Ar-Br and Ar-I substrates).[83] Our analysis of the rate-limiting step in Ni-catalyzed Suzuki-Miyaura CTP is consistent with this proposal, where the catalyst resting state is the $L_nM(Ar)Br$ complex (Fig. 1).[41] Importantly, the rate-determining step may change depending on the electrophile employed in the reaction (e.g. Ar-Cl).

The specific role of the base in transmetalation has been debated, with the two proposed pathways shown in Fig. 4. The oxo-metal pathway proceeds by ligand exchange of the halide for hydroxide in the oxidatively added catalyst. The Lewis acidic boron then coordinates to the M-OH to transfer the aryl group to the metal (Fig. 4, top). Alternatively, the boronate pathway proceeds by transmetalation of an anionic (hydroxy)borate with the metal halide bond (Fig. 4, bottom). The oxo-metal route has been identified as the kinetically favoured pathway in a number of mechanistic investigations.[83-87] Denmark has also demonstrated that both boronic acids and esters can participate in the transmetalation step.[86]

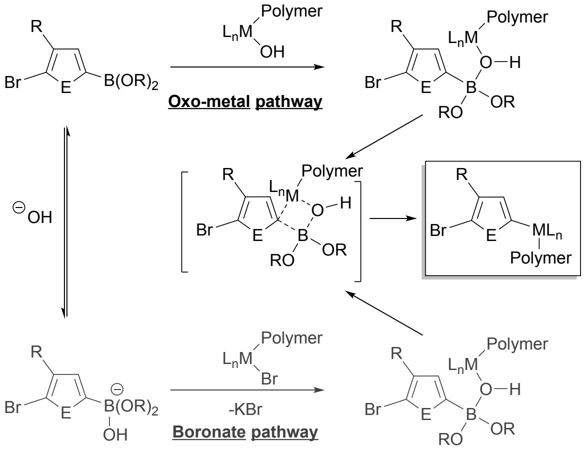


Fig. 4. Simplified proposed mechanism of transmetalation in Suzuki-Miyaura coupling via the "oxo-metal" and "boronate" pathways with the 3-substituted heteroarene monomer (E = element).[82] Metal-hydroxo complexes can be dimeric,[83-87] though not drawn explicitly here.

A variety of inorganic bases can promote transfer of the organic group to the metal. Phase-transfer agents such as 18-crown-6 have also been used in polymerization to aid in extraction of the base into the organic phase.[25, 47, 50, 59] The amount of base used in polymerizations can span a wide range (1 - 20 equivs), which can impact initiation and polymerization rates.[25, 31-59] Jutand and coworkers demonstrated that the base

(OH⁻ or F⁻) plays three roles in Suzuki-Miyaura coupling.[84, 88] First, it enables formation of the M–OH or M–F to promote transmetalation via the oxo-metal pathway. Second, it facilitates reductive elimination through formation of a 5-coordinate metal intermediate. Finally, it also behaves as an antagonist as it retards catalytic turnover by conversion of the boronic ester to an anionic boronate. This anionic boronate is linked with monomer stability, another key consideration for polymerization which is discussed in a later section. Ultimately, the optimal ratios of base, water, and solvent will depend on the organoboron monomer and catalyst. These parameters should be optimized with novel monomers and catalysts.

ORGANOBORONS FOR SM CTP

A small selection of boron derivatives have been used in SM CTP as shown at the top of Fig. 5, with boronic esters being the most common (particularly Bpin). Boronic esters are often isolated using column chromatography and used directly in polymerization. Remarkably, choice of the OR groups on the boron centre can impact the rate of transmetalation. Denmark has noted that 4-fluorophenylboronic acid couples ~4 times faster than the corresponding pinacol ester, and ~4 times slower than its catechol counterpart.[86] This result highlights how the boron group can potentially be used as a tool in polymerization.[86]

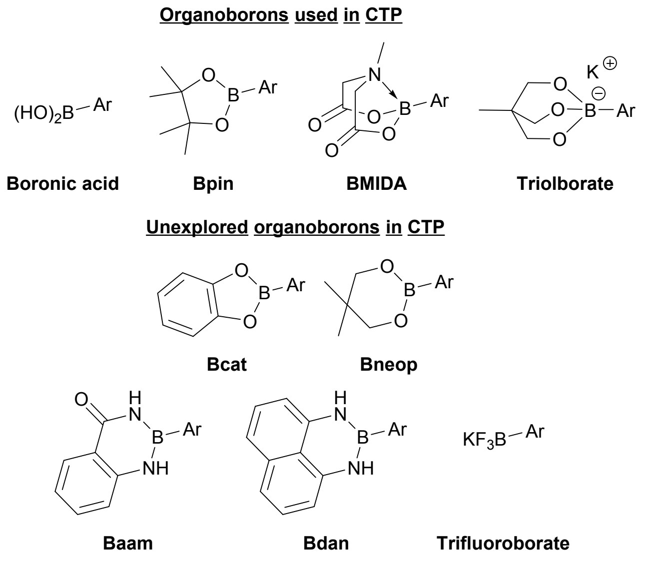


Fig. 5. Organoborons that have been reported in the literature for small molecule cross-coupling. The top group of derivatives have been employed in SM CTP and the bottom group has been used in small molecule coupling, but not in polymerization to date.

Masking groups have also become important derivatives for Suzuki-Miyaura polymerization. A well-known class of masked borons are derived from N-methyliminodiacetic acid (BMIDA in Fig. 5).[89] MIDA boronates are typically air-stable, crystalline solids making them highly attractive in synthesis.[90] Though the MIDA boronate cannot be used directly in coupling due to the tetrahedral boron center, it is hydrolysed to the corresponding boronic acid under basic conditions, so it can still be used directly in Suzuki-Miyaura coupling (Fig. 6).[89] This unmasking strategy was first utilized in polythiophene synthesis by Ingleson and coworkers with M_n values approaching 15 kg/mol, albeit with large dispersity ($Đ$ = 3.5).[91] Choi and coworkers then reported a controlled polymerization of a thiophene MIDA boronate with good control over M_n and dispersity (17.6 kg/mol, $Đ$ = 1.16).[31, 39]

Choi and coworkers also exploited reactivity differences between Bpin and BMIDA moieties to build block copolymers by combination of two monomers in one pot (Fig. 6). The Bpin monomer is consumed first due to its higher reactivity, while the BMIDA monomer hydrolyses slowly, and is consumed after the Bpin monomer. This experiment represents a unique entry to block copolymers for SM CTP, where monomer reactivity can be tuned by identity of the boron group. One-pot block copolymerization of more complex monomer scaffolds could be possible using this strategy.

Pre-activated anionic boronates such as the triolborate are bench stable boron complexes that are highly efficient coupling partners for Suzuki-Miyaura reactions (Fig. 5). These moieties can participate in coupling without base present in the reaction mixture,[92] which is highly beneficial given the intricate role of hydroxide in most coupling reactions. SM CTP using triolborates has been reported for the synthesis of P3HT and polyfluorene.[32, 50] High molecular weight polyfluorenes were prepared and graft copolymers with polystyrene could be produced.[32] The triolborate monomer was beneficial to reduce the water loading during the graft copolymerization, as the polystyrene is not soluble in this solvent. [32]

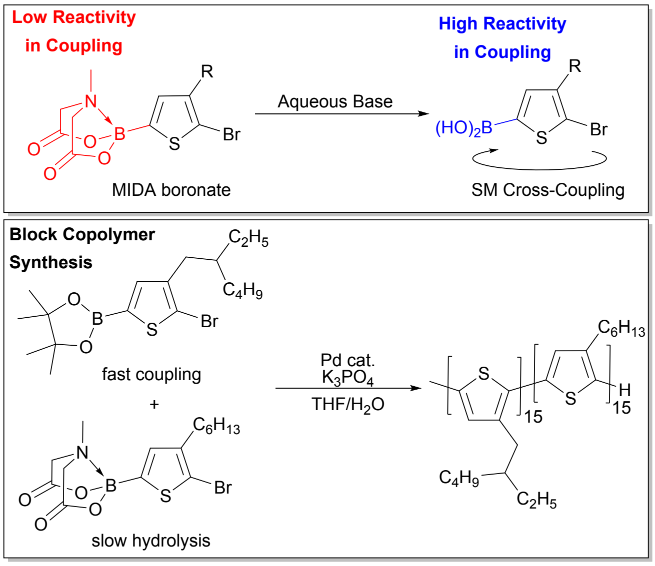


Fig. 6. Top – Unmasking of the MIDA boronate in the presence of base to form the corresponding boronic acid. Bottom - One-pot synthesis of P3EHT-b-P3HT from two monomers which hydrolyse at different rates.

Many other organoborons should be of interest for SM CTP.[90] A few of the possibilities are shown in Fig. 5, though this is by no means exhaustive. Catechol and neopentyl glycol esters (e.g. Bcat, Bneop) have not been used in polymerization, though these have been employed in small molecule cross-coupling.[90] Diaminonaphthalene boronamides[93, 94] (Bdan) and anthranilamide borons (Baam)[95, 96] are both known as remarkably stable organoboron moieties. For the most part these have only been used as protecting groups, though recent work has shown some of these derivatives can participate in coupling directly.[97, 98] The trifluoroborates salts (BF_3K) have not yet been explored for chain-growth polymerizations,[99] but these derivatives are typically compatible with environmentally friendly solvents such as water and alcohol. Pairing trifluoroborates with water-soluble conjugated polymers[100] could be an exciting new strategy to build polyaromatics in environmentally benign media.

PROTODEBORONATION IN SM CTP

Monomer stability is an important consideration in Suzuki-Miyaura polymerization (Fig. 7). Protodeboronation, where a C-B bond is cleaved to form a C-H bond, can occur during coupling.[101-104] This monomer deactivation proceeds from the hydroxyboronate as shown in Fig. 7. The identity of the aromatic ring, the substituents appended to the ring, and the substitution pattern of groups, all impact the rate of protodeboronation.[101-104] To better illustrate this, one can compare the half-lives of a few aryl boronic acids.[101, 102] For example, 2-thienylboronic acid protodeboronates much faster ($t_{1/2}$ < 2 h) than phenyl boronic acid ($t_{1/2}$ ~ 6 months) at a pH of 13 in 1:1 H_2O:1,4-dioxane at 70 °C. Substituents on the phenyl ring and in particular, *ortho*-substituents impact organoboron stability as 4-fluorophenylboronic acid, 2-fluorophenylboronic acid and 2,6-difluorophenylboronic acid have half-lives of 4 months, 19 h, and 5 s respectively (at pH 13 in 1:1 H_2O:dioxane at 70 °C).[101]

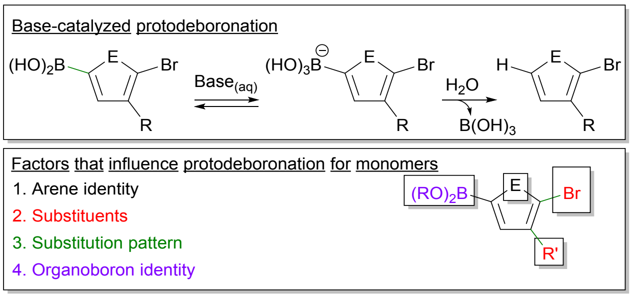


Fig. 7. Factors which impact protodeboronation of arylboronic acids.

Monomers for SM CTP are typically comprised of an aromatic ring bearing a boronic ester, a halide and at least one solubilizing group (Fig. 7). Heterocyclic rings are common building blocks for conjugated polymers, so protodeboronation will be a larger concern with these derivatives. The halogen, which is required for polymerization, will also accelerate this side reaction.[101, 102] More detailed studies are needed on protodeboronation of Suzuki-type monomers used in CTP, especially since these monomers often have boronic esters as opposed to boronic acids which will likely impact the rate of this side reaction. Empirically, we have noted adjusting base strength can help lower the rate of this side reaction as isolated yields of ester-functionalized thiophenes and furans were increased when using CsF rather than K_3PO_4.[35, 46] Regardless, protodeboronation remains a challenging aspect of cross-coupling for unstable boronic acids and esters.[101, 102]

SM CTP EXAMPLES WITH PALLADIUM AND NICKEL CATALYSTS

For a chain-growth mechanism to be operative, a catalyst must promote efficient coupling as well as effective π-complexation to the growing polymer chain. As the electronic properties of conjugated polymers are influenced by the aromatic repeat unit (and by the choice of side-groups), the metal catalyst is critical to achieving a controlled polymerization. Fortunately, Suzuki-Miyaura coupling has been catalysed by nickel and palladium complexes, which ensures the steric/electronic parameters of the catalyst can be easily modulated.

PRECATALYST SELECTION

Formation of the active M(0) catalyst for polymerization can be accomplished from a variety of M(II) precatalysts or by simply combining a M(0) precursor with the desired ligand.[25, 31-48, 50-59] Precatalyst activation is critical in CTP, as this initiation event influences the molecular weight distribution of the final polymer.[105, 106] In the top of Fig. 8, simplified catalyst structures are shown where the metal, the ancillary ligand, and the reactive ligands are represented by M, L and X/X' respectively. Palladacycle precatalysts that have been developed for small molecule coupling[107, 108] have also been used to prepare SM CTP catalysts (Fig. 8).[31, 33, 39, 40, 44, 45] Recent advances with allyl or indenyl precatalysts may prove beneficial for SM CTP in the future.[109-112]

The externally initiated catalysts with a ligand, a halide and an arene (LM(Ar)Br) produce well-defined chain-ends and narrow molar mass distributions in SM CTP. These soluble catalysts are rapidly converted to the active M(0) catalyst as only one transmetalation and reductive elimination is required to enter the catalytic cycle.[25] These are the most common catalysts used in SM CTP. Interestingly they are often targeted even from palladacycle precatalysts.[31, 33, 39, 40]

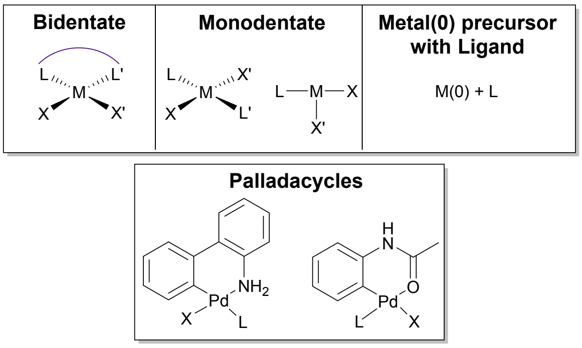


Fig. 8. General scheme of precatalysts for Suzuki-Miyaura cross-coupling polymerization. The metal can be Ni or Pd, the ancillary ligand (L) can be a phosphine, diphosphine or N-heterocyclic carbene and the X /X' groups can be acetates, halides, tosylate, mesylate or a combination of an aryl group and a halide.

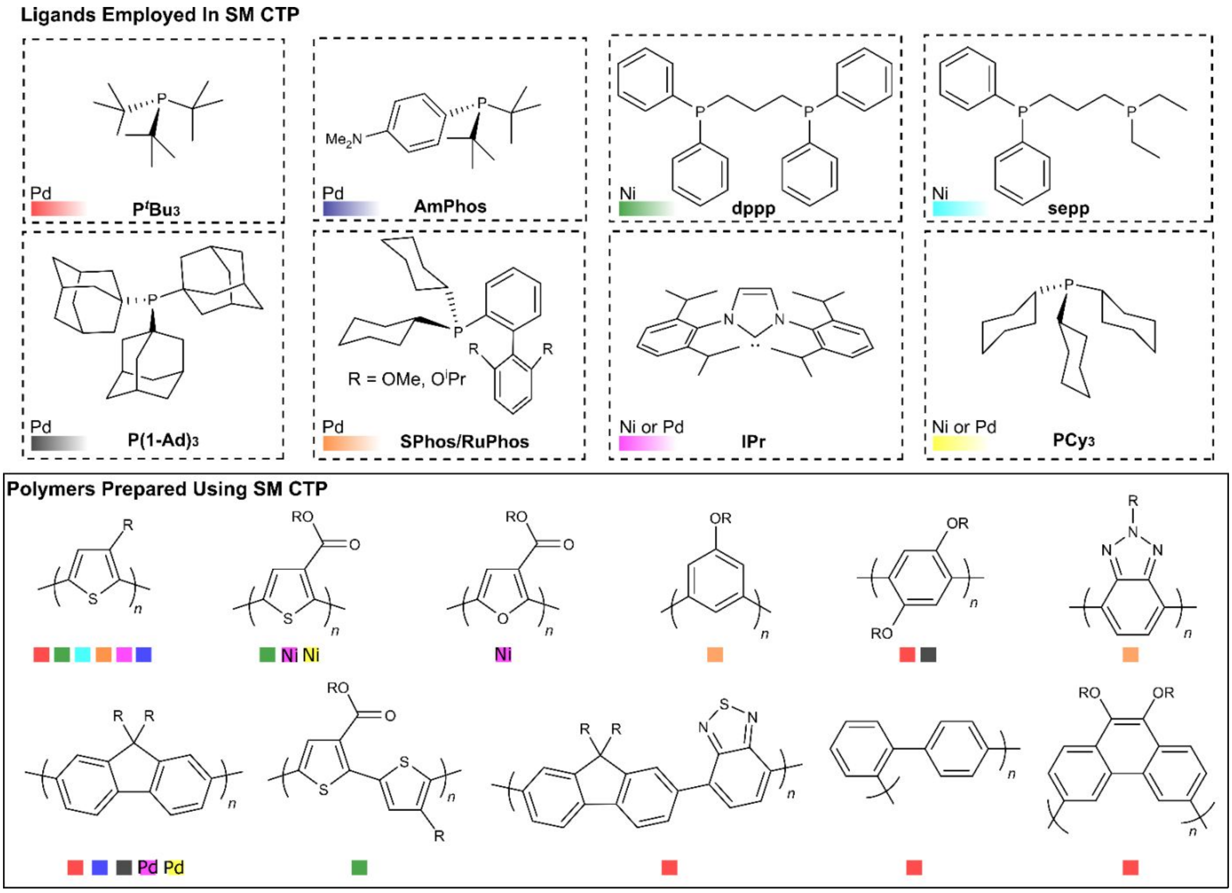


Fig. 9. Top – Ligands used for Suzuki-Miyaura cross-coupling polymerization. Ligand abbreviations: P^tBu_3 = tri-*tert*-butylphosphine, P(1-Ad)$_3$ = tri-1-adamantylphosphine, AmPhos = di-*tert*-butyl(4-dimethylaminophenyl)phosphine, SPhos = 2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, RuPhos = 2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl, dppp = 1,3-diphenylphosphinopropane, IPr = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene, sepp = 1,3-splitdiethyldiphenylphosphinopropane, and PCy$_3$ = tricyclohexylphosphine. Bottom – Homopolymers prepared using SM CTP. For some of the polymers shown, chain-growth character was noted during polymerization, but may not have been classified as SM CTP.

ANCILLARY LIGAND SELECTION

Another important feature to consider when choosing a catalyst for SM CTP is the ancillary ligand. The ligands that have employed in SM CTP to date are illustrated in Fig. 9. The figure is organized with ligands shown on top and homopolymers on bottom. Ligands have been paired with either Pd or Ni (which is noted), and the Fig. is colour coded to reference pairings of catalysts and polymers. Generally, electron rich monophosphines have been used in most SM CTP polymerizations, where the active catalyst is a 12 electron L-Pd(0) complex. Geng and coworkers also reported on an NHC-Pd for thiophene and fluorene polymerization (Pink Squares, Fig. 9).[51]

The most common catalyst system used in SM CTP is $^tBu_3P$–Pd (Red Squares, Fig. 9) with a range of precatalyst variations. This catalyst system has been successful for the controlled polymerization of polythiophenes, polyfluorenes, and various polyphenylenes.[25, 36-38, 42, 43, 45, 48-50, 52-55, 57-59] The success of $^tBu_3P$–Pd has led to investigations to prepare more exotic polymers such as poly(3,6-phenanthrene),[54] poly(fluorene-*alt*-benzothiadiazole),[58] and poly(pyridyl-*alt*-thiophene).[113] For poly(fluorene-*alt*-benzothiadiazole), Huck and coworkers were able to bring about controlled chain-growth polymerization of this large monomer system, though molecular weights were modest (3 - 7.3 kg/mol). Though the phenanthrene and pyridyl-thiophene monomers produced some promising initial results, chain-growth was limited for both systems.[54, 113] Together, these studies highlight how monomer changes can impact controlled polymerization behaviour.

Hu and coworkers have recently demonstrated that the electron releasing bulky (P(1-Ad)$_3$) (Grey Squares, Fig. 9), can be combined with Pd to prepare polyfluorenes, poly(*p*-phenylenes) and poly(*m*-phenylenes) with modest molecular weights and narrow molecular weight distributions (M_n = 2.5 – 11.4 kg/mol, $Đ$ = 1.16).[44] Yokozawa and coworkers discovered that AmPhos (Blue Squares, Fig. 9) can be employed to prepare polythiophenes and polyfluorenes. Interestingly, Yokozawa noted that block copolymers of thiophene and fluorene could be prepared irrespective of which monomer was polymerized first. Triarylamine-based Pd complexes with PEt$_3$, PCy$_3$, and P(*o*-tolyl)$_3$ ligands have also been used to prepare polyfluorenes using SM CTP (Yellow Squares, Fig. 9).[47] The authors noted that the Cy$_3$P–Pd and (*o*-tolyl)$_3$P–Pd produced chain-growth behaviour to some extent.[47]

Recently, dialkylbiarylphosphine palladium catalysts have been explored in SM CTP (Orange Squares, Fig. 9). These catalysts are highly modular, with a rich history in Suzuki-Miyaura cross-coupling.[114] The electron releasing alkyl groups on the phosphine ensure facile oxidative addition of aryl halides to Pd and the biaryl substituent promotes rapid reductive elimination around the metal center. The tunability of the alkyl groups and biaryl structure enables precise fine-tuning of the steric and electronic parameters of the phosphine, to optimize for rapid coupling of a wide range of organoborons using Pd. In CTP, two dialkylbiaryl ligands have received considerable attention, namely SPhos and RuPhos.[31, 33, 39, 69, 115, 116] The first example of these ligands being used in SM CTP of 3-alkylthiophenes appeared in 2006 from Higgins.[69] Though chain-growth polymerization was not the focus of that work, it is clear from the data obtained that the obtained P3HT was highly regioregular, with a narrow molecular weight distribution. Schluter also noted that the polymerization of *m*-phenylene organoboron monomers with an SPhosPd catalyst showed characteristics of a chain-growth polymerization.[56]

Following this work, Choi recently described an approach to synthesize poly(3-alkylthiophenes) via polymerization of MIDA boronates with externally initiated RuPhos and SPhos catalysts.[31, 39] Analysis of the reaction using ^{31}P NMR spectroscopy revealed fast initiation kinetics. In addition, the authors noted that additional equivalents of ligand in the reaction relative to catalyst were key to achieving a controlled polymerization. In our own work, we have also noted the importance of additional equivalents of phosphine and diphosphine in chain-growth polymerizations with both Pd and Ni.[33, 34, 41] Choi even noted that dialkylbiarylphosphines result in superior control as compared to P^tBu_3 in the polymerization of 3-alkylthiophenes.

Building from these reports, our group recently reported a chain-growth polymerization of benzotriazole.[33] SPhos, RuPhos, and DavePhos Pd catalysts were used to prepare polybenzotriazole with relatively narrow dispersities and high molecular weights under mild conditions.[33] In that work, we also noted that the benzotriazole monomer, which bears a pinacol boronic ester, partially hydrolysed during polymerization. In addition, a polybenzotriazole-poly(3-hexylthiophene) block copolymer could be synthesized by sequential addition of the benzotriazole and thiophene monomer. Polymerization of electronically distinct monomers can be challenging,[117] and speaks to the versatility of this ligand family for CTP.

Beyond Pd catalysts, Ni-mediated polymerizations are also of interest due to the low cost, relative abundance and exceptional reactivity of nickel catalysts for Suzuki-cross coupling.[118-121] Our group has shown NHC-Ni complexes (Pink Squares, Fig. 9) are highly effective for alkyl- and ester-functionalized thiophenes.[34, 41, 46] We have also noted that diphosphine catalysts can also be highly effective in 3-alkylthiophene polymerizations (Green/Light Blue Squares, Fig. 9) with fast reaction times and high molecular weights.[34, 41, 46]

In our work, we discovered how critical additional water was for fast turnover in Ni-catalysed SM CTP, and how water can lead to hydrolysis and deactivation of dihalide precatalysts.[41] Fortunately, the hydrolysis event was serendipitous, as it revealed the importance of added ligand in the chain-growth polymerization of thiophenes with diphosphine ligands. With both Ni(dppp) and Ni(sepp) catalysts, additional ligand in the reaction mixture was necessary to achieve good end-group fidelity and narrow dispersities in the polymerization of 3-alkylthiophene. Further analysis into the precise role of the additional ligand is needed, as additional ligand has been shown to be beneficial in palladium reactions as well.[31, 33, 40]

Future Opportunities & Challenges

Though the chain-growth polymerization of thiophene was reported over 15 years ago, synthesis of conjugated polymers by CTP is still centered on the polymerization of monomers such as thiophene and fluorene. The limited choice of aromatic monomers for chain-growth polymerization is, in part, a consequence of the limitations of conventional synthetic methods to make difunctional monomers. Organolithium and organomagnesium reagents are still common strategies to install boryl groups on arenes, but these approaches are not always compatible with complex arene scaffolds. The extensive exploration of arene borylation with transition metals should serve as inspiration to make novel organoboron monomers for CTP.[65-68]

The different borylation methods can offer difunctional monomers with a wide range of conjugated frameworks and perhaps enable preparation of well-defined polymers from ring systems that have been used in conjugated polymer devices (Fig. 10). As novel boron monomers are evaluated in CTP, an improved understanding of the detrimental effects of protodeboronation are needed. Monitoring loss of the boron group should be possible using NMR techniques, and it is anticipated this kind of information can be used to inform better practices for monomer design. Moreover, further exploration of the transmetalation step in SM CTP with different organoborons would be highly valuable for the community. Understanding how monomers transmetalate, and how different organoborons impact the rate, would provide valuable information to enable further improvements in polymerization.

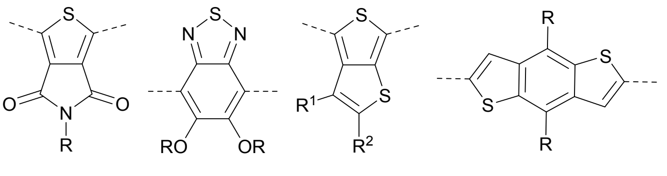


Fig. 10. Common building blocks that have rarely explored in CTP

One general challenge in the controlled synthesis of conjugated polymers is achieving high-molecular weight materials. Most SM CTP examples have a degree of polymerization (DP) less than 100, presumably due to a combination of issues with catalyst stability, undesirable side reactions, and polymer solubility. Realization of low dispersity, high-molecular weight polymers could be particularly relevant with respect to mechanical properties of aromatic polymers.[122] For example, Schluter noted that poly(*m*-phenylenes) of sufficient molecular weight are exceptional high T_g polymers,[123] and illustrated the importance of catalyst choice and initiation in SM CTP of *m*-phenylene organoboron monomers.[56] This study highlights the importance of matching catalyst, monomer and organoboron in any Suzuki-Miyaura polymerization.

Despite the higher complexity of SM CTP relative to Kumada-Corriu CTP, it remains one of the most popular and versatile cross-coupling reactions. Further advances in aromatic building block, organoboron moiety, and choice of catalyst are likely to lead to exciting advances in this field. Further insights into transmetalation and role of additives will pave the way to more diverse well-defined polymers.

Conflicts of interest

There are no conflicts to declare

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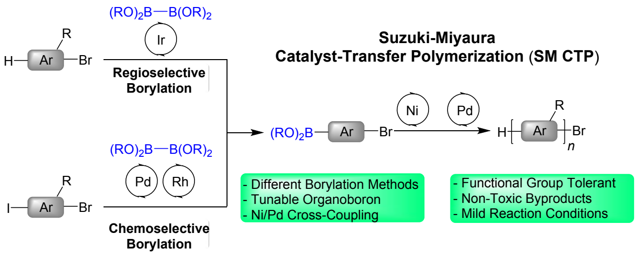

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