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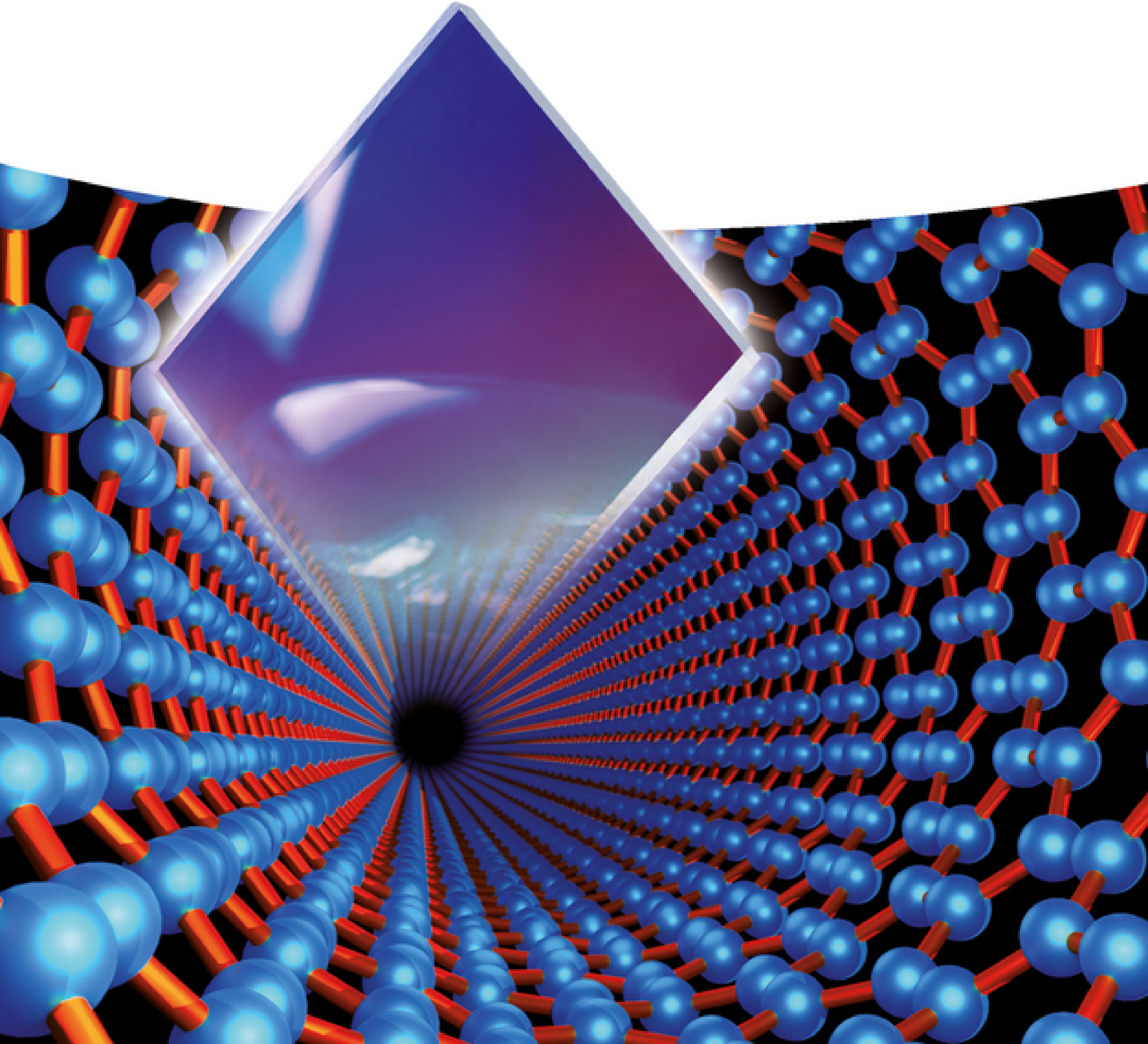
Synthetic Methods for Conjugated Polymer and Carbon Materials



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Edited by Mario Leclerc and Jean-Francois Morin

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1

Stille Polycondensation: A Versatile Synthetic Approach to Functional Polymers

Tianyue Zheng, Alexander M. Schneider, and Luping Yu

1.1 Introduction

The development of functional polymers is a very active research field that covers every aspects of our lives and has had huge impact on human society due to their applications in many cutting-edge technologies, such as energy conversion and storage, electronic devices, biotechnology, and health care, to name a few [1]. Scientists from different disciplines have invented numerous new materials for those purposes. Integral to these efforts is the development of efficient, versatile, and scalable synthesis techniques, which in turn enable the development of new functional materials. Thus, new synthetic methodologies are always a critical research topic that is actively pursued. A large number of recent advances can be cited to support this view, such as ring-opening metathesis polymerization (ROMP), atom transfer radical polymerization (ATRP, a type of "living" radical polymerization), and controlled Ziegler–Natta polymerization [2, 3]. Most recently, polycondensations based on transition metal-catalyzed CC bond formation reactions have emerged as important methodologies for synthesis of electro-optic materials containing large systems. These reactions include Stille, Suzuki, Negishi, Heck, and so on [4–7]. The Stille reaction is one of the best methods for the synthesis of organic functional materials due to its excellent compatibility with various functional groups and high reaction yield.

The most attractive application of the Stille coupling reaction is in the synthesis of conjugated, polyaromatic semiconducting materials, which are an important class of materials for organic electronics. These materials exhibit good solubility in various solvents, which allows them to be fabricated into devices using inexpensive solution-phase printing techniques [8]. Over the past several decades, the development of semiconducting polymers has led to the advent of new technologies for numerous applications, ranging from organic light-emitting diodes (OLEDs), field effect transistor (FET), and organic photovoltaic (OPV) solar cells [7]. Among these semiconducting polymers, the majority of them, especially those containing thiophene moieties, can be synthesized via Stille polycondensation from-related monomers. These polymers bear a wide variety of functional groups and their emergence is enabled by the power and broad scope of the

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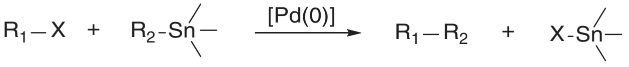
Stille polycondensation. This chapter summarizes recent progress in investigating the Stille polycondensation and its application to the development of functional materials.

1.1.1 History of the Stille Reaction (and Polycondensation)

The Stille coupling reaction refers to the reaction between an organostannane (also called *organotin*) and an organic electrophile in the presence of palladium catalyst to generate new C–C single bond (Scheme 1.1) .



$$R_1-X + R_2\text{-}Sn \xrightarrow{[Pd(0)]} R_1-R_2 + X\text{-}Sn$$

Scheme 1.1 The Stille coupling reaction scheme.

In 1976, Eaborn reported a Pd-catalyzed reaction using bis(tributyltin) to prepare aryltin compounds, where C–Sn bonds were formed (Scheme 1.2) [9]. Later, in 1977, Kosugi used a similar method to report the first C–C bond formation from cross-coupling between acyl chlorides or aryl halides and organostannanes (Scheme 1.3) [10–12]. These disclosures were considered the first examples of cross-coupling reactions between organostannanes and electrophilic partners.

$$ArBr + Bu_3SnSnBu_3 \xrightarrow{Pd(PPh_3)_4} ArSnBu_3 + ArAr + BrSnBu_3$$

Scheme 1.2 Synthesis of aryltin compounds by Eaborn *et al*. [9].

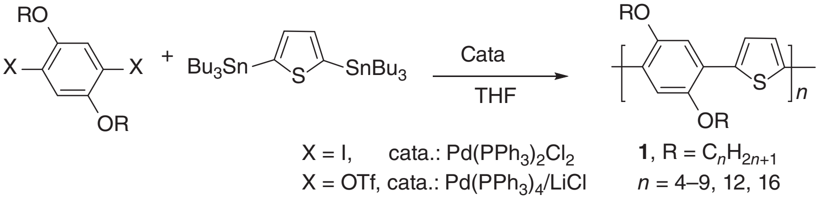
$$RCOCl + Bu_3SnR' \xrightarrow[\text{or } RhCl(PPh_3)_3]{Pd(PPh_3)_4} RCOR' + ClSnBu_3$$

$$ArX + Bu_3SnR' \xrightarrow{Pd(PPh_3)_4} ArR' + XSnBu_3$$

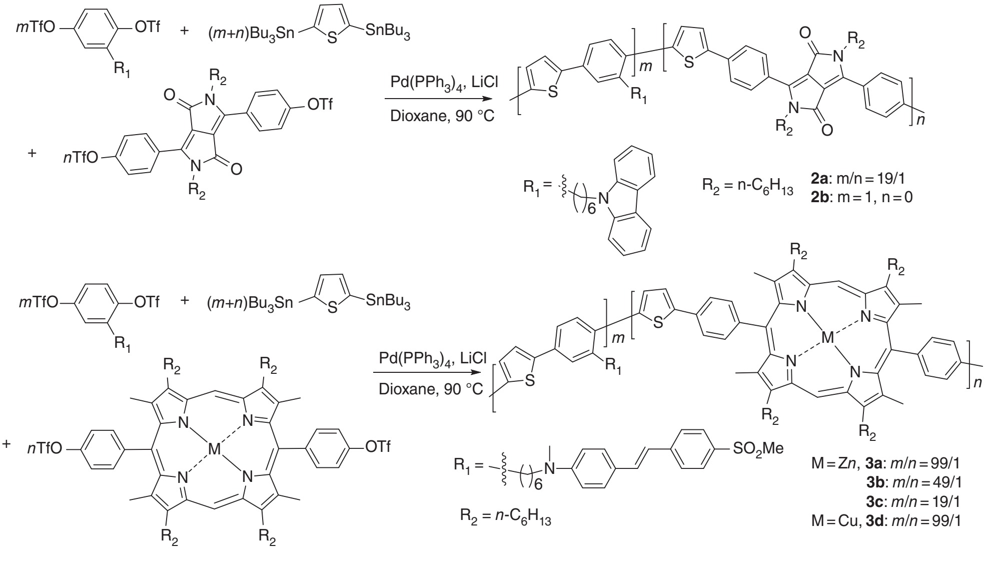
Scheme 1.3 Coupling of halides and organostannanes by Kosugi *et al*. [10–12].

Following these examples, John K. Stille carried out extensive studies on the reaction scope and mechanism beginning in 1978. The original report from Stille and coworkers involved the synthesis of ketones from acyl chlorides and organostannanes [13]. Following that, the general features of this reaction were revealed and it quickly became a standard method in organic synthesis and one of the most useful procedures for carbon–carbon bond formation, especially of sp^2-sp^2 C–C bonds. His major body of work was summarized in a very influential review in 1986 [13–15]. Together with the Suzuki reaction, a palladium-catalyzed cross-coupling of organoboranes and electrophiles, the Stille reaction is one of the most efficient methods for preparing functional materials, especially those containing extended conjugation systems that are linked by sp^2-sp^2 C–C bonds.

By incorporating a ditin compound and a difunctional electrophile, the Stille reaction was used to synthesize polymers as early as the 1980s and the early 1990s, when polycondensation between organo-ditin monomers and dihalide monomers was developed [7]. Yu and coworkers further developed this methodology, including reaction scope and conditions, for making high molecular weight heteroaromatic diblock copolymers in the early 1990s (Schemes 1.4 and 1.5) [16–18].


RO
X
X
OR
+
Bu3Sn
S
SnBu3
Cata
THF
RO
S
n
OR
X = I, cata.: Pd(PPh3)2Cl2
X = OTf, cata.: Pd(PPh3)4/LiCl
1, R = CnH2n+1
n = 4–9, 12, 16

Scheme 1.4 Synthesis of PPT by Stille polycondensation [16, 17].


mTfO
OTf
+
(m+n)Bu3Sn
S
SnBu3
R1
R2
O
N
OTf
+
nTfO
N
O
R2
Pd(PPh3)4, LiCl
Dioxane, 90 °C
S
m
R1
S
O
R2
N
N
R2
O
n
R1 =
6
N
R2 = n-C6H13
2a: m/n = 19/1
2b: m = 1, n = 0
mTfO
OTf
+
(m+n)Bu3Sn
S
SnBu3
R1
R2
R2
+
nTfO
N
N
M
N
N
OTf
R2
R2
Pd(PPh3)4, LiCl
Dioxane, 90 °C
S
m
R1
S
R2
R2
N
N
M
N
N
R2
R2
n
R1 =
6
N
SO2Me
R2 = n-C6H13
M = Zn, 3a: m/n = 99/1
3b: m/n = 49/1
3c: m/n = 19/1
M = Cu, 3d: m/n = 99/1

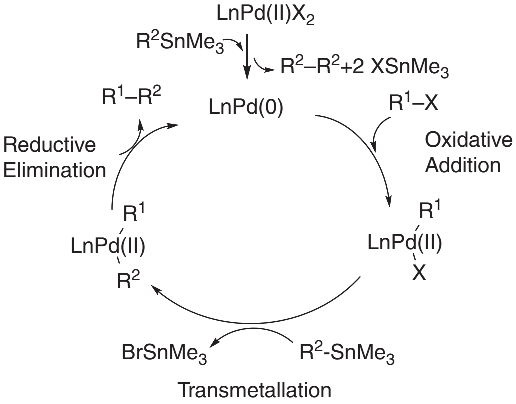
Scheme 1.5 Synthesis of PPTs with metalloporphyrin or pendent carbazole units [18].

1.2 Reaction Mechanism

1.2.1 Simplified Mechanism

The Stille reaction is a Pd(0)-catalyzed cross-coupling reaction. The active Pd(0) species may be generated from Pd(II) precursor that is reduced by the organostannane before entering the catalytic cycle. In his review article in 1986 [15], Stille proposed the reaction mechanism based on the study of coupling between benzoyl chloride and tributyl(phenyl)stannane with Pd(Bn)Cl$(PPh_3)_2$ (PPh_3 = triphenylphosphine) as the catalyst. The proposed mechanism is similar to other Pd(0)-mediated cross-coupling reactions, in which the PdL_2 (L = PPh_3) complex was assumed to be the active catalytic species. The PdL_2 undergoes oxidative addition with organic electrophile R^1-X to form

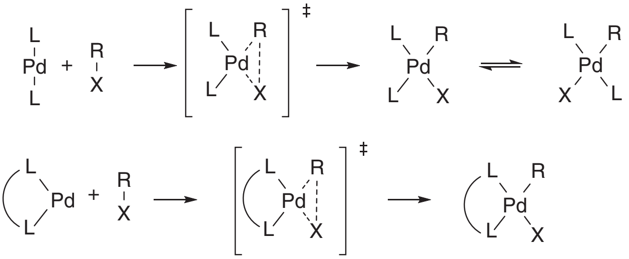
R^1PdL_2X, which then undergoes a slow transmetallation with organostannane R^2SnMe_3 to form $R^1PdL_2R^2$, followed by a reductive elimination step to give the product R^1-R^2 and regenerate the PdL_2 active species. A general feature of this mechanism is that a *trans–cis* isomerization step is needed for the ensued reductive elimination. Though this mechanism (Scheme 1.6) was generally accepted by the research community, more extensive investigation revealed more complexity of the mechanism. Espinet and coworkers have written in-depth reviews of the mechanistic study of the Stille reaction in 2004 [19] and most recently in 2015 [20]. It was shown that the actual mechanism may vary according to different reaction conditions, including catalyst, ligands, solvents, and additives. There is no simple answer to the actual mechanism and thus is referred as the *mechanistic black box* [19]. In the three major steps of the mechanism, the oxidative addition and reductive elimination steps are extensively studied and relatively well understood, but the transmetallation step is more complicated and not well understood.



Scheme 1.6 A simplified mechanism for Stille coupling [7, 19].

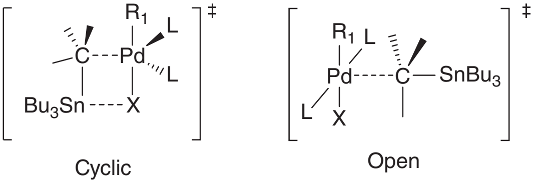
For halides with a $C(sp^3)$–X bond, the oxidative addition of R–X to Pd(0) is usually a bimolecular reaction (S_N2) and the configuration of product will be affected by the choice of different solvents. For $C(sp^2)$–X, this step is considered to go through a three-center transition state between the electrophile R–X and the active $Pd(0)L_2$ (L = ligand) to give a kinetic product of *cis*-$[Pd(II)RXL_2]$ complex, which can isomerize to the more thermodynamically stable *trans*-$[PdRXL_2]$ complex [19]. This *cis*-to *trans*-isomerization is usually fast; very often only the *trans*-complex is found. However, with bidentate ligands to stabilize the intermediate, the *cis* complex may be observed (Scheme 1.7). For example, in the reaction of ArOTf (Ar = C_6F_5, $C_6Cl_2F_3$) and $RSnBu_3$ (R = vinyl), Espinet and coworkers were able to observe the *cis* complexes [(dppe)Pd(Ar)(OTf)] (dppe = 1,2-bis(diphenylphosphino)ethane), which were stable in the solid state and fully characterized by nuclear magnetic resonance (NMR) spectroscopies [21]. Milstein and coworkers studied the mechanism of the oxidative addition of chlorobenzene to $Pd(dippp)_2$ (dippp = 1,3-bis(diisopropylphosphanyl)propane) in dioxane [22]. They monitored the intermediates by ^{31}P NMR and found that the *cis*-(dippp)Pd(Ph)Cl and *trans*-(η^1-dippp)$_2$Pd(Ph)Cl are formed in parallel pathways.

While in equilibrium with each other, the *cis*-complex is favored both kinetically and thermodynamically.



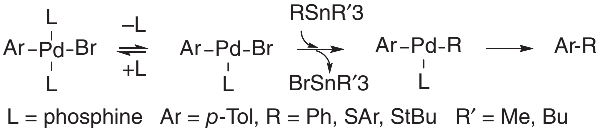
Scheme 1.7 Formation of *cis* complex and *cis–trans* isomerization [19]. L = ligand. (Adapted with permission from [19]. Copyright 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

The major difference between the Stille reaction and other similar Pd-catalyzed cross-coupling reactions is in the transmetallation step. During the transmetallation step, the organostannanes interact with the Pd center, resulting in Sn–C bond cleavage and Pd–C bond formation. Unlike in other modern Pd-catalyzed coupling reactions, the nature of the Sn–C bond is neither as strong nor as polar as other metal–carbon bonds, such as B–C, Zn–C, and Mg–C bonds. Espinet and Echavarren point out that the transmetallation step in the Stille reaction involves the electrophilic cleavage of Sn–C bond (S_E2) by the Pd(II) complex (from oxidative addition), which could also be viewed as a ligand substitution (S_N2) on the Pd(II) complex [19]. These complexes are usually 16-electron, square planar, tetracoordinated, and can experience ligand substitution via two possible pathways. One pathway is dissociative, which would involve a 14-electron, T-shaped intermediate with substitution being determined by the ligand with the highest *trans* influence that weakens the bond *trans* to it. The other is associative, which would involve an 18-electron, trigonal bipyramidal intermediate with substitution being determined by the ligand with the highest *trans* effect that leads the lowest energy transition state [23]. The solvent could play a role in this step, by assisting the ligand substitution or serving as ligand itself, such as THF or DMF [24, 25]. For the intermediate in the electrophilic cleavage process, both an open and cyclic (Scheme 1.8) transition states are possibilities, which have been proposed to explain this (S_E2) step. Stille considered this step to involve an open transition state from his studies on the $[Pd(Bn)Cl(PPh_3)_2]$-catalyzed coupling of benzoyl chloride with (S)-PhCHDSnBu3 [15, 28], which explains the fact that the transmetallation step can be very fast and that the inversion configuration of the alpha carbon sometimes occurs. Espinet and coworkers also reported an open transition state in the coupling of organotriflates, again using triphenylarsine ($AsPh_3$) as ligand [26]. However, with the same ligand but organohalide substrate, Espinet and coworkers reported that the *trans* complex reacts with organostannane through a cyclic transition state with release of ligand [27], which explains the inverse dependence on the concentration of ligand on the reaction rate [15, 23]. All of these findings demonstrate the complexity of the transmetallation step, which may go through different pathways according to different reaction conditions.



Scheme 1.8 Cyclic and open transition states [26, 27].

Reductive elimination leads to formation of the final product and regenerates the active Pd(0) species into the catalytic cycle. Before the formation of the coupled product from the transmetallation intermediate, a *trans*- to *cis*-isomerization places the coupling partners in *cis*-position to each other [15]. A three-coordinate, T-shaped 14-electron complex resulting from ligand dissociation has also been proposed to be the intermediate [15, 19, 23]. For example, Hartwig and coworkers reported the formation of 14-electron ArPdXL ($L = PPh_3$) complexes by dissociation of one ligand L from 16-electron *trans*-$ArPdXL_2$ complexes (Scheme 1.9) [29]. The ArPdXL complexes then react with organostannane to generate the ArPdRL complexes, which then undergo a fast reductive elimination to produce the Ar-R product. The rate of the reductive elimination step is usually fast, but might be slow when allyl groups or chelating ligands are involved [30].

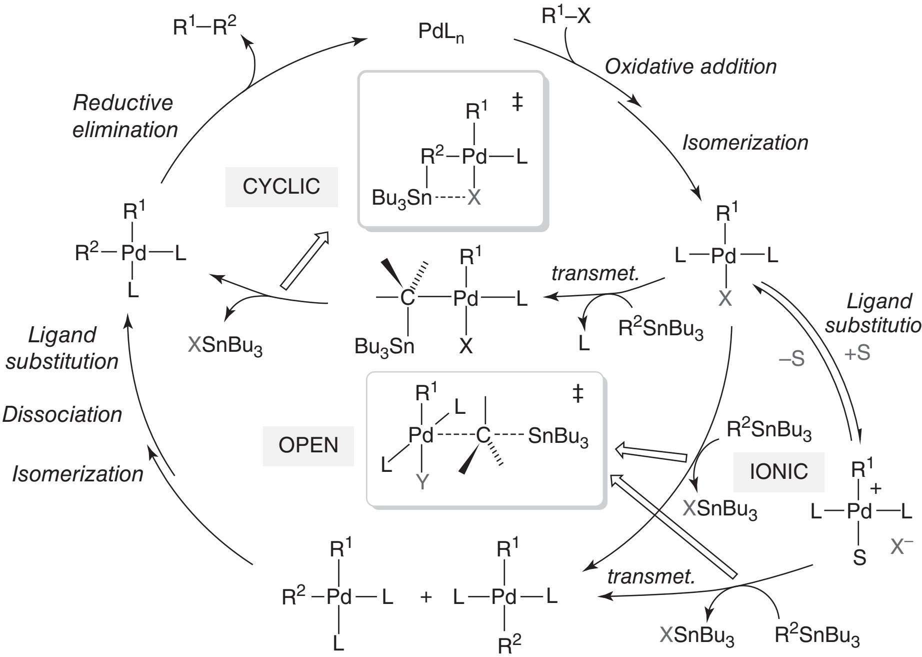


Scheme 1.9 A ligand dissociation to form a T-shaped complex [29].

Taking this knowledge together, a more complicated mechanism has been proposed by Espinet and coworkers (Scheme 1.10) [20]. In this mechanism, in addition to the regular three major steps, more details about the configuration of intermediate species have been added, taking into account the effect of ligands, solvents, and so on. This more detailed mechanism may give clues to the nature of side reactions, which could affect the structure of resulting polymers. A more detailed understanding of reaction mechanism under proper conditions is crucial to synthesize high-quality polymers. This point will be further illustrated in the later section of this chapter.

1.3 Reaction Conditions

The Stille polycondensation reaction involves two types of monomers, an organodihalide (or organoditriflate) and an organodistannane. Typically, diiodo monomers are more reactive than dibromo compounds, and dichlorides are the least reactive primarily due to their low reactivity in the oxidative addition step. However, while organochlorides can be activated in the synthesis of small molecules by using special catalyst systems [31, 32], the examples of using chlorides to synthesize polymers are rare. In general, it has been found that the combination of electron-rich organotin compounds and


R^1–R^2
PdL_n
R^1–X
Oxidative addition
Isomerization
Reductive elimination
CYCLIC
R^2–Pd–L
Bu_3Sn----X
transmet.
R^2SnBu_3
$XSnBu_3$
Bu_3Sn
Ligand substitution
Dissociation
Isomerization
OPEN
SnBu₃
IONIC
Ligand substitution
–S
+S
L–Pd–L
X^-
transmet.
$XSnBu_3$
R^2SnBu_3

Scheme 1.10 A more complex mechanism by Espinet *et al*. [20]. (Reprinted with permission from [20]. Copyright 2015 American Chemical Society.)

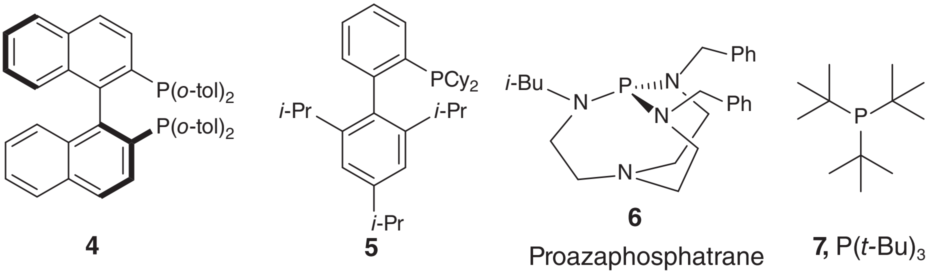
electron-deficient halide or triflate is beneficial for the synthesis of polymers exhibiting high molecular weight, as the electron-withdrawing groups may facilitate the oxidative addition step and the electron-rich organostannane favors the transmetallation step [7, 18].

1.3.1 Catalyst and Ligand

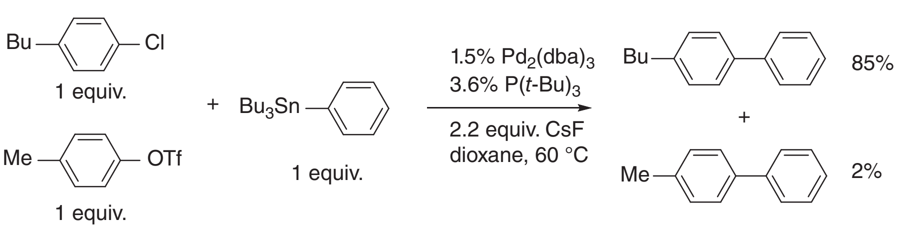
There are many palladium compounds that provide catalytic centers for the Stille reaction, including Pd(II) sources such as dichlorobis(triphenylphosphine)-palladium(II) [$PdCl_2(PPh_3)_2$] and palladium(II) acetate [$Pd(OAc)_2$] and Pd(0) sources such as tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and tris(dibenzylideneacetonyl) dipalladium(0) [$Pd_2(dba)_3$]. However, since the active species in the catalytic cycle is Pd(0) complex, a reducing agent will be needed if Pd(II) is added as the Pd source. For example, adding PPh_3 to $Pd(OAc)_2$ rapidly leads to the formation of [$Pd(OAc)_2(PPh_3)_2$] complex, which undergoes slow intramolecular reduction to form a Pd(0) complex [33]. $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ are the most frequently used, commercially available Pd catalysts for the Stille coupling, particularly for polymerization. $Pd(PPh_3)_4$ is reactive but is not stable against air or moisture, since the free PPh_3 can be easily oxidized by air to form triphenylphosphine oxide ($OPPh_3$), accordingly, $Pd_2(dba)_3$ is a more air-stable compound [7].

In addition to catalyst, the selection of ligand is also important in developing a robust catalytic system. Size and bulkiness, as well as electron-donating ability are some key parameters for ligands applied in the Stille reaction, in which phosphine ligands are the most commonly used ligands. For example, Yu and coworkers examined the reaction scope and conditions of Stille coupling for making high molecular weight conjugated copolymers [18]. It was found that catalyst concentration, different solvents and ligands, and structures of monomers could largely affect the polymerization. If a Pd(II) catalyst is used, a stoichiometric excess of the distannyl monomer is necessary to generate the Pd(0) complex and enhance the molecular weight of the resulting polymer. When different ligands are used, they also found that the molecular weight and dispersity of resulting polymers showed a trend as $AsPh_3 > P(2\text{-furyl})_3 > PPh_3$, indicating the reactivity of ligands.

Though they suffer from sensitivity to trace amounts of oxygen and moisture, the bulky electron-rich phosphine ligands are widely used in the Stille coupling reaction to extend the reaction scope to weakly active organotin and electrophile (**4**–**7**, Scheme 1.11) [34–37]. For example, proazaphosphatrane ligands (**6**) are very effective for enabling the coupling of aryl chlorides with a variety of organostannanes, including sterically hindered ones [36]. Fu and coworkers studied the bulky ligand $P(t\text{-Bu})_3$ (**7**), leading to the first effective Stille couplings of unactivated aryl chlorides with organostannanes [37]. This catalyst system was found to be highly effective; highly hindered tetrasubstituted biaryls may be produced, and the reaction can take place at room temperature in some cases. They also found the unexpected selectivity of Ar-Cl over Ar-OTf in the reaction involving ArCl/ArOTf or ClC_6H_4OTf when $P(t\text{-Bu})_3$ was used (Scheme 1.12).

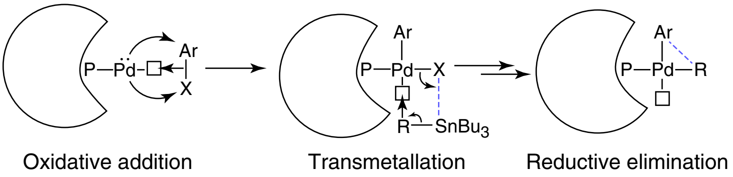


Scheme 1.11 The structure of some bulky phosphine ligands [34–37].



Scheme 1.12 Selectivity of ArCl over ArOTf in Stille coupling [37].

In fact, bulky phosphine ligands can assist every step in the catalytic cycle of the Stille reaction, as concluded by Espinet and coworkers in 2015 (Scheme 1.13) [20]. This is shown to be due to the stabilization of monoligated Pd intermediates due to the bulk of the phosphine ligand. At the oxidative addition step, the monoligated Pd(0) species facilitates nucleophilic attack at the Ar–X bond from the ligand free side; while the electron richness of the phosphine provides efficient electron back-donation to the σ^* Ar–X orbital, making the oxidative addition possible even for Ar–X bond with very low nucleophilicity. At the transmetallation step, a three-centered, 14-electron Pd(II) complex is stabilized by the ligand, beneficial for the nucleophilic attack by the organostannane, the Sn–C bond of which is of low polarity. Moreover, there is no need for *trans-* to *cis*-isomerization as in the case of a tetracoordinated Pd(II) complex, further inducing reductive elimination.



Scheme 1.13 Bulky ligands assist Stille coupling [20]. (Reprinted with permission from [20]. Copyright 2015 American Chemical Society.)

Another factor that is of no less importance is the electronic effect of the ligands. For example, the reduction of $[Pd(OAc)_2(PPh_3)_2]$ to Pd(0) complex will be enhanced by electron-withdrawing groups at the para position of the aryl groups on the phosphine [33]. $[Pd(dba)(AsPh_3)_2]$ was found to be more stable than analogous phosphine complexes $[Pd(dba)L_2]$ ($L = PPh_3$ or tri(2-furyl)phosphine (TFP)) due to its better electron-donating ability [38]. Farina and coworkers carried out a kinetic study of ligands with different donicities [39]. The coupling was between a model reaction system of iodobenzene and vinyltributyltin with $Pd_2(dba)_3$ as the palladium source, and the ligands studied were PPh_3, tri(*p*-anisyl)phosphine (TAP), TFP, and $AsPh_3$. It was shown that the coupling rate when using TFP and $AsPh_3$ is three and four orders of magnitude faster, respectively, than that of PPh_3. They rationalized this by the observed inhibitory effect on the cross-coupling of "strong" ligands, such as both PPh_3 and TAP. Stronger electron-donating ligands are also more easily oxidized, leading to formation of palladium black, deactivating the catalyst [7].

Since the pathways in the Stille coupling reaction may be influenced by the reaction conditions, it is crucial to carefully optimize the conditions in order to obtain desired products. For the Stille polycondensation, the reaction conditions are even more critical because in addition to high yield (thus high degree of polymerization), molecular weight distribution (characterized by dispersity) is important in controlling the quality of the resulting polymers. Selection of the correct set of conditions for Stille polycondensation is often a trial-and-error process when different monomer combinations are used [7]. The optimized catalytic systems for Stille polycondensation to achieve high-quality polymers may vary according to different target polymers.

1.3.2 Solvent

The solvent lays the foundation for the complex system of reaction conditions, which involves the interplay of many factors including catalyst, ligand, and additives, in addition to the solvent. The commonly used solvents for the Stille reaction include benzene, toluene, xylene, tetrahydrofuran (THF), dimethylfluoride (DMF), *N*-methylpyrrolidone (NMP), dioxane, and chloroform. They show a wide range of polarity, as well as solubility toward organic molecules. Choosing the appropriate solvent is critical for the reaction to be efficient, since the solvent not only solubilizes the organic reagents and intermediates, but also takes part in the catalytic cycle by serving as ligand to Pd catalyst or assisting in ligand dissociation. For example, Amatore and coworkers [25] studied the coupling of PhI with tributyl(vinyl)tin in DMF with $[Pd(dba)(AsPh_3)_2]$ as the catalyst, and found that the transmetallation takes place in the solvent-coordinated *trans*-$[PdPhI(AsPh_3)(DMF)]$ complex. Moreover, the solvent is found to affect the configuration (retention or inversion) of final product based on its polarity and coordinating ability [40, 41].

For polymerization, the demand of the solvent is even greater than those in small-molecule Stille coupling. Like in the small-molecule reaction, the solvent should dissolve the starting monomers, stabilize the catalyst, and maintain catalytic ability; for Stille polymerization, the solvent must also keep the growing polymer chain in solution as long as possible in order to obtain polymers with high molecular weight and narrow dispersity. For example, DMF is highly polar and can coordinate to the catalyst center as ligand; however, many polymers, especially conjugated polymers used in functional materials, show low solubility in DMF. On the contrary, polymers show good solubility in toluene, which is less polar and coordinating. Yu and coworkers found that mixed solvents such as toluene/DMF (typically in a 4 : 1 ratio) can provide benefits of each individual solvent while avoiding the disadvantages, enabling a good yield of high molecular weight polymers [18]. In addition, high-boiling solvents are always used for polymerization procedures, which often require high temperature to facilitate the polymerization reaction and increase the solubility of final polymers. As a result, toluene (b.p. = 110 °C) and chlorobenzene (b.p. = 131 °C) are often used in polymerization reactions. For example, Yan and coworkers used chlorobenzene as solvent to carry out the Stille polycondensation either in a conventional or a microwave-assisted conditions, with the reaction temperature reaching over 150 °C in the latter case [42].

1.3.3 Additive

The additives used in the Stille coupling are usually inorganic salts, such as LiCl, CsF, and CuI. The active species may be either anion or cation; the role additives play in the catalytic cycle can be varied according to different combinations of other reaction conditions, such as ligand and solvent.

LiCl is a common additive in the Stille coupling since the very early stages of this methodology. Prof. Stille found that LiCl could accelerate the coupling of organostannanes with vinyl and aryl triflates [43]. LiCl was proposed to transform the triflato complex into the more reactive chloro complex, which then enters the catalytic cycle as with other organic halides. Similar effects have been found with iodide and bromide salts as well [44, 45]. However, Farina and coworkers reported that the effect of LiCl additive was largely dependent on the reaction conditions, leading to both accelerating and retarding effects [39, 46]. For example, in the coupling of vinyl triflate and aryl tributylstanne with $Pd_2(dba)_3$ as the catalyst in NMP, LiCl was found to retard the reaction when TFP or PPh_3 was used as ligand, but accelerate the reaction for $AsPh_3$. Interestingly, they found that the accelerating effect was extremely significant when no additional ligand was added. Espinet and coworkers have also reported both positive and negative effects of LiCl [26]. LiCl favors the coupling of C_6F_5I with organostannanes when catalyzed by $[Pd(AsPh_3)_4]$ in THF, by promoting the oxidative addition step. By contrast, with the more nucleophilic $[Pd(PPh_3)_4]$, LiCl retards the reaction since the oxidative addition has already taken place without LiCl.

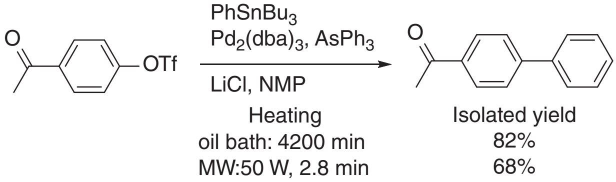
Some Lewis bases have been reported to facilitate Stille coupling by activating the organostannane. The most widely studied are fluoride salts, such as CsF, KF, and Bu_4NF, which can activate the tin compounds due to its fluorophilicity. It is suggested that a pentavalent tin complex with enhanced reactivity toward transmetallation be formed by the coordination of F^- anion to tin compounds [7]. Fu and coworkers used CsF to activate the organostannane, enabling its coupling with aryl chlorides, and particularly with aryl bromides at room temperature, in their Pd/P(t-Bu)$_3$ catalytic system [37]. Examples of applying other Lewis bases have also been reported. Besides fluoride salts, Fu and coworkers have studied the activating effect of bases such as Cs_2CO_3, NaOH, NaOMe, N(i-Pr)$_2$Et, and others in assisting the Stille coupling reaction [47]. In addition, amines can also be beneficial since that they can stabilize the tin compounds by coordination [48]. Finally, reagents such as $(n\text{-Bu})_4N^+Ph_2P(O)O^-$ can act as a “tributyltin scavenger” to improve cross-coupling efficiency, as reported by Liebeskind and coworkers [49].

Another important category of additive is CuIor other Cu(I) salts, which could enhance coupling of Stille reaction, referred as the *copper effect*. Liebeskind and coworkers studied the effect of addition of CuI on the kinetics of Pd-catalyzed coupling between iodobenzene and vinyltributyltin in dioxane [50]. They observed a >100-fold rate increase when a strong ligand, such as PPh_3, was used, but little effect when a soft ligand, such as $AsPh_3$, was used. They concluded that CuI is a scavenger for the free ligand, especially for strong ligands such as PPh_3, which is known to inhibit the transmetallation. In addition, they proposed that in very polar solvents such as NMP and in the absence of strong ligand, a Sn/Cu transmetallation takes place to yield an organocopper species, which more easily transmetallates to the Pd(II) complex. They also observed that a stoichiometric ratio of Pd:L:Cu = 1 : 4 : 2 (L = ligands) gave the best result with both enhanced reaction rate and yield. Further increase of CuI did not increase the rates significantly, but did decrease the yield, because too much CuI removes ligand from the active catalytic species and thus reduces the catalyst stability. Many other Cu(I) salts (CuX, X = Cl, Br, CN, thiophene-2-carboxylate (TC)) have been reported to have similar effect [51–53].

1.3.4 Temperature

Though heating is applied in common Stille reactions, the reaction temperature plays a less important role than the other parameters discussed above, which have largely determined the catalytic cycle already. While temperature generally does not change the reaction pathway, it affects the Stille coupling in many aspects. For example, increasing temperature may improve the reaction rate and perhaps the solubility of relative compounds, especially in the case of Stille polycondensations. On the contrary, possible side reactions and decomposition, if the reagents are not stable against heat, may also take place at higher temperatures. However, high temperature of over 100 °C is usually employed for polymerization. High temperature increases the solubility of the resulting polymers in the reaction mixture so as to keep polymers in solution as the chain grows as long as possible; therefore, high molecular weight and narrow dispersity can be achieved.

From a practical perspective, inexpensive reagents (such as the previously mentioned aryl chlorides), lower reaction temperature, and shorter reaction time are desirable to save resources. Fu and coworkers [37, 47] further developed a room-temperature Stille coupling for aryl bromides. Meanwhile, new ways of heating have been studied to increase heating efficiency. Microwave irradiation has been used in the Stille reaction to reduce the reaction time from hours or days, as in conventional oil bath reactions, to minutes, with only a limited reduction in yield (Scheme 1.14) [54]. This technique enables a more timely way of reaction condition optimization. In this case, energy is directly transferred to the reactants and the temperature of the whole volume rises simultaneously (bulk heating); while in an oil bath, the reaction mixture in contact with the vessel wall is heated first [55]. Microwave-assisted heating has been found to be useful in Stille polycondensation to produce polymers of better quality. For example, Bazan and coworkers reported the synthesis of a low band gap polymer for solar cell applications from dibromobenzothiadiazole and distannylated dithienosilole (DTS). The use of microwave irradiation resulted in improved molecular weight of $M_n = 14-22$ kDa with yields as high as 80%, as well as promising power conversion efficiencies as high as 5.9% [56].



Scheme 1.14 Microwave conditions to shorten reaction time [54].

1.4 Examples of Functional Materials Synthesized by Stille Polycondensation

Due to the tolerance of the Stille reaction toward many different functional groups, the Stille polycondensation is ideal for the synthesis of functional polymers. The first functional polymer synthesized with Stille polycondensation is poly(phenylene-thiophene) (PPT) which was shown to exhibit liquid crystal (LC) properties and nonlinear optical (NLO) properties (Scheme 1.4) [17]. By changing the length of the side chains, physical properties of the polymers, such as phase transition temperatures, solubility, and fusibility, may be fine-tuned. The broad scope of this polycondensation reaction is well demonstrated by Yu *et al.*, who in 1995 synthesized polymers containing metalloporphyrin and carbazole moieties (Scheme 1.5) [18]. Since then, this synthetic approach has emerged as a standard approach toward numerous polyaromatic conjugated polymers exhibiting a range of appealing physical properties. The following section documents typical examples of these polymers and a brief introduction of their applications.

1.4.1 Nonlinear Optical (NLO) polymers

1.4.1.1 Background

Nonlinear optics describes the behavior of light in nonlinear media. The dielectric polarization P of the media responds nonlinearly to the electromagnetic field E of an intense light, such as from a laser, which in return affects the behavior of light, including phase, frequency, and amplitude. The relationship of P and E follows the equation

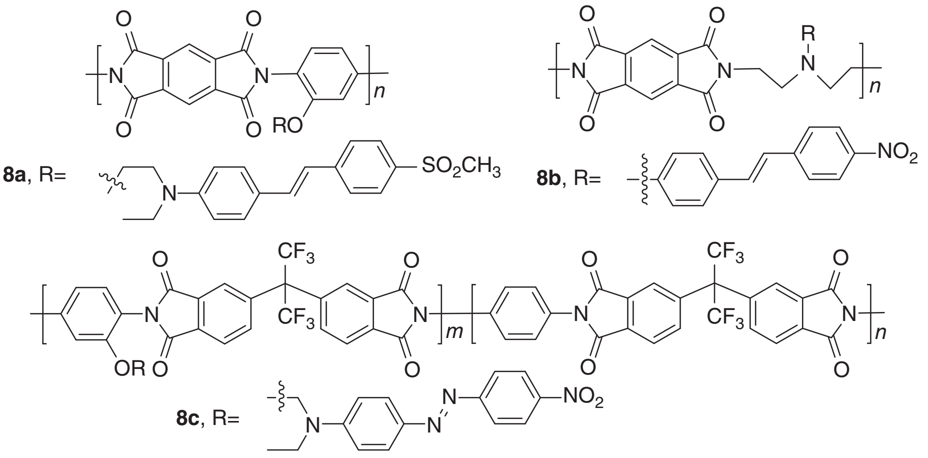
$$P = P_0 + \chi_{ij}^{(1)} E_{ij} + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \cdots$$

where P_0 is the static dipole moment and $\chi^{(n)}$ is the nth order susceptibility. The term $\chi^{(1)}$ describes normal linear behavior (refraction and absorption) and the rest describes nonlinear behavior. The $\chi^{(n)}$ values are nonzero for all media when n is an odd number. When n is an even number, $\chi^{(n)}$ is nonzero only when the media is noncentrosymmetric. NLO materials, particularly second-order NLO, can be very useful in information technology, where light can be used as an information carrier to process, transmit, and store data at extremely high speed. In general, $\chi^{(n)}$ values are small when $n > 3$ and thus only the $\chi^{(2)}$ and $\chi^{(3)}$ parameters are of significant value for possible real-world applications. For materials to be useful in NLO applications, they should display low optical losses from either absorption or scattering, fast response times, easy processability, as well as high chemical and optical stability [7]. Polymers with large second-order optical nonlinearity are usually those containing oriented NLO chromophores with large dipole moments and conjugated polymers have emerged as an important class of third-order NLO materials.

1.4.1.2 Examples of NLO Polymers Synthesized by Stille Polycondensation

Second-order NLO materials are very promising for photonic applications, because they exhibit a linear electro-optic effect in which the refractive index of the material can be controlled by an applied external E [57]. A polymer containing NLO chromophores will become noncentrosymmetric when the chromophores are oriented by applying high external electric field via field–dipole interaction at an elevated temperature, usually past their glass transition temperature, T_g [57, 58]. Cooling will freeze this orientation, resulting in a material with second-order nonlinearity. In polar polymers, this orientation order should be kept over time even at increased temperature in order to maintain second-order nonlinearity.

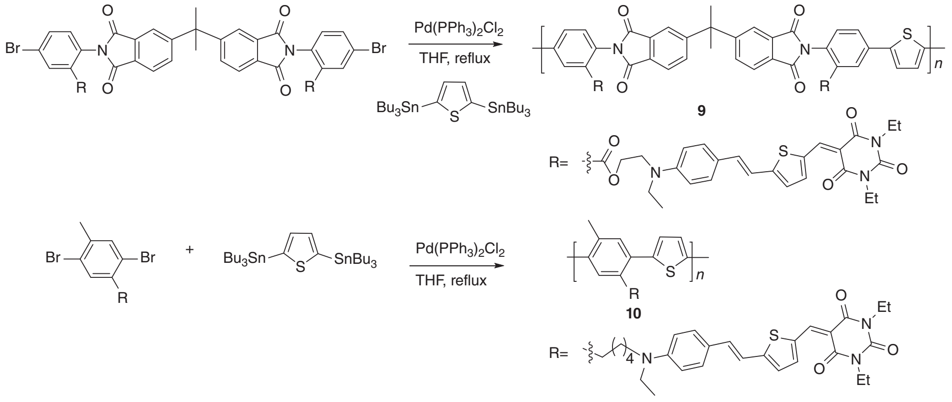
In order to synthesize these polymers, NLO chromophores are usually either grafted as side chains or imparted into the polymer backbone (**8**, Scheme 1.15) [59–61]. To achieve large second-order optical nonlinearity exhibiting high thermal stability in dipole orientation, chromophores with large dipole moments are incorporated to polyimide chains. Unfortunately, these chromophores are usually sensitive to traditional synthetic approaches of polyimides. In order to solve this problem, Yu and coworkers utilized the mild reaction conditions of Stille polycondensation to synthesize functional polyimides. A polyimide derivative (**9**) with an amino chromophore side chain was synthesized (Scheme 1.16) [62]. In the same report, another polymer (**10**) with a similar chromophore but different polymer backbone was also prepared. Polymer **9** showed higher T_g than **10** (170 and 125 °C, respectively), possibly due to the higher molecular weight. Interestingly, while the loading density of chromophore decreased from 65.04% in **10** to 50.85% in **9**, the r_{33} value increased from 9 to 35 pm V^{-1}, indicating a higher orientational stability of the chromophores in **9**. The authors proposed that higher loading will decrease the average distance between chromophores, resulting in increased dipolar repulsion between chromophores, which reduces the electro-optic effect.



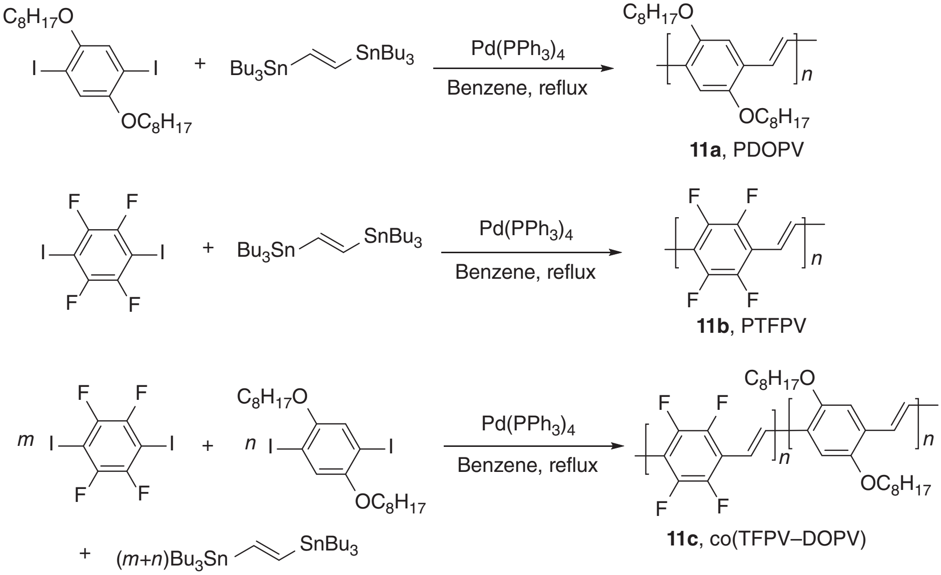
Scheme 1.15 The structure of some polyimide polymers for second-order NLO [59–61].

Third-order nonlinear optic effect can be observed in centrosymmetric media, caused by displacement of electron distribution. This effect is large when the density of polarizable electrons is high, such as in the case of conjugated polymers. Numerous conjugated polymers, such as polyphenylenevinylene (PPV) and polythiophene derivatives, were studied and shown to exhibit interesting third-order NLO properties. For example, Yu and coworkers synthesized a series of PPT polymers by Stille polycondensation with $Pd(PPh_3)_2Cl_2$ catalyst in THF solvent (Scheme 1.4). The polymer with $-OC_{16}H_{33}$ side chains showed a third-order nonlinear susceptibility $\chi^{(3)}$ of 1.77×10^{-13} esu in $CHCl_3$ solution [16]. Naso and coworkers synthesized tetrafluoro- and dialkoxy-substituted PPV polymers with high percentage of fluorinated units (>60%) via Stille polycondensation (**11**, Scheme 1.17) [63]. Fluorinated PPV gave more than 10 times higher third-order susceptibility, $\chi^{(3)}$ ($6 \pm 2 \times 10^{-10}$ esu), than that of the nonfluorinated one. Schrof and coworkers prepared a series of conjugated polymers, including random copolymers, based on a polythiophene backbone through Stille polycondensation (**12**, Scheme 1.18) [64]. These polymers showed red and near-infrared (IR) absorption and high third-order nonlinear behavior with $\chi^{(3)}$ value as high as 10^{-8} esu.

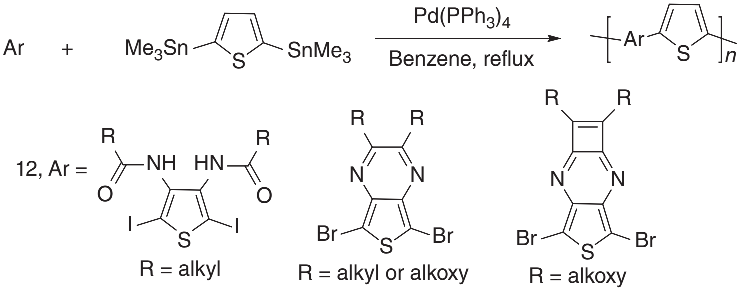
Photorefractive (PR) polymers are also an important class of NLO materials. The PR effect describes the change in the refractive index of a certain material in response to light of varying intensity, under the illumination of low-power lasers. A PR material can be used to record and store optically encoded information such as holograms [57]. A PR polymer normally needs two functions: photoconductivity and electro-optic effect. It consists of a photocharge generator, a charge transporter, a charge trapping center, and an NLO chromophore. For example, Yu and coworkers [65] made PPT derivative


Pd(PPh$_3$)$_2$Cl$_2$
THF, reflux
Bu$_3$Sn
SnBu$_3$
Br
R
n
9
R=
10
Et
+

Scheme 1.16 Synthesis of polymers with NLO chromophores on side chains [62].



Scheme 1.17 Synthesis of fluoro- and alkoxy-substituted PPVs for third-order NLO [63].



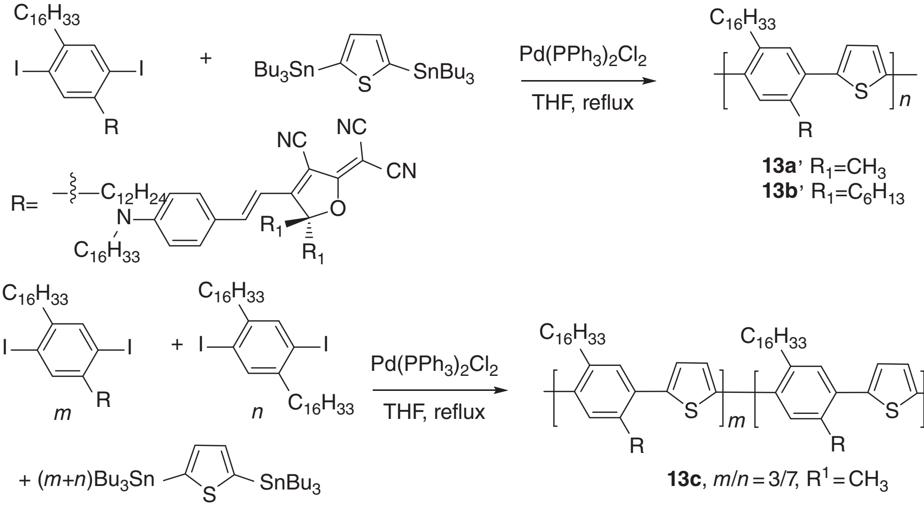
Scheme 1.18 Synthesis of polythiophene derivatives for third-order NLO [64].

polymers **13** via Stille polycondensation (Scheme 1.19). These polymers were PR; a side chain contained an electron-rich amino unit and an electron-withdrawing tricyanodihydrofuran group, creating a strong dipole and thus serving as a second-order NLO chromophore; while the conjugated backbone absorbs visible light with a maximum at about 590 nm and acted as a charge generator and transporter. The best PR results were obtained for **13a**, with a net optical gain coefficient of 158 cm^{-1} at a field of 50 V $\mu\mathrm{m}^{-1}$ and a diffraction efficiency of 68% at a field of 46 V $\mu\mathrm{m}^{-1}$. The synthesis of these multifunctional polymers is difficult with other synthetic approaches due to the sensitivity of NLO chromophores to both basic and acidic conditions, and demonstrated the broad utility of the Stille polycondensation.

1.4.2 Organic Photovoltaic Polymers

1.4.2.1 Background

The triumph of the Stille polycondensation is its broad application in the synthesis of donor–acceptor (D–A) semiconducting polymers for OPV solar cell applications.



13a' R_1=CH_3
13b' R_1=C_6H_{13}

13c, $m/n = 3/7$, $R^1 = CH_3$

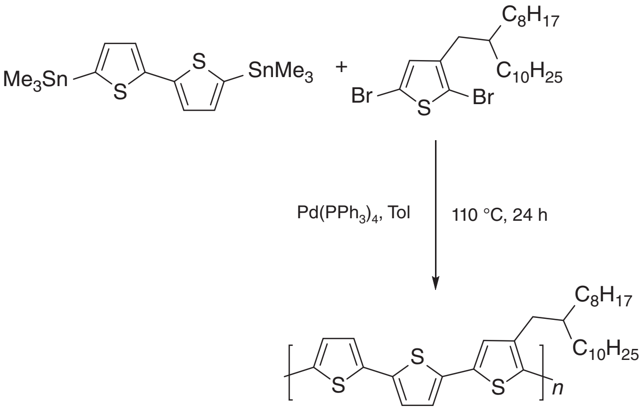
Scheme 1.19 Synthesis of PPTs with tricyanodihydrofuran subunit for PR material [65]

Polymer solar cells (PSCs) for the conversion of solar energy into electricity have been studied extensively in the past decades for their potential in fabricating lightweight and flexible devices, as well as their high-throughput production process and potential low cost [8]. Currently, the bulk heterojunction (BHJ) architecture is the most widely studied design for PSCs, in which donor and acceptor materials are mixed together to form a bicontinuous interpenetrating network between two electrodes. Typically, the donor material is a conjugated polymer, and the acceptor material is a fullerene derivative, such as [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM, which may also refer to the close analog [6,6]-phenyl C_{71} butyric acid methyl ester). Another system, which has been gaining popularity recently, is the all polymer cell, where the fullerene is replaced by another conjugated polymer as acceptor material. The Stille polycondensation has made an irreplaceable contribution to the development of both donor and acceptor polymers.

1.4.2.2 Examples of Donor Polymers

Donor polymers play a key role in BHJ solar cells, because they are the main component for the absorption of light and the generation of electrical current. The common rules for donor polymers include: low band gap to absorb as much solar energy as possible, correct energy level match with the acceptor material, good solubility in common solvents, and miscibility with the acceptor material to form the desired nanoscale morphology, all of which require careful selection of backbone structure, side chains, and substituent groups.

The first polymers for BHJ PSCs were PPV derivatives [66, 67], but their application was limited by the large band gaps (>2 eV) and low photocurrent. Later research interest shifted to polythiophenes, especially poly(3-hexylthiophene-2,5-diyl) (P3HT) [68], which is still a heavily studied system to this day [69]. Regioregular P3HT is normally synthesized by the McCullough method [70]. The Stille polycondensation is also applicable to the synthesis of some polyalkylthiophenes. For example, Yang and coworkers



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Scheme 1.20 Synthesis of a polyalkylthiophene polymer [71].

(**14**, Scheme 1.20) [71] synthesized a regioregular polythiophene, bearing fewer alkyl chains than typical polyalkylthiophenes, using $Pd(PPh_3)_4$ as the catalyst and toluene as the solvent at 110 °C. This system resulted in a polymer with $M_w = 18.9$ kDa and dispersity (Đ) = 1.8. A maximum power conversion efficiency (PCE) of 3.4% was achieved in the polymer/PCBM devices.

The most recent breakthrough in the design of solar cell polymers has been the introduction of D–A alternating copolymers [42, 72–74]. Unlike homopolymer P3HT, where a single moiety is used as the repeating unit, these low band gap polymers incorporate a backbone, which alternates between one electron-rich moiety (donor) and one electron-deficient moiety (acceptor). One unique feature of these polymers is that their HOMO and LUMO energy levels are largely determined by the HOMO energy level of the donor and the LUMO energy level of the acceptor, respectively [75]. Therefore, the energy levels of polymers can be tuned by modifying the donor and acceptor units separately by introducing different functional groups [7, 76]. Due to its tolerance of a wide variety of functional groups, the Stille polycondensation is highly competitive for the synthesis of these polymers. Some design principles for the construction of D–A copolymers are that the building moieties should have proper electron-donating or -accepting abilities, available sites for side chain and functional group modifications, and are favorable for conjugated polymer propagation. Through these rules, and the use of the Stille polycondensation, many high-performance polymers have been developed by combining various donor and acceptor moieties.

The benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) unit is an important electron-rich building block for high-performance solar cell polymers. The PTB series of polymers incorporating BDT and thieno[3,2-*b*]thiophene (TT), developed by Yu and coworkers, showed excellent solar cell performance [74, 77, 78]. They were prepared by Stille polycondensation, with $Pd(PPh_3)_4$ catalyst, toluene/DMF mixed solvent at 120 °C (Scheme 1.21). High molecular weight can be obtained for polymers of this series due to their excellent solubility, which allows them to stay in solution in the reaction mixture until the growing polymer chains are very large. These polymers were widely investigated for OPV cells [78]. Developed in 2010, PTB7, when combined with