

Stille Polycondensation for Synthesis of Functional Materials

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1. INTRODUCTION

The Stille coupling reaction between stannanes and aryl halides to form new carbon–carbon bonds has become a versatile synthetic methodology and has been widely applied to the syntheses of numerous organic compounds.^{1–4} The major advantages of this reaction are that it can tolerate different functional groups and requires mild reaction conditions. These features are especially important for the synthesis of functional polymers, oligomers, and small molecules for applications ranging from nonlinear optics to biological sensing.⁵ Because the halides involved can be extensively functionalized before subjecting them to the Stille condensation, the Stille protocol offers the opportunity to design polymers with functional moieties manifesting many highly desirable properties.

The most attractive application of the Stille coupling reaction is in the synthesis of conjugated polyaromatic systems that exhibit semiconducting properties. Throughout the past 2 decades, semiconducting polymers have played a pivotal role in emerging materials technology. With the push toward inexpensive, solution-processable organic materials to alleviate the economic pressures surrounding production of solid-state inorganic semiconducting materials, the emergence of semiconducting polymers has led to the realization of commercial devices including Sony's organic light-emitting diode (OLED) televisions and the Samsung Impression cellular phone using OLED technology, among a host of other examples. During the process of development of semiconducting polymers, palladium-mediated coupling reactions, including the Suzuki–Miyaura, Sonogashira, Heck, and Stille reactions, have played a crucial role in their syntheses. A survey of the literature of semiconducting polymers will quickly advance the idea that thiophene-bearing polymers in particular play a key role in emergent organic semiconducting materials technology. Many different synthetic methods may be employed to prepare semiconducting polymers; however, the method of Stille polycondensation has emerged as one of the most significant. While this method is broadly applicable to the preparation of a wide variety of different polymers, in the particular case of thiophene-bearing polymers, it has clearly emerged as the method of choice. Taking advantage of the pairing of highly electron-rich thiophene monomers with electron-deficient halide and triflate monomers, the Stille coupling reaction provides a facile route to high molecular weight,

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narrowly dispersed polymers under mild conditions, while tolerating a wide variety of functional groups.^{6,7}

1.1. History of the Stille Coupling Reaction

While the first examples of cross-coupling reactions between organostannanes and electrophilic partners appeared between 1976 and 1977 in works by Eaborn⁸ and Kosugi,^{9,10} the body of work soon to be known under the collective title of the Stille coupling¹¹ appeared in 1978,^{1,12} followed by a 1986 review of the methodology.² The initial paper by J. K. Stille and co-workers reported the use of palladium-catalyzed cross-coupling in the preparation of ketones from acyl chlorides and organostannanes.^{1,12} Following this, the Stille reaction quickly took its place as one of the most useful protocols for forming sp^2 carbon–carbon bonds in organometallic chemistry. Along with the method of Suzuki–Miyaura coupling, the palladium-catalyzed cross-coupling of organoboranes,¹³ the Stille reaction has streamlined the process of polymer synthesis. While some early work had been done involving preparation of polymers from organotin and dihalide monomers by the groups of Bochmann in 1989,¹⁴ Schulz in 1990,¹⁵ and Galarini in 1991,¹⁶ Yu and co-workers in 1993 further developed this methodology for use in polycondensation reactions for preparation of heteroaromatic diblock copolymers, examined its scope, and optimized reaction conditions for preparation of high molecular weight polymers.^{6,17}

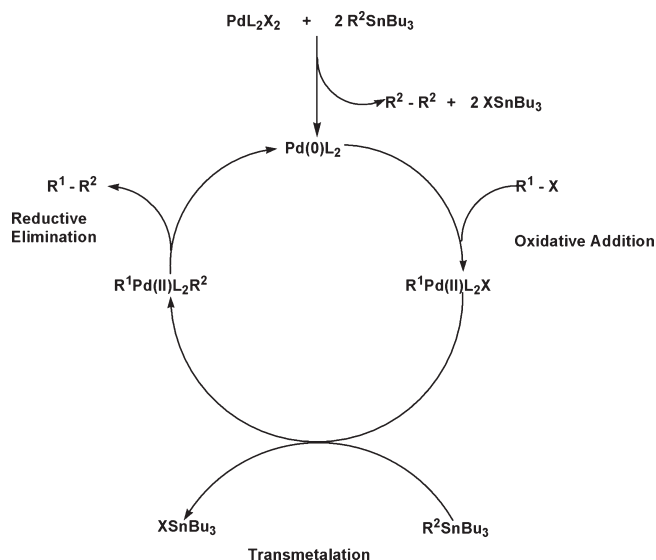
1.2. Advantages of the Stille Polycondensation

A variety of different organometallic reactions have been utilized in the formation of sp^2 – sp^2 carbon–carbon bonds, as typically found in semiconducting polymers, including the Heck,¹⁸ Suzuki–Miyaura,¹³ Sonogashira,¹⁹ and Yamamoto²⁰ reactions. However, the Stille coupling reaction is one of the most versatile. Advantages include the fact that the Stille reaction is stereospecific, regioselective, and typically gives excellent yields. Organotin and organohalide compounds can be conveniently prepared, typically without the requirement for protecting functionalities present in the monomers, and are far less oxygen- and moisture-sensitive than many of their other organometallic counterparts, e.g., Grignard reagents, organolithium reagents, and others. With its mild reaction conditions, high monomer solubility, tolerance for a wide range of functional groups, and facile preparation of monomers, the Stille reaction represents one of the most versatile protocols in the arsenal of organometallic chemistry.² The Suzuki–Miyaura reaction, for example, suffers from a few key drawbacks, the first of which is the requirement for basic conditions. A number of monomers may be labile to basic conditions, thus rendering this methodology impractical for these applications, or require more complex protection–deprotection strategies. Also, the Suzuki–Miyaura reaction requires a two-phase system; thus, polymers that rapidly decrease in solubility as molecular weight increases may form in poor yields or display very low molecular weights and high polydispersities under Suzuki–Miyaura conditions. Similarly, the Yamamoto methodology may be effective in the preparation of homopolymers but essentially ineffective in the preparation of regioregular diblock copolymers, in which the Stille method has been found to be highly effective. The Heck and Sonogashira coupling methods, while effective in context, limit the selection of monomer. Thus, the Stille methodology remains one of the most versatile methods for a wide variety of synthetic applications.

1.3. Scope of Review

This review is mainly synthetic in nature and will focus on the applications of the Stille coupling, as this method has been used

Scheme 1. General Mechanism of the Stille Reaction



throughout the literature for the preparation of various semiconducting polymers. In the interest of furthering some aspects of current research, the conditions for the Stille polycondensation as applied to such areas as nonlinear optical (NLO) polymers, polymers for organic photovoltaic cells (OPVs), polymer light-emitting devices (PLEDs), organic field effect transistors (OFETs), sensing polymers, and other applications will be examined. In this review, we will present a comprehensive treatment of the most relevant examples of Stille polycondensation, examining the role of catalyst, solvent, and various facets of the reaction conditions as they have evolved and changed throughout the past 2 decades.

Thiophene-containing polymers have emerged as an important class of semiconducting polymers. From applications to organic photovoltaics to light-emitting devices, this class of polymers has proven itself to be at the forefront of emerging organic materials technology, particularly in the field of energy-related polymers. Polymers from these highly electron-rich thiophene monomers are easily synthesized using Stille coupling; thus, the method of Stille coupling conveys a key advantage in this area.

2. MECHANISM OF THE STILLE COUPLING REACTION

The Stille reaction encompasses $Pd(0)$ -mediated cross-coupling of organohalides, triflates, and acyl chlorides with organostannanes.² The general mechanism of the Stille reaction shown in Scheme 1 follows closely that of other $Pd(0)$ -mediated reactions, involving an oxidative addition step, a transmetalation step, and reductive elimination step, which yields the product and regenerates the catalyst. The $Pd(0)$ species is the active catalyst; thus, $Pd(II)$ catalysts used in these reactions are reduced to $Pd(0)$ by the organostannane monomers, enabling entry into the catalytic cycle. While the steps in the simplified mechanism originally proposed by Stille are generally accepted, the process itself is known to be far more complex and has been the subject of extensive work. An in-depth discussion of all relevant work surrounding the mechanism of the Stille reaction is beyond the scope of this review; however, an excellent mechanistic review has been published by Espinet and co-workers.²¹ Choices

of ligands, solvents, and additives have all played a major role in the outcome of the Stille reaction, and alternative mechanistic pathways have been shown to exist on the basis of varying reaction conditions. The interplay of these three variables has gone a long way toward elucidating the mechanism. We will attempt to present the most relevant results regarding the mechanistic work that has been done in this area.

The first step in the catalytic cycle, oxidative addition, occurs when the organohalide or triflate oxidatively adds to the Pd(0) active catalyst, forming a Pd(II) intermediate $[\text{PdL}_2\text{R}^1\text{X}]$ (L = ligand; R^1 = alkenyl, alkynyl, aryl; X = Br, I, Cl, or OTf). Espinet and Casado²² found that this step is followed by a rapid cis–trans isomerization, giving *trans*- $[\text{L}_2\text{PdR}^1\text{X}]$. Espinet and co-workers²³ also isolated and characterized the key intermediates in the Stille coupling of $\text{C}_6\text{F}_5\text{OTf}$ (Ar = C_6F_5 , $\text{C}_6\text{Cl}_2\text{F}_3$) with $\text{CH}_2=\text{CHSnBu}_3$ by ^1H , ^{19}F , and ^{31}P NMR spectroscopy. The coupling was performed using a palladium catalyst with bidentate ligand dppe [1,2-bis(diphenylphosphino)ethane], which stabilized intermediates, allowing for their characterization. The intermediate of oxidative addition was found to be $[\text{Pd}(\text{Ar})(\text{OTf})(\text{dppe})]$.

The second major step in the process, transmetalation, is generally regarded to be the rate-determining step.^{2,21,24} This step is the most complex and thus has been the subject of much debate. As detailed by Espinet et al. in their 2004 review,²¹ the transmetalation process in general is a process of ligand substitution on a Pd(II) complex. Specifically, transmetalation as it applies to Stille coupling is cleavage of the Sn–C bond by an electrophilic Pd(II) complex.² These complexes are typically 16-electron, square planar, four-coordinate complexes that can undergo substitution via either dissociative or associative pathways. Farina and Roth²⁵ state that nucleophilic substitution of square planar Pd(II) complexes typically takes place via an associative mechanism. Dissociative substitution would involve a 14-electron, T-shaped intermediate in which substitution “is determined by the ligand with the highest trans influence, which weakens the bond trans to it,”²⁵ whereas substitution via an associative pathway would involve an 18-electron, trigonal bipyramidal complex with substitution being determined by the ligand with the highest trans effect, with the expectation that the lowest energy transition state would prevail.²⁵ Additionally, in the associative mechanism, both a direct and a solvent-assisted substitution may operate simultaneously, both of which contribute to the overall rate of substitution. Also of note, water, olefins, and coordinating solvents may also function as ligands. Farina and Roth²⁵ propose that ligand “dissociation” is key to the transmetalation step, with transmetalation occurring via an intermediate possessing a solvent molecule in its coordination sphere, $[\text{PdRL}[\text{S}]\text{X}]$ (R = alkenyl, alkynyl, aryl, L = ligand, S = solvent, X = Br, I, Cl, OTf). Indeed, Espinet and co-workers²³ observed the ionic species $[\text{Pd}(\text{Ar})(\text{dppe})(\text{THF})]\text{OTf}$, from which transmetalation was then stated to occur to yield the species $[\text{Pd}(\text{Ar})(\text{CH}=\text{CH}_2)(\text{dppe})]$. Espinet and Casado²⁶ reported in 1998 for organohalide couplings using AsPh_3 as ligand that the *trans* complex reacts with the tin compound via an associative $\text{S}_{\text{E}}2(\text{cyclic})$ mechanism with release of ligand, explaining the free-ligand retardation effect observed by Farina and co-workers,²⁵ described in section 3.1. Espinet and co-workers²⁷ later reported an $\text{S}_{\text{E}}2(\text{open})$ transition state in the case of couplings involving organotriflates, again using AsPh_3 as ligand. Thus, the nature of the transition state may also depend upon the substrate involved in the coupling. More recently, Amatore and

co-workers²⁸ studied the transmetalation step using electrochemical techniques in DMF solvent using AsPh_3 as the ligand and showed that the species $\text{PhPdI}(\text{AsPh}_3)(\text{DMF})$ is the species that reacts with the stannane. Santos and co-workers²⁹ also reported isolation and characterization of the major intermediates of the Stille reaction by electrospray ionization mass spectrometry.

Reductive elimination is the final step in the process, which generates the desired product and allows the palladium catalyst to reenter the catalytic cycle. A *trans*–*cis* isomerization immediately precedes this step, placing the coupling partners *cis* to one another. This is reported to be a fast step in the process following which the product is quickly eliminated and the Pd(0) catalyst is eliminated.² A three-coordinate, T-shaped complex via ligand dissociation has also been proposed as the intermediate from which reductive elimination takes place.^{25,30,31} Espinet and co-workers²³ identified stable dppe complexes such as $[\text{Pd}(\text{dppe})(\eta^2\text{-CH}_2=\text{CHC}_6\text{Cl}_2\text{F}_3)]$ in which the coupling product remained coordinated.

3. REACTION SCOPE

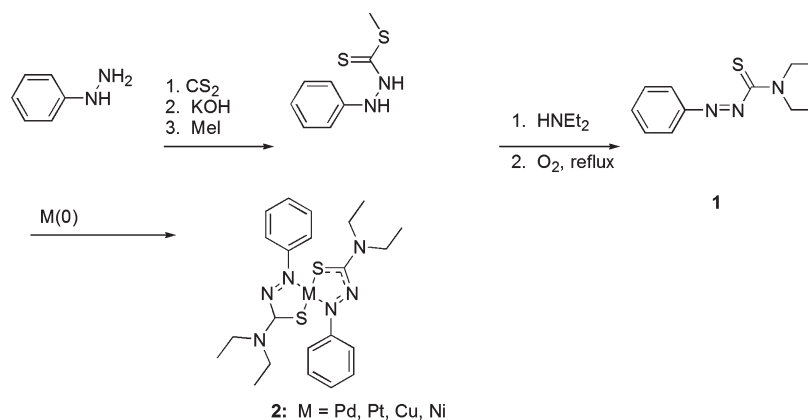
3.1. Catalytic Systems and Ligand Effect

The most commonly employed catalyst in the Stille reaction, and indeed the most common in its extension to polycondensation, has been tetrakis(triphenylphosphine)palladium(0) $[\text{Pd}(\text{PPh}_3)_4]$. This complex, while frequently employed, suffers from a number of drawbacks, one of which being its instability to oxidation in air, as it is oxidized by traces of oxygen to its oxide, Ph_3PO . Also, excess PPh_3 is a known inhibitor of the Stille reaction;³² thus, any excess ligand must be slowly oxidized by adventitious oxygen before the reaction can function efficiently. Similar known catalytic systems such as $\text{PdCl}_2(\text{PPh}_3)_2$, while lessening the effect of free PPh_3 ligand, suffer from even more pronounced instability in air.²⁵ Ishii and co-workers³³ reported the preparation of a more air-stable source of palladium(0), tris(dibenzylideneacetonyl)dipalladium $[\text{Pd}_2(\text{dba})_3]$, which has been widely used in Stille cross-coupling procedures.

The catalyst benzyl(chloro)bis(triphenylphosphine) palladium(II)² has also been widely used in the Stille reaction. Additionally, bis(acetonitrile)palladium(II) dichloride has been used as well as 1,1'-bis(diphenylphosphino)ferrocene palladium(II) dichloride and allylpalladium(II) chloride dimer.³

Beletskaya et al. reported couplings under “ligandless conditions” in which solvent acts as the ligand.³⁴ In this instance, increased coupling rates were observed. Originally, Stille rationalized that the increased rates under ligandless conditions were due to the steric bulk of triphenylphosphine slowing the reaction. However, it has been shown by Farina and co-workers that the Stille reaction is far more sensitive to electronic effects, such as that of ligand donicity, than that of steric bulk alone.²⁵

The choice of ligand clearly plays a critical role in the kinetics of the Stille reaction, as emphasized by Farina and Roth.²⁵ Farina and co-workers³² carried out a number of kinetic experiments beginning with the model system coupling of iodobenzene and vinyltributyltin with $\text{Pd}_2(\text{dba})_3$ as the catalyst. The ligands employed in the model system were $(4\text{-MeO-C}_6\text{H}_4)_3\text{P}$, triphenylphosphine (PPh_3), tri(2-furyl)phosphine, and triphenylarsine (AsPh_3). They found rate accelerations over the rate observed using PPh_3 of 3 and 4 orders of magnitude when using tri(2-furyl)phosphine and AsPh_3 , respectively. Additionally, they observed that both PPh_3 and $(4\text{-MeO-C}_6\text{H}_4)_3\text{P}$ exhibited a large inhibitory effect on the cross-coupling reaction. “Weak” or “soft”

Scheme 2. Synthesis of *N,N*-Diethylphenylazothioformamide and Metal Chelation of Pd, Pt, Cu, and Ni

ligands such as AsPh₃ were not observed to appreciably slow the reaction; thus, excess free ligand present in the reaction mixture did not inhibit the reaction as it did in the case of PPh₃. An inverse correlation between coupling rate and donicity of ligands was shown. Stronger donating ligands are also more easily oxidized, leading to formation of palladium black (and the oxide of the ligand); thus, the catalyst stability is greater using “weak” ligands. Tri(*o*-tolyl)phosphine ligands have also been employed as ligands of lower donicity.³

Fu et al.³⁵ reported Stille cross-couplings of aryl chlorides with organostannanes in addition to room-temperature couplings involving aryl bromides using the catalyst Pd/P(t-Bu)₃. In addition, the Fu group reported extension of the Stille reaction to include couplings of alkyl bromides and iodides with aryl- and vinylstannanes in the presence of alkyldiaminophosphane [PR(NR')₂]₂ ligands.³⁶ The Fu group also reported room-temperature couplings of alkyl halides with alkenylstannanes using the catalysts Pd/P(t-Bu)₂Me,³⁷ and Pd/PCy(pyrrolidinyl)₂.³⁶

Fu and co-workers³⁸ have also recommended conversion of air-sensitive phosphine ligands into their corresponding phosphonium salts. Their in situ deprotonation by a Brønsted base liberates the trialkylphosphine.

The means of optimization of catalytic systems to achieve high molecular weight polymers via Stille coupling depends largely on the polymers being synthesized. An additional challenge in polymer chemistry has been optimization of not only yield but degree of polymerization in order to achieve high molecular weight polymers. The matching of reactive partners is a key parameter in achieving high molecular weight. Similarly, precise stoichiometric balance is much more critical in polymer chemistry than in single-molecule cross-coupling reactions, because slight imbalances can have a large detrimental effect on degree of polymerization. Solvent also plays an even more critical role in polymerization because not only must catalytic activity be considered but also the continued solubility of the growing polymer chain. Optimization of reaction conditions for a particular set of polymers is often a trial-and-error process. While Stille polycondensation uses the same catalysts, ligands, solvents, and additives used in single-molecule applications, finding the right set of conditions to obtain high molecular weight polymers often requires a great deal of optimization. For example, after surveying a number of different catalysts, ligands, and catalyst: ligand ratios, Moreau and co-workers³⁹ found that a catalytic

system employing Pd₂(dba)₃(CHCl₃) formed in situ in addition to using a 1:4 ratio of Pd/PPh₃ was effective in generating a high yield of high molecular weight, regioregular poly(3-alkylthiophenes). The authors found that the catalytic system generated in this case was more active than Pd(PPh₃)₄. Also, they noted that when using a 1:2 ratio of Pd/PPh₃, they obtained a poor yield, and that other ligands including P(*p*-tol)₃, P(C₆H₁₁)₃, and P(OPh)₃ also gave poor yields and low molecular weight polymers.

Finally, the presence of palladium black formed as a byproduct of the Stille coupling reaction is known to adversely affect the electronic properties of the final polymers. Typically, this is removed by filtration over Celite, though more recently reports of the use of chelating reagents such as *N,N*-diethylphenylazothioformamide^{40,41} 1, reported in 2005 by Krebs and co-workers (Scheme 2), or *N,N*-bis[tetra(ethylene glycol) monomethyl ether]phenylazothioformamide, reported by Nielsen and co-workers, have emerged as effective for removal of metals.^{41,42} These reagents form soluble complexes such as 2, making their removal from the final polymers easier. The amount of palladium present in the final product was found to be less than 0.1 ppb⁴⁰ when using *N,N*-diethylphenylazothioformamide, which can be synthesized from phenylhydrazine. More recently, Fréchet et al.⁴³ reported use of this compound in purification of polymers for highly efficient organic photovoltaic materials, as discussed in section 4.4.2

3.2. Solvent Effect

The interplay of catalyst, ligand, additives, and solvent is complex. As will be discussed in section 3.4, the choice of solvent may determine whether an additive is required, and may dictate whether a particular additive, such as LiCl, has an enhancing or retarding effect on the reaction. Also, the role of commonly used copper salts such as CuI can change on the basis of whether the additive is used in a polar or nonpolar solvent. While the chosen solvent clearly plays a large role in single-molecule syntheses via Stille coupling, the solvent is even more important in polymerization reactions. The solvent must not only dissolve starting monomers, stabilize the catalyst, and maintain these in solution but it must also maintain the growing polymer in solution for as long as possible in order to achieve high molecular weight. The solvents employed in Stille polycondensation vary as widely as those used in single-molecule couplings, including benzene, toluene, xylene, mesitylene, THF, DMF, NMP, DMSO, dioxane, and chloroform.

The solvent must also sustain the high temperatures often required for polymerization procedures. Many of these procedures are carried out at temperatures in excess of 120 °C; thus, toluene is a solvent frequently employed in Stille polycondensation. Some microwave-assisted Stille polycondensation reactions, employing temperatures as high as 200 °C,⁴⁴ use the higher boiling chlorobenzene as solvent. Highly polar solvents such as DMF and NMP are known to act as coordinating ligands to the palladium center; however, many conjugated polymers are insoluble in these highly polar systems. Ethereal solvents such as THF and dioxane offer some catalyst stabilization, while maintaining polymers in solution. Often, highly polar solvents are used in conjunction with toluene or another cosolvent. Mixed solvent systems such as toluene/DMF or toluene/NMP are common. Yu and co-workers⁷ found that mixed solvent systems such as these combined the catalyst-stabilizing effects of highly polar solvents with increased polymer solubility and enabled a high yield of high molecular weight polymers to be obtained.

3.3. Additives and Their Effects

In J. K. Stille's 1986 review of the methodology,² he stated that triflate coupling cannot take place without the use of the LiCl additive. Stille postulated that this was because nucleophilic chloride facilitates transmetalation in couplings involving triflates by replacing the inert Pd–O bond with the more reactive Pd–Cl bond. As reported by Roth and co-workers,⁴⁵ however, the effect of LiCl additive is largely dependent on the reaction conditions. For example, in the coupling of aryl triflates with phenyltributyltin using Pd₂(dba)₃ as catalyst, LiCl was shown to have an inhibitory effect when PPh₃ was used as the ligand in NMP solvent, while LiCl was a requirement when the same reaction was carried out in dioxane. When the coupling was performed using AsPh₃ as the ligand, coupling rates in NMP solvent were not affected substantially by addition of LiCl, while its addition was again required to affect coupling in dioxane. The group further reported that LiCl most likely played a dual role in the Stille reaction involving triflates. One role was to stabilize the oxidative addition product as [PdRL₂Cl] (R = aryl; L = ligand). Second, they suggested that LiCl played a role in nucleophilic assistance at the departing tin in transmetalation. Espinet et al.²⁷ reported that LiCl actually exhibited a retarding effect on triflate couplings carried out in THF solvent when using Pd(PPh₃)₄ as catalyst.

ZnCl₂ has also been employed and reported to enhance the Stille reaction in couplings involving triflates. Stille² proposed that an organozinc intermediate was responsible for the enhancement; however, Farina and co-workers⁴⁶ proposed that the enhancement was actually due to its water of hydration, since anhydrous ZnCl₂ showed no enhancement.

Liebeskind and co-workers⁴⁷ reported a more than 100-fold rate acceleration of the Stille reaction by addition of Cu(I) salts such as CuI. Very little acceleration was observed in the presence of "soft" ligands, such as AsPh₃, however. This led them to the conclusion that the copper salts acted as scavengers of free ligand, as strong ligands were known to inhibit the Stille reaction. Copper-assisted ligand dissociation was reported to lead to a solvent-occupied coordination site on palladium, a species such as [RPd[S]LX] (R = alkenyl, alkynyl, aryl; S = solvent; X = Br, I; L = ligand), thus facilitating the transmetalation of the tin compound. They also observed that the ability to enhance the reaction with CuI was highly dependent on the amount of CuI added. Too little was ineffective at scavenging free ligand, while too much was found to

remove ligand from the active catalyst, thus destabilizing the catalyst. Farina and Roth²⁵ stated that the ideal ratio of copper to palladium was 2:1. A second role for copper was also proposed. Liebeskind and co-workers observed that in highly polar solvents such as NMP in the absence of strong ligand inhibition, unsaturated stannanes reacted with CuI via Sn/Cu transmetalation to yield an organocopper species, which more easily transmetalated onto the Pd(II) species. Farina and Roth⁴⁸ also reported a heterogeneous system involving Pd/C as catalyst with CuI cocatalyst. In this instance, the CuI catalyst both enhanced the yield and decreased the reaction time over the use of Pd/C alone.

Corey and co-workers⁴⁹ reported acceleration of the Stille reactions involving sterically hindered vinyl stannanes using CuCl as an additive. Corey also invoked a faster transmetalation involving a vinyl copper intermediate as the explanation for the acceleration.

Nucleophiles are known to enhance the reactivity of organotin reagents via hypercoordinate intermediates.³⁵ Martinez and co-workers⁵⁰ showed that tetrabutylammonium difluorotriphenylstannane was highly reactive with alkenyl triflates. Cross-coupling proceeded without the need for the LiCl additive.

Organotin reagents can be activated through intramolecular coordination with Lewis bases. For example, Cs₂CO₃ and NaOH are both reported to assist.⁵¹ Vedejs and co-workers⁵² also reported stabilization of organotin reagents via intramolecular coordination with amines. Similarly, Brown and co-workers⁵³ reported significant acceleration of palladium- and nickel-catalyzed arylations when a neighboring tertiary amine was present on the organotin compound. Fu et al.³⁷ also studied a series of Lewis basic additives and their effect on the coupling of alkenyltin compounds with alkyl bromides, including CsF, KF, NaOMe, N(*i*-Pr)₂Et, Bu₄NF·3H₂O, Me₄NF/3 Å molecular sieves, the latter of which was shown to function as a highly effective activator. Baldwin et al.⁵⁴ reported a tandem effect of CuI and CsF in enhancing the Stille coupling, which they attributed to the removal of Bu₃SnI as insoluble Bu₃SnF, thus regenerating the more active CuI. Fouquet et al.⁵⁵ reported use of TBAF (tetrabutylammonium fluoride) as activator, reportedly via formation of a pentavalent difluorinated tin compound due to the known fluorophilicity of tin.

Gronowitz and co-workers⁵⁶ also reported the efficacy of the copper(II) salt CuO to enhance Stille coupling reactions. Both yields and reaction times were reported to improve in coupling procedures involving 2-tributylstannylpyridine and various halo-benzenes.

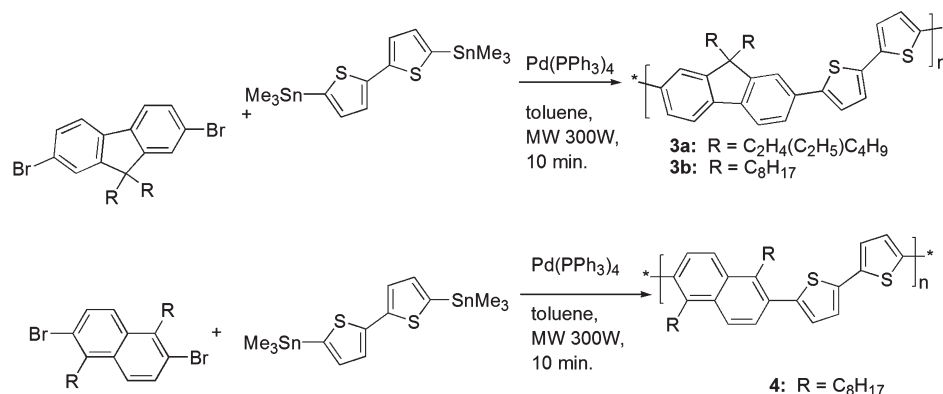
Liebeskind and co-workers^{57–59} reported use of copper(I) thiophenecarboxylate (CuTC) as cocatalyst in palladium-mediated cross-couplings of thioether compounds with organostannanes. The thioether formed a complex with CuTC that permitted oxidative addition of palladium into the C–S bond. This additive extended the range of monomers available for cross-couplings with organotin compounds, as discussed further in section 3.2.

Liebeskind and co-workers⁶⁰ also reported the use of Ph₂P(O)O[–]*n*-Bu₄N⁺ as a "tributyltin scavenger." Cross-coupling efficiency was significantly improved by employing this additive.

3.4. Types of Monomers

The Stille coupling reaction generally includes couplings of unsaturated organohalides (generally iodides and bromides) and organotriflates with organostannanes. In the case of Stille polycondensation, it is understood that polymerization is carried out

Scheme 3. Synthesis of Fluorene- and Naphthalene-Containing Polymers 3 and 4



using difunctionalized monomers; thus, the monomers involved are diorganohalides/ditriflates and distannanes. Generally, diiodo monomers show higher reactivity than dibromo monomers. The use of aryl chlorides in Stille coupling reactions in general has been sparse, primarily due to their low reactivity in oxidative addition to Pd(0). Fu and co-workers⁵¹ reported a general method for couplings involving chlorides; however, the extension of this method to polycondensation has yet to be seen. Some reported success of Stille coupling of aryl chlorides in ionic liquid medium⁶¹ exist in small-molecule applications; however, the extension of the method to encompass a broad scope of these substrates, particularly in polymerization, also remains a challenge for the future. Liebeskind and co-workers reported palladium-catalyzed copper-mediated cross-couplings of thioether-bearing compounds with organostannanes using copper(I) thiophenecarboxylate (CuTC) cocatalyst.^{57,58} This so-called Liebeskind-Srogl cross-coupling protocol effectively extended the range of monomers available for palladium-mediated cross-coupling beyond halides and triflates.

Typically, pairing of electron-rich organotin compounds with electron-deficient halide or triflate coupling partners facilitates synthesis of high molecular weight polymers. This is presumably due to the fact that oxidative addition to the active catalytic species is facilitated by electron-withdrawing groups, while the transmetalation step may also be facilitated by electron-rich organotin compounds. In the case of thiophene-based monomers, the lone-pair on the sulfur heteroatom, in addition to the delocalization of six electrons over a five-atom system, render this monomer significantly electron-rich such that high molecular weights can be obtained using this methodology.^{7,62}

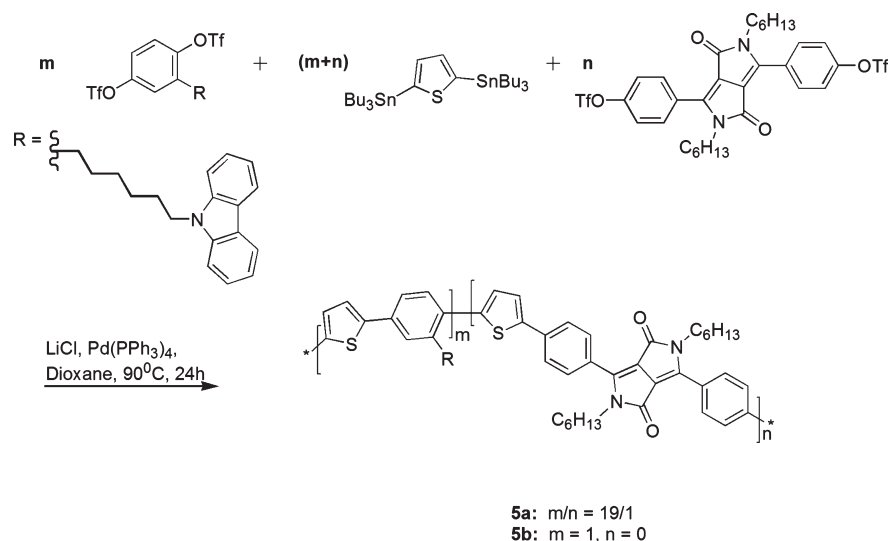
Another key issue is the balancing of monomer stoichiometry. It is well-known that precise stoichiometric balance is required to achieve high molecular weight in polycondensation reactions. However, the nature of the Stille coupling cycle may have an adverse effect on stoichiometric balance. This is due to the imbalance occurring when Pd(II) catalysts are used due to the reduction of the catalyst to the active Pd(0) species by the organotin monomer. Homocoupling of the ditin compound may also pose a problem in maintaining a stoichiometric match in order to obtain high molecular weight. In these instances, both the catalyst concentration and organotin monomer concentration may be adjusted to maintain stoichiometric balance.⁷ While the Stille coupling conditions themselves may tolerate a variety of functional groups, the conditions required for preparation of

ditin monomers may pose a problem, since organolithium or Grignard reagents are required intermediates to the organostannanes. The use of reagents such as butyllithium may interfere with functional groups present on the ditin monomers. Purification of organotin monomers can also present an issue. While many ditin compounds such as 2,5-bis(tributylstannyl) thiophene can be purified by vacuum distillation, and many solid trimethylstannyl compounds can be purified by recrystallization, many tin compounds are too unstable for column chromatography on silica gel to be a viable purification option. Given the fact that extremely pure monomers are a requirement to maintain precise stoichiometry and thus obtain high molecular weight, limited purification options can pose a substantial problem. Thus, the selection of butyl vs methyl tin monomers depends upon the intended final monomer and the desired method of purification, among other factors. The reactivity of trimethyltin chloride is known to be much greater than that of tributyltin chloride.⁶³ Additionally, recrystallization of the final monomers is often the only means of purification available for large, multi-step monomers; thus, the more reactive tin chloride may be the better choice to maximize conversion to the ditin compound. While trimethyltin compounds may often be easier to purify than their tributyl counterparts, there is a trade-off in that the toxicity of trimethyltin chloride is 100 times²⁵ greater than that of tributyltin chloride. Also, the trimethyl derivatives tend to be more volatile; thus, the possibility of exposure increases when these are used. Careful consideration of these trade-offs is necessary in selection of ditin monomer.

3.5. Microwave-Assisted Stille Polycondensation

In addition to Stille polycondensation reactions being performed using conventional heating, several groups found improvement of molecular weight and polydispersity when using microwave irradiation. The use of microwave irradiation is reported to improve results in cross-coupling reactions, mainly because of the direct transfer of energy to reactants, which significantly reduces reaction times. This technique lends itself very well to polymerization, because conditions can be optimized quickly. Scherf and co-workers⁶⁴ reported in 2004 the syntheses of polymers 3a,b and 4 (Scheme 3). The group found that in the microwave-assisted synthesis of 4 from reportedly less-active 1,5-dioctoxy-2,6-dibromonaphthalene, irradiation at 300 W for 10 min resulted in improvement in number-averaged molecular weight (M_n), yield, and polydispersity index (PDI). M_n more

Scheme 4. Synthesis of Conjugated Polymers Bearing Pendant Carbazole Moieties



than doubled, with PDI dropping from 6.4 to 2.8, and yield improved from 34 to 52% over conventional heating conditions. In the case of **3a**, yield improved from 55 to 83%, as did the yield of **3b** from 52 to 72%.

Similarly, Tierney and co-workers⁴⁴ employed microwave conditions in the syntheses of soluble polythiophenes **31** (Scheme 26) for OFET applications, as shown in section 4.3.2. They reported the use of chlorobenzene as solvent, which enabled heating to 200 °C, resulting in improved M_n (4.7 versus 1.8 kDa) over that obtained from the same reaction in THF with only a 10 min reaction time.

More recently, in 2009, Bazan and co-workers⁶⁵ reported high molecular weights in the microwave-assisted syntheses of narrow band gap polymers **51** for solar cell applications, as shown in section 4.4.2. Significantly, they reported low molecular weights when attempting the polymerization of dibromobenzothiadiazole and distannylated dithienosilole moieties using conventional heating and $\text{Pd}(\text{PPh}_3)_4$ as catalyst. The use of microwave irradiation resulted in M_n values ranging from 14 to 22 kDa, in yields as high as 80%. The solar cell properties of the materials synthesized by this method also showed promise with power conversion efficiencies as high as 5.9%, which is further discussed in section 4.4.2.

The reaction conditions used in Stille polycondensation vary widely on the basis of the system in question. The purpose of this review is to examine the various aspects of the Stille reaction in context. The following examples of polymers from some of the most important applications should serve as a starting point for further applications of the Stille reaction to the next generation of functional polymers.

4. EXAMPLES OF FUNCTIONAL POLYMERS

4.1. Synthesis of Various Conjugated Polymers

The most important advantage of the Stille polycondensation over other methods is the wide tolerance of the method to a variety of functional groups. The use of this method in the preparation of functional materials has been demonstrated by a number of groups, producing many examples of conjugated polymers with multifunctional groups. Yu and co-workers⁷ demonstrated this advantage in developing numerous functional

polymers containing metal complexes, nonlinear optical chromophores, and carbazole species, as shown in Schemes 4 and 5. These polymers showed interesting electro-optical properties to be discussed in more detail in the following sections.

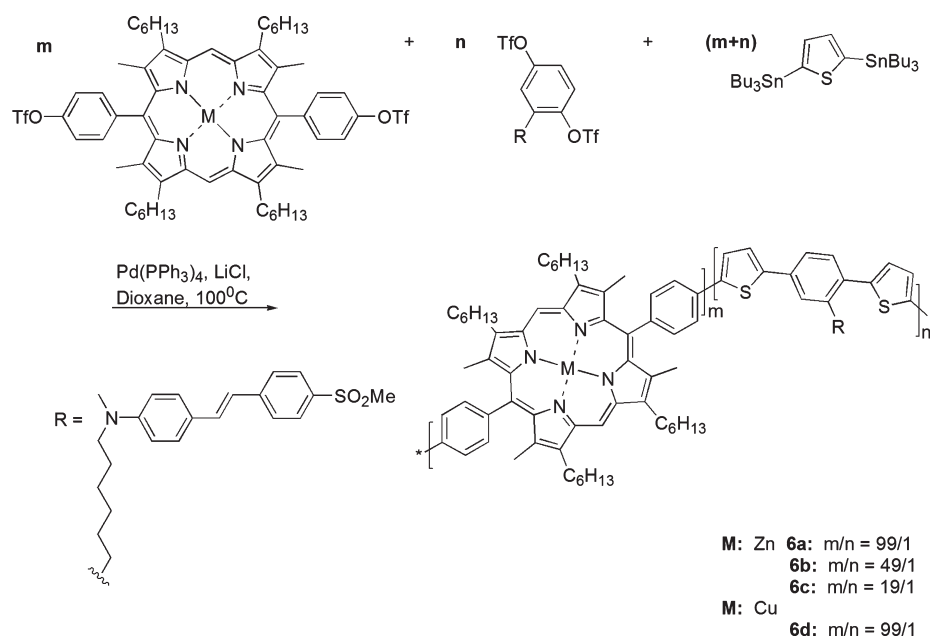
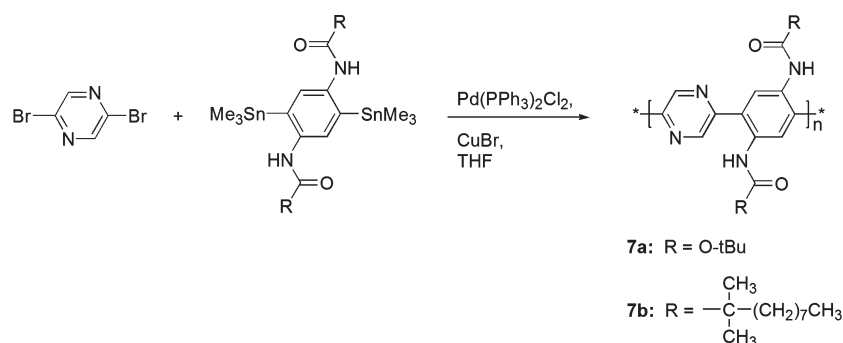
The synthesis of thienylpyrrole polymers was reported in 1996 by Cava et al.⁶⁶ using Stille coupling methodology. Incorporation of an *N*-alkyl chain improved solubility of the final polymers. Pyrazines and amides are also tolerated under Stille coupling polymerization conditions. Meijer and co-workers⁶⁷ synthesized a series of alternating polymers **7a,b** and well-defined oligomers composed of 2,5-linked pyrazines and *N,N'*-diacylated phenylene-1,4-diamines using Stille cross-coupling (Scheme 6). The presence of intramolecular hydrogen bonding was found to lead to spontaneous formation of a ladder-type structure in which the arylene units tended to become coplanar.

Four and co-workers have shown that nitro,⁶⁸ ketone, amine, and quinone groups^{69,70} are all compatible with the Stille polycondensation conditions as shown in polymers **8a–c** (Scheme 7). These low optical band gap polymers based on polythiophenes were prepared by a modified Stille polymerization using a Pd(0) and CuI precatalyst system in which electron-deficient aryl dibromides coupled with electron-rich aryldistannanes. In one example, copolymerization of an *N,N'*-bis(*tert*-butoxycarbonyl)-3,4-diaminothiophene distannane and 3,4-dinitrothiophene dibromide led to polymers with the optical spectra showing λ_{max} values ranging from 526 to 662 nm, consistent with a decrease in their band gaps.

Similarly, Scherf et al.⁷¹ synthesized polyketones via the Stille coupling method. It was found that these could be further cyclized to form soluble, fully conjugated ladder polymers. Sterzo and co-workers⁷² found that direct formation of alkynylstannanes was possible when lithium diisopropylamide (LDA) was added to aromatic acetylides formed in situ. The formation of bisalkynylstannanes in this manner afforded acetylenic polymers without the need for isolation of the acetylene group.

Okamoto and co-workers⁷³ introduced the oxazoline group into the polymer chain of an optically active, regioregular polythiophene, poly[(*R*)-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl) thiophene]. This polymer, **9** (Scheme 8), was found to show a unique induced circular dichroism (ICD) signature on coordination of

Scheme 5. Synthesis of Polymers Containing Metalloporphyrins

Scheme 6. Synthesis of Polymers Composed of 2,5-Linked Pyrazines and *N,N'*-Diacylated Phenylene-1,4-diamines

metal ions. Significantly, a hydrolyzed derivative of the polymer was found to exhibit chiral recognition ability. Complexation with chiral amines also gave a unique ICD signature in the UV–visible region, based on the chirality of the amines. Similarly, Cheng et al.⁷⁴ reported that 1,3,4-oxadiazole units incorporated into polymers could function as fluorescent chemosensors for selective detection of metal ions.

Yamamoto et al.^{75,76} showed that imidazole groups could also be introduced into the conjugated polymer chain of **10a–c** (Scheme 9) via the Stille reaction. They found that alternating copolymers of benzimidazole and thiophene blocks showed interesting photoluminescent properties, with absorbances and photoluminescence maxima at approximately 436–460 and 520–530 nm, respectively. The photoluminescence quantum yields of the polymers were reported to be between 21 and 37% in DMF. Also, they reported that the addition of sodium hydroxide induced an absorbance red-shift of approximately 70 nm.

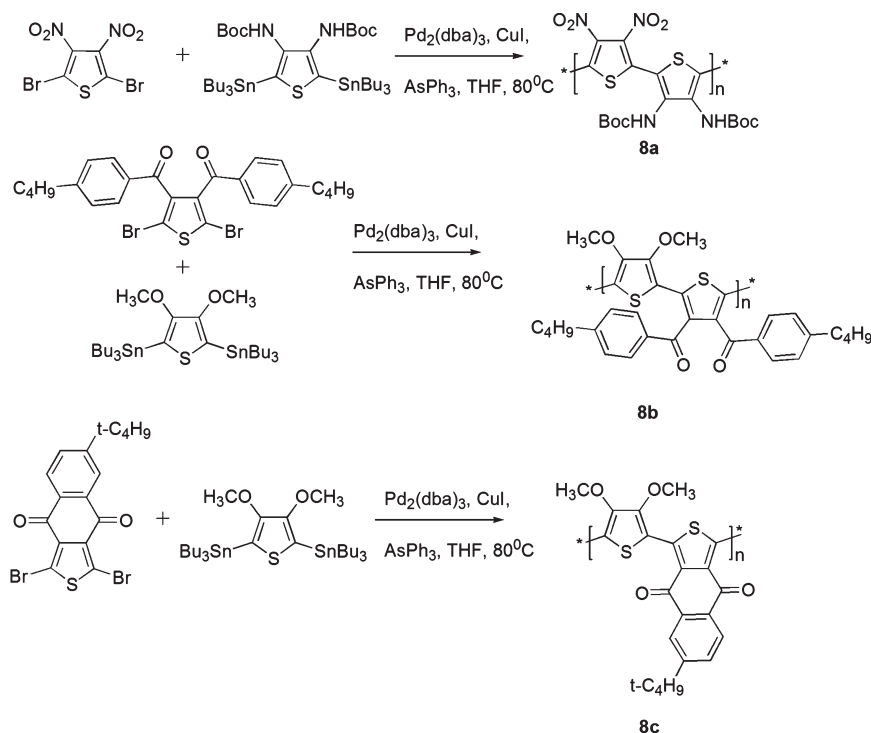
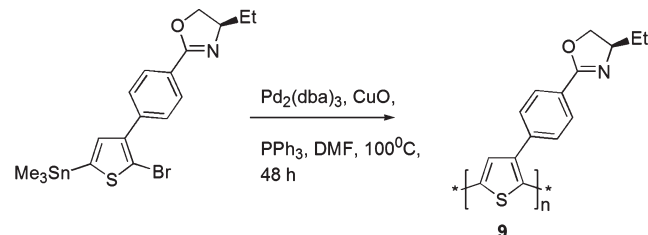
Mucci et al.^{76,77} showed that the cysteine moiety could also be introduced into the backbone of a conjugated polymer in biomimetic applications. They reported the synthesis of a polythiophene polymer **11** (Scheme 10) from dibromomethyl-*N*-(*tert*-butoxycarbonyl)-*S*-thien-3-ylcysteinate and distannylthiophene.

The polymer was shown to form a self-assembling hydrogen bond network in both solid and solution states.

Mucci et al.⁷⁸ also reported the syntheses of thiophene-based polymers bearing free carboxylic acid moieties **12** (Scheme 11). The Stille reaction protocol was found to tolerate the presence of the free carboxylic acid group, and polymers were found to precipitate from the reaction medium. Significantly, molecular weights and PDIs of the carboxylic acid-bearing polymers ($M_n = 4.1$ kDa, PDI = 1.2) were more favorable when compared to those of polymers obtained by Stille coupling of the ester-bearing monomers followed by hydrolysis ($M_n = 2.6$ kDa, PDI = 2.1).⁷⁹

Chan et al.⁸⁰ reported the use of Stille coupling to prepare rhenium-containing polymers such as **13** (Scheme 12) for organic solar cell applications. These polymers were obtained in acceptable molecular weights with $M_n = 3.2$ kDa and PDIs of 1.8. Upon complexation of rhenium(I) pentacarbonyl chloride, the polymers were reported to exhibit a broadened absorption spectrum and concomitant lowering of their band gaps. While the overall power conversion efficiencies of 0.1% for these polymers were low, the polymers were found to show extremely low band gaps of 1.34 eV.

Scheme 7. Low Band Gap Polythiophenes Bearing Nitro, Amine, Quinone, and Ketone Functional Groups

Scheme 8. Synthesis of Poly[(*R*)-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene]

4.2. Stille Polycondensation for Preparation of Nonlinear Optical Polymers

4.2.1. Background of Nonlinear Optical Materials. The palladium-catalyzed Stille polycondensation was widely investigated to produce conjugated polymers possessing interesting electronic and optical properties. Materials with low optical losses (α), fast response times (τ), high degrees of processability, in addition to high degrees of chemical and optical stability, show promising optical nonlinearities. The synthesis of nonlinear optical materials has been a topic of considerable interest. To this end, conjugated polymers have been shown to be an important class of active nonlinear optics materials (NLO).

4.2.2. Third-Order Nonlinear Optical Effect. Yu and co-workers synthesized third-order nonlinear optical polymers via Stille polycondensation. These were poly(1,4-phenylene-2,5-thiophenes), soluble conjugated polymers **14** (Scheme 13).⁸¹ These polymers were also found to be nonlinearly optically active, exhibiting a $\chi^{(3)}$ value of 1.77×10^{-13} esu. This was determined in chloroform solution with a concentration of 0.527 g/L using degenerate four-wave mixing. Pure chloroform has a $\chi^{(3)}$ value of 0.602×10^{-13} esu at 532 nm. The polymers were

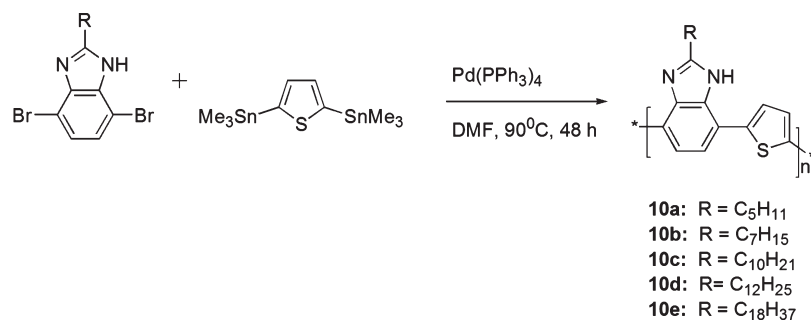
also shown to exhibit a nematic liquid crystallinity phase, the transition temperature of which was affected by alkyl chain length.

Schrof and colleagues⁸² applied the Stille coupling reaction to the synthesis of novel low-band gap polythiophenes with interesting third-order nonlinear optical properties. In contrast to the low environmental stability observed in polyacetylene samples, polythiophenes are much more stable due to the presence of an aromatic system in the conjugated backbone. Polymers with tailor-made band gaps and nonlinearities were achieved by varying both the substituent groups as well as the number and alternation of substituted versus unsubstituted thiophene units, as shown in Schemes 14 and 15. Degenerate four-wave mixing measurements and Raman spectroscopy were carried out to further investigate their optical nonlinearities. High values of the third-order susceptibility, $\chi^{(3)}$, of 10^{-8} esu, were reported.

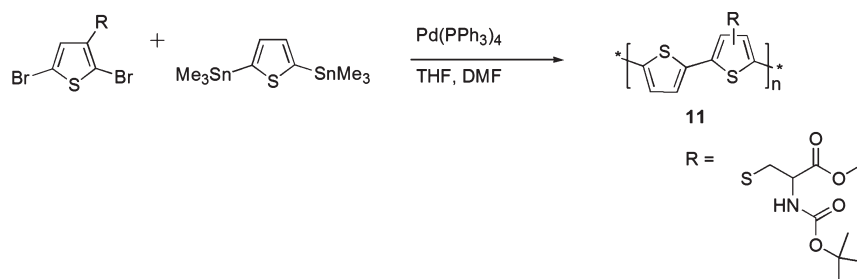
Naso and co-workers⁸³ reported a copolymer of tetrafluoro and dialkoxy-substituted poly(*p*-phenylenevinylene) (PPV) with a high percentage of fluorinated units, which was synthesized using the Stille cross-coupling reaction. The introduction of electron-deficient aromatic rings gave a high $\chi^{(3)}$ coefficient ($6 \pm 2 \times 10^{-10}$ esu) of the copolymer, which is more than 1 order of magnitude larger than that of its homopolymeric counterpart in the absence of fluorinated units, as shown in 17–19 (Scheme 16).

4.2.3. Second-Order Nonlinear Optical Materials. Polymeric second-order NLO materials were envisioned to possess advantages over their inorganic counterparts in photonic technologies. A few requirements must be met for practical applications, including large nonresonant second-order nonlinearities, a high degree of chemical and thermal stability under both operating and fabrication conditions, and low optical loss. The incorporation of chromophores into the polymer backbone has been a widely adopted strategy in this area. For example, Wright

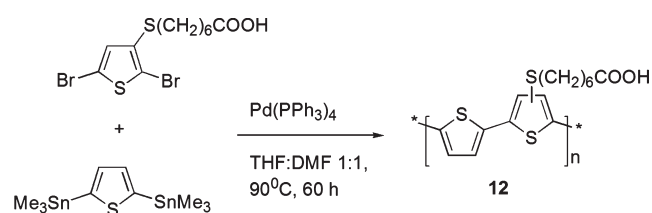
Scheme 9. Synthesis of Alternating Copolymers Composed of Benzimidazole and Thiophene Blocks



Scheme 10. Synthesis of Polythiophene Functionalized with the Cysteine Moiety



Scheme 11. Synthesis of Polythiophenes Bearing Free Carboxylic Acids



and co-workers reported a ferrocene-containing polymer.⁸⁴ Ferrocene has long been recognized to stabilize α -carbocations and can serve as an excellent donor for an NLO-chromophore. The ferrocene–fluorene complex **20** (Scheme 17) was the first conjugated organic polymer backbone to possess pendant ferrocene moieties.

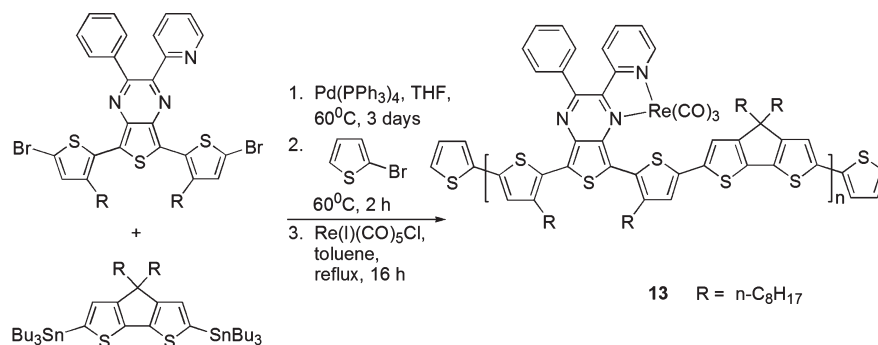
Functionalized aromatic polyimides were promising for the investigation of second-order NLO materials because their high glass transition temperatures could be utilized to stabilize the dipole orientation of the NLO chromophore after electric polling at high temperatures. Yu and co-workers explored the Stille reaction to synthesize imide-containing polymers⁸⁵ **21** and **22** (Schemes 18 and 19). As the loading of the NLO chromophore increased, the average distance between chromophore dipoles decreased and the antiparallel chromophore–chromophore electrostatic dipole interaction became stronger. These strong interactions will cancel the nonlinear optical contributions of the chromophores. With the loading density for **21** decreased from 65.04% of **22** to 50.85%, the glass transition temperature (T_g) and r_{33} values both increased, which implied a higher orientational stability of the chromophores. The T_g values for polymers **21** and **22** were 125 and 170 °C, respectively, while their r_{33} values were 9 and 35 pm/V, respectively.

While it has long been known that chromophores must be oriented in a noncentrosymmetrical way to be useful for NLO applications, chromophores tend to have high dipole moments above a critical loading density. Because of this, electrostatic interactions occur that favor centrosymmetrical ordering of the chromophores in the polymer matrix. Several approaches have been investigated to diminish the dipolar interactions. Samyn^{86,87} proposed a chiral, helical polybinaphthalene matrix using Stille polycondensation. There were two main advantages of this approach. First, the rigidity of the backbone could greatly diminish unwanted dipolar interactions between the chromophores, allowing a very high chromophore density. Second, when chiral polymers were used, the system could benefit from its chirality, giving rise to the relaxation of the need for polar order and the presence of contributions, inherent to chirality, which could increase the nonlinear optical response, as shown in polymer **23** (Scheme 20). Differential scanning calorimetry (DSC) and second-harmonic generation experiments revealed that the mobility of the chromophore in the polymers, prepared from optically impure monomers, is much higher than that in polymers obtained by polymerization of optically pure monomers. Hyper-Rayleigh scattering measurements demonstrated that this difference in mobility is due to a different macromolecular structure.

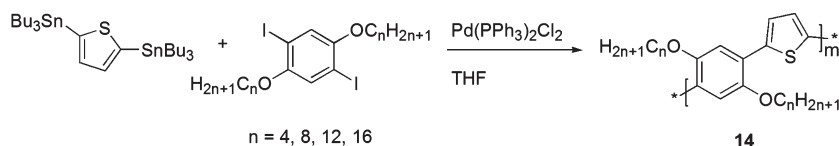
Further research regarding the influence of optically impure binaphthalene monomers on the conformation and properties was carried out in 2005 by Samyn and co-workers.⁸⁸ The Stille coupling reaction was applied to this system and it was demonstrated that impurity of monomers led to nonhelical polymers. In the meantime, the results confirmed that there was no preference for enantiomers to react with monomers in the same configuration.

4.2.4. Photorefractive Materials. Photorefractive (PR) materials are another important class of NLO polymers that can be used to record and erase holograms many times without the need for chemical processing. To manifest PR effects, a

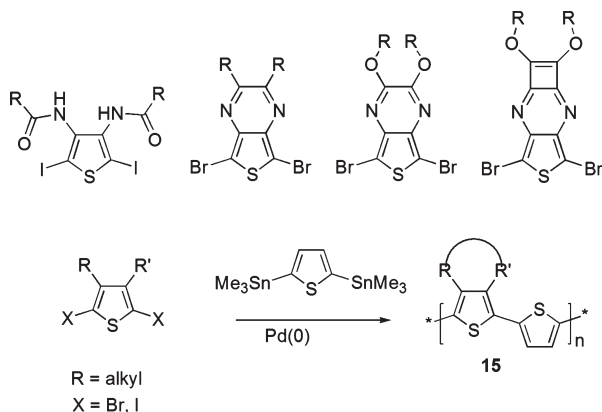
Scheme 12. Synthesis of Rhenium(I)-Containing Conjugated Polymers



Scheme 13. Synthesis of Poly(1,4-phenylene-2,5-thiophene)s



Scheme 14. Monomers Used and Examples of the Stille Reaction for Synthesis of Polythiophenes

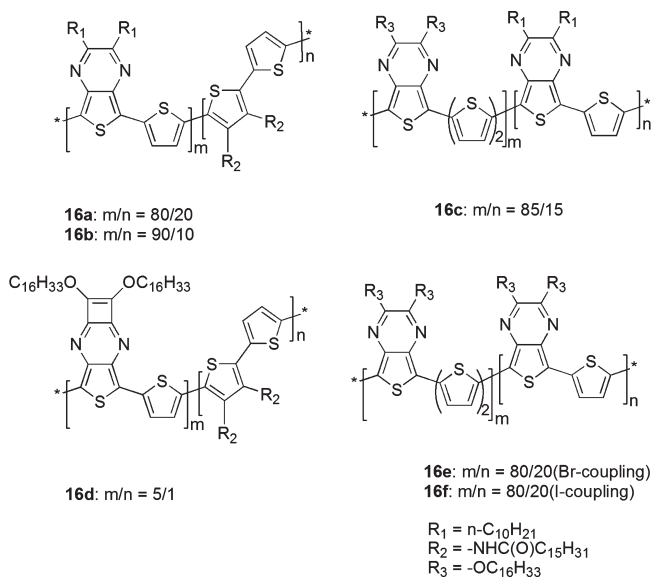


polymer must possess a photocharge generator, a charge transporter, a charge trapping center, and a nonlinear optical chromophore. A PR polymer, containing a conjugated backbone, a second-order NLO chromophore, and a small amount of charge trapping species was developed by Yu and co-workers.^{89–91} The conjugated backbone was shown to absorb photons in the visible region and could play the triple role of charge generator, charge transporter, and backbone. Polymers such as **24** (Scheme 21), incorporating the dihydropyrrolopyrroldione moiety, are known to exhibit strong absorption in the visible region. Conjugated polymers containing this moiety have also recently become interesting photovoltaic materials. New PR polymers **25–27** (Scheme 22) containing electron-withdrawing tricyanodihydrofuran derivatives exhibited high PR performances. An optical gain coefficient of 158 cm^{-1} at a field of $50 \text{ V}/\mu\text{m}$ and a diffraction efficiency of 68% at a field of $46 \text{ V}/\mu\text{m}$ for **25** were obtained, which are among the best values for fully functionalized PR polymers.

4.3. Polymer Field Effect Transistors (OFET)

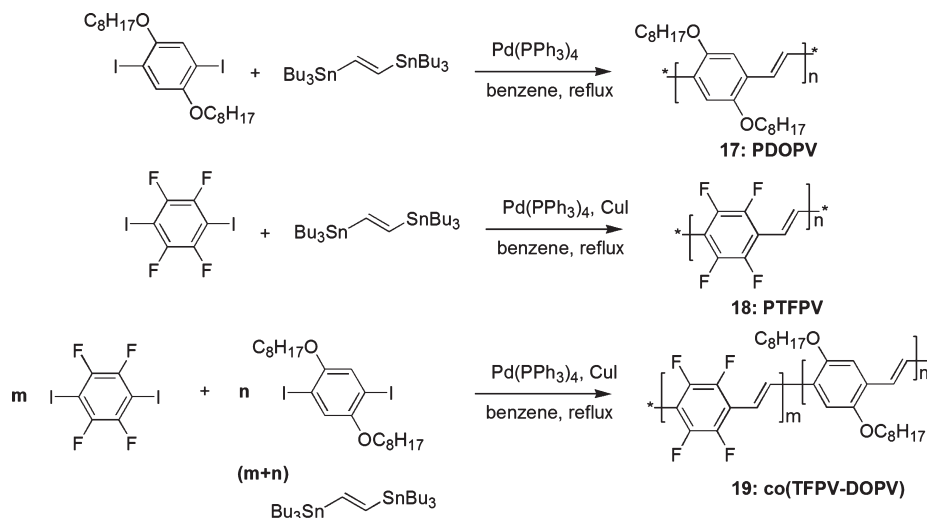
4.3.1. Background and Organic Field Effect Transistor Concept. Organic field effect transistors (OFET) are another

Scheme 15. Structural Formulas of the Polythiophenes Investigated

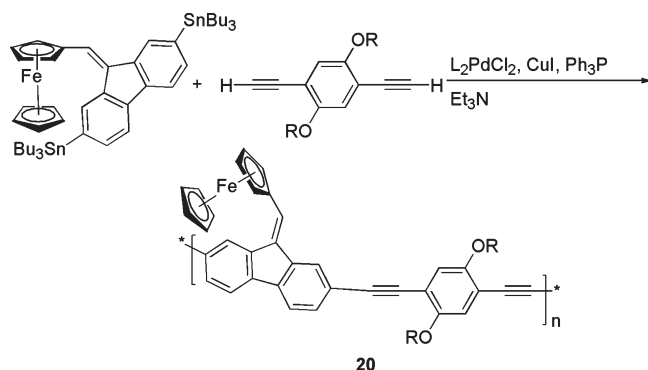


important application area of semiconducting polymers. The interest in the development of polymer FETs has surged in the last 2 decades due to all of the advantages inherent to organic electronics, such as the ability to produce flexible displays, low-cost fabrication, and solution processability. Typical FET devices consist of a gate electrode, a dielectric insulating layer, and a polymer semiconducting material sandwiched between a source and drain electrode. When zero bias is applied to the gate electrode, there is nearly zero current between the source and drain electrode. Once a bias is applied to the gate electrode, a field is generated at the polymer semiconductor–dielectric interface, which shifts the HOMO and LUMO energy levels of the semiconducting polymer. Therefore, electrons can flow from the HOMO to the electrode or from the electrode to the LUMO, forming a conducting channel between the source and drain electrodes to form the current.

Scheme 16. Syntheses of Tetrafluoro and Dialkoxy-Substituted Poly(phenylenevinylene)s



Scheme 17. Synthesis of Conjugated Polymer with a Pendant Ferrocene Group



For a semiconducting polymer to function as an OFET, the polymers must satisfy the following conditions: the HOMO energy level (or the LUMO energy level) should be matched with the work function of electrodes, the polymer should be stable to oxidation, and it should exhibit high carrier (hole or electron) mobility.^{92–97} In the field of polymer FETs, the Stille polycondensation has been effectively employed for the syntheses of high-performance polymers.

4.3.2. Examples of Polymers for OFET Applications.

Thiophene-based polymers have been extensively employed in OFETs and many of them have been prepared via Stille polycondensation. McGehee et al.⁹⁸ synthesized regioregular polythiophenes containing electron-withdrawing carboxylate substituents, **28** (Scheme 23), by using the Stille coupling method, employing $\text{Pd(PPh}_3)_4$, in toluene and heating at 115 °C. Although their reported molecular weight was only around 6.6 kDa, these polymers provided better oxidative doping stability than conventional polythiophenes due to the lowering of their HOMO energy levels. The top-contact organic thin-film transistors (OTFTs) fabricated entirely in air had measured mobilities averaging 0.06 $\text{cm}^2/\text{V}\cdot\text{s}$ with on/off ratios $>10^5$.

Tierney and co-workers reported⁹⁹ two polythiophenes, **29a,b** (Scheme 24), exhibiting number-averaged molecular weights of

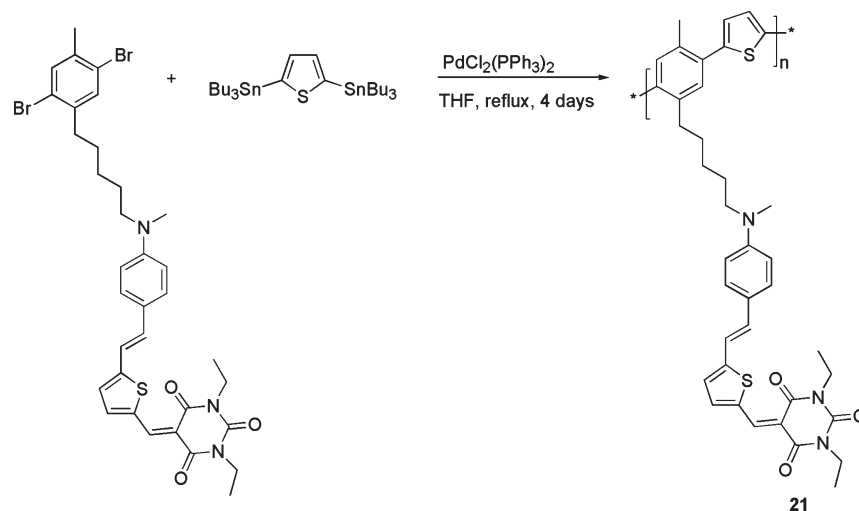
approximately 13 and 30 kDa, respectively. The OTFTs exhibited charge carrier mobilities as high as 0.03 $\text{cm}^2/\text{V}\cdot\text{s}$ and on/off ratios of $10-10^4$ when measured in air. The polymers were synthesized using $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$, with toluene as solvent and microwave irradiation.

McCulloch and co-workers¹⁰⁰ prepared a thieno[2,3-*b*]-thiophene based polymer, **30** (Scheme 25), where thieno[2,3-*b*]thiophene was incorporated into a polythiophene backbone using the Stille polycondensation. The polymerization was performed under microwave irradiation using $\text{Pd}_2(\text{dba})_3$, $\text{P}(o\text{-tolyl})_3$ as catalyst, resulting in improved molecular weight and reduced reaction times compared to conventional heating. The OTFTs exhibited charge carrier mobilities of up to 0.15 $\text{cm}^2/\text{V}\cdot\text{s}$ and on/off ratios greater than 10^5 when measured in air.

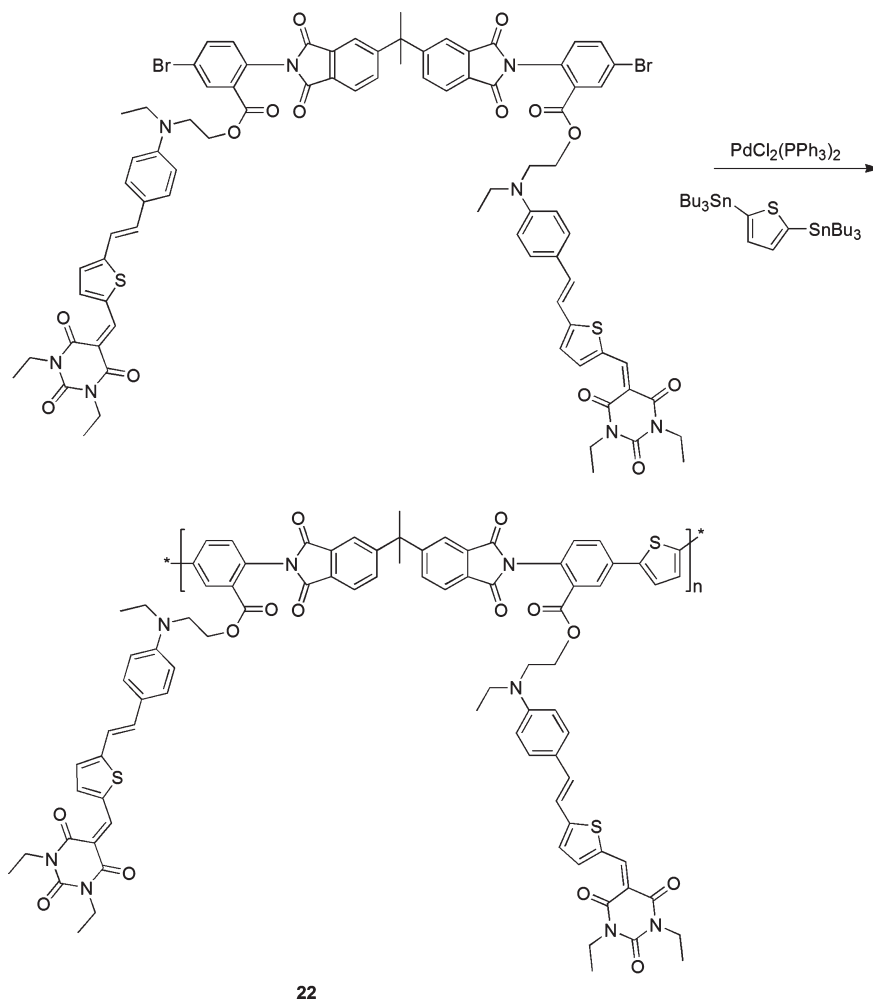
In 2005,⁴⁴ McCulloch and co-workers studied the influence of reaction conditions including solvent, catalyst, and additives to the molecular weight of polythiophene **31** (Scheme 26) in microwave-assisted Stille polycondensations. When employed in the reaction, chlorobenzene yielded polythiophenes with improved molecular weights compared to those obtained using THF after a 10 min heating ($M_n = 4.7$ versus 1.8 kDa, respectively). The reason for the improvement was reportedly because chlorobenzene has a higher boiling point and can maintain the growing polymer in solution very well. Different $\text{Pd}(0)$ catalysts were tested, where Pd(II) catalysts were excluded in order to avoid potential stoichiometric imbalances stemming from consumption of organotin reagent. Including $\text{Pd(PPh}_3)_4$, a series of catalytic systems were investigated, namely $\text{Pd}_2(\text{dba})_3/\text{AsPh}_3$ and $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$. When $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$, LiCl additive, and chlorobenzene solvent were used for the microwave-assisted polycondensation, the molecular weight of the polymer ($M_n = 16.8$ kDa) was reportedly higher than that ($M_n = 3.0$ kDa) prepared by conventional heating using the same catalyst and solvent.

Marder and co-workers¹⁰¹ synthesized electron-transporting polymers based on alternating perylene diimide and dithienothiophene units, **32** (Scheme 27). Their weight-averaged molecular weights (M_w) and polydispersity indexes were 15.0 kDa and 1.5, respectively. The Stille polycondensation conditions used

Scheme 18. Synthesis of Conjugated Polymer 21 with Pendant Imide-Bearing NLO Chromophore



Scheme 19. Synthesis of Conjugated Polymer 22 with Pendant Imide-Bearing NLO Chromophore

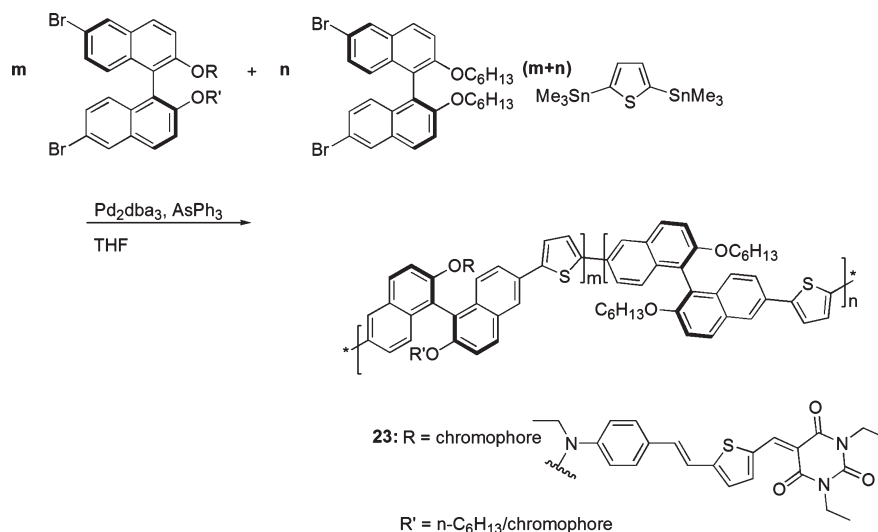
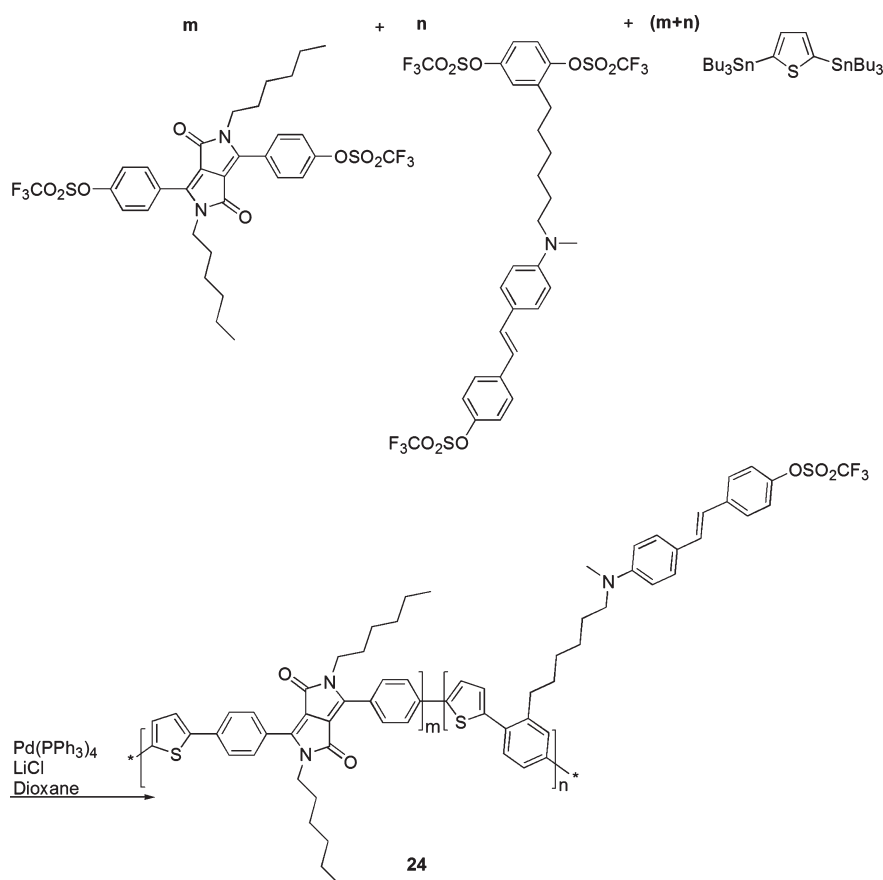


employed $\text{Pd}(\text{PPh}_3)_4$ as catalyst and toluene as solvent and required heating at 90 °C.

Toney and co-workers¹⁰² synthesized semiconducting liquid-crystalline thieno[3,2-*b*]thiophene-based polymers, 33a–c

(Scheme 28), using $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$ as catalyst and dichlorobenzene as solvent and requiring heating in the microwave reactor. They obtained the polymer with M_n of 54 kDa. Mobilities equivalent to those found in amorphous

Scheme 20. Synthesis of Chiral Polybinaphthalenes

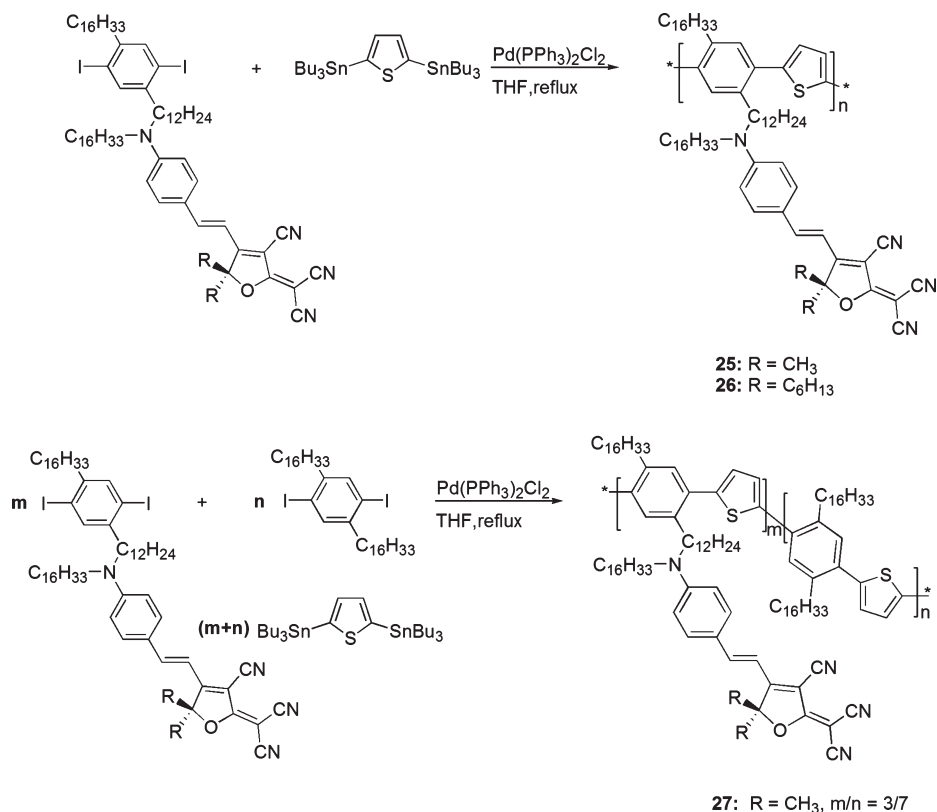
Scheme 21. Synthesis of Polymers Containing Pyrrole[3,4-*c*]pyrrole-1,3-dione-3,6-diyl Units

silicon were achieved with printable semiconducting polymers.

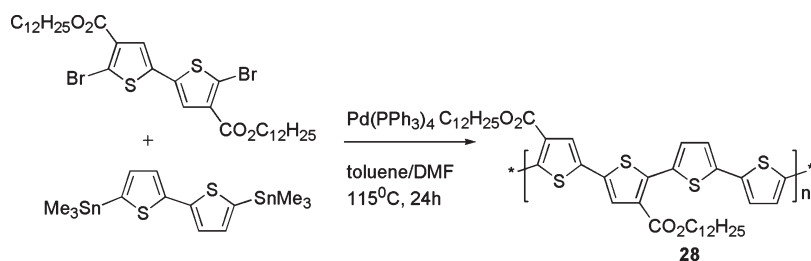
Marc's et al.¹⁰³ synthesized a series of dithienosilole based polymers, **34a–c** (Scheme 29). The polymers were prepared via a Stille polycondensation using the catalyst Pd(PPh₃)₂Cl₂. The molecular weights were reportedly between $M_n = 26$ and 41 kDa, and all polymers showed good thermal and air stability.

4.4. Polymer Solar Cell Materials (OPVs)

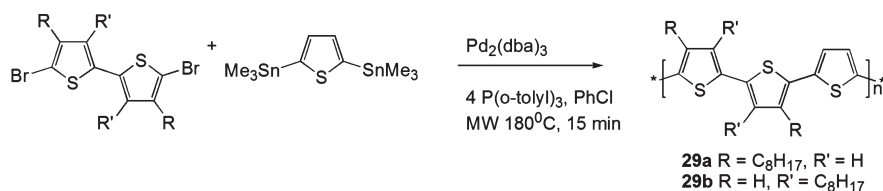
4.4.1. Background and General Concept of Polymer Organic Solar Cells. Polymer-based organic solar cells (PSCs) have emerged as a promising low-cost alternative to inorganic solar cell materials. They have the potential to provide technologies to fabricate flexible, large, and lightweight devices in a more cost-effective manner using solution processing.^{104–107}

Scheme 22. Synthesis of Tricyanodihydrofuran-Bearing Poly(*p*-phenylenethiophene)s

Scheme 23. Synthesis of Regioregular Polythiophenes with Carboxylate Substituents

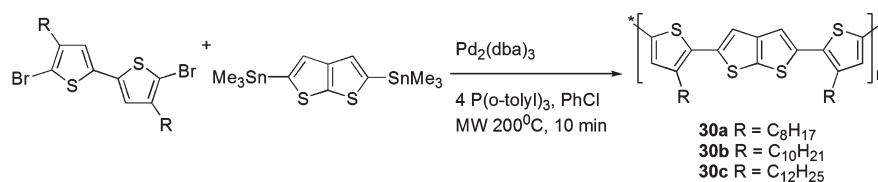


Scheme 24. Synthesis of Polythiophenes 29a and 29b



The most efficient and feasible approach for PSCs is represented by the bulk heterojunction (BHJ) model, consisting of a bicontinuous composite of donor and acceptor phases between electrodes with different work functions. The general working principle in BHJ devices includes the photoexcitation of an electroactive material (usually p-type polymers) by the absorption of light-energy to generate excitons. These excitons diffuse to the donor–acceptor (D–A) interface, where exciton dissociation occurs via an electron-transfer process. The fully

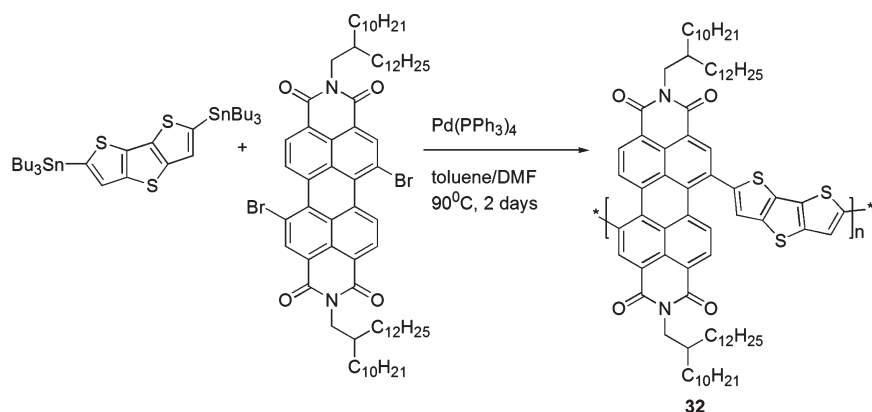
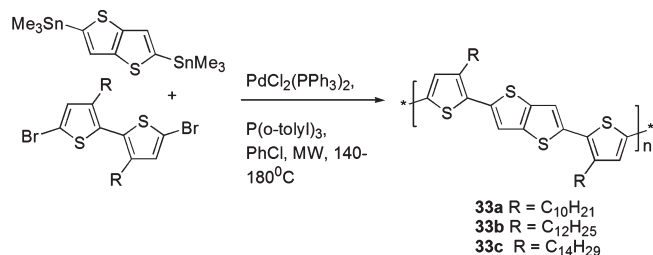
dissociated free charge carriers transport to the respective electrodes in opposite directions, with the driving force being the internal electric field and chemical potential differences between electrodes. This in turn generates the photocurrent and photovoltage. Since nanoscale phase separation in BHJs enables maximization of interfacial areas between two components, efficient charge separation can be attained and polymer solar cells with reliable efficiencies between 5 and 6% were reported by employing conjugated polymer–fullerene

Scheme 25. Synthesis of Thieno[2,3-*b*]thiophene-Based Polymers

Scheme 26. Microwave-Assisted Synthesis of High Molecular Weight Polythiophenes



Scheme 27. Synthesis of Polymers Based on Alternating Perylenediimides and Dithienothiophene Units

Scheme 28. Synthesis of Semiconducting Liquid-Crystalline Thieno[3,2-*b*]thiophene-Based Polymers

composites. Numerous polymers were developed for PSCs with high performance. Those polymers are primarily thiophene-based low band gap materials.^{108–112}

4.4.2. Examples of Polymer Solar Cell Materials. The most reliable and efficient methodology for the synthesis of thiophene-based conjugated polymers reported thus far has been the Stille coupling polymerization in which $\text{Pd}(\text{PPh}_3)_4$ is employed as catalyst and toluene or another relatively high boiling point solvent is usually used. Li and co-workers¹¹³ synthesized a series of polythiophene derivatives **35a–c** (Scheme 30) with bi(thienylenevinylene) side chains using this $\text{Pd}(0)$ catalyst. These polymers showed M_w values from 20 to 50 kDa and, compared with the UV–visible absorption spectra of poly(3-hexylthiophene) (P3HT), cover a more broad absorption range

due to absorption in the region between 350 and 450 nm of the conjugated bi(thienylenevinylene) side chains. The maximum power conversion efficiency (PCE) of the solar cell device based on **35b** reached 3.18% under AM 100 mW/cm^2 , which represents a 38% efficiency increase in comparison with that of the devices based on P3HT under the same conditions (2.41%).

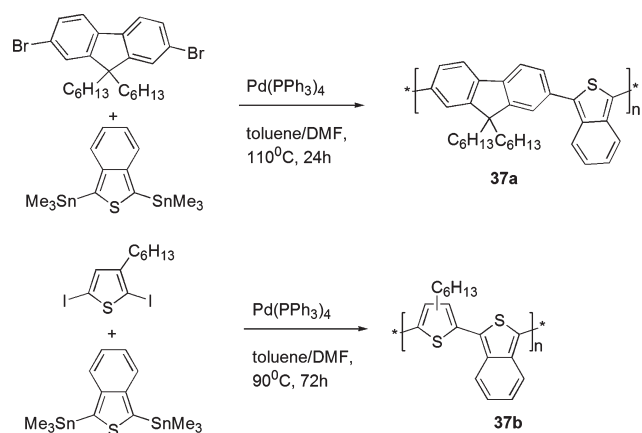
In order to adjust the band gap of polythiophenes, which usually have relatively high band gaps of approximately 2.0 eV, Yu et al.¹¹⁴ prepared a series of copolymers **36a–d** (Scheme 31) including different ratios of thieno[3,4-*b*]thiophene. Using the $\text{Pd}(\text{PPh}_3)_4$ catalyst and a mixed solvent system of toluene/DMF at 120 °C, they prepared the copolymers with weight-averaged molecular weights as high as 130 kDa. These were much greater than those reported for other thiophene-based polymers prepared by the step-growth polymerization method. The composition of these polymers could be fine-tuned by adjusting the feed ratios of monomers. Thus, the band gap and the physical properties of the resulting polymers could be controlled by adjusting their compositions.

Yu and co-workers¹¹⁵ also synthesized a thieno[3,4-*b*]thiophene-based polymer **37** (Scheme 32) containing a perfluorinated alkyl chain on thieno[3,4-*b*]thiophene with the same reaction conditions. However, this polymer had a lower M_w value of 19 kDa, which corresponded to only approximately six repeating units. This result was attributed to the limited solubility of the polymer. These polymers were shown to yield single layer solar cells with PCE values between 1.5 and 2.8%.

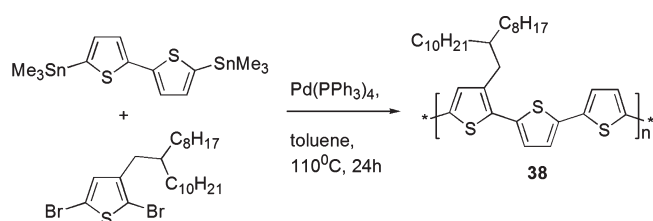
the copolymers and PC₆₁BM gave power conversion efficiencies ranging from 0.12% to 0.42%.

In 2009, Yang and co-workers¹¹⁷ employed Stille coupling polymerization to prepare a regioregular polythiophene with fewer alkyl side chains than typical polyalkylthiophenes in order to reduce the electron-donating effect of the alkyl side chains. Compared to the McCullough-type method typically used in

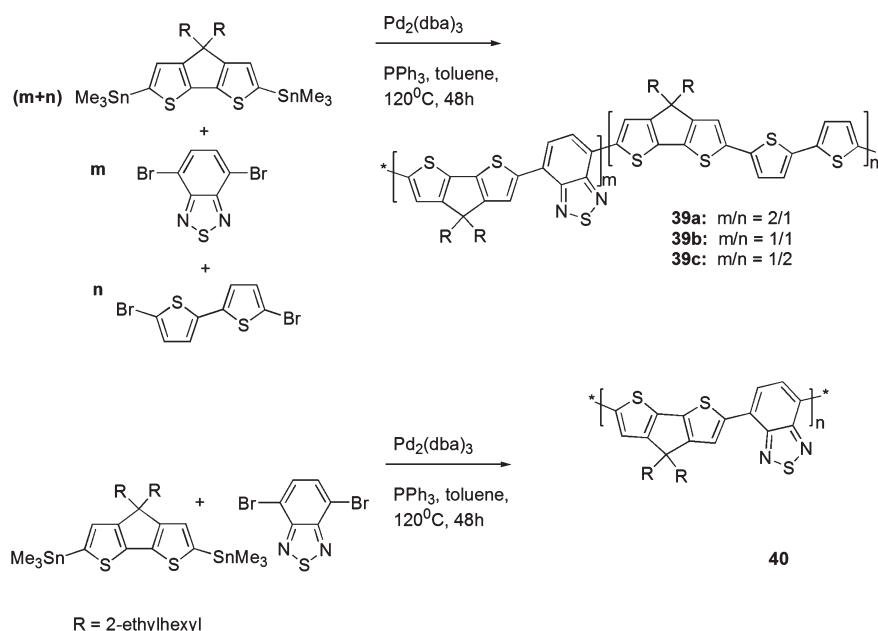
Scheme 33. Synthesis of Fluorene–Isothianaphthene and Thiophene–Isothianaphthene Copolymers



Scheme 34. Synthesis of Poly(3-alkylthiophene) Polymer P3HDTT



Scheme 35. Synthesis of Random Copolymers Containing 4,4-Bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and Benzothiadiazole Units

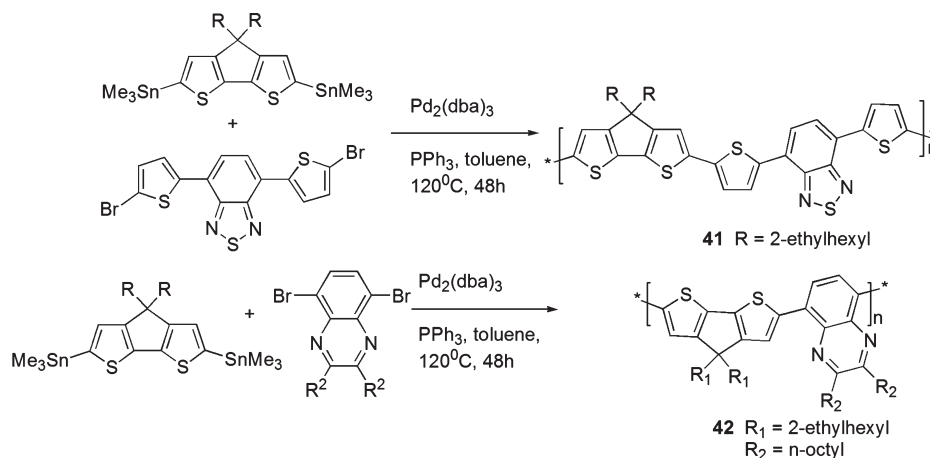
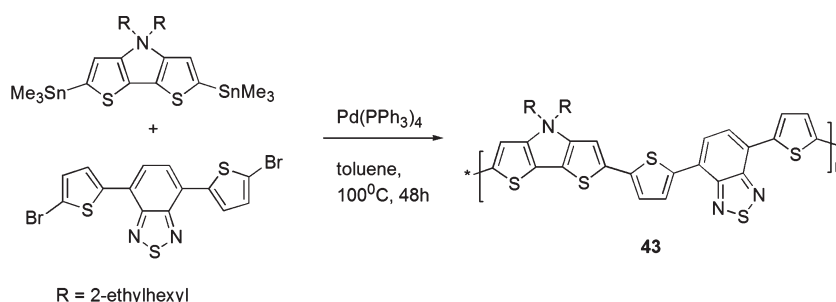


preparation of polyalkylthiophenes, Stille coupling conditions using the $\text{Pd}(\text{PPh}_3)_4$ catalyst, toluene solvent, and reflux gave the polymer 38 (Scheme 34) with acceptable molecular weight ($M_w = 18.9$ kDa with a PDI of 1.8). The solar cells prepared from the polymer and PCBM exhibited a maximum PCE of 3.4% with a V_{oc} of 0.82 V under illumination of AM1.5G, 100 mW/cm^2 .

Various 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophenes (CPDTs), which have analogous structures to that of fluorene, were synthesized and employed in low band gap polymers for polymer solar cells. Due to their planar structures, they are known to effectively reduce the band gap of the polymer and improve charge carrier mobility. Various polymers including CPDTs with different bridge atoms such as silicon, carbon, and nitrogen were prepared using the Stille polycondensation. Brabec and co-workers¹¹⁸ synthesized random copolymers including 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene units using the $\text{Pd}_2(\text{dba})_3/\text{PPh}_3$ catalytic system (Scheme 35). These polymers were obtained with relatively narrow polydispersities of about 1.5. The solar cell devices prepared using 40 showed a PCE of 3.5% under the standard AM1.5 conditions.

Copolymers of 4,4-bisalkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 2,1,3-benzothiadiazole with various alkyl chains were synthesized via a Stille coupling method in several groups.^{118,119} In 2007, the copolymer of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 2,1,3-benzothiadiazole reported by Bazan et al.¹²⁰ showed 5.5% power conversion efficiency. Subsequently, 4,4-bisalkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene was used as an electron-donating building block for the synthesis of a series of donor–acceptor type conjugated polymers, 41 and 42 (Scheme 36). In addition to benzothiadiazole, other electron-accepting compounds such as quinoxaline and dithiophene-ylbenzothiadiazole were also copolymerized with 4,4-bisalkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene using Stille coupling polymerization.¹²¹

Hashimoto et al.¹²² synthesized an alternating copolymer of 2,6-dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) and 2,1,3-benzothiadiazole which showed a molecular weight of 6.0 kDa using

Scheme 36. Synthesis of Copolymers Containing Cyclopenta[2,1-*b*:3,5-*b'*]dithiophene and Benzothiadiazole UnitsScheme 37. Synthesis of Copolymers Containing 2,6-Dithieno[3,2-*b*:2',3'-*d*]pyrrole and Benzothiadiazole Units

$\text{Pd}(\text{PPh}_3)_4$ as catalyst (Scheme 37). The photovoltaic device based on **43**:PC₆₀BM bulk heterojunction showed a power conversion efficiency of 2.18%.

Various copolymers, **44** and **45** (Scheme 38), including 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, with silane bridges were reported by several different groups.^{123–125} Most often, a 2,1,3-benzothiadiazole was used as comonomer and the polymers exhibited narrow band gaps due to their donor–acceptor structures. The substitution of silicon atoms with silicon on the main chain of a conjugated polythiophene gives a polysilole with higher crystallinity, improved charge transport, reduced bimolecular recombination, and reduced formation of charge transfer complexes when blended with a fullerene derivative.

Recently, the benzo[1,2-*b*:4,5-*b'*]dithiophene has emerged as an important building block for synthesis of low band gap polymers with high hole mobility. Yu and co-workers¹²⁶ synthesized such a low band gap polymer via Stille coupling polymerization. This synthesis employed $\text{Pd}(\text{PPh}_3)_4$ as the catalyst and toluene/DMF as the solvent and was carried out at 120 °C. A series of derivatives of these polymers,¹⁰⁸ **46a–e** (Scheme 39), were also prepared using the same polymerization conditions. All polymers showed narrow polydispersities of 1.2–1.5 with weight-averaged molecular weights of approximately 25 kDa. The bulk heterojunction photovoltaic devices based on these polymers in a blend with PC₆₁BM showed power conversion efficiencies as high as 6%.

Several other benzo[1,2-*b*:4,5-*b'*]dithiophene-based copolymers with various alternating units were also reported. Yang and co-workers¹²⁷ synthesized several copolymers, **47a–h** (Scheme 40), including benzo[1,2-*b*:4,5-*b'*]dithiophene and

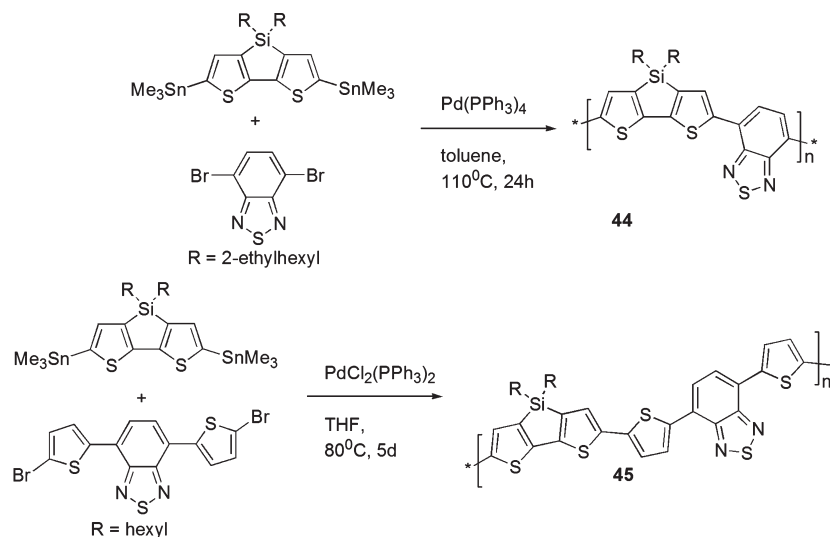
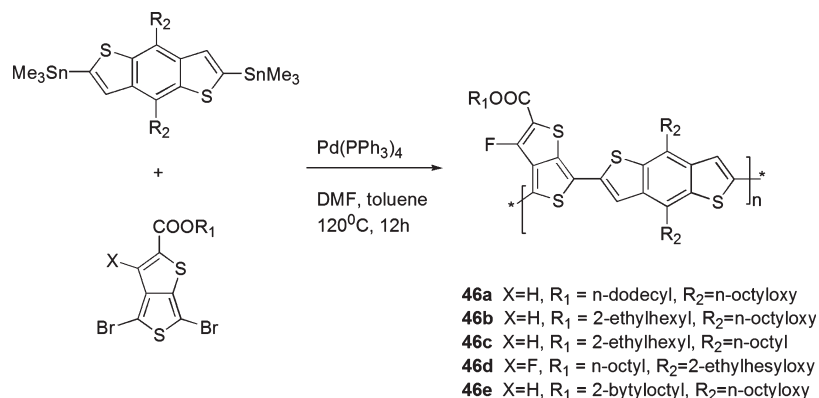
different monomers using Stille coupling polycondensation. They also investigated the relationship between polymer structure and molecular energy levels.

In 2010, Yu et al.¹⁰⁹ synthesized copolymer **48** (Scheme 41) of benzo[1,2-*b*:4,5-*b'*]dithiophene and thieno[3,4-*b*]thiophene using $\text{Pd}(\text{PPh}_3)_4$ as catalyst. The molecular weight of this polymer was approximately 100 kDa, which is 4 times greater than that of other polymers incorporating the same backbone structure. They showed totally different M_w values despite using the same polycondensation conditions. This is most likely due to the different solubility of the polymer chains. The solar cell device based on this polymer showed very high power conversion efficiency, with values between 7.4 and 7.8%.

The thieno[3,2-*b*]thiophene moieties are also attractive building blocks for low band gap polymers in the polymer solar cell field because the fused thiophene ring is known to improve the charge carrier mobility. Polymers **49** and **50** (Scheme 42) were prepared using the $\text{Pd}(\text{PPh}_3)_4$ -catalyzed Stille coupling method by Li and co-workers. These polymers showed very narrow polydispersity values of 1.1.¹²⁸

Because the carrier mobility of polymers in solar cell devices tends to increase with high molecular weight, many groups have tried to increase the molecular weight by changing polymerization conditions. Bazan and co-workers⁶⁵ synthesized the polymer **51** (Scheme 43) using two different sets of conditions. When using $\text{Pd}(\text{PPh}_3)_4$ catalyst and heating at 120 °C for 48 h, the M_n value of the polymer was reported as 7–10 kDa, but with the same catalyst and 30 min heating under microwave irradiation, the M_n was reported to increase to 44 kDa. The polymer with higher molecular weight showed a much higher current density in

Scheme 38. Synthesis of Polymers Containing Cyclopentadithiophenes with Silane Bridges

Scheme 39. Synthesis of Copolymers of Fluorinated Thieno[3,4-*b*]thiophene and Benzodithiophene Units

a solar cell device when compared to the polymer of lower molecular weight; thus, optimization of reaction conditions played a critical role in improving device efficiency. Bazan and co-workers¹²⁹ also reported PCEs as high as 1.86% for polymers incorporating biselenophene and cyclopentadithiophene moieties synthesized via Stille coupling. The highest efficiencies were obtained from blend films with PC₇₁BM as acceptor.

Other palladium compounds with different ligands have also been used as catalysts. A benzo[1,2-*b*:4,5-*b'*]dithiophene-based polymer with thieno[3,4-*c*]-4,6-dione, **52** (Scheme 44), reported by Leclerc and co-workers¹³⁰ was prepared using the Stille polycondensation with Pd₂(dba)₃, P(*o*-tolyl)₃ as catalyst and toluene as solvent and heating at 110 °C.

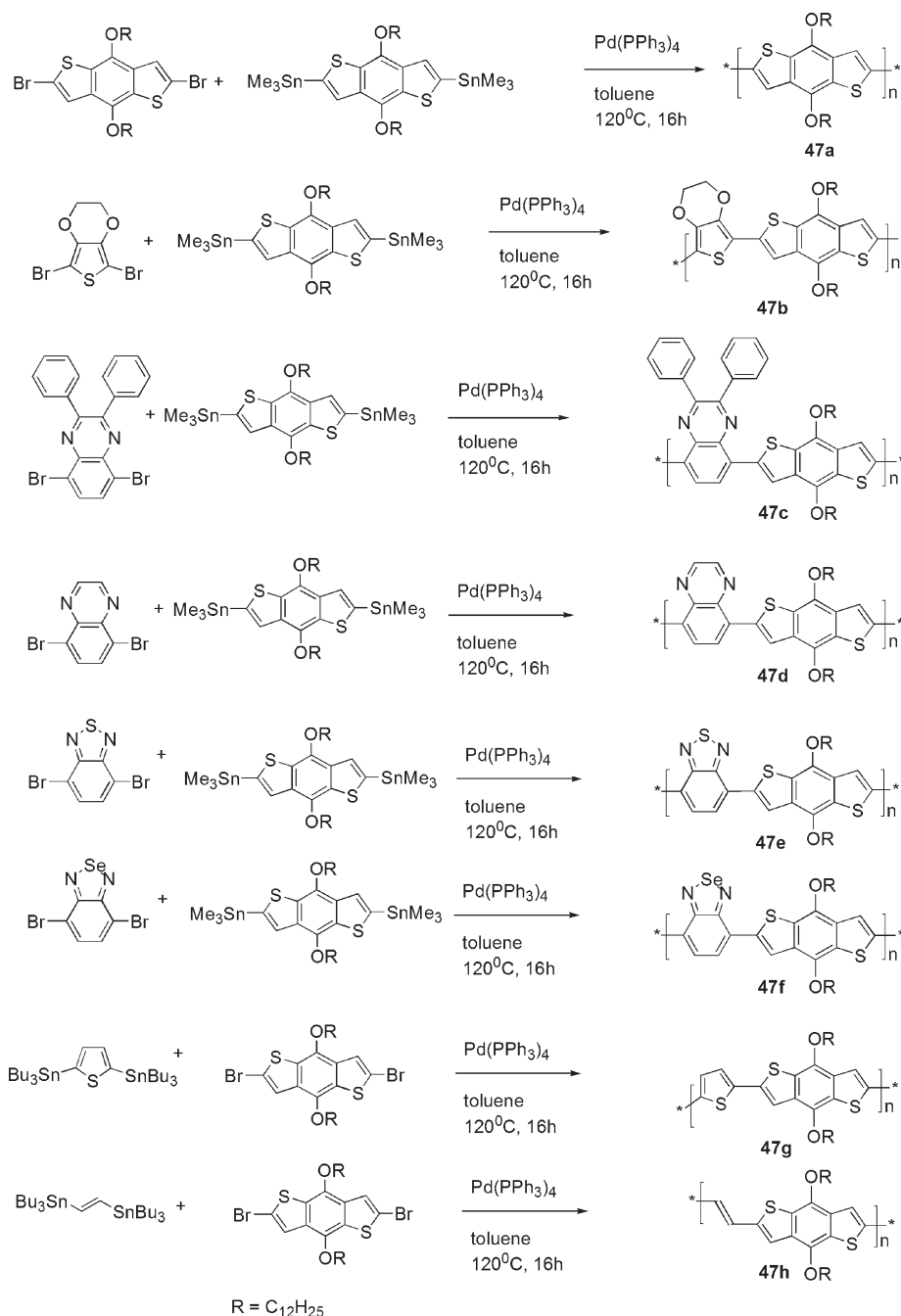
Krebs and co-workers¹³¹ synthesized a series of polymers, **53a–f** (Scheme 45), based on thiophene, benzothiadiazole, and benzobis(thiadiazole) using Pd(PPh₃)₂Cl₂ catalyst. Pd(PPh₃)₂Cl₂ is known to be more stable to oxygen and light.

Geng et al.¹³² in 2009 reported PCEs as high as 2.23% for so-called “black” polymers. These polymers, composed of thiophene and benzothiadiazole units, showed band gaps in the range of 1.52–1.56 eV, covering with absorption between 400 and 800 nm. In 2010, Bao et al.¹³³ reported PCEs as high as 1.42% for polymers prepared via Stille coupling. These random polymers

were composed of benzothiadiazole and fluorene units. Significantly, the *V*_{oc} of these polymers reached as high as 0.765 V with *J*_{sc} of 5.82 mA/cm². Leclerc et al.¹³⁴ reported PCEs as high as 1.8% for thiophene polymers also incorporating 2,1,3-benzothiadiazole together with thieno[3,2-*b*]thiophene.

Fréchet and co-workers⁴³ reported in 2010 the synthesis of polymers **54a–c** (Scheme 46) based on *N*-alkylthieno[3,4-*c*]pyrrole-4,6-dione and benzodithiophene blocks. The solar cell devices based on **54a–c** showed power conversion efficiencies of 3.9, 5.4, and 6.6%, respectively. They also reported a correlation between higher PCE and the steric bulk of the alkyl chain. As noted, **54c** showed the highest PCE of 6.6%, where the *N*-substituted *n*-octyl chain showed the least amount of steric bulk when compared to **54a** substituted with the 2-ethylhexyl side chain.

You and co-workers^{135–138} reported a series of polymers incorporating soluble thiadiazole[3,4-*c*]pyridine (PyT) and various “weak” donors, including naphtha[2,1-*b*:3,4-*b'*]dithiophene (NDT), dithieno[3,2-*f*:2',3'-*h*]quinoxaline (QDT), and benzo[1,2-*b*:4,5-*b'*]dithiophene (BnDT). The polymer PBnDT–DTPyT showed a high *V*_{oc} of 0.85 V, a *J*_{sc} of 12.78 mA/cm², and a PCE as high as 6.32%.

Scheme 40. Synthesis of Benzo[1,2-*b*:4,5-*b'*]dithiophene-Based Copolymers

4.5. Organic Light-Emitting Device (OLED) Polymer Materials

4.5.1. Background and General Concept of OLEDs.

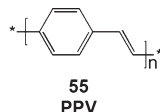
While both polymer-based organic photovoltaic devices and organic field-effect transistor devices are extremely timely and important emerging technologies, some of the first commercially viable devices in organic materials appeared in the area of organic light-emitting diode technology. From the seminal work in small-molecule based LEDs by Tang et al.¹³⁹ to the realization of commercial devices such as the Samsung Impression cell phone, one of the first devices on the U.S. market, the path to success for polymer LED devices has been long and arduous. The general phenomenon of electroluminescence has long been known in in-

organic materials, with the first observation of this phenomenon in organic materials appearing in 1963 in anthracene crystals.^{140,141} The earliest reported conjugated organic polymer-based electroluminescent materials were reported in 1989 utilizing poly(*p*-phenylene vinylene) (PPV, 55) based materials. While a thorough treatment of the literature of OLED and PLED devices is beyond the scope of this review, an extremely comprehensive review of the synthesis, history, and applications of these devices has been published, to which the reader is referred.¹⁴¹

Electroluminescence is the generation of light on application of an electric field. Charge injection into the active material results in the generation of an exciton, an electron, and a hole pair. Exciton recombination results in a singlet excited state.

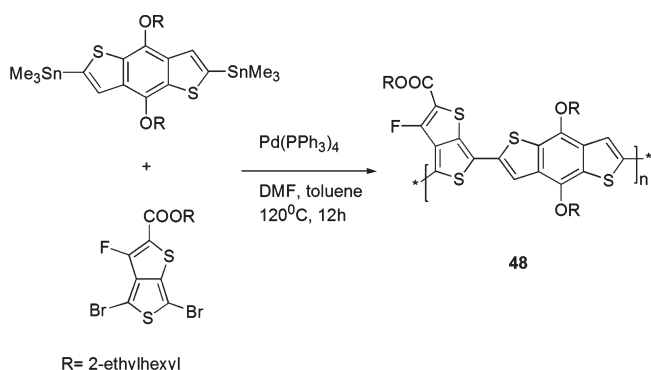
Radiative emission from this excited state is perceived as visible light if the wavelength of the emitted photon falls within the visible range of the spectrum.

Typical PLED device structure consists of the active polymer between two electrodes (anode and cathode). In typical devices, the anodic material consists of conductive indium tin oxide (ITO) on a glass or polymer substrate, while the cathode is typically a vacuum-deposited metal electrode. The active polymer is usually applied to the device via spin-coating. Notably, insoluble polymers such as PPV (**55**) can be deposited as soluble precursors that can then be converted into the final polymer structure either thermally or by photoirradiation.¹⁴¹

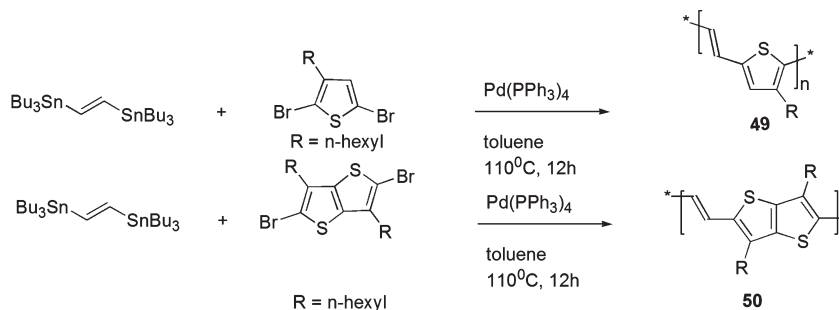


The theoretical efficiency of PLED devices depends on a number of parameters. The maximum theoretical efficiency of a single-layer polymer device is generally believed to be 25% due to the generation of a 3:1 ratio of triplet to singlet excited states.¹⁴¹ The optimization of device performance hinges upon optimal matching of HOMO and LUMO energy levels of the active polymer with the work functions of the anode and cathode, respectively. The choice of electrode materials and rational design of new polymers is clearly informed with these parameters in mind. The external quantum efficiency (EQE) of these devices is the measure of the overall device efficiency and essentially represents the amount of emitted light from the device based upon the charges injected into the material. One of the most

Scheme 41. Synthesis of 2-Ethylhexyl-Substituted Benzo[1,2-*b*:4,5-*b'*]dithiophene and Fluorinated Thieno[3,4-*b*]thiophene Copolymer



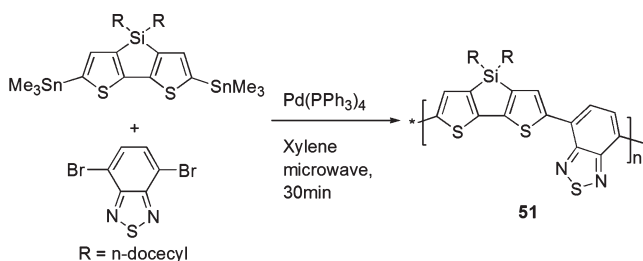
Scheme 42. Synthesis of Thieno[3,2-*b*]thiophene Polymers



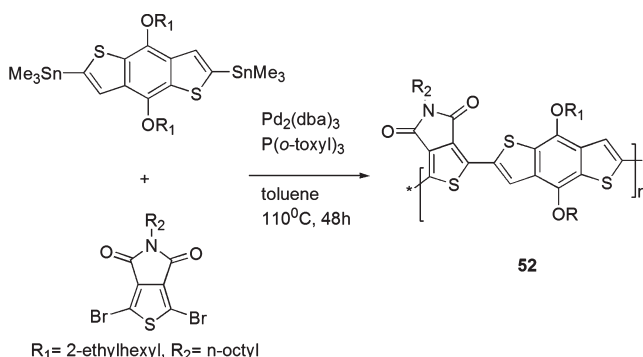
important components of device optimization has been prevention of incorporation of known fluorescence-quenching functional groups (i.e., halides) as defects in the final active polymer. These are known to substantially decrease device efficiency; thus, careful synthetic design, control of reaction conditions, and optimal purification are important in maximizing device efficiency.¹⁴¹ Throughout the evolution of synthetic methods for efficient preparation of electroluminescent polymers, the Stille coupling method has been instrumental in preparing polymers with minimal defects, therefore enabling optimal device efficiency.

4.5.2. PLED Polymers Synthesized by Stille Polycondensation. As with organic photovoltaic polymers, commonly employed reaction conditions for formation of PLED polymers include the use of 1–6 mol % of palladium catalyst including Pd(PPh₃)₄, Pd(OAc)₂, Pd(PPh₃)₂Cl₂, and Pd₂(dba)₃. The choice of solvent depends largely on the solubility of the final polymer species, and the ability to obtain high molecular weight hinges upon selection of optimal solvent. As typical for this reaction, a polar, aprotic solvent is desired, such as THF or

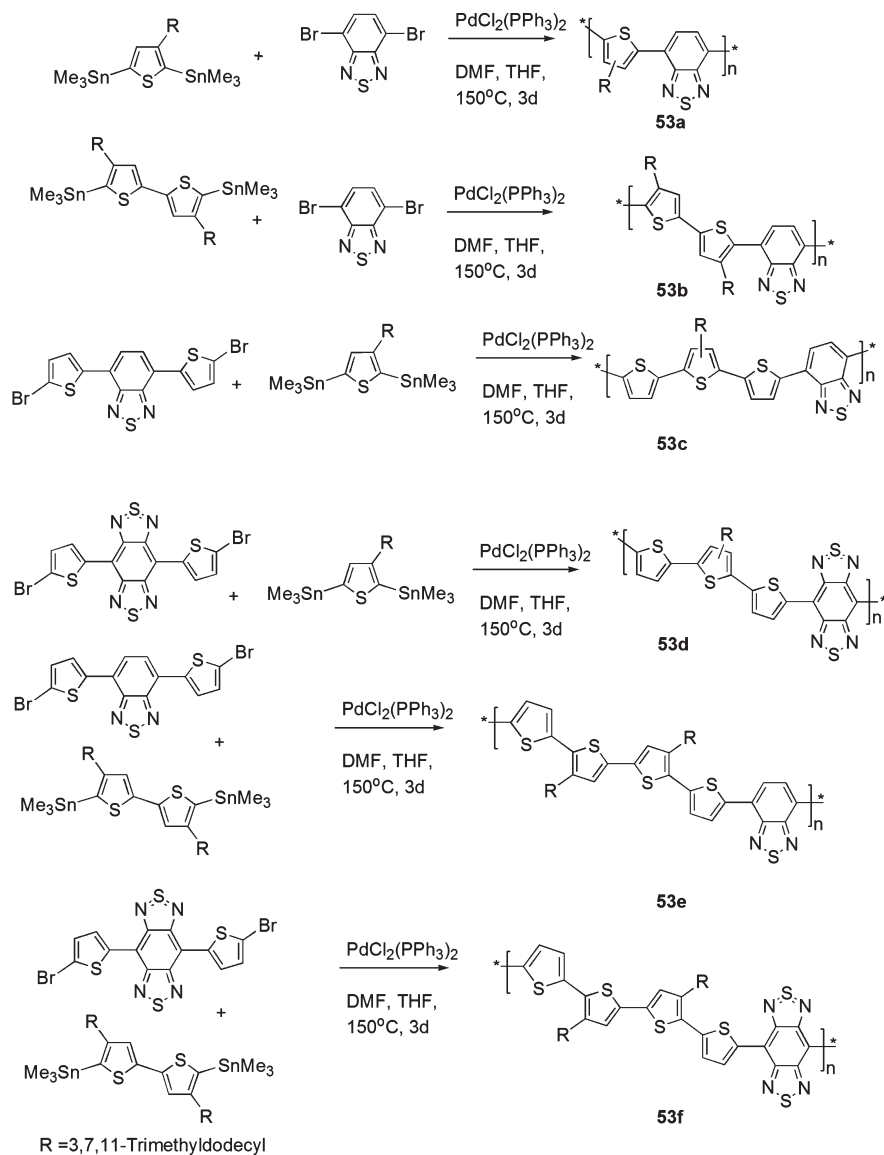
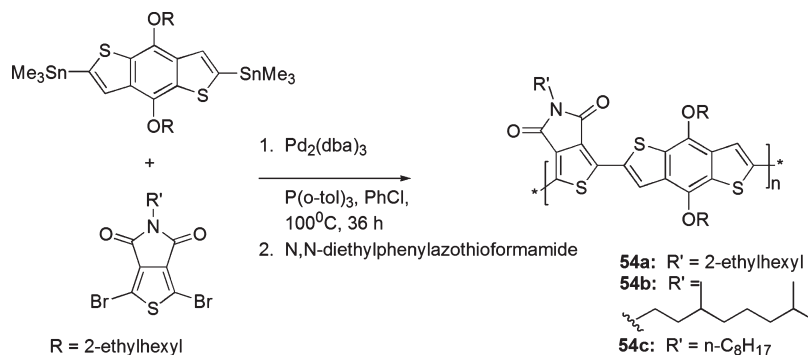
Scheme 43. Synthesis of Copolymer Containing Benzothiadiazole and Dithienosilole Blocks



Scheme 44. Synthesis of Benzo[1,2-*b*:4,5-*b'*]dithiophene-Based Polymer with Thieno[3,4-*c*]-4,6-dione Units



Scheme 45. Synthesis of Thiophene, Benzothiadiazole, and Benzobis(thiadiazole)-Based Polymers

Scheme 46. Synthesis of Copolymers of *N*-Alkylthieno[3,4-*c*]pyrrole-4,6-dione and Benzodithiophene Blocks

DMF; however, an array of different solvents have also been used, including toluene,^{5,142–146} NMP,^{147–151} benzene,¹⁵² and chlorobenzene,¹⁵³ as well as mixed solvent systems.^{154,155}

While in all cases the active catalytic species is known to be Pd(0), a few deviations from the typical Pd(PPh₃)₄ system are

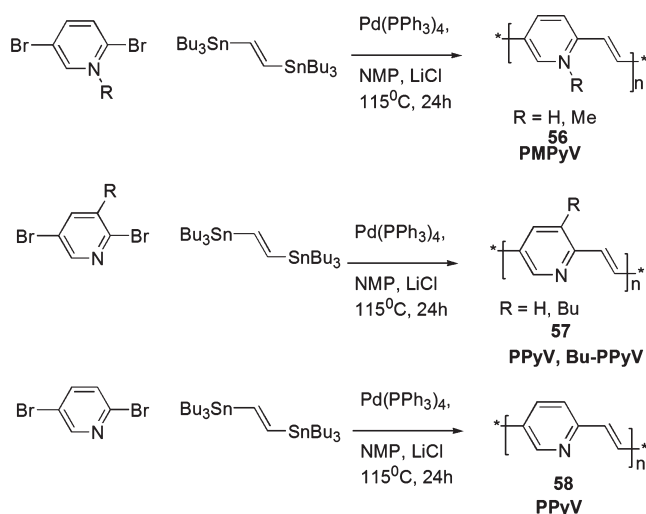
reported in which additives such as LiCl are employed as in single-molecule Stille couplings, particularly in the preparation of polymethylpyridinium vinylenes and related PPV-derived polymers, as shown in examples 56–58 (Scheme 47).

Swager et al. prepared 57 (PPyV and Bu-PPyV), reporting number

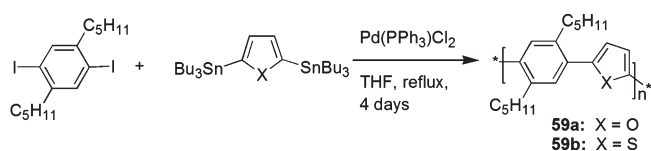
averaged molecular weights (M_n) of approximately 7.0 kDa. Notably, the highest external quantum efficiency (EQE) achieved from Bu-PPyV (**57**) devices was 0.05% for the device with configuration ITO/Bu-PPyV/Al with a PPV hole-transporting layer. These polymers were reported to emit orange-red light consistent with their photoluminescence spectra (photoluminescence maximum = 610 nm), showing an electroluminescence emission maxima of 625 and 690 nm for the nonprotonated and N-protonated forms of **57**, respectively. Devices were reported to operate for 1 h at less than 25 V applied bias. Onoda and co-workers reported an improved result for the same polymer, synthesizing PPyV (**58**) under similar conditions to obtain the final polymer with M_n = 7.3 kDa. This group reported a maximum EQE of 0.08% using a PPV hole-transport layer, with emission of yellowish-orange light (electroluminescence maximum = 585 nm).

In preparation of thiophene-based polymers, the catalysts of choice are typically $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ or $\text{Pd}_2(\text{dba})_3$,¹⁵⁶ both of which are reduced in situ to the active Pd(0) species. In the case of **59a,b** (Scheme 48), Yu and co-workers¹⁵⁷ prepared poly(phenylene)furans and poly(phenylene)thiophenes in yields greater than 90%, reporting M_n = 9.5 kDa. In this instance, the

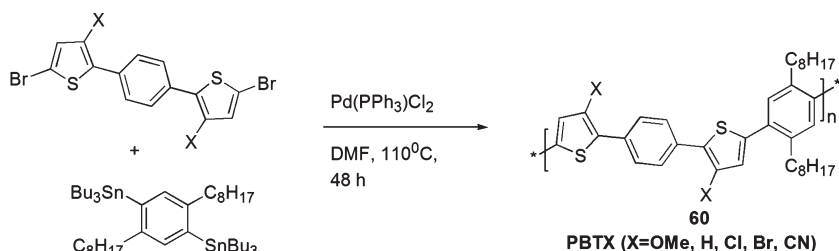
Scheme 47. Synthesis of Polymethylpyridinium Vinylenes and Related Pyridine-Derived Polymers



Scheme 48. Synthesis of Poly(phenylene)furans and Poly(phenylene)thiophenes



Scheme 49. Synthesis of Soluble Thienylene/Phenylene-Based Polymers



poly(phenylene)furan polymer exhibited a greater EQE than that observed in the analogous poly(phenylene)thiophenes, with EQE values for **59a** of 0.1% compared to 0.03% for the thiophene-containing polymer; however, more than 50% of the furan-based device was shown to decay within around 2 h due to photochemical instability.

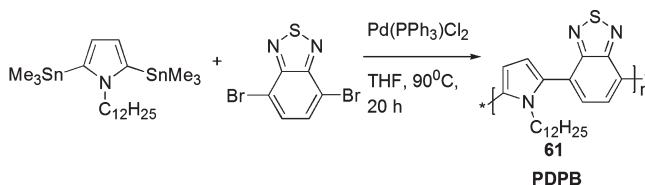
Ng et al.¹⁵⁸ also prepared a series of thiophene-based polymers using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ as catalyst, though the molecular weights were relatively low, with M_n between 1.8 and 2.7 kDa and polydispersities between 1.1 and 1.4. The polymer **60** (PB-TOME, Scheme 49), containing a methoxy group attached to the thiophene moiety, was shown to exhibit a substantial red shift in its film emission spectrum (λ_{max} = 540 nm) relative to the unsubstituted PBTH, which showed film emission maxima between 467 and 483 nm.

Janssen et al.¹⁵⁹ reported a promising red-emitting polymer, PDPB **61** (Scheme 50), which showed a photoluminescence emission maximum at 640 nm. The polymer was prepared in 60% yield, with relatively high molecular weight, with M_n between 7.1 and 14.6 kDa, with a PDI of 2.06. Notably, the authors reported initial solubility trouble using DMF as solvent due to polymer precipitation from solution; thus, the procedure was carried out in THF, which alleviated this problem.

Ramey et al.¹⁶⁰ reported thiophene–dialkoxybenzene-based copolymer **62** bearing tertiary amine substituents in its side chain (Scheme 51), in addition to optimization of reaction conditions for this system. The tertiary amine side chains were shown to readily form quaternary ammonium salts when reacted with bromoethane. Both Stille and Suzuki–Miyaura coupling methods were used in this instance; however, better PDIs (1.68–1.71) were obtained with Stille coupling than with Suzuki–Miyaura coupling (1.52–2.20), with best results from Stille coupling obtained with dropwise addition of the ditin compound over 24 h followed by a 96-h reaction time at 70 °C. The best PLED device showed an EQE of 0.017%, with emission maximum at 558 nm, yellow-orange light.

Cao and co-workers¹⁶¹ prepared a thiophene–benzothiadiazole-based polymer **63** (Scheme 52), which was reported to be applicable to near-IR (NIR) LED devices. The polymer showed emission at 830 nm for the device configuration ITO/PEDOT:

Scheme 50. Synthesis of Red-Emitting Copolymer Containing Benzothiadiazole and N-Alkylpyrrole Units



PSS/PDDBT/Ba/Al and showed an EQE of 0.08% at a turn-on voltage of 3.5 V.

While $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ is commonly used in the preparation of thiophene-based polymers, $\text{Pd}_2(\text{dba})_3$ is also used extensively in Stille polycondensation for LED applications. McCullough and co-workers¹⁵¹ prepared a series of regioregular poly(thienylenevinylenes) **64a,b** (Scheme 53), with the regioregular polymer prepared via Stille coupling, while the regiorregular polymer was prepared via Heck reaction conditions. Polymers were prepared in relatively high molecular weights with M_n between 8.0 and 15.0 kDa and PDIs between 1.8 and 1.9. Of note, the group reported a much more substantial bathochromic shift in absorbance maximum in transition from solution to film for the regioregular polymer (40 nm) when compared to the regiorregular polymer (12 nm). This difference is attributed to a lower degree of structural ordering in the polymer prepared by Heck polycondensation due to the potential presence of α -coupling in addition to cis and trans coupling, decreasing the effective conjugation length.

Melucci and co-workers¹⁴⁴ utilized similar reaction conditions to synthesize v-shaped thiophene polymer (Scheme 54) **65** (V-PT), which although showing somewhat low photoluminescence efficiency in thin film (PL quantum yield 1–2%), reportedly showed the highest luminance for a polymer incorporating

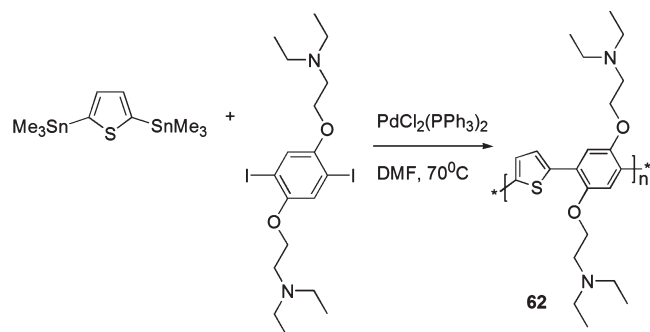
thienyl S,S-dioxide units. The reported luminance of the single-layered device was 948 cd/m^2 .

Mishra et al.¹⁵³ reported extremely high yields (78–89%) and high molecular weights between 45 and 53 kDa in syntheses of **66a–c** (Scheme 55) using $\text{Pd}_2(\text{dba})_3$ catalyst, (o-tol)₃P ligand, chlorobenzene solvent, and CuO as additive heating for 72 h at 150 °C. Authors reported a 5-fold increase in molecular weight with the addition of CuO additive attributed to improvement of polymer solubility. The electroluminescence device with configuration ITO/PEDOT:PSS/polymer/BCP/Alq₃/LiF/Al showed red light emission with maximum emission values between 795 and 814. In addition, the polymers showed extremely low band gaps between 1.35 and 1.43 eV. The maximum luminance values achieved for EL devices was 54 cd/m^2 at a turn-on voltage of 9 V.

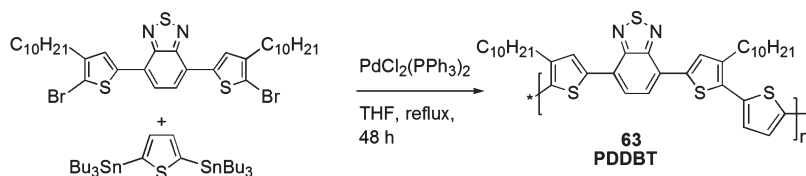
Similar use of additives has been reported to enhance molecular weight by facilitating the transmetalation step, as discussed in section 3.3. As previously reported, LiCl is frequently used in this capacity, as observed in **56–58** (Scheme 47).^{142,143,147–149} In addition, many examples of CuI as cocatalyst have also been reported in the preparation of silole-containing polymers **67** and **68a,b** (Scheme 56). In these, Ohshita et al. reported failure of FeCl_3 -mediated oxidative polymerization. While these polymers also showed very little electroluminescence, they were found to be useful as hole-transporting materials in multilayered EL devices, and the use of both $\text{Pd}(\text{PPh}_3)_4$ - and $\text{Pd}(\text{OAc})_2$ -mediated oxidative homocoupling represents a less prominently employed example of the cross-coupling of distannanes. The decomposition of the silole ring system was noted to be the most prevalent side reaction occurring in this polymerization when the reaction was carried out in refluxing THF. Optimal temperature was found to be 0 °C, where minimal decomposition was reported, though with a concomitant decrease in molecular weight.^{156,162}

The additive CuO was also used by Osuga et al. in the preparation of oligomers **69** (Scheme 57), producing materials of $M_n = 2.1$ kDa with PDI of 1.4. Synthetic conditions employed 6% $\text{Pd}(\text{PPh}_3)_4$ and 1.5 equiv of CuO in refluxing toluene for 39 h, which resulted in 92% yield. These materials were developed to tune emission color through control of bridging units. Various oligomers were prepared via Stille, Suzuki–Miyaura, Wittig, Heck, and Sonogashira coupling protocols, which incorporated

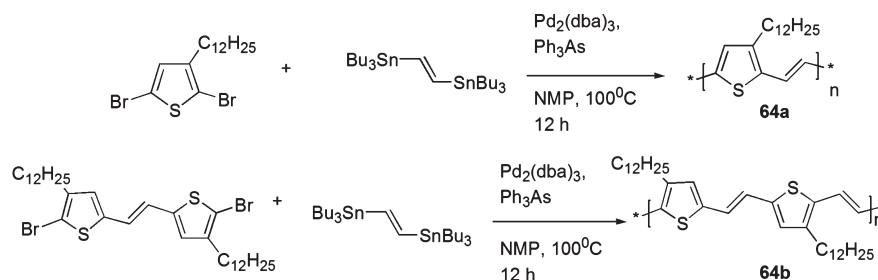
Scheme 51. Synthesis of Polymers Bearing Amine-Substituted Side Chains



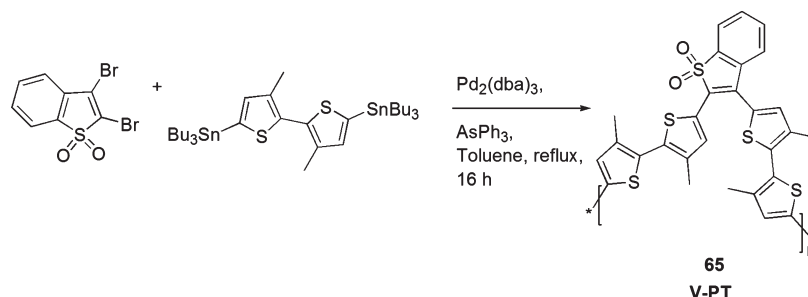
Scheme 52. Synthesis of Polymers Containing Thiophene and Benzothiadiazole Units



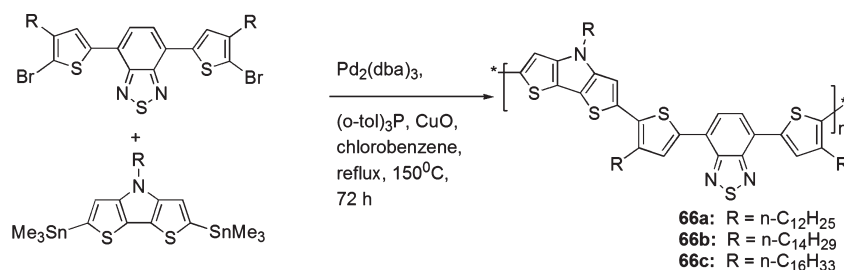
Scheme 53. Synthesis of Regioregular Poly(thienylenevinylenes)



Scheme 54. Synthesis of v-Shaped Polythiophene V-PT



Scheme 55. Synthesis of Polymers Composed of Carbazole, Thiophene, and Benzothiadiazole Units



various bridging moieties, such as vinylene (Heck), ethynylene (Sonogashira), or those which were directly linked, which were prepared via Stille coupling. It was found that the emission color varied from blue to yellow on the basis of the length of the chain, with oligomers of 5, 10, and 14 benzodithiophene (BDT) units being almost identical in color. The film emission maxima were reported at 540, 544, and 534 nm, respectively.¹⁶³

The optimization of catalytic conditions for preparation of 3-alkylpolythiophenes has been investigated by Moreau et al., yielding the result that the optimal catalyst for this system was Pd₂(dba)₃(CHCl₃) at a 1:4 ratio of catalyst:PPh₃ ligand. In this case, a 90% yield with >95% head-to-tail regioselectivity was reported for **70** (Scheme 58). This regioselectivity and resultant effects on physical properties were also observed by McCullough et al. in the synthesis of **64a,b**. This can be attributed to the mechanism of Stille coupling, in which oxidative addition to the active catalyst is favored at the 5-position in thiophenes, which results in a large amount of monovinyl thiophene intermediate. Since a single coupling with the tributylstannyl monomer occurs much faster than the second coupling, large amounts of this monocoupled intermediate can self-couple in a highly regioselective form. McCullough and co-workers observed differences in UV–visible absorbance maxima as large as 66 nm in **64a,b**.¹⁵¹

Moreau et al. reported significant red shifts in the UV–visible absorbance maxima of regioregular polymers **70** relative to their regiorandom counterparts, with chloroform solution maxima for regioregular and regiorandom polymers reported at 448 and 466 nm, respectively. Similarly, film absorbance maxima were reported at 515 and 575 nm for the regiorandom and regioregular polythiophenes, respectively. The differences were attributed to a greater degree of torsion in the polymer backbone in regiorandom polymers due to the presence of tail-to-tail (TT) linkages, which disrupted the planar structure of the polymer. The highest molecular weights obtained were $M_n = 142.02$ kDa with the highest PDI reported to be 1.1. While various Pd

catalysts were used in synthesis, Moreau and colleagues reported optimal results with 1.0 mol % of Pd catalyst at 80 °C, heating for 72 h, and using a 1:4 or greater catalyst:ligand ratio.³⁹

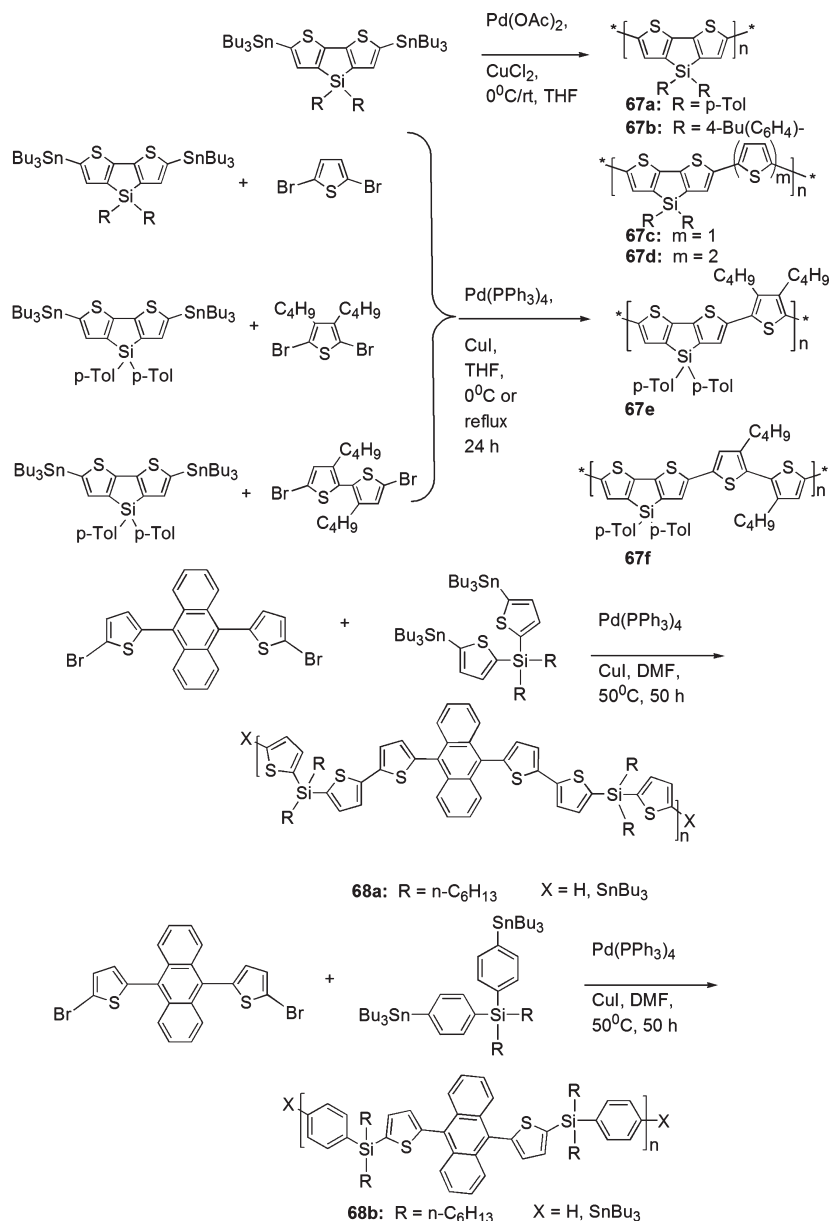
An example of Ni(0) catalysis has also been reported by Wu et al. for coupling of dibromopyridine with trimethylstannylthiophene in the synthesis of **71** (Scheme 59). Weight-averaged molecular weight (M_w) was reported at 6.04 kDa, with a PDI of 1.6. While further synthetic details were not reported, the authors reported use of Stille coupling was successful in overcoming synthetic difficulties encountered in attempting to prepare the same polymers via oxidative polymerization of 2-(3-octylthiophene-2-yl)pyridine with FeCl₃, which had failed.¹⁶⁴

As previously mentioned, a common choice of ligand in polycondensation reactions is PPh₃; however, a few reports of AsPh₃ are also known, as previously mentioned for **65** and **66** (Schemes 54 and 55).^{144,153} As previously mentioned, the choice of ligand has been exploited in order to increase reactivity of the catalyst, presumably by accelerating the transmetalation step.^{32,45} Choice of solvent reportedly factored largely into the ability to obtain high molecular weights, with premature precipitation of polymer being the largest challenge to be overcome. In one relatively early application of the Stille reaction to PLED polymer **72** (Scheme 60), extremely poor results were obtained using DMF as solvent; however, use of benzene was reported to alleviate this problem.¹⁵²

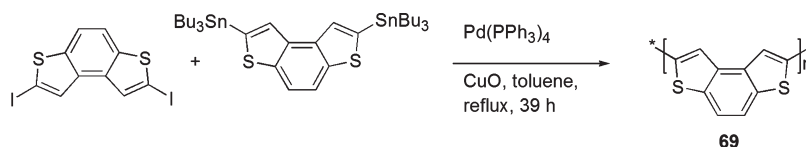
Use of NMP solvent in place of DMF also gave high molecular weights in nitrogen-containing heterocyclic polymers, such as polymethylpyridinium vinylenes **56–58**,^{142,143,147,150,151} as well as some polythiophenes such as **64a,b** (Scheme 53).¹⁵¹ The use of mixed solvent systems has also been reported to enhance molecular weight, presumably also by mediation of polymer–solvent interactions. Mixed systems of 1:1 THF:DMF^{165,166} as well as 2:1 toluene:DMF have been reported.^{154,155}

Moreau et al. reported use of 1:1 THF/DMF solvent system in synthesis of polymers **73** and **74a–c** (Scheme 61). This system

Scheme 56. Synthesis of Cyclopentadithiophene Polymers with Alkylated Silole Bridges



Scheme 57. Synthesis of Benzodithiophene Oligomers



yielded weight-averaged molecular weights between 3 and 4 kDa, with PDI values between 1.4 and 1.8. These red-emitting polymers showed photoluminescence emission maxima between 620 and 636 nm.¹⁶⁵ Significantly higher molecular weights were achieved in syntheses of alternating thiophene–dialkoxybenzene polymers **74a–c**, with M_w between 13.7 and 25.6 kDa and PDI values between 1.89 and 2.93. These polymers were reported to exhibit promising qualities for orange-red-emitting PLED devices, with film emission maxima between 610 and 625 nm.¹⁶⁶

Cao and co-workers¹⁵⁵ synthesized polymers **75a,b** (Scheme 62) using a mixed 2:1 toluene:DMF system. **75b**, PMOPV-BTV polymers, were shown to be deep red light emitting materials, exhibiting electroluminescence maxima between 659 and 724 nm in a device with configuration ITO/PEDOT:PSS/polymer/Ba/Al. These values increased with increasing benzothiadiazole content of the polymers, resulting in red shifts between 68 and 133 nm relative to the PMOPV homopolymer **75a**. Notably, emission was exclusively red. The

authors attributed this to the incorporation of the benzothiadiazole as a narrow band gap unit, which served as a trap center. Intramolecular exciton confinement was reported to enable color tuning. The same group also reported near-IR emitting polymers¹⁵⁴ **76a,b** (Scheme 62), which incorporating benzothiadiazole and benzoselenadiazole units. These were prepared with M_n values between 3.99 and 5.10 kDa, with PDI values between 2.2 and 3.1. The variation of starting monomer ratio was reported to have an adverse effect on the molecular weight, however, this variation was necessary in this case in order to investigate the effect of varying amounts of benzothiadiazole and benzoselenadiazole in the respective polymers. The polymer **76b** (PMOPV-TBSV) showed an electroluminescence maximum of 800 nm with 30% TBSV content. Notably, EQE values were also

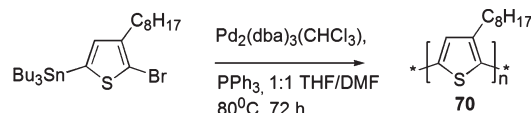
relatively high for these polymers, with **76a** showing the highest EQEs of 0.27% and 0.31% for polymers incorporating benzothiadiazole ratios of 0.5 and 1.0, respectively. The selenium counterparts showed EQE values of 0.01 and 0.16% for benzo-selenadiazole ratios of 0.3 and 1.0, respectively.

The Stille coupling has been instrumental in providing a solution for a number of difficulties encountered with other methods of polymer preparation. One of the first known examples of this was in the preparation of poly(phenylene vinylene)s (PPVs) and their derivatives. The initial work in polymer-based OLED materials was done on poly[phenylene vinylene)s (PPVs),^{167,168} one of the earliest examples of which touts the Stille coupling method of polymerization as highly advantageous over the previously employed "precursor method" in that use of palladium-catalyzed cross-coupling supplants the need for a thermal elimination step.¹⁶⁷

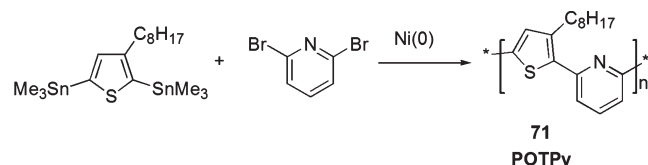
The Stille polycondensation has also been employed where other polymerization methods have failed. For instance, in the preparation of diblock copolymers of thiophene and fluorene **77a–d** (Scheme 63) by Scherf et al.,⁵ thienyl diboronic acids were found to be unstable to the basic conditions required for Suzuki–Miyaura coupling; thus, Stille polymerization was the method of choice for preparation of the desired polymers. Polymers were prepared in 60–85% yield, with M_n between 9 and 16 kDa and PDI values between 1.3 and 1.9. The polymers showed thin film photoluminescence emission maxima between 504 and 575 nm, with bathochromic shifts observed with extension of thienyl units in the polymer.

The Stille coupling enabled the preparation of diblock copolymers of thiophene and pyridine monomers as shown in **78a–c** in Scheme 64 (and as previously shown in **71**, Scheme 59), where

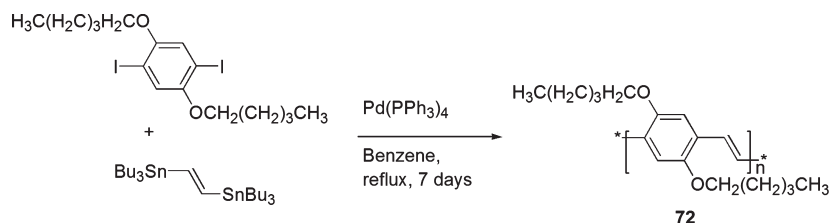
Scheme 58. Synthesis of Regioregular Polythiophenes



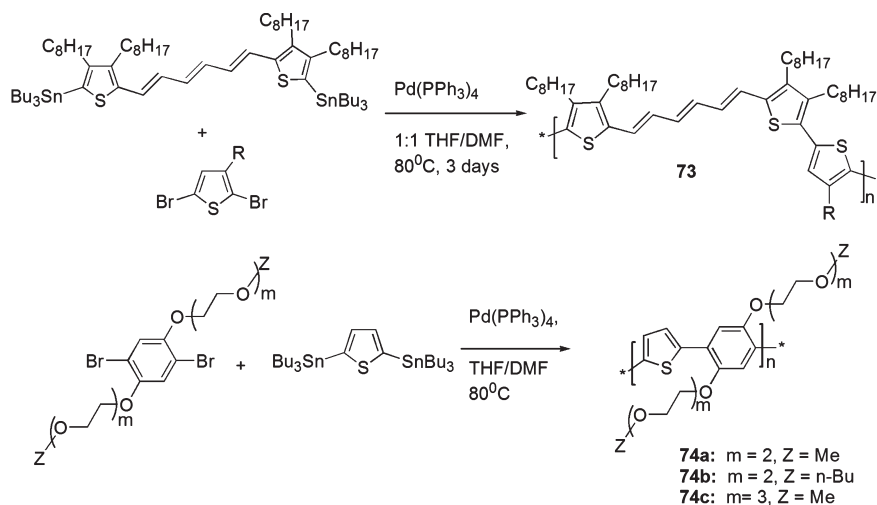
Scheme 59. Synthesis of POTPy Incorporating Thiophene and Pyridine Blocks



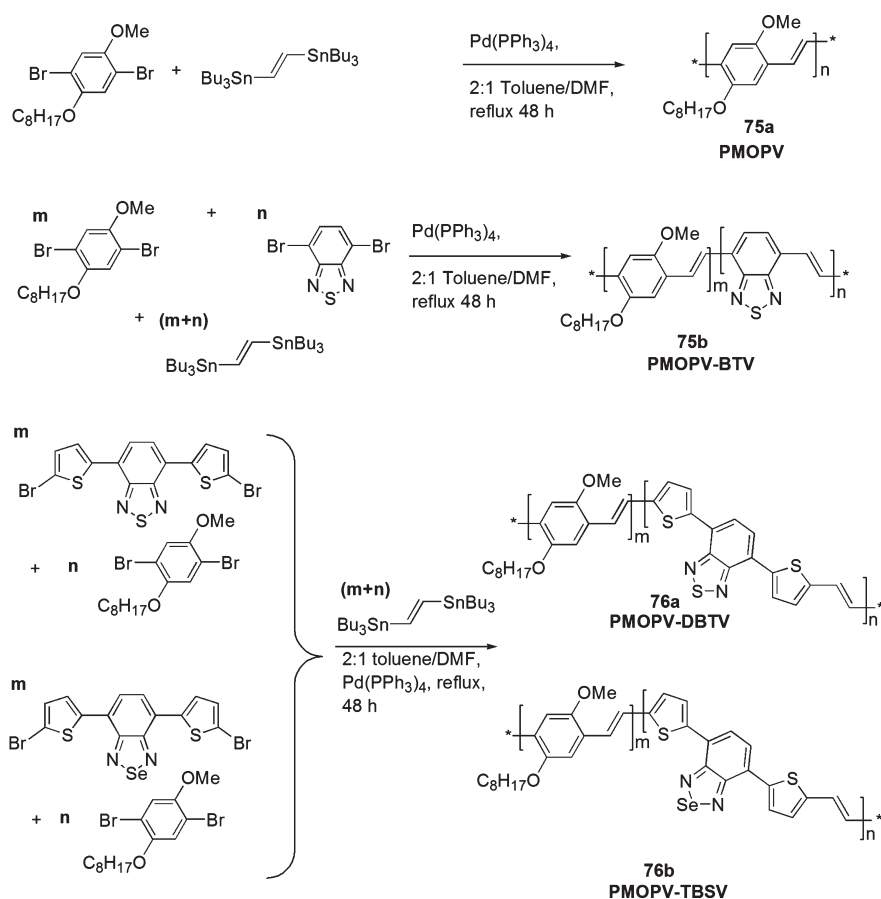
Scheme 60. Synthesis of Soluble PPV-Derived Polymer with Alkoxy Substituents



Scheme 61. Synthesis of (Thienylene)–[1,6-Dithienylhexa-1,3,5-trienylene] Copolymers **73 and Thienylene–Phenylene Copolymers with Oligo(ethylene oxide) Side Chains **74a–c****



Scheme 62. Synthesis of Poly(*p*-phenylenevinylene) Copolymers PMOPV, PMOPV-BTV, PMOPV-DBTV, and PMOPV-TBSV Containing Benzothiadiazole and Benzoselenadiazole Units



the presence of the pyridine group precluded use of FeCl_3 -mediated oxidative cross-coupling. In preparation of **78a–c**, Ng et al.¹⁶⁹ found that the presence of the pyridine moiety offered an acid-sensitive, electron-withdrawing group that could be used to tune the properties of the polymer. However, the presence of this moiety precluded the use of FeCl_3 -mediated oxidative cross-coupling. Stille coupling, however, offered a viable alternative, and the desired polymers were prepared in 65–75% yields with M_n values between 5.4 and 12.7 kDa and PDIs between 1.36 and 1.80. Authors reported that the polymers containing 2,5-linked pyridine moieties exhibited red shifts in UV–visible spectra relative to their 2,6- and 3,5-linked counterparts. The film emission maxima of **78a–c** were almost identical at 540, 540, and 541 nm, respectively. Cyclic voltammetry measurements showed electron affinity values between 2.57 and 2.60 eV, which the authors stated is due to incorporation of the electron-withdrawing pyridine moiety, effectively lowering the LUMO energy level and potentially facilitating electron injection into the active layer of PLED devices.

4.6. Sensor Materials and Other Polymers

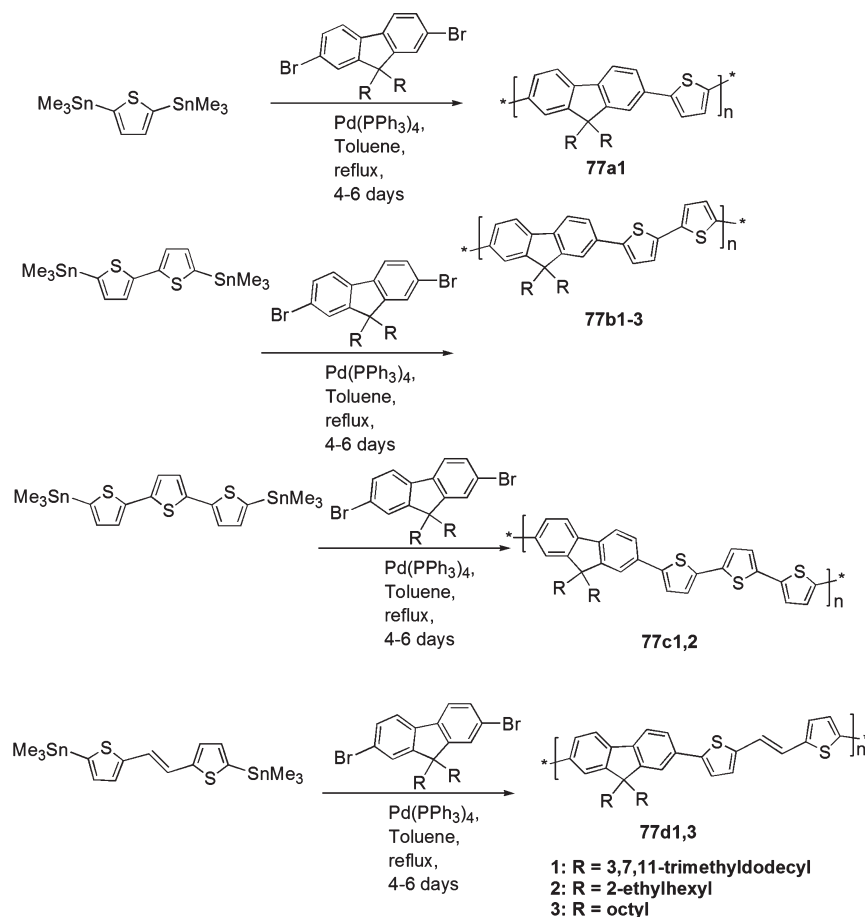
Yet another interesting application of functional polymers is in the realm of chemical sensors, which have been widely investigated over the past decade. While there are numerous highly relevant examples of these types of polymers, we have selected a few to show the expanse of applications of the Stille polycondensation. This presentation is by no means a complete account of all known examples in this area.

As shown in Scheme 65, the enantiopure 1,1'-binaphthyl-based oligomer **83** was synthesized by three different synthetic routes by Lin and co-workers: two of them using Stille coupling and one using Suzuki–Miyaura coupling.¹⁷⁰ In the following fluorescence quenching experiments, **84** showed very good chirality-based fluorescence quenching selectivity for 1,2-diaminocyclohexane molecules compared to that of 1,1'-bi-2-naphthol.^{171,172}

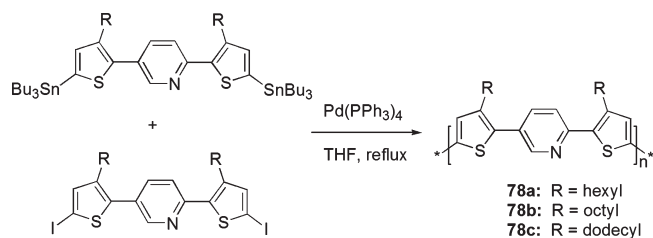
Swager et al.¹⁷³ reported the synthesis of polythiophene-based pseudorotaxane sensory materials. The polymers, which bore cyclophane receptors, were capable of forming pseudorotaxane complexes with paraquat by self-assembly, the formation of which induced electrostatic perturbations, causing a decrease in carrier mobility and resultant lowering of conductivity. Swager and co-workers¹⁷⁴ also reported the synthesis of polythiophenes bearing calyx[4]arene substituents. These were shown to exhibit ion-selective voltammetric, chromic, fluorescent, and resistive responses. Ionoresistivity was shown to be the most ion-selective response.

A series of organometallic polymers with organic spacers and platinum or palladium have also been reported for chemical sensing applications. These applications include surface acoustic wave humidity sensors, in which the transition metal was shown to be responsible for the differential sensitivity to the environment.⁷⁹ Fratoddi et al.¹⁷⁵ used a modified Stille coupling reaction,^{2,176} referred to as EOP (extended one pot), to synthesize an organometallic copolymer Pt-DOB, **85** (Scheme 66). As compared to another similar copolymer with a longer organic spacer, they demonstrated that the organic spacers would

Scheme 63. Synthesis of Diblock Copolymers Containing Thiophene and Fluorene Units



Scheme 64. Synthesis of Polymers Containing 2,5-Linked Pyridine Moieties



also greatly influence the sensor response properties. The chemical structures of Pt-DOB (**85**) and Pt-TRI (**86**) and the EOP synthetic route for the former are shown in Scheme 66.

In this instance, the polymerization proceeded very well and a relatively high molecular weight was achieved with $M_w = 26.7$ kDa and $M_n = 15.8$ kDa, corresponding to approximately 20–28 repeating units. The response of the organometallic polymers to ethanol and 2-propanol vapors had been studied using a quartz crystal microbalance (QCM) device. It has been revealed that two of the organometallic polymers, Pt-DOB and Pt-TRI, were sensitive to the ethanol vapors, but the chemical sensor behavior was different. The frequency of Pt-DOB¹⁷⁵ with a short organic spacer in the polymer chain was 2 times that of Pt-TRI with a long organic spacer in the polymer chain.

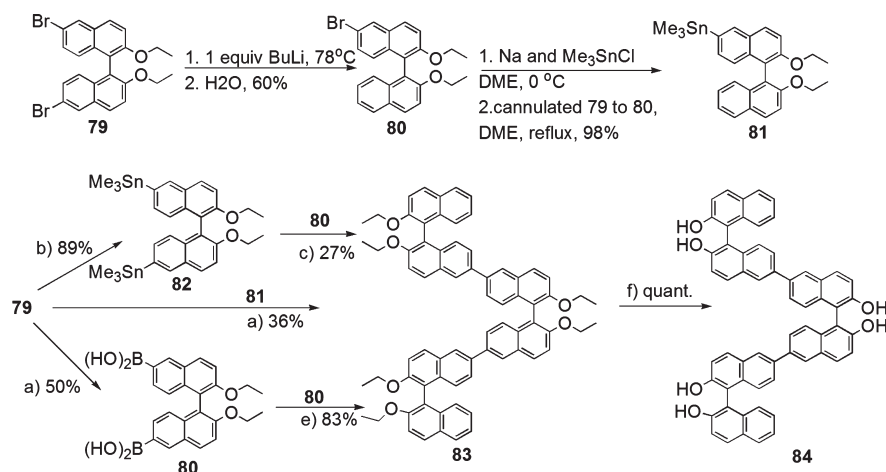
McCullough and co-workers¹⁷⁷ synthesized water-soluble polythiophenes for ionochromatic sensing applications. The polymers showed different chromic responses based on counterion size. The McCullough group¹⁷⁸ also reported the synthesis of amine-functionalized polythiophenes. The salts of one example of this class of polymers were found to be water-soluble and became helically ordered on addition of DNA.

Fréchet and Malenfant¹⁷⁹ reported synthesis of a polythiophene bearing only dendrimers as solubilizing groups. These materials exhibited conductivities as high as 200 S/cm.

Holdcroft and co-workers¹⁸⁰ utilized a postfunctionalization strategy based on the susceptibility of the 4-position in poly(3-hexylthiophene) to electrophilic substitution. This enabled further cross-coupling chemistry to be used to functionalize the polymer.

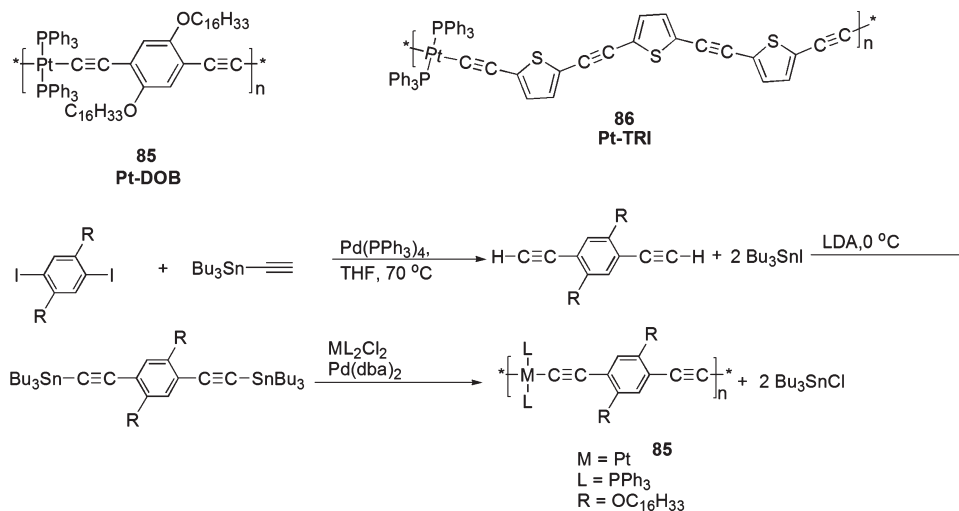
Swager and co-workers¹⁸¹ also developed a series of water-soluble N-type polymers containing the pyridinium unit. The polymer **88** (Scheme 68) showed high conductivity ($\sigma_{\text{max}} = 160$ S/cm) and high electron-affinity of 4.14 eV, comparable to the electron-affinity of PCBM (4.2 eV). Because of this, the polymer shows potential as an acceptor material in all-polymer organic photovoltaic applications.

Swager et al.¹⁸² also developed a series of azepine-containing polymers for use in electrochemically driven actuators. Dithieno[3,2-*b*:2',3'-*f*] azepines such as polymer **87** (Scheme 67) showed stability even in highly oxidized states, an excellent property for “artificial muscles” driven by electrochemical stimuli.

Scheme 65. Synthesis of 7a and 7b Using Different Routes^a

^a Reagents and conditions: (a) 81, $\text{PdCl}_2(\text{PPh}_3)_2$, THF, reflux, 60 h. (b) (i) Na and Me_3SnCl , DME, 0 °C; (ii) cannulated (i) into 79, DME, reflux, overnight. (c) 80, $\text{PdCl}_2(\text{PPh}_3)_2$, THF, reflux, 84 h. (d) (i) BuLi, THF, -78 °C, 2 h; (ii) $\text{B}(\text{OEt})_3$, rt, overnight; (iii) HCl. (e) 80, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , THF, reflux, 69 h. (f) BBr_3 , from 0 °C to rt.

Scheme 66. Structures of Pt-TRI and Pt-DOB and Synthesis of Organometallic Polymers Pt-DOB by the Extended One Pot (EOP) Method



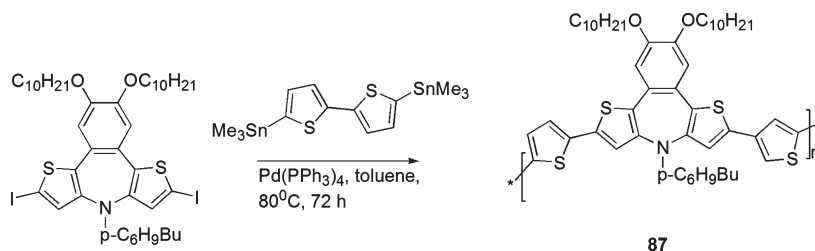
5. CHALLENGES FOR THE FUTURE

While there are many advantages to the Stille methodology for polymerization, one of the most important disadvantages is the formation of highly toxic SnR_3X , halogenated tin byproducts, which are known to be harmful to the environment. Additionally, complete removal of tin from the final product is difficult, presenting another key disadvantage. Farina and Roth²⁵ reported that use of 1 M aqueous potassium fluoride solution and extraction of the product in a hydrocarbon solvent was an effective means of removing tributyltin halides. Filtration of insoluble tributyltin fluoride [actually an insoluble polymer with the structure $-(\text{R}_3\text{SnF})-_n-$] was reported to remove the majority of the tin from the product. In 2008, Espinet et al.¹⁸³ reported using stannylated norbornene polymers as efficient R-transfer reagents during Stille coupling reactions of small molecules. Carrying out the reaction using these polymers led to very efficient removal of tin from the final products. Reportedly, products showed a tin content of

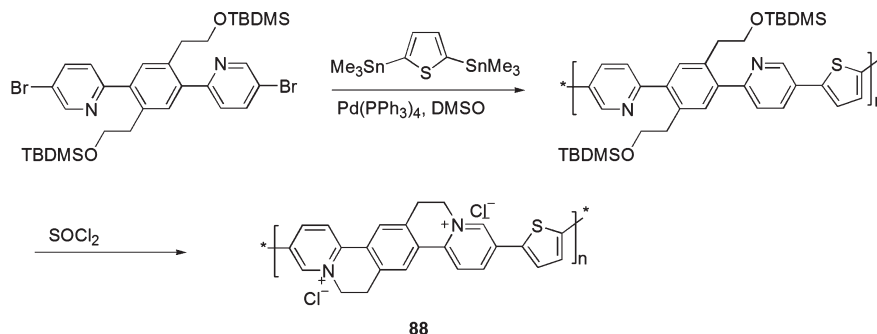
approximately 0.05 wt % in the final products. While this method was not applied directly to polymerization, the potential remains for a “green” Stille polymerization protocol.

Another potential drawback has been the use of highly expensive and potentially also toxic phosphine ligands as stabilizers for the active catalyst. Additionally, the low reactivity of aryl chlorides under these conditions presents another challenge. The use of aryl chlorides in Pd-catalyzed cross-coupling would present a great advantage, since these substrates are often less expensive and more commercially available than their bromo and iodo counterparts. Some groups have begun to address these issues, using ionic liquids as reaction media for metal-catalyzed cross-couplings.¹⁸⁴ To this end, Caló et al.⁶¹ reported a Pd nanoparticle-catalyzed cross-coupling of a nitrophenyl chloride with tributylstannylbenzene (among other examples) in ionic liquid medium without the need for phosphine ligands, as shown in Scheme 69. The reaction medium was the quaternary ammonium salt tetrabutylammonium bromide, and the palladium nanoparticle

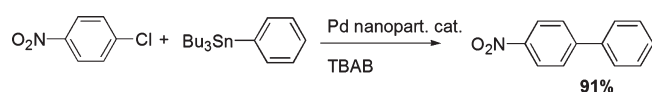
Scheme 67. Synthesis of Dithieno[3,2-b:2',3'-f]azepine Polymers for “Artificial Muscle” Applications



Scheme 68. Synthesis of High Electron-Affinity N-Type Polymers Containing the Pyridinium Unit



Scheme 69. Palladium Nanoparticle-Catalyzed Cross-Coupling of Nitrophenyl Chloride with Tributylstannyl Benzene in Ionic Liquid



was formed by adding 2.5 mol % $\text{Pd}(\text{OAc})_2$ and 5% tetrabutylammonium acetate. The reaction yield was reported to be 91%. The ability to recycle the catalyst was also reported.

6. CONCLUDING REMARKS

In summary, the progress made in the past 2 decades in the development of the Stille coupling reaction for the preparation of functional polymers has been tremendous. The clear advantages of the synthetic methodology discussed herein are the ease of synthesizing functional dihalide monomers and its compatibility with various functional groups, which have made the syntheses of numerous functional polymers possible. The impact of this methodology has been spread to material areas ranging from optical materials, electronic materials, and biological sensors. We expect many more future applications in these areas. However, this methodology is by no means problem-free, as stated above. In addition, the synthesis of distannane monomers requires use of reactive organometallic compounds, such as organolithium or Grignard reagents, which impose problems in monomer functional group compatibility. The distannane monomers are usually difficult to purify when they are not crystallizable. Palladium catalysts are relatively expensive and palladium black formed during polymerization could be detrimental to electrical properties of the resulting polymers if they are not properly removed. The methodology still gives only low molecular weight polymers, quite often, only oligomers. This may be adequate for electronic applications, because many electronic properties will become saturated when the conjugation length reaches a limited value. For other applications requiring

high molecular weight, this may impose a problem. Fourth, side reactions such as homocoupling of distannane compounds exist in the Stille coupling reaction, which change the stoichiometric balance of monomers and may be one of the reasons for low molecular weight observed in many reports. We believe that all of these issues present challenges and opportunities for future research efforts.

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BIOGRAPHIES

Bridget Carsten was born in 1978 in Phoenix, AZ. She received her B.S. in chemistry from Northern Arizona University in 2007, working with Dr. Edgar Civitello. She then received her M.S. in chemistry from the University of Chicago in 2008, working with Dr. Luping Yu. Currently, she is pursuing her Ph.D. at the University of Chicago. Her current work focuses on design and synthesis of new low band gap organic semiconducting polymer materials for organic photovoltaic applications.



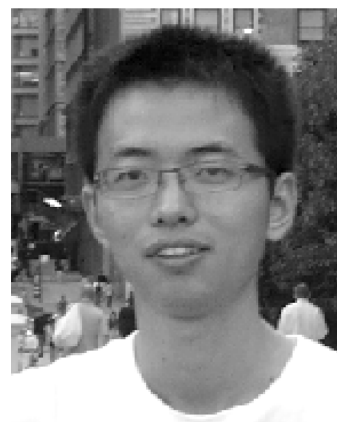
Feng He was born in 1979 in Hubei Province, People's Republic of China. He received his B.E. degree in 2002 and Ph.D. degree in polymer chemistry in 2007 from Jilin University under the supervision of Prof. Yuguang Ma. Then he moved to the University of Toronto, Canada, for his postdoctoral research with Prof. Mitchell A. Winnik on the design and synthesis of fluorescent block copolymers as well as their supramolecular self-assembly. In 2009, he joined Prof. Luping Yu's group as a postdoctoral scholar at the University of Chicago, where his research interests are the synthesis of low band gap copolymers for organic solar cell applications.



Hae Jung Son was born in Busan, Republic of Korea, in 1977. She received her B.S. degree in chemistry in 2000 from Sungkyunkwan University and her M.S. degree in organometallic chemistry in 2002 under the supervision of Prof. YoungKyu Do from the Korea Advanced Institute of Science and Technology (KAIST). After graduation, she worked for Samsung Advanced Institute of Technology (SAIT) as a research staff member from 2002 to 2004. Presently, she is a Ph.D. student under the direction of Prof. Luping Yu at the University of Chicago. Her current research focuses on the development of novel conjugated polymers for organic solar cells.



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