Chapter 8
Cross-Coupling Polymerization

Take-aki Koizumi and Takaki Kanbara

Abstract Organometallic cross-coupling reactions directed toward the synthesis of aromatic polymers are reviewed. The progress of this methodology has made the syntheses of numerous functional polymers possible, which includes the synthesis of well-defined π-conjugated polymers and buildup molecular architectures. The polycondensation has been spread out to material areas ranging from optical and electronic materials to biological sensing materials. The use of organometallic direct arylation and carbon-heteroatom bond formation for the synthesis of functional polymers has also been dealt with.

8.1 Introduction

The organometallic catalyzed cross-coupling reactions of various organometallic (Mg, Zn, Sn, B, and Si) reagents and aryl halides to form new carbon–carbon bonds have emerged as versatile synthetic techniques that are widely employed for the syntheses of a variety of organic compounds [1–9]. The pioneering work of Profs. Heck, Suzuki, and Negishi on the Pd-catalyzed cross-coupling reactions in organic synthesis was recognized with the 2010 Nobel Prize in Chemistry [10–12]. Recently a wide range of aromatic functional materials has been developed using such cross-coupling reactions.

The most commonly employed transition metal catalysts in cross-coupling reactions are nickel and palladium-based complexes. The general mechanism of the reactions is shown in Scheme 8.1 [1–9]. In general, cross-coupling reactions involve

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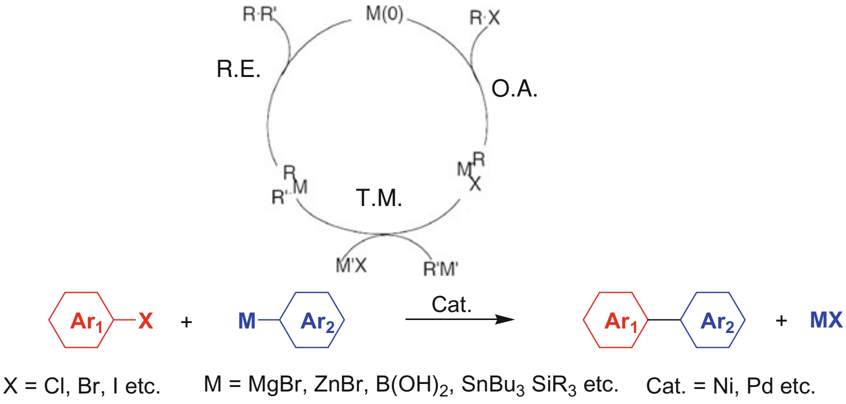


Scheme 8.1 Transition metal catalyzed cross-coupling reaction

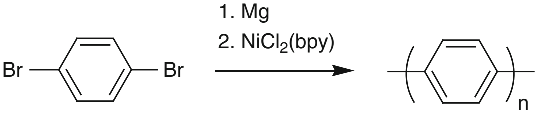
three steps: an oxidative addition reaction across the C-halogen bond as an electrophile, transmetalation with the main group in the organometallic reagents acting as nucleophiles, and reductive elimination resulting in the formation of the carbon-carbon bond and regeneration of the active catalyst. Organometallic reagents such as Grignard reagents (Kumada-Tamao-Corriu) [1m], zinc (Negishi) [1n], stannane (Migita-Kosugi-Stille) [1o], boron (Suzuki-Miyaura) [1p], silane (Hiyama) [1q], copper (Sonogashira) reagents [1r], or lithium and mercury compounds can be used.

In the field of polymer chemistry, cross-coupling reactions are particularly important in the synthesis of conjugated aromatic oligomers and polymers [13–17]. Over the last three decades, conjugated polymers have attracted widespread attention owing to their high conductivity and interesting optoelectronic properties, resulting in their application to optoelectronic devices such as light emitting diodes, field-effect transistors, and photovoltaic systems. Organometallic methodologies are useful for preparing well-defined conjugated polymers, especially when a high regioselectivity is required in the polymeric backbone [18, 19]. Since the development of conducting polymers by Profs. Heeger, MacDiarmid, and Shirakawa in 1977, which was recognized with the 2000 Nobel Prize in Chemistry [20–22], various aromatic monomers have been employed to develop conjugated polymers. This chapter describes the organometallic catalyzed cross-coupling polycondensation used in the synthesis of various conjugated polymers. The utilization of organometallic carbon-heteroatom bond formations in the synthesis of functional polymers is also described.

8.2 Ni-Catalyzed Polycondensation

The application of transition metal catalyzed cross-coupling reactions to polymeric materials was first reported by Yamamoto and co-workers in the synthesis of poly(*p*-phenylene), which is prepared by nickel-catalyzed Grignard coupling of

1,4-dibromobenzene [23–25]; one of the C–Br bonds reacts with magnesium to form the Grignard reagent, which undergoes further coupling reaction (Eq. 8.1). Polythiophene (PTh) and poly(3-alkylthiophene)s (P3RThs) were prepared using the same protocol (Eq. 8.2) [26]. The introduction of the alkyl group to PTh resulted in enhanced solubility of the polymer. The nickel-catalyzed polycondensation of dihalogenated-thiophenes in the presence of zinc also yielded PTh derivatives (Eq. 8.3) [27].



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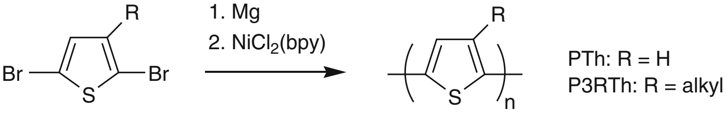

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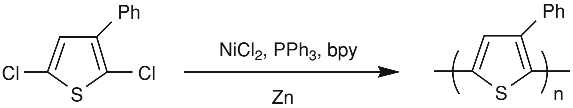


(8.3)

The reactions are simple and they yield several conjugated aromatic polymers with well-defined linkages between the monomer units. However, the regioregularity cannot be controlled using this protocol (Chart 8.1). The synthesis of regioregular poly(3-alkylthiophene)s (P3RThs), which involve head-to-tail (HT) repeating units, such as poly(3-hexylthiophene) (HT-P3HTh), can be realized by the Ni-catalyzed polycondensation of regio-controlled organomagnesium reagents. This is achieved by the regioselective lithiation of 2-bromo-3-alkylthiophene with lithium diisopropylamide (LDA), followed by transmetalation with magnesium bromide, yielding an organometallic intermediate (Chart 8.2a) [28]. Regio-controlled organozinc reagents also afforded regioregular P3RThs (Chart 8.2b) [29]. Regioregular poly(3-hexylthiophene) (HT-P3HTh) is of particular interest because the polymer exhibits remarkable physical properties such as higher crystallinity and electrical conductivity in the solid state, as compared to the regio-random polymers [13, 30, 31]. Their application to flexible electronic devices such as organic thin-film solar cells and organic field effect transistors has been investigated.

Because the molecular weight of the polymer prepared by condensation polymerization is generally difficult to control, the polydispersity index theoretically approaches two at high conversions. Both Yokozawa and McCullough groups reported the first chain-growth synthesis of regioregular P3RThs via the

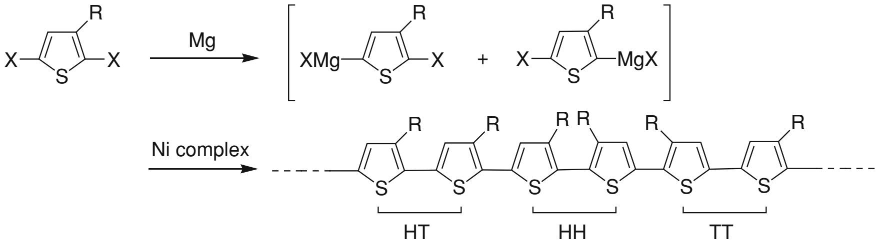


Chart 8.1 Synthesis of regioirregular poly(3-alkylthiophene)

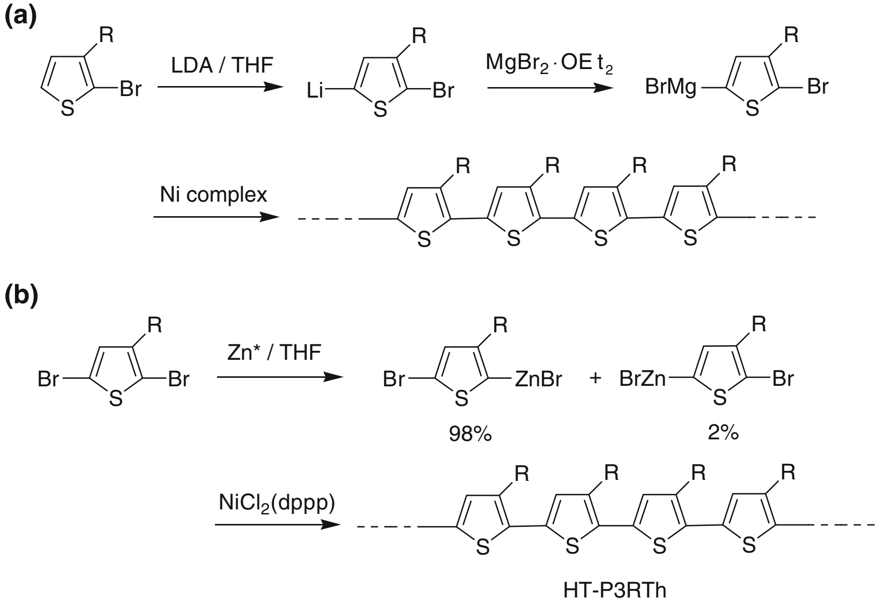
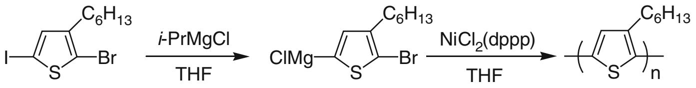


Chart 8.2 Synthesis of regioregular poly(3-alkylthiophene)

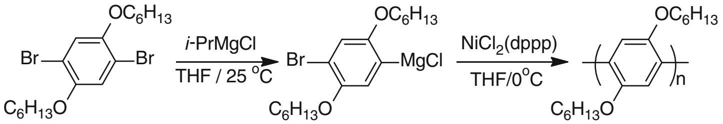
polymerization of Grignard-type monomers catalyzed by dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) ($NiCl_2$(dppp)) (Eq. 8.4). The products have controlled molecular weights and narrow molecular weight distributions (M_w/M_n ratios around 1.1, M_n up to 28,700 g/mol) [18, 19, 32, 33]. The M_n values and the M_w/M_n ratios of the polymers were strongly affected by the ligands of the Ni catalyst (dppp > dppe > PPh_3; dppe = 1,2-bis(diphenylphosphino)ethane). In these reactions, the regio-controlled Grignard reagent was prepared by a selective Grignard exchange reaction with *i*-PrMgCl. The C–H functionalization of 2-chlorothiophene derivatives with the formation of magnesium amides in situ also afforded similar regio-controlled Grignard monomers [34, 35].



(8.4)

In their proposed mechanism, the chain-growth polymerization is induced by the “ring-walking process” of the Ni catalyst, whereby the Ni(0) species is transferred intramolecularly along a polymer chain to its end, where it oxidatively inserts into the C–Br bond (Chart 8.3) [36].

Owing to the protocol, all polymer chains are equipped with the same end groups, i.e., bromine and hydrogen atoms after quenching with acid. Therefore, it can allow control of the molar mass by adjusting the feed ratio of the monomer to the Ni catalyst. The catalyst-transfer condensation polymerization has also been demonstrated for other monomers; well-defined conjugated polymers such as polyphenylenes, polypyrroles, and polyfluorenes have been prepared (Eqs. 8.5–8.7) [18, 19, 37–39].



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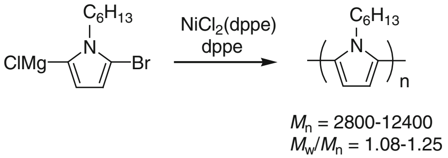

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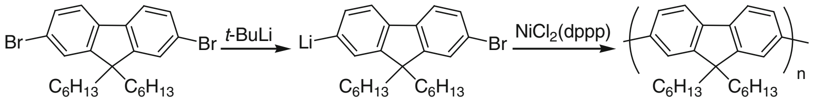


(8.7)

The important advantage of this catalyst-transfer condensation polymerization over other methods is the possible formation of block copolymers by successive monomer additions (Chart 8.4) [40]. Because several aromatic monomers undergo catalyst-transfer condensation polymerization in a living polymerization manner, a variety of block copolymers has been synthesized by successive polymerizations performed in one pot (Chart 8.5) [18, 19, 38, 41–44].

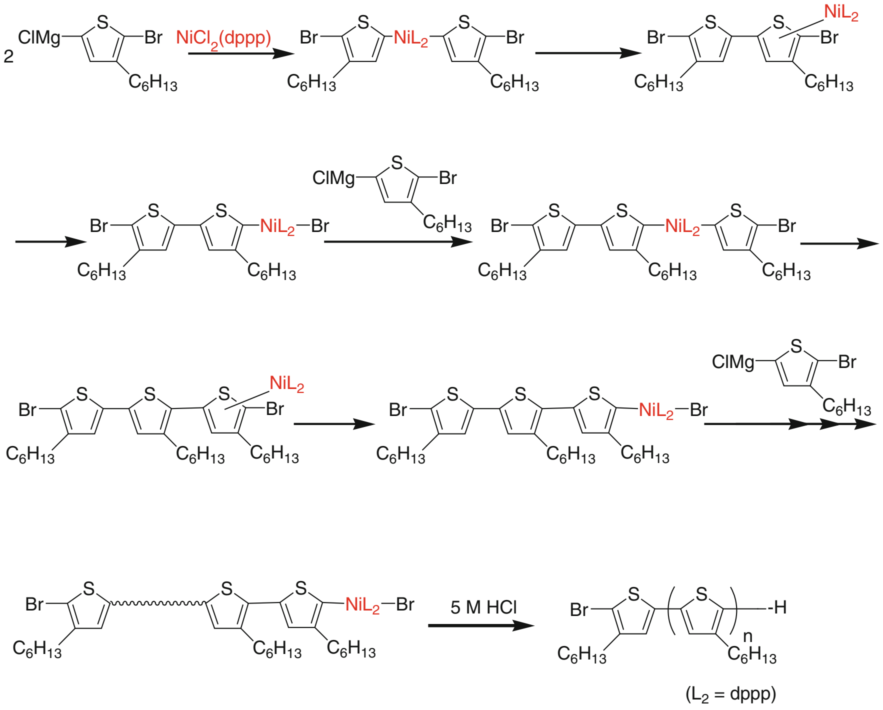


Chart 8.3 Chain-growth synthesis of poly(3-hexylthiophene)

8.3 Pd-Catalyzed Polycondensation

During the early development of cross-coupling reactions, Ni complexes were identified as useful reagents and catalysts. In the intervening years, more attention was invested in the development of Pd catalysts, particularly for Pd-catalyzed Migita-Kosugi-Stille, Suzuki-Miyaura, Sonogashira, and Mizoroki-Heck coupling reactions. These reactions have been utilized in the synthesis of a variety of conjugated polymers owing to some inherent advantages such as increased diversity and tenability of the catalysts, oxidative and aqueous stability, and relatively facile isolation and structural analysis of the complexes, which aids their mechanistic and methodological developments [13–17].

The Migita-Kosugi-Stille coupling reaction is a versatile carbon-carbon bond formation between stannanes and aryl halides (Eq. 8.8), whereas the Suzuki-Miyaura coupling reaction is the palladium-catalyzed cross-coupling reaction between organoboronic acid and aryl halides (Eq. 8.9) [1–12, 17]. One important difference between the Suzuki-Miyaura and the Migita-Kosugi-Stille coupling reactions is that in the former reaction, the boronic acid requires activation, for example with a base. This activation of the boron atom enhances the polarization

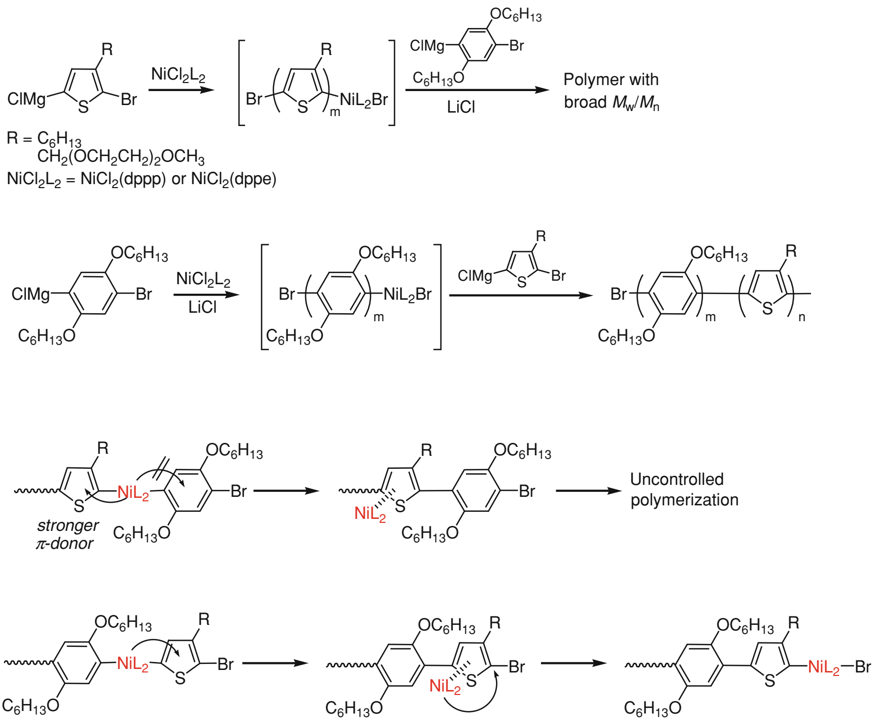
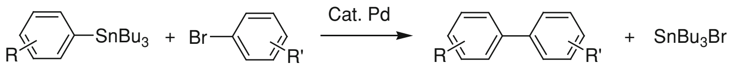


Chart 8.4 Synthesis of block copolymer by the catalyst-transfer condensation polymerization

of the organic substituent, and facilitates transmetalation, as shown in Scheme 8.2. Recently developed catalysts and methods have broadened their possible applications enormously, so that the range of the reactants is not restricted to aryls, but also includes alkyls, alkenyls, and alkynyls.



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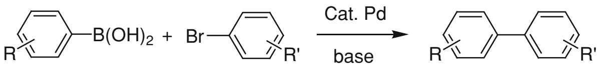
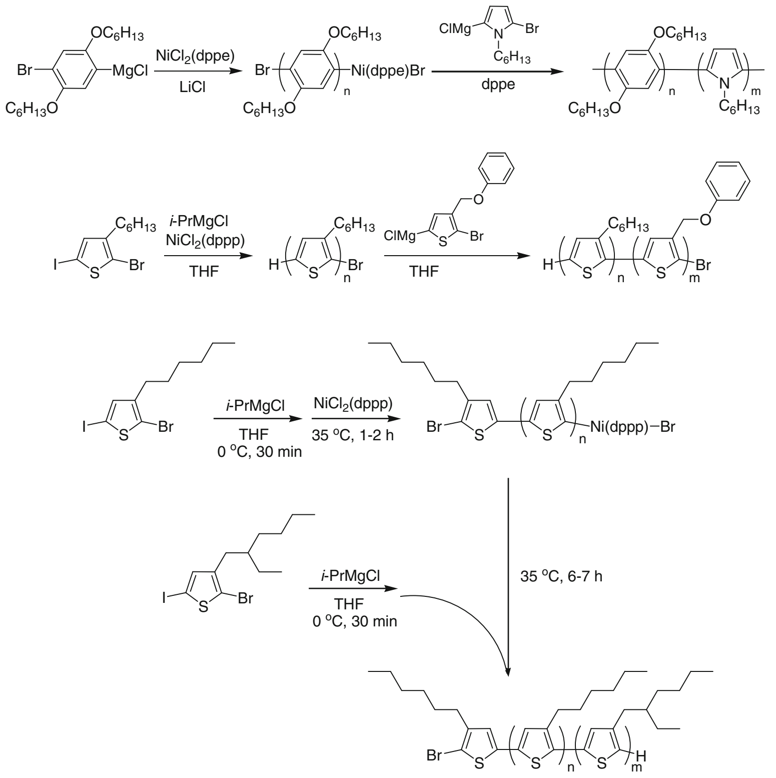


(8.9)

The major advantage of these cross-coupling reactions is that they can tolerate various functional groups and proceed under mild reaction conditions. The Suzuki-Miyaura coupling reaction can be conducted even in aqueous media. Because the aryl halides involved can be extensively functionalized before subjecting them to



Feed molar ratios of 3-hexylthiophene to 3-(2-ethylhexyl)thiophene are 25:75, 50:50, and 75:25.

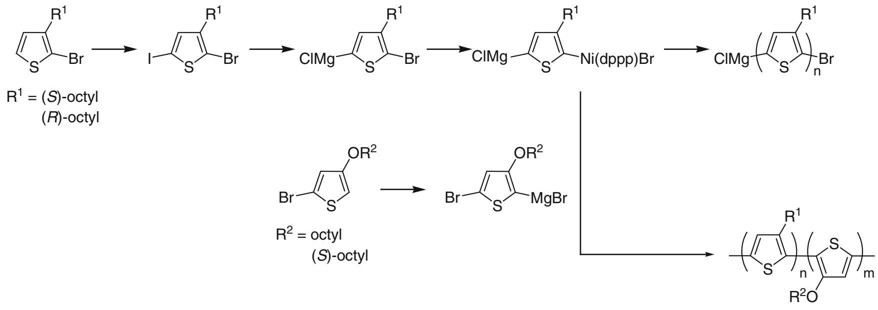
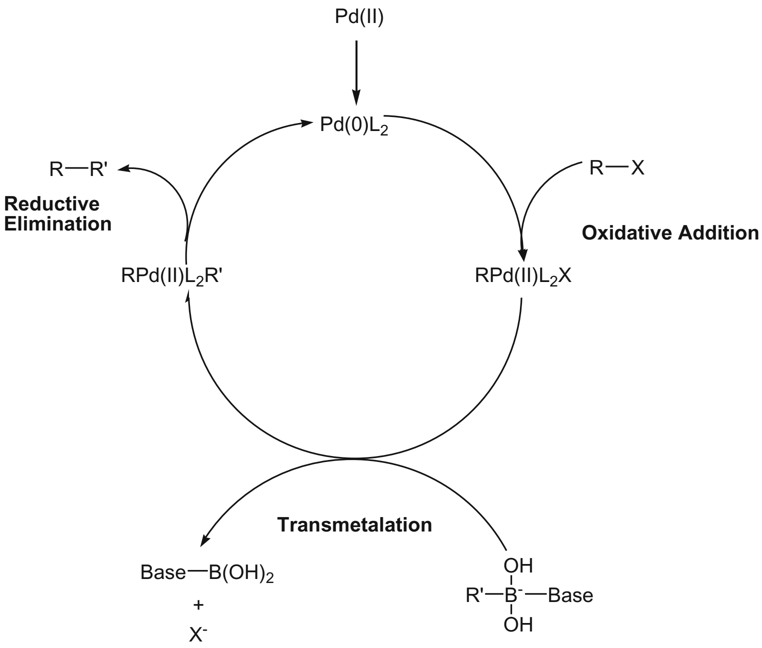
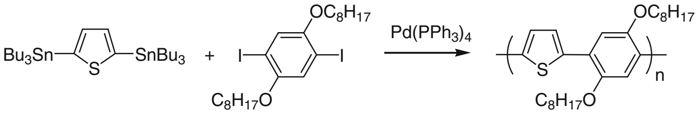


Chart 8.5 Synthesis of several block copolymers in one pot



Scheme 8.2 Suzuki-Miyaura coupling reaction

the coupling reaction, these reactions allow for the preparation of different products from all of the combinations of halides and stannanes or boron reagents. This feature of the coupling reactions offers the opportunity to design a variety of conjugated polymers as well as alternating copolymers with functional moieties manifesting many highly desirable properties (Eqs. 8.10–8.12) [16, 17, 45–47].



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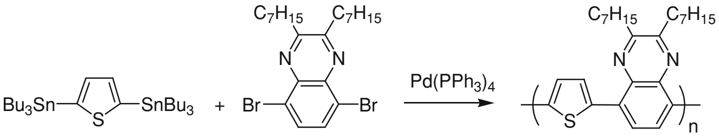

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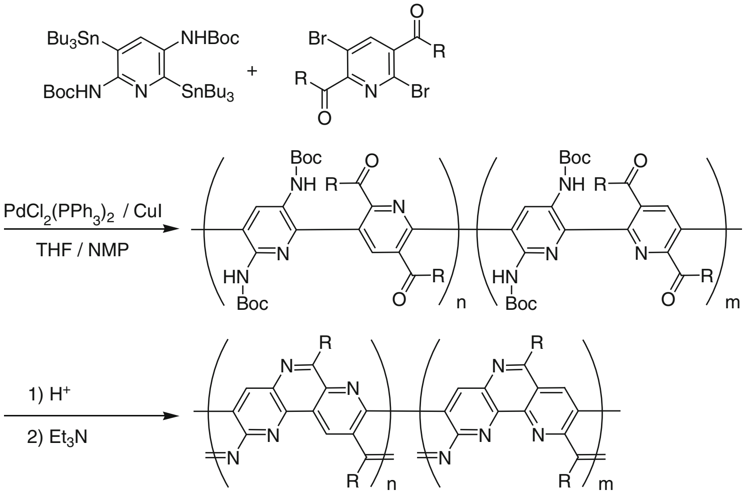
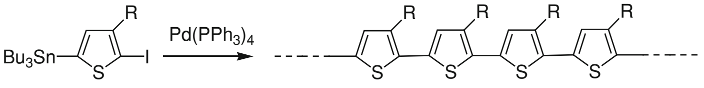


(8.12)

The coupling reactions can also yield highly regioregular poly(3-alkylthiophene)s (HT-P3RTh), when the 3-alkylthiophene derivatives shown in Eqs. 8.13 and 8.14 are employed [48, 49].



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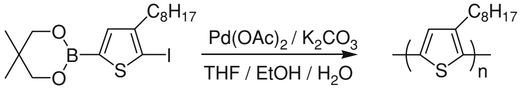
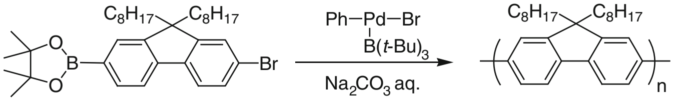


(8.14)

Catalyst-transfer condensation type Suzuki-Miyaura coupling polymerization was achieved by Yokozawa and coworkers (Eqs. 8.15 and 8.16) [50, 51]; polyfluorene with a narrow polydispersity has also been prepared. The polycondensation proceeded in a chain-growth polymerization manner from the initiator unit derived from the Pd catalyst.



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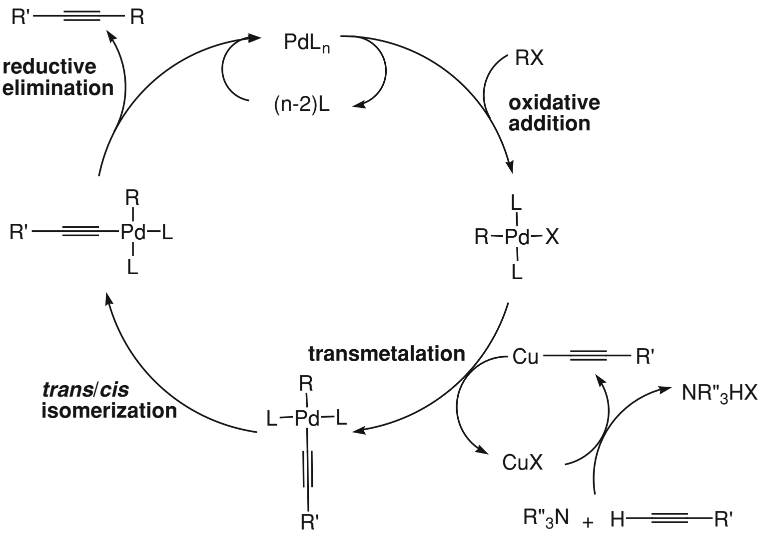
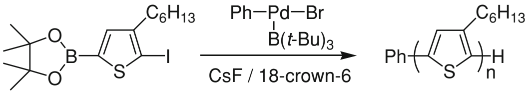
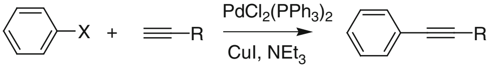


Scheme 8.3 Sonogashira coupling reaction



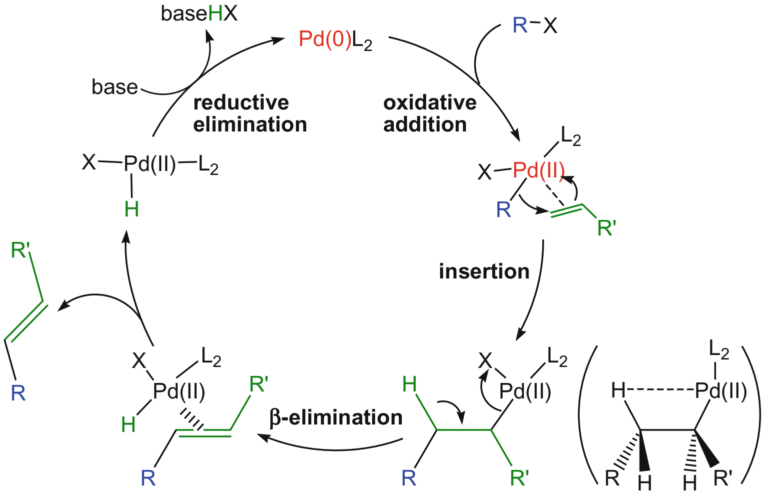
(8.16)

The Pd-catalyzed cross-coupling reaction of aryl and vinyl halides with terminal alkynes employing co-catalytic copper(I) halides and an amine base is known as the Sonogashira coupling reaction (Eq. 8.17) [1–9]. In this reaction, copper(I) halides react with the terminal alkyne and produce copper(I) acetylide, which acts as an activated species for the coupling reactions. Then, transmetalation proceeds in the usual manner for the Pd complex (Scheme 8.3). Because the reaction forms C_{sp}–C_{sp2} bonds, the polycondensation between dihalogenated and diethynyl aromatic compounds gives poly(arylene ethynylene) type conjugated polymers (Chart 8.6) [14, 52].



(8.17)

The Mizoroki-Heck reaction is the palladium-catalyzed addition of aryl, vinyl, or substituted vinyl groups to aryl halides or triflates (Eq. 8.18) [1–9, 12]. The Mizoroki-Heck reaction differs significantly from the other Pd-catalyzed cross-coupling reactions because (1) it involves an insertion step after the oxidative addition step, and (2) the coupling products are produced via a β-hydrogen



Scheme 8.4 Mizoroki-Heck coupling reaction

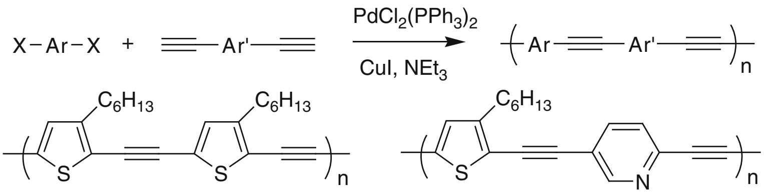
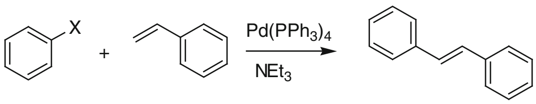


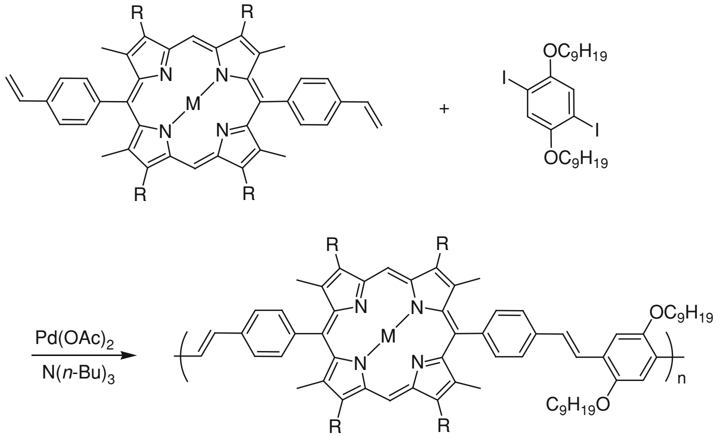
Chart 8.6 Synthesis of poly(arylene ethynylene)s

elimination, whereas the other coupling products are associated with reductive elimination (Scheme 8.4).



(8.18)

In the β-hydrogen elimination step, the atom in the Pd–C–C–H group must be included in a plane for the reaction to take place, as this is a *syn* elimination process. For steric reasons, the R group will tend to eclipse the smallest group on the adjacent carbon as elimination occurs, leading predominantly to a *trans* double bond in the product. Owing to this *trans* selectivity, the Mizoroki-Heck reaction has been successfully applied to the synthesis of several poly(phenylene vinylene) (PPV) analogs having *trans*-C=C bonds. PPV analogs have attracted considerable attention owing to their high electrical conductivity and optoelectronic properties harnessed in electroluminescent applications (Eqs. 8.19 and 8.20) [53, 54].



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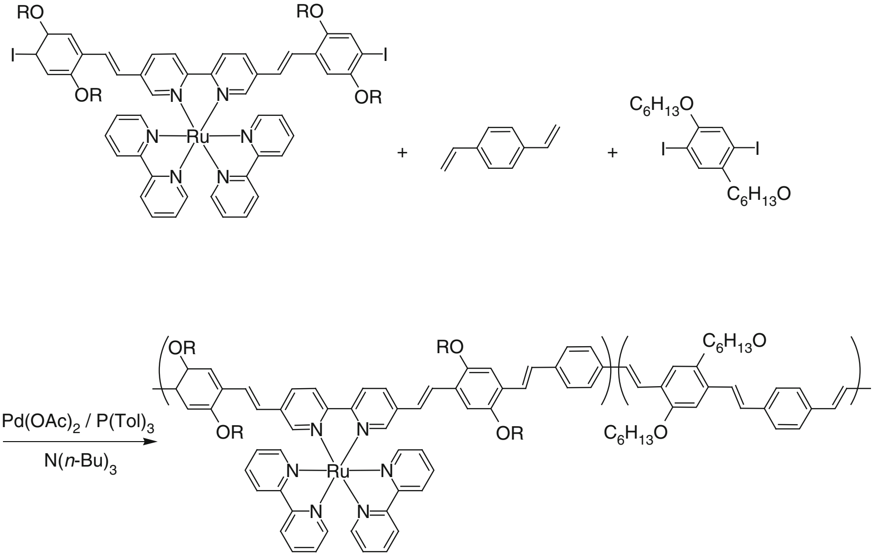
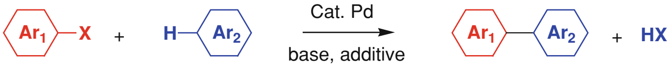


(8.20)

Recently, the catalytic dehydrohalogenative cross-coupling of heteroarenes with aryl halides (a so-called direct arylation) has attracted a great deal of attention as an alternative to the various cross-coupling reactions described above (Eq. 8.21)

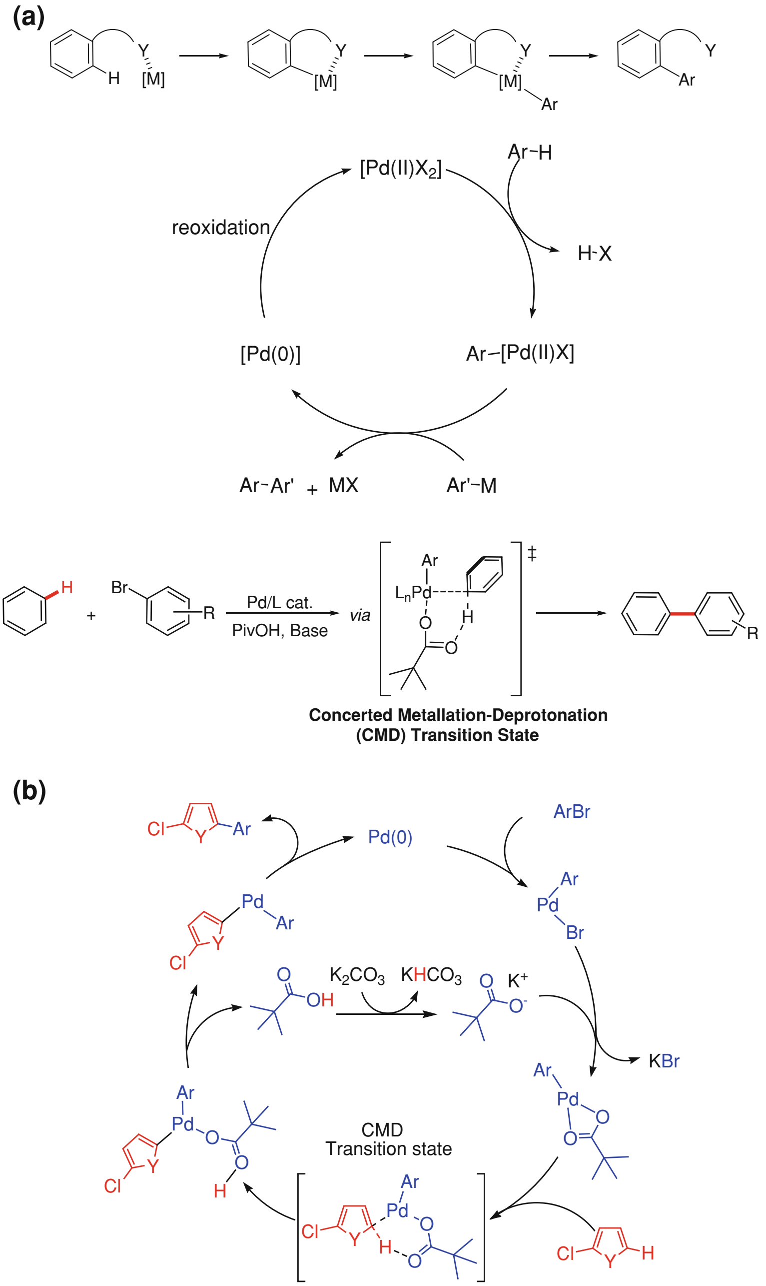
[55, 56]. Since this class of cross-coupling reactions does not require preparation of organometallic reagents and does not form metallic salts as a by-product, this method serves as a cost-effective and environmentally friendly alternative for the preparation of arylated heteroaromatic compounds.



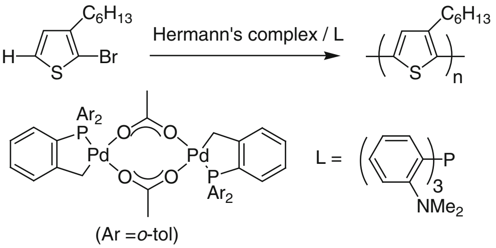
(8.21)

The most common mechanism of C–H bond cleavage promoted by a metal is electrophilic aromatic substitution (SE_{Ar}) involving the reaction of an electrophilic metal catalyst with an electron-rich, nucleophilic aromatic ring. Cyclometalation-based approaches constitute the general strategy towards the arylation of C–H bonds, which results in the functionalization of the *ortho* position to a directing group (Scheme 8.5a). Alternatively, a mechanism based on the metal/base-promoted cleavage of C–H bonds involving a concerted metalation-deprotonation (CMD) pathway has been proposed, instead of the SE_{Ar}. In this mechanism, the carboxylato ligands act as an internal base to achieve the deprotonation of the arenes and the concurrent metalation (Scheme 8.5b). It has been found that palladium(II) acetate is generally the best source of the transition metal catalyst to be used, because the acetate ligand is believed to play multiple roles in cyclometalation reactions. In terms of the iron-catalyzed direct arylation, the transformation proceeds through an aryl radical transfer pathway [57]. The development and mechanistic studies of C–H functionalization are currently underway.

The direct arylation protocol should be of great benefit to polymer synthesis with respect to reducing the waste formation and decreasing number of the reaction steps. However, the development of dehydrohalogenative polycondensation reactions can prove a significant challenge owing to the highly efficient regioselective cross-coupling bond formation required to achieve well-defined linkages between the monomer units. Ozawa and co-workers successfully synthesized poly(3-alkylthiophene)s with high molecular weight and high regioregularity via direct arylation of 2-bromo-3-hexylthiophene (M_n = 30,600 g/mol, M_w/M_n = 1.60). The key to the high catalytic performance reported is the use of Hermann's complex (*trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium) and tris(*o*-*N*,*N*-dimethylaminophenyl)phosphine as catalyst precursors (Eq. 8.22) [58]. The dehydrohalogenative polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene yields the corresponding conjugated polymer with a high molecular weight (M_n = 31,500 g/mol) (Eq. 8.23) [59]. This is attributed to the fluorine substituted aryl compounds which causes the effective direct arylation leading to the coupling products in excellent yields [60].



Scheme 8.5 Catalytic direct arylation with **a** organometallic reagents and **b** aryl halides



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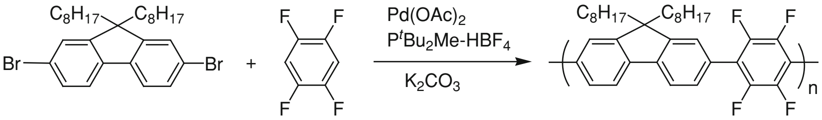
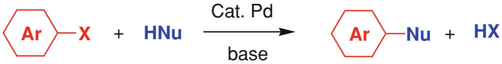


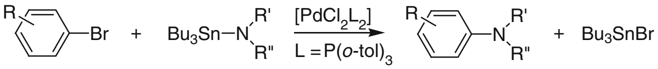
(8.23)

As described above, Pd-catalyzed cross-coupling reactions have proven to be a powerful method for the formation of carbon–carbon bonds, and they are extensively employed across a wide range of areas in synthetic organic chemistry. Meanwhile, the transition-metal catalyzed carbon-heteroatom bond forming reactions have rapidly become valuable synthetic tools because aryl amines and aryl esters are ubiquitous in numerous fields of chemistry (Eq. 8.24) [3, 61–66]. In terms of polymer chemistry, the Pd-catalyzed synthesis of aryl amines by the reaction of aryl halides with primary or secondary amines, commonly known as the Buchwald-Hartwig cross-coupling reaction, has particularly attracted much attention because triarylamine-based polymers are reported to be suitable for use in organic optoelectronic devices, as well as being investigated as typical high-spin organic materials.

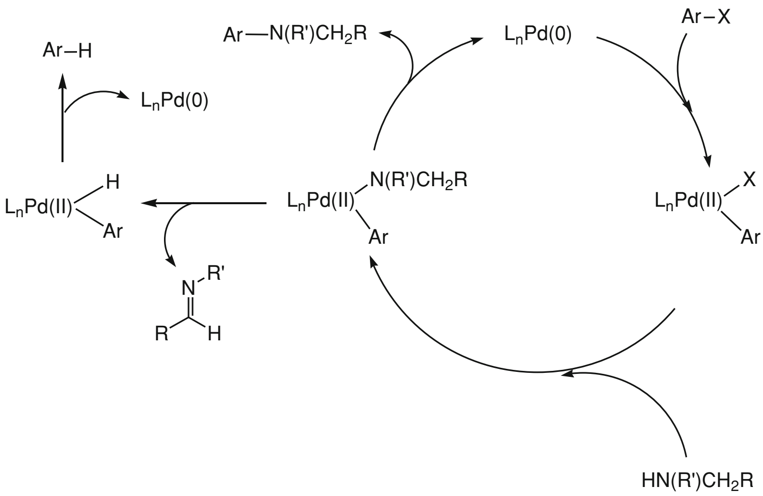


(8.24)

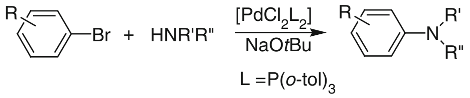
The first Pd-catalyzed aryl amination reaction, reported by Migita and coworkers, is shown in Eq. 8.25 [67]. The reaction was considered to proceed in the same way as the Migita-Kosugi-Stille coupling reaction via the transmetalation of the tin amide compounds to the Pd complex. Problems associated with the use of stannane reagents were overcome by the Buchwald and Hartwig groups (Eq. 8.26) through the use of sodium *tert*-butoxide as a base [68, 69]. This base was effective in the deprotonation of the reacting amine, and the sodium amide generated in situ was used instead of the corresponding tin amide species.



(8.25)



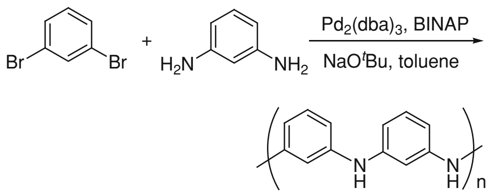
Scheme 8.6 Buchwald-Hartwig cross-coupling reaction



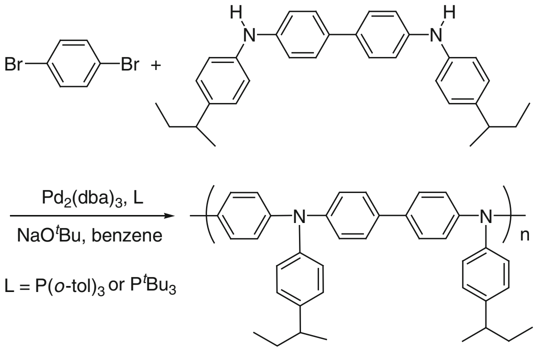
(8.26)

The generally proposed mechanism for this transformation is shown in Scheme 8.6. The catalytic cycle is believed to involve the oxidative addition of an aryl halide, followed by the coordination and deprotonation of the amine. Finally, the reductive elimination of the *N*-aryl product takes place. Since the side products form via β-hydrogen elimination, design of the catalyst systems, especially selection of the ligand, plays a key role in the aryl amination reaction.

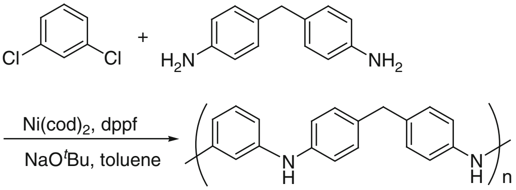
The Buchwald-Hartwig cross-coupling reaction is an efficient tool for syntheses of poly(*m*-aniline) analogs and poly(triarylamine)s, which are rarely prepared by conventional oxidative polymerization. Because the ligand in a catalytic system plays an important role in smooth polymerization, it is essential to choose a suitable ligand for the desired polymer structure. 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) is a suitable ligand for the synthesis of poly(*m*-aniline) analogs bearing a secondary amine unit (Eq. 8.27). Tri-*t*-butylphosphine (P^tBu_3) is one of the optimal ligands for the synthesis of poly(triarylamine)s (Eq. 8.28) [70–74]. Analogous Ni-catalyzed aryl amination reactions have also been applied to polycondensation (Eq. 8.29) [75].



(8.27)

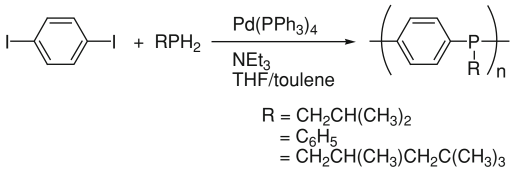


(8.28)



(8.29)

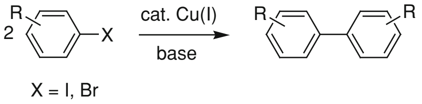
Other Pd-catalyzed carbon-heteroatom (i.e., C–O, C–S, C–P) bond forming reactions essentially proceed in the same manner. The polycondensation using a C–P coupling reaction yields poly(*p*-phenylphosphine) (Eq. 8.30); analogs of polyaniline exhibit electronic delocalization through the extension of conjugation through the phosphorus atom [76–78].



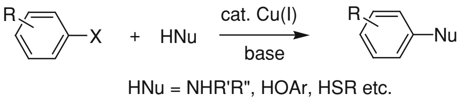
(8.30)

8.4 Cu-Catalyzed Polycondensation

Since copper is a cheaper metal with lower-toxicity than Pd and Ni, an increased interest in the Cu-catalyzed cross-coupling reaction, referred to as the Ullmann condensation, has arisen. This is supported by the recent observations that appropriate ligands can modulate the reactivity of less reactive transition metals than Pd etc. and achieve effective and versatile catalytic systems [79–82]. The classical Ullmann reaction is defined as the synthesis of symmetric biaryls using Cu-catalyzed coupling (Eq. 8.31). Meanwhile, "Ullmann-type" cross-coupling reactions include Cu-catalyzed nucleophilic aromatic substitutions between various nucleophiles (e.g., substituted phenoxides) with aryl halides (Eq. 8.32).



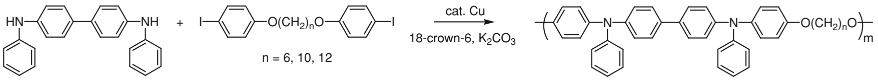
(8.31)



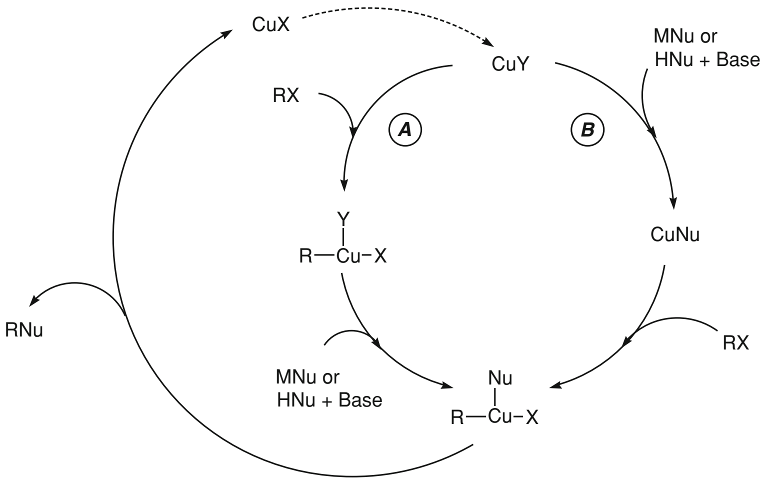
(8.32)

Copper can take part in the cross-coupling chemistry in a way similar to palladium as shown in Scheme 8.7. The most important difference with respect to copper is an easy accessibility of four oxidation states (0 to +3) of the metal; the cross-coupling catalytic cycle with copper is most likely served by the +1/+3 oxidation states.

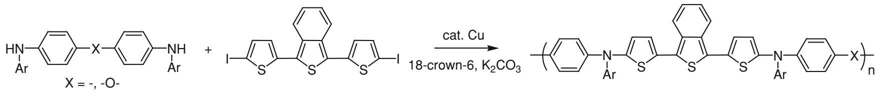
The classical Ullmann coupling reaction has several drawbacks including the necessity of high reaction temperatures and of large amounts of copper. However, with the development for milder reaction conditions and increasing tolerance to sensitive functionalities, the deficiencies of the conventional Ullmann coupling reactions have been overcome. The modified Ullmann coupling reaction in the presence of 18-crown-6 as a phase transfer catalyst was adopted for the synthesis of soluble poly(triarylamine)s (Eq. 8.33) [83]. The coupling reaction procedure could also be used to prepare poly(triarylamine)s containing light-harvesting dyes with a low band gap ($E_g < 1.8$ eV) (Eq. 8.34) [84]. The combination of CuCl/quinoline and sodium hydroxide is a suitable catalyst/ligand and base system for preparation of hyperbranced poly(phenylene oxide) (Eq. 8.35) [85]. Analogous Cu-catalyzed aryl amidation of aromatic dihalides with diamides yielded the corresponding aromatic polyamides (Eq. 8.36) [86, 87].



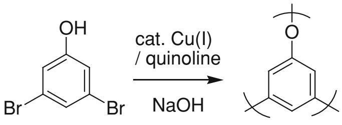
(8.33)



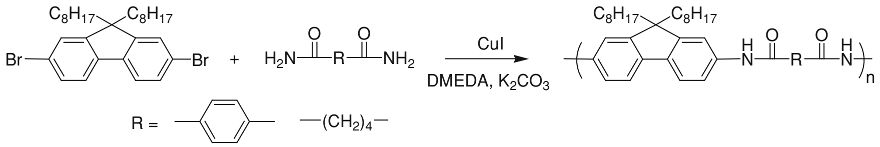
Scheme 8.7 Ullmann-type cross-coupling reaction



(8.34)



(8.35)



(8.36)

8.5 Recent Topics of the Polymers Synthesized by Using Cross-Coupling Polymerization Methods

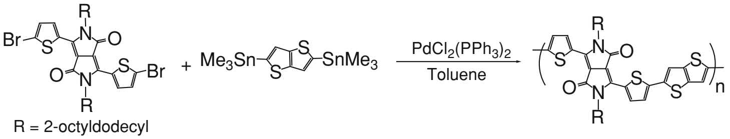
The development of diverse cross-coupling methods has made possible the preparation of a wide variety of polymers containing various monomer units. As mentioned in the previous section, cross-coupling methods can be employed to control the linkage position when an aromatic-aromatic bond is formed. Therefore, they are very helpful in preparing various polymers with precisely controlled linkage positions. By applying the various cross-coupling methods to generate π-conjugated polymers consisting of a variety of aromatic compounds, regioregular homopolymers and alternating copolymers can be produced easily; they are difficult to create using traditional oxidative polymerization or electrochemical oxidative polymerization methods. Various π-conjugated polymers have greatly contributed to the development of optical materials, electronic and photovoltaic devices, etc. [88–98] (For recent reviews, see: [99–119]). In this section, recent research on π-conjugated polymers developed using cross-coupling reactions is described, concentrating on their applications to field effect transistors (FETs), solar cells, and light emitting diodes (LEDs).

An FET is a transistor that controls the current between source and drain terminals through a voltage applied to a gate electrode. This voltage establishes a gate in the flow of electrons or holes using an electric field in a channel. These features enable FETs to be used as switching devices, amplifying elements, etc. Since FETs have a planar structure, they are easy to prepare and integrate. Therefore, they are indispensable elements in the integrated circuits currently used in electronic devices. Recently, extensive research on the creation of new π-conjugated polymers that can be used as low-cost electronic materials has been conducted (For recent reviews, see: [120–123]). In particular, development of materials that show higher mobility of holes and electrons has been emphasized.

The p-type semiconducting π-conjugated polymers are used to form a hole-transportation layer. The rapidly growing range of conducting polymers that show field-effect mobilities exceeding 0.1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ is contributing to improvement in basic device performance. For many years, it appeared difficult to achieve such high mobilities with π-conjugated polymers other than regioregular poly-3-hexylthiophene (P3HT) [124, 125]. However, π-conjugated polymers containing various units have since been developed widely. More recently, the semiconducting polymers with mobility values exceeding 1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$ have been reported.

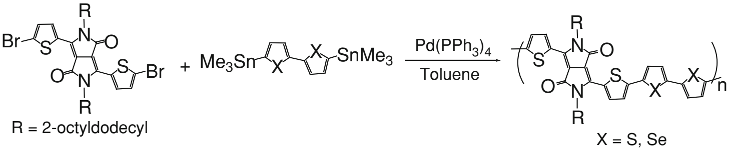
Diketopyrrolopyrole (DPP) has a planar bicyclic structure that leads to a strong π–π interaction. Therefore, π-conjugated polymers containing DPP as a co-monomer unit are expected to be high-performance organic semiconductors. Recently, several DPP-containing alternating π-conjugated polymers have been developed, and their transistor properties were elucidated.

Li et al. reported that an alternating copolymer of DPP and oligothiophene could be synthesized using the Migita-Kosugi-Stille coupling polymerization (Eq. 8.37) and that the copolymer showed a high hole mobility of 0.89 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$. After annealing of the polymer at 100 °C, the hole mobility was increased to 0.97 cm^2 V^{-1} s^{-1} [126, 127].



(8.37)

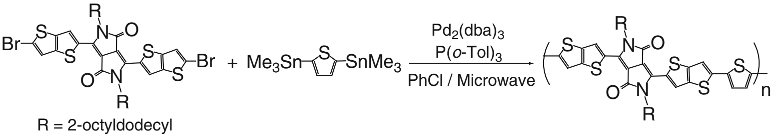
Choi et al. synthesized DPP-based alternating donor-acceptor type copolymers using the Migita-Kosugi-Stille coupling reaction (Eq. 8.38) [128].



(8.38)

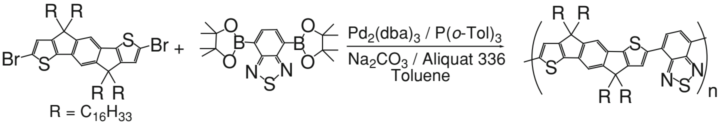
They reported that these polymers showed hole mobilities of *ca.* 0.6 cm^2 V^{-1} s^{-1}. The mobility of one polymer (X=S) was enhanced after annealing at 150 °C to 1.04 cm^2 V^{-1} s^{-1}, and that of another polymer (X=Se) was increased to 1.5 cm^2 V^{-1} s^{-1} after annealing at 180 °C.

Bronstein et al. prepared alternating copolymers consisting of DPP and thieno[3,2-*b*]thiophene using the Migita-Kosugi-Stille coupling reaction (Eq. 8.39) [129]. This polymer showed very high hole mobility of 1.95 cm^2 V^{-1} s^{-1} with no high-temperature annealing.



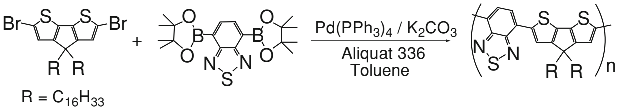
(8.39)

Other polymers with high hole mobilities have also been developed by several groups. Zhang et al. synthesized alternating copolymers consisted of indacenodithiophene and benzothiadiazole using the Suzuki-Miyaura coupling polymerization (Eq. 8.40). This copolymer also showed a high hole mobility of *ca.* 1.0 cm^2 V^{-1} s^{-1} [130].



(8.40)

Müllen et al. reported that alternating copolymers consisting of 2,1,3-benzothiadiazole and a cyclopentadithiophene derivative were synthesized using the Suzuki-Miyaura coupling polymerization (Eq. 8.41) [131] and exhibited a very high hole mobility of 3.3 $cm^2\ V^{-1}\ s^{-1}$ [132, 133].

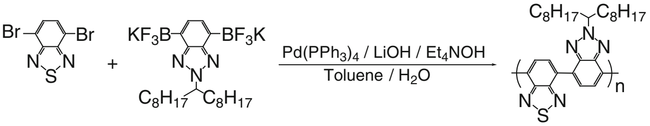


(8.41)

These values are among the highest values obtained from a homogeneous polymer system.

The π-conjugated polymers in which all the unit(s) are formed by electron-accepting monomers are expected to show interesting physical and chemical properties as optoelectronic devices. Since these polymers show features of n-type semiconductors, they are expected to function as an electron-transporting material [134–136]. However, examples of the preparation of such polymers are limited [137–140]. Because it is difficult to make polymers composed only of electron-withdrawing units using oxidative polymerization methods, cross-coupling polymerization methods are particularly useful for producing such polymers.

Ober et al. reported a new class of π-conjugated polymers composed only of electron-accepting monomers prepared using the Suzuki-Miyaura cross-coupling polymerization (Eq. 8.42) [141].

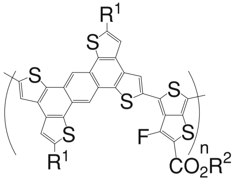
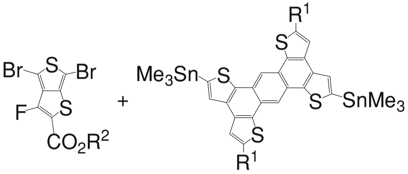
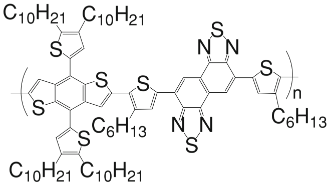
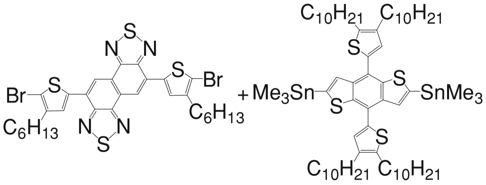
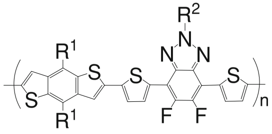
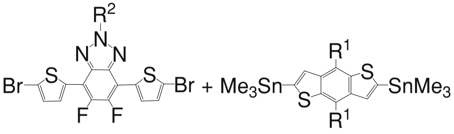
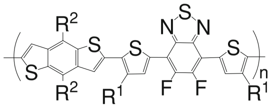
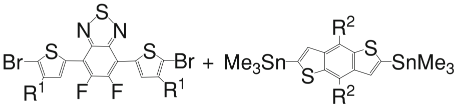


(8.42)

This polymer showed a high electron mobility of $\mu_e = 2 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$. This is the first example of a π-conjugated polymer composed only of electron-accepting units synthesized using the Suzuki-Miyaura coupling. Cross-coupling polymerization methods are very useful in the development of n-type FET materials.

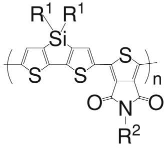
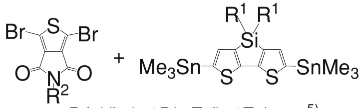
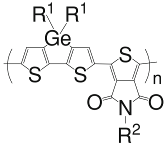
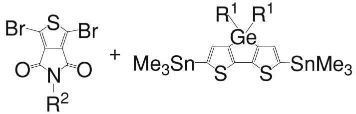
Bulk-heterojunction solar cells (BHSCs) are more cost-effective than inorganic devices, making them an attractive altenative. Since BHSCs were discovered in 1995 [142–144], photovoltaic (PV) devices based on conjugated polymers have attracted much interest. With further development of solar cells using conducting polymers the structures and manufacturing processes of the cells could be further simplified beyond those of the current dye-sensitized solar cells (DSSC). The main disadvantages associated with organic photovoltaic cells are low power conversion efficiency (PCE), low stability, and low strength compared to inorganic photovoltaic cells. Previously, conducting-polymer-based solar cells showed very low PCEs of 10^{-2}–10^{-1} % [145, 146]. The discovery of photoinduced electron transfer in composites of conducting polymers as donors and buckminsterfullerene and its

Table 8.1 Recent development of alternating copolymers for solar cells

Structure	Preparation method	PCE$_{av}$ (PCE$_{max}$)/%
 R^1 = 2-butyloctyl R^2 = 2-ethylhexyl	 $Pd(PPh_3)_4$ / Toluene / DMF	5.6 [170]
	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / toluene	6.00 [171]
 R^1 = 3-butylnonyl R^2 = 2-butyloctyl	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / *o*-Xylene	6.81 (7.10) [172]
 R^1 = 2-ethylhexyl R^2 = 3-butylnonyl	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / *o*-Xylene / microwave	6.9 (7.2) [173]

(continued)

Table 8.1 (continued)

Structure	Preparation method	PCE$_{av}$ (PCE$_{max}$)/%
 R^1 = 2-ethylhexyl R^2 = octyl	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / Toluene[5)] $Pd(PPh_3)_4$ / Toluene / DMF[6)]	6.6 [174] 7.3 [175]
 R^1 = 2-ethylhexyl R^2 = octyl	 $Pd_2(dba)_3$ / P(*o*-Tol)$_3$ / Toluene	7.3 [174]

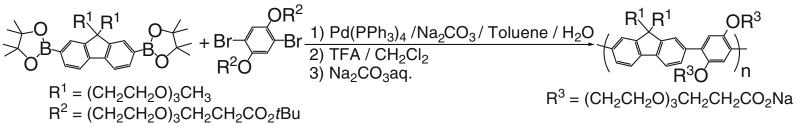
derivatives as acceptors [147] provided a molecular approach to high-efficiency photovoltaic conversion [148, 149]. Since then, many bulk heterojunction polymer solar cells have been developed using π-conjugated polymers containing various monomer units (For recent reviews, see: [150–169]).

In recent years, solar cells using conducting polymers that exhibit high PCEs exceeding 6 % have been developed. Table 8.1 shows recently reported high-PCE-producing π-conjugated polymers prepared by cross coupling polymerization methods.

More recently, Mitsubishi Chemical developed an organic thin film solar cell that used for benzoporphyrin as a p-type organic semiconductor in which the PCE exceeded 10 % [176]. This value is comparable to those of thin-film-type silicon solar cells, which have the highest PCE values in the world. Since polymer-based organic thin film solar cells have the merits quoted above, improvements in high-performance photovoltaic devices through further improvement of the PCE are expected.

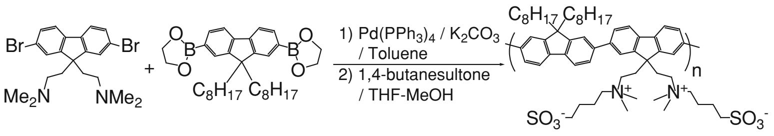
The first polymer light-emitting diode (PLED) composed of π-conjugated polymers was produced in 1990 [177]. Since then, versatile classes of conjugated polymers have been prepared and diverse synthetic methods have been developed (For recent reviews, see: [178–180]). These days, development of new materials that focuses on the luminescence response time is progressing rapidly.

In recent years, conjugated polyelectrolytes have attracted much attention for PLED applications, because they function as electron injection layers (EIL) efficiently and effectively [181–187]. Nguyen et al. reported that a fluorene-phenylene alternating copolymer with an ion-conducting polyethylene pendant was prepared using the Suzuki-Miyaura polymerization (Eq. 8.43) [188] and that this polymer could be used as an EIL in PLEDs [189]. As a result, a fast luminescence temporal response time (200 μs) can be achieved.



(8.43)

Huck et al. reported the preparation of a zwitterionic conjugated polyelectrolyte that had cationic ammonium and anionic sulfonate units in the same side chain (Eq. 8.44). They used this polymer as an EIL and succeeded in creating a high-performance PLED that showed a very fast-response time of less than 10 μs [190].



(8.44)

8.6 Summary

A wide variety of metal-catalyzed cross-coupling reactions has been developed, and a huge number of polymers for functional materials of various natures have resulted from this methodology. Cross-coupling polymerization methods are applicable to the synthesis of varied polymers using diverse monomer materials. Furthermore, since the linkage position between the monomer units is strictly controllable by the design of the monomer(s), regioregular polymers can be invented easily. The methods have distinct potential in the preparation of π-conjugated polymers, since couplings between aryl, alkenyl, and alkynyl species are the most successful confirmed reactions. It is fully expected that these polymerization methods will play a role in the development of not only π-conjugated polymers but also various polymers for functional materials, thus greatly contributing to the development of the material chemistry field.

References

1. Miyaura N, Suzuki A (1995) Chem Rev 95:2457–2478
2. Rosen BM, Quasdorf KW, Wilson DA, Zhang N, Resmerita AM, Garg NK, Percec V (2011) Chem Rev 111:1346–1416
3. Martin R, Buchwald SL (2008) Acc Chem Res 41:1461–1473
4. Suzuki A (1999) J Organomet Chem 576:147–168
5. Tamao K, Sumitani K, Kiso Y, Zembayashi M, Fujioka A, Kodama S, Nakajima I, Minato A, Kumada M (1976) Bull Chem Soc Jpn 49:1958–1969
6. Negishi EI (2007) Bull Chem Soc Jpn 80:233–257
7. Fugami K, Kosugi M (2002) Top Curr Chem 219:87–130
8. Hiyama T, Shirakawa E (2002) Top Curr Chem 219:61–85
9. Sonogashira K (2002) J Organomet Chem 653:46–49
10. Suzuki A (2011) Angew Chem Int Ed 50:6723–6737
11. Negishi EI (2011) Angew Chem Int Ed 50:6738–6764
12. Heck RF (2006) Synlett 18:2855–2860
13. Yamamoto T (2002) J Organomet Chem 653:195–199
14. Yamamoto T (2010) Bull Chem Soc Jpn 83:431–455
15. Babudri F, Farinola GM, Naso F (2004) J Mater Chem 14:11–34
16. Cheng YJ, Luh TY (2004) J Organomet Chem 689:4137–4148
17. Carsten B, He F, Son HJ, Xu T, Yu L (2011) Chem Rev 111:1493–1528
18. Yokozawa T, Yokoyama A (2009) Chem Rev 109:5595–5619
19. Osaka I, McCullough RD (2008) Acc Chem Res 41:1202–1214
20. Shirakawa H (2001) Angew Chem Int Ed 40:2575–2580
21. MacDiarmid AG (2001) Angew Chem Int Ed 40:2581–2590
22. Heeger AJ (2001) Angew Chem Int Ed 40:2591–2611
23. Yamamoto T (1992) Prog Polym Sci 17:1153–1205
24. Yamamoto T, Yamamoto A (1977) Chem Lett 6:353–356
25. Yamamoto T, Hayashi Y, Yamamoto A (1978) Bull Chem Soc Jpn 51:2091–2097
26. Yamamoto T, Sanechika KI, Yamamoto A (1983) Bull Chem Soc Jpn 56:1497–1502
27. Ueda M, Miyaji Y, Ito T, Oba Y, Sone T (1991) Macromolecules 24:2694–2697
28. McCullough RD, Lowe RD (1992) J Chem Soc Chem Commun 70–72

29. Chem T-A, Wu X, Rieke RD (1995) J Am Chem Soc 117:233–244
30. Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, Spiering AJH, Janssen RAJ, Meijer EW, Herwig P, de Leeuw DM (1999) Nature 401:685–688
31. Gangopadhyay P, Voorakaranam R, Lopez-Santiago A, Foerier S, Thomas J, Norwood RA, Persoons AA, Peyghambarian N (2008) J Phys Chem 112:8032–8037
32. Yokoyama A, Miyakoshi R, Yokozawa T (2004) Macromolecules 37:1169–1171
33. Iovu MC, Sheina EE, Gil RR, McCullough RD (2005) Macromolecules 38:8649–8656
34. Tamba S, Shono K, Sugie A, Mori A (2011) J Am Chem Soc 133:9700–9703
35. Tamba S, Tanaka S, Okubo Y, Meguro H, Okamoto S, Mori A (2011) Chem Lett 40:398–399
36. Tkachov R, Senkovskyy V, Komber H, Sommer JU, Kiriy A (2010) J Am Chem Soc 132:7803–7810
37. Miyakoshi R, Shimono K, Yokoyama A, Yokozawa T (2006) J Am Chem Soc 128:16012–16013
38. Yokoyama A, Kato A, Miyakoshi R, Yokozawa T (2008) Macromolecules 41:7271–7273
39. Jhaveri SB, Peterson JJ, Carter KR (2008) Macromolecules 41:8977–8979
40. Miyakoshi R, Yokoyama A, Yokozawa T (2008) Chem Lett 37:1022–1023
41. Ohshimizu K, Ueda M (2008) Macromolecules 41:5289–5294
42. Zhang Y, Tajima K, Hashimoto K (2009) Macromolecules 42:7008–7015
43. Van den Bergh K, Cosemans I, Verbiest T, Koeckelberghs G (2010) Macromolecules 43:3794–3800
44. Kim J, Song IY, Park T (2011) Chem Commun 47:4697–4699
45. Bao Z, Chan W, Yu L (1993) Chem Mater 5:2–3
46. Kanbara T, Miyazaki Y, Yamamoto T (1995) J Polym Sci Part A Polym Chem 33:999
47. Yao Y, Lamba JJS, Tour JM (1998) J Am Chem Soc 120:2805–2810
48. Iraqi A, Barker GW (1998) J Mater Chem 8:25–29
49. Bidan G, Nicola AD, Enée V, Guillerez S (1998) Chem Mater 10:1052–1058
50. Yokoyama A, Suzuki H, Kubota Y, Ohuchi K, Higashimura H, Yokozawa T (2007) J Am Chem Soc 129:7236–7237
51. Yokozawa T, Suzuki R, Nojima M, Ohta Y, Yokoyama A (2011) Macromol Rapid Commun 32:801–806
52. Yamamoto T, Yamada W, Takagi M, Kizu K, Maruyama T (1994) Macromolecules 27:6620–6626
53. Bao Z, Chen Y, Yu L (1994) Macromolecules 27:4629–4631
54. Peng Z, Yu L (1996) J Am Chem Soc 118:3777–3778
55. Ackermann L, Vicente R, Kapdi AR (2009) Angew Chem Int Ed 48:9792–9826
56. Lapointe D, Fagnou K (2010) Chem Lett 39:1118–1126
57. Vallée F, Mousseau JJ, Charette AB (2010) J Am Chem Soc 132:1514–1516
58. Wang Q, Takita R, Kikuzaki Y, Ozawa F (2010) J Am Chem Soc 132:11420–11421
59. Lu W, Kuwabara J, Kanbara T (2011) Macromolecules 44:1252–1255
60. Lafrance M, Rowley CN, Woo TK, Fagnou K (2006) J Am Chem Soc 128:8754–8756
61. Hartwig JF (1998) Acc Chem Res 31:852–860
62. Hartwig JF (1998) Angew Chem Int Ed 37:2046–2067
63. Yang BH, Buchwald SL (1999) J Organomet Chem 576:125–146
64. Muci AR, Buchwald SL (2002) Top Curr Chem 219:131–209
65. Hartwig JF (2006) Synlett 9:1283–1294
66. Hartwig JF (2008) Acc Chem Res 41:1534–1544
67. Kosugi M, Kameyama M, Migita T (1983) Chem Lett 12:927–928
68. Louie L, Hartwig JF (1995) Tetrahedron Lett 36:3609–3612
69. Gram AS, Rennels RA, Buchwald SL (1995) Angew Chem Int Ed 34:1348–1350
70. Kanbara T, Izumi K, Nakadani Y, Narise T, Hasegawa K (1997) Chem Lett 26:1185–1186
71. Spetseris N, Ward RE, Meyer TY (1998) Macromolecules 31:3158–3161
72. Goodson FE, Hartwig JF (1998) Macromolecules 31:1700–1703

73. Kanbara T, Oshima M, Imayasu T, Hasegawa K (1998) Macromolecules 31:8725–8730
74. Yasuda T, Suzuki T, Takahashi M, Tsutsui T (2009) Chem Lett 38:1040–1041
75. Kanbara T, Miyazaki Y, Hasegawa K, Yamamoto T (2000) J Polym Sci, Part A Polym Chem 38:4194–4199
76. Jin Z, Lucht BL (2002) J Organomet Chem 653:167–176
77. Jin Z, Lucht BL (2005) J Am Chem Soc 127:5586–5595
78. Kanbara T, Takase S, Izumi K, Kagaya S, Hasegawa K (2000) Macromolecules 33:657–659
79. Hua F (2011) Synlett 745–769
80. Ma D, Cai Q (2008) Acc Chem Res 41:1450–1460
81. Beletskaya IP, Cheprakov AV (2004) Coord Chem Rev 248:2337–2364
82. Das P, Sharma D, Kumar M, Singh B (2010) Curr Org Chem 14:754–783
83. Ostrauskaite J, Karickal HR, Leopold A, Haarer D, Thelakkat M (2002) J Mater Chem 12:58–64
84. Kisselev R, Thelakkat M (2004) Macromolecules 37:8951–8958
85. In I, Lee H, Kim SY (2003) Macromol Chem Phys 204:1660–1664
86. Ghaemy M, Barghamadi M (2009) J Appl Polym Sci 111:1588–1593
87. Ghaemy M, Barghamadi M (2009) J Appl Polym Sci 114:3464–3471
88. Brédas JL, Chance RR (eds) (1982) Conjugated polymeric materials: opportunities in electronics, optoelectronics, and molecular electronics. Kluwer Academic Publishers, Dordrecht
89. Alcácar L (ed) (1987) Conducting polymers. D. Reidel Publishing Company, Dordrecht
90. Kuzmany H, Mehring M, Roth S (eds) (1987) Electronic properties of conjugated polymers. Springer, Heidelberg
91. Kuzmany H, Mehring M, Roth S (eds) (1989) Electronic properties of conjugated polymers III. Springer, Heidelberg
92. Skotheim TA (ed) (1991) Electroresponsive molecular and polymeric systems. Marcel Dekker, New York
93. Kuzmany H, Mehring M, Roth S (eds) (1991) Electronic properties of polymers. Springer, Heidelberg
94. Salaneck WR, Clark DT, Samuelsen EJ (eds) (1991) Science and applications of conducting polymers. IOP Publishing, Norfolk
95. Brédas JL, Silbey R (eds) (1991) Conjugated polymers. Kluwer Academic Publishers, Dordrecht
96. Zerbi G (ed) (1992) Polyconjugated materials. North-Holland, Netherlands
97. Salaneck WR, Lundström I, Rånby B (eds) (1993) Conjugated polymers and related materials. Oxford University Press, New York
98. Schopf G, Koßmehl G (eds) (1997) Polythiophenes-electrically conductive polymers. Springer, Berlin
99. For recent reviews, see: Advincula RC (2011) Funct Polym Film 1:379–399
100. Lehnherr D, Tykwinski RR (2011) Aust J Chem 64:919–929
101. Brinkmann M (2011) J Polym Sci B Polym Phys 49:1218–1233
102. Haussler M, Tang BZ (2011) Hyperbranched Polym 273–300
103. Morisaki Y, Chujo Y (2011) Polym Chem 2:1249–1257
104. Feist FA, Basche T (2011) Angew Chem Int Ed 50:5256–5257
105. Da Como E, Lupton JM (2011) Funct Supramol Architect 2:589–610
106. Comoretto D, Morandi V, Galli M, Marabelli F, Soci C (2011) Funct Supramol Architect 2:567–588
107. Xu Y, Zhang F, Feng X (2011) Small 7:1338–1360
108. Akeroyd N, Klumperman B (2011) Eur Polym J 47:1207–1231
109. Balan A, Baran D, Toppare L (2011) Polym Chem 2:1029–1043
110. Baibarac M, Baltog I, Lefrant S (2011) Curr Org Chem 15:1160–1196
111. Liu C-L, Lin C-H, Kuo C-C, Lin S-T, Chen W-C (2011) Prog Polym Sci 36:603–637
112. Reiss P, Couderc E, De Girolamo J, Pron A (2011) Nanoscale 3:446–489

113. Lange U, Roznyatovskaya NV, Hao Q, Mirsky VM (2011) Artificial receptors for chemical sensors. Wiley-VCH Verlag & Co. KGaA, Weinheim, pp 361–390
114. Andrew TL, Swager TM (2011) J Polym Sci B Polym Phys 49:476–498
115. Klingstedt T, Nilsson KPR (1810) Biochim Biophys Acta Gen Subjects 2011:286–296
116. Pina J, Costa T, Seixas de Melo JS (2010) Photochem 38:67–109
117. Gangopadhyay P, Koeckelberghs G, Persoons A (2011) Chem Mater 23:516–521
118. Kim FS-J, Ren G-Q, Jenekhe SA (2011) Chem Mater 23:682–732
119. Hwang I, Scholes GD (2011) Chem Mater 23:610–620
120. For recent reviews, see: Akagi K (2005) Adv Mater 17:2281–2305
121. Sirringhaus H, Bird M, Zhao N (2010) Adv Mater 22:3893–3898
122. Lu K, Liu Y (2010) Curr Org Chem 14:2017–2033
123. Liu Y, Liu Y, Zhan X (2011) Macromol Chem Phys 212:428–443
124. Bao Z, Dodabalapur A, Lovinger AJ (1996) Appl Phys Lett 69:4108
125. Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, Spiering AJH, Janssen RAJ, Meijer EW, Herwig P, de Leeuw DM (1999) Nature 401:685–688
126. Li Y, Singh SP, Sonar P (2010) Adv Mater 22:4862–4866
127. Li Y, Sonar P, Singh SP, Soh MS, van Meurs M, Tan J (2011) J Am Chem Soc 133:2198–2204
128. Ha JS, Kim KH, Choi DH (2011) J Am Chem Soc 133:10364–10367
129. Bronstein H, Chen Z, Ashraf RS, Zhang W, Du J, Durrant JR, Tuladhar PS, Song K, Watkins SE, Geerts Y, Wienk MM, Janssen RAJ, Anthopouos T, Sirringhaus H, Heeney M, McCulloch I (2011) J Am Chem Soc 133:3272–3275
130. Zhang W, Smith J, Watkins SE, Gysel R, McGehee M, Salleo A, Kirkpatrick J, Ashraf S, Anthopoulos T, Heeney M, McCulloch I (2010) J Am Chem Soc 132:11437–11439
131. Zhang M, Tsao HN, Pisula W, Yang C, Mishra AK, Müllen K (2007) J Am Chem Soc 129:3472–3473
132. Tsao HN, Cho D, Andreasen JW, Rouhanipour A, Breiby DW, Pisula W, Müllen K (2009) Adv Mater 21:209–211
133. Tsao HN, Cho DM, Park I, Hansen MR, Mavrinskiy A, Yoon DY, Graf R, Pisula W, Spiess HW, Müllen K (2011) J Am Chem Soc 133:2605–2612
134. Newman CR, Frisbie CD, da Silva Filho DA, Brédas JL, Ewbank PC, Mann KR (2004) Chem Mater 16:4436–4451
135. Facchetti A (2007) Mater Today 10:28–37
136. Wen Y, Liu Y (2010) Adv Mater 22:1331–1345
137. Kanbara T, Yamamoto T (1993) Chem Lett 419–422
138. Hu Y, Alam MM, Jenekhe SA (2003) Macromolecules 36:8958–8968
139. Tanimoto A, Yamamoto T (2004) Adv Synth Catal 346:1818–1823
140. Yamamoto T, Sakai Y, Aramaki S (2006) Bull Chem Soc Jpn 79:956–961
141. Lee J-K, Gwinner MC, Berger R, Newby C, Zentel R, Friend RH, Sirringhaus H, Ober CK (2011) J Am Chem Soc 133:9949–9951
142. Yu G, Heeger AJ (1995) J Appl Phys 78:4510–4515
143. Halls JJM, Walsh CA, Greenham NC, Marseglia E, Friend RH, Moratti SC, Holmes AB (1995) Nature 376:498–500
144. Shaheen S, Ginley DS, Jabbour GE (eds) (2005) MRS bull. Special issue on organic based photovoltaics, vol 30, pp 10–52
145. Karg S, Riess W, Dyakonov V, Schwoerer M (1993) Synth Met 54:427–433
146. Antoniadis H, Hsieh BR, Abkowitz MA, Jenekhe SA, Stolka M (1994) Synth Met 62:265–271
147. Sariciftci NS, Smilowitz L, Heeger AJ, Wudl F (1992) Science 258:1474–1476
148. Lee CH, Yu G, Moses D, Pakbaz K, Zhang C, Sariciftci NS, Heeger AJ, Wudl F (1993) Phys Rev B 48:15425–15433
149. Yu G, Pakbaz K, Heeger AJ (1994) Appl Phys Lett 64:3422–3424
150. For recent reviews, see; Hoppe H, Sariciftci NS (2006) J Mater Chem 16:45–61

151. Mozer AJ, Sariciftci NS (2006) CR Chim 9:568–577
152. Güenes S, Neugebauer H, Sariciftci NS (2007) Chem Rev 107:1324–1338
153. Cravino A (2007) Polym Int 56:943–956
154. Li Y, Zou Y (2008) Adv Mater 20:2952–2958
155. Chen J, Cao Y (2009) Acc Chem Res 42:1709–1718
156. Cheng Y-J, Yang S-H, Hsu C-S (2009) Chem Rev 109:5868–5923
157. Helgesen M, Sondergaard R, Krebs FC (2010) J Mater Chem 20:36–60
158. Skompska M (2010) Synth Met 160:1–15
159. Inganaes O, Zhang F, Tvingstedt K, Andersson LM, Hellstroem S, Andersson MR (2010) Adv Mater 22:E100–E116
160. Lee T-W, Lim K-G, Kim D-H (2010) Elect Mater Lett 6:41–50
161. Boudreault P-LT, Najari A, Leclerc M (2011) Chem Mater 23:456–469
162. Zhan X, Zhu D (2010) Polym Chem 1:409–419
163. Duarte A, Pu K-Y, Liu B, Bazan GC (2011) Chem Mater 23:501–515
164. Facchetti A (2011) Chem Mater 23:733–758
165. Zhang W, Cheng Y, Yin X, Liu B (2011) Macromol Chem Phys 212:15–23
166. Zhou Y, Eck M, Krueger M (2010) Energy Environ Sci 3:1851–1864
167. Palewicz M, Iwan A (2011) Curr Phys Chem 1:27–54
168. Gendron D, Leclerc M (2011) Energy Environ Sci 4:1225–1237
169. Chochos CL, Choulis SA (2011) Prog Polym Sci 36:1326–1414
170. He F, Wang W, Chen W, Xu T, Darling SB, Strzalka J, Liu Y, Yu L (2011) J Am Chem Soc 133:3284–3287
171. Wang M, Hu X, Liu P, Li W, Gong X, Huang F, Cao Y (2011) J Am Chem Soc 133:9638–9641
172. Price SC, Stuart AC, Yang L, Zhou H, You W (2011) J Am Chem Soc 133:4625–4631
173. Zhou H, Yang L, Stuart AC, Price SC, Liu S, You W (2011) Angew Chem Int Ed 50:2995–2998
174. Amb CM, Chen S, Graham KR, Subbiah J, Small CE, So F, Reymonds JR (2011) J Am Chem Soc 133:10062–10065
175. Chu T-Y, Lu J, Beaupré S, Zhang Y, Pouliot J-R, Wakim S, Zhou J, Leclerc M, Li Z, Ding J, Tao Y (2011) J Am Chem Soc 133:4250–4253
176. http://www.mitsubishichem-hd.co.jp/group/strategy/major_project/solar_cell.html
177. Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burn PL, Holmes AB (1990) Nature 347:539–541
178. For recent reviews, see: Morin J-F, Leclerc M, Adès D, Siove A (2005) Macromol Rapid Commun 26:761–778
179. Iwan A, Sek D (2008) Prog Polym Sci 33:289–345
180. Al Salhi MS, Alam J, Dass LA, Raja M (2011) Int J Mol Sci 12:2036–2054
181. Wu H, Huang F, Mo Y, Yang W, Wang D, Peng J, Cao Y (2004) Adv Mater 16:1826–1830
182. Wu H, Huang F, Peng J, Cao Y (2005) Org Electron 6:118–128
183. Ma W, Iyer PK, Gong X, Liu B, Moses D, Bazan GC, Hegger AJ (2005) Adv Mater 17:274–277
184. Yang R, Wu H, Cao Y, Bazan GC (2006) J Am Chem Soc 128:14422–14423
185. Garcia A, Yang R, Jin Y, Walker B, Nguyen T-Q (2007) Appl Phys Lett 91:153502
186. Zeng W, Wu H, Zhang C, Fuang F, Peng J, Yang W, Cao Y (2007) Adv Mater 19:810–814
187. Hoven CV, Garcia A, Bazan GC, Nguyen T-Q (2008) Adv Mater 20:3793–3810
188. Wang F, Bazan GC (2006) J Am Chem Soc 128:15786–15792
189. Garcia A, Bakus RC II, Zalar P, Hoven CV, Brzezinski JZ, Nguyen T-Q (2011) J Am Chem Soc 133:2492–2498
190. Fang J, Wallikewitz BH, Gao F, Tu G, Müller C, Pace G, Friend RH, Huck WTS (2011) J Am Chem Soc 133:683–685