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Transition Metal-catalyzed Polycondensation

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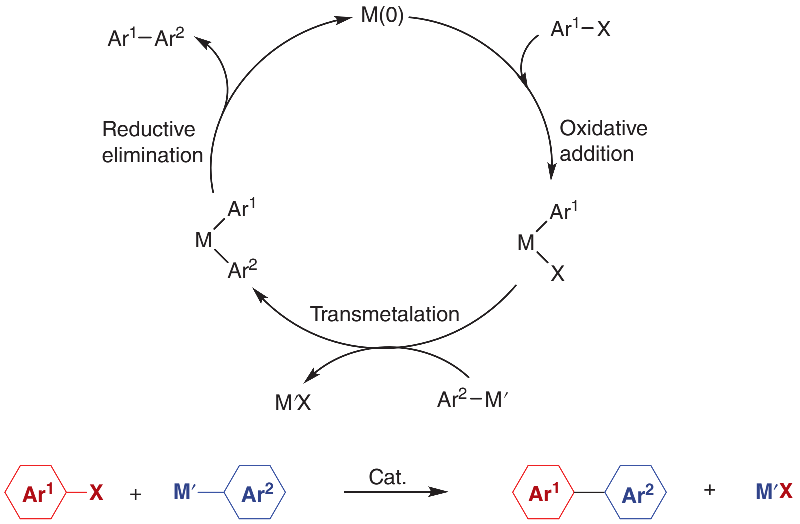
1.1 Introduction

Transition metal-catalyzed homo- and cross-coupling reactions have emerged as versatile synthetic methodologies that are widely employed for the synthesis of a variety of organic compounds [1–9]. Cross-coupling reactions of various organometallic (Mg, Zn, Sn, B, and Si) reagents and aryl halides are suitable for bond formation at sp^2 and sp carbons. Profs. Negishi, Suzuki, and Heck were awarded the Nobel Prize in Chemistry in 2010 for their pioneering work on Pd-catalyzed cross-coupling reactions in organic synthesis [10–13].

Scheme 1.1 shows the general mechanism of cross-coupling reactions. Ni- and Pd-based complexes are commonly employed as transition metal catalysts. In general, cross-coupling reactions involve three steps: an oxidative addition reaction across the carbon–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 bonds and regeneration of the active catalyst. Various organometallic reagents, including Grignard reagents (Kumada–Tamao–Corriu), zinc (Negishi), stannane (Migita–Kosugi–Stille), boron (Suzuki–Miyaura), silane (Hiyama), copper (Sonogashira), lithium, and mercury compounds, can be used [1–13].

In terms of polymer synthesis, various π-conjugated polymers have been designed and developed by the transition metal-catalyzed homo- and cross-coupling polycondensation over the last few decades [14–17]. This chapter describes a fundamental overview of the transition metal-catalyzed homo- and cross-coupling polymerization reactions used in the synthesis of various π-conjugated polymers. The utilization of transition metal-catalyzed C—H bond functionalization and carbon–nitrogen bond formations in synthesizing π-conjugated polymers is also involved.

Conjugated Polymer Synthesis and Materials Applications, First Edition. Edited by Yoshiki Chujo.



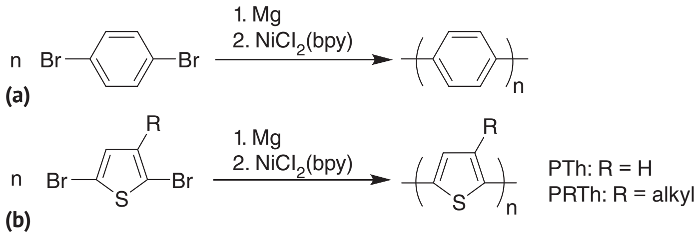
X = Cl, Br, I etc.   M = MgBr, ZnBr, $B(OH)_2$, $SnBu_3$ SiR_3 etc.   Cat. = Ni, Pd etc.

Scheme 1.1 General mechanism of metal-catalyzed cross-coupling reaction. Ar^1 and Ar^2 denote aromatic units, M and M′ represent an organometallic moiety, and X represents halogen or pseudo-halogen.

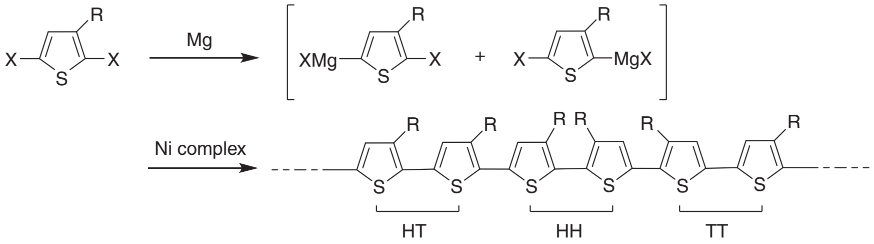
1.2 Ni-catalyzed Polycondensation

The utilization of transition metal-catalyzed cross-coupling reactions to π-conjugated polymers was first reported by Yamamoto et al. in the synthesis of poly(*p*-phenylene), which was prepared by Ni-catalyzed Grignard coupling of 1,4-dibromobenzene [14, 18, 19]. One of the C—Br bonds reacts with Mg to form the Grignard reagent and undergoes further coupling reactions based on the Kumada–Tamao–Corriu cross-coupling reaction (Scheme 1.2a). Polythiophene (PTh) and poly(3-alkylthiophene) s (PRThs) were synthesized using the same protocol (Scheme 1.2b) [20].

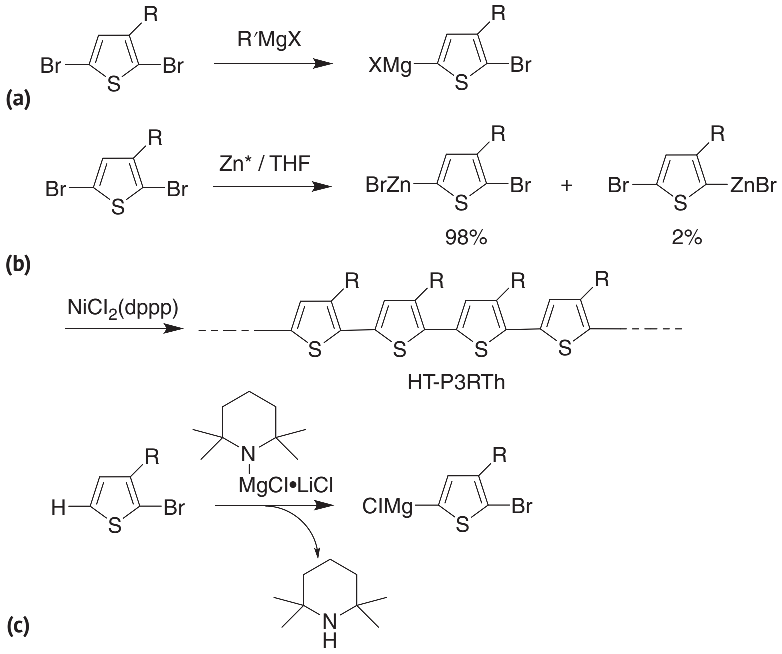
While the reactions are simple and provide several π-conjugated polymers, the regioregularity cannot be controlled using the conventional protocol (Scheme 1.3). The synthesis of regioregular PRThs involving head-to-tail (HT) repeating units can be realized by the Ni-catalyzed polycondensation of regio-controlled organometallic monomers (Scheme 1.4). The reaction of 2,5-dibromo-3-alkylthiophene with metallic Mg or Zn was shown to give the organometallic species at the 5-position. Further addition of the Ni catalyst initiated polymerization to give PRThs with high HT regioregularity (HT-P3RTh, Schemes 1.4a, b) [21–23]. The active monomers for regioregular PRThs were also generated by deprotonation of 2-bromo-3-alkylthiophene with Knochel–Hauser base, 2,2,6,6-tetramethyl piperidinyl magnesium chloride lithium chloride complex (TMPMgCl·LiCl) (Scheme 1.4c) [23]. Regioregular PRThs have been of particular interest because regioregular polymers exhibit remarkable physical properties such as higher crystallinity and electrical conductivity in the solid state than regio-random PRThs [14, 24]. It should be noted



Scheme 1.2 Ni-catalyzed Grignard coupling polycondensation of (a) 1,4-dibromobenzene and (b) 2,5-dibromo-3-alkylthiophene.



Scheme 1.3 Synthesis of regioirregular PRTh.



Scheme 1.4 Synthesis of regioregular PRTh mediated by (a) Grignard reagent, (b) Rieke zinc, and (c) Knochel–Hauser base.

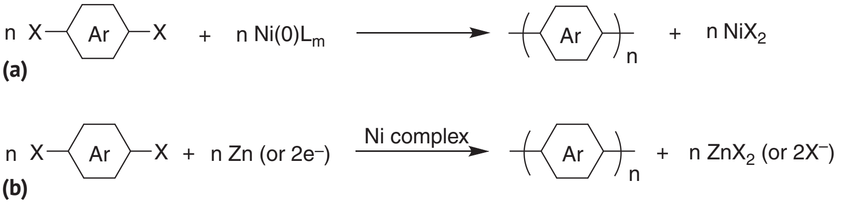
that the polymerization reaction in Scheme 1.4 could proceed in a chain-growth manner, in which propagation occurs at the polymer end, despite the reaction being based on a polycondensation. Thus, the reaction allows the control of the molecular weight with a narrow molecular weight distribution and the formation of block copolymers by successive monomer additions [23, 25–30]. Chapter 2 will provide a detailed description of the chain-growth polycondensation.

Dehalogenative homo-coupling polycondensation of dihaloaromatic monomers using zerovalent Ni complexes ($Ni(0)L_m$) such as $Ni(PPh_3)_4$ and $Ni(cod)_2$ (cod = 1,5-cyclooctadiene), has also contributed to design various π-conjugated polymers (Scheme 1.5a) [14, 18]. The protocol proceeds under mild conditions and enables the polycondensation of dihaloaromatic monomers, such as 2,5-dibromopyridine and 1,4-dichloroanthracene, which has not been achieved by other polycondensation methods. While the reaction generally requires a stoichiometric amount of Ni(0) complex, the $Ni(0)L_m$ complexes formed in situ by chemical (e.g. by Zn, NaH, and hydrazine hydrate) or electrochemical reduction of Ni(II) compounds are available for polycondensation [31–35] thus facilitating the following catalytic reactions (Scheme 1.5b).

1.3 Pd-catalyzed Polycondensation

Pd complexes are known as useful catalysts for various C—C coupling reactions, particularly the Pd-catalyzed Migita–Kosugi–Stille, Suzuki–Miyaura, Sonogashira, and Mizoroki–Heck coupling reactions have been utilized for polycondensation giving various π-conjugated polymers [14–17]. This is due 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 aid their mechanistic and methodological developments. With the development of these cross-coupling reactions utilized polycondensation, π-conjugated polymers consisting of alternating aromatic units have been prepared easily, and the variation of the π-conjugated polymers has been dramatically increased.

The Migita–Kosugi–Stille coupling reaction is a Pd-catalyzed cross-coupling reaction between aryl halides and organostannic compounds and the Suzuki–Miyaura coupling reaction is a versatile C—C bond formation reaction between aryl halides

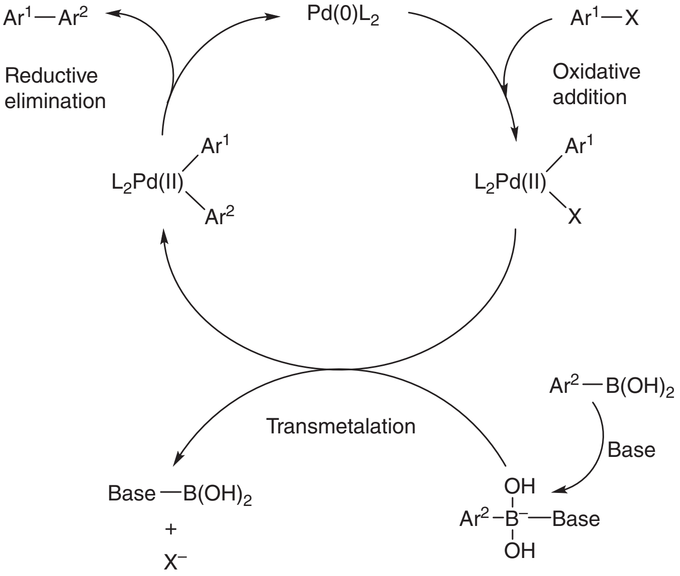


Scheme 1.5 Dehalogenative homo-coupling polycondensation using (a) a stoichiometric amount of Ni(0) complex and (b) Ni(0) complexes formed by chemical and electrochemical reduction.

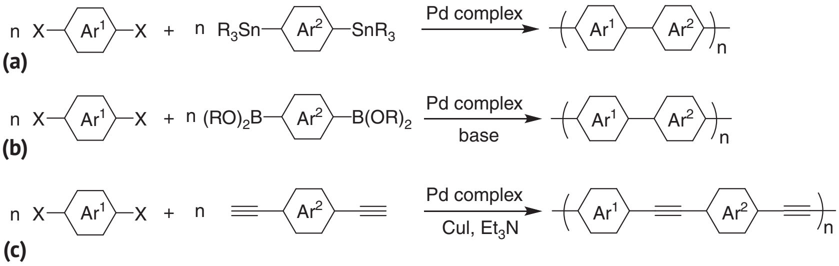
and organoboronic acids. One important difference between the cross-coupling reactions is that the Suzuki–Miyaura coupling reaction requires the activation of the organoboronic acid with a base. This activation facilitated transmetalation (Scheme 1.6). The major advantage of these cross-coupling reactions is that they can tolerate various functional groups and proceed under mild conditions. The Suzuki–Miyaura coupling reaction can even be conducted in aqueous media. The feature of the coupling reactions offers the opportunity to design a variety of π-conjugated polymers with functional moieties manifesting many highly desirable properties (Scheme 1.7a, b) [14–17, 36, 37]. In addition, these cross-coupling polymerization protocols also proceed in a chain-growth polymerization manner from the initiator unit derived from the Pd catalyst [25–30]; the details are to be described in Chapter 2.

The Pd-catalyzed cross-coupling of aryl halides with terminal alkynes employing co-catalytic Cu(I) halides and an amine base is referred as the Sonogashira coupling reaction [9]. The polycondensation reactions between dihaloaromatic monomers and diethynyl aromatic monomers give poly(arylene ethynylene) type π-conjugated polymers (Scheme 1.7c) [38]. In this reaction, the Cu(I) halides react with the terminal alkyne to produce a Cu(I) acetylide, which serves as an activated species for the coupling reaction. Transmetalation proceeded in the usual manner for the Pd complex (Scheme 1.1). A Cu-co-catalyzed mechanism for the Sonogashira coupling reaction was also proposed since the rate of the reaction was affected by the nature of the substituent and the halide of the copper(I) salt as well as the aryl halide [39].

The Mizoroki–Heck coupling is a Pd-catalyzed cross-coupling reaction between aryl halides and alkenes in the presence of a base to form aryl alkenes [12]. The reaction differs from other Pd-catalyzed cross-coupling reactions because it does



Scheme 1.6 Reaction mechanism of the Suzuki–Miyaura coupling reaction. Ar^1 and Ar^2 denote aromatic units and X denotes halogen or pseudo-halogen.



Scheme 1.7 Pd-catalyzed polycondensation via (a) Migita–Kosugi–Stille, (b) Suzuki–Miyaura, and (c) Sonogashira coupling reactions.

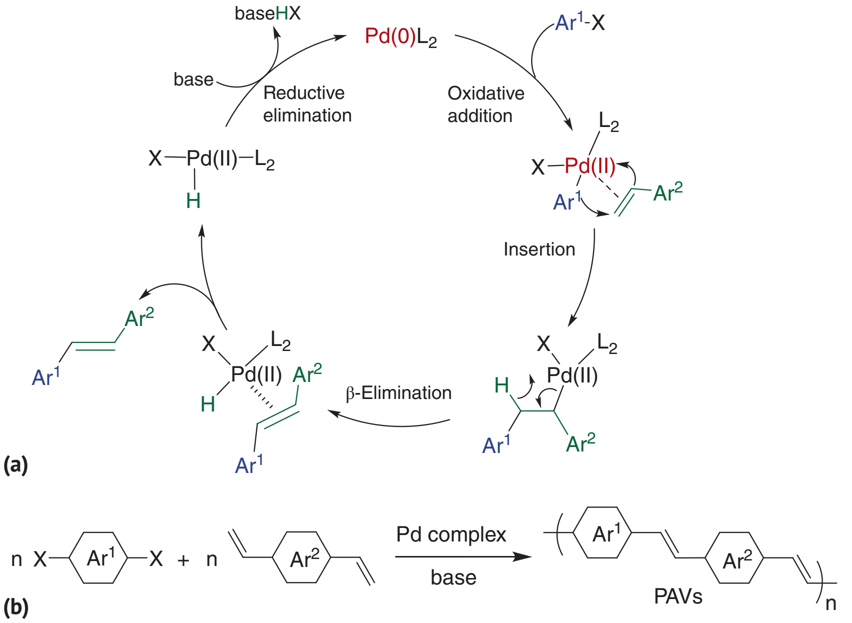
not involve a transmetalation step. Alternatively, after the oxidative addition step, the alkene inserts into the Pd—C bond, and the coupling products are produced via a β-hydrogen elimination (Scheme 1.8a). The Mizoroki–Heck reaction is compatible with the synthesis of several poly(*p*-phenylene vinylene) (PPV) derivatives and their analogs, namely poly(arylene vinylene)s (PAVs, Scheme 1.8b) [40]. PPV and PAVs have attracted considerable attention because of their high electrical conductivity and optoelectronic properties [41, 42].

Pd-catalyzed carbon–heteroatom bond formation reactions have also become valuable synthetic tools. In particular, the Pd-catalyzed amination of aryl halides, commonly known as the Buchwald–Hartwig coupling reaction, has attracted attention [43, 44]. The catalytic cycle involves the oxidative addition of aryl halides, followed by the coordination and deprotonation of the amine. The use of bases such as sodium *tert*-butoxide is effective for the deprotonation of the reacting amine. Finally, the reductive elimination of the *N*-aryl product occurs (Scheme 1.9). The aryl amination reaction relies on the design of the catalyst systems, particularly the choice of a ligand, to prevent a side reaction through β-hydrogen elimination.

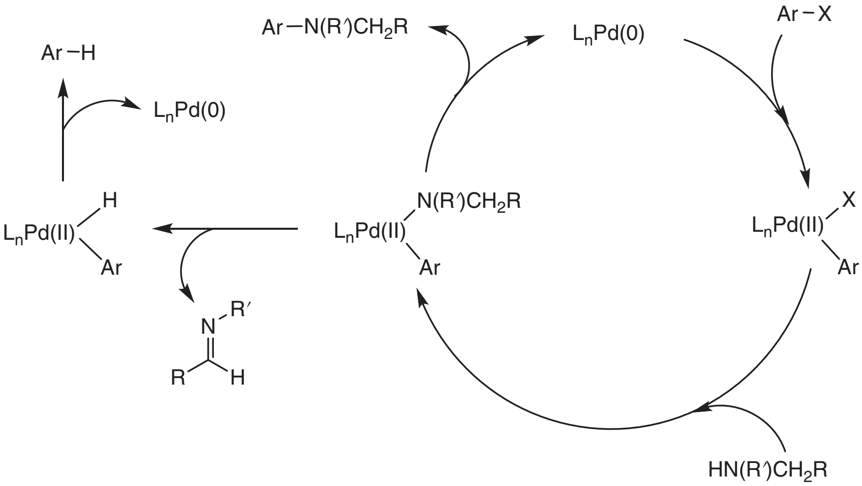
The Buchwald–Hartwig aryl amination reaction is an effective tool for the synthesis of polyaniline analogs and poly(triarylamine)s, which are difficult to prepare via conventional oxidative polymerization (Scheme 1.10) [45]. It is essential to select a suitable ligand for the desired polymer structure. While 2-(di-*tert*-butylphosphino) biphenyl or 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos) is a suitable ligand for the synthesis of polyaniline analogs bearing a secondary amine unit (Scheme 1.10a–c) [46–48], tri-*tert*-butylphosphine $\left(P^{t}Bu_3\right)$ is one of the optimal ligands for the synthesis of poly(triarylamine)s (Scheme 1.10d, e) [49–52]. Analogous Ni-catalyzed aryl aminations are also compatible with polycondensation [53].

1.4 Pd-catalyzed Polycondensation via C—H Bond Functionalization

As mentioned above, various π-conjugated polymers have been synthesized by metal-catalyzed cross-coupling reactions. Recently, direct arylation reactions using the C—H bonds of aromatic compounds as the reaction points have attracted

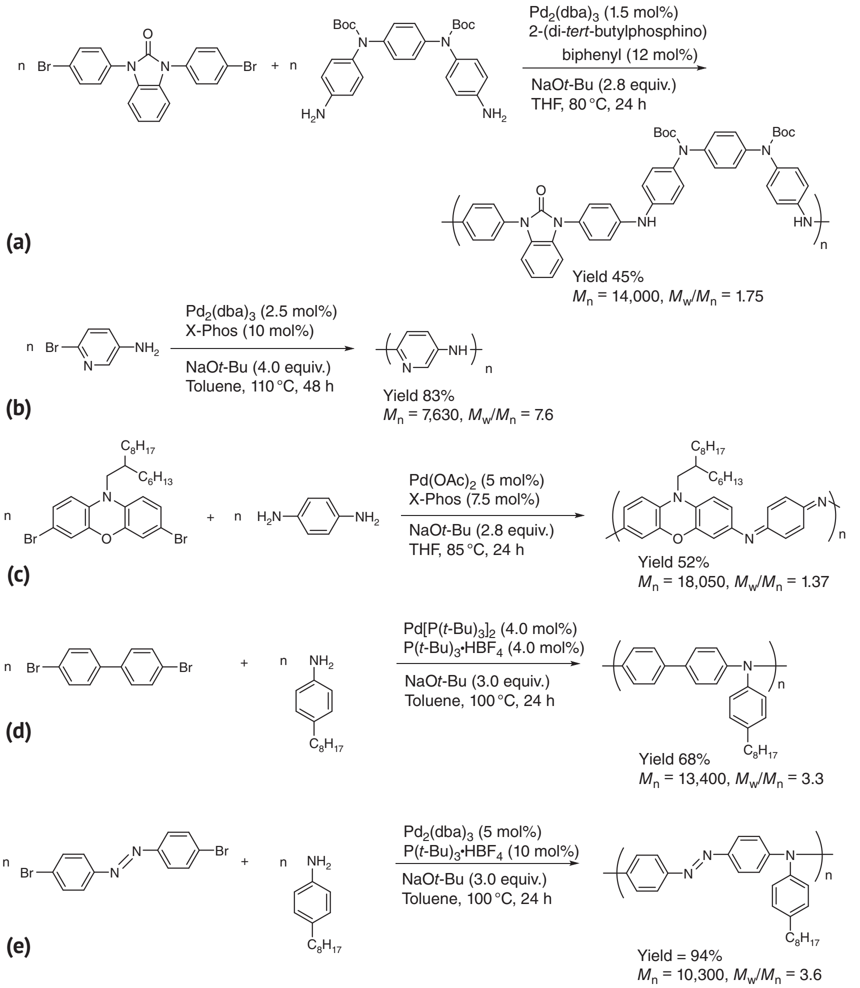


Scheme 1.8 (a) Reaction mechanism of the Mizoroki–Heck coupling reaction. Ar^1 and Ar^2 denote aromatic units and X denotes halogen or pseudo-halogen. (b) Synthesis of PAVs via the Mizoroki–Heck coupling reaction.

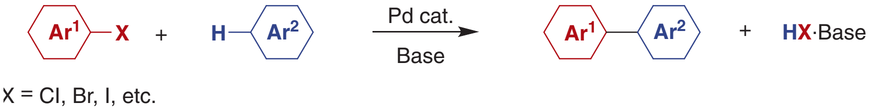


Scheme 1.9 Reaction mechanism of the Buchwald–Hartwig aryl amination reaction. Ar denotes aromatic units, R and R′ denote alkyl or aryl groups, and X represents halogen or pseudo-halogen.

attention as alternatives to conventional cross-coupling reactions (Scheme 1.11) [54–56]. This reaction does not require the introduction of an organometallic moiety into the reactant, thus reducing the number of synthetic steps. Furthermore, while cross-coupling reactions produce metal-containing by-products, the formal



Scheme 1.10 Pd-catalyzed polycondensation via the Buchwald–Hartwig aryl amination reaction. Synthesis of (a–c) polyaniline analogs and (d, e) poly(triarylamine)s.



Scheme 1.11 General scheme of a Pd-catalyzed direct arylation reaction. Ar^1 and Ar^2 denote aromatic units, and X represents halogen or pseudo-halogen.

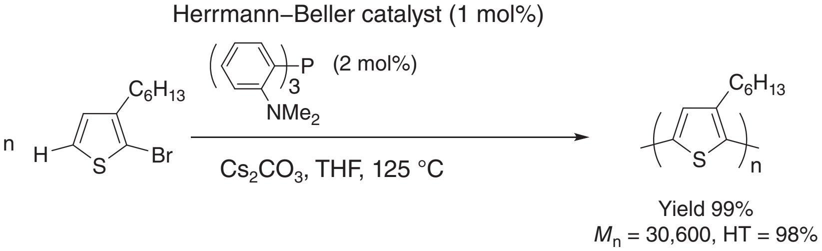
by-product of the direct arylation reaction is hydrogen halides (HX), which reduces the environmental impact. Owing to these advantages, polycondensation reactions involving direct arylation have been actively developed in recent years [57–61].

Lemaire et al. reported the first direct arylation polycondensation of 2-bromo-3-octylthiophene for the synthesis of poly(3-octylthiophene) [62, 63]. Although these studies pioneered a novel synthetic methodology, the regioregularities and molecular weights of the resulting polymers were inferior to those prepared by conventional cross-coupling polycondensation. In 2010, Ozawa et al. reported the successful synthesis of high-molecular-weight poly(3-hexylthiophene) with high regioregularity from 2-bromo-3-hexylthiophene, using their original catalytic system (Scheme 1.12) [64].

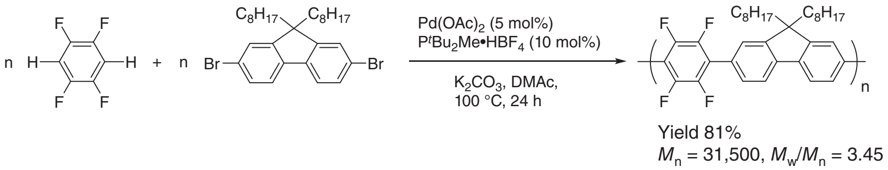
Subsequently, the direct arylation polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene afforded the corresponding polymer with a high molecular weight in good yield (Scheme 1.13) [65]. This molecular weight is higher than that prepared by conventional polycondensation using the Suzuki–Miyaura coupling [66]. The polymer exhibited efficacy as a hole-blocking material in organic light-emitting diodes, which can be attributed to the low HOMO energy levels resulting from the presence of multiple F substituents [67].

Scheme 1.14 shows the general reaction mechanism for the direct arylation [68]. As in conventional cross-coupling reactions, direct arylation is initiated by the oxidative addition across the carbon–halogen bond. Subsequently, ligand exchange occurs between the halogen and carboxylate, which is generated by the reaction of a carboxylic acid additive with a base. The carboxylato-Pd complex undergoes C—H bond cleavage with the assistance of the carboxylato ligand and Pd—C bond formation in a concerted manner. This process is referred as the concerted metallation–deprotonation (CMD) pathway [69]. The reductive elimination of the biaryl complex results in the formation of the product and the regeneration of the active Pd catalyst. Carboxylic acid additives are important for direct arylation because they affect the transition state of CMD.

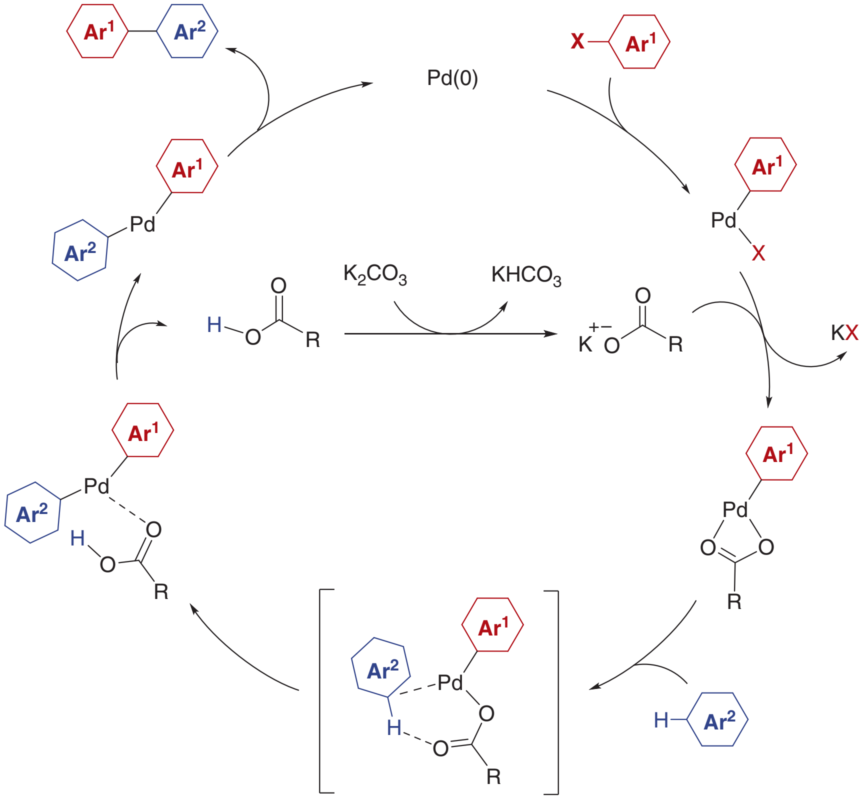
The effects of carboxylic acid additives were investigated in a model reaction using 3,4-ethylenedioxythiophene (EDOT) as the C—H monomer (Scheme 1.15) [70]. Weak carboxylic acids with bulky substituents, such as 1-adamantanecarboxylic acid (1-AdCOOH) and pivalic acid, are effective additives because of the high molecular weight of the resultant polymers and high yield. Weak acidity is advantageous because a weak acid acts as a strong conjugate base in the coordination sphere of the transition state of the CDM pathway. In addition, bulkiness might prevent the aggregation of the Pd catalyst, which facilitates the reaction [71]. Owing to the high efficiency of the catalytic system with 1-AdCOOH, only 1 mol% of $Pd(OAc)_2$ was



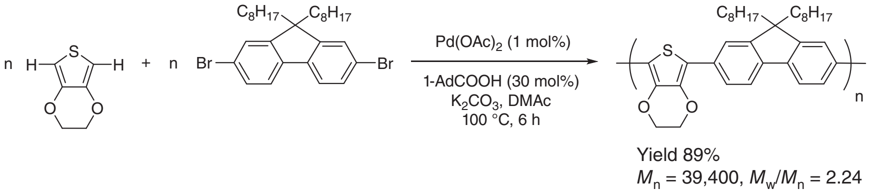
Scheme 1.12 Synthesis of poly(3-hexylthiophene) by direct arylation polycondensation.



Scheme 1.13 Direct arylation polycondensation of tetrafluorobenzene.



Scheme 1.14 Reaction mechanism of a Pd-catalyzed direct arylation reaction. Ar^1 and Ar^2 denote aromatic units, R denotes an alkyl group, and X represents halogen or pseudo-halogen.



Scheme 1.15 Direct arylation polycondensation of EDOT.

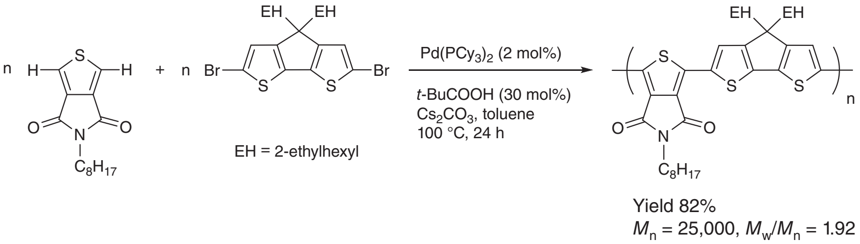
required to afford a high-molecular-weight polymer in good yield (Scheme 1.15) [70]. The advantages of using bulky carboxylic acids, such as neodecanoic acid, have also been reported [72, 73]. Direct arylation polycondensation of thiophene monomers bearing electron-donating substituents is generally conducted in polar solvents such as *N*,*N*-dimethylacetamide (DMAc) [74–76].

Scheme 1.16 shows the direct arylation polycondensation reaction for the synthesis of a donor–acceptor-type conjugated polymer suitable for organic photovoltaic applications [77]. The optimal reaction conditions for the direct arylation of acceptor monomers bearing electron-withdrawing substituents are different from those for donor monomers such as EDOT, as shown in Scheme 1.15 [78]. For acceptor monomers, the combination of a phosphine ligand (PCy_3) and low-polarity solvent (toluene) is effective for obtaining the targeted polymer.

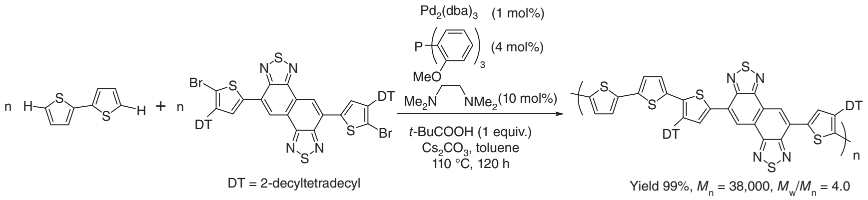
The catalytic system with the phosphine and nitrogen ligands demonstrated high selectivity and yielded polymers without structural defects (Scheme 1.17) [79]. In direct arylation reactions, there are potential concerns regarding side reactions involving C—H bonds at undesired positions and C—H/C—H and C—Br/C—Br homo-coupling reactions. The mixed-ligand approach minimizes these side reactions and prevents the formation of branching, crosslinking, and homo-coupling defects, even in difficult-to-control monomers, such as unsubstituted bithiophene [80]. The obtained polymers could serve as high-performance materials for organic photovoltaics.

Polycondensation using the C—H/C—H homo-coupling reaction is a facile method for synthesizing homopolymers because there is no need for reactive functional groups such as halogens and metal moieties. This method is referred to as oxidative direct arylation polymerization [81]. Scheme 1.18 shows the oxidative direct arylation polymerization of thiazole-based monomers using a Pd catalyst and metal oxidants such as $Cu(OAc)_2$ [82, 83]. Further investigations have led to the development of an environmentally friendly oxidative direct arylation polymerization method that does not utilize a metal oxidant and employs oxygen as the oxidant [84].

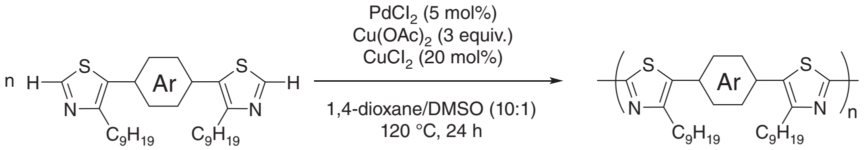
Polycondensation reactions using cross-dehydrogenative coupling (C—H/C—H cross-coupling) allow the synthesis of polymers that link two monomers in a short synthetic process [85–87]. However, to achieve this, it is necessary to suppress undesired homo-coupling reactions because both reaction points are C—H bonds [88].



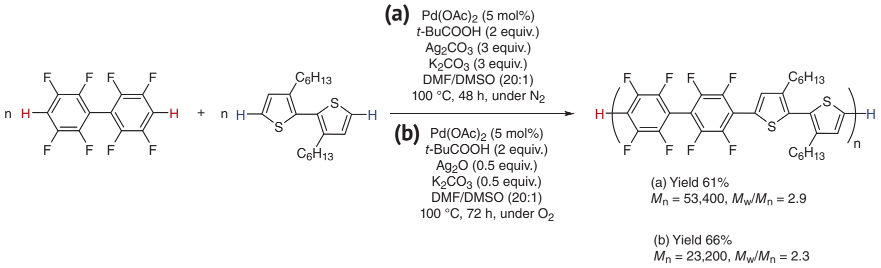
Scheme 1.16 Direct arylation polycondensation of an electron-deficient thiophene derivative.



Scheme 1.17 Synthesis of a defect-free conjugated polymer by direct arylation polycondensation.



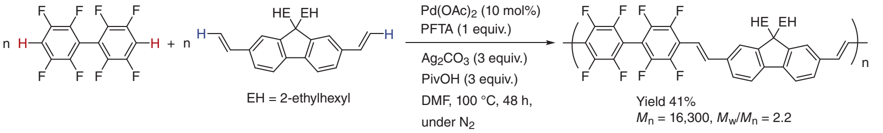
Scheme 1.18 Oxidative direct arylation polycondensation.



Scheme 1.19 Cross-dehydrogenative-coupling polycondensation.

Scheme 1.19 shows cross-dehydrogenative-coupling polycondensation of 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl with 3,3′-dihexyl-2,2′-bithiophene [89]. The resultant polymer had a highly alternating structure with only minor homo-coupling defects (approximately 4%). Silver salts are responsible for cleaving the C—H bonds of octafluorobiphenyl, in addition to acting as oxidants. The combined action of the Pd catalyst and the Ag salt prevents homo-coupling [90, 91]. The reaction also proceeded in air, and the use of O_2 as a terminal oxidant resulted in a lower Ag oxidant loading (Scheme 1.18) [89]. Reports on the associated direct sp^2 C—H coupling polycondensation of thiophene derivatives have also been published [92–96].

The dehydrogenative alkenylation of arenes, known as direct alkenylation, is applicable to the synthesis of PAVs (Scheme 1.20) [97–99]. This protocol is a promising alternative to the Mizoroki–Heck-type polycondensation, allowing straightforward access to PAVs without bromo groups in the monomers [40, 100]. The Pd-catalyzed direct alkenylation polycondensation afforded the corresponding PAV in a *trans* configuration (Scheme 1.20) [101]. The polymer contained only 3% homo-coupling defects. The obtained polymer was used as the emitting material in an OLED device.



Scheme 1.20 Direct alkenylation polycondensation.

In addition, the direct alkenylation polymerization of diketopyrrolopyrrole monomers [102] and polymerization using directing groups have also been reported [103].

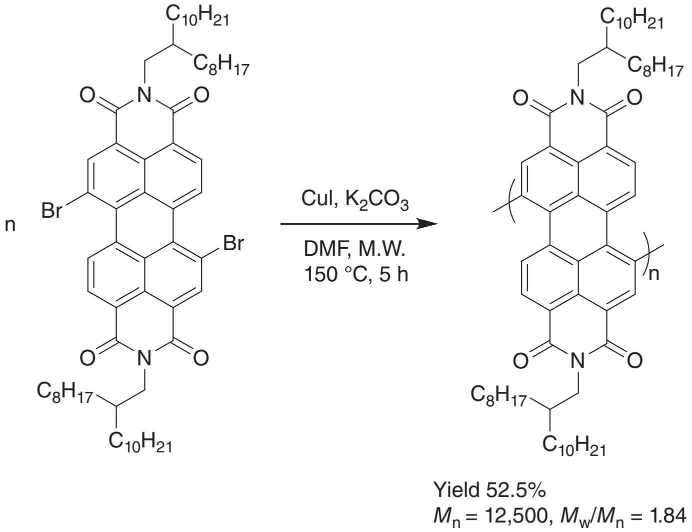
1.5 Cu- and Fe-catalyzed Polycondensation

Because Cu is an earth-abundant metal with lower toxicity than Pd and Ni, there has been increased interest in Cu-catalyzed homo- and cross-coupling reactions. The classical Ullmann coupling reactions involve the synthesis of symmetric biaryl compounds. While the traditional Ullmann coupling reaction has some drawbacks, including the necessity of high temperatures and large amounts of Cu, the use of appropriate ligands can modulate the reactivity and achieve an effective and versatile catalytic system [104–107]. Microwave-assisted Ullmann homo-coupling reaction has been applied to the synthesis of acceptor-type π-conjugated polymers (Scheme 1.21) [108].

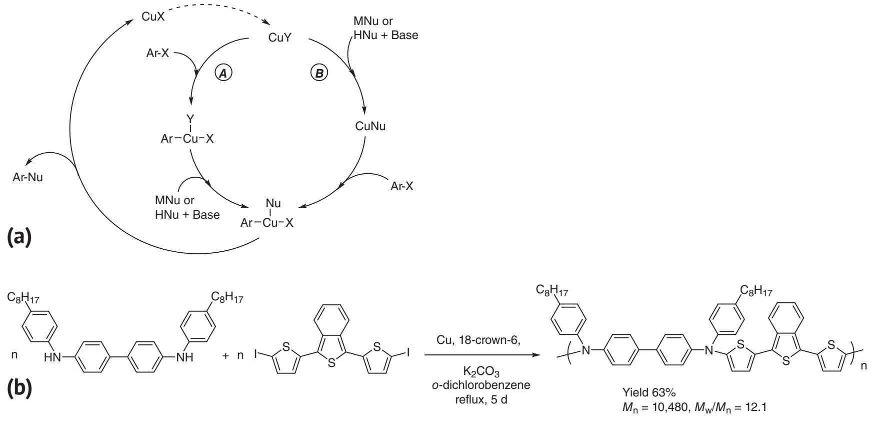
The Ullmann-type cross-coupling reactions involve nucleophilic aromatic substitutions of aryl halides with various nucleophiles, such as amines. Cu can participate in cross-coupling reactions in a manner similar to that of Pd. An important difference with respect to Cu is the easy accessibility of the four oxidation states (0 to +3) of the metal; the cross-coupling catalytic cycle with Cu is most likely serviced by the +1/+3 oxidation states (Scheme 1.22a). The Cu-catalyzed aryl amination reaction can also be used to prepare poly(triarylamine)s containing light-harvesting dyes with low bandgaps (Scheme 1.22b) [109, 110].

It has been reported that CuI/PPh$_3$ or phenanthroline-based catalysts promote the direct arylation of heteroaromatic compounds with aryl halides [111, 112]. Cu-catalyzed direct arylation polycondensation has also been reported by Thompson et al. (Scheme 1.23a) [113]. While the Cu catalyst does not show high reactivity and broad availability compared with those of the Pd catalyst at present, the use of CuBr(phen)(PPh$_3$) as a precatalyst could overcome these issues (Scheme 1.23b) [114]. Furthermore, Cu-catalyzed direct arylation achieved C—H bond activation at the 2-position in thiazole-based monomers (Scheme 1.23c). This is in contrast to Pd-catalyzed direct arylation, in which the C—H bond at the 5-position of the thiazole moiety is highly reactive [115, 116]. The site selectivity could apply to the unique molecular design of π-conjugated polymers.

The 2-position of the thiazole moiety is also highly reactive in Cu-catalyzed aerobic oxidative C—H/C—H homo-coupling reactions [117]. Cu-catalyzed aerobic oxidative homo-coupling polycondensation affords thiazole- and benzodiimidazole based π-conjugated polymers (Scheme 1.24) [118, 119]. The synthetic method is a



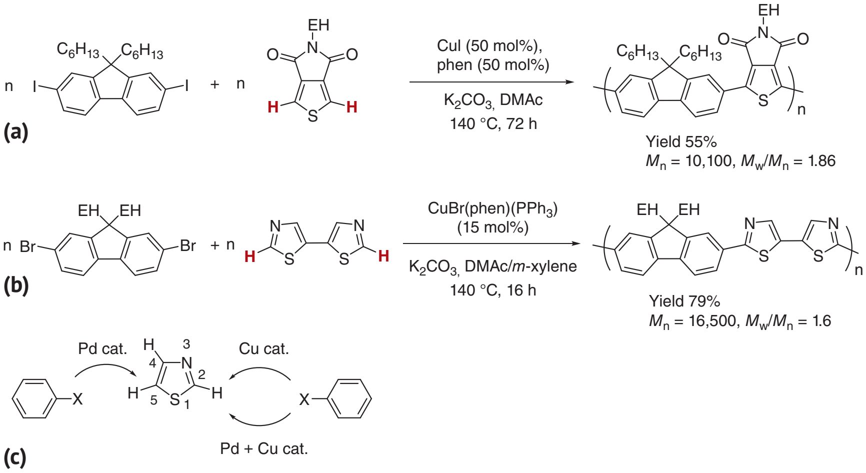
Scheme 1.21 Ullmann homo-coupling polycondensation.



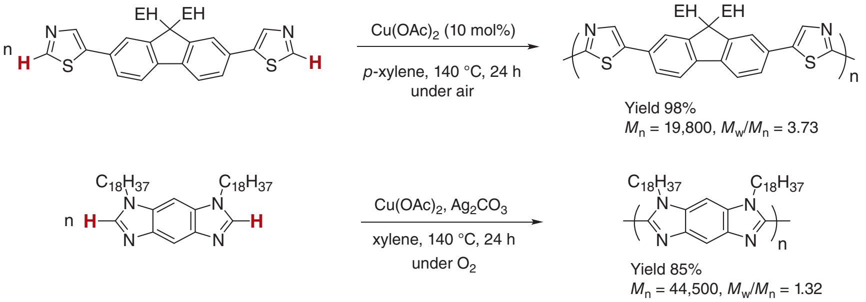
Scheme 1.22 (a) Reaction mechanism of the Ullmann-type cross-coupling reaction. Ar denotes aromatic unit, Nu denotes nucleophilic species, and X and Y represent halogen or pseudo-halogen. (b) Synthesis of poly(triarylamine) by the Ullmann-type cross-coupling polycondensation.

low-cost and environmentally friendly process because of the naturally abundant feedstock of dioxygen and harmless by-products, such as water.

Iron is the best alternative to precious metals as an earth-abundant catalyst. Nakamura et al. demonstrated the Fe-catalyzed regioselective C—H/C—H homo-coupling polycondensation of thiophene derivatives (Scheme 1.25a) [120]. The use of conjugated tridentate phosphine as a ligand suppresses catalyst deactivation, whereas diethyl oxalate, used together with $AlMe_3$, acts as a two-electron acceptor in C—H activation. The polycondensation reaction proceeds under



Scheme 1.23 Cu-catalyzed direct arylation polycondensation of (a) thieno[3,4-c]-pyrrole-4,6-dione and (b) 5,5′-bithiazole. (c) Selective direct arylation on thiazole unit.

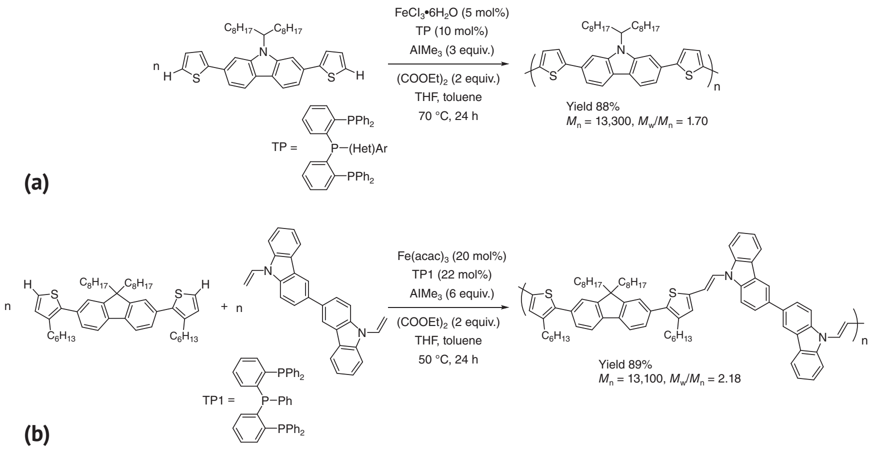


Scheme 1.24 Cu-catalyzed aerobic oxidative homo-coupling polycondensation.

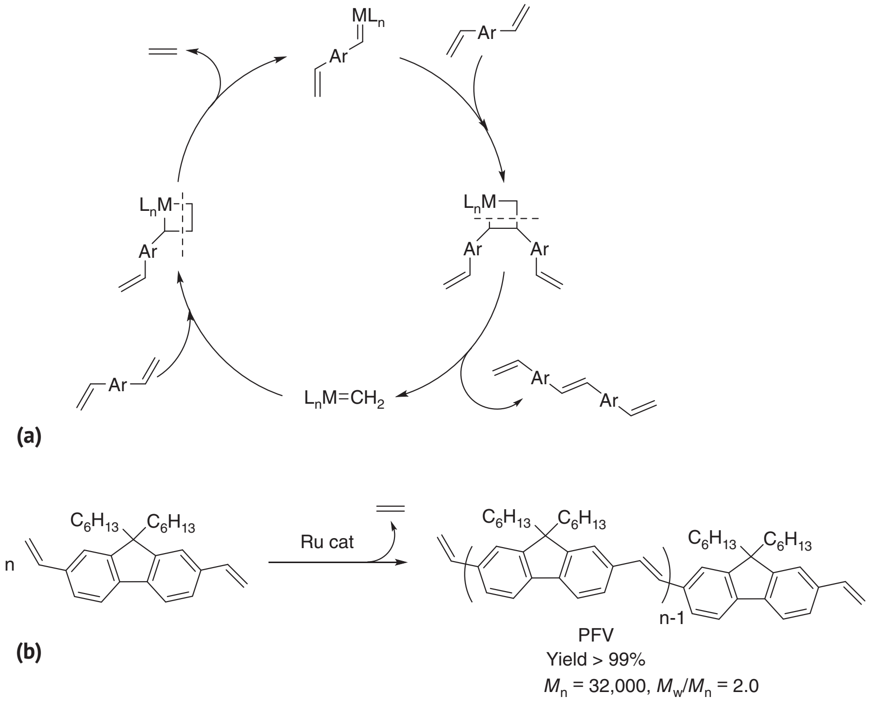
mild conditions and affords a variety of thiophene-based π-conjugated polymers bearing electron-donative π motifs. The cooperative catalytic systems using two earth-abundant metals, Fe and Al, are also compatible with C—H/C—H cross-coupling reaction between thiophenes and enamines and its application to polycondensation of bisenamine and bisthiophene derivatives (Scheme 1.25b) [121].

1.6 Other Transition Metal-catalyzed Polymerization

The acyclic diene metathesis (ADMET) polycondensation of divinyl aromatic monomers is another promising synthetic method for PAVs [122–125]. The catalytic cycle begins with the metathesis of the terminal olefin of a divinyl monomer using a metal alkylidene catalyst. The newly formed metal alkylidene species then undergoes metathesis with another terminal olefin of the monomer to recover the metal methylidene species and produce an internal olefin (Scheme 1.26a). Because ADMET is an equilibrium reaction, the removal of ethylene by-products from the reaction



Scheme 1.25 Fe-catalyzed dehydrogenative (a) homo-coupling and (b) cross-coupling polycondensation.



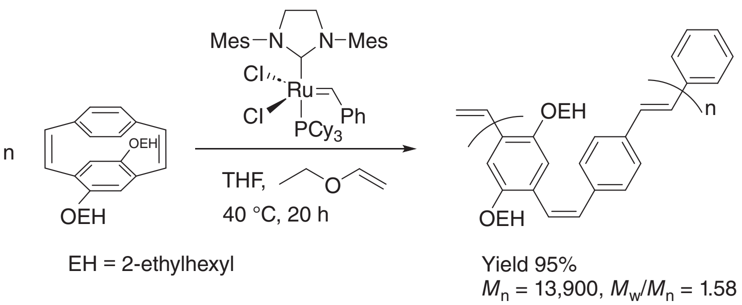
Scheme 1.26 (a) Reaction mechanism of an acyclic diene metathesis (ADMET) polycondensation. Ar denotes aromatic unit. (b) Ru-catalyzed ADMET polycondensation.

medium is a prerequisite for obtaining PAVs with high molecular weights. ADMET polycondensation of 2,7-divinyl-9,9-dialkylfluorenes by Ru-carbene catalysts provides all-*trans* poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) with a high molecular weight, defect-free, and well-defined chain ends (Scheme 1.26b) [122, 125].

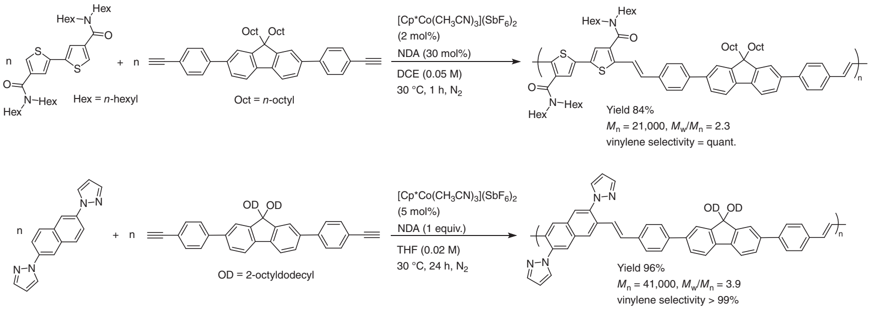
PPV derivatives have also been prepared by the ring-opening metathesis polymerization (ROMP) of strained cyclophanedienes initiated by Ru-carbene catalysts (the second-generation Grubbs catalyst) (Scheme 1.27) [126]. Once the cyclophanediene has been consumed completely, the polymer chain end is still active, and the addition of further cyclophanediene gives block copolymers. This protocol was also applicable to the synthesis of block copolymers of PAVs consisting of donor–acceptor fractions [127].

Polyaddition via the hydroarylation of aromatic diynes with arenes is a promising alternative synthetic methodology for PAVs because the production of by-products from monomers can be eliminated. The synthesis of PAVs via the Rh-catalyzed hydroarylation of internal diynes has been reported [128], whereas the Cp*Co(III)-catalyzed hydroarylation polyaddition of aromatic terminal diynes to arenes bearing directing groups provides the corresponding PAVs under mild reaction conditions (Scheme 1.28) [129–132]. The protocol includes an *ortho*-metalation process, which facilitates site-selective reaction. However, the reaction sometimes produces a 1,1-vinylidene unit from a side reaction during the migratory insertion of the alkyne unit into the Co catalyst, which lowers the regioselectivity of PAVs. The presence of 1,1-vinylidene unit serves as a defect in π-conjugated polymer materials that decreases the semiconducting device performance [129]. This difficulty has been overcome by designing targeted aromatic monomers bearing appropriate directing groups, resulting in site-specific and regioselective polymerization. The synthesized PAVs serve as emitting materials and p-type semiconductors for organic optoelectronic devices [131, 132]. Mn-catalyzed hydroarylation is compatible with the polyaddition protocol, affording pyrrole-based PAVs with quantitative site- and regioselectivity [133].

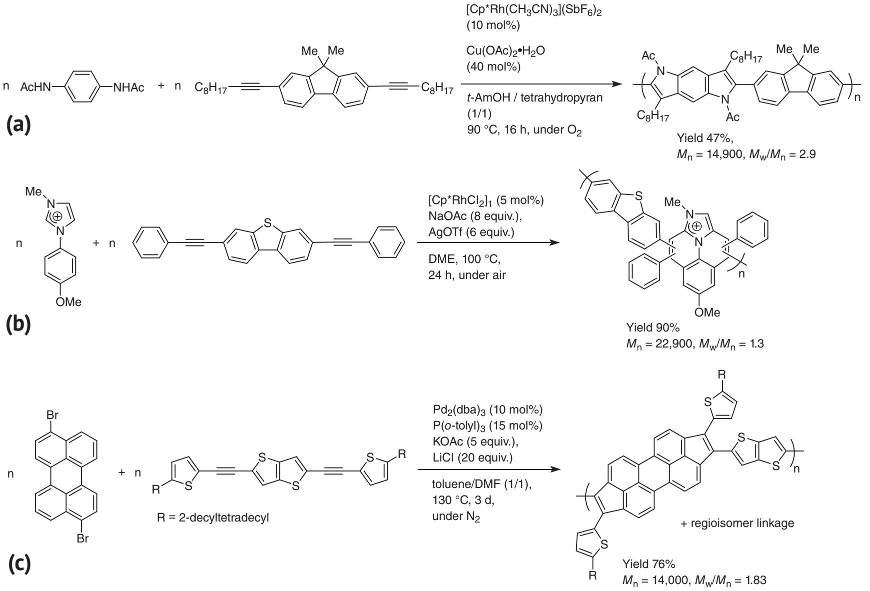
Transition metal-catalyzed C—H bond activation followed by alkyne insertion is a useful method for the synthesis of fused aromatic rings. Rh-catalyzed C—H bond cleavage of the acetanilide and alkyne insertion forms indoles [134]. The annulation reaction applied to polycondensation of 1,4-bis(acetylamino)benzene and various diynes, affording π-conjugated polymers containing benzodipyrrole moieties with high regioselectivity (Scheme 1.29a) [135]. Oxidative Rh-catalyzed successive C—H activation–annulation reactions of 1-phenylimidazole with alkynes were also applicable to polycondensation, affording main chain-charged conjugated



Scheme 1.27 Ru-catalyzed ring-opening metathesis polymerization.



Scheme 1.28 Co-catalyzed hydroarylation polyaddition.



Scheme 1.29 Successive C—H activation–annulation polycondensation of (a) 1,4-bis(acetylamino)benzene, (b) 1-phenyl-imidazolium compound, and (c) 3,9-dibromoperylene with aromatic diynes.

polyelectrolytes consisting of cationic ring-fused heteroaromatic structures (Scheme 1.29b) [136, 137]. Although the regioregularity of polyelectrolytes has not been controlled, they form multicolored fluorescent microfibers for biomedical applications. Polycondensation via the Pd-catalyzed cyclopenta-annulation of brominated polycyclic aromatic hydrocarbons with alkynes has also been reported (Scheme 1.29c) [138, 139]. The reaction involves oxidative addition of C—Br bond, followed by alkyne insertion into the Pd—C bond and C—H activation of the adjacent C—H bond, and reductive elimination forms π-extensive annulated products.

1.7 Summary

Transition metal-catalyzed homo- and cross-coupling reactions are essential tools for the synthesis of varied π-conjugated polymers using diverse monomer materials. To produce high-performance organic optoelectronic materials, the synthesized π-conjugated polymers must have a high molecular weight, defect-free structure, and high purity [16, 140]. Thus, polymerization reactions should proceed efficiently without side reactions because regioirregular structures in the polymer chain cannot be removed from the polymer backbone, even in the purification step. Therefore, appropriate monomer choices and detailed optimization of the reaction conditions are vital. Conversely, the chemical structures of state-of-the-art π-conjugated polymer materials tend to be too complex to meet the requirements for qualifying as materials for organic optoelectronic devices. Complex structures bearing multi-component units require numerous synthesis steps. The synthetic routes of monomers have to be more sophisticated in terms of a reaction step because a successful practical application of π-conjugated polymers will depend on the overall synthetic route [141–145]. Polymerization through direct C—H bond functionalization should contribute to the practical use of π-conjugated polymer materials. In addition, catalysts that enable highly efficient and new coupling reactions with less environmental impact should be developed and polymerization protocols must be updated to incorporate them.

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