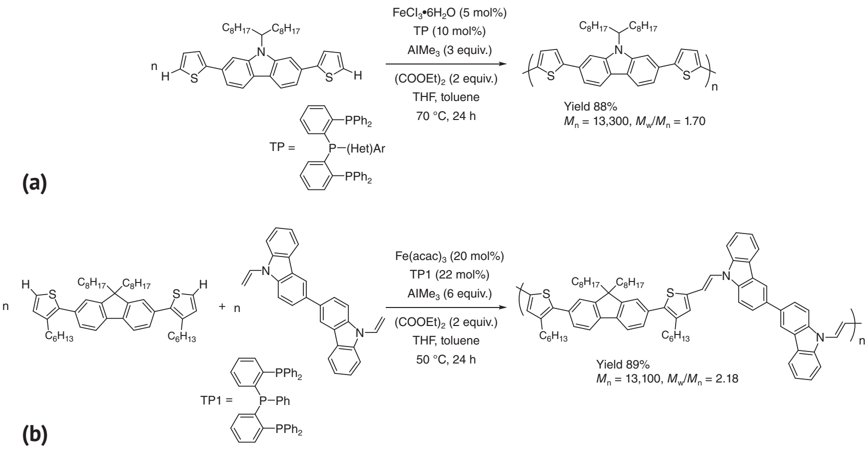
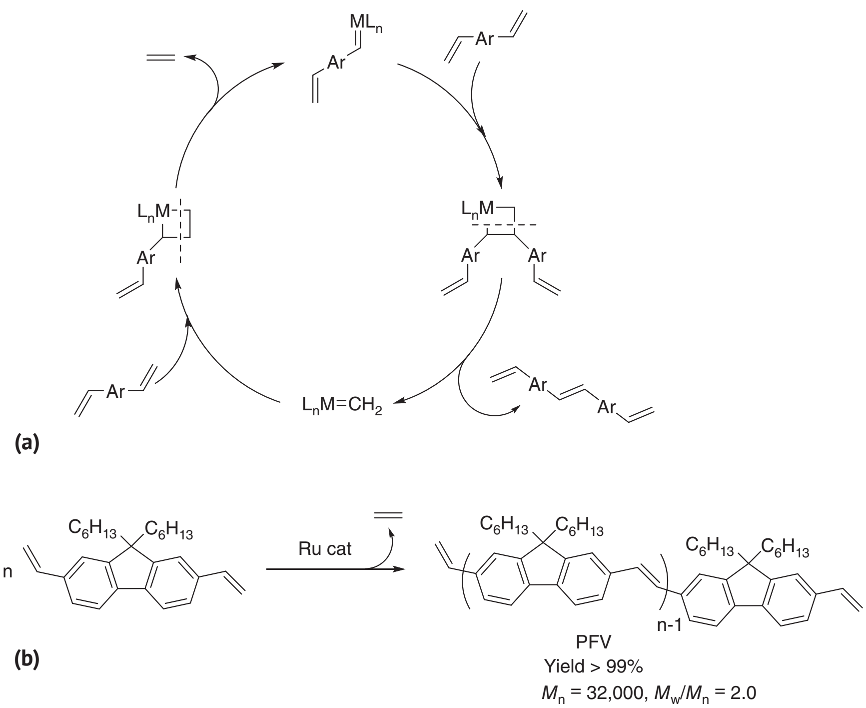


Scheme 1.25 Fe-catalyzed dehydrogenative (a) homo-coupling and (b) cross-coupling polycondensation.



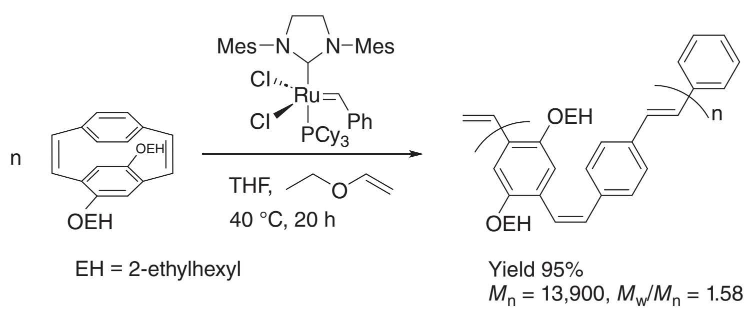
Scheme 1.26 (a) Reaction mechanism of an acyclic diene metathesis (ADMET) polycondensation. Ar denotes aromatic unit. (b) Ru-catalyzed ADMET polycondensation.

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].

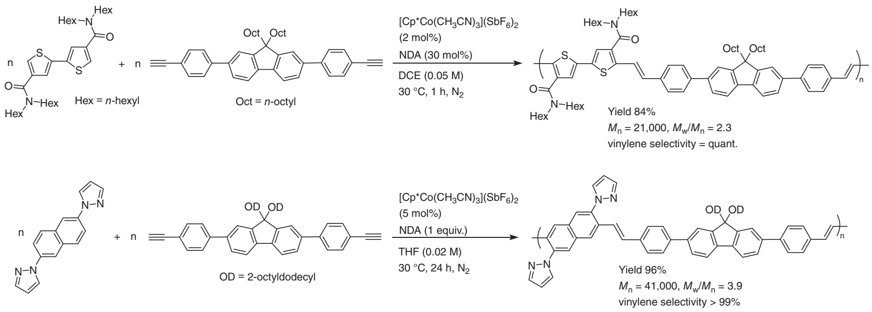
PPV derivatives have also been prepared by the ring-opening metathesis polymerization (ROMP) of strained cyclophanedienes initiated by Ru-carbene catalysts (the second-generation Grubbs catalyst) (Scheme 1.27) [126]. Once the cyclophanediene has been consumed completely, the polymer chain end is still 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].

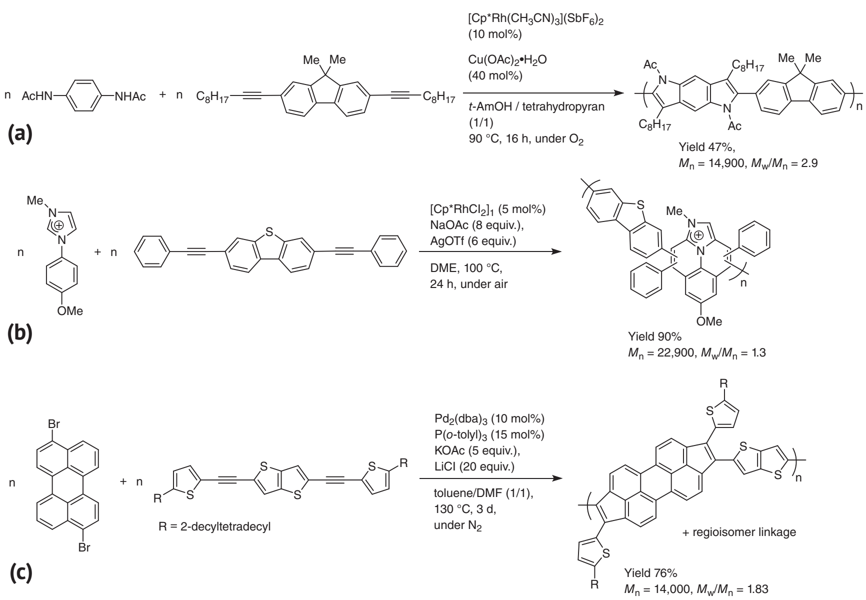
Transition metal-catalyzed C—H bond activation followed by alkyne insertion is a useful method for the synthesis of fused aromatic rings. Rh-catalyzed C—H bond cleavage of the acetanilide and alkyne insertion forms indoles [134]. The annulation reaction applied to polycondensation of 1,4-bis(acetylamino)benzene 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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