Review

Recent Advances in the Synthesis of Substituted Polyacetylenes

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Abstract: Recent developments in the synthesis of substituted polyacetylenes have considerably benefitted from advancements in organometallic catalysis; however, most important developments rely on the advent of Rh-catalyzed living polymerizations. The latter not only allow the tailoring of well-defined degrees of polymerization with low and narrow polydispersity but also enable access to stereochemical well-defined *cis*-transoidal polymers with a helical structure. These novel polymers open new avenues for application in photonics and electronics. Rh-catalyzed living polymerizations are mild and concise metal-catalyzed polymer syntheses that not only allow for the decoration of sidechains with multiple functionalities, including chiral units, but also enable enantioselective induction of helical chirality, memory of chirality, well-defined copolymerization, and end-group functionalization at both termini. This review summarizes recent developments in metal-catalyzed syntheses of substituted polyacetylenes, with a special focus on Rh-catalyzed living polymerizations.

Keywords: conducting polymers; functional π-systems; polyacetylenes; Rh-catalyzed living polymerization; transition metal catalysis

1. Introduction

Conductive organic polymers have represented a significant paradigm shift because organic materials and, in particular, polymers have long been considered to be insulating materials. Less than fifty years ago, electrically semiconducting and conducting polymers began their remarkable rise, becoming essential components of organic electronics with significant technical potential [1–3]. Their applications are multifold, spanning electroluminescence in organic light-emitting diodes (OLEDs) for converting electricity into light [4,5], to photoconductors [6] and organic solar cells (OSCs) for converting sunlight into electricity [7,8]. Consequently, numerous updates on the synthesis, characterization, properties, and applications of electrically conductive organic polymers have been published over time [9–11].

From a structural point of view, (semi)conducting organic polymers are widely extended π-electron systems, and first materials, such as aniline black, date back to the early days of organic chemistry in the first half of the 19th century. Many other polycondensates were prepared thereafter; however, without knowledge of their unusual conductivity potential [12–14]. It was not until Shirakawa, Heeger, and MacDiarmid in the 1970s achieved a breakthrough by synthesizing and characterizing an electrically conductive "doped" polyacetylene film [15,16]. In 2000, the three pioneers were awarded the Nobel Prize in Chemistry for their success in synthesizing the first stable organic polymer with a specific electrical conductivity similar to that of metals—electrically conductive polyacetylene [17].

This discovery opened up a whole new world of "plastic electronics" and conjugated polymers, such as polyacetylene (PA), poly-*p*-phenylene (PPP), polypyrrole, polythiophene, and many others, were suddenly seen in a whole new light as (semi)conductive organic materials (Figure 1).
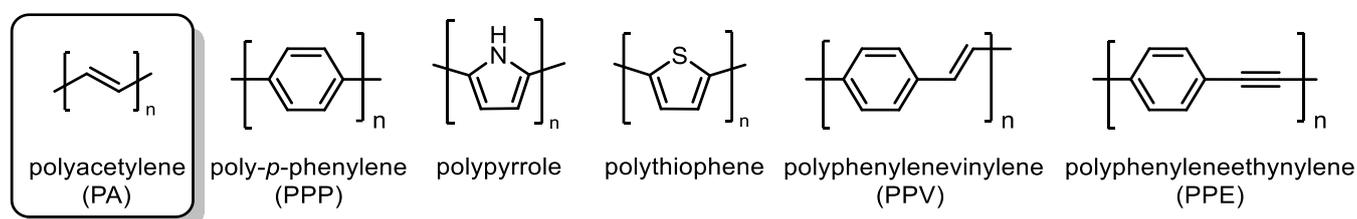
Figure 1. Selected conjugated polymers.

From the perspective of basic research, PA is an excellent model for one-dimensional conductors with considerable potential for the discovery of novel electronic materials, including magneto-optical properties [18]. With the disclosure of new PA syntheses, such as metathesis-based processes [19–21], increasingly substituted PAs have become available [22]. These materials differ significantly from traditional unsubstituted PAs in terms of conjugation, synthesis, architectural diversity, and functionality. These materials can show high gas permeability, improved mechanical properties (e.g., softness and ductility), thermal stability, helicity, photoelectronic functionalities, and nonlinear optical and magnetic properties. In particular, the Rh-catalyzed polymerization of substituted acetylenes has opened new avenues to network-type conjugated PAs [23] and helical PAs with circular polarized luminescence (CPL) [24] for potential application in displays, biomedical diagnostics, and sensorics [25]. In addition, helical PAs can be employed for transformation into helical graphite [26]. PAs functionalized with electron-donating substituents have been shown to exhibit hole-conducting properties, rendering them potential organic photoconductors in xerography [27–29]. Finally, due to their rigidity, disubstituted PAs form micropores, which are suitable for gas and liquid separation and the highest permeability has been observed in poly[1-(trimethylsilyl)-1-propyne] (PTMSP) [30,31]. Therefore, this overview summarizes recent developments in the synthesis of substituted PAs by catalytic methods.

2. Structural Aspects of Substituted Polyacetylenes and Mechanistic Scenarios of Polymerization

Despite the described metallic character of doped unsubstituted PA, its potential industrial use is limited due to its inherent instability against oxidation and hydrolysis, as well as its poor solubility [12]. The processability can be significantly improved by the targeted functionalization of PAs with solubility-enhancing and electron-rich substituents [32,33]. Substituted PAs can be prepared through the polymerization of mono- or disubstituted acetylenes. As with unsubstituted PAs, transition metal complexes are suitable catalysts for polymerization. For successful polymerization, the catalyst system must exhibit high oxidation stability and tolerance towards various functional groups, considering stereoelectronic effects [34]. Furthermore, the catalyst influences important parameters, such as the degree of polymerization, polydispersity, and stereoregularity of the substituted PA [35]. In principle, PA adopts *trans*- or *cis*-configurations of the double bonds, including transoidal and cisoidal conformations, with respect to the orientation of the substituents within the polyene backbone (Figure 2).
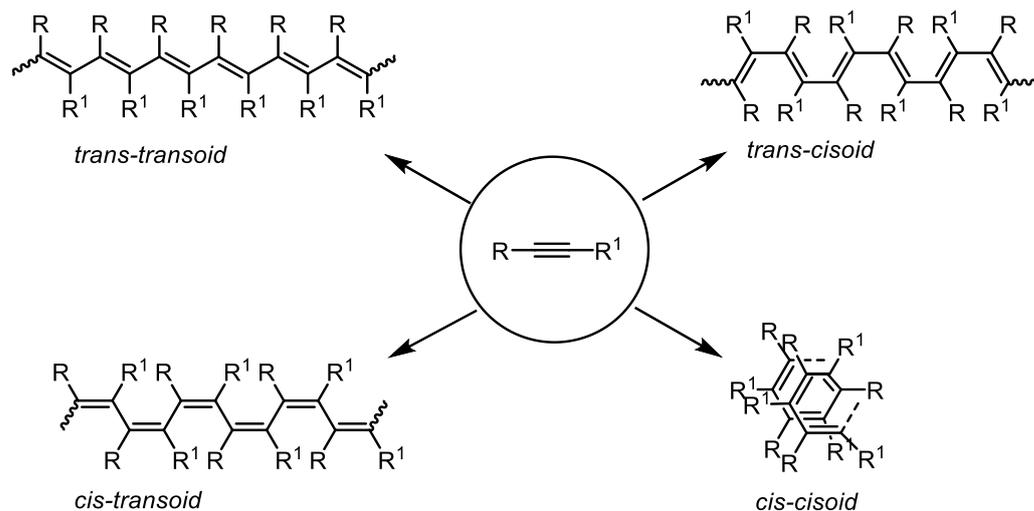
Figure 2. Possible configurational conformers of substituted PAs [32].

Although the isomers can undergo thermal or photochemical isomerization, the stereoregular preparation of both isomers is possible using the correct catalyst system [36,37]. Polymerization can proceed through two mechanistic scenarios. According to the metathesis mechanism, the formation of *trans*-PAs occurs, whereas *cis*-PAs are accessible via the 2,1-insertion mechanism (Scheme 1). Both mechanisms have been elucidated in detail through ^{1}H NMR and IR experiments [35]. The insertion mechanism can be described in analogy to Ziegler–Natta polymerization (Scheme 1, top) [38]. Initially, the PA coordinates with the metal. Subsequently, the alkyne inserts into the metal–carbon bond in a *cis*-fashion. The free coordination site on the metal allows this step to be repeated multiple times, constructing the *cis*-polyene backbone. The metathesis mechanism was first described by Chauvin for olefin metathesis and later extended to acetylene polymerization through the experimental findings of Masuda and Katz (Scheme 1, bottom) [39–41]. Initially, the alkyne coordinates side-on to the metal carbenoid. A [2+2]-cycloaddition forms a metallacyclobutene intermediate, which then opens via a [2+2]-cycloreversion. The resulting metal carbenoid allows the continuous insertion of additional monomer units.

Insertion pathway
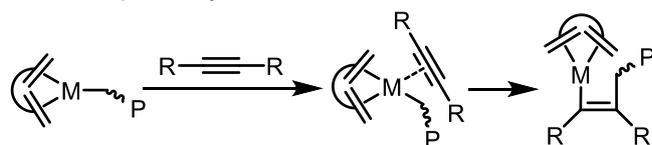
Metathesis pathway
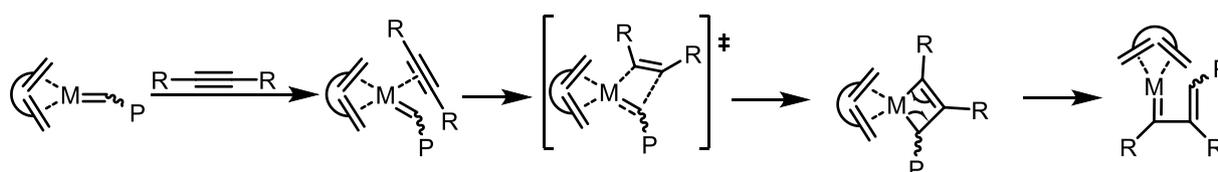
Scheme 1. Schematic representation of the two possible mechanistic scenarios of metal-catalyzed acetylene polymerization: insertion (**top**) and metathesis (**bottom**) pathways [35].

Additionally, PAs can be obtained from precursors in the form of cyclic olefins or macromolecules [42]. Substituted PAs are accessible via the ring-opening metathesis polymerization (ROMP) of cyclooctatetraenes [43,44]. Alternatively, PAs can also be prepared

through the post-polymerization modification of polyvinyl chloride (PVC) via dehydro-halogenation [45,46].

3. Catalyst Systems for the Polymerization of Substituted Acetylenes

The synthesis of substituted PAs is typically carried out using transition metal catalysts [42,47–49]. The search for a universally applicable catalyst system, considering the sensitivity of functional groups, presents a significant methodological challenge as the substituents on the acetylene influence both the reactivity of the monomer and the control of polymerization [33]. Generally, both early (e.g., Nb, Ta, Mo, and W) and late transition metal complexes (e.g., Fe, Ru, Pd, and Rh) are suitable for the polymerization of monosubstituted acetylenes. Rhodium catalysis is particularly important as it allows for controlled living polymerization [35,50,51]. Therefore, rhodium-catalyzed polymerization will be discussed separately (vide infra).

For disubstituted acetylenes, the number of suitable catalyst systems is significantly limited due to the restricted accessibility of the reaction center caused by the steric effects of the substituents [32,33]. Sterically demanding diarylacetylenes generally cannot be polymerized in the presence of late transition metals, but require early transition metal catalysts, such as tantalum, tungsten, molybdenum, and niobium complexes. Transition metal chlorides are often combined with organometallic cocatalysts based on stannanes. Prominent examples include WCl_6-Ph_4Sn and $TaCl_5$-Bu_4Sn [52,53]. However, the applicability of these catalysts is limited due to their high oxophilicity, meaning various polar functional groups and electron-withdrawing substituents are not tolerated [54]. The use of palladium catalysts in combination with sterically demanding monophosphane ligands offers the possibility to extend the substrate scope of polydiarylacetylenes (Scheme 2) [54]. Recently, a similar catalyst system demonstrated excellent functional group tolerance, efficiently polymerizing various propargyl compounds into *cis*-transoidal PAs with molecular weights of 5−15 kDa and narrow dispersities (1.4–2.1) [55].
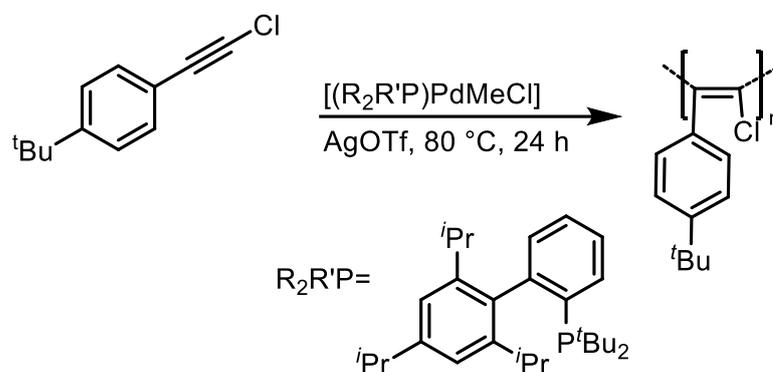
Scheme 2. Palladium-catalyzed polymerization of disubstituted acetylenes according to Castanon [54].

Initially, early transition metals based on the Ziegler–Natta catalyst were used for the polymerization of monosubstituted acetylenes [32]. However, this polymerization method was characterized by poor control and resulted mostly in polymers with high polydispersities and low stereoregularities. This issue was mitigated by the use of late transition metals. Palladium and ruthenium catalysts, for instance, have been developed for the efficient polymerization of acetylenes (Figure 3) [34]. Pyrazole-coordinated palladium complexes generally require activation with silver triflate [56]. *ortho*-Substituted phenylacetylenes can be polymerized in the presence of ruthenium carbene complexes [57]. Additionally, nickel carbene complexes can be used after activation with methylaluminoxane (MAO) [58].
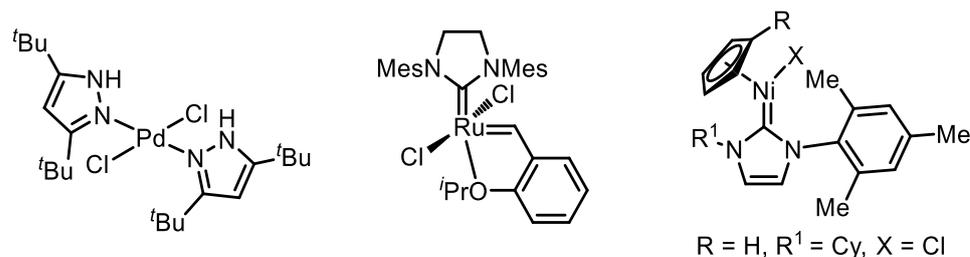
Figure 3. Examples of catalysts for the polymerization of monosubstituted acetylenes: pyrazole palladium complexes by Darkwa (**left**) [56], Grubbs–Hovyda ruthenium catalyst (**center**) [57], and nickel–carbene complexes by Buchowitz (**right**) [58].

4. Rhodium-Catalyzed Polymerization of Monosubstituted Acetylenes: The Path to Living Polymerization

Modern catalytic systems for the polymerization of monosubstituted acetylenes are predominantly dominated by rhodium(I) complexes, which exhibit high reactivity towards acetylenes [35]. In particular, such complexes are characterized by high stability in the presence of various functional groups, such as nucleophilic amines, hydroxy groups, or azo compounds, considerably expanding the class of monosubstituted polyacetylenes and controlling processability [32]. Furthermore, rhodium(I) complexes exhibit high tolerance towards polar and protic solvents, allowing polymerizations to be conducted in THF, dichloromethane, alcohols, and even water [59]. This approach can counteract the known solubility issues of terminal alkynes, and the substituted polyacetylenes obtained as polymerization products can be precipitated in methanol [50]. Due to the low oxophilicity of rhodium, rhodium(I) complexes demonstrate low sensitivity to hydrolysis and oxidation, making them stable for storage [60].

Commercially available phenylacetylene can be considered the simplest terminal alkyne as a model system for investigating the polymerization of monosubstituted acetylenes. Initial studies on the rhodium-catalyzed polymerization of phenylacetylenes date back to 1969 [61]. For instance, the preparation of poly(phenylacetylene) in the presence of the Wilkinson catalyst, already established for the reaction of olefins, was possible at high temperatures. However, as confirmed by Kern, the material could only be obtained with a low degree of polymerization and molecular weights of 1100 Da [62]. It was only through the contributions of Tabata that access to high-molecular-weight poly(phenylacetylene) using dimeric rhodium(I) complexes became possible. The activation of [Rh(nbd)Cl$_2$] occurred through dimer cleavage in the presence of triethylamine (Scheme 3) [63].

Scheme 3. Base-mediated activation of the dimeric rhodium complex for the polymerization of phenylacetylenes.

The obtained polyphenylacetylenes exhibited high polydispersities, indicating poor reaction control. To counteract the high polydispersities, the diene ligands of the binary rhodium complex can be varied (Figure 4). The complex with tetrafluorobenzobarrelene (tfbb) as a ligand exhibits particularly high reactivity [64].

cod   dcp   nbd   tfbb (X=F)

tcbb (X=Cl)
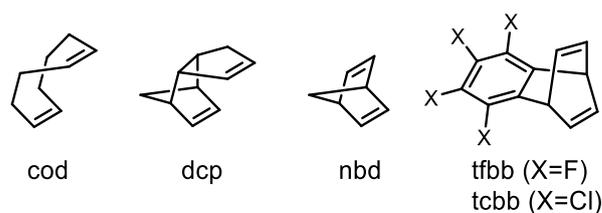
Figure 4. Various diene ligands in binuclear rhodium complexes for the polymerization of monosubstituted acetylenes.

The catalytic activity of binuclear rhodium complexes can be significantly increased by the cocatalytic action of selected organometallic compounds, such as methyllithium and triethylaluminum, allowing phenylacetylenes with high molecular weights to be obtained in quantitative yields [65]. Additionally, according to Alper, zwitterionic rhodium complexes can also be utilized for the production of stereoregular polyphenylacetylenes (Figure 5). However, their activity requires the addition of hydrosilylation reagents, such as triethylsilane [66].
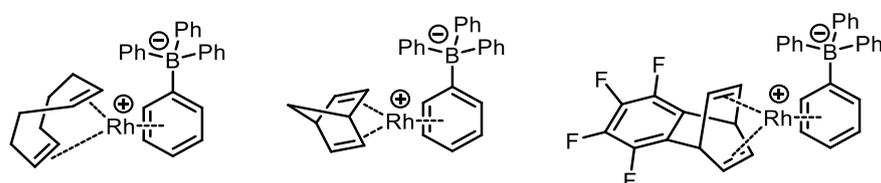
Figure 5. Selected examples of zwitterionic rhodium-(diene)-tetraphenylborate complexes for the stereoregular polymerization of phenylacetylenes according to Alper [66].

For the application of substituted polyacetylenes in organic electronics, both polydispersity and stereospecificity are of central importance [32]. However, the presented catalyst systems based on active rhodium complexes only allow access to monosubstituted polyacetylenes with high degrees of polymerization and broad molecular weight distributions [62]. A solution is provided by the concept of living polymerization, established by Szwarc [67], which was demonstrated as early as 1936 by Ziegler through the anionic polymerization of styrene and butadiene. Formally, living polymerization requires the simultaneous growth of all chains, with the chain ends remaining active, or "alive", after polymerization. This approach inhibits chain termination and chain transfer reactions that prevent controlled polymerization [68]. The living chain end can be deactivated only through the targeted addition of termination reagents. Consequently, the degree of polymerization can be controlled via the monomer/catalyst ratio, allowing for the production of polymers with defined molecular weights. There is a linear relationship between conversion and molecular weight [50]. The first suitable catalyst system for the living polymerization of monosubstituted acetylenes was introduced by Noyori in 1994 and could be generated from the established rhodium complex in the presence of lithium phenylacetylide and triphenylphosphane (Scheme 4) [69]. However, controlled polymerization was only possible with the addition of dimethylaminopyridine (DMAP).
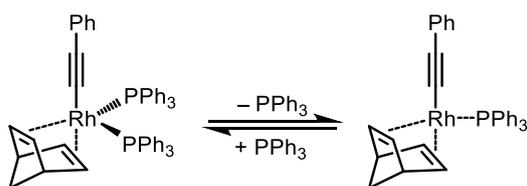
Scheme 4. Active rhodium(I)-alkynyl complex for the controlled living polymerization of phenylacetylene, as developed by Noyori.

The in-situ formation of the rhodium(I)-alkynyl complex is particularly attractive from an atom-economy perspective. For example, the complex established by Noyori can be generated from phenylacetylene, sodium methanolate, and triphenylphosphane and can be used for the polymerization of stereoregular all-*cis*-poly(phenylacetylene) with a polydispersity of Đ = 1.5 (Scheme 5). Due to poor reaction yields, the required addition of Lewis acids for activation, and the lack of possibilities for end-group functionalization, the Noyori catalyst systems need optimization [62].
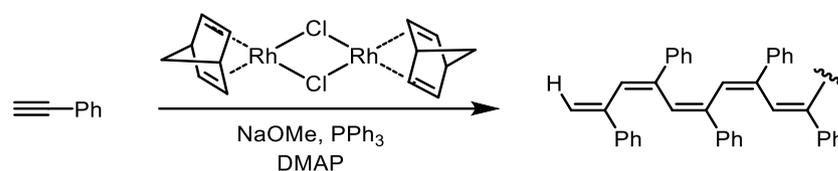
Scheme 5. Stereoregular polymerization of phenylacetylene using the complex [Rh(nbd)Cl]$_2$, according to Noyori.

The fact that the controlled polymerization of phenylacetylenes using rhodium(I) catalysts occurs via a *cis*-insertion mechanism suggests that polymerization proceeds via a reactive vinyl-rhodium species. Accordingly, Masuda developed a highly efficient vinyl-rhodium complex for the living polymerization of phenylacetylenes, which could also be generated in-situ from the binary rhodium complex (Scheme 6) [70].
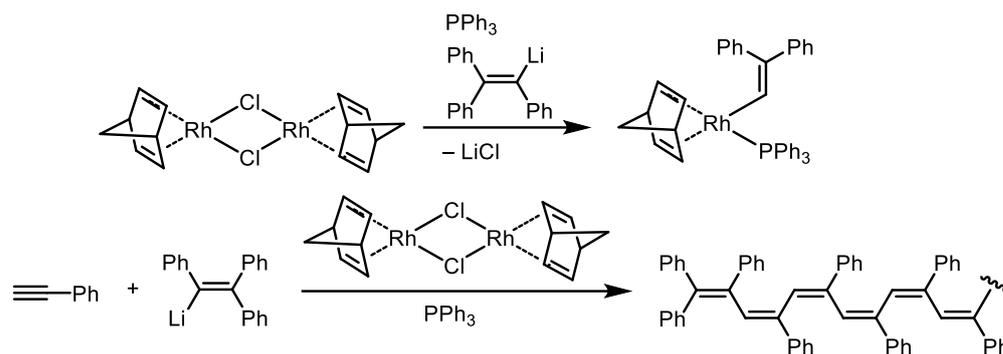
Scheme 6. In-situ formation of the active vinyl-rhodium(I) complex for the living polymerization of phenylacetylene (**top**) and the stereoregular polymerization of phenylacetylene (**bottom**), according to Masuda [50].

For the first time, this catalyst system enabled the controlled polymerization of *para*-substituted phenylacetylenes with electron-donating substituents and various functional groups, such as esters, propiolates, and propargyl derivatives. Inspired by Masuda's work, Taniguchi et al. developed an alternative reaction sequence for the in-situ formation of the active vinyl-rhodium species [50,51]. Starting from the binuclear rhodium complex, with an arylboronic acid and triphenylphosphane, the vinyl-rhodium species can be generated under basic conditions. Furthermore, the choice of the arylboronic acid offers the possibility of end-capping, as the aryl group is mechanistically incorporated into the polyene backbone (Scheme 7) [50].
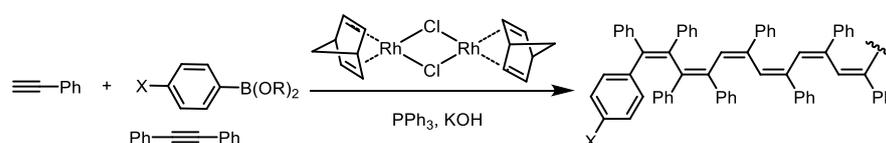
Scheme 7. Rhodium-catalyzed living polymerization of substituted phenylacetylenes according to Taniguchi et al. [50].

The mechanistic scenario of the highly stereoregular polymerization was comprehensively elucidated by Taniguchi et al. through NMR studies of the isolated intermediates, as well as X-ray structural analyses (Scheme 8) [50]. Starting from the binuclear rhodium complex, an active rhodium species is first generated via base-mediated transmetalation. The free coordination site is temporarily occupied by the solvent before tolane coordinates side-on to rhodium. This is followed by the *cis*-insertion of tolane into the rhodium–carbon bond, forming the active vinyl-rhodium species. Mass spectrometric and NMR spectroscopic investigations suggest that there can be a subsequent insertion of another tolane unit. The triphenylphosphane used can coordinate to the free coordination site of the active vinyl-rhodium species.
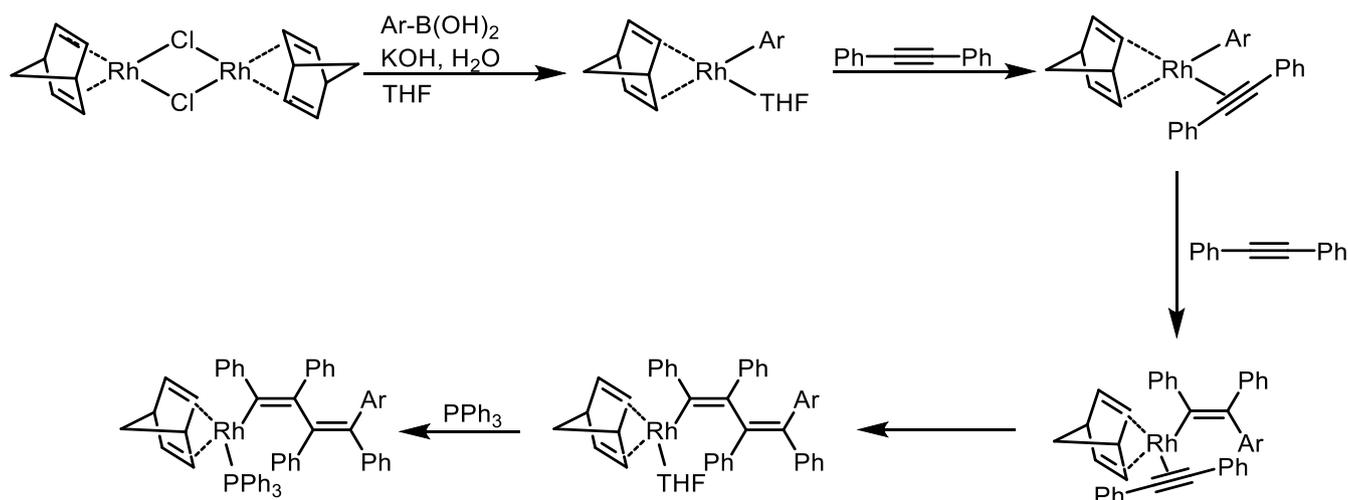
Scheme 8. Postulated mechanism for the formation of catalytically active vinyl-rhodium species for the polymerization of arylacetylenes, according to Taniguchi et al. [50].

Due to steric interactions of triphenylphosphane and the phenyl ring, triphenylphosphane can decoordinate to form an η^5-complex. The intramolecular π-complex can easily cleave in the presence of the terminal alkynes used as monomers, with side-on coordination of the alkyne. The construction of the polyene backbone occurs through the *cis*-2,1-insertion of the alkyne into the rhodium–carbon bond (Scheme 9). The final proto-demetalation with acetic acid allows for termination of the active chain end, resulting in the precipitation of the polymer.
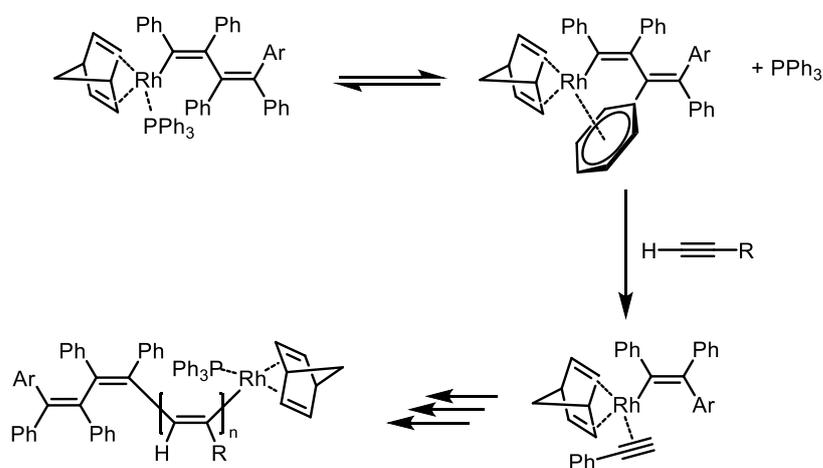
Scheme 9. Rhodium-catalyzed polymerization of monosubstituted arylacetylenes via *cis*-2,1-insertion, according to Taniguchi et al. [50].

In addition to the simple termination of the chain end with acetic acid, targeted end-capping of the polymer is also possible by adding acrylates and acrylamides [71]. Rhodium(I)-catalyzed conjugate addition of boronic acids and the Michael system provides access to telechelics with defined molecular weights. This method also yields chiral polyacetylenes with defined helicities. The method established by Taniguchi et al. for the polymerization of monosubstituted acetylenes can also be transferred from phenylacetylenes to propargylamides [72]. By optimizing the reaction conditions, polymerizations can even be performed in water, yielding water-soluble polyacetylenes [60].

5. Syntheses and Properties of Functional Monosubstituted Arylacetylenes

In recent decades, poly(phenylacetylenes) (PPAs) have shown remarkable potential for forming diverse supramolecular assemblies, such as fibers, nanospheres, liquid crystals, and hybrid materials [73]. Their helical structure, tunable through functional pendants, enables unique properties for applications in asymmetric catalysis, nanoreactors, and chiral recognition. The helicity of PPAs can be proven and investigated using AFM microscopy and CD spectroscopy [74–76]. In particular, the multicomponent catalytic system for the well-controlled living polymerization of phenylacetylenes developed by Taniguchi et al. [50] paved the way for recent applications in synthesizing diversely functionalized substituted PPAs.

Maeda and Yashima summarized various approaches to the construction of one-handed helical polyacetylenes using noncovalent chiral interactions with nonracemic chiral guests, enabling high cooperativity and chiral amplification, inducing nearly single-handed helices in polymer backbones [77]. The "memory effect" allows dynamic helices to transform into stable static ones by increasing helix-inversion barriers. These polymers are useful as chiral materials, such as switchable chiral packing for enantiomer separation, showcasing unique functionalities beyond conventional helical polymers with covalently bonded chiral pendants. This strategy offers new possibilities for creating functional helical polyacetylenes with tunable properties.

Inaba et al. reported the synthesis of star polymers bearing three helical PPA chains with precisely controlled molecular weights and a polydispersity of less than 1.03, employing the multicomponent catalyst system (Scheme 10) [78]. The controlled structure of the polymers was visualized using AFM, corroborating the star-shaped structure. The PA chains ligated by ester groups were also hydrolyzed and analyzed using size exclusion chromatography, demonstrating uniform polymerization on each branch. The chiroptical analysis further reveals chiral amplification of the star-shaped polymer, exerted by the *R*- or *S*-configured *N*-acyl alanine esters.
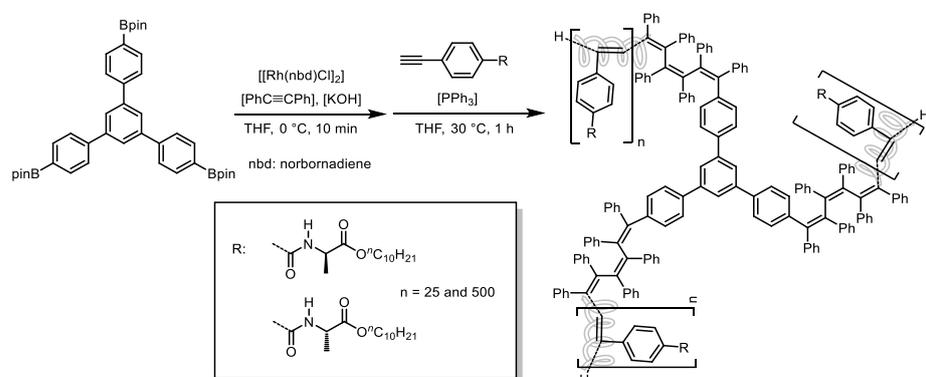
Scheme 10. Rhodium-catalyzed polymerization of 1,3,5-tris(*p*-B(pin)phenyl)benzene bearing *N*-acyl alanine esters to star-shaped polymers with precisely controlled PPA sidearms [78].

Starting with the formation of the linear polymer branch using a triphenylvinyl–rhodium–norbornadiene phosphane complex, Mino et al. prepared star-shaped helical substituted PPAs bearing *L*-valine and *L*-threonine moieties. They showed that the chiroptical intensities of the star-shaped polymers were smaller in comparison to the corresponding linear polymers in solution, but were larger in films (Scheme 11) [79]. Interestingly, the water contact angles and refractive indices of the star-shaped polymers were smaller in comparison to the linear polymers.
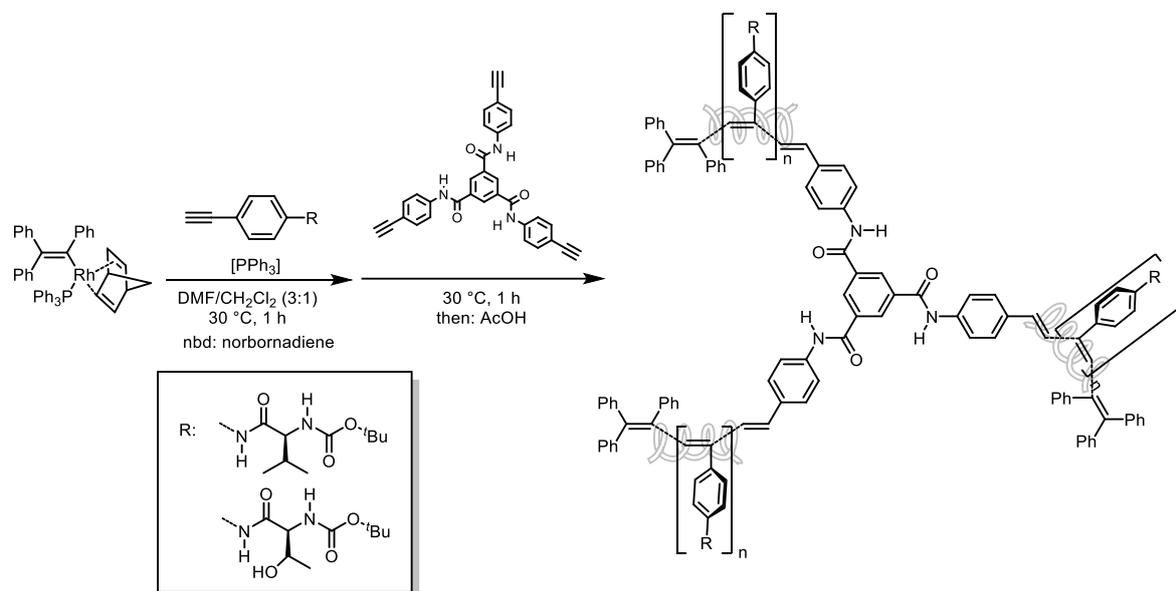
Scheme 11. Rhodium-catalyzed polymerization of *L*-valine and *L*-threonine ligated phenylacetylenes, followed by three-fold ligation to a central trialkynyl core through insertion/proto-demetalation, resulting in star-shaped polymers with PPA sidearms [79].

The Rh-multicomponent catalyst was successfully applied by Lu et al. to synthesize stimuli-responsive helical block copolymers with substituted PPA backbones containing dendritic oligoethylene glycol pendants and photoswitchable spiropyran units (Scheme 12) [80]. These materials unite tuneable thermoresponsivity, amphiphilicity, and reversible helicity switching upon heating. Photoisomerization of the appended spiropyran moieties does not significantly affect helicity, and the block copolymers form long fibers with diameters of 25 nm.

Scheme 12. Rhodium-catalyzed block copolymerization of dendritic oligoethylene glycol phenylacetylene and spiropyran phenylacetylene to PPA block copolymers containing dendritic oligoethylene glycol pendants and photoswitchable spiropyran unit sidearms [80].

Luminescent polyacetylenes (LEPAs) offer a potential application in organic electronics [81]. These polyacetylenes are disubstituted containing electron-rich heterocycles. However, monosubstituted polyacetylenes are typically non-emissive, similar to unsubstituted polyacetylene, due to the unfavorable energetic positioning of the electronic ground and excited states [82]. The emission properties of LEPAs can be controlled by the substitution pattern, as seen for the green fluorescent poly(diphenylacetylene) [42]. Furthermore, by functionalizing with tetraphenylethene or hexaphenylsilole, PAs with aggregation-induced emission (AIE) behavior have been reported [83–85].

Phenothiazine, a strong, reversibly oxidizable heterocyclic donor system, is a constituent of many organic optoelectronic materials [86], polymers for energy storage [87], and fluorescent [88] and OSC dyes [89,90]. However, luminescent phenothiazinyl-based polyacetylenes have remained unknown until recently.

Starting from 3-ethynyl-substituted phenothiazinyl-merocyanines, soluble phenothiazinyl-merocyanine substituted PAs were readily accessed using rhodium-catalyzed polymerization, as recently demonstrated by Pisetsky, Budny, and Müller (Scheme 13) [91]. Optical spectroscopy (absorption and emission) revealed that 7-acceptor-substituted phenothiazinyl polyacetylenes with conjugatively ligated merocyanines are emissive in solution, displaying positive emission solvatochromism. For a few polymers, even distinct solid-state luminescence was detected.

Scheme 13. Rhodium-catalyzed polymerization of 3-ethynyl-substituted phenothiazinyl-merocyanines to emissive phenothiazinyl-merocyanine decorated PAs (inset: emission solvatochromocity of PA (R = indane-1,3-dione-2-ylidene) in solvents of various polarity (from left to right: *n*-hexane, cyclohexane, toluene, benzonitrile, and dichloromethane)) [91].

Similarly, Pisetsky and Müller expanded the polymerization of 3-ethynyl-substituted 7-(hetero)aryl-, 7-(diarylamino)-, and 7-stryryl-phenothiazines to the corresponding 3-functionalized conjugated phenothiazinyl-substituted PAs, bearing extended π-conjugation in the sidechains (Scheme 14) [92]. As in the phenothiazine-merocyanine PA series, narrow molecular weight distributions were obtained in most cases. Selected polymers are luminescent (Φ_f = 0.06), displaying moderate Stokes shifts and positive emission solvatochromism.

Scheme 14. Rhodium-catalyzed polymerization of 3-ethynyl-substituted 7-(hetero)aryl-, 7-(diarylamino)-, and 7-stryryl-phenothiazines to conjugated phenothiazinyl PAs [92].

The multicomponent catalytic system of [Rh(nbd)Cl]$_2$, arylboronic acids, diphenylacetylene, and aqueous KOH, enabling well-controlled, living polymerization, further allows for the introduction of functional groups at the polymer ends and facilitates terminal modifications with α,β-unsaturated carbonyl compounds, yielding telechelic poly(phenylacetylene)s [93]. In addition, novel rhodium complexes isolated from this system provide insights into the polymerization mechanism, which was also extended to water-soluble and non-conjugated acetylenes.

A unique approach to PPAs was recently presented by He et al., who employed the Mizoroki–Heck coupling reaction of vinyl bromides to synthesize linear and branched poly(phenylacetylene)s (Scheme 15) [94]. Starting from α-bromostyrene derivatives as monomers, the polymer-analogous vinylation reaction proceeded efficiently with potassium carbonate as a base, whereas triethylamine did not show any catalytic reactivity. The obtained PPAs exhibited a broad molecular weight distribution, indicating typical step-growth polymerization.
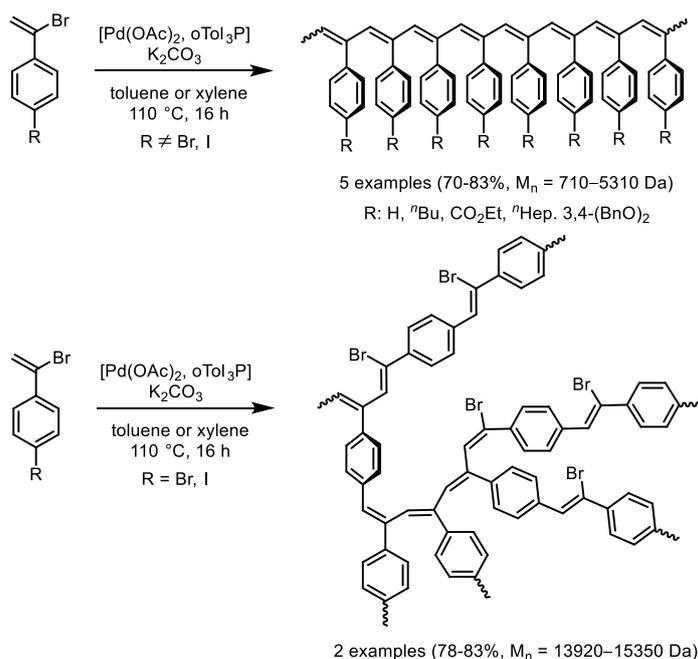
Scheme 15. Palladium-catalyzed Mizoroki–Heck polymerization of arylvinyl bromides to linear and branched PAs [94].

6. Conclusions

Almost 50 years ago, synthetic advances in polyacetylene synthesis and the discovery of their (semi)conductivity upon partial oxidation or reduction caused a paradigm shift in organic (semi)conducting materials, leading to many applications. Although the dream of replacing metals as conductive materials in electronic devices was not fulfilled, completely new avenues for the application of organic (semi)conductors arose, initiating a steady quest for new functional π-systems. Besides long conjugation pathways in polyacetylene, their structural peculiarities, especially with respect to substituted derivatives, have inspired synthetic organometallic chemistry, which ultimately provided new types of structurally well-defined substituted polyacetylenes through living rhodium-catalyzed polymerization and chain-end functionalization. The obtained materials are helical and open numerous options for chiroptic applications in photonics and electronics. This review provides only a snapshot of a rapidly developing and vibrant field in organic materials chemistry. Most importantly, organometallic synthesis and catalysis are sitting at the forefront of discovering exciting properties and structural features.

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