

CONTROLLED AND LIVING POLYMERIZATIONS INDUCED WITH RHODIUM CATALYSTS. A REVIEWJan SEDLÁČEK¹ and Jiří VOHLÍDAL^{2,*}

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In the last fifteen years, a large variety of specialty polymers of diverse chemical structure and functionality have been synthesized with the rhodium-based catalysts. The high tolerance to the reaction medium and functional groups of monomers, as well as ability to control various structure features of the polymer formed are typical properties of these catalysts. In addition, some rhodium catalysts can be anchored to inorganic or organic supports or dissolved in ionic liquids to form heterophase polymerization systems, which opens the way to pure, well-defined polymers free of the catalyst residues, as well as to recycling rhodium

catalysts. This review provides a survey on the polymerization reactions induced with rhodium-based catalysts, in which one or more structure attributes of the polymer formed are subject to control. The structure attributes considered are (i) sequential arrangement of monomeric units along polymer chains; (ii) head-tail isomerism of polymer molecules; (iii) configurational structure of polymer molecules; (iv) conformation of polymer molecules; and (v) molecular weight and molecular-weight distribution of the polymer formed. A review with 188 references.

Keywords: Anchored catalysts; Atom transfer radical polymerization; Cross-dehydrocoupling polymerization; Dehydrocoupling; Helical polymers; Heterophase catalysis; Hydrosilylative addition copolymerization; Immobilized catalysts; Ionic liquids; Living polymerization; Mesoporous molecular sieves; Mesoporous supports; Polyacetylenes; Polyketones; Polyphosphinoboranes; Polysilylenevinylenes; Polyvinylenes; Rhodium diene complexes; Ring-opening polymerization; Substituted acetylenes.

1. INTRODUCTION

Rhodium complexes are mainly well-known as robust, effective catalysts for hydrocarbonylation of olefins (industrial process) and hydrogenation of unsaturated compounds¹. Besides, they also catalyze other transformations of low-molecular-weight compounds, such as isomerization, hydrosilylation and silylation¹⁻³, Kharash addition⁴, methanation of carbon oxides⁵ and transformations of diazo compounds⁶. High stability in air and high tolerance to the reaction medium and functional groups of reactants are typical properties of Rh catalysts. Therefore, they can be used for the activation of various organic compounds in chemical transformations under mild conditions (room or slightly elevated temperature, in solvents from water to hydrocarbons, and in the presence of air), which balances the high cost of these catalysts.

Unlike rhodium-based catalysts, typical polymerization catalysts are often unstable in air and sensitive to functional groups of monomers, which brings about complications in their use and limitations of their applicability as to the monomer functionality and choice of suitable solvents. These problems were successfully overcome in the case of large-scale commodity polymers, which have no or rather limited chemical functionality. However, these difficulties are a serious obstacle in smooth preparation and/or production of specialty polymers of varied chemical functionality, for which new, more stable and more robust catalysts are required. Concerning the above-mentioned properties of Rh-based catalysts, it is natural that rhodium complexes have attracted attention of scientists searching for advanced polymerization catalysts. In the last decade, numerous new, as well

as already known Rh complexes have been designed, prepared and tested as catalysts for the polymerization of various unsaturated and cyclic monomers. Many of them were found to control the stereochemistry of formed macromolecules, and some of them were also found to control the molecular weight distribution of the polymers formed. The advances achieved in this field are reported in the present paper, which, for the sake of completeness, also includes information on earlier applications of rhodium catalysts.

2. BUTA-1,3-DIENE (BUTADIENE)

Butadiene can polymerize by the 1,2-addition (like a vinyl monomer) yielding 1,2-units or by the 1,4-addition (conjugative addition) giving 1,4-units, which can be of the *cis* or *trans* configuration (Fig. 1). If only 1,2-addition takes place in a polymerization, the polymer formed is referred to as 1,2-polybutadiene, *i.e.*, poly(1-vinylethylene); it can be of various tacticity (atactic or isotactic or syndiotactic). Configurationally pure butadiene polymers formed by the 1,4-addition, poly(but-1-ene-1,4-diyl)s, are usually referred to as *cis*- and *trans*-1,4-polybutadiene.

Rinehart *et al.*⁷ reported in 1961 a stereoregular polymerization of butadiene with RhCl_3 , $\text{Rh}(\text{NO}_3)_3$, $\text{Na}[\text{RhCl}_4]$ and $\text{NH}_4[\text{RhCl}_4]$ to the *trans*-1,4-polybutadiene of high configurational purity (99% *trans*). They examined ethanol, dimethylformamide, water and aqueous solutions of sodium dodecylbenzenesulfonate as reaction media and found a strong solvent effect in this polymerization. For example, they observed that RhCl_3 is inactive in the polymerization carried out in ethanol even under reflux as well as in water (formation of a complex mixture of more than twenty steam-volatile hydrocarbons was observed), whereas $\text{Rh}(\text{NO}_3)_3$ gives reasonable yields of crystalline polybutadiene in both solvents under the same reaction conditions. On the other hand, RhCl_3 becomes an active catalyst in water in the presence of anionic emulsifiers, while the emulsifiers have a much lower effect in the case of the rhodium nitrate catalyst.

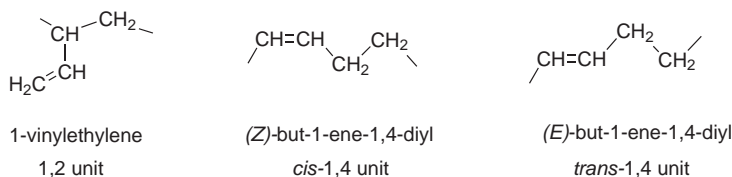


FIG. 1
Monomeric units of linear polybutadienes

Polymerization of butadiene with Rh(III) salts proceeds without an induction period, it is of the zero reaction order with respect to butadiene and of the first order with respect to the catalyst⁸ if the catalyst concentration is neither too low nor too high (*ca* from 1 to 50 mmol/l). The lower catalyst concentration limit occurs owing to the participation of radical polymerization, which is quenched by Rh(III) salt at an increased concentration. Evidences for this explanation were obtained from the polymerization kinetics as well as from the polymer structure analysis: the presence of *cis*- and 1,2-units in the polybutadiene prepared using a low concentration of the Rh salt. The upper concentration limit is ascribed to the formation of oligomeric Rh species in solutions^{8,9}. In context with the observed precise trans-stereocontrol of the butadiene polymerization by Rh species, Rinehart *et al.* also examined the *cis*-to-*trans* isomerization of pure *cis*-1,4-PB by RhCl₃ (ref.⁸). The reaction proceeded to the equilibrium *cis/trans* content (*ca* 25% *cis*- and 75% *trans*-form) and it was inhibited by butadiene which transforms the isomerization species to the polymerization ones.

Similar results were surprisingly obtained with the $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-Cl})_2]$ catalyst¹⁰ although the oxidation number of rhodium is +1 in this complex, (cod is cycloocta-1,5-diene). However, later on, Teyssié *et al.*¹¹ and Rinehart¹² found that the reaction is accelerated by formic acid and other acids (including water) and by those reducing agents which are capable of reducing Rh(III) to Rh(I) in aqueous systems (particularly cyclohexa-1,3-diene). These observations were interpreted in terms of stabilization of low-valent rhodium species, which are the real growing species. Ligands such as organic amines, as well as bromide and iodide anions, were found to act as retarders or even inhibitors. Rinehart¹² suggested a mechanism in which the active species is η^3 -allylrhodium hydride, an initiation occurring by hydride shift, and propagation occurring by a ligand displacement processes.

Further research^{13,14} has revealed that the molecular weight of *trans*-1,4-PB formed with Rh catalysts increases proportionally to the monomer consumption but, on average, two polybutadiene macromolecules (growing species) are formed per one Rh atom. Therefore, it was concluded that (i) the initiation is practically quantitative, (ii) chain transfer takes place in the overall reaction, and (iii) the low reaction rate generally observed for this polymerization is the result of a slow propagation.

Attempts were also made to copolymerize with butadiene and homopolymerize other conjugated dienes (isoprene, 2,3-dimethylbutadiene, cycloocta-1,3-diene) and styrene using Rh(III) catalysts¹¹. None of the monomers was found to form a copolymer or to enhance the rate of butadiene polymerization. On the contrary, a decrease in the reaction rate as

well as the polymer regularity was observed. As to the homopolymerization, only styrene was found to form an atactic homopolymer in the presence of rhodium catalysts but the reaction was found to be of the radical polymerization class (details are not given).

The polymerization of butadiene with rhodium catalysts is a dormant or dead subject today; research in this field has stopped in the early 1970's mainly because of low interest of practice in *trans*-1,4-polybutadiene and a high cost of rhodium catalysts. Nevertheless, the reviewed studies clearly revealed the ability of Rh catalysts to induce well-controlled polymerization giving highly stereoregular polymers of tunable molecular weight under mild conditions (air, water, low temperature). The knowledge obtained by those studies is of importance in the context of increasing interest in polymerizations of other monomers catalyzed with Rh compounds.

3. PROPADIENE (ALLENE) AND SUBSTITUTED PROPADIENES

Double bonds in propadiene and its derivatives are not conjugated and hence these monomers polymerize by 1,2- or 2,3-addition, *i.e.*, in a similar way to vinyl monomers. As a result, macromolecules of polypropadienes are of unique structure: they are composed of a saturated main chain which, however, involves unsaturated carbon atoms that are parts of unsaturated side groups (Fig. 2).

Propadienes can be polymerized using various transition metal complexes, mainly nickel, cobalt, palladium and rhodium complexes. The polymerization catalyzed with Rh complexes has been studied from the end of the 1960's, when it was found that this reaction can give high-molecular-

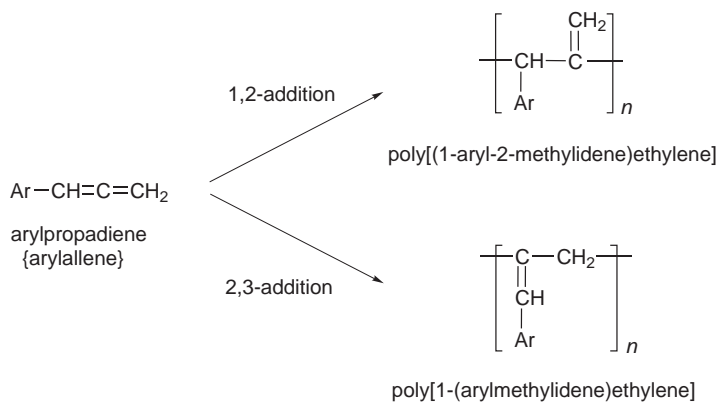


FIG. 2
Modes of polymerization of substituted propadienes

weight polymers (usually crystalline)^{15–18} or cyclooligomers^{19–22} or both, depending on the ligands of the Rh complex and the reaction conditions. The Rh(I) complexes containing Cl and CO ligands and no or only one PPh₃ ligand were found to give crystalline (*i.e.*, regular) polymers together with small amounts of cyclooligomers, which can be removed by dissolving in acetone^{16,17}. The activity of Rh complexes in polymerization of propadiene was found to decrease in the order: [RhCl(CO)₂(PPh₃)] > {[Rh(CO)₂]₂(μ-Cl)₂} > [RhCl(CO)₃]. The reaction order with respect to the catalyst was found to be one for the [RhCl(CO)₂(PPh₃)] and [RhCl(CO)₃] catalysts but only 1/2 for the bridged {[Rh(CO)₂]₂(μ-Cl)₂} complex. This indicates that the dissociation to mononuclear species is the first step of the initiation with the last catalyst, which is also active in the polymerization of phenylpropadiene¹⁸. Polymerization occurred in a weakly coordinating solvent such as ethanol but not in strongly coordinated solvents such as dimethyl sulfoxide and hexamethylphosphoramide. The suggested mechanism assumes initiation by hydrogen transfer from a monomer molecule to a single Rh species to give a rhodium hydride species, on which the propagation starts *via* insertion of propadiene molecules.

Rhodium complexes involving more than one PPh₃ ligand, such as [RhCl(CO)₂(PPh₃)₂], [RhCl(CH₂=CH₂)₂(PPh₃)₂] and [RhCl(PPh₃)₃], are inactive in the polymerization but active in the cyclooligomerization of propadiene^{16,19–22}. Evidently, the reactivity of these complexes is not limited by steric factors, because other complexes with even more crowded central Rh atom polymerize substituted propadienes. Choi *et al.*²³ polymerized various arylpropadienes (where aryl is phenyl, 4-methylphenyl, 2-naphthyl) with nonplanar Rh(I) hydride complexes carrying bulky ligands, such as with [RhH(PPh₃)₄], [RhH(CO)(PPh₃)₃], [RhH(dppe)₂] (dppe is Ph₂PCH₂CH₂PPh₂), and η³-allyl complex [Rh(η³-C₃H₄-Ph)(CO)(PPh₃)₂]. Polymerization is assumed to proceed on η³-allyl species (Fig. 3) and it

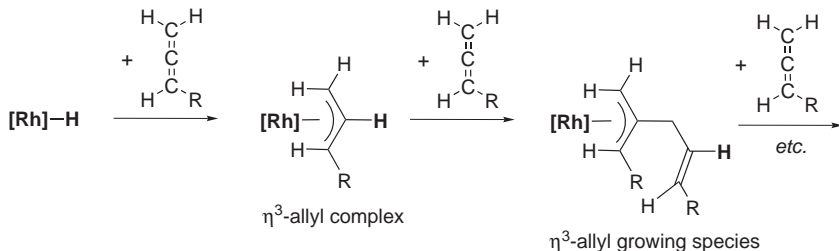


FIG. 3

Propagation in polymerization of propadienes

exclusively proceeds by the 2,3-addition (Fig. 2) giving regular, high-molecular-weight polymers with saturated main chains and *exo*-aryl-methylidene pendant groups. The electronic effects, in particular lowered electron density on the monomer double bonds, cannot be considered a crucial controlling factor because [4-(trifluoromethyl)phenyl]propadiene and (4-fluorophenyl)propadiene give only low-molecular-weight oligomers under the same reaction conditions. Thus, it is clear that the reaction path of a particular monomer–catalyst system is a result of a complex interaction of several factors that are not easy to tune, because Rh complexes can interact with propadienes in various ways (Fig. 4), each way having different steric and electronic requirements for reactants.

In order to obtain a better insight into these interactions, Choi *et al.*^{24,25} studied a single and multiple insertion of substituted propadienes into the Rh–H bond to give η^3 -allylrhodium at room temperature (polymerizations are typically performed at 60 °C). They isolated single η^3 -allyl complexes $[\text{Rh}(\eta^3\text{-C}_3\text{H}_4\text{-X})(\text{CO})(\text{PPh}_3)_2]$ (X is OMe, Ph or 4-substituted Ph) from equimolar reaction mixtures of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ and a corresponding propadiene. On the other hand, reaction with $[\text{RhH}(\text{PPh}_3)_4]$ preferably provides complexes containing tetrameric η^3 -allyl ligand with the tail-to-tail linked end unit (Fig. 5). The same tetrameric η^3 -allyl complexes are also formed by the interaction of either $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{Rh}(\eta^3\text{-C}_3\text{H}_4\text{-X})(\text{CO})(\text{PPh}_3)_2]$ with an excess of monomer at room tempera-

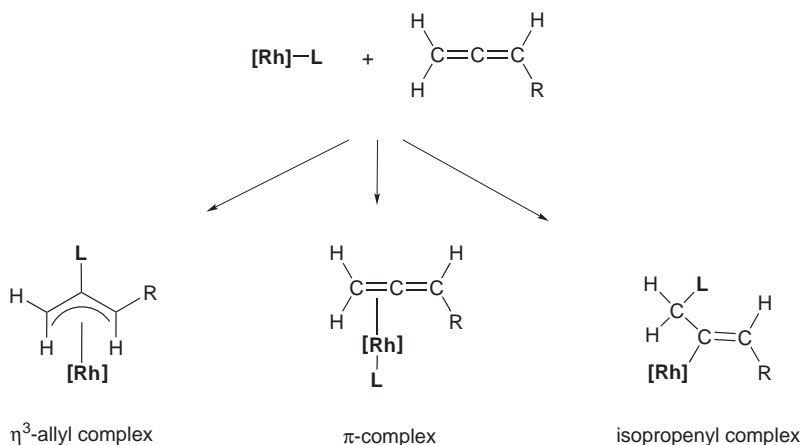


FIG. 4

Classes of complexes formed in the interaction of propadienes with Rh species (R = H, alkyl, aryl, hetaryl, alkoxy, *etc.*; L = H, halogen, alkyl, acyl, *etc.*)

ture. The corresponding dimeric and trimeric species were not observed. The mechanism proposed for the tetrameric species formation involves (i) transformation of the monomeric η^3 -allyl species into dimeric isopropenyl species during tail-to-tail addition of the second diene molecule, (ii) head-to-tail addition for the two next molecules to the growing isopropenyl species, and (iii) back isomerization of the isopropenyl species to the η^3 -allyl one. The reasons for the observed unique stability of η^3 -allyl tetrameric species at room temperature are not yet clear.

Unlike the hydride complexes, rhodium chloro complexes with PR_3 ligands, such as $[\text{RhCl}(\text{PR}_3)_3]$ and $[\{\text{Rh}(\text{PR}_3)_2\}_2(\mu\text{-Cl})_2]$ (R is Me, Et, *i*Pr, Ph), react with arylpropadienes at room temperature to give classic π -complexes with η^2 -coordinated 2,3- π -bond ($\text{CH}_2=\text{C}$) and benzene ring inclined toward the Rh atom²⁶ (Fig. 6). If the auxiliary phosphine ligands of the Rh complex are PMe_3 , the formed π -complex can add a second propadiene molecule giving rhodacyclopentane species with benzylidene side group (Fig. 6). It should be noted here that Kishimoto *et al.*²⁷ also isolated a rhodacyclopentane complex formed as a side product in the initiation of polymerization of phenylacetylenes with Rh(I) complexes.

The above-mentioned Rh(η^3 -allyl) complexes with tetrameric η^3 -allyl ligands catalyze not only the polymerization of propadienes but also the

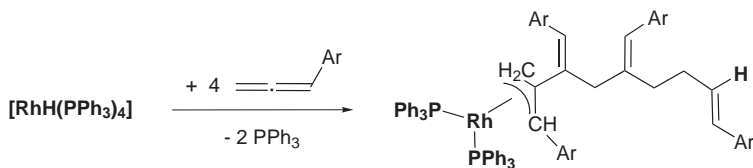


FIG. 5

Structure of rhodium species with tetrameric η^3 -allyl ligand isolated by Choi *et al.*²⁵

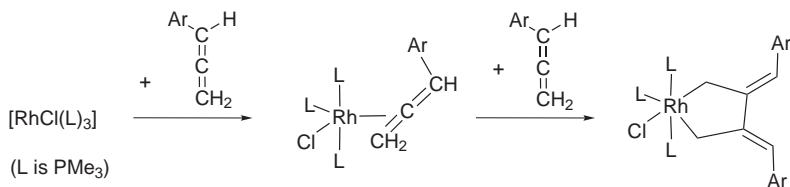


FIG. 6

Formation of rhodium η^3 -propadiene complex and rhodacyclopentane species

copolymerization of substituted propadienes with carbon monoxide to give alternating copolymers of the polyketone class²⁸⁻³⁰ (Fig. 7). These catalysts are active in polymerization of aryl as well as alkyl propadienes and they show high initiator efficiency (practically 100%). The polymers prepared are of low polydispersity and their number-average molecular weight, M_n is close to that calculated from the monomer-to-catalyst molar ratio, indicating the living character of the polymerization²⁸. These polyketones can also be prepared as polymer networks if a difunctional monomer such as dipropadienylbenzene is added to the polymerization mixture. Rh complexes with tetrameric η^3 -allyl ligand were also found to induce living alternating copolymerization of CO and propadienes with the azobenzene moiety to give liquid-crystalline polyketone^{30,31} (Fig. 7, X = O(CH₂)₁₂O-C₆H₄-N=N-Ph). Mechanistic studies have revealed that CO insertion is the rate-determining step for these copolymerizations.

As it can be seen, many rhodium complexes are available, which induce controlled polymerization of propadienes to regular polymers and strictly controlled copolymerization of propadienes with carbon monoxide to alternating copolymers. Even polymerization systems are known in which both the polymer structure and polymer molecular weight are precisely controlled. It is worth noting that the more frequently used Ni catalysts do not provide so strict control of the polymer structure as the rhodium catalysts (see, *e.g.*, refs³²⁻³⁴), although they also induce living polymerization. The scope of use of Rh catalysts in polymerization of propadienes can be further extended, *e.g.*, in copolymerizations of propadienes with isocyanides (isonitriles), since the latter monomers are also polymerizable with rhodium catalysts³⁵. The new knowledge of the scope and mechanism of polymerization of propadienes revealed in the last years is deep and it opens the way to the design and synthesis of new reactive and functional specialty polymers.

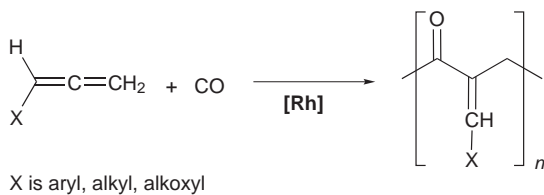


FIG. 7
Synthesis of polyketones by alternating polymerization of arylpropadiene and CO

4. SUBSTITUTED ACETYLENES - HOMOGENEOUS POLYMERIZATION

Stability in a variety of solvents, unprecedented tolerance to functional groups, precise control of the stereochemistry of propagation, and accessibility of living polymerization systems are the properties that make Rh(I)-based catalysts attractive for polymerization of acetylenes, despite their high cost. Therefore, in the last decade, rhodium complexes became the catalysts that are unequivocally most often used in polymerization of monosubstituted acetylenes and, simultaneously, substituted acetylenes became the monomers number one among those polymerized with Rh catalysts. Research in this field is driven by potential applications of conjugated polymers as functional materials in electronics, optoelectronics, molecular electronics and related fields. It is notable that, for example, carotenes, retinals, zeaxanthines and related compounds, which, from the structural viewpoint, are oligomers of substituted acetylenes (oligovinylenes), effectively function as molecular wires in the living matter (photosynthesis systems, vision) for hundreds millions of years.

The term "polyacetylenes" is a source-based class name for polymers prepared from acetylene (ethyne) and/or substituted acetylenes. These polymers can have various structures, depending on the mode of polymerization. They can be polymerized by processes in which triple bonds are opened, such as by the insertion or metathesis coordination polymerization, to give polyvinylenes, the most frequent kind of polyacetylenes (Fig. 8). Besides, they can also be polymerized by processes in which triple bonds are preserved, such as metathesis polycondensation, metathesis ring-opening polymerization and Sonogashira coupling, to give polymers containing main-chain triple bonds or by cyclopolymerization processes based on cyclotrimerization of alkynes, yielding polymers with benzene rings as branching and/or knot points. Since polymers prepared by polymerization of acetylene and its derivatives with Rh catalysts are from the structural

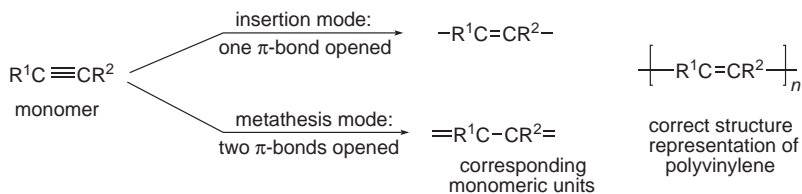


FIG. 8

Modes of polymerization of acetylenes to polyvinylenes ($R^1, R^2 =$ hydrogen, alkyl, aryl, heteroaryl, etc.)

point of view exclusively polyvinylenes, we shall use this structure-based term throughout this paper instead of the currently but incorrectly used term polyacetylenes.

4.1. Isomerism of Polyvinylene Macromolecules

The isomerism of polyvinylenes derived from monosubstituted or asymmetrically substituted acetylenes is very complex, involving configurational and constitutional (head-tail, HT) isomerism. Due to conjugation, free rotation along the main-chain C-C single bonds is restricted and, as a result, these bonds exhibit the *cisoid-transoid* isomerism (i.e., *cis*-like-*trans*-like isomerism). As a result, there are four different basic configurations of the unsubstituted polyvinylene chain (Fig. 9a). In addition, three different HT isomers can be derived for each of basic configurations in the case of polyvinylenes derived from asymmetrically substituted acetylenes (see iso-

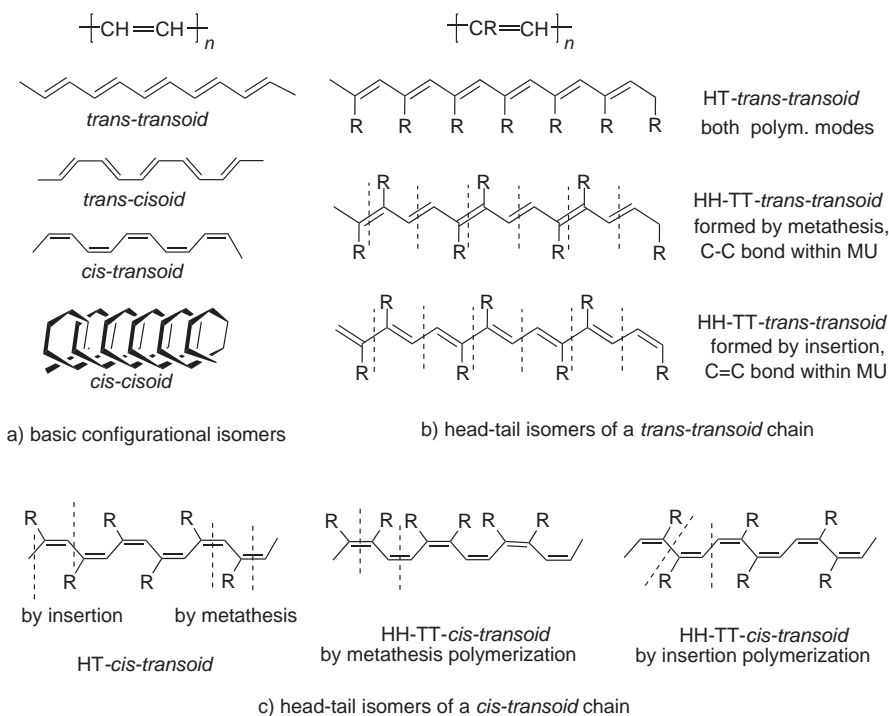


FIG. 9
Configurational and head-tail isomerism of polyvinylene chains

mers of a *trans-transoid* chain, Fig. 9b, and *cis-transoid* chain, Fig. 9c). This means that there are in total twelve possible basic structures of a regular polyvinylene chain composed of asymmetric monomeric units (MU) of one kind. Rh(diene) catalysts typically provide the only one: HT-*cis-transoid* form, out of all twelve possible basic isomeric forms and virtually infinite number of their combinations, which clearly shows their unique product selectivity in polymerization of acetylenic monomers. Other catalysts do not show such a high stereoselectivity in propagation³⁶.

The *cis-transoid* structure for poly(phenylacetylene), PPA, prepared with Rh-based catalyst was identified as early as 1969 by Kern³⁷, who polymerized phenylacetylene (PA) with the Wilkinson catalyst [RhCl(PPh₃)₃]. He observed (i) micro-crystallinity of the prepared PPA and proposed a helical conformation of PPA macromolecules in the solid state, (ii) *cis-to-trans* isomerization of PPA induced by pyridine, and (iii) a close correlation between the microstructure, color and crystallinity of PPA. These results, corresponding well to the present knowledge, are outstanding taking into account the instrumentation available at that time. However, the era of expanding research in this field, still lasting, has started in the 1990's being initiated by the discovery of Furlani *et al.*³⁸⁻⁴⁰ (1986) that Rh^I(η²:η²-diene) complexes such as [Rh(cod)₂(μ-Cl)₂], [Rh(cod)(bipy)]PF₆, [Rh(nbd)(bpy)]PF₆ and others (cod stands for cycloocta-1,5-diene, nbd for norborna-1,4-diene and bpy for 2,2'-bipyridine) selectively polymerize PA to stereoregular *cis-transoid*-PPA with high yields. Various Rh(diene) complexes, mainly dinuclear Rh(nbd) and Rh(cod) complexes with bridge chloro and methoxo ligands, have been used in the early nineties for the polymerization of substituted acetylenes to stereoregular *cis-transoid* polyvinylenes⁴¹⁻⁴⁷.

The HT-*cis-transoid* structure of polyvinylenes prepared with Rh(diene) catalysts found by Kern and recognized by Furlani *et al.* is well established today²⁷ on the basis of detailed NMR studies. This structure is characterized by well resolved, sharp ¹H NMR signals which, for PPA, occur at 5.84 ppm (s, CH=), 6.63 ppm (d, 2 H, *ortho*-H) and 6.94 ppm (m, 3 H, arom. H), and ¹³C NMR signals at 126.7, 127.5 and 127.8 ppm (arom. C), 131.8 ppm (CH=), 139.3 ppm (C=) and 142.8 ppm (*ipso*-C). The HT-*cis-transoid* polymers of substituted PA also show a sharp singlet of olefinic hydrogen in the region from 5 to 6 ppm, while signals of their aromatic protons are displaced depending on the substituent structure (see, *e.g.*, ref.²⁷ and references given in Table I).

The experimentally determined content of *cis*-units in a prepared polyvinylene is usually lower than 100%. In spite of that, it is almost certain that Rh(I) catalysts indeed operate as the *cis*-stereospecific ones. The ob-

served small configurational defects can be namely ascribed to an additional, rather rapid *cis*-to-*trans* isomerization of formed *cis*-polyvinylene molecules in solution^{48,49}, which, undoubtedly, takes also place during polymerization and NMR analysis. The presence of oxygen in the polymerization mixture can further decrease the *cis*-regularity of the formed polyvinylene molecules because they are often unstable in air undergoing autoxidative degradation^{48–53}. Their degradation in solution can be so rapid that it even affects the results of the polymer SEC analysis^{53–56}. It is important that autoxidative degradation of *cis*-*transoid* polymers is faster than that of the irregular or the *trans*-rich ones^{52,53}. In addition, the degradation speeds up the *cis*-to-*trans* isomerization of high-*cis* polymers, as can be seen in Fig. 10.

The occurrence of the HH-TT sequences in polyvinylenes must be taken into consideration mainly in the case of polymers prepared with metathesis catalysts, because the head-to-head reaction of substrate molecules is typical of metathesis. Recently, the presence of HH-TT sequences was demonstrated in poly[2-(trifluoromethyl)phenyl]acetylene prepared with the MoOCl₄/Bu₄Sn/EtOH catalyst⁵⁷. However, indirect evidences of the presence of HH-TT sequences in substituted polyvinylenes were obtained much earlier, from results of the thermal degradation study on ring-substituted PPAs. Blum *et al.*⁵⁸ have found that polyvinylenes prepared with Rh catalysts degrade at 200–225 °C selectively under the formation of

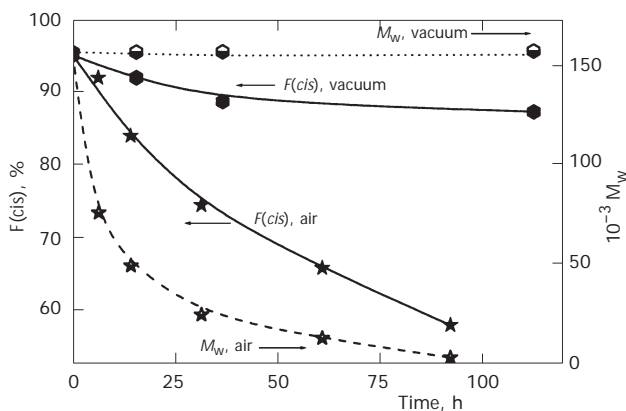


FIG. 10

Time dependence of the weight-average molecular weight, M_w , and fraction of *cis*-units, $F(cis)$, in poly[(4-fluorophenyl)acetylene] prepared with $[Rh(nbd)_2](\mu-OMe)_2$, when kept in THF solution at room temperature in vacuum or exposed to air (unpublished data of the authors)

1,3,5-trisubstituted benzene derivatives. These results were later confirmed by fast pyrolysis gas chromatography⁵⁹, in which the polymer is decomposed at 500 °C within *ca* 0.5 s, and the decomposition products are on-line analyzed by GC/MS. If a regular HT chain undergoes cyclotrimerization cleavage, only 1,3,5-trisubstituted benzene is formed as the product. However, if HT irregularities occur in the chain, also 1,2,4-trisubstituted benzene together with isomers of disubstituted and tetrasubstituted benzenes are formed (Fig. 11).

4.2. Monomer Structure Requirements

Rhodium catalysts effectively operate under mild conditions in solvents typically used in coordination polymerization, such as in hydrocarbons, chlorinated hydrocarbons and ethers, as well as in solvents that are rather rare in this field, such as amines, alcohols and water (see review, ref.⁶⁰). This opens up a wide scope of possibilities of tailoring the polymerization conditions for a given monomer. The Rh(I) complexes also show unusually high tolerance to functional groups of monomers and so the scope of substituted acetylene monomers which were polymerized with Rh(I)-based catalysts is very wide (Table I). Disturbing effects on the polymerization show mainly compounds that can reduce Rh(I) to Rh(0), such as aldehydes. Acetylene monomers bearing a carboxylic group should be polymerized under alkaline conditions (*i.e.*, transformed into salts) or in the form with protected carboxyl groups, as carboxylic acids easily form Rh(I) carboxylato complexes, which usually show low or no polymerization activity in the polymerization of acetylenes^{27,61}.

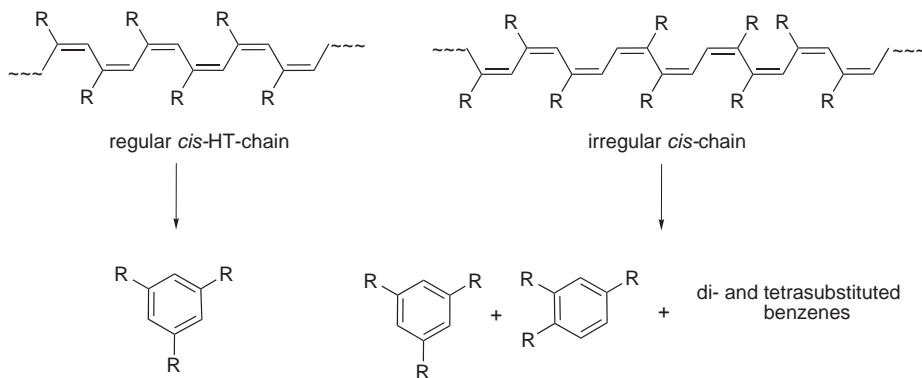


FIG. 11

Scheme of cyclotrimerization cleavage of a regular and irregular polyvinylene chain

TABLE I
Substituted acetylenes polymerized with various Rh(diene) complexes:

1 $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$	1* $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-Cl})_2]$
2 $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-OMe})_2]$	2* $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-OMe})_2]$
3 $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{PPh}_3)_2]$	4 $[\text{Rh}(\text{CPh}=\text{CPh}_2)(\text{nbd})(\text{PPh}_3)_2]$
5* $[\text{Rh}^+(\text{cod})\{\text{CH}_3\text{CO}^-\text{CHCOO}(\text{CH}_2)_2\text{OCOC}(\text{CH}_3)=\text{CH}_2\}]$	
6 $[\text{Rh}^+(\text{nbd})(\eta^6\text{-Ph-BPh}_3)^-]$	7* $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-S-C}_6\text{F}_5)_2]$
8 $[\text{Rh}^+(\text{nbd})(\text{Tosyl}^-)(\text{H}_2\text{O})]$	8* $[\text{Rh}^+(\text{cod})(\text{Tosyl}^-)(\text{H}_2\text{O})]$
9* $[\text{Rh}^+(\text{cod})(\text{tripyrazolylborate})^-]$	10* $[\text{Rh}(\text{cod})_2]\text{BF}_4^-$

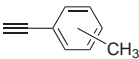

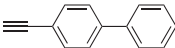
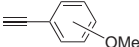
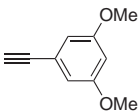
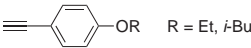
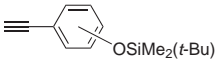
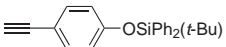
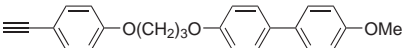
Monomer	Catalyst	References
Substituted phenylacetylenes		
	1,1*,2,2*,3,4,5*,6,7,8,8*,9	<i>o</i> - ^{27,62} ; <i>p</i> - ^{49,63-66}
	1,2*	Bu, <i>t</i> -Bu ⁵² ; 1-C ₅ H ₁₁ ^{67,68}
	1,3	27,69
	1,2,2*,3,4,6,7*	<i>o</i> - ^{27,70} ; <i>m</i> - ^{27,70} <i>p</i> - ^{27,52,63,64,70-72}
	3	27
	1	72,73
	1	<i>m</i> -; <i>p</i> - ⁶⁹
	1	69
	3	74

TABLE I
(Continued)

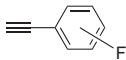
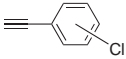
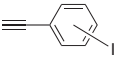
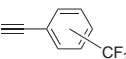
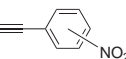
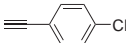
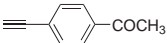
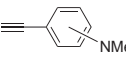
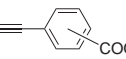
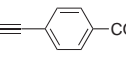
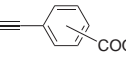
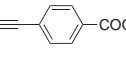
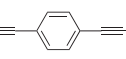
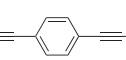
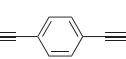
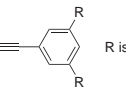


Monomer	Catalyst	References
Substituted phenylacetylenes		
	2*	<i>o</i> - ⁶⁷ ; <i>p</i> - ^{67,68}
	1,4,9*	<i>m</i> - ^{41,42} ; <i>p</i> - ^{41,47,63,66}
	2,2*	<i>m</i> -, <i>p</i> - ^{75,76}
	1,2,2*,3,6	<i>o</i> - ^{27,57,70}
	1,2,9*	<i>p</i> - ^{41,77,63}
 	9*	66
	1	<i>p</i> - ⁴¹
	1,2,3,4,6,7*,9*	<i>m</i> - ^{27,70} ; <i>p</i> - ^{27,52,63,64,66,70,71}
	4	78
	3	<i>p</i> - ²⁷
	1	<i>n</i> = 6, 12 ⁷⁹
	2,2*,3	76,80,81
 X = H, I, CN	2*,3	76
	2*,3	76,80
 R is:  or 	1	82

TABLE I
 (Continued)

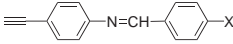
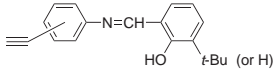
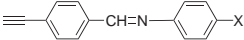
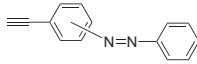
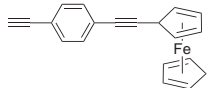
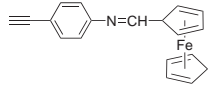
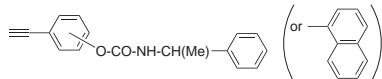
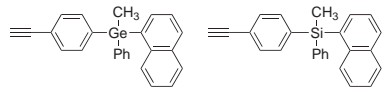
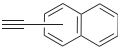




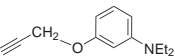
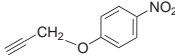
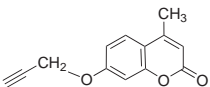
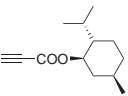
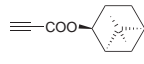

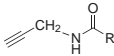
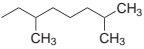
Monomer	Catalyst	References
Substituted phenylacetylenes		
	X = H, Me, <i>t</i> -Bu, F, Br, CN, NO ₂ , NMe ₂ , OH, C≡CSiMe ₃	1*, 2* 76,83,84
		1 <i>m</i> -, <i>p</i> - ⁸⁵
	X = Me, <i>t</i> -Bu, F, Br, I, CN, NO ₂ , C≡CSiMe ₃	2* 76,83
		1 <i>m</i> -, <i>p</i> - ⁸⁶
		2 76,87
		2* 76
		1 <i>m</i> -, <i>p</i> - ⁶⁹
		1 88,89

TABLE I
(Continued)

Monomer	Catalyst	References	
Other substituted acetylenes			
	1	α - ⁹⁰ ; β - ⁶⁹	
\equiv - <i>t</i> Bu	6	70	
  	6	70	
	1	61	
 	2*,3	76	
	3	76	
 	1	91,92	
\equiv -COOH \equiv -COONa	10*	93	
\equiv -COO(CH ₂) ₆ OCO-  -O(CH ₂) ₆ CH ₃	1	94	
\equiv -COOR	R = (CH ₂) _n CH ₃ (n = 2 to 14), (CH ₂) ₄ Cl, (+) or (-)-(CH ₂) _n CH(CH ₃)C ₂ H ₅ (where n = 0 to 5)	1	92,95,96
 R = Me, Et, Pr, <i>i</i> -Pr, Bu, <i>t</i> -Bu, pentyl, heptyl		6	97

* The list of monomers as well as catalysts and papers is not comprehensive.

So far only monosubstituted acetylenes (ethynyl monomers) have been polymerized with Rh(I) complexes to give polyvinylenes (see Table I). There is no example of successful homopolymerization of a disubstituted acetylene published in the literature; only negative results are reported, *e.g.* ref.⁶² However, Jun *et al.*⁹⁸ have recently reported the alternating copolymerization of disubstituted acetylenes and aldehydes to give polyketones with saturated main chains (see below). It further seems that only monosubstituted acetylenes which contain an electron-withdrawing substituent can be polymerized with neutral Rh(I) complexes (in cyclohex-1-en-1-yl-acetylene, the electron density on the triple bond is lowered due to conjugation). Alkylacetylenes have been polymerized only by the ionic Rh complex **6** and, recently, also with the [Rh(nbd)(acac)] complex⁹⁹. Zwitterionic complex **9*** was found to be inactive.

The above observations suggest that the polymerizability of an ethynyl monomer is a function of its ethynyl group acidity, besides other factors. The existence of such a dependence was demonstrated on a systematic series of 4-substituted *N*-(4-ethynylbenzylidene)anilines, for which a close correlation between the Hammett σ constant and the ¹H NMR shift of acetylenic proton and polymer yield has been observed^{83,100}. Qualitatively similar results were obtained with a series of 4-substituted PAs, for which the polymerization rate increases in the following order of substituents: OMe < H < COOCH₃ (ref.⁶⁴). The last observation as well as solvent effects observed in the polymerization of PA, has led Ogawa *et al.*⁶⁴ to the proposal of a propagation mechanism in which proton transfer from a coordinated monomer molecule to the last monomeric unit of the growing chain is assumed. However, a solid evidence for such mechanism has not yet been given.

4.3. Living Polymerization of Acetylenes with Rhodium Catalysts

The first partly successful approach to the living polymerization of acetylenes with a rhodium catalyst was accomplished as early as in 1990 by Tabata *et al.*⁴² who polymerized (3-chlorophenyl)acetylene with [Rh(nbd)₂(μ -Cl)₂] in the presence of triethylamine (Et₃N). They found that Et₃N increases the catalyst efficiency (up to a value of 0.2) as well as the lifetime of growing species.

A true living polymerization of a substituted acetylene with the Rh-based catalyst was first reported in 1994 by Kishimoto *et al.*⁷¹, who polymerized PA with the mononuclear complex [Rh(C \equiv CPh)(nbd)(PPh₃)₂] (Fig. 12) in the presence of 4-(dimethylamino)pyridine (DMAP). The latter was found

to be essential for the living polymerization to be achieved. They also prepared the poly[PA-*block*-(4-methoxyphenyl)acetylene] block copolymer, thus strongly supporting their discovery. They prepared the catalyst by reacting $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$ with $\text{LiC}\equiv\text{CPh}$ and PPh_3 (mole ratios 1:2.5:4.5) in diethyl ether, and characterized it by single-crystal X-ray analysis. The *in situ* formation of the complex is also possible: it was shown to proceed in the systems in which either $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-OMe})_2]$ or a mixture of $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$ and NaOMe is reacted with PA in the presence of PPh_3 (Fig. 12)^{27,74}. Detailed NMR analysis of the copolymer of PA and ^{13}C -labeled PA ($\text{H}^{13}\text{C}\equiv^{13}\text{CPh}$) demonstrated⁷¹ that the PA molecule enchainment takes place by the insertion mode (see Fig. 8). A solid-state NMR study of the labeled copolymer¹⁰¹ has confirmed the conclusion.

Kishimoto *et al.* have assembled series of evidences^{27,71,74} that enabled them to formulate a mechanism of PA polymerization with their catalyst system. As to the propagation, the main evidences are as follows:

- The isolated PPA with a narrow molecular weight distribution (MWD) prepared by the living polymerization induced with $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{PPh}_3)_2]$ in the presence of DMAP contains on average: 1 Rh(I) atom, 1 atom P, and 1 nbd molecule, per one macromolecule.

- The above PPA induces polymerization of another portion of PA (or a ring-substituted PA), during which the narrow polymer MWD is preserved if 1 equivalent of PPh_3 (relative to Rh) is added to the reaction mixture, but broadened if PPh_3 is not added (see also ref.¹⁰²).

These observations strongly indicate that the growing species contain, in addition to a growing PPA molecule, two permanently bound ligands: nbd and PPh_3 , and that the added PPh_3 controls the propagation process *via* si-

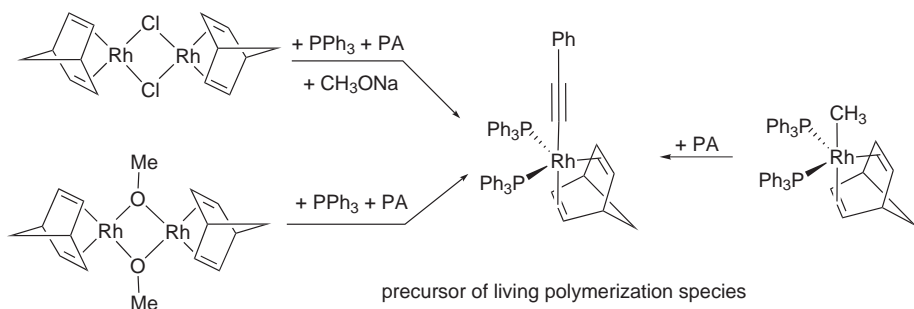


FIG. 12

Catalyst for living polymerization introduced by Kishimoto, Noyori *et al.*^{27,71,74}

multaneous coordination to the growing species. These conclusions are consistent with the propagation mechanism shown in Fig. 13.

Evidences providing an insight into the initiation mechanism and a role of DMAP in the living polymerization system are as follows:

- Low-molecular-weight PPA prepared by using the ^{13}C -labeled catalyst, $[\text{Rh}(^{13}\text{C}\equiv^{13}\text{CPh})(\text{nbd})(\text{PPh}_3)_2]$, is not ^{13}C -enriched, which indicates that the polymerization does not start by the direct insertion of a PA molecule into the $\text{Rh}-\text{C}(\equiv\text{CPh})$ bond.

- Diphenylbuta-1,3-diyne is formed as side product of the polymerization conducted in the presence of DMAP and, if the ^{13}C -labeled initiator is used, the labeled $\text{PhC}\equiv\text{C}-^{13}\text{C}\equiv^{13}\text{CPh}$ isomer is formed (Fig. 14).

- In the absence of DMAP, diphenylbuta-1,3-diyne is not observed among the products of the reaction performed at a catalyst:PA ratio of 1:1.2 but, instead, the dinuclear rhodacyclopentadiene complex (Fig. 15) is isolated (yield 30%; for X-ray crystallographic analysis, see supplement material to ref.²⁷).

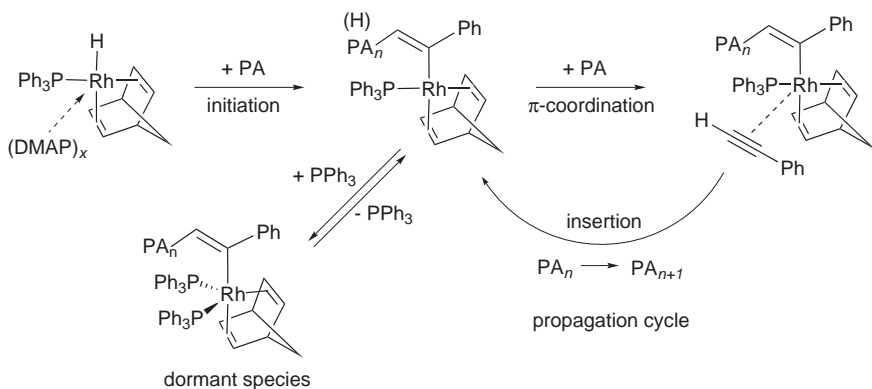


FIG. 13

Proposed mechanism of the initiation and propagation with the Kishimoto-Noyori catalyst

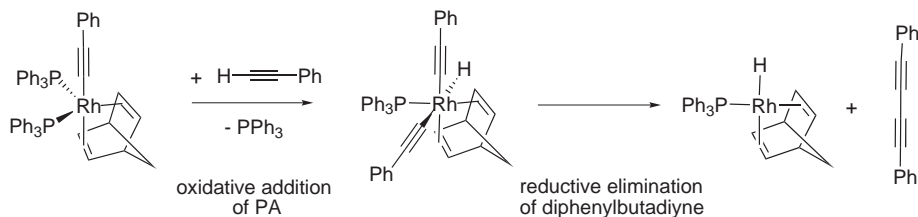


FIG. 14

First steps of the transformation of the Kishimoto-Noyori catalyst to active species

- The rhodacyclopentadiene complex also induces PA polymerization, however, not the living one (it gives 30% yield of PPA of $M_n = 175\ 000$ and $M_w/M_n = 2.45$ after 4 h reaction at a PA/catalyst mole ratio 50).

The above observations indicate that the initiation of PA polymerization starts by the formation of diphenylbuta-1,3-diyne, most probably according to the scheme shown in Fig. 14. Attempts to isolate the proposed Rh hydride species were unsuccessful, which can be explained by their fast transformation to growing species (in the presence of DMAP, see Fig. 13) or to rhodacyclopentadiene species (in the absence of DMAP), or other not yet identified Rh species. Kishimoto *et al.* have suggested a tentative mechanism of the dinuclear rhodacyclopentadiene complex formation (Fig. 15), consisting of (i) the addition of Rh hydride species to a diphenylbuta-1,3-diyne molecule (both being formed in the first stage of initiation, see Fig. 14) to give Rh enyne species, (ii) *cis*-insertion of PA molecule into the Rh-C bond of the Rh enyne species to give Rh species with PA-trimer ligand, and (iii) cyclization of the trimeric ligand. Final oxidative ring-closure is assumed to be assisted by $\eta^2:\eta^2$ -coordination of $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{PPh}_3)_2]$ species to the metallacycle due to the formation of the metal-metal bond, giving a closed-shell structure involving two Rh atoms.

The above findings of Kishimoto *et al.* and the conclusions drawn from them are also of importance for the reaction systems with bridged catalytic species (*e.g.*, systems with μ -chloro and μ -methoxo Rh complexes), in which the formation of Rh ethylidene species is taken into consideration as a part of the initiation (see above). Thus, it seems probable that the formation of rhodacyclopentadiene species is the reason for the low initiator efficiency observed generally for these systems and that the inhibition of side reactions similar to those depicted in Fig. 15 is a rational lying behind the positive effect of Et_3N observed by Tabata *et al.*⁴²

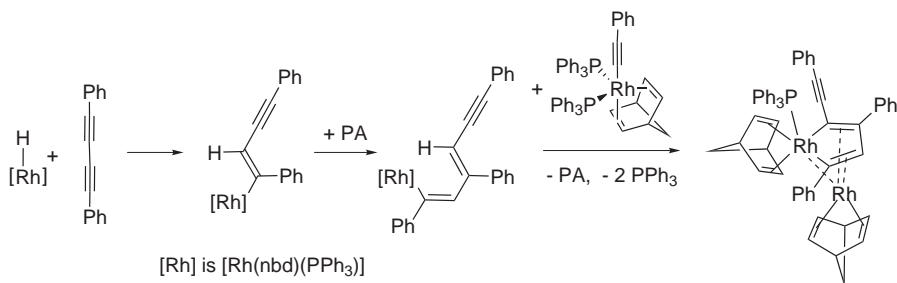


FIG. 15

Proposed mechanism of formation of the dinuclear rhodacyclopentadiene complex

Another path to the Rh-based catalysts for living polymerization of substituted acetylenes has been developed by Masuda *et al.*^{63,103–105} who designed systems in which the initiation does not include the formation of Rh ethynyl species. They reacted the $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$ complex with $\text{Ph}_2\text{C}=\text{CPhLi}$ in the presence of PPh_3 to obtain growing species with σ -bound vinylic ligand directly (Fig. 16). In this tricky way, they avoided the above-discussed complications with side reactions of the Rh ethynyl species.

First the ternary catalyst system composed of $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$, $\text{Ph}_2\text{C}=\text{CPhLi}$ and PPh_3 in the molar ratios 1:4:6 was introduced (the complex contains two Rh atoms and the stoichiometric excess of $\text{Ph}_2\text{C}=\text{CPhLi}$ is used to eliminate partial decomposition of this compound by traces of moisture)¹⁰³. This catalyst system was shown to induce quantitative living polymerization of PA, ring-substituted PAs carrying groups such as CH_3 , OCH_3 , Cl , COOCH_3 and COOCPh_3 in the para position^{63,78}, propiolates (prop-2-ynoates) and propargyl (prop-2-yn-1-yl) derivatives (see below). The catalyst also facilitates synthesis of block copolymers and star polyvinyl-ene¹⁰⁶. The presence of a bulky group such as phenyl or *tert*-butyl group on the α -carbon of the vinyl ligand was found to be a key factor in obtaining a living polymerization system¹⁰⁴. Besides, the presence of free PPh_3 in the reaction mixture is necessary for a good control of MWD of polyvinylene under formation (see Fig. 13).

Attempts to isolate the $[\text{Rh}(\text{nbd})(\text{PhC}=\text{CPh}_2)]$ complex with PPh_3 ligand were not successful. However, analogous complexes with $\text{P}(4\text{-F-Ph})_3$ and $\text{P}(4\text{-Cl-Ph})_3$ auxiliary ligands (where 4-F-Ph stands for 4-fluorophenyl and 4-Cl-Ph for 4-chlorophenyl) were isolated and the latter was characterized by X-ray diffraction¹⁰⁵, which has shown the presence of only one auxiliary ligand in the complex (Fig. 17). This is in accord with the above stated role of the excess PPh_3 consisting in controlling the propagation *via* temporary binding to Rh atoms of active species resulting in slowing down the propagation but narrowing MWD of the resulting polymer. Both these complexes

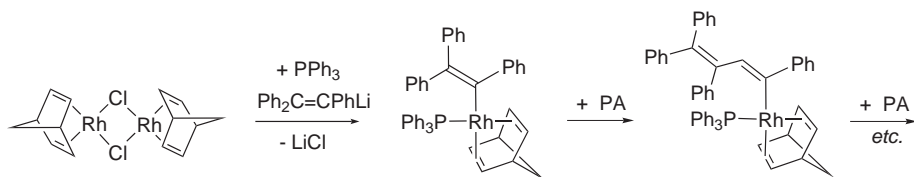


FIG. 16 Catalysts for living polymerization developed by Masuda and Misumi^{63,103–105}

induce living polymerization of PA and PA derivatives¹⁰⁵ giving polymers of low polydispersity (about 1.05) at the initiator efficiency of 100%. They also enable synthesis of conjugated block copolymers.

Masuda *et al.* actually developed not only one catalyst but a new class of catalysts for controlled synthesis of polyvinylenes. They proved namely that the vinylic ligand of their catalysts is transformed to the end group of the formed PPA macromolecule (Fig. 16) and, by using $[4-(\text{Me}_2\text{N})\text{C}_6\text{H}_4]_2\text{C}=\text{CPhLi}$ instead of $\text{Ph}_2\text{C}=\text{CPhLi}$, that a chemical modification of this ligand opens a way to tailored, end-functionalized polyvinylenes¹⁰³ (Fig. 17). Feasibility of this approach was also demonstrated on the synthesis of poly(phenylacetylene-*block*-propiolactone) copolymer¹⁰⁷ by polymerizing PA with the catalyst containing vinylic ligand carrying the *t*-BuMe₂SiO group which was introduced as the end group of the resulting PPA. By treating with Bu₄NF and then with NaH, they transformed the *t*-BuMe₂SiO end groups into ONa groups, on which β -propiolactone was polymerized to obtain the block copolymer in question.

So far the latest described living polymerization system has been reported by Farnetti *et al.*¹⁰⁸ who polymerized PA with $\{[\text{Rh}(\text{nbd})]_2(\mu\text{-OMe})_2\}$ complex in the presence of didentate phosphines $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2, 3$ and 4 ; mole ratio of components 1:1). For the system with 1,4-bis(diphenylphosphino)butane (dppb), they observed a low polydispersity (from 1.09 to 1.33) of the formed PPA, approximately linear increase in its M_n value with increasing PA consumption and no formation of oligomers. However, the experiment with a polymerization of an additional portion of PA was not successful, since only one half of the second PA portion has reacted to give the polymer. The too low initiator efficiency is the weakest point of this catalyst. It provides PPAs with M_n values ranging from 270 000 (at PA:Rh = 25)

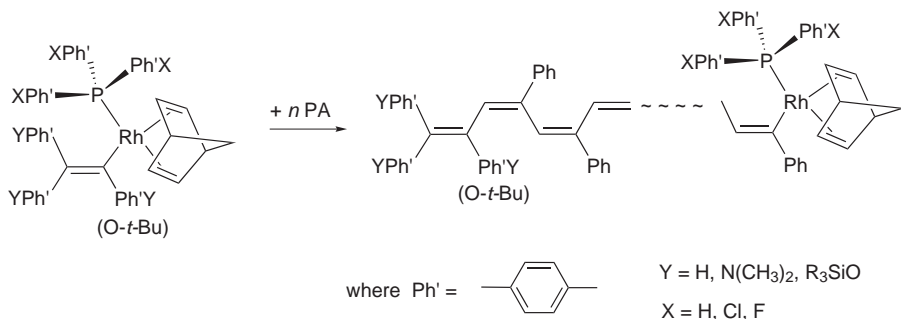


FIG. 17

Synthesis of end-functionalized polyvinylenes by the living polymerization induced with Masuda–Misumi catalysts

to 1 300 000 (at PA:Rh = 150), which gives an initiator efficiency of only 1%. For comparison, the catalyst systems introduced by Kishimoto *et al.* and Masuda *et al.* show an initiator efficiency from 25 to 70% and 100%, respectively.

A rational lying behind living features of the above catalyst systems is not yet fully clear. When developing the living catalyst, Kishimoto *et al.*²⁷ also examined the effect of variation of phosphine ligand on the catalytic properties of $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{PR}_3)_2]$ species and found that a replacement of both PPh_3 ligands with two PPh_2Me ligands or one $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (dppb) didentate ligand makes their catalyst almost or totally inactive. However, Farnetti *et al.* found that the reaction of $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-OMe})_2]$ with dppb gives three different Rh species (Fig. 18): (i) catalytically inactive species **I**, tentatively identified as tetracoordinated cationic species $[\text{Rh}(\text{nbd})(\text{dppb})]^+$, (ii) inactive species **IIa** identified (by NMR) as pentacoordinated $[\text{Rh}(\text{OMe})(\text{nbd})(\text{dppb})]$ having OMe in the axial position and the equatorially bound dppb ligand, and (iii) catalytically active isomeric species **IIb** with OMe in the equatorial position and dppb bound in meridian position (Fig. 18). Upon addition of 10 equivalents of PA to a solution of all the above species in a mixture of $\text{Et}_2\text{O} + \text{C}_6\text{D}_6$ (1:1), in which the formed PPA is insoluble, **IIb** disappears, **I** and **IIa** remain and new unidentified species appear, which are assumed to be formed from **IIb**. It is worth noting that species **IIa** with an axial MeO ligand corresponds to $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{dppb})]$ which was found inactive by Kishimoto *et al.* Therefrom, Farnetti *et al.* concluded that species **IIb** are precursors of the observed living polymerization centers. However, this means that also **IIb** shows very low catalyst efficiency, up to only 3% (taking into account the 35% content of **IIb** in the catalyst system, Fig. 18). It is clear that the Rh(dppb) system needs further investigation and development to become an effective living polymerization system.

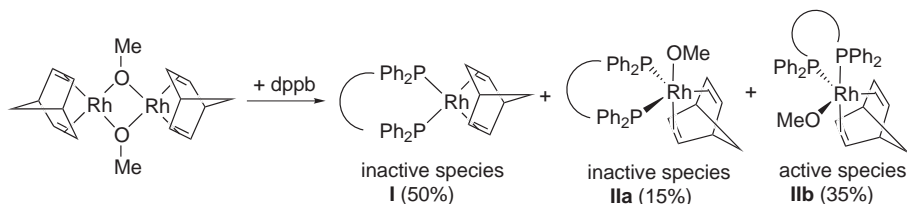


FIG. 18

Polymerization catalyst system introduced by Farnetti *et al.*¹⁰⁸

It is worth mentioning that all the known Rh-based catalysts that induce living polymerization of acetylenes contain exclusively the nbd ligand and that their cycloocta-1,5-diene (cod) counterparts have never been found to induce a living polymerization^{27,36}. The reason is a stronger σ -donating as well as stronger π -back-bonding capability of the nbd ligand compared with the more flexible cod ligand. Individual attributes of the living polymerization, typically consumption of a second monomer portion (see, *e.g.*, refs^{42,83}), are occasionally observed with other systems; however, the other features of the living polymerization, in particular high catalyst efficiency, are usually missing.

4.4. Helical Polyvinylenes, Columnar Structures

Rhodium catalysts have opened a way to substituted polyvinylenes carrying various side groups, through which physical properties of the polymers, such as non-linear optical properties and charge carrier photogeneration and transport in these materials, can be tuned (see, *e.g.* refs^{41,79,81,86}). Another possibility of tuning the functional properties of *cis-transoid* polyvinylenes consists in packing their highly stereoregular molecules to well organized structures. As mentioned above, already Kern³⁷ (in 1969) has proposed the helical conformation for PPA molecules prepared with the Wilkinson catalyst. However, this topic was not studied more in detail until 1991 when Tabata *et al.*¹⁰⁹ observed a solvent-induced crystallization (toluene was found as preferable solvent) of an amorphous, high-molecular-weight *cis-transoid* PPA prepared with $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$. This transition was later observed for other *cis-transoid* polyvinylenes, too^{75,90,110,111}. It was recognized that, in these crystallites, macromolecules adopting the helical conformation are hexagonally packed to regular nanostructures which they called columnar structures^{73,95,96}. Hexagonal packing was interestingly found to make polyvinylenes, mainly poly(propionic ester)s, more resistant to autoxidative degradation^{112,113}. The macromolecules assembled in columnar nanostructures were found to undergo the *cis-to-trans* isomerization when exposed to high pressure^{73,95,110,114,115}, UV or γ irradiation^{116,117}. The radical mechanism has been proposed for this isomerization.

The self-assembling process is accompanied by a deep color change of the polyvinylene (Fig. 19). Amorphous *cis-transoid*-HT-polyvinylenes are usually bright yellow or orange, while those transformed into the hexagonal nanocrystalline state are typically bright red^{73,75,95,96,109,111,112}. The polymer color depends on the achieved degree of microcrystallinity^{95,113}. Perhaps the most interesting is the behavior of polymers of (4-alkoxyphenyl)acetylenes

which, upon transition to the columnar structure state, show profound dependence of the color on the alkyl substituent length. PPAs with short alkyl chains (*ca* up to C₅) in the alkoxy substituent are red while those with longer alkyl chains (about C₁₀) are almost black. The amorphous-to-crystalline state transition of these polymers proceeds quite smoothly being, most probably, facilitated by the fluidity of alkyl chains domains. The amorphous-to-columnar state transitions of these polymers are reported to be reversible; a polymer in the columnar state can be dissolved and precipitated to give the yellow amorphous polymer, which can repeatedly be transformed into the columnar state¹¹⁸.

Research of columnar polyvinylenes has revealed that the unprecedented HT-*cis-transoid* stereospecificity of Rh(I) catalysts affords a synthesis of highly stereoregular polymers that can spontaneously adopt a helical conformation. It was found that *cis-transoid* macromolecules of substituted polyvinylenes with bulky pendent groups partly adopt this conformation also in solution. The more bulky the side groups the longer are helical sequences of dissolved macromolecules^{89,97,119}, which indicates disturbing effect of the microbrownian motion of their segments. In the case of poly(propionic ester)s and poly(propionic amide)s, which smoothly adopt the helix conformation, a stabilization of their regular helical conformations *via* strong interactions associated with the presence of polar carboxy and carboxamide groups can be suggested^{91-94,97,119}.

The presence of chiral pendent substituents increases the tendency of polyvinylene molecule to adopt helical conformation^{89,91,112,120,121}, as intuitively expected due to better preconditions for van der Waals binding of groups located on neighboring threads of the helix. However, if the chiral groups are removed, *e.g.*, by hydrolysis, the modified polymer does not

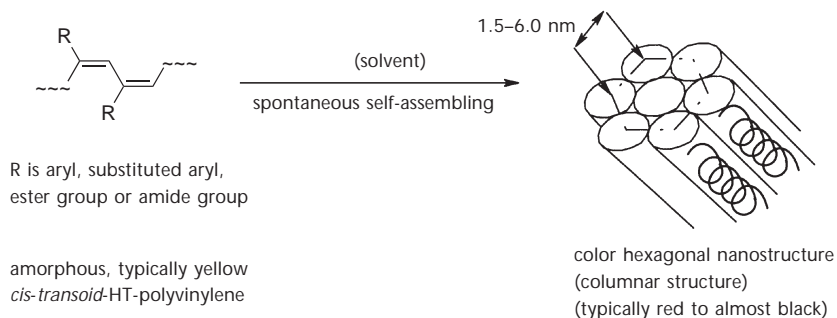


FIG. 19
Solvent-induced formation of hexagonal nanostructures of substituted PPAs

maintain its helical conformation in solution (see note 4 in ref.¹²²), which indicates a close correlation between the chirality of side groups helical conformation of molecules of these polymers.

Aoki *et al.* have recently reported¹²² the synthesis of helical *cis-transoid* polyvinylenes from achiral substituted acetylenes consisting in a use of the chiral Rh catalyst system. They polymerized [4-(dodec-1-yloxy)-3,5-dihydroxyphenyl]acetylene with $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$ in the presence of a chiral amine such as (*R*)-dimethyl(1-phenylethyl)amine, (*S*)-dimethyl(1-phenylethyl)amine and (*R*)-(1-phenylethyl)amine (using Rh/N mole ratio 1/250) and found that these catalyst systems induce a helix-sense-sensitive polymerization of this achiral monomer. They found that the helix sense of formed molecules is controlled by the cocatalyst chirality and that helical conformations of formed molecules are intrinsically stabilized by intramolecular hydrogen bonds involving hydroxyl side groups. The hydrogen-bond stabilization of the helix is lowered in polar solvents so as the polymer shows solvatochromism. A chloroform solution of the prepared helical polymer is reported to show stable circular dichroism for at least 5 months when kept at room temperature as well as when heated to 50 °C for a short time. If one or both OH groups of the monomer are replaced by MeO groups, solutions of corresponding polymers do not show any circular dichroism. If the dihydroxy monomer is copolymerized with the dimethoxy one, helicity of the formed copolymer molecules dramatically decreases with increasing amount of the methoxy comonomer, approaching zero value at about equimolar content of comonomeric units.

Aoki *et al.* suggested the bridge-splitting of $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$ by amines affording mononuclear species $[\text{Rh}(\text{nbd})\text{Cl}(\text{amine})]$ as a rational lying behind the observed effect of chiral amine cocatalysts¹²². The chiral amine bound as a ligand in a mononuclear growing species can really effectively control the stereochemistry of propagation. This is in analogy with explanation suggested by Tabata *et al.* concerning the role of Et_3N in their almost-living polymerization system⁴⁷. The bridge-splitting of dinuclear rhodium species by amines is considered as important step also in the atom transfer radical polymerizations induced with dinuclear Rh catalysts¹²³ (see Chapter 6) and in anchoring Rh complexes on mesoporous supports^{68,124–126} to obtain heterogeneous polymerization catalysts (see Chapter 5).

Research of all the above classes of the helical π -conjugated polymers is undoubtedly important, since such polymers are potentially useful as polarization-sensitive electrooptical materials for asymmetric electrodes and sensors.

4.5. Ring-Opening Polymerization of Cycloalkynes

As mentioned above, no internal alkyne is known that undergoes polymerization to the corresponding polyvinylene under the assistance of a rhodium catalyst. However, Jun *et al.*^{98,127} have recently discovered that, in the presence of 2-amino-3-methylpyridine, cyclohexylamine and a Lewis acid such as AlCl_3 , both $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-Cl})_2]$ catalyze a chelation-assisted hydroacylation of internal alkynes (dimethyl-, diethyl-, diprop-1-yl-, methyl-*t*-butyl- and dipent-1-ylalkynes) followed by retro-Mannich type fragmentation of the resulting α,β -unsaturated ketimine. Hydrolysis of the fragmentation products provides the corresponding ketones. Encouraged by these results, Jun *et al.* carried out this reaction with cyclododecyne as the substrate and obtained oligomeric polyketimidine, which is easily hydrolyzed to the corresponding polyketone (Fig. 20). From the general viewpoint, this reaction can be regarded as the ring-opening polymerization of cycloalkynes to regularly functionalized polymers with saturated main chains.

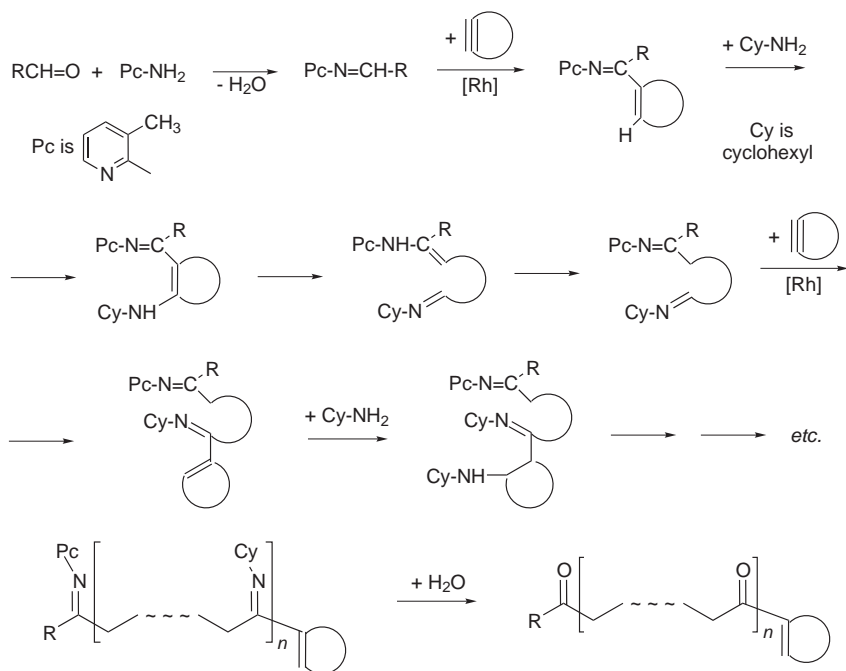


FIG. 20

Scheme of the one-pot ring-opening polymerization of cycloalkynes to regularly functionalized oligomers developed by Jun *et al.*⁹⁸

5. SUBSTITUTED ACETYLENES - HETEROGENEOUS POLYMERIZATION SYSTEMS

5.1. Polymerization with Immobilized Rhodium Complexes

The purity of specialty polymers with potential applications in areas such as electronics, medicine and pharmacy, as well as the possibility of recycling a catalyst, is of increasing importance from the technical, ecological and economical point of view. If a polymer is prepared by homogeneous coordination polymerization, transition-metal-catalyst residues buried in the polymer can prevent it from a practical use. The residues may be toxic, which is inadmissible for any application of the polymer in medicine or pharmacy. In conjugated polymers, the catalyst residues can act as dopants or, on the contrary, as quenchers of excited states or traps of charge carriers. Removal of the residues is a time-consuming, expensive process in which waste solvents are uselessly produced. Besides, rhodium catalysts are rather expensive, so as recycling of them is of high economical importance at considerations on their technological applications. The development of heterogeneous polymerization systems enabling facile isolation of used catalysts from reaction mixtures and their recycling unambiguously meets the above demands of practice for future low-cost, environment-friendly technologies of production of pure specialty polymers.

The idea of the use of recyclable heterogeneous catalysts is simple, well known, and for about hundred years successfully established in the industrial production of low-molecular-weight chemicals. However, the use of recyclable heterogeneous catalysts in polymer synthesis faces difficulties arising from the dimensions of macromolecules, which are too large to be released from the catalyst pores. These so-called transport limitations were clearly demonstrated in the first heterogeneous polymerizations of acetylene monomers, which were performed more than ten years ago. Acetylene, propyne and but-1-yne were polymerized with H-ZSM5 zeolites and Co(II)- and Ni(II)-exchanged zeolites¹²⁸⁻¹³¹. These experiments gave inorganic matrix - conjugated polymer composites; attempts to isolate the formed polymers by dissolving the matrix in dilute hydrofluoric acid were unsuccessful, yielding hydrofluorinated polymers. Nevertheless, composites containing organic-polymer nanowires are also of interest because they are believed to find practical applications in energy storage and related fields¹³²⁻¹³⁴. In the last two years, various composites of polyacetylenes and mesoporous silica and alumina molecular sieves have been prepared and studied as to their functional properties¹³⁴⁻¹³⁷.

The preparation of isolable polymers with microporous catalysts (pore-diameter up to 2 nm) such as those based on classic zeolites is practically impossible because of transport limitations existing for macromolecules in narrow pores. Macromolecules can hardly escape from narrow pores of typical diameter, d , from 0.4 to 1 nm. As a result, they remain confined in pores thus inhibiting further polymerization and, in addition, the formed polymer cannot be isolated without the catalyst decomposition. Transport limitations can be overcome by using mesoporous polymerization catalysts with pore diameter above *ca* 3 nm (Fig. 21) instead of microporous ones. Such catalysts can be prepared by a direct or indirect (*via* anchoring ligands) immobilization of active homogeneous catalysts on inner walls of mesoporous, inorganic or organic supports.

Among inorganic supports, mesoporous molecular sieves are perhaps the most promising materials, since they typically have narrow pore-size distribution and their pore size and pore architecture can be tuned¹³⁸⁻¹⁴¹. They are increasingly used as supports to immobilize transition-metal catalysts for transformations of hydrocarbons^{138,142} and also for the polymerization of alkenes¹⁴³ and ring-opening metathesis polymerization of norbornene¹⁴⁴. Recently, Rh(diene) complexes such as $[\text{Rh}(\text{cod})_2(\mu\text{-Cl})_2]$ and $[\text{Rh}(\text{cod})_2(\mu\text{-OMe})_2]$ have also been anchored on all-siliceous mesoporous sieves MCM-41 ($d = 3.7$ nm), MCM-48 ($d = 3.7$ nm) and SBA-15 ($d = 7.4$ nm) and the resulting mesoporous catalysts have been successfully used in the polymerization of PA⁶⁷ and ring-substituted PAs¹²⁴⁻¹²⁶ giving high yields of isolable *cis-transoid* polymers. $[\text{Rh}(\text{cod})_2(\mu\text{-OMe})_2]$ has been immobilized from solution at room temperature by its direct reaction with silanol groups of the support, in which methanol is formed as a side product. Commercially available $[\text{Rh}(\text{cod})_2(\mu\text{-Cl})_2]$ complex does not react with silanol

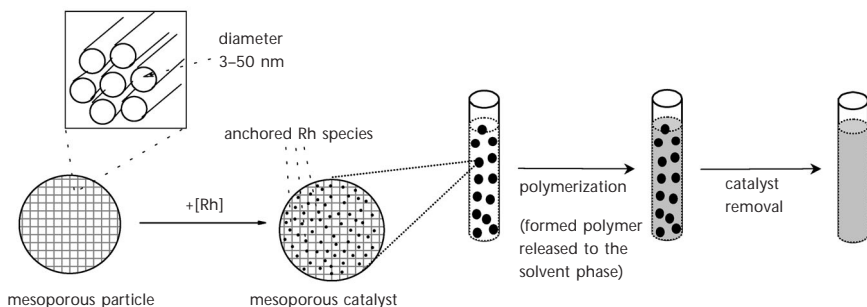


FIG. 21
Polymerization with Rh catalysts immobilized in pores of a mesoporous support

groups under the same reaction conditions. However, it is smoothly anchored on mesoporous sieves modified by a reaction with 3-(trimethoxysilyl)propylamine, in which amino groups are linked to the inner walls of the support as anchoring ligands for the Rh complex (see Fig. 21).

Another support used for immobilization of homogeneous catalysts is commercial (Hoechst-Celanese Corporation) polybenzimidazole (PBI; for the structure see Fig. 22) available as porous beads. PBI is known as a thermally very stable polymer, which is resistant to oxidation, and which is insoluble in common solvents due to the rigidity of polymer chains and interchain hydrogen bonding. Dry PBI beads have a foam-like morphology, as revealed by SEM¹⁴⁵, and they do not appear to be a good support for a catalyst. They have a pore volume of 0.11 cm³/g and the overall BET surface area about 20 m²/g, of which 10 m²/g is the surface of macropores and 10 m²/g the surface of meso- and micropores in the walls between macropores. However, upon exposure to a solvent such as THF, water, and toluene, the inner walls swell and a high number of mesopores of desired diameters is formed in them¹⁴⁵ (Table II). Even if the smallest mesopores would not be accessible, there are many wider mesopores of *d* from 10 to 20 nm in the PBI support, in which catalyst species can be easily immobilized and transport limitations for formed macromolecules should be almost absent.

PBI beads have been already used as a support for immobilization of metal complexes to give oxidation and epoxidation catalysts¹⁴⁶⁻¹⁴⁸. Recently, [Rh(cod)]₂(μ-Cl)₂ has also been anchored on PBI beads to give heterogeneous catalyst that is active in polymerization of PA and ring-substituted PAs to *cis-transoid* polymers⁶⁸. Imidazole moieties of the PBI support are assumed as anchoring ligands for rhodium species in analogy with binding of Rh atom in complexes having modified purine bases as ligands¹⁴⁹. Another polymer-anchored Rh(I) catalyst has been prepared by the copolymerization of an Rh(cod) complex containing 2-(acetoacetoxy)ethyl methacrylate ligand with acrylates and cross-linkers. This catalyst also induces polymerization of PA and 4-methyl-PA to *cis-transoid* polymers¹⁵⁰.

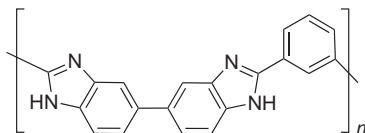


FIG. 22

Structure of polybenzimidazole which was used in the form of porous beads for immobilization of rhodium complexes to obtain heterogeneous polymerization catalysts

Experimental results obtained for both mesoporous-sieves- and PBI-anchored rhodium catalysts indicate that (i) polymerization takes place inside catalyst particles, (ii) the formed macromolecules are continuously released to the surrounding solvent phase, and (iii) leaching of active species from mesoporous supports is negligible^{67,68,124–126}. Such properties are sufficient for a use of these catalysts in a preparation of high-purity polymers. However, both these hybrid catalysts suffer from a termination of their active centers, which significantly lowers their activity if they are reused.

It is worth of noting that Rh complexes have also been anchored on polymers such as poly(styrene-*co*-divinylbenzene) or polyfluoroacrylate copolymers, to which phosphine binding sites have been introduced during copolymerization by using functionalized monomer^{151,152} or by an additional polymer modification¹⁵³. However, these complexes were tested as catalysts in reactions such as hydrogenolysis and hydrogenation but not in polymerization.

5.2. Polymerization in Ionic Liquids

Synthesis of compounds in systems containing an ionic liquid as a separate phase is a rather new method of the preparative chemistry, which is increasingly used in the last few years as an alternative to the heterogeneous catalysis, since it also enables easy isolation and effective recycling of a catalyst (the ionic one in particular). This method is based on a use of two-phase systems composed of a molten salt such as 1-butyl-3-methylimidazolium (BMIM) tetrafluoroborate or butylpyridinium (BuPy) tetra-

TABLE II
Characteristics of 250–500 μm PBI beads (data taken from ref.¹⁴⁵)

Solvent	Specific surface area, m^2/g of mesopores of diameter d , nm			Specific pore volume, cm^3/g of mesopores of diameter d , nm		
	3	10–20	40	3	10–20	40
Toluene	410	384	8	0.31	1.30	0.08
THF	490	643	14.5 ^a	0.37	2.25	0.29 ^a
Water	1040	227	15	0.78	1.02	0.15
No (dry PBI)	10 (micro- and mesopores in total)			0.11 (in total)		

^a $d = 80$ nm.

fluoroborate as a solvent for an ionic catalyst, and an organic liquid immiscible with the ionic one as a solvent for the products. If this method is applied in a polymerization, the formed polymer as well as the unreacted monomer(s) can be easily separated from the catalyst solution in the ionic liquid, which can be reused.

So far this polymerization method is perhaps the most frequently used in the atom transfer radical polymerization (ATRP). However, recently it was also applied in the ring-opening metathesis polymerization of norbornene with a cationic ruthenium allenylidene precatalyst¹⁵⁴ and in the polymerization of PA with complexes $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-Cl})_2]$, $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$, $[\text{Rh}(\text{acac})(\text{cod})]$ and $[\text{Rh}(\text{acac})(\text{nbd})]$ ¹⁵⁵ in the presence of Et_3N . High yields of PPA of M_w from 55 000 to 200 000 were obtained with both BMIM·BF₄ and BuPy·BF₄ ionic liquids and the last catalyst has been recycled without a significant loss in activity.

6. VINYL AND RELATED MONOMERS: ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

As it was already mentioned above (Introduction of this paper), as early as in 1963, Teyssié observed that styrene slowly polymerizes in the presence of Rh(III) catalysts by a free radical mechanism, in contrast to butadiene which polymerizes by a coordination mechanism under the same conditions. Soon after discovery of ATRP, which was accomplished with Ru and Cu complexes¹⁵⁶⁻¹⁵⁸, also rhodium complexes have been tested as to their ATRP activity. The first Rh complex-induced ATRP was accomplished with the Wilkinson catalyst $[\text{RhCl}(\text{PPh}_3)_3]$, styrene as monomer and 4-(CH₃O)C₆H₄SO₂Cl as initiator⁷⁰. However, rather poor control of the polymerization was achieved, $M_w/M_n \geq 1.8$. Better results were obtained for ATRP of methyl (MMA), butyl (BuMA) and 2-hydroxyethyl (HEMA) methacrylates with the same catalyst and (4-ClC₆H₄)₂CO as initiator¹⁵⁹. Polymers with M_w/M_n values down to 1.3 were prepared and shown to act as a macro-initiator in the consecutive polymerization of MMA and BuMA. Besides, a random copolymer of MMA and HEMA was prepared, and a positive effect of added water on the behavior of these ATRP systems was found.

Another ATRP-active Rh catalyst, $[\text{RhCl}(\text{CO})(\text{Et}_2\text{NH})(\text{PPh}_3)]$, was prepared by the bridge-splitting reaction of $[\{\text{Rh}(\text{CO})(\text{PPh}_3)_2(\mu\text{-Cl})_2\}]$ with Et_2NH ¹⁶⁰. Also with this catalyst, the ATRP of MMA yielded better results than that of styrene (M_w/M_n values of 1.43 and 2.08, respectively, are reported). Rh(I)(diene) complexes $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-4-MeC}_6\text{H}_4\text{O})_2]$ and $[\{\text{Rh}(\text{cod})\}_2\{\mu\text{-OCO}(\text{CH}_2)_{20}\text{CH}_3\}_2]$ have been reported as ATRP catalysts recently¹²³. By itself, they promote a con-

trolled polymerization of MMA ($\text{CH}_3\text{-C}(\text{CH}_3)\text{Br-COOME}$ initiator) and styrene (CH_3CHBrPh initiator), affording a medium to good yield of high-molecular-weight (M_w up to 400 000) polymers with M_w/M_n values from 1.45 to 1.65 but too low initiator efficiency (0.04 to 0.20). The addition of Bu_2NH was found to improve the initiator efficiency (up to 0.85) as well as the polymer molecular weight control (M_w/M_n down to 1.27) in both systems, but more distinctly for the μ -docosanoato catalyst. The bridge splitting of the dinuclear Rh complex with Bu_2NH is assumed to be responsible for this improvement, but corresponding mononuclear complexes have not been isolated.

7. SILANES

7.1. Cross-Dehydrocoupling Copolymerizations of Silanes

In the last few years, some Rh complex-catalyzed polymerizations of silanes have been introduced as new effective tools for the preparation of silicon polymers from relatively easily available monomers. One class of these reactions are cross-dehydrocoupling copolymerizations of bis(hydrosilane)s or dihydrosilanes with comonomers containing labile hydrogen, such as with diols¹⁶¹, silanediols¹⁶² and dithiols^{163,164} (Fig. 23), which easily proceed in the presence of the Wilkinson catalyst at ambient or little elevated temperature to give high-molecular-weight polymers including those that are in

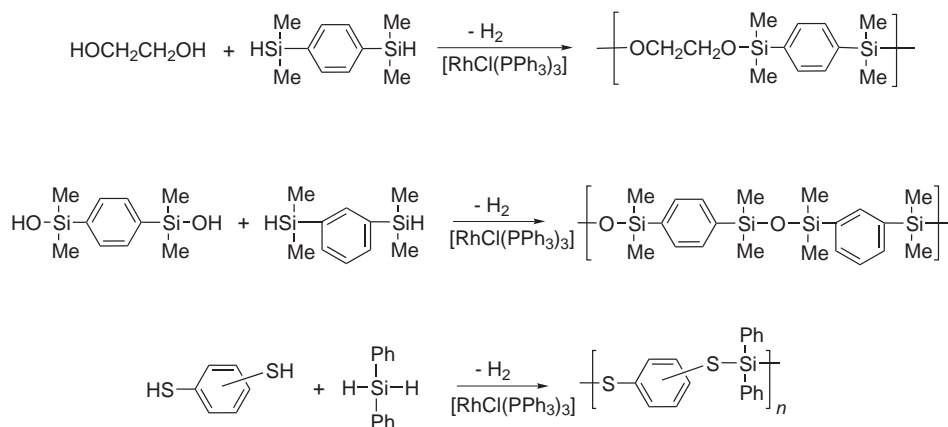


FIG. 23

Examples of the cross-dehydrocoupling copolymerization of hydrogen-containing silanes with a diol¹⁶¹, disilanol¹⁶² and dithiol¹⁶³

this quality hardly accessible by other polymerization reactions (*e.g.*, high-molecular-weight silane/diol copolymers). Also polymers with main-chain organometallic moieties can be prepared by these polycondensations¹⁶⁴.

7.2. Silylative and Hydrosilylative Polymerization

Other newly introduced processes open up the way to poly(silylenevinylene)s and related polymers which meet demands of practice for new field-responsive organic materials. The first of these processes is referred to as silylative coupling polycondensation of divinylsilanes and bis(vinylsilane)s, which, from the formal stoichiometry point of view, proceeds as metathesis, but their mechanism consists of the alternating sequence of Si-C and C-H bond cleavages¹⁶⁵⁻¹⁶⁷ (Fig. 24). The alternative process is based on the hydrosilylation of diethynyl compounds with bis(hydrosilane)s^{168,169}. The polymerization is catalyzed with $[\text{RhI}(\text{PPh}_3)_3]$ or a $[\text{RhCl}(\text{PPh}_3)_3]/\text{NaI}$ mixture, and it shows unusually distinctive, temperature-dependent stereoselectivity: *cis*-selectivity of *ca* 95% is observed at low reaction temperatures (0 to 20 °C) while, at 60 °C, *ca* 95% *trans*-polymer is formed.

7.3. Ring-Opening Polymerization

Cationic $[\text{Rh}(\text{cod})_2]^+\text{A}^-$ and $[\text{Rh}(\text{cod})(\text{dmpe})]^+\text{A}^-$ complexes (A = OTf or PF₆ and dmpe is 1,2-bis(dimethylphosphino)ethane) were recently introduced as catalysts for the ring-opening polymerization of disilacyclobutanes and silicon-bridged ferrocenes (often referred to as [1]silaferrocenophanes)^{170,171}

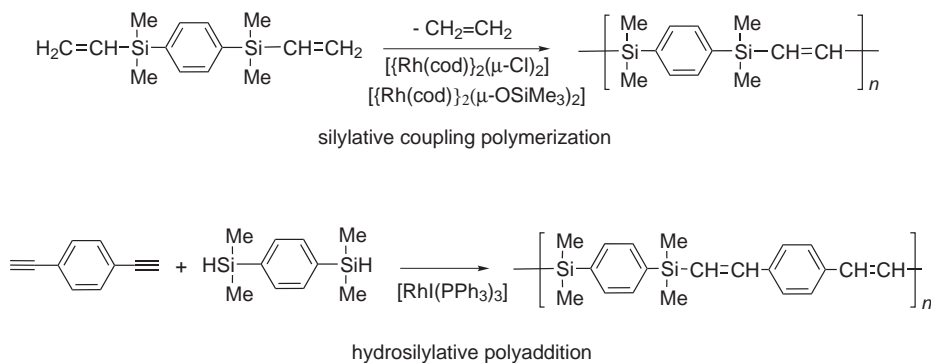


FIG. 24

Examples of Rh-catalyzed silylative and hydrosilylative polymerization reactions

(Fig. 25). The former catalyst gives 100% conversion of silicon-bridged ferrocenes within 2 min, however, it simultaneously cleaves Si-C(ferrocene) bonds in the formed polymer inducing its rapid degradation. On the other hand, the ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is also facile with $[\text{Rh}(\text{cod})_2]^+\text{A}^-$ but the resulting polymer, which does not contain Si-C(ferrocene) bonds, does not undergo subsequent degradation. Thus the observed cleavage of Si-C(unsaturated) bonds in poly[(dialkylsilane)diyl(ferrocene-1,1'-diyl)]s can also be regarded as an additional evidence supporting the mechanism suggested for the silylative coupling polymerization (see above). Complex $[\text{Rh}(\text{cod})(\text{dmpe})]^+\text{A}^-$ shows lower activity in polymerization of silicon-bridged ferrocenes but no activity in the polymer degradation. Stoichiometric excess of cod or dmpe inhibits catalytic activity of Rh complexes in the ring-opening polymerization.

8. OTHER MONOMERS

8.1. Olefins, Norbornene and Norbornadiene; Copolymerization with CO

Copolymerizations of olefins and related monomers with CO to give polyketones have already been reviewed¹⁷² as well as polymerizations of olefins in aqueous media⁶⁰, some of which have also been accomplished with rhodium catalysts. Therefore, we mention here only recent result on the copolymerization of carbon monoxide with norbornene, norbornadiene and derivatives of both, since this reaction can be potentially used in exploitation of industrial overproduction of cyclopentadiene, which is easily

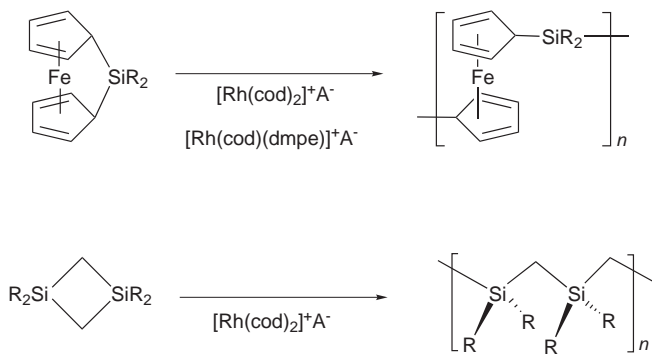


FIG. 25

Rh-catalyzed ring-opening polymerization of silicon-bridged ferrocenes and 1,3-disilacyclobutanes^{170,171}

transformed into these monomers. These copolymerizations are mostly catalyzed with palladium(II) catalyst, which, however, mostly provide branched copolymers if both double bonds of a norbornadiene monomer are unsubstituted¹⁷³⁻¹⁷⁵.

Rhodium catalysts have been recently revealed (Takahashi *et al.*^{176,177}) to induce a copolymerization of norbornadiene as well as norborne monomers with CO to give alternating copolymers, *i.e.*, regular polyketones (Fig. 26), in high yields. These authors found that these copolymerizations are catalyzed with various rhodium compounds, such as by $[\text{Rh}_6(\text{CO})_{16}]$, $[\text{Rh}_4(\text{CO})_{12}]$, $[\{\text{Rh}(\text{nbd})\}_2(\mu\text{-Cl})_2]$ and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and that they provide copolymers of rather low polydispersity ($M_w/M_n = 1.17$ to 1.60). Mechanistic considerations are discussed at length¹⁷⁷.

8.2. Isocyanides

Molecules of isocyanides, $\text{R-N}\equiv\text{C}$, can be enchainned into macromolecules in the same way as molecules of carbon monoxide, *i.e.*, by one carbon atom only, so as their polymers can be described as $[-\text{C}(=\text{NR})-]_n$. Polyisocyanides with bulky substituents R such as *t*-Bu or *ortho*-substituted benzene rings are attractive polymers since their macromolecules can have helical conformation¹⁷⁸. Takahashi *et al.*¹⁷⁹ have recently shown that *ortho*-substituted aryl isocyanides smoothly polymerize with the $[\text{Rh}(\text{aryl})(\text{nbd})(\text{PPh}_3)]$ complexes containing bulky aryl ligands such as 2,6-dimethylphenyl, or 2,4,6-triisopropylphenyl, or biphenyl-2-yl (Fig. 27). They obtained high yields (65 to

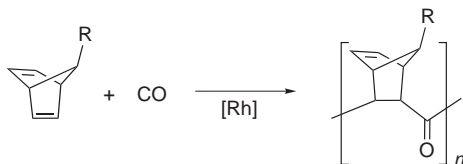


FIG. 26

Alternating copolymerization of norbornadienes and CO induced with Rh catalysts^{176,177}

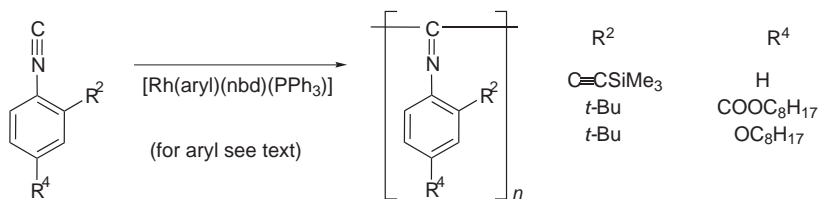


FIG. 27

Scheme of polymerization of arylisocyanides with $\text{Rh}(\text{nbd})$ catalysts¹⁷⁹

95%) of polymers of low-to-medium polydispersity ($M_w/M_n = 1.12$ to 1.51) and a number-average molecular weight close to that calculated from the monomer-to-catalyst mole ratio, however, they also revealed that these polymerizations are not the living ones.

The presence of free PPh_3 in the reaction mixture was found essential for a good course of the polymerization. Without PPh_3 , a polymer together with a significant amount of oligomers is formed. Other phosphines such as PCy_3 , P(OPh)_3 or $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$, inhibit the polymerization. Strong effect of the phosphine structure on the course of an isocyanide molecule insertion has also been observed for the systems with Pd catalysts¹⁸⁰. Rhodium complexes with non bulky ligands, such as $[\text{Rh}(\text{Ph})(\text{nbd})(\text{PPh}_3)]$, $[\text{Rh}(\text{Me})(\text{nbd})(\text{PPh}_3)_2]$ and $[\text{Rh}(-\text{C}\equiv\text{CPh})(\text{nbd})(\text{PPh}_3)_2]$, were found to provide a mixture of polymers and oligomers.

8.3. Phosphine–Borane Adducts

The development of procedures for a preparation of inorganic-main-chain polymers is of importance for accessing advanced functional materials with potential applications in various practical fields^{181,182}. Polyphosphinoboranes, macromolecules of which contain exclusively alternating phosphorus and boron atoms in the backbone, belong to materials that received significant attention in 1950's already, as properties such as flame retardancy and high thermal stability were anticipated for such structures. However, attempts to synthesize them by thermal dehydrocoupling of phosphine–borane adducts, $\text{RPH}_2\cdot\text{BH}_3$ and $\text{R}_2\text{PH}\cdot\text{BH}_3$, were not too successful¹⁸³.

In 1999, Dorn, Manners *et al.*^{184–186} discovered catalytic dehydrocoupling polymerization of phosphine–borane adducts $\text{RPH}_2\cdot\text{BH}_3$ ($\text{R} = \text{Ph}$, or 4-but-1-yl- C_6H_4 , or 4-but-2-yl- C_6H_4 , or 4-dodec-1-yl- C_6H_4) with rhodium compounds such as $\{[\text{Rh}(\text{cod})]_2(\mu\text{-Cl})_2\}$, RhCl_3 and RhCl_3 hydrate (Fig. 28). They obtained reasonable yields (from 50 to 70%) of highly polydisperse polymer with M_w up to ca 170 000. They also found that values of polymer molecular weight were not reproducible, which they ascribe to complications associated with increasing viscosity of the neat reaction mixture at the end of polymerization. Later on, Jaska and Manners *et al.*¹⁸⁷ have shown that rho-

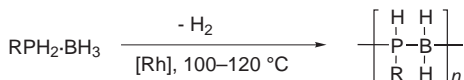


FIG. 28
Scheme of polymerization of phosphine–borane adducts with Rh catalysts

dium compounds also catalyze dehydrocoupling of amino– borane adducts, however, only cyclic oligomers are obtained in this reaction. Recently, also fluorinated polyphosphinoboranes have been prepared¹⁸⁸ and a rapid progress in synthesis of this type of polymers can be expected.

9. CONCLUSIONS

The steadily increasing number of applications in the synthesis of new polymers with one or more well-defined structure features is proving the high potential of rhodium-based catalysts for preparing new useful materials with unusual functional properties. Main advantages of these catalysts are (i) potentiality to polymerize and copolymerize divers classes of monomers including the inorganic ones (ii) high tolerance to the reaction medium and monomer functional groups, (iii) often unique product selectivity, and (iv) capability of forming living polymerization systems. At present, the rhodium-based catalysts have become an efficient tool for synthesis of both organic and inorganic polymers and it can be expected that these versatile and robust catalysts will soon find further interesting and useful applications in polymer science and, perhaps, also in technology.

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