11

Coordination Polymerization

S. Koltzenburg et al., *Polymer Chemistry*, DOI 10.1007/978-3-662-49279-6_11

Nearly half of all polymers produced worldwide are produced by catalytic polymerization reactions carried out in the presence of transition metal compounds. Coordination of a monomer to a metal center is a crucial step in the catalytic cycle. Therefore, these polymerizations are referred to as "coordination polymerizations". Especially polypropylene and a large proportion of polyethylene are produced in this way. Therefore, this chapter deals with the fundamental principles of this industrially enormously important but also academically interesting and multifaceted field of chemistry.

11.1 Polymerization of α-Olefins

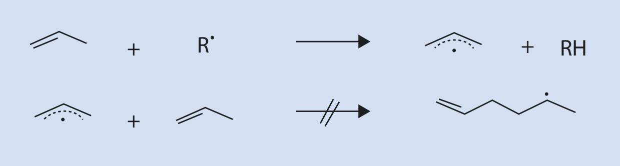
In contrast to many other unsaturated compounds, simple α-olefins cannot be polymerized (with the exception of ethene) via the radical or ionic polymerizations described in the previous chapters. This is because of the chain carrying the active center—for example, a radical—preferring to abstract a hydrogen atom or an ion from the carbon atom adjacent to the double bond. This results in an allyl species, which is so stable that no other monomer can be added because this would lead to the resonance stabilization being lost. An example of this is the reaction of propene with a source of radicals in ◘ Fig. 11.1. The reaction with corresponding anions or cations takes place in an analogous manner.

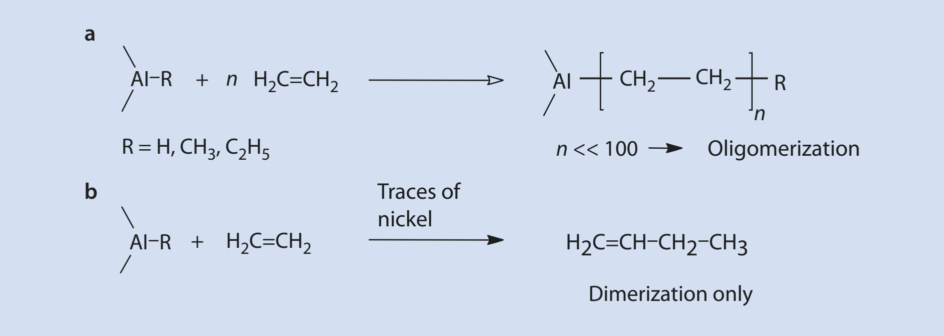
The polymerization of α-olefins only became possible after Karl Ziegler's discoveries at the Max Planck Institute for Carbon Research in Muelheim an der Ruhr (Ziegler et al. 1955).

11.2 Ziegler Catalysts

Karl Ziegler, who was conducting research on the oligomerization of ethene by aluminum alkyls, discovered by accident that transition metals could massively influence this reaction (◘ Fig. 11.2). He noticed that traces of nickel prevented the oligomerization of

◘ **Fig. 11.1** Reaction of propene with a radical





◘ **Fig. 11.2** (**a**) Ziegler's "Aufbaureaktion" (Chain extension reaction). (**b**) The nickel effect

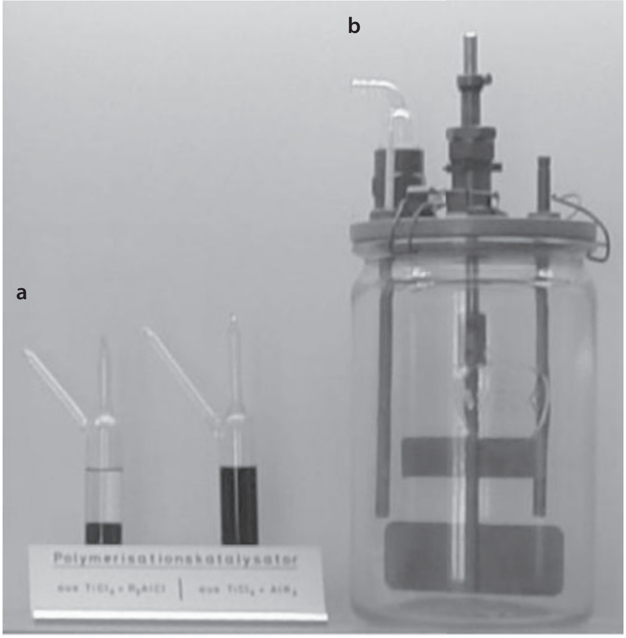


Fig. 11.3 (**a**) Glass containers with two catalysts. (**b**) Ziegler's polymerization reactor (reproduced here with kind permission from Professor Dr. G. Fink)

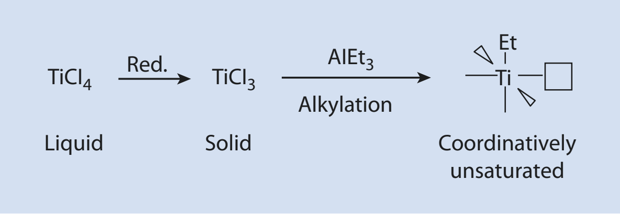
Table 11.1 Examples of Ziegler catalysts and cocatalysts (Et = C_2H_5)

Catalyst	Formula	Cocatalyst	Formula
Titanium tetrachloride	$TiCl_4$	Triethyl aluminum	$AlEt_3$
Zirconium tetrachloride	$ZrCl_4$	Diethyl aluminum chloride	$AlEt_2Cl$
Titanium trichloride	$TiCl_3$	Ethyl aluminum dichloride	$AlEtCl_2$
Titanium tetraisobutylate	$Ti(O\text{-}i\text{-}C_4H_9)_4$	Diisobutyl aluminum hydride	$AlH(i\text{-}C_4H_9)_2$
Vanadium oxytrichloride	$VOCl_3$		

ethene and that in the presence of nickel only dimers are produced. This effect came to be known as the *nickel effect* and spurred Ziegler on to analyze more closely the influence of transition metals on oligomerization. During his research he discovered that a mixture of titanium compounds, such as titanium tetrachloride together with aluminum alkyl compounds, could spontaneously polymerize ethene to macromolecular polyethylene at atmospheric pressure and room temperature.

At that time this procedure was revolutionary because a typical radical polymerization of ethene, involving a very active primary radical at the growing chain end, required extreme reaction conditions: a temperature of 300 °C and a pressure of up to 2000 bar. In contrast to this, the polymerization using Ziegler catalysts takes place at ambient conditions. To highlight this, Karl Ziegler used a converted preserving jar for presentation purposes (Fig. 11.3).

The reaction takes place with organometallic compounds, formally transition metals, and requires a second component, an aluminum alkyl, as a so-called cocatalyst. Examples are given in Table 11.1.



▣ **Fig. 11.4** Initiation process for Ziegler catalysts

Heptane or toluene is used as a solvent. The use of metal alkyls dictates strictly anhydrous conditions. Alternatively, traces of water can be scavenged by a surplus of aluminum alkyls.

The active catalysts discussed above are insoluble in hydrocarbon solvents and can thus be described as *heterogeneous* catalysts.

The following model is the generally accepted one for Ziegler catalysis and is discussed in the following using titanium tetrachloride as an example. The catalytic cycle can be divided into the basic steps—initiation, growth, chain transfer, and termination—analogous to other chain growth reactions, such as radical polymerization.

11.2.1 Initiation

Because of the reducing effect of aluminum compounds, the titanium(IV) chloride is reduced and a solid titanium-containing species is formed.[1] On the surface of the solid particles the titanium centers are alkylated by the aluminum alkyl. During this process one of the chloride ions is swapped for an ethyl group. Some of the metal centers on the surface are coordinatively unsaturated and have a free coordination point. The metal atoms are the catalytically active centers (▣ Fig. 11.4).

11.2.2 Growth

An ethene molecule coordinates with the metal atom via the π-electrons of the double bond as the first part of the growth step. Then an insertion of the ethene molecule over a four-center-four-electron-transition state involving the metal carbon bond already existing takes place. Thus the coordination site that was occupied by the ethyl group becomes available again and so the center is ready for another insertion step (▣ Fig. 11.5). The chain migration during the insertion step leads to a *cis*-addition (this is known as the *chain migratory mechanism*).

Bi-metallic mechanisms, for example involving chloride bridged titanium–aluminum species, have also been described for chain growth but confirmation has proved difficult because of the heterogeneous nature of the catalytic species.

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[1] The reaction is not well defined and the products, because they are insoluble, are not easily analyzed. There are a number of different titanium species in various valence states. Because among the various species formed many catalyze the polymerization of ethene, this system is called a *multi-site* catalyst.

Fig. 11.5 Chain growth with Ziegler catalysts

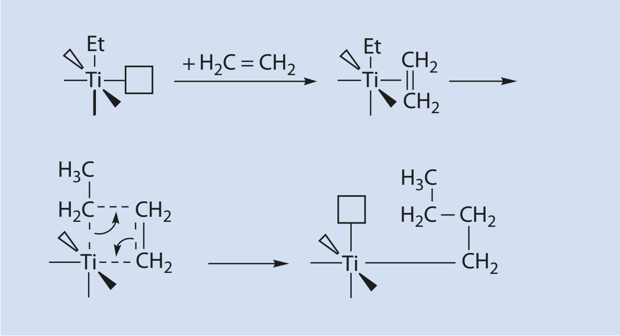
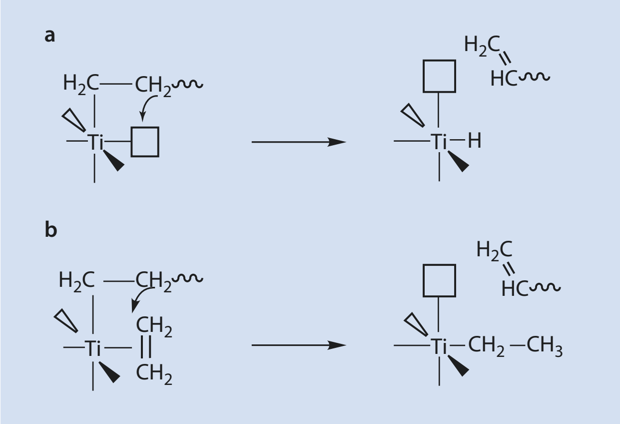


Fig. 11.6 Chain termination and transfer. (**a**) Via ß-hydride-elimination. (**b**) Via ß-hydride-transfer



11.2.3 Termination/Chain Transfer

Instead of an insertion, the *ß*-carbon of the hydrocarbon chain can be transferred in the form of a hydride ion to the free coordination center or to a coordinated monomer molecule (Fig. 11.6). In both cases an unsaturated polymer is formed. These processes are called *ß-hydride-elimination* or *ß-hydride-transfer*, respectively. The titanium alkyl or titanium hydride species formed during these processes are still active polymerization catalysts and can coordinate with further ethene molecules to initiate new polymer chains.

It is possible to distinguish between the two mechanisms by varying the ethene concentration, i.e., the ethene pressure above the liquid phase. If termination takes place via *ß*-hydride-elimination then an increase in the ethene concentration increases the rate of chain growth and the rate of termination remains the same. Thus, the molar mass increases with an increase in ethene pressure. If, however, a catalyst system is used, in which a *ß*-H-transfer onto a coordinated monomer is favored, an increase in ethene concentration is also beneficial for chain growth and the molar mass is independent of the ethene pressure. Generally, however, both reactions occur concurrently.

Furthermore, termination of the catalytic process can take place because of contamination, by water for example.

During catalytic polymerization the molar mass of the polymer is controlled kinetically by the relationship between the rates of chain growth and termination, just as they are during radical or ionic polymerization:

$$\text{Kinetic chain length } \nu = \frac{\text{Olefin insertion rate}}{\text{Rate of } \beta\text{-H-elimination or -transfer}}$$

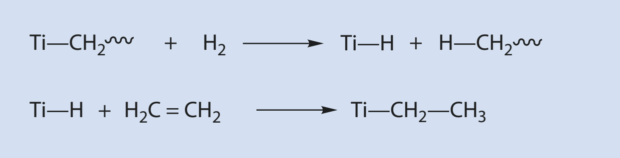
An increase in the reaction temperature benefits especially the rate of β-H-elimination and β-H-transfer as these reactions have large activation energies. Thus, the polymer molar mass decreases as the reaction temperature is increased.

The nickel effect, observed by Ziegler, is attributable to elimination taking place very quickly in the presence of nickel and therefore only a dimerization of the ethene takes place.

The molar mass can be regulated by the addition of hydrogen. Molecular hydrogen splits the titanium–alkyl bond (*hydrogenolysis*). The resulting hydride species can add further monomers so that the rate of polymerization stays the same but shorter polymer chains are formed (Fig. 11.7).

The different variants of the Ziegler “Aufbaureaktion” can be summarized as follows (Fig. 11.8):

Fig. 11.7 Regulation of molar mass with hydrogen



$$Ti{-}CH_2{\sim} + H_2 \longrightarrow Ti{-}H + H{-}CH_2{\sim}$$

$$Ti{-}H + H_2C{=}CH_2 \longrightarrow Ti{-}CH_2{-}CH_3$$

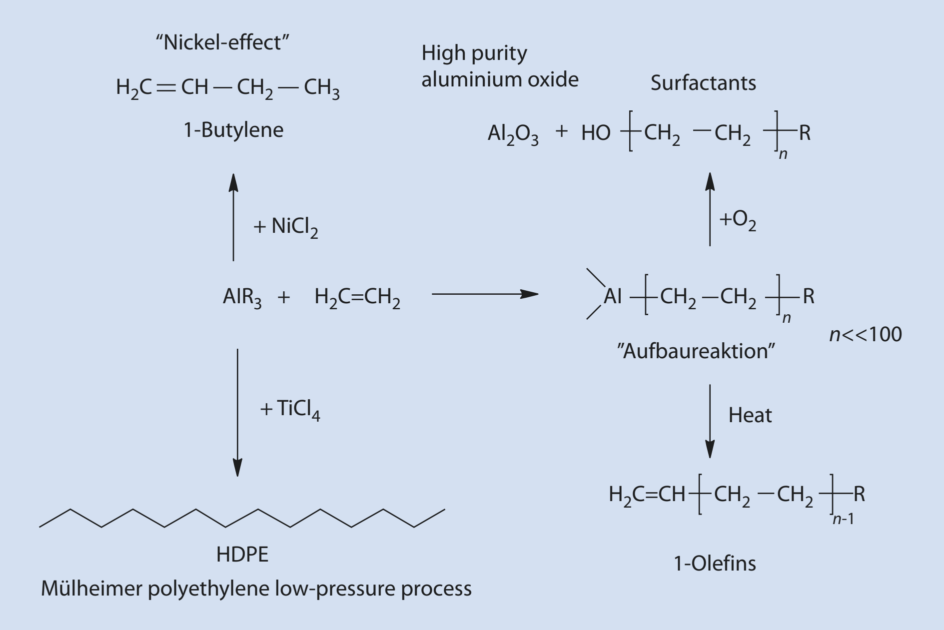


Fig. 11.8 Reactions of aluminum alkyls with ethene. *HDPE* high density polyethylene

- Oligomerization of ethene through the “Aufbaureaktion”
- Dimerization of ethene through the *nickel effect*
- Polymerization of ethene to polyethylene (*Muelheim polyethylene low-pressure process*)

The longer chain aluminum alkyls formed during the “Aufbaureaktion” have a narrow molar mass distribution (Poisson distribution, ▶ Chap. 10) and can be oxidized to alcohols with oxygen. This is a technically used route to valuable raw materials for surfactants. Very pure aluminum oxide is formed as a by-product. As an alternative, olefins can be produced by thermal elimination (▣ Fig. 11.8).

As well as the systems known as *Ziegler catalysts*, chrome-based catalysts have also found their way into technical polymerization processes. These systems, known as *Phillips catalysts*, consist of chromium trioxide on an SiO_2 carrier. Chrome(VI) is probably reduced down to chrome(II) during the reaction. Phillips systems are able to function without a cocatalyst, in contrast to Ziegler catalysts. The mechanism of polyinsertion is suggested to take place in an analogous manner to that described above for titanium-based catalysts. As a group, the reactivity of these systems is somewhat lower than that of Ziegler catalysts so that higher temperatures and higher olefin pressures are necessary and, usually, polymers of low molar mass are produced. Processes based on these catalysts are referred to as medium-pressure processes. The differences are summarized in ▣ Table 11.2.

As early as 1 year after their discovery, the applicability of the titanium catalysts discovered by Ziegler was substantially broadened by the Italian scientist Giulio Natta. Natta discovered that the systems described by Ziegler could polymerize not only ethene but also higher α-olefins. The polypropylene produced using the first generation of, not yet optimized, Ziegler catalysts was essentially atactic or stereo-irregular (▶ Sect. 1.3.2) and thus soluble in the reaction medium. No precipitated polymer could be observed during the reaction, in contrast to insoluble polyethylene, which is probably why this important discovery was overlooked in Karl Ziegler’s laboratories.

If heterogeneous Ziegler catalysts are optimized by adding additional components, they are able to control the stereoregularity of the product (Natta 1964). The mechanism of the stereoregular polymerization of α-olefins is dealt with in the following paragraph (▶ Sect. 11.3) in combination with the polymerization with metallocene catalysts.

Karl Ziegler and Giulio Natta received the 1963 Nobel Prize for Chemistry for the discovery of the catalytic polymerization of α-olefins and the stereospecific polymerization of propene.

▣ **Table 11.2** A comparison of the process parameters for low and medium pressure processes

Process	Low pressure	Medium pressure
Catalyst	$TiCl_4/AlR_3$	CrO_3/SiO_2
p (bar)	1–10	35
T (°C)	70	150–180
M_w (kg/mol)	50–100	5–20

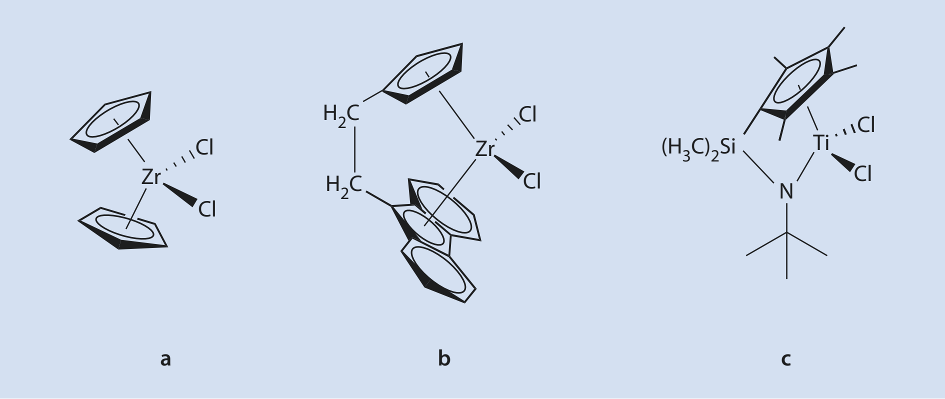
11.3 Homogeneous Polymerization Catalysts

The discovery of highly active and stereoselective metallocene catalysts by Brintzinger in 1995 opened up a further fascinating and, what is now, a widely studied research area of catalytic polymerization. These transition metal compounds are soluble in the reaction medium and are therefore referred to as homogeneous catalysts. Many of the mechanistic details of polyinsertion have been clarified with the aid of these well defined systems so that they have provided essential contributions to our understanding of catalytic polymerization.

Most, in particular the more important, homogeneous catalysts are metallocenes or half-sandwich compounds of the early transition metals titanium and zirconium. Examples are shown in ◘ Fig. 11.9. In principle, hafnium can also be used but the compounds based on this metal are generally less active than their zirconium counterparts—and hafnium is very expensive.

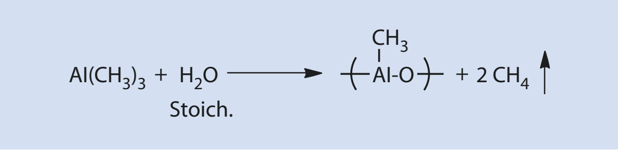
Similar to the heterogeneous Ziegler catalysts, most of the metallocenes are only active with a cocatalyst. Often, aluminum organic compounds are used as cocatalysts. However, the aluminum alkyls used in the heterogeneous systems have not proved to be very effective. Far more active catalyst systems can be obtained if methyl aluminoxane (MAO) is employed as a cocatalyst (◘ Fig. 11.10). This compound is the oligomeric product of the partial hydrolysis of trimethyl aluminum comprising approximately 20 aluminum atoms (Sinn and Kaminsky 1980). The structure of methyl aluminoxane has not been completely determined; it is probably not a linear oligomer, but rather contains cyclic and cage-like structures in which the oxygen atoms coordinate onto several aluminum atoms reflecting the Lewis acidity of aluminum.

However, it has been shown that systems not based on aluminum can also be employed as cocatalysts; only a high Lewis acidity is necessary. Thus, for example, triphenyl methyl cations $[C(C_6H_5)_3]^+$ with weakly coordinated anions such as tetrakis(pentafluorophenyl borane) $[B(C_6F_5)_4]^-$ can be used as cocatalysts.



◘ **Fig. 11.9** Examples of (**a**, **b**) homogeneous metallocene catalysts and (**c**) half-sandwich complexes for the polymerization of olefins

◘ **Fig. 11.10** Synthesis of methyl aluminoxane via partial hydrolysis of trimethyl aluminum



$$Al(CH_3)_3 + H_2O \xrightarrow[\text{Stoich.}]{} \left[\overset{CH_3}{\overset{|}{Al}}-O\right] + 2\,CH_4\uparrow$$

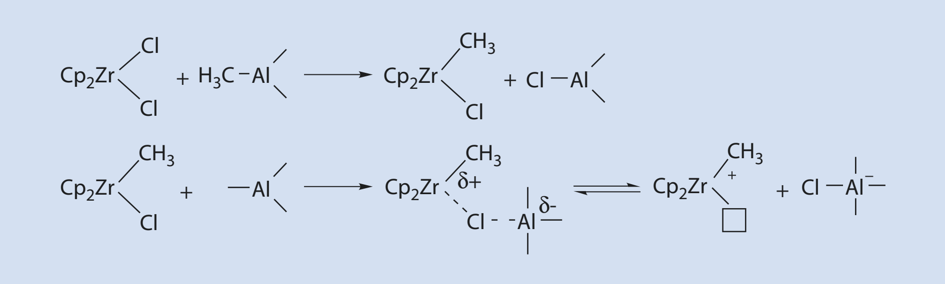
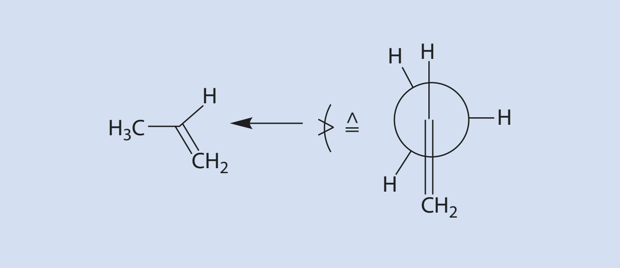


Fig. 11.11 Formation of the catalytically active moiety from a metallocene and a cocatalyst (here: methyl aluminoxane)

Fig. 11.12 Newman projection of propene along the C2–C3 bond



In contrast to the chemically relatively undefined heterogeneous systems, metallocene catalysts are well defined entities. Generally, there is only one, well defined, catalytically active component, which is why these systems are referred to as *single-site catalysts*. The uniform nature of the catalytic centers has considerably facilitated the mechanistic analyses of these catalyst systems.

For the polyinsertion of olefins, as a first step, the metallocene, which is mostly employed as a dichloride, is alkylated by the cocatalyst, such as methyl aluminoxane. In the next step, a further ligand is abstracted from the transition metal by the Lewis acid center of the cocatalyst. It is during this step that the active polymerization species moiety is formed, a cationic species which has the electron configuration d^0 (◘ Fig. 11.11). As this is only formed by reaction of the metallocene with the cocatalyst, the metallocene is also referred to as a *precatalyst* or *precursor*. Coordination and insertion take place in the manner described for heterogeneous systems in ▶ Sect. 11.2.

The mechanism of stereo control of the polyinsertion reaction can be most easily understood using metallocene catalysts as an example.[2] It is assumed here that the different stereoisomers dealt with in ▶ Chap. 1 are understood.

Propene is a prochiral molecule (◘ Fig. 11.12). This means that if an addition reaction takes place at the double bond of the C2 carbon atom, a chiral compound is produced (unless, coincidentally, after the addition step the two substituents at C2 are identical).

Whether the addition of the catalytically active metal alkyl complex takes place from the re or the si side of the propene[3] is decisive in determining the stereochemistry that results at C2 (◘ Fig. 11.13).

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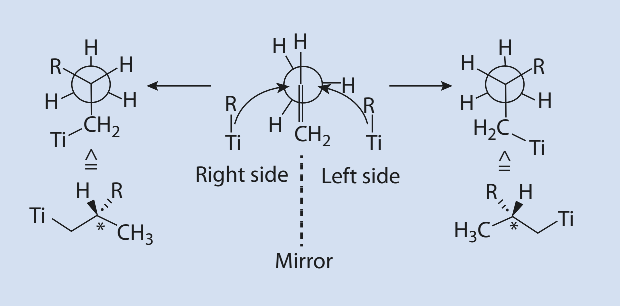
[2] The following discourse describes the basic mechanisms of stereo control. For a detailed discussion of stereo control during catalytic polymerization the reader is referred to the literature (e.g., Brintzinger et al. 1995; Angermund et al. 2000).

[3] The re/si nomenclature denotes the sides of a planar, sp^2-hybridized center, from which, after a reaction in which a further substituent is added, a chiral center is formed.

Fig. 11.13 Stereochemistry of an addition of a titanium alkyl to propene molecule



A stereoregular product is formed if addition takes place in a regular sequence. There are three possibilities for this; addition always takes place:

- From the left side in Fig. 11.13
- From the right side in Fig. 11.13
- Alternately from each side

For the first two cases the configuration at the prochiral carbon atom is the same along the chain; isotactic polypropylene is formed. In the third case, polypropylene with an alternating sequence of stereo configurations is formed, syndiotactic polypropylene. If the catalyst system used is unable to control the stereochemistry of the insertion reaction, then atactic polypropylene results. All stereochemical variants can be deliberately obtained using metallocene catalysts.

11.3.1 Catalysts for Isotactic Polypropylene

An example of an isoselective metallocene—a metallocene that predominantly catalyzes the formation of isotactic polymers—is shown in Fig. 11.14. The symmetry of the metallocene is identical to that of the point group C_2; the molecule has an axis of symmetry.[4] Because of this, the chlorine atoms of the metallocene, or both coordination points formed after the alkylization and formation of the d^0-cation, are identical in that they can be transferred into one another by rotating the molecule; such molecules are referred to as being *homotopic*.

There are four stereochemically different possibilities shown in Fig. 11.15 for the olefin to approach the catalytically active, tetrahedrally coordinated center. Complexes I and II are energetically unfavorable as the methyl group of the propene molecule points towards the ligand structure of the metallocene. This results in a sterically unfavorable interaction and causes insertion to take place in such a way that the transition metal adds to the C1 atom of the propene molecule and not the prochiral C2 atom. Option III is energetically disadvantaged in comparison to configuration IV as the ligand system forces the methyl group of the propene molecule into a position as far away as possible from the sterically demanding indenyl ligands. The most energetically favorable insertion option is the stereochemistry represented by IV. These effects can be modeled and quantitatively predicted using force field calculations (Angermund et al. 2000).

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[4] For a more detailed discussion of point groups and the elements of molecular symmetry, the interested reader is referred to the literature (Willock 2009)

Fig. 11.14 Example of an isoselective metallocene and its simplified representation (in order to provide a better overview the chlorine atoms and the silyl bridges have been left out here and in the following figures)

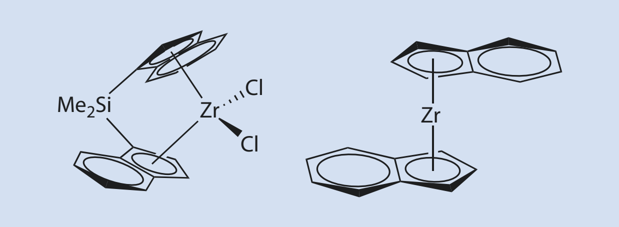


Fig. 11.15 Stereochemical options for the approach of a propene molecule to a metallocene with C_2-symmetry. *Pol*: the growing polymer chain

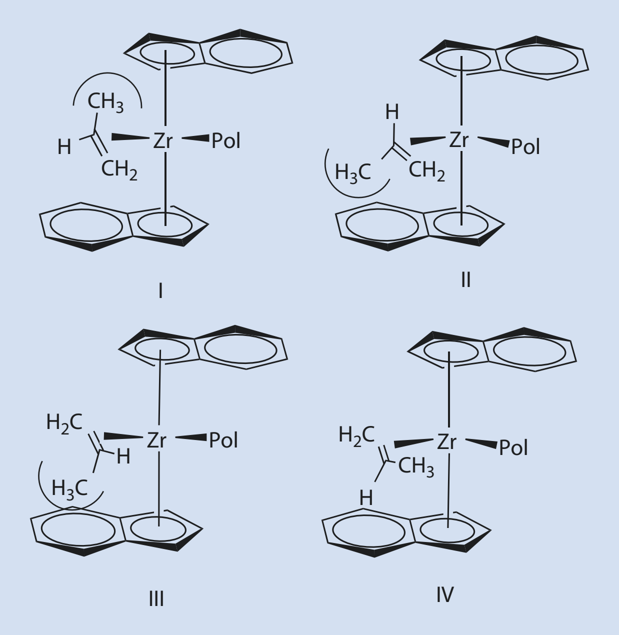
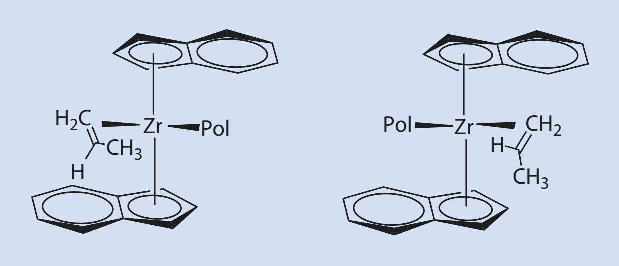


Fig. 11.16 Homotopy of the possible configurations when a propene molecule coordinates with an isoselective metallocene. *Pol*: the growing polymer chain



As has been explained above, both equatorial ligand positions are stereochemically identical at the transition metal (homotopic) in catalysts with C_2-symmetry. The configuration given by IV in Fig. 11.15 for a coordination of olefin with the 'left' coordination point is identical to the alternative coordination at the opposite ligand position (Fig. 11.16). Even though the polymer chain changes its position in the ligand structure every time an insertion step takes place (*chain migratory mechanism*, Sect. 11.2), every insertion takes place in a manner leading to the same configuration at the C2-atom of the inserted monomer unit. Isotactic polypropylene is formed (it-PP).

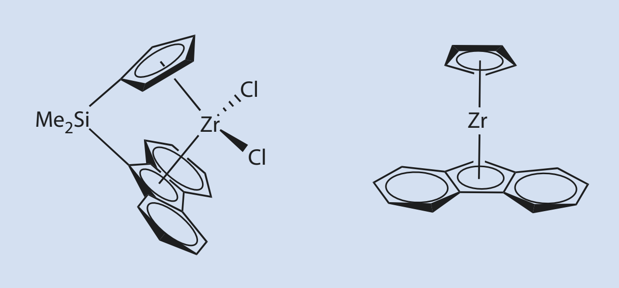
Metallocenes with a symmetry that deviates from that of the point group C_2 can also produce isotactic polypropylene (Brintzinger et al. 1995). It is only necessary that in every case the monomer approach is directed by the ligand structure of the metallocene to ensure that the insertion at both coordination sites always takes place from the same side (re or si) of the propene molecule.

11.3.2 Catalysts for Syndiotactic Polypropylene

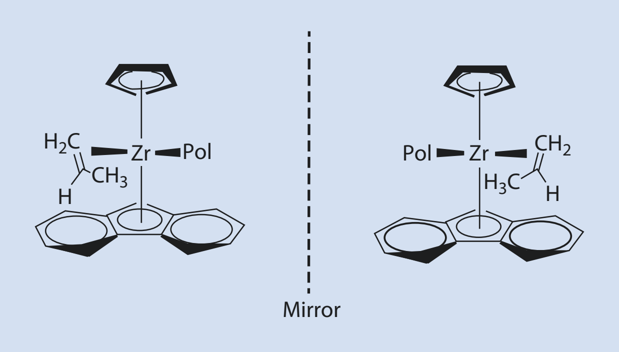
Control of the stereochemistry by *syndioselective* metallocenes takes place in a very similar way. An example of this type of catalyst is shown in ◘ Fig. 11.17.

In contrast to isoselective metallocenes, syndioselective metallocenes belong to the point group C_S and have a mirror plane in the molecule. For this reason, both chlorine atoms are *enantiotopic* and not homotopic; their substitution results in an enantiomeric molecule.

The control of the stereochemistry follows the same principles as for isoselective catalysts: the methyl group of the coordinated propene monomer is directed away from the ligand structure (this results in the addition of the metal to the C1-atom) and positioned so that steric interaction with the ligands—in this case the fluorenyl system—is minimized. The ligand positions at which insertion takes place are, in contrast to the isoselective catalysts, enantiotopic. The transition states of the insertion steps are thus mirror images of each other and produce antipodal stereochemistry at the prochiral carbon atom (◘ Fig. 11.18). As the two transition states alternate with one another because of the *chain migratory mechanism,* syndiotactic polypropylene is formed.



◘ **Fig. 11.17** Example for a syndioselective metallocene and its simplified representation



◘ **Fig. 11.18** Enantiotopicity of the possible configurations when a propene molecule coordinates with a syndioselective metallocene. *Pol*: the growing polymer chain

Considerable rigidity of the ligand structure is necessary to control the stereochemistry of both iso- and syndioselective metallocenes. This can be achieved by covalently linking both aromatic systems as shown in ◘ Figs. 11.14 and 11.17. Suitable bridges are ethylene or silyl moieties and, less commonly, a single carbon atom. The length of the bridges determines the angle of the aperture of the metallocene. As the bridge between the ligands is similar in form to a handle, these types of bridged metallocenes are referred to as *ansa*-metallocenes, after the Greek word for handle.

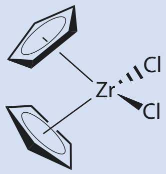
11.3.3 Catalysts for Atactic Polypropylene

Metallocenes that yield atactic polyolefins do not have an asymmetrical ligand structure. The simplest example of this type of catalyst is the metallocene of the point group C_{2v} shown in ◘ Fig. 11.19.

Because of the highly symmetrical nature of the molecule, neither of the stereochemically possible coordination options of the monomer and the active center is energetically favored. The configuration of the resulting stereocenter is therefore completely random and results in an atactic macromolecule.

Although the discovery of metallocene catalysts has led to a veritable flood of academic and industrial research work, the use of homogeneous catalysts is technically limited to niche markets. This is because of the high price of these catalysts, generated by the elaborate synthesis of tailor-made ligand structures. As well as this, there have been many patent litigations which have blocked a broad technical use of this new technology. The high price is only compensated for by a few tangible advantages in practice. Among them are a narrower molar mass distribution and the homogenous integration of comonomers. These aspects are briefly discussed in the following paragraphs.

Heterogeneous Ziegler catalyst systems have, as has already been mentioned, a number of different active centers. These centers are all different with respect to their insertion kinetics and their readiness to incorporate higher α-olefins as comonomers. As a consequence, a polymer is formed with a very broad molar mass distribution. It has also



◘ **Fig. 11.19** Zirconocene dichloride as an example of a metallocene which is not stereoselective

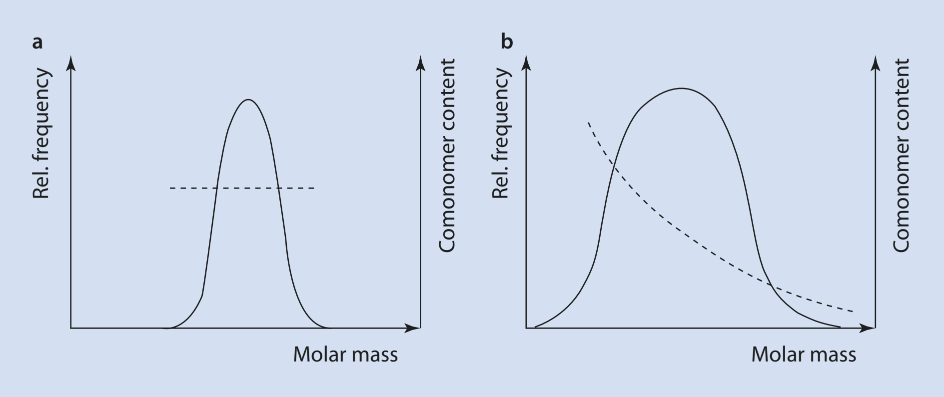


Fig. 11.20 (**a**) Homogeneous and (**b**) heterogeneous Ziegler catalysts. *Solid line:* molar mass distribution, *Dashed line*: comonomer fraction

been observed in practice that especially those active centers that incorporate α-olefins particularly readily tend to yield polymers of low molar mass, whereas the other centers tend to yield high molar mass homopolymers. Thus the product is a mixture of high polymers with a low concentration of comonomer and lower molar mass polymers with a higher concentration of comonomer (Fig. 11.20). This can result in extreme cases where the different macromolecules are immiscible and the product is inhomogeneous.

This, for the most part undesirable effect does not occur with homogeneous *single-site* catalysts. In practice, however, this rarely has an economic advantage. A technically relevant process in which polypropylene produced by metallocene catalysis is used is the high speed spinning of PP fibers. During the spinning process (▶ Chap. 17), the polymer molecules have to orientate themselves in the direction of the fiber axis. As is described in ▶ Chap. 17, this is facilitated by the polymer having a narrow molar mass distribution. Molecules with a too high degree of polymerization are difficult to orientate; molecules with a low molar mass negatively affect the mechanical properties of the fibers. Thus a narrow molar mass distribution is desirable for process optimization.

11.4 Catalysts Made from Late Transition Metals

In addition to the widely discussed catalysts made from early transition metals, which were dealt with in ▶ Sects. 11.2 and 11.3, in the last few years catalysts made from late transition metals such as iron, nickel, or palladium have also been studied. Figure 11.21 shows examples of nickel-based polymerization catalysts (Mülhaupt 2003). The catalysts shown at Fig. 11.21d and e can produce high molar mass polymers but the catalysts shown at Fig. 11.20a–c tend to result in the formation of oligomers. Nevertheless, this reaction has also become technically important for the commercial production of α-olefins from ethene and is known as the *Shell Higher Olefin Process (SHOP)*.

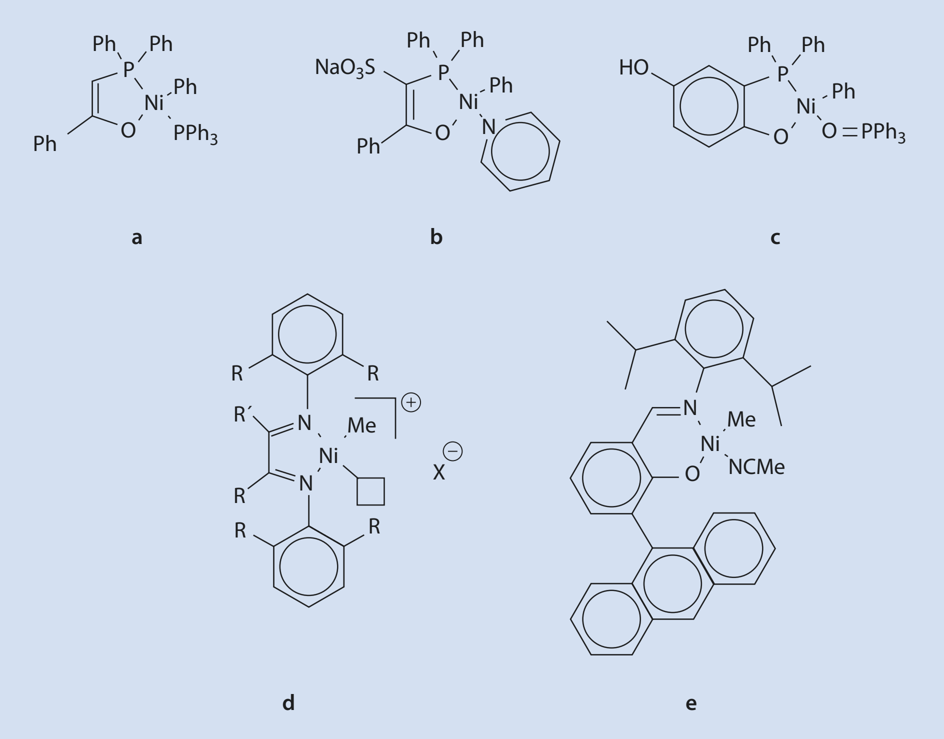


Fig. 11.21 Examples of nickel-based polymerization catalysts. Complexes described by (**a**) Keim, (**b**) Klabunde, (**c**) Ostoja-Starzewski, (**d**) Brookhardt, and (**e**) Grubbs

Catalysts based on late transition metals have the advantage of being less sensitive to the presence of substances containing hetero atoms, especially water, so that in principle a catalytic polymerization of α-olefins in aqueous emulsion is possible.

11.5 Technical Processes

Modern polymerization processes are often gas phase processes and do not involve solvents. The catalyst particles are brought into contact with the olefin in a fluidized bed reactor. Because of the special significance of the so-called gas phase polymerization, it is dealt with in more detail here.

A number of technical advances, which are discussed below, were necessary for the development of the gas phase polymerization of α-olefins, in which transition metals are used as catalysts.

11.5.1 Supports for Ziegler Catalysts

The activity of the first Ziegler catalysts—expressed as the amount (in grams) of polymer per amount of titanium (in grams)—was relatively low, because in these systems a large part of the metal is inside the insoluble titanium chloride particle and is not available for the reaction taking place at the surface. This is the reason why the first polymers produced using these catalyst systems contained rather high titanium concentrations. As titanium residues in the polymer can catalyze photochemical degradation reactions, they had to be removed from the reaction product after polymerization, which was technically complex as well as expensive. Newer catalyst systems have core-shell structures in which the core of the catalyst particle is composed of magnesium chloride with a very thin layer of active titanium centers precipitated on the surface (Böhm 2003). These structures naturally contain substantially less titanium than solid titanium chloride particles. Nevertheless, they exhibit similar activity because only the titanium chloride on the surface of the particles is catalytically active. The activity of Ziegler catalysts could be increased to more than a ton of polyolefin per gram of catalyst because of this clever piece of technical engineering. The products from such catalysts contain less than 1 ppm of titanium and its removal is unnecessary. The magnesium chloride that exists in place of the titanium chloride is inert and does not affect the product. These catalysts are often referred to as *leave-in catalysts*.

11.5.2 Optimization of Stereoselectivity of Heterogeneous Catalysts

Because of the less well defined character of the active centers of the heterogeneous Ziegler catalysts, many experiments were necessary to increase the consistency of the active centers. This can be achieved by the addition of Lewis bases such as alkyl benzoates, phthalates, or 1,3-diethers such as dimethoxy propane. The addition of these bases increases the stereoselectivity of the catalyst system. It is assumed that this is the result of the base reacting with non-stereoselective active polymerization centers on the surface of the catalyst particle which leads to their deactivation. This explanation is plausible if one considers that if a titanium atom is sterically so non-specific that even a relatively large Lewis base can coordinate with it, then it cannot be expected that the local geometry is so severely constricted that the catalytic center can stereoselectively direct the approach of the much smaller propene molecule.

By adding bases to the catalytic system the activity of the system decreases but the stereoselectivity of the system can be significantly increased. Because of this it was no longer necessary to remove the hitherto formed portion of (sticky!) atactic PP, which had been effected by elaborate extraction.

11.5.3 Control of Particle Morphology

Control of the morphology of the catalyst and polymer particles was also essential for the development of modern gas phase processes. In the most optimized processes, extremely porous agglomerates of very fine, catalytically active particles are employed. Because of this superstructure the catalyst particles can absorb the monomer as does a sponge and 'swell' as polymer is formed. After polymerization the polymer particles correspond to a significantly enlarged image of the original catalyst particles.

The use of such catalysts considerably simplifies the process; the product requires no further manufacturing, such as extrusion and pelletizing, to enable its easy handling (► Chap. 17).

The three developments dealt with in the Sects. 11.5.1–11.5.3 have significantly reduced the complexity of the production process of polyolefins. In the first few years of polyolefin manufacture the following process sequence was necessary:

- Polymerization reaction
- Catalyst deactivation
- Removal of the solvent
- Removal of catalyst residue
- Removal of atactic fraction
- Conversion into a manageable form, e.g., by extrusion

By application of the solvent-free gas phase process, this process sequence is simplified to one single production step and yields a dust-free product with acceptable levels of residual titanium and free of a troublesome, atactic fraction. Because polyolefins are large volume thermoplastics the technical optimization of the process was essential for the production of these products in a very competitive market.

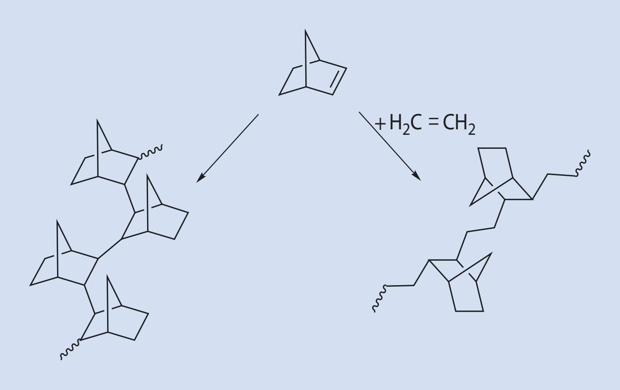
11.6 Cycloolefin Copolymers

Cyclic olefins can also be polymerized by transition metal catalysts. Homo- and copolymers of norbornene and its derivatives are of special importance in this context. Ethene is the most often used comonomer (■ Fig. 11.22).

Cycloolefin copolymers (*COCs*) are engineering plastics and find application as medical packaging, optical fibers, adhesives and photo resists. As well as copolymers with ethene, terpolymers of ethene, propene, and ethylidene norbornene (■ Fig. 11.23) are a large volume elastomer. The market relevance of the thermoplastic cycloolefin copolymers is, however, not remotely comparable to that of polyolefins.

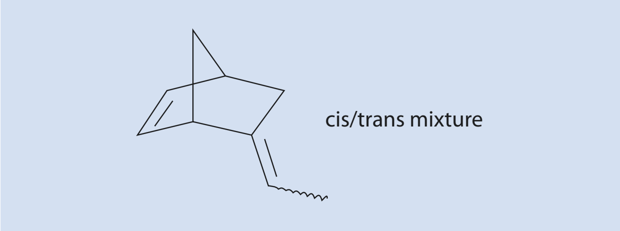
If cyclopentene is catalytically polymerized an anomaly occurs. The isomer, poly(1,3-cyclopentene) is obtained rather than the expected poly(1,2-cyclopentene) (■ Fig. 11.24).

The reason for this initially surprising result is that the metal alkyl compound formed by the insertion of cyclopentene is sterically too restricted to allow a further cyclopentene insertion. Thus, initially a *β*-H-elimination occurs and the product can then insert a further cyclopentene molecule in an alternative orientation (■ Fig. 11.25). This explains the 1,3-insertion.

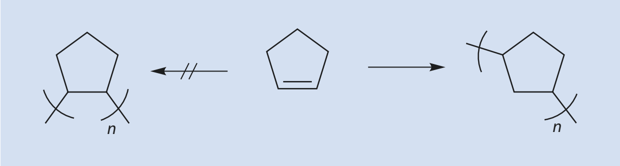


■ **Fig. 11.22** Homopolymers and ethene copolymers from norbornene

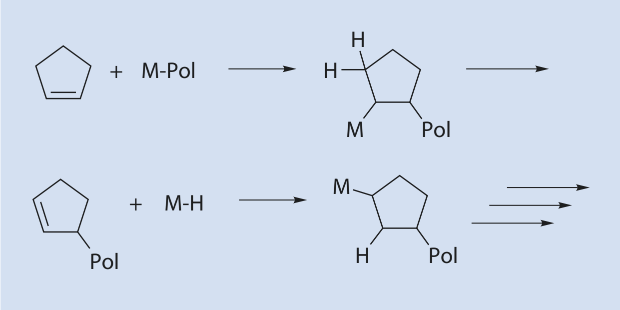
◘ **Fig. 11.23** Ethylidene norbornene



◘ **Fig. 11.24** Product of the catalytic polymerization of cyclopentene



◘ **Fig. 11.25** Elimination and reinsertion during the catalytic polymerization of cyclopentene



11.7 Olefin Metathesis

One of the most promising developments in synthesis chemistry is the metathesis of olefins. The discoverers of this development (Grubbs, Schrock, and Chauvin) were awarded the Nobel Prize in 2005. Recently, because of well defined catalysts, even functionalized monomers can be employed in metathesis reactions.

11.7.1 Metathesis Mechanism

Olefin metathesis is, formally, a reaction in which the double bond is split and alkylidene groups are exchanged between two olefins (◘ Fig. 11.26) (Calderon 1972).

The current, generally accepted mechanism in which metal carbene complexes and metallacyclobutane rings play a key role was suggested by Chauvin very early on (Hérisson and Chauvin 1971) (◘ Fig. 11.27).

Fig. 11.26 Metathesis of two olefins

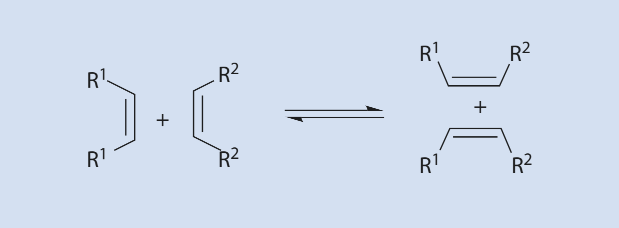


Fig. 11.27 Metallacyclobutane mechanism for olefin metathesis

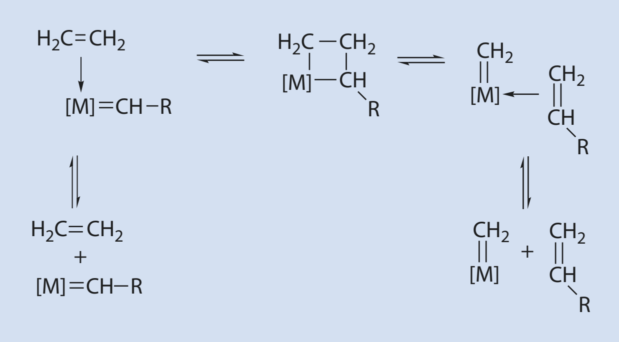


Table 11.3 Heterogeneous metathesis catalysts

WO_3/Al_2O_3	MoO_3/Al_2O_3
WO_3/SiO_2	MoO_3/SiO_2
Re_2O_7/Al_2O_3	MoO_3/TiO_2
Re_2O_7/SiO_2-Al_2O_3	MoO_3/ZrO_2

11.7.2 Metathesis Catalysts

Metathesis catalysts can be divided into three groups: heterogeneous, homogeneous, and immobilized homogeneous catalysts.

11.7.2.1 Heterogeneous Catalysts

Classical heterogeneous metathesis catalysts are oxides of transition metals of the sixth group on Lewis acid oxide carriers. They are robust, durable, and can be regenerated. Typical examples are shown in Table 11.3.

These catalysts generally require high temperatures (for example 400 °C for WO_3/Al_2O_3). Some, however, are very effective even at room temperature (MoO_3/ZrO_2). Most of them do not tolerate other functional groups.

11.7.2.2 Homogeneous Catalysts

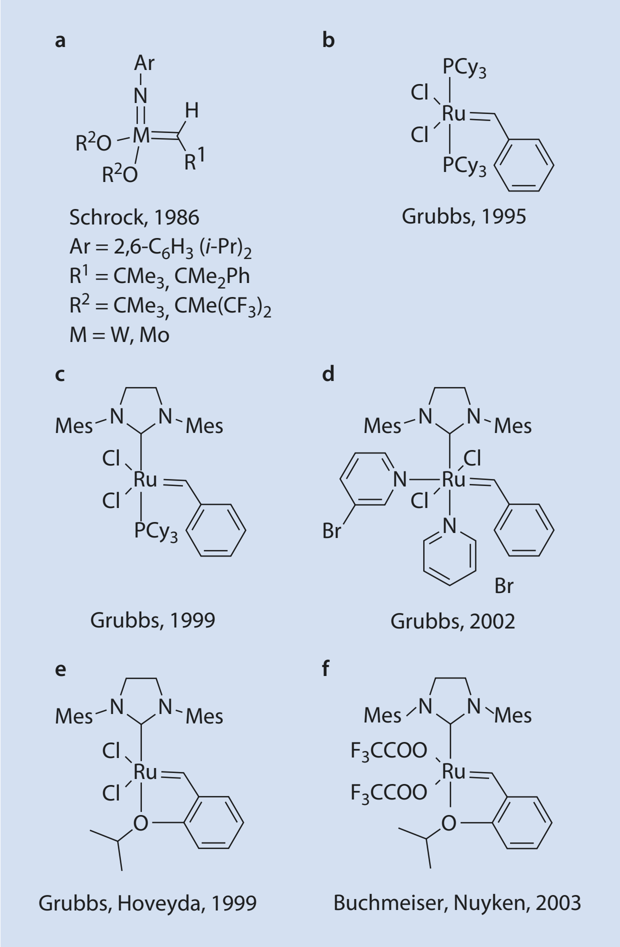
Homogeneous metathesis catalysts are nitrosyls, chlorides, or oxychlorides of tungsten or molybdenum in their higher oxidation states in combination with organotin compounds as cocatalysts (Table 11.4).

These systems can be used at room temperature. Their most serious disadvantage is that organometallic cocatalysts have to be used.

Table 11.4 Homogeneous metathesis catalysts

$WCl_6/EtOH/EtAlCl_2$	$MoCl_5/Ph_4Sn$
$WCl_6/BuLi$	$MoCl_3(NO)/EtAlCl_2$
$WOCl_4/EtAlCl_2$	

Fig. 11.28 A selection of well defined, homogeneous metathesis catalysts: (**a**) Schrock (1986), (**b**) Schwab et al. (1995), (**c**) Scholl et al. (1999), (**d**) Love et al. (2002), (**e**) Kingsbury et al. (1999), (**f**) Krause et al. (2003). *Mes*: 2,4,6-trimethyl phenyl, *Cy*: Cyclohexyl



The exceptionally active tungsten and molybdenum amido complexes, introduced by Schrock in 1986, were the starting molecules in the search for further, well defined catalysts (Schrock 1986). The ruthenium catalysts synthesized by Grubbs constituted a further breakthrough. Selected examples of well defined homogeneous catalysts are shown in Fig. 11.28.

Table 11.5 demonstrates how ruthenium-based metathesis catalysts triumph over the others. Although titanium-based catalysts do not tolerate any other functional groups, tungsten-based catalysts can tolerate esters and amides, molybdenum-based catalysts tolerate esters, amides, and ketones, and ruthenium-based catalysts are stable and active in the presence of nearly all functional groups. Ruthenium catalysts can even be used for metathesis in water.

Table 11.5 A comparison of the reactivity of metathesis complexes based on the most important metals with respect to olefins and other functional groups (decreasing reactivity from top to bottom) (Grubbs 1994)

Titanium	Tungsten	Molybdenum	Ruthenium
Alcohols, water	Alcohols, water	Alcohols, water	Olefins
Acids	Acids	Acids	Alcohols, water
Aldehydes	Aldehydes	Aldehydes	Acids
Ketones	Ketones	Olefins	Aldehydes
Esters, amides	Olefins	Ketones	Ketones
Olefins	Esters, amides	Esters, amides	Esters, amides

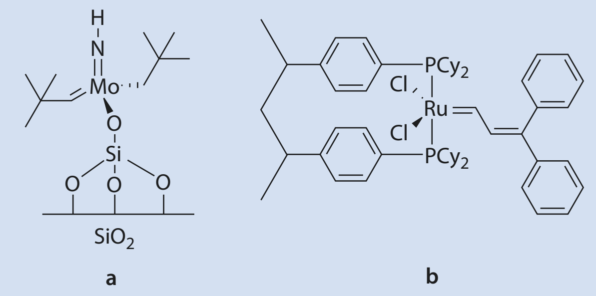


Fig. 11.29 The immobilization of well defined metathesis catalysts. (**a**) Schrock-type on SiO$_2$. (**b**) Grubbs-type on polystyrene

11.7.2.3 Immobilized Catalysts

The disadvantage of homogeneous metathesis catalysts is their insufficient reusability because the complex compounds are destroyed during the isolation of the products and undesirable transition metal traces remain in the product.

This problem can be overcome by immobilizing homogeneous catalysts on insoluble carriers. In this way the advantages of the homogeneous catalysts can be exploited, their disadvantages can be avoided, and the catalyst can be recovered by simple filtration for reuse. Two examples are shown in Fig. 11.29.

11.7.3 Metathesis Reactions

The most important metathesis reactions of olefins are summarized in Fig. 11.30.

As well as making unusual monomers accessible by disproportionation, the reciprocal transformation of monomers via metathesis is also of interest. Thus, for example, ethene reacts with 2-butene to give propene, a reaction which can also be reversed (Fig. 11.31).

Route b (Fig. 11.30) is most important for the synthesis of polymers by metathesis but they can also be synthesized using ADMET (route e, Fig. 11.30). By adding additional monomer the molar mass of the metathesis products can be reduced (i.e., reverse reaction of route e, Fig. 11.30). The ring closure metathesis (route c) and degradation

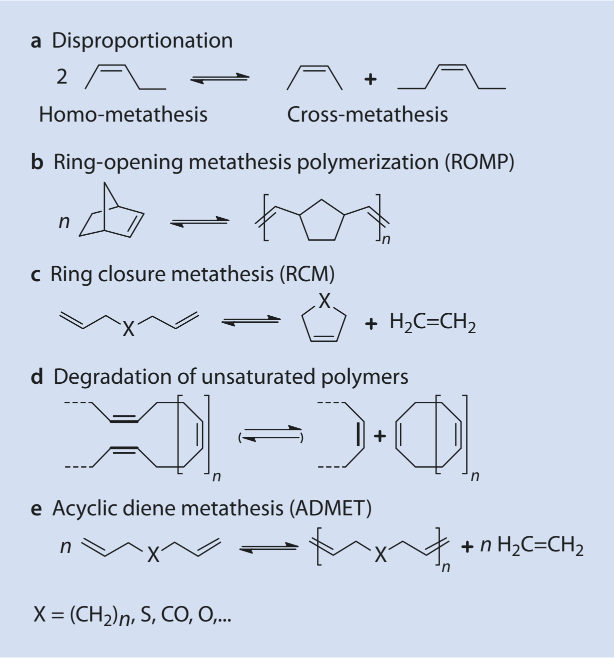
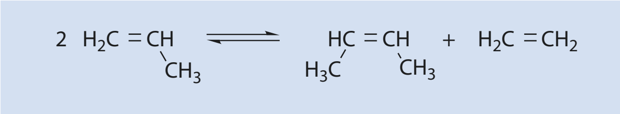


Fig. 11.30 Important metathesis reactions



$$2\ H_2C=CH-CH_3 \rightleftharpoons H_3C-HC=CH-CH_3 + H_2C=CH_2$$

Fig. 11.31 Reciprocal transformation of propene and ethene

reactions (route d, Fig. 11.30) are especially well suited to the synthesis of some special organic molecules.

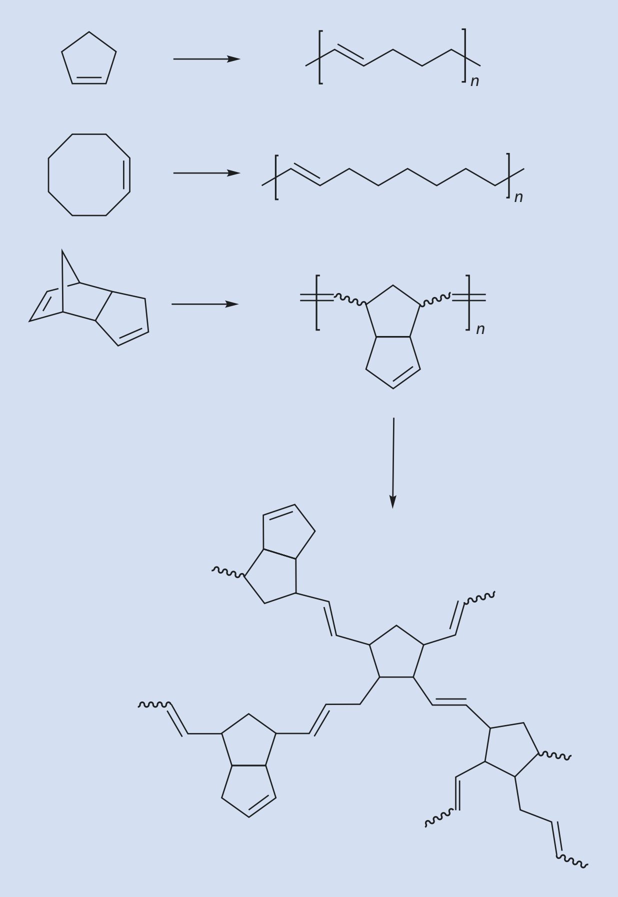
Important polymers produced by ROMP (Fig. 11.32) are polycyclopentene (Polypentenamer®), polycyclooctene (Vestenamer®), and polydicyclopentadiene, sold under several names.

Norbornenes can also be polymerized by ROMP. This reaction broadens the spectrum of interesting norbornene polymers that were already introduced in connection with polyinsertion (Fig. 11.22). Figure 11.33 gives an overview of the technically relevant structures. As ROMP-polymers have double bonds after polymerization, their resistance to atmospheric oxygen is limited (formation of allyl radicals!) and they are often hydrogenated to make them more weather-resistant.

A special case of a monomer that can be polymerized by metathesis catalysts is acetylene. Its polymerization (Fig. 11.34) is possible with classical metathesis catalysts as well as with Schrock systems whereas most of the ruthenium-based systems, such as the Grubbs' systems, are not suitable (Krause 2004).

This polymer is exceptional in that it has a continuous conjugated, pure sp^2-system along the polymer backbone; above and below the main polymer chain there is an unusually large, conjugated π-electron system. For this reason the polymer is black and electrically conductive when appropriately doped. Levels of conductivity can be reached that are

Fig. 11.32 Important polymers synthesized using ROMP



similar to those of conductive metals. However, two serious disadvantages have prevented the use of this fascinating material up to now. First, the very expansive π-electron system is very sensitive to oxidation so that polyacetylene (especially in its doped form) is sensitive to air; second, it is insoluble and infusible, which not only makes its processing but also its characterization difficult. Nevertheless, Heeger, MacDiarmid, and Shirakawa's work on polyacetylene was awarded the Nobel Prize for Chemistry in 2000.

Other monomers capable of metathesis are dialkynes, such as those shown in Fig. 11.35.

Dialkynes can be transformed using molybdenum catalysts of the Schrock kind or with special ruthenium catalysts (Fig. 11.28 (Buchmeiser, Nuyken)) into either perfect six-ring structures (molybdenum catalysts) or into five-ring structures (ruthenium systems) (Krause et al. 2004). These polymers are highly conjugated, similar to polyacetylene; they are however, significantly more stable and soluble, particularly in conventional solvents such as $CHCl_3$ and THF.

The living character of diyne-polymerizations can be exploited for the formation of block copolymers of the AB- and ABA-types. Monomers from Fig. 11.35 (forming the A-block) can, therefore, be combined with norbornenes (forming the B-block), for example.

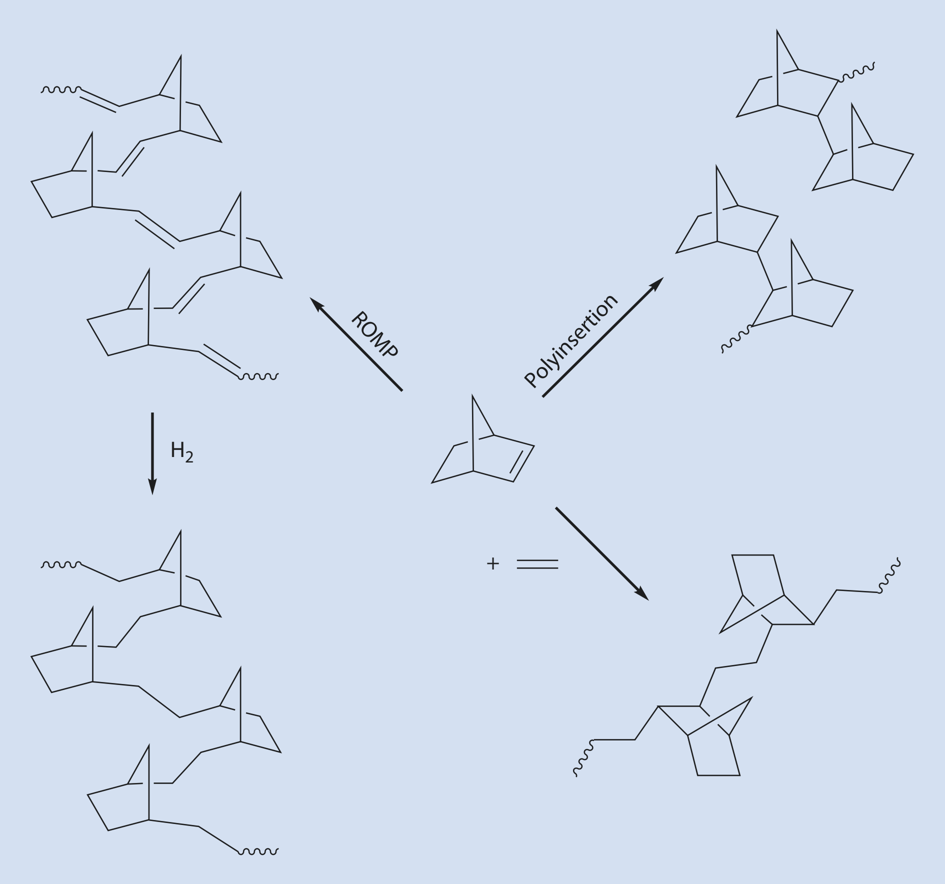


Fig. 11.33 Polymers based on norbornene

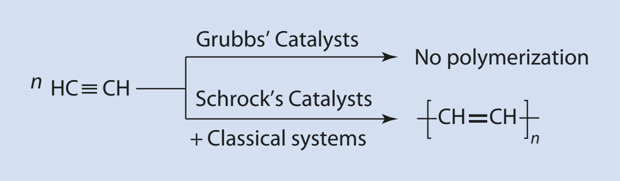


Fig. 11.34 Polymerization of acetylene with metathesis catalysts

11.8 Copolymerization with Polar Comonomers

Most of the transition metal catalysts capable of polymerizing olefins are very sensitive to hetero atoms. This can be explained by the low nucleophilicity of the olefin double bond in comparison to most hetero atoms. This is why the copolymerization of olefins with monomers that are known from ionic or radical polymerizations has its limitations. Some cases exist, in which olefins or epoxides can be catalytically copolymerized with polar monomers and they are discussed in the following paragraphs.

Fig. 11.35 The cyclopolymerization of 1,6-heptadiynes to five- and six-membered ring structures

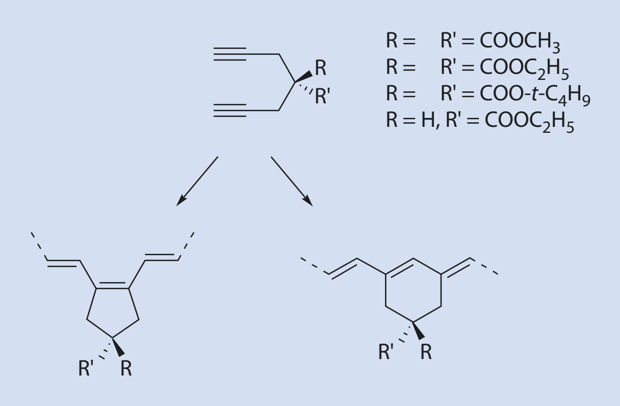
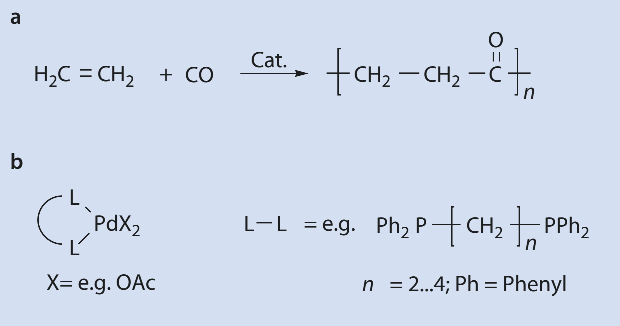


Fig. 11.36 (**a**) Copolymerization of ethene with carbon monoxide. (**b**) Possible catalysts



11.8.1 Olefin-CO Copolymers

A strictly alternating copolymer can be obtained by the copolymerization of ethene with carbon monoxide (Fig. 11.36). This copolymer is a polyketone. Palladium phosphine complexes are used as catalysts.

The mechanism (Fig. 11.37) is similar to that for olefin polymerization with metallocene catalysts. The monomers are coordinated and then inserted via chain migration.

The strictly alternating sequence of the two monomers is caused by the different stabilities and reactivities of the species formed during the catalytic cycle. The insertion of carbon monoxide into a palladium acyl compound is thermodynamically unfavorable. The insertion of an ethene molecule therefore always follows a CO-insertion. Conversely, the insertion of ethene is kinetically very inhibited. The rate of the insertion of a CO molecule is therefore significantly faster so that the insertion of carbon monoxide quickly follows the insertion of ethene and an alternating copolymer results.

As in the case of ethene, higher α-olefins can also be polymerized with CO. The generic polymer structure shown in Fig. 11.38 results. The insertion takes place in a regioselective manner, i.e., the substituent is bound to every third carbon atom along the polymer backbone in a regular fashion. The stereochemistry of the polymer can be controlled using catalysts with suitable symmetry.

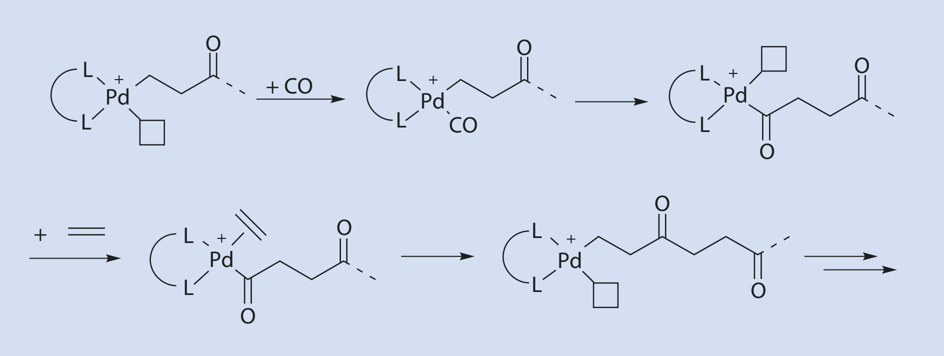
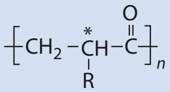


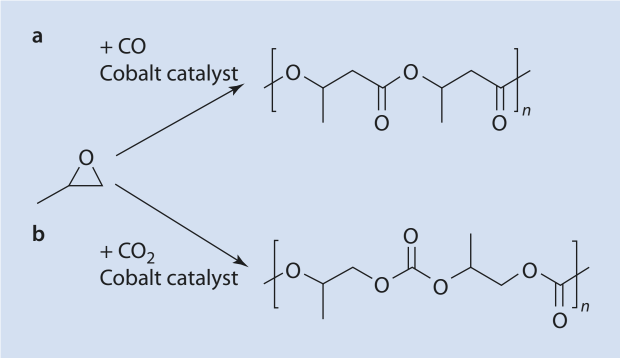
Fig. 11.37 Mechanism for the copolymerization of ethene and carbon monoxide

Fig. 11.38 Generic structure of copolymers from CO and α-olefins



$$\left[CH_2-\underset{R}{\underset{|}{\overset{*}{C}H}}-\overset{O}{\overset{\|}{C}} \right]_n$$

Fig. 11.39 Copolymerization of epoxides with (**a**) CO and (**b**) CO_2



11.8.2 Copolymers From Epoxides and Carbon Oxides

Epoxides can be copolymerized with carbon monoxide as well as with carbon dioxide using cobalt catalysts to yield polyesters or polycarbonates, respectively (Fig. 11.39).

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