

Review

Metal catalysts for the vinyl polymerization of norbornene

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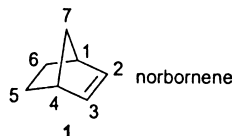
Abstract

A full literature and patent account (about 100 references) is given on work describing the vinyl polymerization to homo-polynorbornene. The interest in vinyl homo-polynorbornene is driven by its dielectric and mechanical properties for the technical application as an interlevel dielectric in microelectronics applications. The norbornene/olefin copolymerization is covered to some extent for comparison. The metal catalysts are presented and important polymer product properties are emphasized. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Bicyclo[2.2.1]hept-2-ene, better known by its trivial name norbornene (**1**) and its derivatives can be polymerized in three different ways (Fig. 1).



It is important to note that each route leads to its own polymer type which is different in structure and properties from the other two.

The best known polymerization of norbornene is the ring-opening metathesis polymerization (ROMP) [1]. The reaction is technically applied in the Norsorex process. The polymer thus, obtained is a polyalkenamer — it still contains double bonds in the polymer backbone. Through the double bonds the polymer

chains can be crosslinked, i.e. vulcanized. The vulcanized polynorbornene product is used as an elastomeric vulcanizable material for vibration and sound damping. It has specialist applications for engine mounts, shock-proof bumpers, and flexible couplings. In addition, porous polynorbornene is a soaking material for oil spills. Polynorbornene oil spill sponges can absorb up to 400% of their own mass as oil. Most publications on norbornene polymerization deal with the ring-opening metathesis reaction. The commercial polymerization process uses an RuCl_3/HCl catalyst in butanol.

Other technical ROMP processes generally employ tungsten, molybdenum, rhenium or ruthenium catalysts as metal halides, metal oxides or metal oxo-chlorides in combination with alkylating agents (e.g. R_4Sn , Et_2AlCl) and promoting agents (e.g. O_2 , EtOH , PhOH) [1]. While the industrial catalysts are usually heterogeneous, little-defined systems, academic research has focused on molecular single-component catalysts. Many of these latter well-defined catalysts are metal-carbene com-

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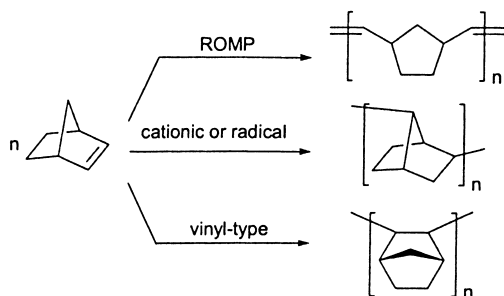


Fig. 1. Schematic representation of the three different types of polymerization for norbornene.

plexes. They are also predominantly based on tungsten (for examples of tungsten-carbene complexes for ROMP see [2–7]), molybdenum (for examples of molybdenum-carbene complexes for ROMP see [8–11]), and ruthenium (for examples of ruthenium-carbene complexes for ROMP see [12–14]). The possibility of a ring-opening metathesis polymerization of norbornene with catalyst systems based on titanium [15], tantal [16], and osmium [17] has been reported.

The control of stereochemistry in unsubstituted polynorbornene is possible through the choice of reaction conditions, such as catalyst, cocatalyst, activator, solvent, and temperature. Highly *cis*-polynorbornene was obtained with the catalyst system $\text{ReCl}_5/\text{EtAlCl}_2$ /ethyl acrylate; *trans*-polynorbornene with the system $\text{IrCl}_3 \cdot x\text{H}_2\text{O}/\text{EtAlCl}_2$. A higher stereoregularity in polynorbornene increases the glass temperature. The introduction of tacticity increased the permeability coefficient and improved the polymer stability [18].

Little is known about the cationic and the radical polymerization of norbornene. This route was first described in 1967 [19–22]. The result is a low molar mass oligomeric material with 2,7-connectivity of the monomer. Initiators for the radical polymerization were, for example, azoisobutyronitrile (AIBN), *tert*-butyl peracetate or *tert*-butyl perpivalate. The cationic polymerization was started with EtAlCl_2 [19].

It is also possible to polymerize norbornene and to leave the bicyclic structural unit intact, i.e. to open only the double bond of the π -component. Such a polymerization which is akin to the classical olefin polymerization is termed a vinyl polymerization here. The product does not contain anymore double

bonds. The vinyl polymerization of norbornene can take place as a homo- or as a copolymerization. The vinyl polymerization is much less developed for norbornene than ROMP. Common chemistry dictionaries or macromolecular textbooks do not make reference to the vinyl polymerization of norbornene. Occasionally the vinyl polymerization of cyclic olefins is also termed “addition polymerization” [23–25].

Of interest is the vinyl copolymerization of cyclic and acyclic (especially ethene and propene) olefins [26–30]. For specific work on ethene–norbornene copolymers (zirconocene/MAO catalysts: see [31–33], with Co(II) catalysts: [34] and [35–40]). Cycloolefin copolymers (COC) are produced by copolymerization of these cyclic olefins with ethene or α -olefins. Such a copolymerization can be carried out with metallocene and half-sandwich/MAO-catalysts [35–40]. The COC’s can be melt-processed. The materials can be extruded to foils, tubes, pipes, fibers, etc. Their high transparency makes them ideally suited for optical applications. Cycloolefin copolymers have high refractive indices close to crown glass. Thus, they can be applied as a glass substitute in lenses, prisms, carrier plates and foils for optical data storage, video and compact disks. They are envisioned as cover and focusing plates for solar cells or in glass fiber optics [26]. Hoechst and Mitsui Sekka have jointly developed a highly transparent technical plastic: a thermoplastic olefin polymer of amorphous structure (TOPAS). TOPAS is a copolymer from norbornene and ethene made through metallocene catalysis [41,42]. Cycloolefin copolymerization and COC’s have in part been included in some overviews on metallocene catalysts [43–49]. So, we mainly point to some of the literature references here, while a more detailed overview on the current state of the vinyl homo-polymerization of norbornene will be given in this article.

The homo-polymer vinyl polynorbornene is surely a special polymer. Its mechanical properties, heat resistivity, good solubility in organic solvents, and transparency are emphasized. Vinyl homo-polynorbornene is investigated inter alia as a deep UV photoresist and interlevel dielectric in microelectronics applications. Low dielectric constant interlevel dielectrics are seen as critical to the realization of high performance interconnections. High glass transition temperature polynorbornenes exhibit many of the key performance criteria necessary for these demanding applications,

which include good adhesion to a variety of films and substrates, thermal stability, high elongation-to-break values, and low stress [50]. The vinyl norbornene polymer is also said to have a cost advantage over related materials [51]. Films made from norbornene vinyl polymer are excellent in transparency and heat resistance and have unchanged viscoelastic and electric characteristics to markedly high temperatures. Such a film is suitable for a condenser or an insulator [52]. Homo-polynorbornene films are applied as cover layers for liquid-crystal displays. The polymer is developed by the B.F. Goodrich Co. under the trade name Avatrel[®] dielectric polymer [50,51]. The sometimes poor adhesion of homo-polynorbornene can be improved by attaching triethoxysilyl groups to the polymer backbone. Alkyl groups on the backbone lower the rigidity of the system and result in higher elongation-to-break values and a decrease in residual stress [50].

Catalysts containing the metals titanium, zirconium, cobalt, chromium, nickel and palladium are described in the literature for the vinyl homo-polymerization of norbornene and strained cyclic olefins in general [23]. Fig. 2 summarizes the possible metals for the two coordination polymerization types, ROMP and vinyl polymerization. It is evident that the different directions of double bond opening usually require different metals. Titanium and cobalt are interesting cases where both reactions become possible depending on the co-catalyst ratio (Ti) [25,53,54] or the type of cocatalyst employed (Co) [24].

From their metal composition the catalysts for vinyl polymerization can be divided into three groups: (a) early transition metals, especially the metallocene

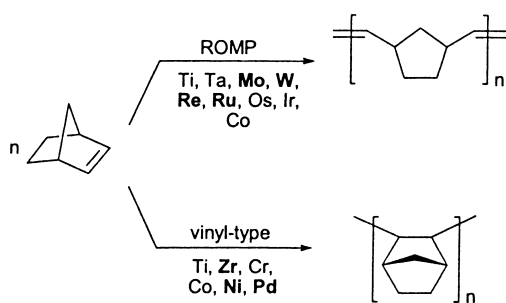


Fig. 2. Schematic representation of the two types of coordination polymerization for norbornene together with the metals used in the catalytic systems. Predominant metals are given in bold.

catalysts of zirconium; (b) the late transition-metal palladium(II) and nickel(II) catalysts; (c) the less used and seldom mentioned central transition metals chromium and cobalt. These three groups will be treated separately in the following. Generally, the neutral pre-catalytic metal complexes require a cocatalyst for their activation, with MAO being the activator of choice here. While the cationic palladium complexes are active without a cocatalyst [55]. These palladium systems of the general formula $[\text{Pd}(\text{NCR})_4]^{2+}2\text{L}^-$ contain weakly bound nitrile ligands and “non”-coordinating counter ions, such as BF_4^- .

1.1. Vinyl polymerization with early transition metals

1.1.1. Titanium catalysts

The first vinyl polymers of norbornene were obtained with a $\text{TiCl}_4/\text{Al}^i\text{Bu}_3$ catalyst with an Al:Ti ratio of 1:2 in the early 1960s [53,56]. In the case of the similar catalyst system $\text{TiCl}_4/\text{AlEt}_3$ it was shown that an increase in the Al:Ti ratio resulted in a mixture of metathesis polymer and vinyl polymer [54]. Also, amine addition to the system $\text{TiCl}_4/\text{AlEt}_3$ alters the polymerization exclusively to the ring-opening type [57]. There is a report on the ionic species $[\text{Cp}_2\text{TiCH}_3]^+[\text{Cl-MAO}]^-$ together with evidence for the synthesis of polyethene–polynorbornene di-block copolymers in an addition polymerization [32].

1.1.2. Metallocene catalysts of zirconium (and hafnium)

Metallocene catalysts which consist of a “metallocene” of group IV (mostly zirconium) and methylalumoxane (MAO) (Fig. 3) are covered in a large number of review articles [43–49,58–66]. The term “metallocene” often refers to a metallocene dichloride as the pre-catalyst.

The metallocene catalysts allowed apparently for the first time for a general facile polymerization of cyclic olefins without ring-opening. Classical, heterogeneous Ziegler–Natta catalysts could polymerize strained cyclic alkenes only with difficulty. A study by Kaminsky described the polymerization of the cycloolefins cyclobutene, cyclopentene and norbornene with the chiral metallocenes $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (**2**) and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ (**3**), in combination with MAO [67].

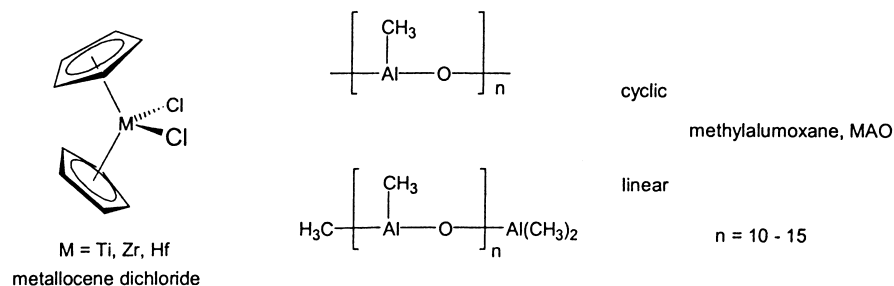
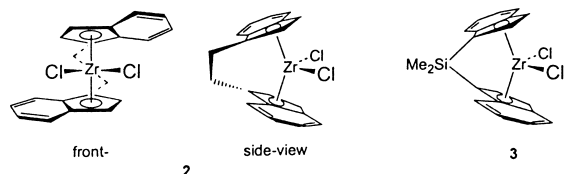
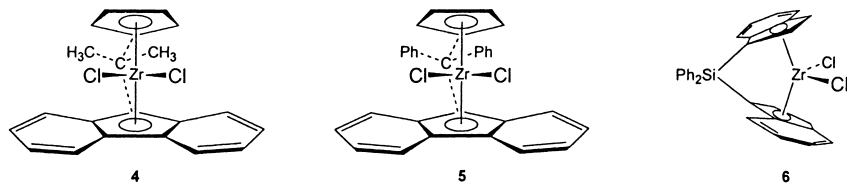


Fig. 3. Basic features of metallocene catalysts: the metallocene dichloride precatalyst and the MAO cocatalyst.



In a series of experiments it was shown that the catalytic systems **2**/MAO or **3**/MAO showed a considerably higher polymerization activity towards cyclobutene and cyclopentene than towards norbornene. Between the two catalysts, **3** was the more active one. However, catalyst **2**/MAO was still 100 times more active than the simple Cp₂ZrCl₂/MAO-system. The copolymerization of norbornene and ethene was investigated. The copolymerization was strongly influenced by the monomer ratio and the reaction temperature. The catalyst **2**/MAO had a maximum activity at a molar ratio of ethene:norbornene of 1:1. The norbornene–ethene copolymer possessed a statistical monomer distribution. Block formation occurred at a high norbornene concentration [67].

Another study by Kaminsky and coworkers was carried out with the C_s-symmetrical complexes [Me₂C(Fluo)(Cp)]ZrCl₂ (**4**) and [Ph₂C(Fluo)(Cp)]ZrCl₂ (**5**) together with the C₂-symmetrical pre-catalysts [Me₂Si(Ind)₂]ZrCl₂ (**3**) and [Ph₂Si(Ind)₂]ZrCl₂ (**6**). Activation was done with MAO [68].



The polymerization reactions were carried out under an argon atmosphere and in toluene as a solvent.

The copolymerization of norbornene and ethene was investigated in more detail. It became clear that the polymerization rates were quite different for the two types of catalysts. The C₂-symmetrical catalysts **3** and **6**/MAO were highly active in the ethene polymerization. In both cases the activities dropped rapidly with an increasing norbornene–ethene ratio [68]. Whereas the C_s-symmetrical catalysts **4** and **5** had a completely different copolymerization behavior. Both compounds showed a slight maximum in activity as a function of monomer ratio $c_{\text{norb.}} : c_{\text{ethene}}$. For system **4** this maximum was at $c_{\text{norb.}} : c_{\text{ethene}} = 3$ and for **5** at $c_{\text{norb.}} : c_{\text{ethene}} = 0.6$. At higher monomer ratios both compounds had a constant activity of 2200 and 2400 kg copolymer/(mol Zr bar h) for **4** and **5**, respectively. This reaction behavior clearly indicated better sterical prerequisites of the C_s-symmetrical catalysts **4** and **5** for the insertion of bulky olefins. The shorter bridge of the C_s-catalysts results in a wider opening angle of the ring ligands around zirconium, thus, creating a larger coordination gap [69,70]. The catalyst symmetry could also be correlated with the stereochemistry of the polymer chain [71]. The mechanism of the alternating ethene–norbornene copolymerization was studied in detail using [Me₂C(Fluo)(3-¹BuCp)]ZrCl₂/MAO. Copolymerization models were developed and applied [72].

The vinyl polymerization and copolymerization of norbornene and other cycloolefins with metallocene

catalysts has been described in a number of patents. A summary of the patent literature with metallocenes and other early transition-metal catalysts for the vinyl polymerization of norbornene follows. We give a brief overview by listing the patent title and the catalyst systems that have been mentioned in the experimental section of the patent. The norbornene monomer is unsubstituted (2-)norbornene; copolymerization was with ethene; the cocatalyst is a methylalumoxane solution in toluene, unless noted otherwise. In some of the patents hafnium is also mentioned as the metal.

Title: bulk polymerization with metallocene catalyst for the preparation of cycloolefin polymers.

Catalysts used: diphenylmethylen-(9-fluorenyl)-cyclopentadienyl-zirconiumdichloride, isopropylene-(9-fluorenyl)-cyclopentadienyl-zirconium dichloride, dicyclopentadienylzirconium dichloride, (*rac*-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride, methyl (phenyl)-methylene-(9-fluorenyl)-cyclopentadienyl-zirconium dichloride, diphenylmethylene-(9-fluorenyl)-cyclopentadienyl-hafnium dichloride [26].

Title: cycloolefinic(co)polymer with a narrow molecular weight distribution and process for preparing same.

Catalysts used: *rac*-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride, fluorenyl-cyclopentadienyl-diphenyl-carbyl-zirconium dichloride [27].

Title: process for the preparation of chemically homogenous cycloolefinic copolymers.

Catalysts used: isopropylene-(9-fluorenyl)(1-(3-isopropyl) cyclopentadienyl)-zirconium dichloride, isopropylene-(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)-zirconium dichloride, diphenylmethylen-(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)-zirconium dichloride, methylphenylmethylen-(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)-zirconium dichloride, dimethylsilyl-(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)-zirconium dichloride, diphenylsilyl-(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)-zirconium dichloride, diphenylmethylen-(9-fluorenyl)(1-(3-*tert*-butyl) cyclopentadienyl)-zirconium dichloride, isopropylene-(9-fluorenyl)(1-(3-*tert*-butyl) cyclopentadienyl)-zirconium dichloride, [and the corresponding hafnium dichlorides], *meso*-dimethylsilyl-bis(1-(3-methyl)cyclopentadienyl)-zirconiumdichlorid, *meso*-dimethylsilyl-bis(1-(2,4-dimethyl)cyclopentadienyl)-zirconium dichloride, *meso*-dimethylsilyl-bis(1-indenyl)-zirconium dichloride, *meso*-diphenylsilyl-bis(1-

indenyl)-zirconium dichloride, *meso*-isopropylene-bis-(1-indenyl)-zirconium dichloride, *meso*-diphenylmethylen-bis(1-indenyl)-zirconium dichloride, *meso*-methylphenylmethylen-bis(1-indenyl)-zirconium dichloride, *meso*-diphenylsilyl-bis(1-indenyl)-hafnium dichloride, *meso*-dimethylsilyl-bis(1-indenyl)-hafnium dichloride, *meso*-1,2-ethylen-bis(1-indenyl)-zirconium dichloride, *meso*-1,2-ethylen-bis(1-indenyl)-hafnium dichloride [28].

Title: process for preparing cycloolefin polymers.

Catalysts used: *rac*-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride, *rac*-dimethylgermyl-bis-(1-indenyl)-zirconium dichloride, *rac*-phenylmethylsilyl-bis-(1-indenyl)-zirconium dichloride, *rac*-phenylvinylsilyl-bis-(1-indenyl)-zirconium dichloride, 1-silacyclobutyl-bis-(1'-indenyl)-zirconium dichloride, *rac*-ethylen-bis-(1-indenyl)-zirconium dichloride, *rac*-diphenylsilyl-bis-(1-indenyl)-hafnium dichloride, *rac*-phenylmethylsilyl-bis-(1-indenyl)-hafnium dichloride, *rac*-dimethylsilyl-bis-(1-indenyl)-hafnium dichloride, *rac*-diphenylsilyl-bis-(1-indenyl)-zirconium dichloride, diphenylmethylen-(9-fluorenyl)cyclopentadienyl-zirconium dichloride, isopropylene-(9-fluorenyl)cyclopentadienyl-zirconium dichloride [73].

Title: cycloolefin copolymers and a process for their preparation.

Catalysts used: diphenylmethylene-(cyclopentadienyl)-(9-fluorenyl)-zirconium dichloride [74].

Title: process for the preparation of cycloolefin polymers.

Catalysts used: *rac*-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride, *rac*-dimethylgermyl-bis-(1-indenyl)-zirconium dichloride, *rac*-phenylmethylsilyl-bis-(1-indenyl)-zirconium dichloride, *rac*-phenylvinylsilyl-bis-(1-indenyl)-zirconium dichloride, 1-silacyclobutyl-bis-(1'-indenyl)-zirconium dichloride, *rac*-ethylen-bis-(1-indenyl)-zirconium dichloride, *rac*-diphenylsilyl-bis-(1-indenyl)-hafnium dichloride, *rac*-phenylmethylsilyl-bis-(1-indenyl)-hafnium dichloride, *rac*-dimethylsilyl-bis-(1-indenyl)-hafnium dichloride, *rac*-diphenylsilyl-bis-(1-indenyl)-zirconium dichloride, diphenylmethylene-(9-fluorenyl)cyclopentadienyl-zirconium dichloride, isopropylene-(9-fluorenyl)cyclopentadienyl-zirconium dichloride [75].

Title: blends of polyolefins and syndiotactic vinyl polymers.

Catalysts used: (Me₂Si)Ind₂ZrCl₂ (in combination with CpTiCl₃ and aluminum triisobutyl in

toluene; copolymerization with styrene and propylene) [76].

Title: polymer blends of cycloolefin polymers and polyolefins.

Catalysts used: diphenylcarbyl-(cyclopentadienyl)-(9-fluorenyl)-zirconium dichloride, *rac*-dimethylsilyl-bis-(1-indenyl)-zirconium dichloride [77].

Title: cycloolefin copolymers and process for their preparation.

Catalysts used: diphenylmethylene-(cyclopentadienyl)-(9-fluorenyl)-zirconium dichloride (copolymerization with ethylene and 5-vinylnorbornene-2) [78].

Title: cycloolefin copolymers and process for their preparation.

Catalysts used: diphenylmethylene-(9-fluorenyl)-cyclopentadienyl zirconium dichloride, bis-(indenyl)-zirconium dichloride (copolymerization with ethylene and 5-vinylnorbornene-2) [79].

Title: cycloolefin copolymers and process for their preparation.

Catalysts used: diphenylmethylene-(9-fluorenyl)-cyclopentadienyl zirconium dichloride, dimethyl-(metylenbisindenyl) zirconium dichloride (copolymerization of 2-norbornene with ethylene and 5-vinylnorbornene-2, respectively 2,5-norbornadiene, 5-ethylidene-2-norbornene) [80].

Title: process for preparation and purification of material of a cycloolefin copolymer.

Catalysts used: isopropylene-(9-fluorenyl)(1-(3-methyl)-cyclopentadienyl) zirconium dichloride (copolymerization of 2-norbornene with ethylene, respectively ethylene and decahydronaphthalene) [81].

1.1.3. Vanadium catalysts

There is one report on the use of vanadium complexes for the vinyl polymerization of norbornene in the form of a patent.

Title: homogeneous addition copolymers of ethylene and cycloolefin monomers and the production thereof.

Catalysts used: VCl₅, VOCl₃, VCl₃, VO(OC₂H₅)₂Cl, VO(OCH₃)₂Cl, VO(OCH₃)Cl₂, VO(OCH₃)₃, VO(OC₃H₇)Cl₂, VCl₄, VO(OC₃H₇)₃.

Cocatalysts used: Al(CH₃)₂Cl, AlCH₃Cl₂, Al(OC₄H₉)(C₄H₉)Cl, Al(C₂H₅)₂Cl, Al₂(C₂H₅)₃Cl₃.

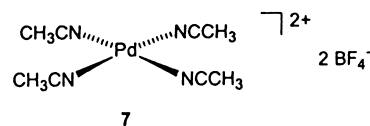
Norbornene monomers used: 5-methyl-2-norbornene, 2-norbornene, 5-ethyl-2-norbornene, 5-propyl-2-norbornene [82].

1.2. Vinyl polymerization with late transition metals

1.2.1. Palladium catalysts

To the best of our knowledge, the first vinyl polymerization of norbornene and substituted norbornene derivatives with palladium catalysts was mentioned in 1966 using PdCl₂ [83,84] and then again in the late 1970s using Pd(C₆H₅CN)₂Cl₂ [21,22,85] and also Pd(Ph₃P)₂Cl₂ [85].

Eventually, the cationic palladium(II) catalyst-system [Pd(CH₃CN)₄](BF₄)₂ (**7**) became the most frequently mentioned one for norbornene polymerization. The system was first introduced by the Sen-team in 1981 with regard to the polymerization of olefins [86,87].



Complex **7** with the weakly bound acetonitrile ligands was examined for its catalytic properties regarding the polymerization of olefins and that of norbornene as well. The compound was catalytically active without the presence of a cocatalyst. The vinyl polymerization of norbornene was carried out by adding 100 equivalents of monomer to a solution of **7** in nitromethane (CH₃NO₂) under Schlenk-conditions at 25°C. After only 5 min a polymer yield of more than 90% was obtained. The average molar mass, however, could not be determined, since the polymer was insoluble in tetrahydrofuran (THF), CHCl₃, CH₂Cl₂, and C₆H₆ [86–88].

An interesting complex may also be [Pd(PPh₃)_n(CH₃CN)_{4–n}](BF₄)₂ (*n* = 1–3). Although mainly used for the copolymerization of carbon monoxide with ethene, it may also prove valuable for the polymerization of norbornene [89].

For many years, the vinyl polymerization of norbornene did not raise much interest and research with the late transition metals almost came to a standstill. In 1991, Risse took up the research on palladium(II)-catalysts again [25,90]. It was found that the resulting vinyl polynorbornene had a relatively good solubility in tetrachloroethene, trichloromethylbenzene, chlorobenzene, and 1,2-dichlorobenzene. This allowed for polymer characterization by size exclusion chromatography (SEC, GPC), vapor phase osmometry (VPO), and solution viscosimetry. All

Table 1
Norbornene polymerization results with $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, **7** [25,90]

(Norbornene): 7 ^a	$\eta_{\text{inh}}/(\text{dl g}^{-1})^{\text{b}}$	$M_n/\text{g mol}^{-1\text{c}}$	M_w/M_n	$M_n/\text{g mol}^{-1}$ (VPO) ^e	$M_n/\text{g mol}^{-1}$ (SEC) ^f	$M_{n,\text{theor.}}/\text{g mol}^{-1\text{g}}$
20	0.07	— ^d	— ^d			
100	0.22	24000	1.41			
200	0.31	38000	1.45			
333	0.45	70000	1.36			
1000	1.10	— ^d	— ^d			
91				6200	11300	6700
67				5000	9500	5000
50				4600	8000	3800
40				3500	5000	3000

^a Initial molar ratio norbornene: **7**.

^b Inherent viscosity η_{inh} in chlorobenzene (25°C).

^c Determined by SEC in chlorobenzene (vs. polystyrene standards).

^d Not determined.

^e Determined at 90°C in chlorobenzene.

^f Determined by SEC in chlorobenzene (vs. polystyrene standards).

^g $M_{n,\text{theor.}} = ([\text{norbornene}]/[\mathbf{7}]) (\text{yield in \%}/100\%) M_{\text{norb.}}$; under the assumption of a living polymerization, i.e. one chain per Pd-complex and each Pd complex being catalytically active.

of the polymerizations were performed using the Schlenk-technique by adding a solution of norbornene in CH_3NO_2 to **7** in CH_3NO_2 . The polymer precipitated within 5 min. Some results of the polymerization are summarized in Table 1.

Among other things it turned out that increasing the ratio of norbornene to the catalyst **7** resulted in the formation of higher molar mass polymers. A certain drawback was the then limited solubility of norbornene in CH_3NO_2 . This especially affected reactions using a monomer-to-catalyst ratio larger than 100:1. Premature precipitation of the polymer resulted in slightly reduced yields and molar masses and also in a broadening of the molar mass distributions [25,90].

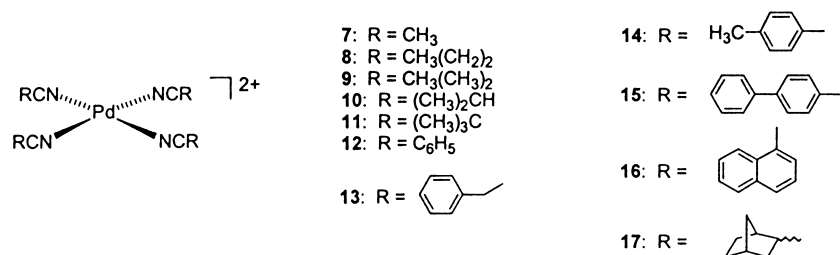
The possibility of a nearly homogeneous polymerization of norbornene with **7** was investigated with a solvent mixture of nitrobenzene and chlorobenzene (volume ratio = 1:2) [91]. Under these conditions chain growth continued after renewed monomer additions, indicating rare chain transfer and chain termination. Also, the polydispersity was reduced considerably in these experiments. The polymerizations were run, for example, to 35 and 54% conversion at 0°C, obtaining polydispersities M_w/M_n as low as 1.07. Even for monomer conversions up to 80% polydispersities were well below 1.2 [91].

A study on the polymerization of norbornene in a water dispersion or in an aqueous emulsion has been reported [92]. The polymerization was carried out in

a water dispersion by heating water, norbornene and PdCl_2 (molar ratio norbornene:catalyst = 100 : 1) at 70°C over 24 h. After a 15–20 min induction period, the polymer precipitated as a powder. The polynorbornene was insoluble in conventional solvents. After 24 h a polymer yield of 70% was obtained. A corresponding polymerization in aqueous emulsion was supplemented with sodium dodecylsulphate (SDS) and then carried out in the same way. Depending on the SDS-concentration, polymers (yields between 80 and 90%) with an average molar mass of $M_n = 690$ (at 1 wt.% SDS), $M_n = 840$ (at 3 wt.% SDS) and $M_n = 1010$ (at 6 wt.% SDS) were obtained.

The vinyl polymerization of exo- and endo-substituted norbornene derivatives was investigated. Substitution included polycyclic norbornenes as well as ester groups [93–95]. The Pd(II) catalyst **7** was found to tolerate the ester functionality. However, the rate of polymerization was reduced in comparison to unsubstituted norbornene [94].

In a study by Heitz and Wendorff the residues of the nitrile ligands in the catalyst system $[\text{Pd}(\text{RCN})_4]^{2+}$ were varied (see also [25]), with the complexes being used in the polymerization of norbornene [96]. The catalysts could be dissolved in the same solvent which contained polynorbornene, so that the polymerization was performed in a homogeneous phase. The following chart shows the residues R which were used.



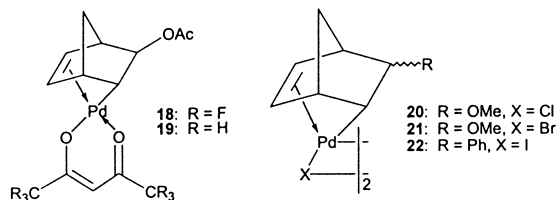
The work by Heitz and Wendorff indicated that for nearly all the catalysts **7–17** polymer yields were very similar to each other. The only exception represented catalyst **7**. It was especially important that the yields were independent of the nature of the nitrile residue, i.e. whether the nitrile ligands were aliphatic or aromatic. A polydispersity M_w/M_n between 1.3 and 1.5 indicated a living polymerization. Under the assumption of a living polymerization, i.e. one polymer chain per Pd center, a theoretical molar mass was calculated according to the formula $M_{n,theor.} = ([\text{norbornene}]/[\text{Pd}]) (\text{yield in } \%/100\%) M_{\text{norb.}}$. This assumes, of course, that every Pd center becomes catalytically active [96].

A second set of experiments showed that the presence of acetone led to the deterioration of yields and polydispersities. The catalyst system **17** was soluble in C₆H₅Cl, so that a polymerization of norbornene could be carried out in this solvent. Under standard conditions (reaction time 1 h, room temperature), a yield of only 45% was obtained. However, the yield could be improved by increasing reaction temperature and time [96].

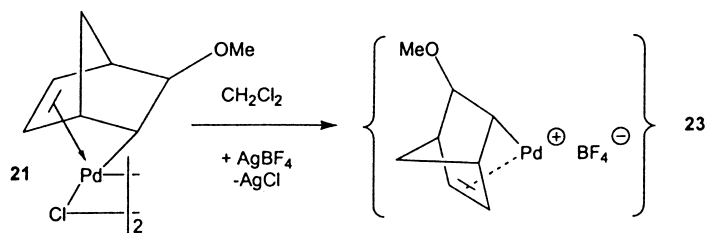
Another study by Heitz et al. investigated inter alia the influence of counterions in the catalyst system $[\text{Pd}(\text{CH}_3\text{CN})_4]^+$ (**7**) on the polymerization of norbornene [97]. Counterions used were BF₄⁻, OSO₂CF₃⁻, SbCl₆⁻, and SnCl₆²⁻. The results showed that with the smallest counterion BF₄⁻, the polynorbornene had a significantly higher average molar mass under standard conditions (1 h, room temperature, [norbornene] : [**7**] = 500:1).

The vinyl polymerization of norbornene with $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (**7**) in the presence of ethene resulted in polynorbornene with narrow molar mass distribution. Neither termination and transfer reactions were found, nor could any incorporation of ethene be detected [97].

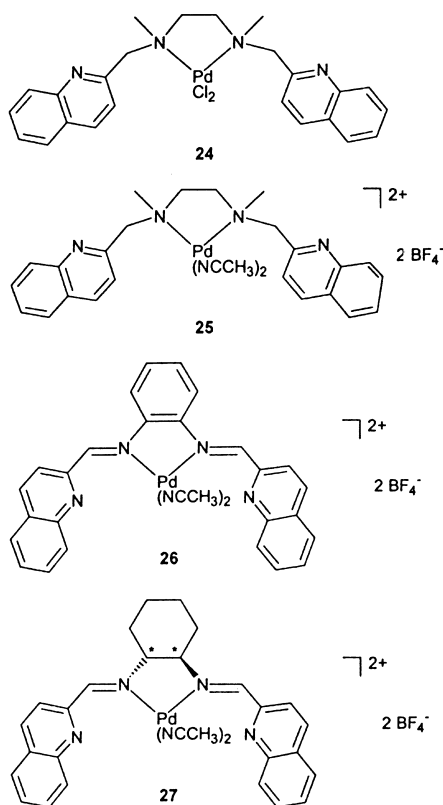
In 1995, Safir and Novak introduced a new series of palladium(II)-catalysts for the 1,2-polymerization of bicyclic olefins. They had found that norbornene can be quantitatively polymerized by the σ -, π -bicyclic catalysts **18–22** in less than 15 min using even wet solvents such as THF [98,99]. Before their study, an uncharacterized π -allylic complex which was prepared from β -pinene and Pd(C₆H₅CN)₂Cl₂ was already employed in the polymerization of olefins, including norbornene [100].



In 1997, Heitz and Wendorff et al. published a study on the further development of these catalysts. Poly(norbornene-carboxylic esters) could be obtained in relatively high yields and high molecular weights by the catalyst system **23** [101]. Follow-up studies with these novel catalyst systems included norbornene derivatives and copolymerization [102,103].



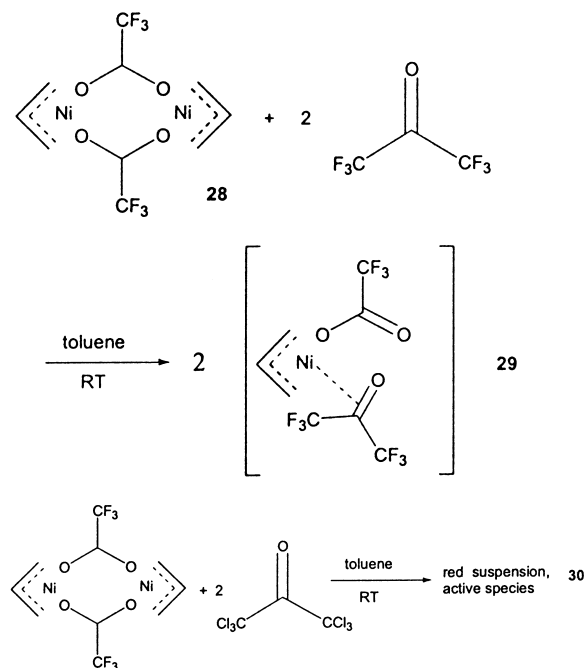
The induction of stereoregularity into polynorbornene requires a chiral and C_2 -symmetric ligand arrangement around the active metal center. This was the case in the metallocene catalysts **2**, **3**, and **6**. As a means to introduce C_2 -symmetrical chirality into palladium complexes, the following compounds **24–27** were synthesized and tested by Rieger et al. towards norbornene polymerization. The palladium(II) compounds carry possibly tetradentate chelate ligands which bear sterically demanding 2-quinolinyl moieties. A fluxional coordination of the 2-quinolinyl side groups was hoped for to help in a control of the stereochemistry of polymerization reactions. Complexes **24–27** were found active in norbornene homo-polymerization without a cocatalyst and in a solvent mixture of CH_2Cl_2 and 1,2-dichlorobenzene. From complexes **26** and **27** the polymers were insoluble. Comparison of the ^{13}C NMR spectra and the decomposition temperature TGA for polymers obtained with chiral **27** and with achiral **7** seemed to indicate a certain degree of stereoregularity in the former [104].



An overview on the patent literature of palladium is combined with the nickel catalysts at the end of the following section. The vinyl polymerization and copolymerization of norbornene and other cycloolefins with both palladium and nickel catalysts has mostly been described within the same patent.

1.2.2. Nickel catalysts

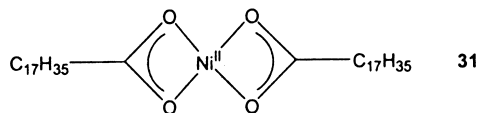
Nickel complexes for the vinyl polymerization of norbornene were introduced in the 1990s. In 1993, Deming and Novak presented the nickel catalyst systems **28**, **29** and **30** [105].



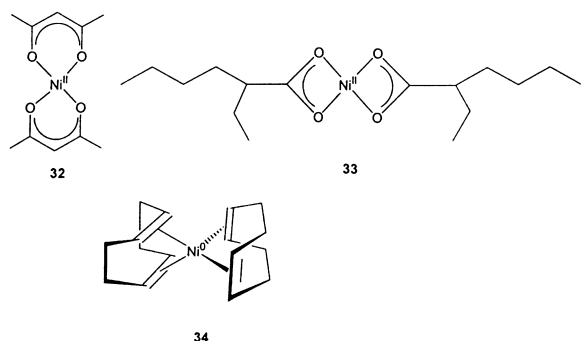
With respect to the polymerization of norbornene, compound **28** was found inactive. System **29** and **30**, however, have been demonstrated as very active catalysts for the polymerization of norbornene, with no cocatalyst necessary [105]. The dimeric structure of **28** with substituted allyl groups was later substantiated by X-ray crystallography. With 1-phenylallyl compound **28** was at the same time able to polymerize norbornene with low activity to an oligomer with $M_n = 1300 \text{ g mol}^{-1}$ and a polydispersity of 1.1 [106].

Usually, the vinyl polymerization of norbornene with nickel catalysts is carried out in combination with MAO as a cocatalyst [107,108]. The nickel-stearate

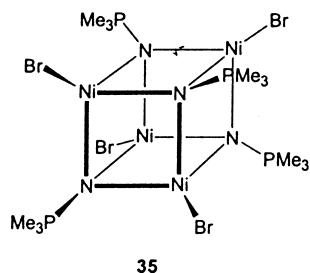
complex **31**/MAO polymerized norbornene under a nitrogen atmosphere in toluene and in chlorobenzene at room temperature.



An article by Arndt and Gosmann reports a study on the polymerization of norbornene with the catalysts Ni(acac)₂ (**32**), Ni(2-ethylhexanoate)₂ (**33**), and (COD)₂Ni⁰ (**34**) (COD = cyclooctadiene) in combination with the cocatalyst MAO. The polymerizations were carried out at room temperature, in toluene and under an argon atmosphere [108].



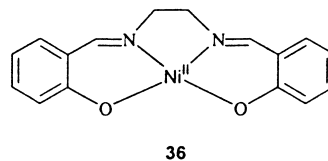
Another highly active catalyst for the polymerization of norbornene is the complex [BrNi(NPMe₃)]₄ (**35**) in combination with MAO. Greiner et al. could observe catalyst activities up to 20.5 t/(mol Ni h) and polymer molar masses up to 3.4 × 10⁶ g mol⁻¹ [109].



The polymer yield or catalyst activity of **35**/MAO and the molar mass of the polynorbornene could be controlled through the reaction parameters temperature, time and the molar ratios Al:Ni and norbornene:Ni. The molar ratio Al:Ni had a significant

impact on the polymer yield, yet, it did not affect the molar mass much. An increase in the monomer:Ni ratio, concomitant with the monomer concentration, increases both the catalyst activity and the polymer molar mass. The molar mass increases almost linearly with a decrease in reaction temperature from +40 to -40°C. The catalyst activity remained constant down to -20°C. An increase in reaction time showed some molar mass dependency whereas the yield increase and the activity decrease were as expected.

Nickel(salen) **36** together with MAO catalyzes the addition polymerization of norbornene. Normal MAO and AlMe₃-free MAO was investigated as a cocatalyst. Polymerization was carried out in chlorobenzene and the polymer was soluble in 1,2,4-trichlorobenzene [110].



The vinyl polymerization and copolymerization of norbornene and other cycloolefins with palladium and nickel catalysts has mostly been described in joint patents. A summary of the patent literature with late transition-metal catalysts for the vinyl polymerization of norbornene follows. We give a brief overview by listing the patent title and the catalyst systems that have been mentioned in the experimental section of the patent. The norbornene monomer is unsubstituted (2-)norbornene; copolymerization was with ethene; the cocatalyst is a methylalumoxane solution in toluene, unless noted otherwise.

Title: norbornene-based polymer, process for production of said polymer, film of said polymer, and process for production of said film.

Catalysts used: nickel bis(acetylacetonate), allyl-cyclopentadienylnickel, dichlorobis(benzonitrile)-palladium, dichloro(1,5-cyclooctadiene)palladium.

Cocatalysts used: methylalumoxane, trimethylaluminum, triisobutylaluminum.

Norbornene-monomers used: 2-norbornene, 5-ethylidene-2-norbornene [111].

Title: process for making polymers containing a norbornene repeating unit by addition polymerization using an organo (nickel or palladium) complex.

Catalysts used: $[(\eta^3\text{-crotyl})(\text{cycloocta-1,5-diene})\text{nickel}]$ hexafluorophosphate, tetrakis(acetonitrile)-palladium(II) tetrafluoroborate, $[(\eta^3\text{-crotyl})(\text{cycloocta-1,5-diene})\text{nickel}]$ tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate, [6-methoxynorbornen-2-yl-5-palladium(cyclooctadiene)]hexafluorophosphate, $[(\eta^3\text{-crotyl})(\text{cycloocta-1,5-diene})\text{palladium}]$ hexafluorophosphate, nickel ethylhexanoate, η^3, η^2, η^2 -dodeca-2(E), 6(E), 10(Z)-triene-1-ylnickel hexafluorophosphate, tetrakis(octanitrile)palladium(II) tetrafluoroborate, $[(\eta^3\text{-cyclooctenyl})(\text{cycloocta-1,5-diene})\text{nickel}]$ tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate, $\{\text{CH}_3\text{Ni}(\text{C}_2\text{H}_4)_2\}^- \text{Li}\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}^{2+}$, bis(η^3 -allyl nickel trifluoroacetate), η^3, η^2, η^2 -dodeca-2(E), 6(E), 10(Z)-triene-1-ylnickel, η^3 -crotyl(cycloocta-1,5-diene)nickel, manganese lin-all, molybdenum hex-chem.

Norbornene-monomers used: 2-norbornene, 5-decyl-norbornene, 5-methylnorbornene, 5-(hexadecyl)norbornene, ethylidenenorbornene, 5-(non-afluorobutyl)-norbornene [112].

Title: nickel catalyst for polymerization.

Catalysts used: $\text{Ni}(\text{cyclooctadiene})_2$, $\text{Ni}(\text{allyl})_2$, Ni-acetylacetonate, Ni-octanoate, Ni-stearate [113].

Title: palladium-catalyst for polymerization.

Catalysts used: $[\text{PdPh}(\text{Ph}_2\text{PCHCPhO})(\text{Ph}_3\text{PCH}_2)]$, $[\text{PdMe}(\text{Ph}_2\text{PCHCPhO})(\text{Ph}_3\text{PCH}_2)]$, $[\text{PdPh}(\text{Ph}_2\text{PCHCPhO})(\text{Ph}_3\text{P})]$, $[\text{PdMe}(\text{Ph}_2\text{PCHCPhO})(\text{Ph}_3\text{P})]$, $[\text{PdMe}(\text{Ph}_2\text{PCHCPhO})(\text{Et}_3\text{P})]$, $[\text{PdMe}(\text{Ph}_2\text{PCHCPhO})(\text{Ph}_3\text{PNH})]$, $[\text{PdMe}(\text{Ph}_2\text{PCHCPhO})(\text{C}_5\text{H}_5\text{N})]$.

Cocatalysts used: tri(pentafluorophenyl)borane, $\text{HB}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4$, methylalumoxane [114].

A patent by Goodall et al. uses nickel ethylhexanoate (**32**) along with HSbF_6 for the homo-polymerization of norbornene [115].

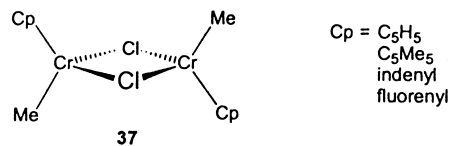
1.3. Vinyl polymerization with central transition metals

1.3.1. Chromium and cobalt catalysts

Catalysts based on the metals chromium and cobalt give satisfactory results in terms of the vinyl polymerization of norbornene, yet, relatively few reports have appeared so far.

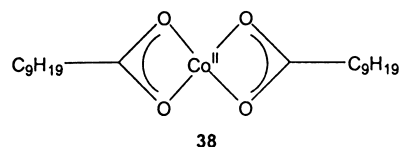
A paper by Peuckert and Heitz in 1998 describes both the homo-polymerization of norbornene as well as the copolymerization with ethene with a homo-

geneous Cr(III)-catalyst of the type $[\text{CpCrMeCl}]_2$ (**37**)/MAO [116]. The cyclopentadienyl (Cp) ligand was varied. The homo-polymers formed were partly crystalline and insoluble in typical organic solvents.



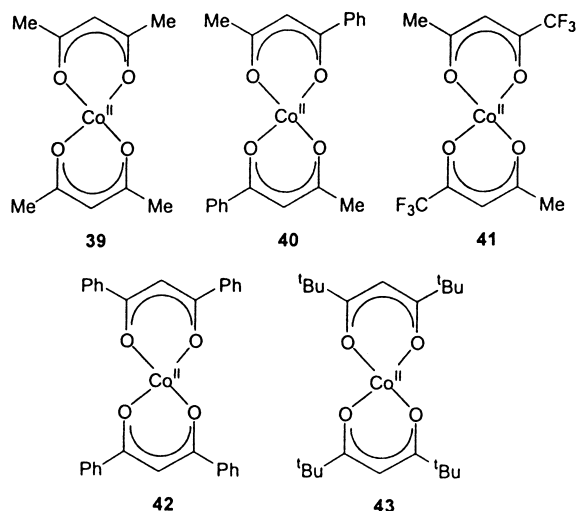
An influence of the Cp-type ligand on the polymer parameters could be observed. The activity increases with the electron-donor character of the ligand. The degree of crystallinity can to some extent be correlated with the steric demand of the Cp-ligand.

In 1995, Goodall and coworkers presented simple cobalt complexes which allowed for both a ring-opening metathesis polymerization (ROMP) as well as a vinyl polymerization of norbornene. Control of the reactivity direction was achieved through the cocatalyst [24]. Cobalt salts such as Co-neodecanoate (**38**) and Co-acetylacetonate (**39**) together with triethyl or triisobutyl aluminum as cocatalyst gave a ring-opening polymerization of norbornene. The product had a high molar mass ($M_w = 720,000 \text{ g mol}^{-1}$) and was shown by ^1H NMR and ^{13}C NMR spectroscopy to be an all-*cis* polynorbornene.

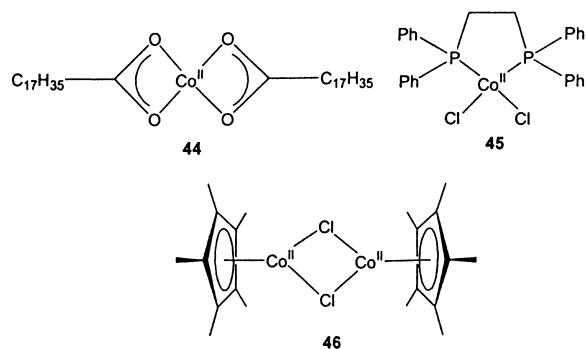


On the other hand, the polymerization of Co-neodecanoate (**38**) and methylalumoxane (MAO) as cocatalyst afforded a polynorbornene formed through the vinyl insertion. The vinyl product had a molar mass of about $M_w = 1,600,000 \text{ g mol}^{-1}$, a glass temperature of 380°C and a remarkable good solubility in simple hydrocarbons, e.g. in cyclohexane [24].

In the presence of ethene, oligomers of low molar mass ($M_n = 1100\text{--}6000 \text{ g mol}^{-1}$) were obtained from the cobalt(II) complexes **40** and **41** together with MAO in toluene or chlorobenzene [34].



The norbornene homo-polymerization with the substituted bis(1,3-diketone)cobalt(II) complexes **39**–**43**/MAO and also with the other cobalt(II) complexes **44**–**46**/MAO is reported. The use of pure chlorobenzene as a solvent (including the synthesis of MAO therein) strongly increased the activity over toluene as a solvent. An activity of 2.7 t polynorbornene/(mol Co h) could be achieved with **40** in chlorobenzene. The amorphous polymers are soluble in chlorobenzenes, cyclohexane and decahydronaphthalene even at high molar mass values, up to $M_w = 1.5 \times 10^6 \text{ g mol}^{-1}$ [117].

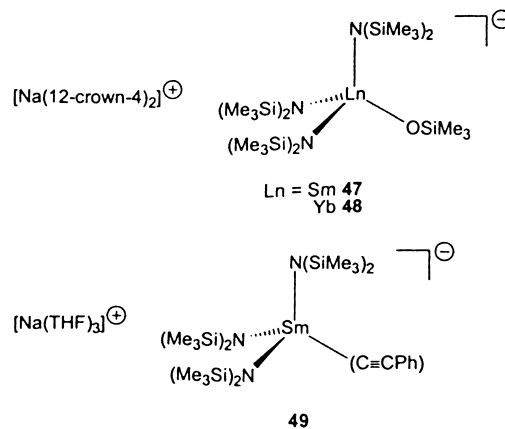


Please note that the analogous nickel complexes to **39** and **44** (**32** and **31**, respectively) were investigated by others [107,108]. Also, the cobalt(II) complexes **38**–**44** are drawn in a simplified square-planar coordination environment. The actual complexes are six-coordinated with the remaining two sites being

occupied by aqua ligands or organic solvent molecules in the pre-catalytic state.

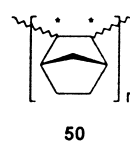
1.4. Vinyl polymerization with rare-earth metals

The amido complexes **47**–**49** were tested with MAO as catalysts for the vinyl polymerization of norbornene. They were found to give an insoluble polynorbornene in low yield only (<10%) in toluene or chlorobenzene as a reaction solvent [118].

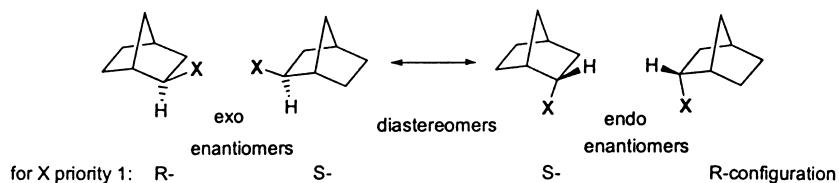


1.5. Polynorbornene stereochemistry

Polycycloolefins possess two stereo centers per monomer repeat unit (see **50**).



In addition, in the case of a bicyclic system such as a norbornyl group an exo- and endo-stereo isomerism is possible as shown in **51**. The exo- and endo-prefixes describe the position of a substituent on one of the bridges relative to the other two unsubstituted remaining bridges if they are of unequal length. The prefix endo is used when the substituent is closer to the longer, here the ethanediyl ($-\text{CH}_2\text{CH}_2-$) bridge; the exo-prefix is used when the substituent is closer to the shorter, here the methanediyl ($-\text{CH}_2-$) bridge [119].



51

The bicyclic backbone apparently makes the direct experimental characterization of the polymer microstructure for polynorbornene by NMR difficult [51]. The determination and interpretation of the tacticity in vinyl polymers of cyclic olefins is much less developed than for acyclic olefins, such as propene [120,121], or even for the ring-opened metathesis polymers [122]. ^{13}C NMR signals are reported in [104,110]. Solution characterization by NMR is further hampered by the insolubility of some norbornene polymers even at elevated temperature. The insoluble polymers are said to be semi-crystalline due to a certain stereoregularity. Such polymers are obtained with zirconocenes and chromium catalysts and with

the chiral palladium complexes (**27**). Whereas the soluble polymers are viewed to be amorphous with little stereoregularity. Solubility can then be achieved particularly in chlorinated (aromatic) hydrocarbons but also in cyclohexane. Catalysts leading to soluble polymers are the cobalt, nickel and palladium systems [117].

The *exo*- and *endo*-differentiation together with the *R*-, *S*-configuration leads in principle to six isomeric stereoregular norbornene polymers (assuming only *cis*-double-bond opening, see Fig. 4). In the form of tetrameric units (or tetrads) these six different stereoregular norbornene polymers are illustrated in Fig. 4.

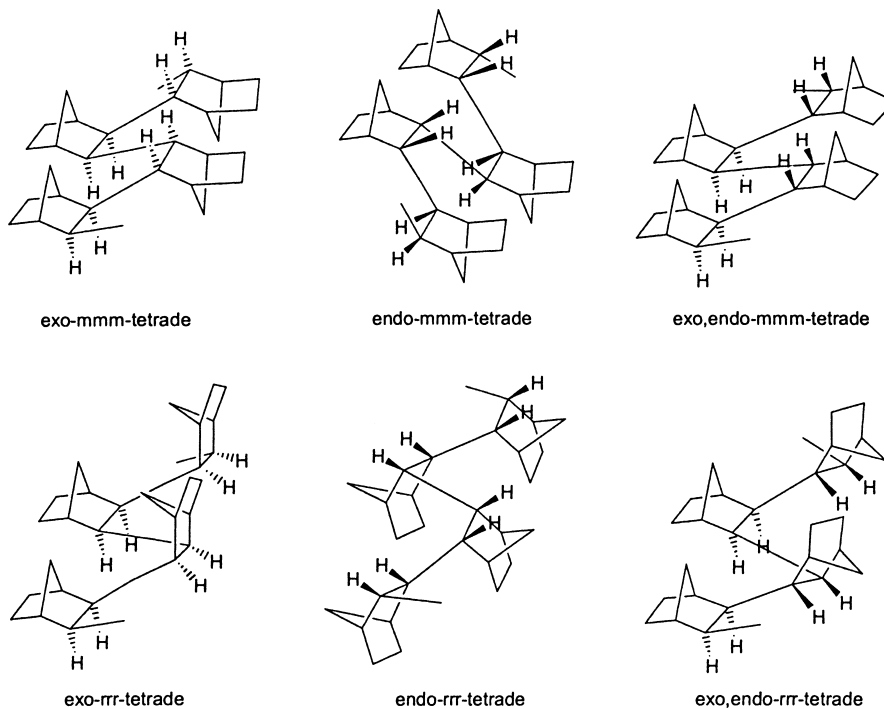
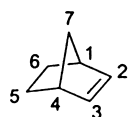
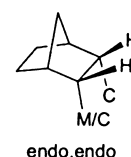
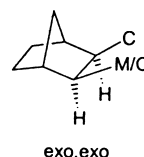


Fig. 4. The six different isomeric stereoregular norbornene polymers, shown as tetrameric units or tetrads. Solely *cis*-double-bond opening is assumed for the six isomeric forms (see text).

Once formed polynorbornene and also an ethene–norbornene copolymer may still undergo conformational conversion into more stable conformers [33]. It is suggested that norbornene undergoes an exo–exo–enchainment during polymerization. This would lead to polymers with exo–mmm units (erythro–diisotactic) or exo–rrr units (threo–disyndiotactic) [51]. A rotational isomeric state treatment is available for polynorbornene [123]



2,3-insertion
cis double-bond opening
(cis-insertion)



52

and for alternating ethylene–norbornene copolymers [124]. With respect to conformational constraints and dynamics for polynorbornene chains, a few reports deal with theoretical simulations using ab initio methods, semi-empirical quantum-mechanical methods, and force field methods [51,96,123,125,126].

The formation of stereoregular norbornene polymers requires a single-site catalyst which can exert a precise control on the polyolefin stereochemistry [127]. The metal center has to differentiate between an exo- and endo-approach and an up/down coordination relative to the last inserted monomer unit (Fig. 5).

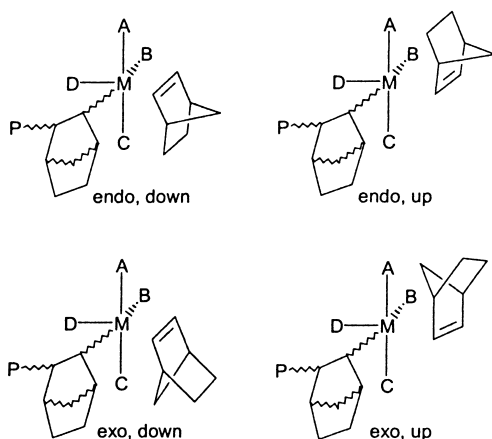


Fig. 5. Principle stereo differentiation at the catalytic center for norbornene insertion.

It is presumed that the zirconocene catalysts (see above) form the highly stereoregular erythro–diisotactic polynorbornene (exo–mmm, cf. Fig. 4) [123]. The high stereoregularity is suggested because the polymer is insoluble in any organic solvent. Other catalyst systems probably lead to other stereochemistries, because polynorbornene products of different solubilities are reported (see Fig. 5 and Scheme below). Such stereochemistries have yet to be assigned, though.

The pictures of the norbornene polymers in Fig. 4 assume a usual “1,2-insertion” together with a *cis*-opening of double bond for the monomer (52). Because of the numbering convention for norbornene, this is also termed a 2,3-insertion here. The vinyl homo-polymer is correctly named poly(2,3-bicyclo[2.2.1]hept-2-ene). So far, there is no evidence to the contrary of a 2,3-insertion and *cis*-double-bond opening for norbornene.

We just note that this is different for cyclopentene. For polycyclopentene the initial formulation as a 1,2-insertion product [128] was later proven incorrect. Instead it was shown that incorporation of the monomer proceeded in *cis*- and *trans*-1,3-manner to give poly(1,3-cyclopentene) [129–132].

Acknowledgements

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