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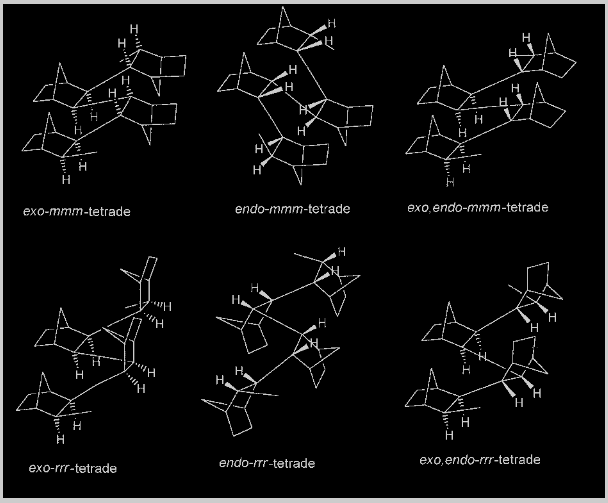
Review: A full literature and patent account (about 100 references) is given on work describing vinyl polymerization to form the homopolymer poly(norbornene). The interest in vinyl-poly(norbornene) is driven by its dielectric and mechanical properties for the technical application as an interlevel dielectric in microelectronics applications. For comparison, the norbornene/olefin copolymerization is discussed also. The metal catalysts are introduced and important polymer product properties are emphasized. The six possible isomers for stereoregular poly(norbornene) are presented.



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

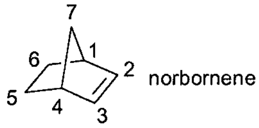
The Vinyl Homopolymerization of Norbornene

Christoph Janiak, Paul G. Lassahn*

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany
E-mail: janiak@uni-freiburg.de

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 (Figure 1).



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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 poly(norbornene) product is used as an elastomeric material for vibration and sound damping. It has specialist applications for engine mounts, shock-proof bumpers, and flexible couplings. In addition, porous poly(norbornene) is a soaking material for oil spills. Poly(norbornene) 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.

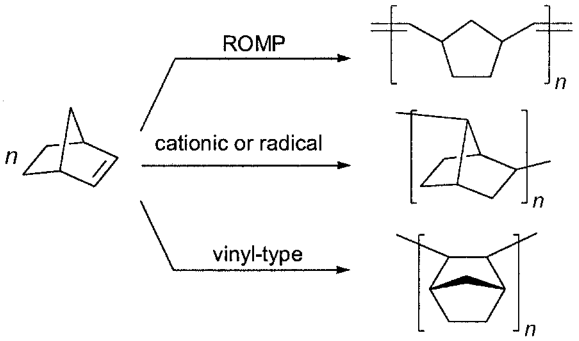

Figure 1. Schematic representation of the three different types of polymerization for norbornene.

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 complexes.

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They are also predominantly based on tungsten,[2] molybdenum,[3] and ruthenium.[4,5] The possibility of a ring-opening metathesis polymerization of norbornene with catalyst systems based on titanium,[6] tantalum[7] and osmium[8] has been reported.

The control of stereochemistry in unsubstituted poly(norbornene) is possible through the choice of reaction conditions, such as catalyst, cocatalyst, activator, solvent and temperature. Highly *cis*-poly(norbornene) was obtained with the catalyst system $ReCl_5/EtAlCl_2$/ethyl acrylate; *trans*-poly(norbornene) with the system $IrCl_3 \cdot xH_2O/EtAlCl_2$. A higher stereoregularity in poly(norbornene) increases the glass temperature. The introduction of tacticity increased the permeability coefficient and improved the polymer stability.[9]

Little is known about the cationic (or radical) polymerization of norbornene. This route was first described in 1967.[10–12] 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 $EtAlCl_2$.[10]

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 any double bonds. The vinyl polymerization of norbornene can take place either as a homo- or as a copolymerization. The product is termed vinyl-poly(norbornene) to show its means of preparation. Vinyl polymerization is much less developed for norbornene than is 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".[13–15]

Of interest is the vinyl copolymerization of cyclic and acyclic (especially ethene and propene) olefins.[16–20] For specific work on ethene/norbornene copolymers see ref.[21–25] Cyclo-olefin 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.[25] 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. Cyclo-olefin copolymers have high refractive indices close to those of crown glass. Thus, they can be applied as a glass substitute in lenses, prisms, carrier plates and foils for optical data storage, video and compacts disks. They are envisioned as cover and focussing plates for solar cells or in glass fiber optics.[16] 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.[26,27] Cyclo-olefin copolymerization and COC's have been included, in part, in some overviews on metallocene catalysts.[28–30] So, we mainly point to some of the COC literature references here, while a more detailed overview on the current state of the vinyl homopolymerization of norbornene will be given in this article.

The homopolymer vinyl-poly(norbornene) is surely a specialty polymer. Its mechanical properties, heat resistivity, good solubility in organic solvents, and transparency are emphasized. Vinyl-poly(norbornene) is investigated inter alia as a deep ultraviolet photoresist and interlevel dielectric in microelectronics applications. Low

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Christoph Janiak was born in Berlin, Germany in 1961. He studied chemistry at the TU Berlin and the University of Oklahoma in Norman. His Ph.D. thesis was completed in 1987 under the guidance of Prof. Herbert Schumann. After postdoctoral work with Prof. Roald Hoffmann at Cornell and with the polyolefin division of BASF AG at Ludwigshafen, he returned to the TU Berlin for his "Habilitation" which was concluded in 1995. In 1996 he moved to Freiburg where he is now a professor of inorganic and analytical chemistry. The research interests of Prof. Janiak extend from metal-coordination polymers over weak interactions in the solid state (π-stacking, hydrogen bonding) to olefin polymerization with single-site catalysis.

Paul-Gerhard Lassahn was born in Karlsruhe, Germany in 1973. He received his "Staatsexamen" in chemistry and mathematics at the Albert-Ludwigs-Universität in Freiburg in 1999. After completing his Master's thesis in the summer of 2000, he began his Ph.D. studies in Prof. Janiak's group.

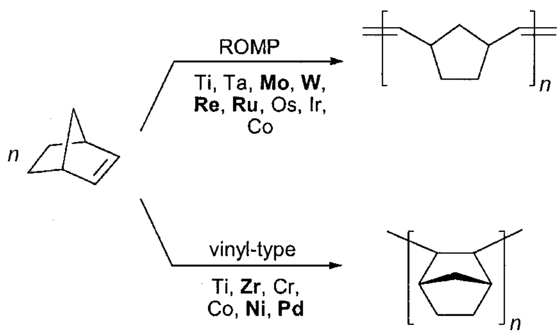


Figure 2. Schematic representation of the two types of coordination polymerization for norbornene together with the metals used in the catalytic systems. Predominant metals are given in bold.

dielectric constant interlevel dielectrics are seen as critical to the realization of high performance interconnections. High glass transition temperature poly(norbornene)s exhibits 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.[31] The vinyl norbornene polymer is also said to have a cost advantage over related materials.[32] Films made from this polymer are excellent in transparency and heat resistance and have unchanged viscoelastic and electric characteristics to markedly high temperatures. Such films are suitable for condensors or insulators.[33] Homopolymer poly(norbornene) films are applied as cover layers for liquid-crystal displays. The polymer is developed by the B.F. Goodrich Corp. under the trade name Avatrel® dielectric polymer.[31,32] The sometimes poor adhesion of the poly(norbornene) homopolymer 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.[31]

Catalysts containing the metals titanium, zirconium, cobalt, chromium, nickel and palladium are described in the literature for the vinyl homopolymerization of norbornene and strained cyclic olefins in general.[13] Figure 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 cocatalyst ratio[15,34,35] or the type of cocatalyst employed,[14] respectively.

Based on their metal composition, the catalysts for vinyl polymerization can be divided into three groups: (a) early transition metals, especially the metallocene catalysts of zirconium; (b) the late transition metal palladium (II) and nickel(II) catalysts and (c) the less used and seldom mentioned central transition metals chromium and cobalt. These three groups will be treated separately. Generally, the *neutral* precatalytic metal complexes require a cocatalyst for their activation, with MAO being the activator of choice here, whereas the *cationic* palladium complexes are active without a cocatalyst.[36] These palladium systems of the general formula $[Pd(NCR)_4]^{2+}2L^-$ contain weakly bound nitrile ligands and "non"-coordinating counter ions, such as BF_4^-.

Vinyl Polymerization with Early Transition Metals

Titanium Catalysts

The first vinyl polymers of norbornene were obtained with a $TiCl_4/Al($*iso*$-Bu)_3$ catalyst with an Al:Ti ratio of 1:2 in the early 1960's.[34,37] In the case of the similar catalyst system $TiCl_4/AlEt_3$ it was shown that an increase in the Al:Ti ratio resulted in a mixture of metathesis polymer and vinyl polymer.[35] Also, amine addition to the system $TiCl_4/AlEt_3$ alters the polymerization exclusively to the ring-opening type.[38] There is a report on the ionic species $[Cp_2TiCH_3]^+[Cl\text{-}MAO]^-$ together with evidence for the synthesis of polyethene-poly(norbornene) diblock copolymers in an addition polymerization.[22]

Metallocene Catalysts of Zirconium (and Hafnium)

Metallocene catalysts which consist of a "metallocene" of group 4 (mostly zirconium) and methylalumoxane (MAO) (Figure 3) are covered in a large number of review articles.[28,29,30,39] The term "metallocene" often refers to catalysts derived from metallocene dichloride precatalysts.

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 cyclo-olefins cyclobutene, cyclopentene and norbornene with the chiral metallocenes $Et(indenyl)_2ZrCl_2$ (**2**) and $Me_2Si(indenyl)_2ZrCl_2$ (**3**), in combination with MAO.[40]

In a series of experiments it was shown that the catalytic systems **2** /MAO or **3** /MAO showed a considerably

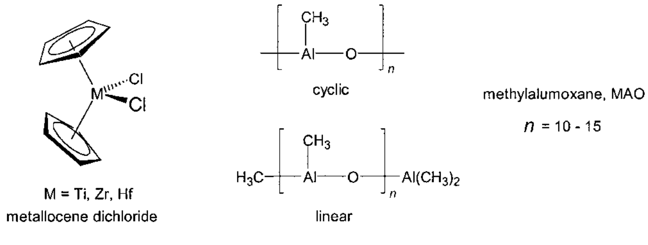
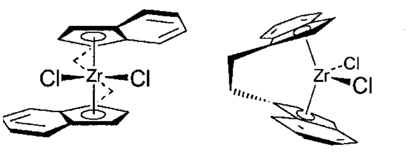


Figure 3. Basic features of metallocene catalysts: The metallocene dichloride precatalyst and the MAO cocatalyst.



front- side-view

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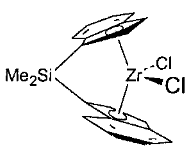

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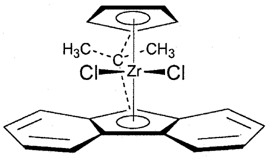
higher polymerization activity towards cyclobutene and cyclopentene than towards norbornene. The copolymerization of norbornene and ethene was investigated. The copolymerization was strongly influenced by the monomer ratio and the reaction temperature. The catalyst **2**/MAO had a maximum activity at 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.[40]

Another study by Kaminsky and coworkers was carried out with the C_s-symmetrical complexes [Me_2C(fluorenyl)(Cp)]$ZrCl_2$ (**4**) and [Ph_2C(fluorenyl)(Cp)]$ZrCl_2$ (**5**) together with the C_2-symmetrical pre-catalysts [Me_2Si(indenyl)$_2$]$ZrCl_2$ (**3**) and [Ph_2Si(indenyl)$_2$]$ZrCl_2$ (**6**). Activation was done with MAO.[41]



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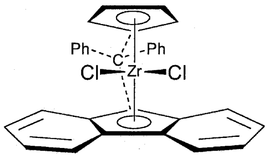

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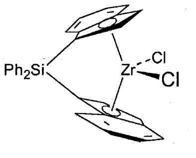

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The copolymerization of norbornene and ethene was investigated in more detail. It became clear that the polymerization rates were quite different for the two types of catalysts. The C_2-symmetrical catalysts **3** and **6**/MAO were highly active in the ethene polymerization. In both cases the activities dropped rapidly with an increasing norbornene/ethene ratio.[41] 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 maxiumum 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 for **4** and 2400 kg copolymer · (mol Zr)$^{-1}$ · bar^{-1} · h^{-1} for **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 ansa-catalysts results in a wider opening angle of the ring ligands around zirconium, thus, creating a larger coordination gap.[42] The catalyst symmetry could also be correlated with the stereochemistry of the polymer chain.[43] The mechanism of the alternating ethene/norbornene copolymerization was studied in detail using [Me_2C(fluorenyl)(3-*tert*-BuCp)]$ZrCl_2$/MAO. Copolymerization models were developed and applied.[44]

The vinyl polymerization and copolymerization of norbornene and other cyclo-olefins 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 and the cocatalyst is a MAO solution in toluene, unless noted otherwise. In some of the patents hafnium is also mentioned as the metal.

Title: "*Bulk polymerisation with metallocene catalyst for the preparation of cyclo-olefin polymers*".

Catalysts used: Diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride, isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride, dicyclopentadienylzirconium dichloride, (*rac*-dimethylsilylbis(1-indenyl)zirconium dichloride, methyl(phenyl)methylene(9-fluorenyl)cyclopentadienylzirconium dichloride, diphenylmethylene(9-fluorenyl)cyclopentadienylhafnium dichloride.[16]

Title: "*Cyclo-olefinic(co)polymer with a narrow molecular weight distribution and process for preparing same*".

Catalysts used: (*rac*-dimethylsilylbis(1-indenyl)zirconium dichloride, fluorenylcyclopentadienyldiphenylcarbylzirconium dichloride.[17]

Title: "*Process for the preparation of chemically homogenous cyclo-olefinic copolymers*".

Catalysts used: Isopropylene(9-fluorenyl)(1-(3-isopropyl)-cyclopentadienyl)zirconium dichloride, isopropylene(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)zirconium dichloride, diphenylmethylene-(9-fluorenyl)(1-(3-methyl) cyclopentadienyl)-zirconium dichloride, methylphenylmethylene(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, diphenylmethylene(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*-dimethylsilylbis(1-(3-methyl)cyclopentadienyl)zirconium dichloride, *meso*-dimethylsilylbis(1-(2,4-dimethyl)cyclopentadienyl)zirconium dichloride, *meso*-dimethylsilylbis(1-indenyl)zirconium dichloride, *meso*-diphenylsilylbis(1-indenyl)zirconium dichloride, *meso*-isopropylenebis(1-indenyl)zirconium dichloride, *meso*-diphenylmethylenebis(1-indenyl)zirconium dichloride, *meso*-methylphenylmethylenebis(1-indenyl)zirconium dichloride, *meso*-diphenylsilylbis(1-indenyl)hafnium dichloride, *meso*-dimethylsilylbis(1-indenyl)hafnium dichloride, *meso*–1,2-ethylenebis(1-indenyl)zirconium dichloride, *meso*–1,2-ethylenebis(1-indenyl)hafnium dichloride.[18]

Title: "*Process for preparing cyclo-olefin polymers*".

Catalysts used: *rac*-Dimethylsilylbis(1-indenyl)zirconium dichloride, *rac*-dimethylgermylbis(1-indenyl)zirconium dichloride, *rac*-phenylmethylsilylbis(1-indenyl)zirconium dichloride, *rac*-phenylvinylsilylbis(1-indenyl)zirconium dichloride, 1-silacyclobutyl-bis(1′-indenyl)zirconium dichloride, *rac*-ethylene-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*-diphenylsilylbis(1-indenyl)zirconium dichloride, diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride, isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride.[19]

Catalysts used: Diphenylcarbyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, *rac*-dimethylsilylbis(1-indenyl)-zirconium dichloride.[45]

Title: "*Cyclo-olefin copolymers and a process for their preparation*".

Catalysts used: Diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride.[46]

Title: "*Process for the Preparation of cyclo-olefin polymers*".

Catalysts used: *rac*-Dimethylsilylbis(1-indenyl)zirconium dichloride, *rac*-dimethylgermylbis(1-indenyl)zirconium dichloride, *rac*-phenylmethylsilylbis(1-indenyl)zirconium dichloride, *rac*-phenylvinylsilyl-bis(1-indenyl)zirconium dichloride, 1-silacyclobutylbis(1′-indenyl)zirconium dichloride, *rac*-ethylene-bis(1-indenyl)zirconium dichloride, *rac*-diphenylsilylbis(1-indenyl)hafnium dichloride, *rac*-phenylmethylsilyl-bis(1-indenyl)hafnium dichloride, *rac*-dimethylsilyl-bis(1-indenyl)hafnium dichloride, *rac*-diphenylsilylbis(1-indenyl)zirconium dichloride, diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride, isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride.[47]

Title: "*Blends of polyolefins and syndiotactic vinyl polymers*".

Catalysts used: $(Me_2Si)Ind_2ZrCl_2$ (in combination with $CpTiCl_3$ and aluminum triisobutyl in toluene; copolymerisation with styrene and propylene).[48]

Title: "*Polymer blends of cyclo-olefin polymers and polyolefins*".

Catalysts used: Diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride, isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride, *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride.[49]

Title: "*Cyclo-olefin copolymers and process for their preparation*".

Catalysts used: Diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride (copolymerisation with ethylene and 5-vinylnorbornene-2).[50]

Title: "*Cyclo-olefin copolymers and process for their preparation*".

Catalysts used: Diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride, bis(indenyl)zirconium dichloride (copolymerisation with ethylene and 5-vinylnorbornene-2).[51]

Title: "*Cyclo-olefin copolymers and a process for their preparation*".

Catalysts used: Diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium dichloride, dimethyl(methylenbisindenyl)zirconium dichloride (copolymerisation of 2-norbornene with ethylene and 5-vinylnorbornene-2, respectively: 2,5-norbornadiene, 5-ethylidene-2-norbornene).[52]

Title: "*Process for preparation and purification of material of a cyclo-olefin copolymer*".

Catalysts used: Isopropylene(9-fluorenyl)(1-(3-methyl)cyclopentadienyl)zirconium dichloride (copolymerisation of 2-norbornene with ethylene respectively ethylene and decahydronaphthalene).[53]

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 cyclo-olefin monomers and the production thereof*".

Catalysts used: VCl_5, $VOCL_3$, VCl_3, $VO(OC_2H_5)_2Cl$, $VO(OCH_3)_2Cl$, $VO(OCH_3)Cl_2$, $VO(OCH_3)_3$, $VO(OC_3H_7)Cl_2$, VCl_4, $VO(OC_3H_7)_3$.

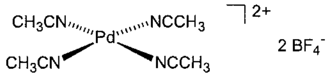
Cocatalysts used: $Al(CH_3)_2Cl$, $AlCH_3Cl_2$, $Al(OC_4H_9)(C_4H_9)Cl$, $Al(C_2H_5)_2Cl$, $Al_2(C_2H_5)_3Cl_3$.

Norbornene monomers used: 5-Methyl-2-norbornene, 2-norbornene, 5-ethyl-2-norbornene, 5-propyl-2-norbornene.[54]

Vinyl Polymerization with Late Transition Metals

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 $PdCl_2$[55,56] and then again in the late 1970's using $Pd(C_6H_5CN)_2Cl_2$[12,57] and also $Pd(Ph_3P)_2Cl_2$.[57]



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Eventually, the cationic palladium(II) catalyst system $[Pd(CH_3CN)_4](BF_4)_2$ (**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.[58]

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 (CH_3NO_2) 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 as the polymer was insoluble in tetrahydrofuran (THF), $CHCl_3$, CH_2Cl_2, and C_6H_6.[58,59]

An interesting complex may also be $[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$ (n = 1–3). Although mainly used for the copolymerization of carbon monoxide with ethene, it may also prove valuable for the polymerization of norbornene.[60]

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.[15,61] It was found that the resulting vinyl-poly(norbornene) had relatively good solubility in tetrachloroethene, trichloromethylbenzene, chlorobenzene, and 1,2-dichlorobenzene. This allowed for polymer characterization by size exclusion chromatography/gel permeation chromatography (SEC/GPC), vapour phase osmometry (VPO), and solution viscosimetry. All 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.

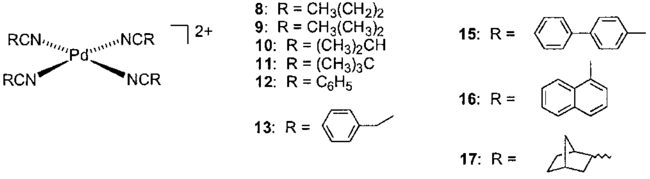
Among other things, it turned out that increasing the ratio of norbornene to the catalyst **7** resulted in the formation of higher molar mass polymers. A certain drawback was the then limited solubility of norbornene in CH_3NO_2. This especially affected reactions using a monomer-to-catalyst ratio larger 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.[15,61]

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).[62] 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 $\overline{M}_w / \overline{M}_n$ as low as 1.07. Even for monomer conversions up to 80% polydispersities were well below 1.2.[62]

A study on the polymerization of norbornene in a water dispersion or in an aqueous emulsion has been reported.[63] The polymerization was carried out in a water dispersion by heating water, norbornene and $PdCl_2$ (molar ratio norbornene:catalyst = 100) at 70 °C over 24 h. After a 15–20-min induction period, the polymer precipitated as a powder. The poly(norbornene) 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 $\overline{M}_n$ = 690 (at 1wt.-% SDS), $\overline{M}_n$ = 840 (at 3 wt.-% SDS) and $\overline{M}_n$ = 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.[64–66] The Pd(II) catalyst **7** was found to tolerate the ester functionality. However, the rate of polymerization was reduced in comparison to unsubstituted norbornene.[65]

In a study by Heitz and Wendorff the residues of the nitrile ligands in the catalyst system $[Pd(RCN)_4]^{2+}$ were varied (see also ref.[15]), with the complexes being used in the polymerization of norbornene.[67] The catalysts could be dissolved in the same solvent which contained poly(norbornene), so that the polymerization was performed in a homogeneous phase. The following chart shows the residues R which were used.

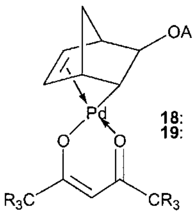


The work by Heitz and Wendorff indicated that for nearly all the catalysts **7–17** polymer yields were very similar to each other. The only exception represented catalyst **7**. It was especially important that the yields were independent of the nature of the nitrile residue, i.e., whether the nitrile ligands were aliphatic or aromatic. A polydispersity $\overline{M}_w/\overline{M}_n$ 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. This assumes, of course, that every Pd center becomes catalytically active.[67]

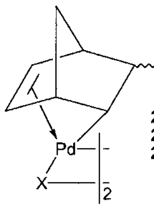
A second set of experiments showed that the presence of acetone led to the deterioration of yields and polydispersities. The catalyst system **17** was soluble in C_6H_5Cl, so that a polymerization of norbornene could be carried out in this solvent. Under standard conditions (reaction time 1 h, room temperature), a yield of only 45% was obtained. However, the yield could be improved by increasing reaction temperature and time.[67]

Another study by Heitz et al. investigated inter alia the influence of counterions in the catalyst system $[Pd(CH_3CN)_4]^+$ (**7**) on the polymerization of norbornene.[68] Counterions used were BF_4^-, $OSO_2CF_3^-$, $SbCl_6^-$, and $SnCl_6^{2-}$. The results showed that with the smallest counterion BF_4^-, the poly(norbornene) had a significantly higher average molar mass under standard conditions (1 h, room temperature, [norbornene]:[**7**] = 500:1).

The vinyl polymerization of norbornene with $[Pd(CH_3CN)_4](BF_4)_2$ (**7**) in the presence of ethene resulted in poly(norbornene) with narrow molar mass distribution.



18: R = F
19: R = H

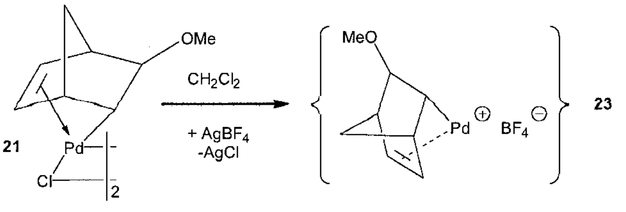


20: R = OMe, X = Cl
21: R = OMe, X = Br
22: R = Ph, X = I

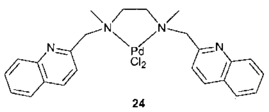
Neither termination and transfer reactions were found, nor could any incorporation of ethene be detected.[68]

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.[69,70] Before their study, an uncharacterized π-allylic complex which was prepared from β-pinene and $Pd(C_6H_5CN)_2Cl_2$ was already employed in the polymerization of olefins, including norbornene.[71]

In 1997, Heitz, Wendorff and coworkers 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**.[72] Follow-up studies with these novel catalyst systems included norbornene derivatives and copolymerization.[73,74]



The induction of stereoregularity into poly(norbornene) 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 homopolymerization 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.[75]



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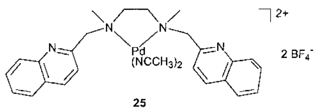

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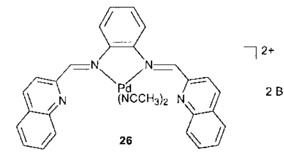

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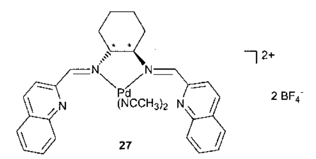

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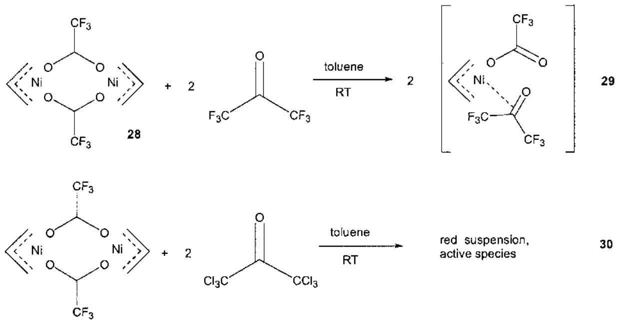
An overview on the patent literature of palladium is combined with the nickel catalysts at the end of the following section. The vinyl polymerization and copolymerization of norbornene and other cyclo-olefins with both palladium and nickel catalysts has mostly been described within the same patent.

Nickel Catalysts

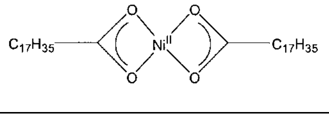
Nickel complexes for the vinyl polymerization of norbornene were introduced in the 1990's. In 1993, Deming and Novak presented the nickel catalyst systems **28**, **29** and **30**.[76]



With respect to the polymerization of norbornene, compound **28** was found inactive. System **29** and system **30**, however, have been demonstrated as very active catalysts for the polymerization of norbornene – with no cocatalyst necessary.[76] 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 $\overline{M}_n$ = 1300 g · mol^{-1} and a polydispersity of 1.1.[77]

Usually, the vinyl polymerization of norbornene with nickel catalysts is carried out in combination with MAO as a cocatalyst.[78,79] 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-



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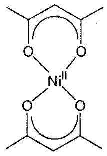

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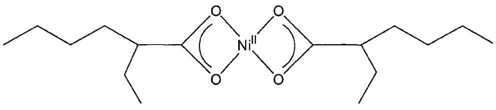

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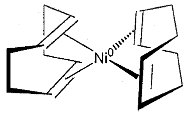

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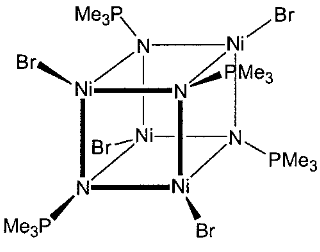
$(acac)_2$ (**32**), Ni(2-ethylhexanoate)$_2$ (**33**), and $(COD)_2Ni^0$ (**34**) (COD = cyclooctadiene) in combination with the cocatalyst MAO in toluene.[79]

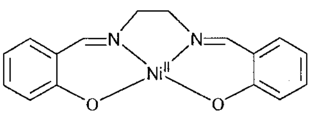
Another highly active catalyst for the polymerization of norbornene is the complex $[BrNi(NPMe_3)]_4$ (**35**) in combination with MAO. Greiner et al. could observe catalyst activities up to 20.5 t · (mol Ni)$^{-1}$ · h^{-1} and polymer molar masses up to 3.4 × 10^6 g · mol^{-1}.[80]

The polymer yield or catalyst activity of **35**/MAO and the molar mass of the poly(norbornene) 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, concomittant 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 °C 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.



35

Nickel(salen) **36** together with MAO catalyzes the addition polymerization of norbornene. Normal MAO and $AlMe_3$-free MAO was investigated as a cocatalyst. Polymerization was carried out in chlorobenzene and the polymer was soluble in 1,2,4-trichlorobenzene.[81]



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The vinyl polymerization and copolymerization of norbornene and other cyclo-olefins 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 MAO 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), allylcyclopentadienylnickel, dichlorobis(benzonitrile)palladium, dichloro(1,5-cyclooctadiene)palladium.

Cocatalysts used: Methylalumoxane, trimethylaluminium, triisobutylaluminum.

Norbornene-monomers used: 2-Norbornene, 5-ethylidene-2-norbornene.[82]

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

Catalysts used: $[(\eta^3$-Crotyl)(cycloocta-1,5-diene)nickel] hexafluorophosphate, tetrakis(acetonitrile)palladium(II) tetrafluoroborate, $[(\eta^3$-crotyl)(cycloocta-1,5-diene)nickel] tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate, [6-methoxynorbornene-2-yl-5-palladium(cyclooctadiene)]hexafluorophosphate, $[(\eta^3$-crotyl)(cycloocta-1,5-diene)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, $[(\eta^3$-cyclooctenyl)(cycloocta-1, 5-diene)nickel] tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate, $\{CH_3Ni(C_2H_4)_2\}^-$ $Li\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}^{2+}$, bis($\eta^3$-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 hexchem.

Norbornene-monomers used: 2-Norbornene, 5-decylnorbornene, 5-methylnorbornene, 5-(hexadecyl)norbornene, ethylidenenorbornene, 5-(nonafluorobutyl)norbornene.[83]

Title: "*Nickel catalyst for polymerization*".

Catalysts used: Ni(cyclooctadiene)$_2$, Ni(allyl)$_2$, Ni-acetylacetonate, Ni-octanoate, Ni-stearate.[84]

Title: "*Palladium-catalyst for polymerization*".

Catalysts used: $[PdPh(Ph_2PCHCPhO)(Ph_3PCH_2)]$, $[PdMe(Ph_2PCHCPhO)(Ph_3PCH_2)]$, $[PdPh(Ph_2PCHCPhO)(Ph_3P)]$, $[PdMe(Ph_2PCHCPhO)(Ph_3P)]$, $[PdMe(Ph_2PCHCPhO)(Et_3P)]$, $[PdMe(Ph_2PCHCPhO)(Ph_3PNH)]$, $[PdMe(Ph_2PCHCPhO)(C_5H_5N)]$.

Cocatalysts used: Tri(pentafluorphenyl)borane, $HB(C_6H_3(CF_3)_2)_4$, MAO.[85]

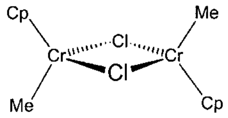
A patent by Goodall et al. uses nickel ethylhexanoate (**32**) along with $HSbF_6$ for the homopolymerization of norbornene.[86]

Vinyl Polymerization with Central Transition Metals

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 homopolymerization of norbornene as well as the copolymerization with ethene with a homogeneous Cr(III) catalyst of the type $[CpCrMeCl]_2$ (**37**)/MAO.[87] The cyclopentadienyl (Cp) ligand was varied. The homopolymers formed were partly crystalline and insoluble in typical organic solvents.



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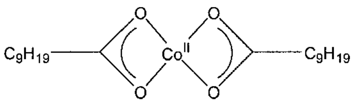
Cp = C_5H_5
C_5Me_5
indenyl
fluorenyl

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.[14] 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 ($\overline{M}_w$ = 720000 g · mol^{-1}) and was shown by ^{1}H NMR and ^{13}C NMR spectroscopy to be an all-*cis* poly(norbornene).



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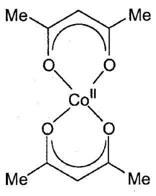
On the other hand, the polymerization of Co-neodecanoate (**38**) and MAO as cocatalyst afforded a poly(norbornene) formed through the vinyl insertion. The vinyl product had a molar mass of about $\overline{M}_w$ = 1600000 g · mol^{-1}, a glass temperature of 380 °C and a remarkably good solubility in simple hydrocarbons, e.g., in cyclohexane.[14]

In the presence of ethene, oligomers of low molar mass ($\overline{M}_n$ = 1100–6000 g mol^{-1}) were obtained from the cobalt(II) complexes **40** and **41** together with MAO in toluene or chlorobenzene.[24]



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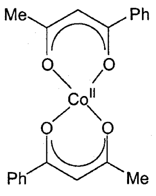

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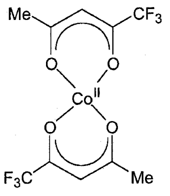

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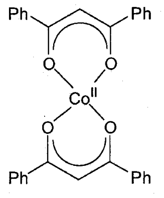

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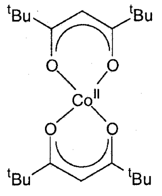

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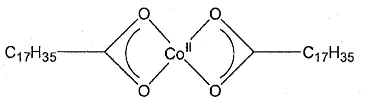

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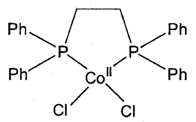

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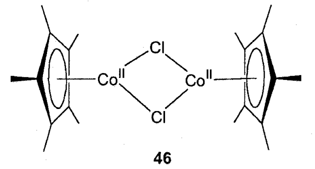

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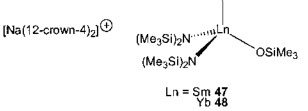
Norbornene homopolymerization with the substituted bis(1,3-diketo)cobalt(II) complexes **39**–**43**/MAO and also with the other cobalt(II) complexes **44**–**46**/MAO is reported. The use of pure chlorobenzene as a solvent (including the synthesis of MAO therein) strongly increased the activity over toluene as a solvent. An activity of 2.7 t poly(norbornene) · (mol Co)$^{-1}$ · h^{-1} could be achieved with **40** in chlorobenzene. The amorphous polymers are soluble in chlorobenzenes, cyclohexane and decahydronaphthaline even at high molar mass values, up to $\overline{M}_w$ = 1.5 × 10^6 g · mol^{-1}.[88]

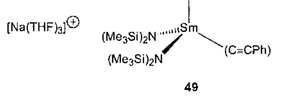
Please note that the analogous nickel complexes to **39** and **44** (**32** and **31**, respectively) were investigated as well by other groups.[78, 79]

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 poly(norbornene) in low yield only (< 10%), in toluene or chlorobenzene as a reaction solvent.[89]



Ln = Sm **47**
Yb **48**



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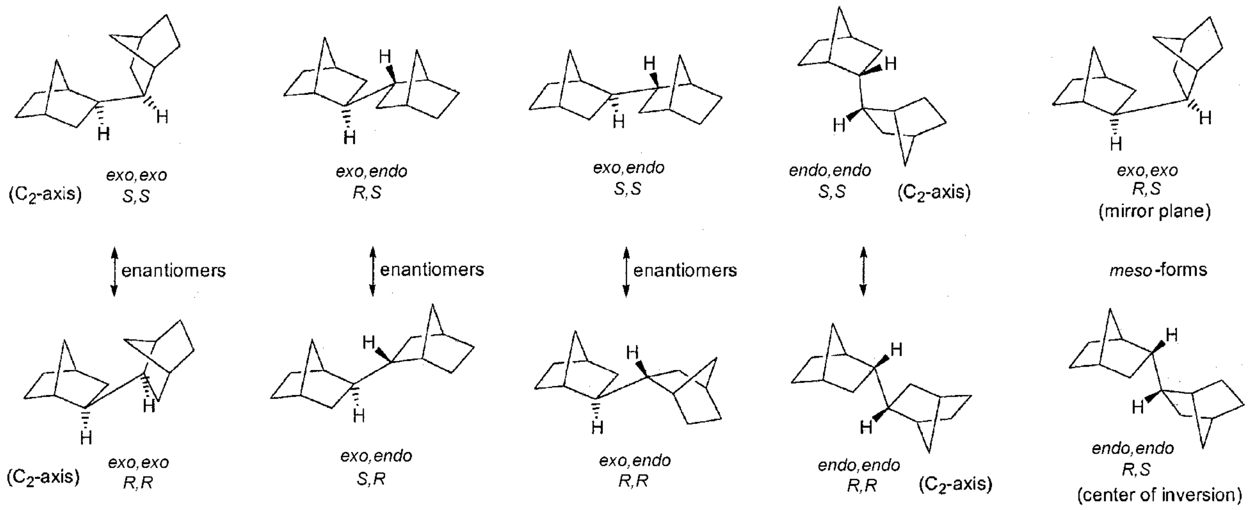
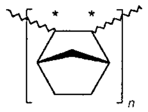


Figure 4. The ten different stereo isomers for dimeric units of (dihydro) norbornene.

The Stereochemistry of Vinyl-Poly(norbornene)

Poly(cyclo-olefin)s possess two stereo centers per monomer repeat unit (see **50**).



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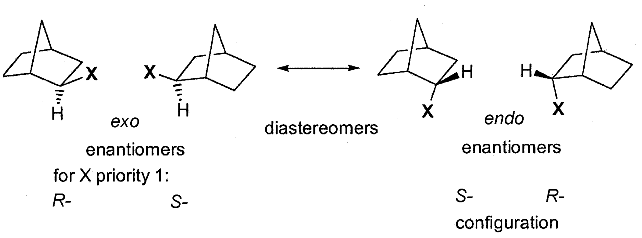
In addition, in the case of a bicyclic system such as a norbornyl group an *exo*/*endo* stereoisomerism is possible as shown in **51**. The prefices *exo*/*endo* describe the positon of a substituent on one of the bridges relative to the other two unsubstituted remaining bridges if they are of unequal length. The prefix *endo* is used when the substituent is closer to the longer, here the ethanediyl (—CH_2CH_2—) bridge; the prefix *exo* is used when the substituent is closer to the shorter, here the methanediyl (—CH_2—), bridge.[90]



51

Figure 4 illustrates the structures of the ten different isomers (enantiomers and diastereomers) for dimeric units of (dihydro-) norbornene. These ten isomers consist of four enantiomeric pairs and two *meso* forms.

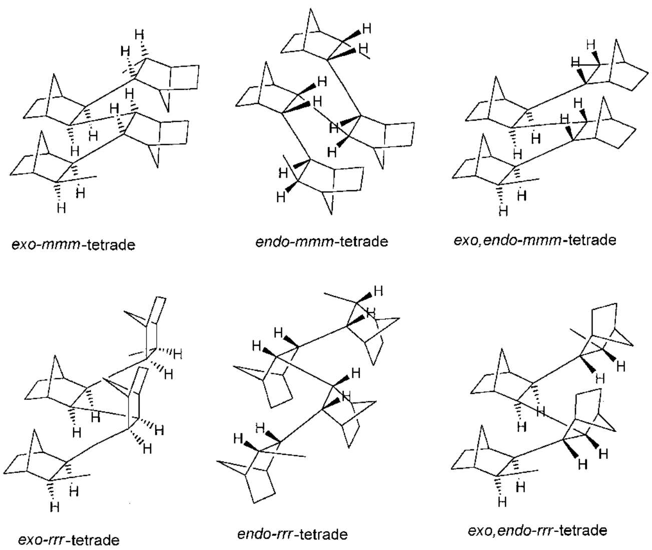


Figure 5. The six different isomeric stereoregular norbornene polymers, shown as tetrameric units or tetrades. Solely *cis* double-bond opening is assumed for the six isomeric forms (see text).

Thus, the *exo*/*endo* differentiation together with the *R*, *S*-configuration leads in principle to six isomeric stereoregular norbornene polymers (assuming only *cis* double-bond opening, see below). In the form of tetrameric units (or tetrades) these six different stereoregular norbornene polymers are illustrated in Figure 5.

The six stereoregular norbornene polymers will be of different energy, due to different repulsive interactions between neighboring monomer units. Once formed poly-(norbornene) and also an ethene/norbornene copolymer may still undergo conformational conversion into more stable conformers.[23] 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).[32] A rotational isomeric state treatment is available for poly(norbornene)[91] and for alternating ethylene/nor-

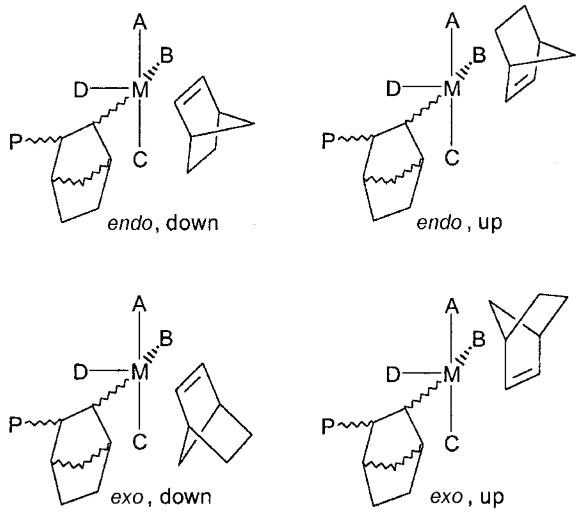


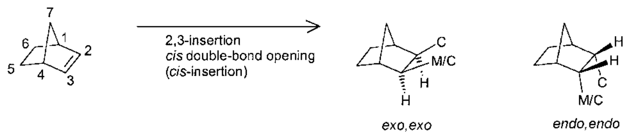
Figure 6. Principle stereo differentiation at the catalytic center for norbornene insertion.

bornene copolymers.[92] With respect to conformational constraints and dynamics for poly(norbornene) chains, a few reports deal with theoretical simulations using ab initio methods, semiempirical quantum-mechanical methods, and force field methods.[32,67,91,93,94]

The formation of stereoregular norbornene polymers would require a single-site catalyst which can exert a precise control on the polyolefin stereochemistry.[95] Thus, the metal center should differentiate between an *exo*/*endo* approach and an up/down coordination relative to the last inserted monomer unit (cf. Figure 6).

It is presumed that the zirconocene catalysts (see above) form the highly stereoregular *erythro*-diisotactic poly(norbornene) (*exo-mmm*, cf. Figure 5).[91] The high stereoregularity is suggested because the polymer is insoluble in any organic solvent. Other catalyst systems probably lead to other stereochemistries, because poly(norbornene) products of different solubilities are reported (see above and below). Such stereochemistries have yet to be assigned, though.

The pictures of the norbornene polymers in Figure 5 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 homopolymer 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.



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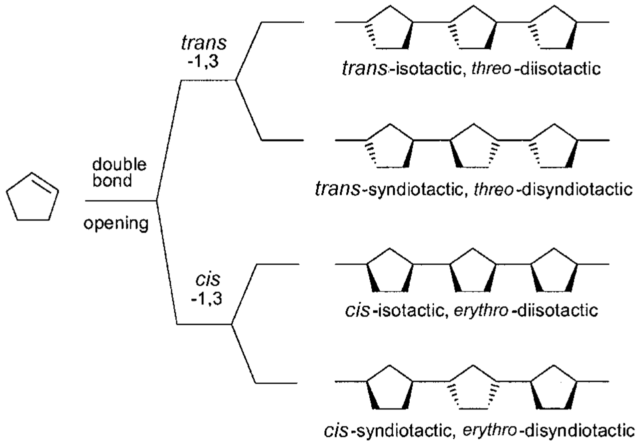

Figure 7. Polycyclopentene microstructures.

We just note that this is different for cyclopentene. For polycyclopentene the initial formulation as a 1,2-insertion product[96] 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) (Figure. 7).[97–99] In poly(1,3-cyclopentene) four regular microstructures can be distinguished: *cis*-iso/syndio-tactic and *trans*-iso/syndio-tactic.

The above comment on the possible stereochemistry in norbornene dimers and polymers is substantially expanded towards previous considerations outlined by Kaminsky and coworkers. They had suggested the formation of *erythro*-di-isotactic or *erythro*-di-syndiotactic structures depending on the C_2- or C_s-symmetry of the catalyst using *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$ (**2**) (C_2-symmetry), Cp_2ZrCl_2 (C_{2v}-symmetry) and [Ph_2C(Fluo)(Cp)]$ZrCl_2$ (**5**) (C_s-symmetry).[99]

NMR Characterization of Vinyl-Poly(norbornene)

The bicyclic backbone apparently makes the direct experimental characterization of the polymer microstructure for poly(2,3-bicyclo[2.2.1]hept-2-ene) by NMR difficult.[32] The determination and interpretation of the tacticity in vinyl polymers of cyclic olefins is much less developed than for acyclic olefins, such as propene,[100] or even for the ring-opened metathesis polymers.[101] In the ^{13}C NMR spectrum two broad peaks at 37.7–40.9 ppm and 53.9–58.8 ppm are observed for a stereoirregular soluble vinyl-poly(norbornene) prepared by [$Pd(CH_3CN)_4$]$(BF_4)_2$ (**7**). Whereas a presumably more stereoregular soluble poly(norbornene) from **27** gave six broad signals at 29.8, 35.3, 39.8, 49.8, 52.5, and 58.2 ppm.[75] For a poly(norbornene) prepared with Ni(salen)/MAO (**36**) the (solid-state) CP-MAS ^{13}C NMR spectrum displayed a sharp peak at 30.6 ppm (assigned to C_5 and C_6) and 39.1 ppm (C_1 and C_3) together with incompletely resolved, broader peaks around 34.6, 47.0, and 51.7 ppm.[81]

Solution characterization by NMR can be hampered by the insolubility of the polymer 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.[88]

Conclusions

In comparison to other vinyl polymers, such as polypropene or polystyrene, little is known in the vinyl polymerization of norbornene concerning the nature of the catalytically active metal species, the stereochemistry during the insertion mechanism and the polymer microstructure. Especially when MAO is used as a cocatalyst with nickel complexes it is not clear, to what extent the original ligands remain bound to the active metal. A variety of metal catalysts is available for the vinyl polymerization of norbornene, yet, the correlation between catalyst and polymer microstructure is poor. This stems mainly from a difficulty to elucidate the polymer stereoregularity or crystallinity. It is hoped for that this review may initiate research activities geared towards a better understanding of the vinyl-poly(norbornene) microstructure.

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