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Polymerization Reactions

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Dedicated to the memory of Professor Paolo Corradini

7.1 An Introductory Overview

The tremendous growth of polymer production since the middle of the twentieth century has been intimately connected with the development of new types of catalysts. A notable example in this regard is the field of polyolefin materials.

While catalysts are also used in the production of other types of polymers, the properties of most of these materials are not particularly dependent on the type of catalyst employed. Many *polycondensation* reactions, e. g. the formation of polyesters, polyamides or urea-formaldehyde resins, are speeded up by addition of some Brønsted or Lewis acids. Since relevant properties of these polymer products, such as their average chain lengths, are controlled by *equilibrium parameters*, primarily by the reaction temperatures and molar ratios of the monomers employed, and since their linkage patterns are dictated by the functional groups involved, addition of a catalyst has little leverage on the properties of the resulting polymer materials.

For typical *polyolefin* materials, on the other hand, the most relevant properties depend in addition to the types and molar ratios of the monomers used quite critically on the catalyst used for their production. This is due to the large numbers of different structural elements which can be formed with practically equal free energies by *polymerization* reactions even of simple olefins such as ethylene and/or propylene (Figure 1). The proportions with which each of these concatenation patterns occurs in a particular polymer product are thus controlled by the *relative rates* of their formation, i.e. by the selectivity with which these patterns are produced in the course of the polymerization process employed, rather than by any equilibrium parameters.

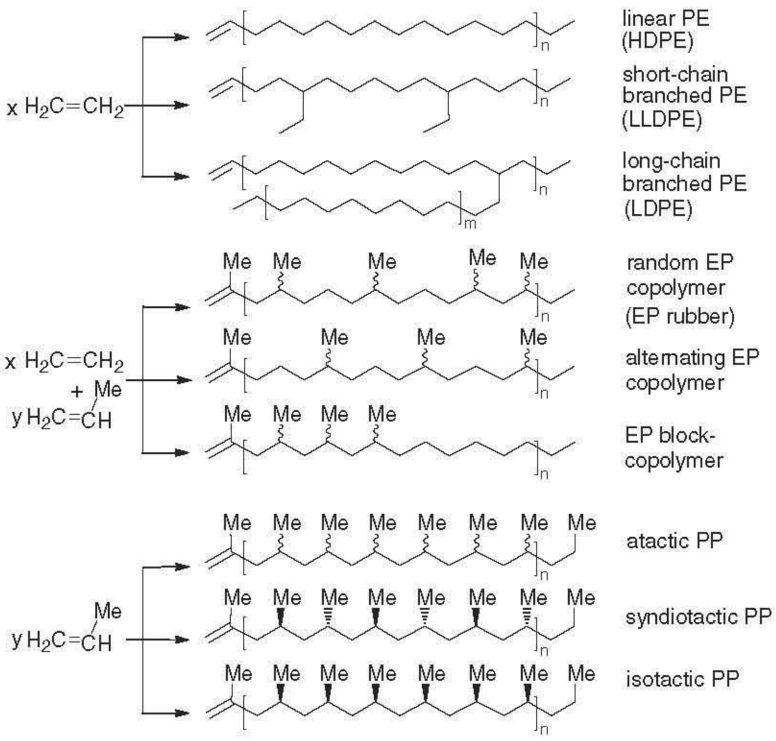


Figure 1 *Polymer enchainment patterns occurring in polyethylene (PE), ethylene-propylene copolymer (EP), and polypropylene (PP) chains (HDPE = crystalline high-density polyethylene, LLDPE = linear low-density polyethylene, LDPE = low-density polyethylene, EP rubber = elastomeric ethylene-propylene copolymer).*

Among the processes used for the formation of polyolefins, the longest-known but least selective one is *free radical polymerization.* A free radical species $X^\bullet$ produced e.g. by thermolysis of benzoyl peroxide or by photolysis of azabisisobutyronitrile (AIBN) can react with the double bond of a vinyl derivative $H_2C{=}CHR^\bullet$ to form a new radical of the type XCH_2-CHR which can then add another $H_2C{=}CHR$ unit; repetition of this process leads to polyolefin formation (Figure 2, top). This process works best for vinyl derivatives with unsaturated side groups, which provide *resonance stabilization* for an adjacent radical centre, e.g. with vinyl and acrylic esters, vinyl cyanides and vinyl chloride and with styrene and 1,3-dienes. It is extensively used in the emulsion polymerization of vinylic and acrylic derivatives and in the light-induced formation of photoresists for the nanofabrication of semiconductor chips and integrated electronic circuits.

Formally similar reaction sequences occur in *anionic polymerization.* Here, a $H_2C{=}CHR$ double bond reacts with a strongly nucleophilic anion X^- to form a new carbon-centred anion $XCH_2\text{-}CHR^-$. Continuation of this process leads to the formation of polymer chains, especially again for those vinyl derivatives

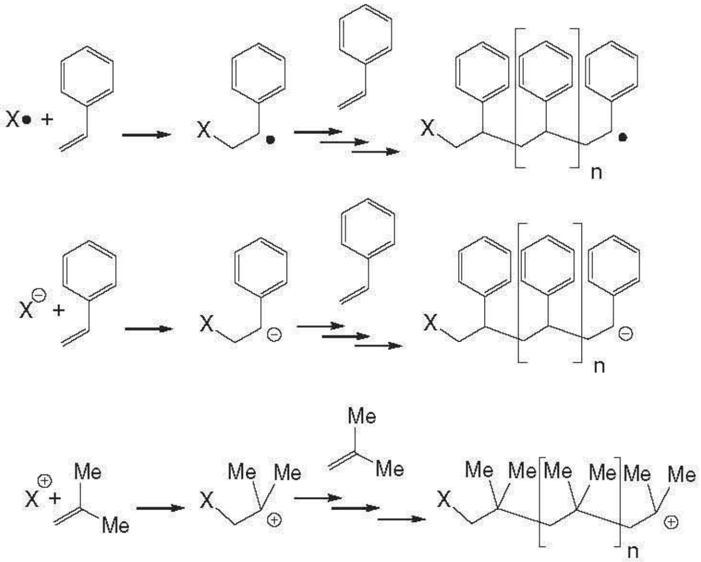


Figure 2 *Free radical polymerization (top) and anionic polymerization (middle) of styrene and cationic polymerization of iso-butene (bottom). For the nature of initiators X see text.*

where an unsaturated substituent R stabilizes the adjacent anionic charge (Figure 2, middle). Typical initiators for anionic polymerizations e.g. of styrene or of 1,3-dienes, are potassium amide or n-butyl lithium. In contrast to free radical polymerizations, where active species disappear rather rapidly (e.g. by radical combination), resonance-stabilized anions often are quite long-lived in aprotic media. As a consequence, *living polymerization* is frequently observed in these reaction systems: The anionic chain ends will continue to grow upon addition of new monomer until they are quenched, e.g. by addition of a protic reagent.

Atom-transfer and *group-transfer* polymerizations are variants of these processes, in which radical or anionic chain ends instead of occurring freely as such are temporarily released by breaking a suitably labile, but otherwise protective bond (e.g. to a Cu atom or to a Me_3Si group) which then gets reattached to the newly-formed chain end.

In *cationic polymerizations,* initiation occurs by attachment of a proton or some other Lewis-acidic cation X^+ to the $H_2C{=}CR_2$ double bond of a vinyl monomer to form a new carbon-centred cation of the type $XH_2C\text{-}CR_2{}^+$, which then grows into a polymer chain by subsequent $H_2C{=}CR_2$ additions (Figure 2, bottom). This type of polymerization works well and is used in practice only for olefins such as isobutene, where 1,1-disubstitution stabilizes the formation of a cationic centre. Since side reactions, such as release of a proton from the cationic chain end, occur rather easily, cationic polymerization usually gives shorter chains than anionic polymerization.

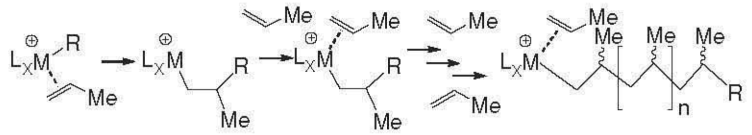


Figure 3 *Propylene polymerization by successive olefin insertions into metal-alkyl bonds.*

In all the processes described so far, the initiator is in principle not attached to the carbon centre by which a polymer chain continues to grow and is thus not in a position to control the type or the stereochemical orientation of an entering olefin substrate. These processes are, in addition, not well-suited for the polymerization of ethylene, propylene and other simple α-olefins, as these do not efficiently stabilize radical, anionic or cationic centres. These industrially abundant and least costly monomers are best polymerized by catalysts which operate by way of *insertion polymerization.* Here a positively charged metal catalyst centre is connected to a chain end which bears a partial negative charge, while at the same time binding and thus suitably polarizing a monomer molecule (Figure 3). Due to its position adjacent both to the growing chain end and to the entering monomer, these insertion-type polymerization catalysts are in principle best suited to control the selective formation of one or other of the polymer enchainment patterns outlined in Figure 1. Catalysts of this type, which are available today for practically all of the *3d* transition metals and some of their *4d* homologues, will be the main topic of this chapter.

Titanium-based *solid-state catalysts* for the industrial production of polyolefin materials were discovered in the early 1950's and have been continually improved since then (see Section 7.3). Due to the high degree to which they have been perfected for the production of large-volume polyolefin commodities, they continue to dominate the processes presently used for polyolefin production. Despite (or because of) this product-oriented perfection, only limited degrees of variability with regard to some relevant polymer properties appear to be inherent in these solid-state catalysts.

Access to polyolefins with a wider choice of properties has more recently been provided by various homogeneously soluble organometallic catalysts. Some of these catalysts, in particular those based on sandwich and half-sandwich complexes of zirconium and titanium and on nitrogen-containing complexes of group 4 and of some of the group 8 10 metals (see Section 7.4), are thus likely to be increasingly used for the production of polyolefins for special-purpose applications, which require properties not easily accessible otherwise.

7.2 Industrial Aspects of Polyolefin Production

During the last five decades, industrial production of polyolefin materials has experienced strong increases in production volumes as well as changes in production procedures. Here we give an overview of the situation in 2005 (Boxes 1 and 2).

Box 1 Raw Materials for Polyolefin Production

The most important monomers for the production of polyolefins, in terms of industrial capacity, are ethylene, propylene and butene, followed by isobutene and 4-methyl-1-pentene. Higher α-olefins, such as 1-hexene, and cyclic monomers, such as norbornene, are used together with the monomers mentioned above, to produce copolymer materials. Another monomer with wide application in the polymer industry is styrene. The main sources presently used and conceivably usable for olefin monomer production are: petroleum (see also Chapters 1 and 3), natural gas (largely methane plus some ethane, *etc.*), coal (a composite of polymerized and cross-linked hydrocarbons containing many impurities), biomass (organic wastes from plants or animals), and vegetable oils (see Chapter 3).

Box 2 Polyolefin Production Volumes and Major Producers

About 50% of the present world-wide plastics production (>200 Mt/a) is based on polyethylene and polypropylene. When polystyrene is included, this percentage rises to 60%. With regard to their total production volumes, polyolefin materials thus are among the top 10 of all products generated in chemical industry. Major producers of polyethylene and polypropylene are shown, together with their production capacities, in Figure 4.

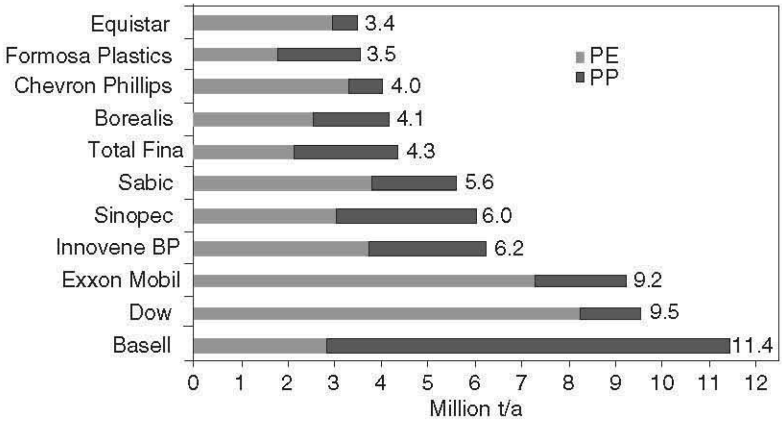


Figure 4 *Major producers of polyethylene (PE) and polypropylene (PP) in 2004/2005, with best-guess production capacities (including joint ventures).*

Almost all current large-scale polymerization plants for catalytic polyethylene and polypropylene production are suited only for the use of solid-state catalysts, which are introduced into the reactor in the form of grains or pellets by a suitable feed system and activated *in situ* by addition of an aluminium alkyl activator (see Section 7.3). Reaction conditions, such as pressure, temperature and monomer composition, are varied to afford polymers with different properties and morphologies.

Discussion Point DP1: *At present the production of polyolefin materials is based almost exclusively on petroleum. However further increases in crude-oil prices might make other potential sources competitive. Identify three alternative olefin sources, formulate the essential chemical reactions necessary for each production process and try to assess advantages, disadvantages and relative likelihoods of industrial implementation for such processes.*

7.2.1 Polyethylene Production

The catalytic polymerization of ethylene is usually conducted by one of the following methods:

Phillips Particle-forming process (Figure 5): In a double-loop reactor, constructed from wide-bore jacketed pipe, the catalyst and growing polymer particles are suspended in a slurry and kept in rapid circulation to avoid polymer deposits on the reactor walls. Due to its high surface-to-volume ratio, this reactor facilitates heat removal and allows short residence times. Typical reaction conditions are 100°C and 30–40 bar. Isobutane, a poor solvent for polyethylene, is used as a diluent and as a vehicle to introduce the catalyst into the reactor. The solid polymer is collected from a sedimentation leg and passed to a flash tank where the monomer and isobutane diluent are separated by evaporation and subsequently recondensed and recycled, while the polymer powder is fed into an extruder and formed into pellets.

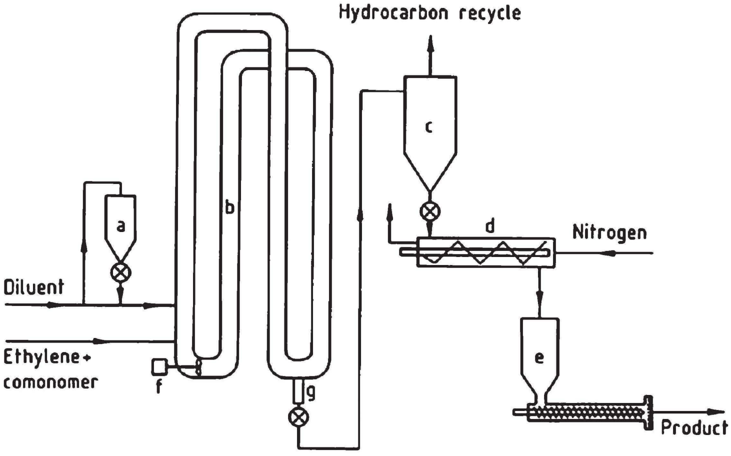


Figure 5 *Phillips Particle-forming process: a) catalyst hopper; b) double loop reactor; c) flash tank; d) purge drier; e) powder-fed extruder; f) impeller; g) sedimentation leg.*

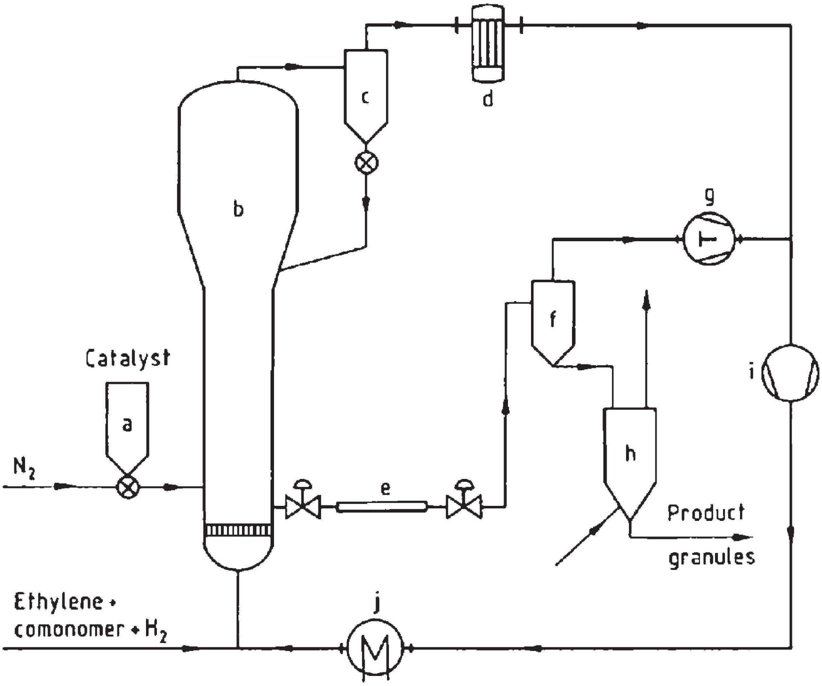


Figure 6 *Union-Carbide process. a) catalyst hopper; b) fluidized-bed reactor; c) cyclone; d) filter; e) polymer take-off system; f) product recovery cyclone; g) monomer recovery compressor; h) purge hopper; i) recycling compressor; j) recycle gas cooler.*

Union Carbide fluidized-bed process (Figure 6): The reactor, about 30 m high, has a characteristic shape with a lower cylindrical reaction section, and an upper expanded section in which the gas velocity is reduced to allow entrained particles to fall back into the bed. The feed gas enters the reactor from the bottom through a distributor plate which provides an even upward flow of gas and prevents polymer powder from falling. Depending on the product being made, reaction temperatures range between 80 and 100°C and pressures between 7 and 20 bar. Most often ethylene conversion is only *ca.* 2% per pass; the unreacted monomer is then recycled. The process operates close to the melting point of the polymer; accurate temperature control is thus necessary to avoid particle agglomeration. The final reaction mixture is fed into a powder cyclone from which residual monomers are recovered and recompressed.

7.2.2 Polypropylene Production

This is often conducted to make impact-resistant polyolefin blends. For this purpose, isotactic polypropylene, which is tough but somewhat brittle, is produced on the catalyst pellet in a first reaction step, using highly active stereospecific catalysts. Within this polymer matrix further polymer, usually a softer copolymer, is then deposited in a second reaction chamber. Four large-scale polymerization processes are used.

Spheripol Process: In a first reaction step homopolymerization is conducted in liquid propylene at 70°C in two loop reactors (Figure 5) connected in series. Since the first few seconds of polymerization with a highly active catalyst are decisive for the polymer morphology, catalyst particles are in some cases prepolymerized under milder conditions and charged into the loop reactor together with the cocatalyst to improve the particle forming process. By connecting two loop reactors in series, a more uniform residence time distribution of the catalyst grains is obtained. The polymer particles are collected in a cyclone and then either deactivated by treatment with steam, to obtain the final granular product, or else fed into a second polymerization, fluidized-bed reactor (Figure 6). Most often, ethylene and propylene are copolymerized onto the previously formed polypropylene matrix at 15–35 bar and 80°C in this second reactor. The resulting impact-resistant copolymer is fed into a cyclone and then worked up by deactivating catalyst residues with steam.

Novolen Process (Figure 7): With this technology, which comprises two vertical stirred gas-phase reactors in series, homopolymers as well as impact and random copolymers are produced. The first reactor operates at 80°C and 20–35 bar monomer pressure and is used exclusively for the homopolymerization of propylene. Propylene is injected as a liquid and cools the exothermic polymerization by its

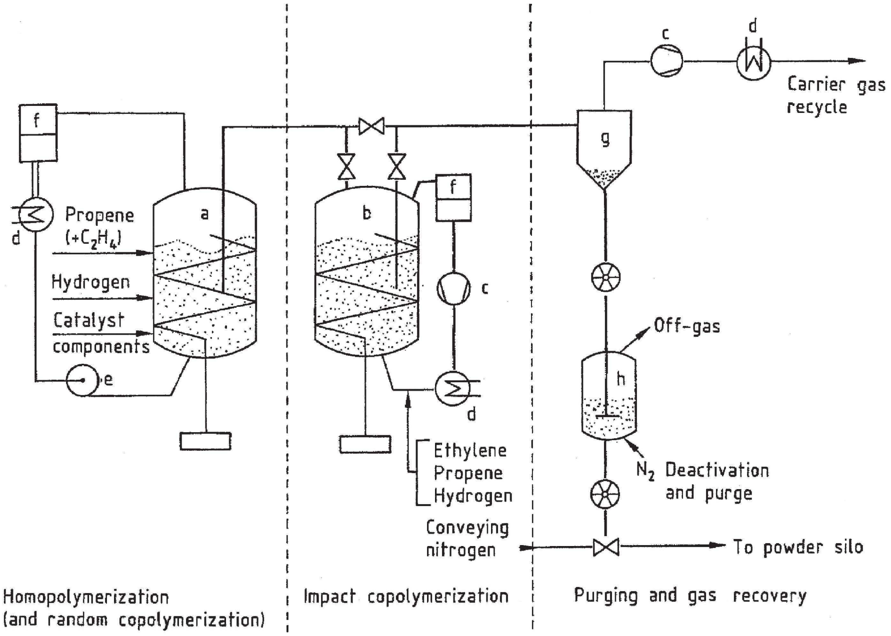


Figure 7 *Novolen process: a) first reactor, b) second reactor for impact copolymers, c) compressor, d) condensation, e) pump, f) filter, g) cyclone, h) deactivation and purge.*

evaporation in the reactor. The product mixture is continuously transferred from the reactor into a cyclone and then either deactivated or further polymerized in a second gas-phase reactor to produce impact-resistant copolymers under milder reaction conditions (10 25 bar and 60°C).

Amoco-Chisso Process: This process resembles the Novolen process except that the two reactors connected in series are stirred horizontally with blades and operated at 90°C and 20 bar. Polymers produced with the Amoco-Chisso technology show high uniformity, as particle residence time distribution in the reactor is particularly narrow.

Fluid-Bed Process: Union Carbide and Shell technologies are combined in this process: Two fluidized-bed reactors are used in series to produce impact-resistant polypropylene. As with other processes, reaction conditions are 50 100°C and 10 40 bar, with particle residence times between 1 and 4 hours.

Due to the use of advanced, highly active and selective solid-state catalysts (sections 7.3), the processes described above produce polymers from which neither stereoirregular polymer components nor catalyst residues need be removed. This has resulted in substantial reductions in the costs of investments, energy and maintenance, compared to slurry processes with first-generation catalysts. Ongoing developments are aimed at increased process flexibility and at process adaptation to the use of supported metallocene catalysts (Section 7.4).

Discussion Point DP2: *Olefin polymerization is an exothermic process. Estimate the heat of reaction released per day by a polymerization reactor with a typical production capacity of about 1000 t of PE or PP per day. Identify the means which can be used to remove this amount of heat from the reactor. What are their relative merits (and limits) in terms of energy use or recycling? Some (e.g. cationic) polymerization reactions proceed rapidly and give products with excellent properties when conducted at temperatures below 0°C. What makes such processes uneconomical?*

7.3 Solid-State Polymerization Catalysts

This category comprises two types of catalysts:

Titanium-containing catalysts, generally called *Ziegler-Natta* catalysts, in honour of Karl Ziegler, who discovered them in 1953, and Giulio Natta, who initiated and developed their use for stereospecific propylene polymerization, and

chromium-containing catalysts, usually called *Phillips* catalysts, with reference to the U.S. petroleum company where they were discovered in 1951 by Paul Hogan and Robert Banks.

7.3.1 Ziegler-Natta Catalysts

In their presently used form, Ziegler-Natta catalysts are typically prepared by adsorbing $TiCl_4$ onto small grains of a *$MgCl_2$ support*, with diameters of ca 50 μm, which are obtained either by prolonged grinding of $MgCl_2$ in a steel-ball mill or by its precipitation from a soluble precursor in the presence of some Lewis base, a so-called "*inner donor*", such as ethyl benzoate or a 1,3-diether. Subsequently a second, so-called "*outer donor*", e.g. a silyl ether or a phthalic acid diester, is often added. Upon being injected into the polymerization reactor these catalysts, which contain about 5 20% (w/w) of $TiCl_4$, are activated by reaction with aluminium alkyls, mainly *triethylaluminium*, to very high levels of *productivity*. Each gram of catalyst will typically produce 50 100 kg of polyethylene or polypropylene in the course of a few hours, its normal residence time in the reactor. The growth of the polymer also takes place inside the catalyst grains; thus each grain is disintegrated into several hundred minuscule particles with diameters of only 1 2 nm, which remain imbedded in a polymer pellet with a diameter of about 1 mm, i.e. with a volume several thousand times greater than the catalyst grain from which it had grown (Figure 8). Because of their small mass and size, the catalyst fragments can remain in the final polymer product without interfering with its chemical, mechanical or optical properties.

Box 3 Typical Polyolefin End Uses

Polyolefin materials have entered into so many varied applications in everyday life that a complete overview is not possible here. Table 1 summarizes the sectors which consume the greatest proportions of ethylene- and propylene-based polyolefin materials.

Table 1 *Uses of ethylene- and propylene-based polyolefin materials (estimated percentage of total plastic application in Europe in 2003, from www.plasticseurope.org; for list of abbreviations see Glossary)*

Packaging	37%	Films for cooking (HDPE), food packaging (LDPE, PE-co-norbornene, PMP), paper laminating (PP, PIB), milk packaging (LDPE, PP), chewing gums (PIB) and cookery (PMP), containers (HDPE) and caps (LDPE)
Building and construction	18%	Pipes (HDPE, LLDPE, PP, isotactic-PB, PMP, ABS), carpets (PP), storage tanks (HDPE, PB), asbestos replacement (PP), hot-melt adhesive (atactic PB), insulating foils (PP, PIB)
Transportation	6%	Transport tanks and containers (HDPE), lubricant (PIB), seals (EPD)
Electronic and electrical devices	9%	Electrical home devices (PP, PS, ABS), cables (PMP), technical parts (PP), lamps (PS)
Agriculture	2%	Crop protection (PE), twines, stripes and strings (PE, PP)
Medical	1%	Blister packaging (PE-co-norbornene), medical devices (PMP)
Sports		Sporting goods (ABS, PS)

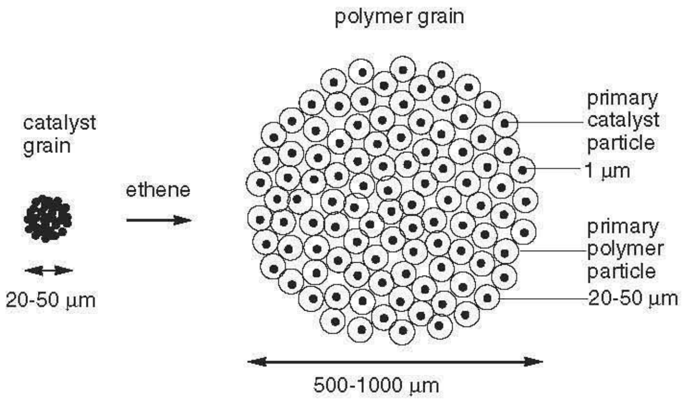


Figure 8 *Simplified model for the fragmentation of $MgCl_2$-supported Ziegler-Natta catalyst grains to primary catalyst particles and shape conservation of growing polymer grains.*

Box 4 Polyolefin Waste and Recycling

As plastic wastes are proliferating at increasing rates, infrastructures for waste recycling are developing in almost all areas of major polymer consumption. Policies in this regard are based on four main steps: *i*) prevention/reduction of plastic waste, *ii*) material recycling (mechanical recycling, feedstock recycling), *iii*) energy recovery and *iv*) dumping.

Feedstock recycling (chemical recycling) is the chemical reconversion of polymers to raw materials, i.e. to monomeric olefins. Suitable pyrolysis and gasification processes are being tested but have not yet become commercially competitive with the use of petrochemicals from crude oil. On the other hand, energy recovery, the combustion of polyolefin wastes in incineration plants to produce energy in the form of heat and electricity, appears to be the most efficient and unproblematic polyolefin waste utilization, since the chemical composition of these materials (which are free of chlorine, sulfur and nitrogen) is practically indistinguishable from that of heavy oils, which are burned in incineration plants, together with normal waste, to ensure temperatures sufficiently high for the complete destruction of toxic effluents.

$MgCl_2$ is ideal as a support for polymerization catalysts since it consists of loosely aggregated, crystalline sub-particles, which are extensively fragmented already by initial polymer formation; hence high polymerization rates are reached immediately. Disadvantageous however, is the high fragility of the initial $MgCl_2$ support, which can lead to formation of polymer fines (dust) due to the turbulence of gas-phase polymerizations. Good morphology control of the polymer grains is achieved however when a pre-polymerization step is applied under mild conditions. Since the catalyst support fragments are now kept embedded in the polymer matrix, polymer grains form good replicas of the original catalyst grains in the subsequent main polymerization.

Even the most advanced Ziegler-Natta catalysts contain distinctly non-uniform catalytic sites. Although most of the less selective (and hence undesirable) sites present in catalysts made by older recipes appear to be eliminated or blocked by the "inner" and "outer" donors now used to condition these catalysts, the polymers they produce still show large variations in molar mass, stereoregularity and comonomer distributions, which indicate that they originate from distinct catalytic sites.

Despite their complexity, Ziegler-Natta catalyst systems have been intensively studied by experimental and theoretical methods and the following model of these catalysts appears to be commonly accepted [G. Monaco, M. Toto, G. Guerra, P. Corradini, L. Cavallo, *Macromolecules* 2000, **33**, 8953; M. Seth, T. Ziegler, *Macromolecules* 2003, **36**, 6613]. After reduction by the alkylaluminium activator, the active sites of the catalyst contain *Ti(III) ions*, which are deposited on disordered surface layers of the minute $MgCl_2$ crystallites. Essential in this regard appears to be the structural similarity of $MgCl_2$ and $TiCl_3$ crystals, both of which form layer structures with similar lattice constants. The presence of "inner" and "outer" donors appear to favour, at the expense of alternative species, Ti(III) centres placed at a 110 edge of the $MgCl_2$ layer lattice, where each Ti(III) ion is surrounded by five Cl^- ions and of related Ti(III)/Ti(IV) pairs placed at a 100 edge. To comply with the stoichiometry $TiCl_3{=}TiCl_{4/2}Cl$, four Cl^- ions are in bridging positions and thus not easily exchanged, while the fifth is a terminal Ti-Cl bond and is thus readily exchanged for an alkyl group upon reaction with the alkylaluminium activator (Figure 9).

The vacant sixth coordination site of these Ti centres can take up an olefin molecule to form the reaction complex required for the initiation and subsequent growth of polyolefin chains. Due to their octahedral dichelate-type structure, these Ti(III) centres are *chiral* and thus able to steer each incoming molecule into a preferred enantiofacial orientation. The *stereospecificity* with which subsequent propylene units insert into the growing polymer chain is most likely based on a mechanism analogous to that determined for soluble polymerization catalysts (Section 7.4.3).

Present-day Ziegler-Natta catalysts are supremely suitable for the production of linear polyethylene and of highly isotactic polypropylene. They are also used to produce the softer ethylene-propylene *copolymers*, used for packaging and related purposes. Due to the presence of distinct catalyst sites in typical Ziegler-Natta catalysts, these copolymers suffer from non-uniformity however, and copolymers which contain increased amounts of higher α-olefins, desirable for certain applications, cannot easily be made with these catalysts.

7.3.2 Phillips Catalysts

Chromium-containing Phillips catalysts are prepared by adsorption of a chromium compound, mostly *chromium trioxide*, onto an amorphous silica support and a subsequent reduction by exposure to ethylene. The resulting catalysts are

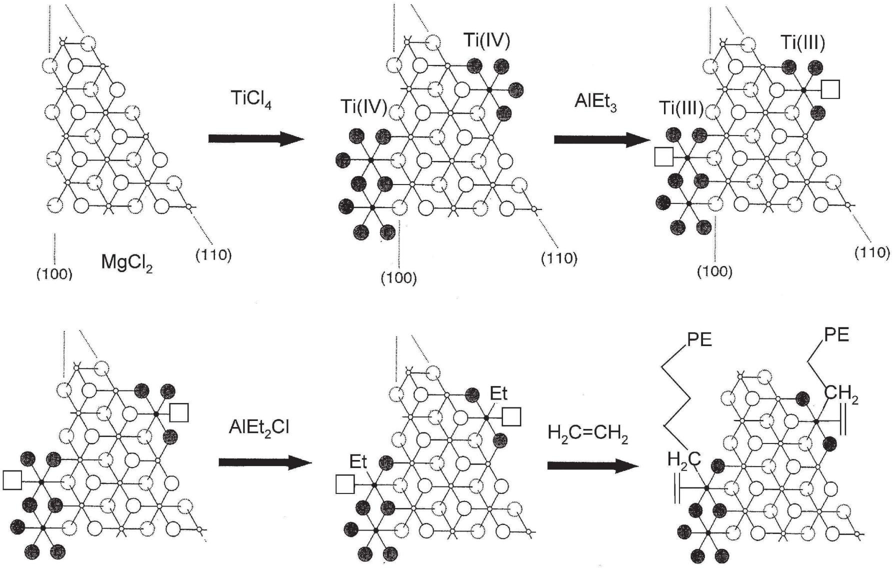


Figure 9 *Simplified model for the formation of active centres of Ziegler-Natta catalysts by adsorption of* $TiCl_4$ *on solid* $MgCl_2$*, reduction of Ti(IV) to Ti(III) chloride-alkyl exchange with aluminium alkyls and polyethylene (PE) formation by coordination and insertion of ethylene molecules.*

highly active and do not require further activation. These catalysts, while not able to generate polypropylene or higher polyolefins, are used extensively for the production of the strictly linear, so-called *high-density polyethylene* (HDPE) with particularly high molar mass and, hence, optimal mechanical and thermal strength. Their active sites are generally considered to consist of *Cr(II) centres*, but the ligand environment of these centres and the pathways by which they induce the insertion of ethylene molecules into growing polymer chains are still very incompletely understood [E. Groppo, C. Lamberti, S. Bordiga, G. Spoto, A. Zecchina, *Chem. Rev.* 2005, **105**, 115].

7.4 Soluble Olefin Polymerization Catalysts

Polymerization catalysis with soluble complexes of group IV transition metals, in particular with hydrocarbon-soluble titanocene complexes, was discovered in the 1950's, shortly after the appearance of Ziegler's and Natta's reports on solid-state catalysts, and rather thoroughly studied from then on. Alkylaluminium compounds, such as $AlEt_2Cl$, are required to activate also these soluble catalysts. In distinction to their solid-state counterparts, however, early soluble catalysts were able to polymerize only ethylene, and not any of its higher homologues. After their activation by methylalumoxanes had been discovered (Section 7.4.1), soluble catalysts became as efficient as solid-state catalysts – in

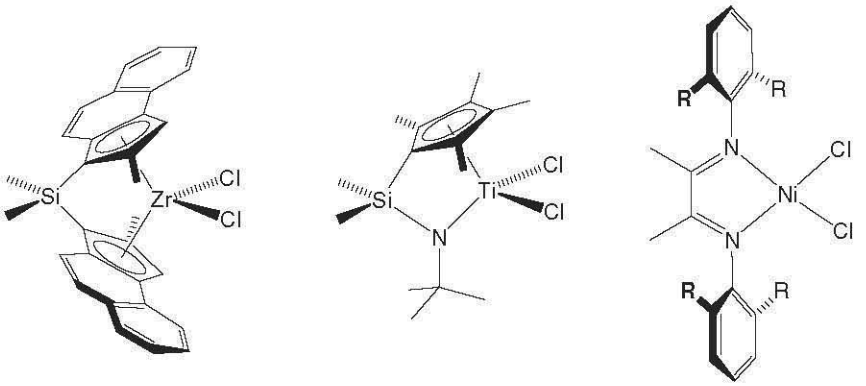


Figure 10 *Precursors for soluble polymerization catalysts: ansa-zirconocene complex (left), constrained-geometry titanium complex (middle) and nickel diimine complex (right).*

some aspects even more so for the polymerization of all types of olefins. Today, soluble olefin polymerization catalysts are available from practically all 3*d*-transition metals as well as from some of their 4*d* homologues.

The presently most advanced, with regard to industrial applications, are variously substituted and/or ring-bridged zirconocene catalysts, and related, so-called "constrained geometry" catalysts (Figure 10). Most of our understanding with regard to the basic functioning and limitations of polymerization catalysis in general comes from studies on soluble catalysts of this type and, in particular, on catalysts derived from a series of nickel and palladium complexes (see Figure 10). These catalysts are thus included in the following discussion, although their industrial applications are still lagging behind those of the group 4 catalysts.

7.4.1 Activation Reactions

For practical reasons, catalysts for olefin polymerizations are usually prepared *in situ* from a stable *pre-catalyst* by exposure to some suitable *activator* (or *co-catalyst*). The resulting *catalyst system* then contains highly reactive catalyst species which are capable of inducing the growth of polymer chains in the presence of suitable monomers. The elementary reactions involved in activation processes of this kind are particularly well-defined for zirconocene-based catalysts.

Air-stable zirconocene dichlorides of the type $Cp^x{}_2ZrCl_2$ ($Cp^x{}_2$ being a particular pair of substituted and/or bridged cyclopentadienyl ligands) are converted to active catalysts, for example by reaction with an aluminium trialkyl compound and dimethylanilinium tetrakis(perfluorophenyl) borate, $PhNMe_2H^+$ $(C_6F_5)_4B^-$, one of a number of so-called *cationization reagents*. Spectroscopic data indicate that the main species in the resulting catalyst system is an ion pair which contains an alkyl *zirconocenium cation* $Cp^x{}_2Zr\text{-}R^+$ in direct coordinating contact with its counter-anion $(C_6F_5)_4B^-$ (Figure 11). $(C_6F_5)_4B^-$ is a *weakly coordinating anion*, due to a high degree of delocalization of its anionic charge and to the inert C-F

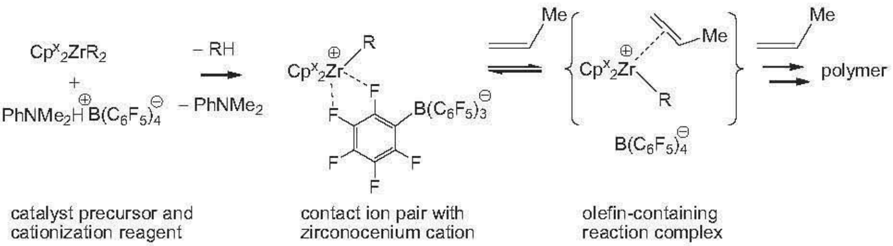


Figure 11 *Formation of a cationic olefin-containing reaction complex (right) by reaction of a zirconocene dialkyl precursor complex with a cationization reagent (left), via a highly reactive contact ion pair containing an alkyl zirconocenium cation (middle).*

lining of its surface. Such an anion can be expected to be rather easily displaced from the Zr centre by an olefin monomer to form an *outer-sphere ion pair*, which contains the cationic *reaction complex* $Cp^x{}_2Zr\text{-}R(olefin)^+$. This is thought to be the site of polymer growth by olefin insertions first into the Zr-R bond and then into successively formed Zr-polymer bonds.

Cations of the same type are also produced, with release of $Ph_3C\text{-}R$, by reaction of $Cp^x{}_2ZrCl_2/AlR_3$ mixtures (or of the dimethyl complex $Cp^x{}_2ZrMe_2$) with Ph_3C^+ $(C_6F_5)_4B^-$, trityl perfluorotetraphenyl borate. In addition to its action as an *alkyl donor* to the Zr centre the trialkylaluminium AlR_3 functions as a *scavenger* by freeing the reaction mixture from protonic or oxidizing impurities. Higher concentrations of AlR_3, in particular of $AlMe_3$, tend to interact with cations such as $Cp^x{}_2Zr\text{-}Me^+$ with formation of binuclear adducts, $Cp^x{}_2Zr\text{-}(\mu\text{-}Me)_2AlMe_2{}^+$, which stabilize these cations against destructive side reactions [M. Bochmann, *J. Organomet. Chem.* 2004, **689**, 3982]. However they also diminish their reactivity *vis-a-vis* olefin monomers, since the olefin now has to displace the trialkylaluminium from the Zr center to form the reaction complex $Cp^x{}_2Zr\text{-}R(olefin)^+$. Triisobutylaluminium, $Al(CH_2CH(CH_3)_2)_3$, is less prone to form adducts with a zirconocene alkyl cation due to the diminished tendency of its bulky alkyl groups to act as bridges between Zr and Al centers and is thus often used as an activator/scavenger reagent.

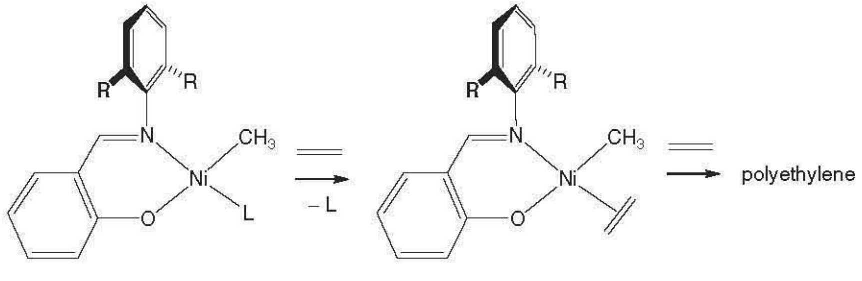
Active catalyst systems are also formed when a *Lewis acid,* LA, reacts with a stable dialkyl zirconocene complex $Cp^x{}_2ZrR_2$ provided that the anion $R\text{-}LA^-$, formed by alkyl abstraction by the Lewis-acid LA, is only weakly coordinated. An example is the Lewis acid perfluorotriphenylboron, $(C_6F_5)_3B$. It reacts with dimethyl zirconocenes to form an ion pair $Cp^x{}_2Zr\text{-}Me^+ \ldots MeB(C_6F_5)_3{}^-$. These catalyst systems usually require higher temperatures to achieve their full activities (and often give shorter polymer chains) than those described above, most likely due to the more "sticky" (*i.e.* more strongly coordinating) nature of $MeB(C_6F_5)_3{}^-$ as compared to $B(C_6F_5)_4{}^-$ anions.

Catalyst sytems with activities less sensitive to impurities are obtained when a zirconocene dichloride complex is reacted with *methylalumoxane,* the Lewis-acidic product of partial hydrolysis of trimethylaluminium, often abbreviated as *MAO*

[W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, **1998**, 1413]. Hydrocarbon solutions of MAO contain various species of general composition $(AlMe)_m(AlMe_2)_nO_{m+n/2}$ with m ≈ n ≈ 10 100, with six- and four-membered $(\text{-AlO-})_x$ rings and with Al centres of coordination number four as well as three. Some of these Al centres appear to be highly Lewis-acidic. A *MeMAO$^-$ anion* is thus generated, together with the cation $Cp^x{}_2Zr\ Me^+$, by methide abstraction from $Cp^x{}_2ZrMe_2$. $MeMAO^-$ appears to be displaced from $Cp^x{}_2Zr\ Me^+$ by olefin monomer about as easily as $B(C_6F_5)_4{}^-$ is from $Cp^x{}_2Zr\text{-}Me^+ \ldots B(C_6F_5)_4{}^-$. The most highly Lewis-acidic species appear to be present in normal MAO mixtures to only a small extent. Rather high [Al]:[Zr] ratios of ≥ 1000 are thus required to induce maximal activity in MAO-activated catalyst systems.

Since substantial amounts of "free" trimethylaluminium (*i.e.* Al_2Me_6) are present in normal MAO preparations, cationic *trimethylaluminium adducts* $Cp^x{}_2Zr\text{-}(\mu\text{-}Me)_2AlMe_2{}^+$, in outer-sphere association with their $MeMAO^-$ counteranions, are in general the dominant species in MAO-activated catalyst systems [D. E. Babushkin, N. V. Semikolenova, V. A. Zakharov, E. P.Talsi, *Macromol. Chem. Phys.* 2000, **201**, 558]. While being quite stable against destructive side reactions MAO-activated catalyst systems are thus often less active than those obtained with the cationization reagents described above.

In a few cases, active catalysts can be obtained without any activator, when release of a neutral stabilizing ligand entity from a precursor complex generates a neutral, coordinatively unsaturated and hence highly reactive metal centre. Examples of such *single-component catalysts* are a number of Ni(II) catalysts which are formed by release of a phosphine or pyridine ligand from neutral nickel alkyl or aryl precursors containing imino-phenolate or other monoanionic N,O or P,O chelate ligands (Figure 12). Some representatives of this class of catalysts, while not as productive as those described above, are inert enough to be usable as catalysts for *emulsion polymerization* of ethylene in water-hydrocarbon mixtures [E. F. Connor, T. R. Younkin, J. I. Henderson, A. W. Waltmann, R. H. Grubbs, *Chem. Comm.* **2003**, 2272; L. Kolb, V. Monteil, R. Thomann, S. Mecking, *Angew. Chem. Int. Ed. Engl.* 2005, **117**, 433].



L = phosphine, pyridine

Figure 12 *Activation of phenoxy-imine nickel complexes by loss of a phosphine or pyridine ligand.*

***Discussion Point DP3**: Organic derivatives of the group 13 elements aluminium and boron are needed as essential components for almost all of the insertion-catalyzed olefin polymerizations. List four such compounds of interest and describe for each of them the structural and reactivity properties relevant to its action as activator/cocatalyst. Outline some of the features of polymerization catalysts that do not require any Al- or B-containing cocatalysts.*

7.4.2 Polyolefin Chain Growth

The processes by which growth of a polymer chain is engendered in a homogeneously soluble catalyst system are best documented for some of the cationic alkyl Ni(II) and Pd(II) complexes with neutral diimine ligands. Low-temperature NMR studies show that the *resting state* of the catalyst (*i.e.* the form in which most of the catalyst accumulates in the presence of ethylene) is an outer-sphere ion pair in which a weakly coordinating $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$ anion has been displaced from the cationic metal centre by an ethylene molecule. The *rate-limiting step* for polymer production is the *migratory insertion* of ethylene into the adjacent metal-alkyl or metal-polymer bond. This step occurs more easily in Ni(II) catalysts than in their Pd(II) analogues. The electron-deficient primary insertion product is probably stabilized by a *β-agostic bond;* in the presence of ethylene however this bond is immediately broken under formation of a new ethylene complex (Figure 13).

Propylene and higher olefins, on the other hand, do not bind to the metal centre strongly enough to induce complete formation of the olefin-containing reaction complex from the β-agostic insertion product. The latter appears to be more stable here and will thus form the catalyst resting state. Olefins other than ethylene must form the required olefin-containing reaction complex in a *pre-equilibrium* reaction step. The β-agostic resting state appears to be destabilized by the presence of bulky ortho-substituents at both imino-aryl groups; olefin uptake can then occur more easily, as indicated by increased activities of the correspondingly substituted catalysts for the polymerization of propylene.

A crucial property of a polyolefin is its *regioregularity*. It is governed by the catalyst used for its production, i.e. by the *regioselectivity* with which it controls the direction of olefin insertion into a metal-alkyl bond. For example, propylene can insert either with its CH_2 or its CHMe end toward the metal. The first

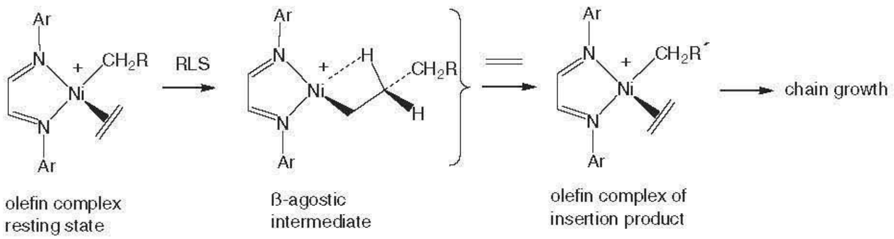


Figure 13 *Chain growth by ethylene insertion in diimine nickel catalysts (RLS = rate-limiting step).*

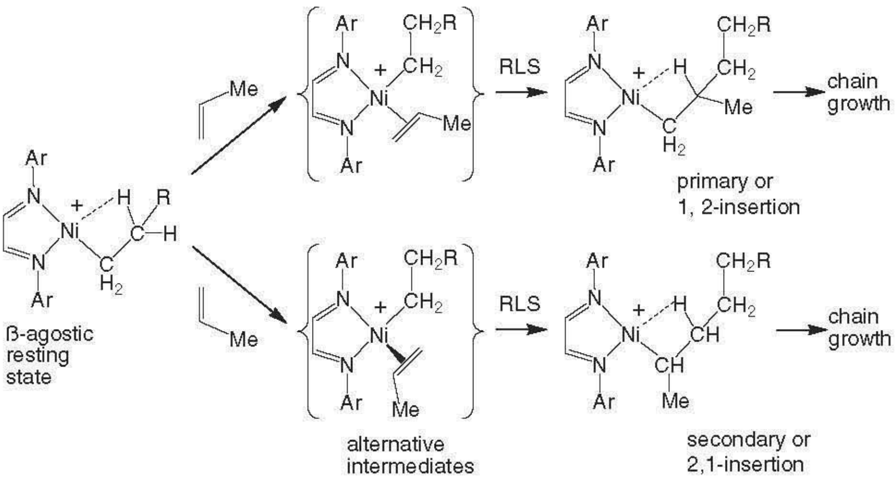


Figure 14 *Alternative propylene insertion modes in diimine-nickel catalysts (RLS = rate-limiting step).*

mode is called *primary* or *1,2-insertion,* whereas attachment of the CHMe end at the metal centre leads to *secondary* or *2,1-insertion* (Figure 14). As with other types of catalytic reactions (e.g. olefin hydrogenation or hydroformylation) this choice is mainly decided by steric factors. Narrow coordination sites will generally favour formation of the slimmer primary insertion product, while the less-hindered olefin end will otherwise be the preferred site of attack of a migrating alkyl group. Both reaction modes occur to comparable extents for most Ni(II) and Pd(II) polymerization catalysts.

A remarkable feature of Ni(II)- and Pd(II)-based catalysts is their amazing propensity for *chain migration,* i.e. for the stepwise movement of the metal centre along the newly formed polymer chain. By repeated β-H transfer with elimination of a polyolefin and reinsertion of the latter with reversed orientation (Figure 15), the metal is able to migrate to each of the enchained C atoms, passing in some cases even tertiary C atoms. Each of the ensuing metal-attachment sites can, in principle, become the starting point of another chain segment by renewed olefin insertions. A number of otherwise unexpected structural elements are thus found in polymers produced with catalysts of this type.

Due to this chain-migration process ethylene is polymerized to macromolecules containing multiple branches rather than to the linearly enchained polymer obtained with classical solid-state catalysts. In propylene polymerization with these catalysts 1,2-insertions give the normal methyl-substituted polymer chains, but after each 2,1-insertion the metal centre is blocked by the bulky secondary alkyl unit and can apparently not insert a further propylene. Instead the metal must then first migrate to the terminal, primary C atom before chain growth can continue by further propylene insertions. By this process, also called *1,ω-enchainment* or *polymer straightening,* some of the methyl or (in the case of higher olefins) alkyl substituents are incorporated into the chain.

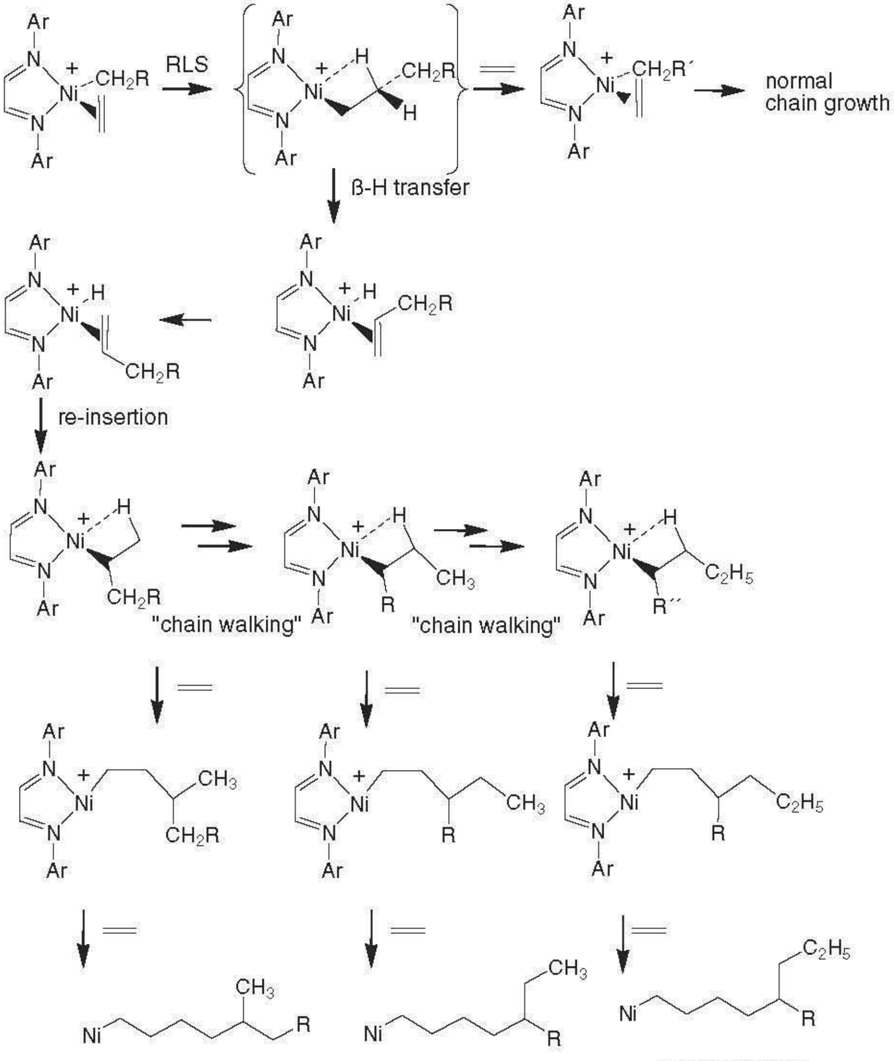


Figure 15 *Formation of branches in polyethylene by chain walking of diimine-nickel catalyst.*

Some Ni(II)-catalysts polymerize higher olefins by *2,ω-enchainment*. Here even the primary insertion product appears too bulky for further chain growth due to its adjacent alkyl branch; the metal thus has to migrate to the unencumbered end of the alkyl side chain before another insertion can occur [V. Möhring, G. Fink *Angew. Chem. Intern. Ed. Engl.* 1985, **24**, 1001].

In zirconocene-catalyzed olefin polymerizations similar processes are involved. Here polymerization rates depend at least linearly on olefin concentrations; an olefin-containing reaction complex thus cannot be the catalyst resting state. Instead the fourth coordination site of the metal centre might be occupied by an agostic bond to the metal-bound polymer chain, as in Ni(II)- and Pd(II)-catalyzed α-olefin polymerizations, by direct contact to a weakly coordinating Me-MAO$^-$ or perfluoroarylborate anion, or by the formation of a trialkylaluminium adduct. Low-temperature NMR studies on relatively slow catalyst systems point to contact-ion pairs as the dominant resting-state species [C. R. Landis, K. A. Rosaeen, D. R. Sillars, *J. Am. Chem. Soc.*, 2003, **125**, 1710]. In faster catalyst systems at above-ambient temperatures where an insertion occurs every few milliseconds, the nature of the predominant species, from which the reaction complex is formed by uptake of an olefin, is still under discussion [I. E. Nifantiev, L. Y. Ustynyuk, D. N. Laikov *Organometallics* 2001, **20**, 5375; Z. Xu, K. Vanka, T. Ziegler, *Organometallics* 2004, **23**, 104; F. Song, S. J. Lancaster, R. D. Cannon, M. Schormann, S. M. Humphrey, C. Zuccaccia, A. Macchioni, M. Bochmann, *Organometallics* 2005, **24**, 1315].

Transition states for α-olefin insertions have been shown from measurements of *kinetic isotope effects* to involve an agostic interaction of an α-H atom of the growing chain with the metal centre of the metallocene catalyst [W. E. Piers, J. E. Bercaw, *J. Am. Chem. Soc.* 1990, **112**, 9406; H. Krauledat, H.-H. Brintzinger, *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 1412]. This interaction which becomes a γ-agostic bond in the primary insertion product, appears to relieve some of the increasing electron deficiency as the complex proceeds along the insertion reaction coordinate.

Due to their narrow aperture, zirconocene-based catalysts insert olefins almost exclusively in the 1,2- or primary direction. Small proportions of 2,1-inserted propylene units and, for some catalysts, 1,3-inserted units derived from them by chain straightening, are a cause of melting-point lowering in some metallocene-produced polypropylenes.

Group 4 metal catalysts of the constrained-geometry type generally follow similar patterns in their polyolefin formation reactions. These catalysts, which can be operated at rather high temperatures, are able probably due to their more open coordination sites to incorporate into a polymer chain also the unsaturated ends of polyolefins, i.e. of *macromonomers*, which are hardly touched by metallocene-based or by Ni(II)- or Pd(II)-based catalysts (Figure 16). Consequently, constrained-geometry catalysts form a peculiar type of long-chain branched polyethylene (Figure 1), which possesses remarkable elasticity and toughness [J. C. Stevens in *Catalyst Design for Tailor-Made Polyolefins*, ed. K. Soga, and M. Terrano, Kodansha Elsevier, Tokyo 1994, p. 277; K. W. Swogger, *ibid.*, p. 285).

Discussion Point DP4: *Figures 13 and 14 represent reaction schemes for the polymerization of ethylene and of propylene by diimine-nickel catalysts. From these schemes predict how the rates of polyethylene and of polypropylene formation should depend on the concentrations of the respective monomers. What influence should the kind of anion present be expected to have on the rates of polymer formation in each of these cases? How would these answers differ from those to the same questions with regard to zirconocene-based polymerization catalysts (Figure 11)?*

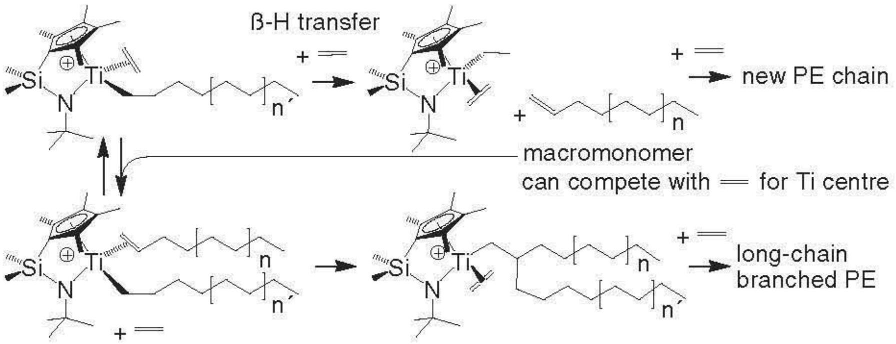


Figure 16 *Formation of long-chain branched polyethylene by a constrained-geometry catalyst through macromonomer insertion.*

Discussion Point DP5: *The previously unexpected observation of side-chain branches in diimine-nickel catalyzed polyethylene formation is explained by the reaction scheme represented in Figure 15. Propose related "chain migration" schemes which explain i) the "chain straightening", i.e. the incorporation of propylene methyl substituents into the backbone of polypropylene chains produced by these catalysts, ii) the 2,ω-concatenation of higher α-olefins by some Ni-based catalysts, and iii) the introduction of stereoerrors in isotactic polypropylene by chain-migration of chiral ansa-zirconocene catalysts.*

7.4.3 Stereochemistry of α-Olefin Enchainment

The thermal and mechanical properties of polypropylene and other polymers produced from α-olefins depend just as much as on their regioregularity on the *stereoregularity* of consecutive olefin insertions, i.e. on the relative configuration of the tertiary C atoms which occupy every other position in the polymer backbone. Some of the diastereomeric structures are represented as Fischer-type projections in Figure 2.

If consecutive olefin insertions all occur with the same stereochemical orientation, i.e. on the same *olefin enantioface*, all alkyl substituents at the polymer backbone will have the same orientation. In such an *isotactic* polymer chain, all the tertiary C atoms inside its backbone are of the same configuration. If all consecutive olefin insertions occur with opposite enantiofacial orientation, the resulting *syndiotactic* polymer contains in its backbone tertiary C atoms of strictly alternating configuration. An *atactic* polymer will finally result when olefin insertions occur randomly, without enantiofacial preference.

Isotactic polypropylene is a rather stiff and tough solid material with a melting point of 164°C. Closely packed, CH_3-studded helices (Figure 17), rigidly interwoven in crystalline domains (Figure 18), account for the mechanical and thermal resistance of isotactic polymers. Syndiotactic polypropylene has a related crystalline structure, but atactic polymers are amorphous and form oily or waxy materials depending on chain lengths.

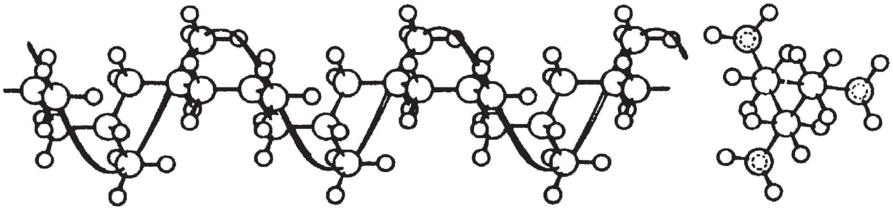


Figure 17 *Helical structure of isotactic polypropylene.*

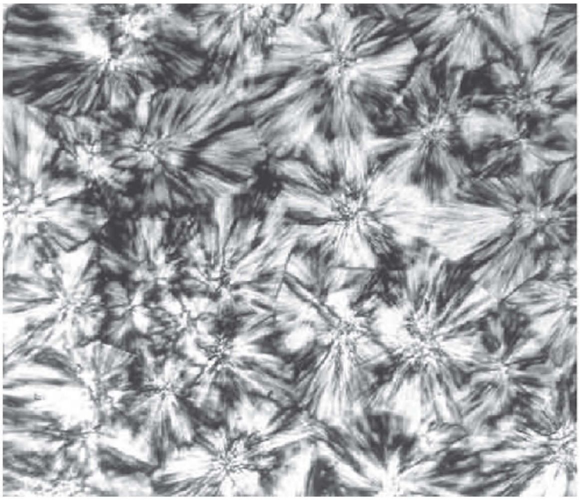


Figure 18 *Spherulite crystals of isotactic polypropylene.*

Highly isotactic polymers, with stereoregularities similar to those obtained with the solid-state catalysts discussed in Section 7.3, are produced by zirconocene catalysts which have a bridged and appropriately substituted ligand framework of C_2 symmetry, such as that shown in Figure 16. The Me_2Si-bridge of these *ansa-zirconocene* complexes renders the ligand framework particularly stereorigid, while the spatially demanding extensions of each C_5 ring provide for efficient chirality at each of the coordination sites.

Studies on catalysts carrying ^{13}C-labeled alkyl groups at their metal centre have shown that a chain with at least two C atoms is required for an efficient control of the enantiofacial orientation of an inserting olefin [A. Zambelli, C. Pellechia, *Makromol. Chem., Macromol. Symp.* 1993, **66**, 1]. This observation, together with molecular-mechanics model calculations, has led to the concept that catalytic-site control is *chain-segment mediated* [G. Guerra, P. Corradini, L. Cavallo, M. Vacatello, *Makromol. Chem., Macromol. Symp.* 1995, **89**, 77]. The metal-bound C(α)-C(β) chain segment will orient itself into the most open sector of the catalyst's ligand framework so as to minimize steric repulsions. An incoming olefin then must adopt that enantiofacial orientation which places its alkyl substituent *trans* to the C(α)-C(β) segment along the incipient C(2)...C(α) bond (Figure 19). All available evidence indicates that analogous mechanisms are also responsible for the stereoselectivity of the Ziegler-Natta catalysts described in Section 7.3.1.

Further studies on kinetic isotope effects, observed with 1-D labeled α-olefins, have added to this picture the notion of *α-agostic assistance*: Of the two C(α)-H bonds only one can interact with the electron-deficient metal centre so as to place the C(α)-C(β) chain segment in an open ligand sector. The resulting four-membered cyclic transition state acquires added conformational rigidity by this agostic stabilization, which probably contributes to the high stereoselectivities of these catalyst systems [M. K. Leclerc, H.-H. Brintzinger, *J. Am. Chem. Soc.* 1996, **118**, 9024].

Similar considerations hold also for syndio-specific polymerization catalysts, for which the C_S-symmetric zirconocene complex shown in Figure 19 is a prototype. Here the two coordination sites have opposite chirality. The preferred orientation of the C(α)-C(β) segment of the polymer chain and hence the preferred enantiofacial orientation of the inserting olefin will thus alternate with each consecutive insertion, by which the Zr-CH_2(polymer) bond moves from one coordination site to the other.

In distinction to C_2-symmetric, iso-specific catalysts, however, stereoerrors can arise here also when the growing chain moves from its original coordination site to the other, without the intervention of an olefin insertion. These *skipped insertions* become frequent at low olefin concentrations for syndiospecific catalysts shown in Figure 19, since then site-exchange of the polymer chain without insertion becomes competitive with further chain growth.

In other cases, for example in syndiotactic propylene polymerization with certain unbridged O,N-chelated Ti complexes, chain-end chirality can control the stereochemistry of 2,1-olefin insertions by adjusting the chirality of a ligand framework so as to minimize mutual repulsions [P. Corradini, G. Guerra, L. Cavallo, *Acc. Chem. Res.* 2004, **37**, 231].

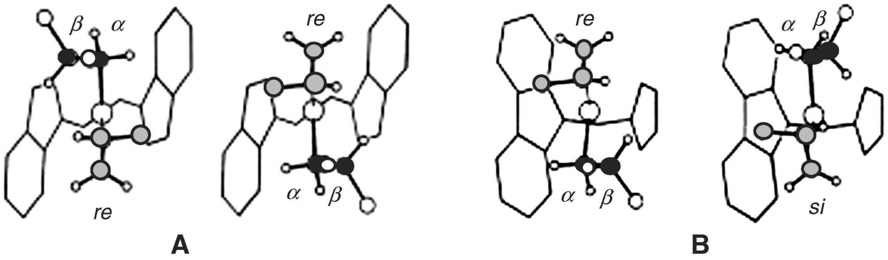


Figure 19 *Stereoselective insertions of propylene (grey) under catalytic-site control, mediated by the α,β segment of the growing polymer chain (black), for isospecific polymerization by a C_2-symmetric catalyst (A, left) and for syndiospecific polymerization by a C_S-symmetric catalyst (B, right).*

7.4.4 Chain-Growth Termination and Re-initiation

Simple zirconocene catalysts, such as the system $(C_5H_5)_2ZrCl_2$/MAO, produce relatively short-chain polypropylenes with several hundred to a few thousand monomer units. More practically useful polymers, with chain lengths of some ten to hundred thousand monomer units, i.e. with molar masses of about half a million to several millions, are available using more elaborated zirconocene catalysts such as that represented in Figure 10. For polymers of the type considered here, average chain lengths, as measured by the mean degree of polymerization, P_N, are approximately equal to the ratio of insertion and termination rates, $P_N = v_i/v_t$. In addition to high rates of chain growth, reduced rates of chain-growth termination by release of the polymer from the catalyst centre, are thus essential for the production of long-chain polymers.

Release of the unsaturated chain end of a polyolefin can occur by *β-H transfer to the metal* or *to a monomer* molecule (see Appendix 1 for backgound material). A metal-alkyl species, i.e. the starting unit for a new polymer chain, arises from the metal-hydride species formed in the first case by insertion of an olefin, or it can be formed directly by *β-H transfer to a monomer* (Figure 20). While the results are thus identical, the two reaction paths differ in their respective kinetics: In the first case, the rate-limiting β-H transfer is independent of the olefin concentration, while the rate of β-H transfer to a monomer requires the formation of an olefin-containing reaction complex and will thus increase linearly with olefin concentration.

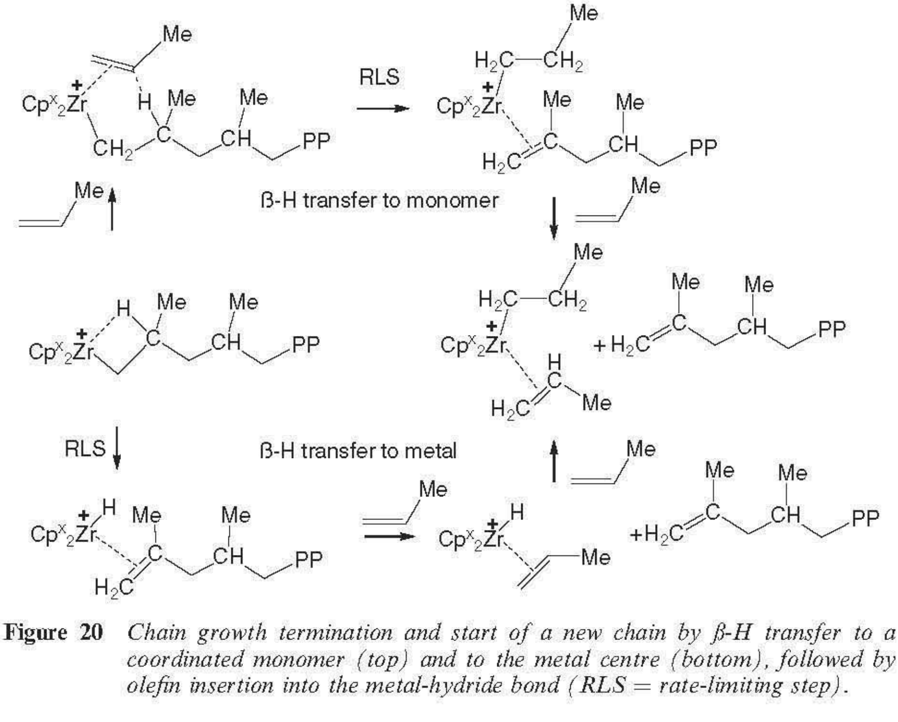


Figure 20 *Chain growth termination and start of a new chain by β-H transfer to a coordinated monomer (top) and to the metal centre (bottom), followed by olefin insertion into the metal-hydride bond (RLS = rate-limiting step).*

Since its dependence on olefin concentration is the same as that observed for chain-growth by olefin insertion, β-H transfer to a monomer has the consequence that average chain lengths P_N are not affected by changes in olefin concentration, since the latter cancels between the numerator and denominator of the expression $P_N = v_i/v_t = k_i \cdot [M]/k_t \cdot [M] = k_i/k_t$. For β-H transfer to the metal, however, chain lengths increase with olefin concentration, since the latter affects only the numerator of the expression $P_N = v_i/v_t = k_i \cdot [M]/k_t$.

Of the two mechanisms, the quasi-degenerate β-H transfer to an olefin requires lower activation energies and is thus likely to occur at higher rates. But this reaction path requires a more highly organized and spatially more demanding arrangement of its reaction participants. It is thus rather efficiently suppressed in catalysts as that shown in Figure 10 which carry space-filling methyl or other alkyl substituents in their lateral positions. Accordingly these catalysts are apt to produce particularly long-chained polypropylene and other polyolefins, especially at high olefin concentration, e.g. in liquid propylene.

Space-filling substituents induce increased chain lengths also with Ni-based polymerization catalysts. Here a spatially demanding transition state, required for β-H transfer to a monomer molecule and subsequent release of the unsaturated polymer chain end, appears to be suppressed by ligand substituents which block the coordination positions above and below the tetragonal coordination plane (Figure 21).

Other processes also contribute to chain growth termination under special conditions. In particularly crowded catalysts, *β-methyl transfer* to the metal centre can occur instead of β-H transfer. When other reaction paths are blocked, *σ-bond metathesis*, i.e. transfer of an H atom from a monomer to the metal-bound alkyl C atom can release a polymer with a saturated chain end with formation of a new unsaturated metal-bound chain start. Saturated chain ends will also result when H_2 gas is added to a catalyst system thus leading to the production of shortened polymer chains. Such an H_2 addition will often also cause an increase in overall catalyst activity, since H_2 will predominantly react with species such as occasional 2,1-inserted units which are rather

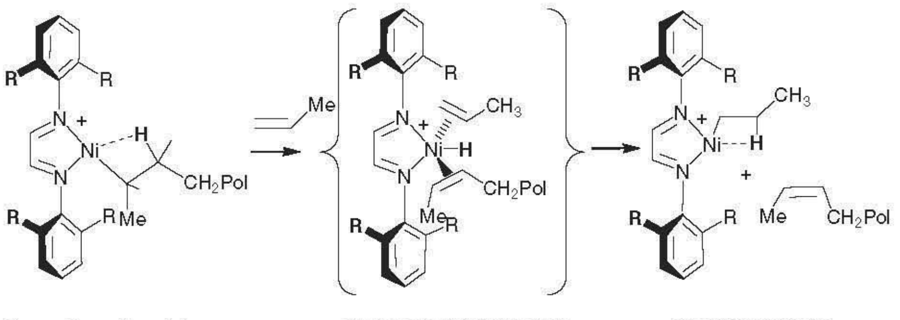


Figure 21 *Chain growth termination by β-H transfer and displacement of unsaturated chain end from nickel centre by a monomer, hindered by bulky substituents R.*

unreactive to olefin insertion and would thus tend to slow further polymer production [V. Busico, R. Cipullo, S. Ronca, *Macromolecules* 2002, **35**, 1537].

In many instances, particularly with MAO-activated zirconocene catalysts carrying bulky ring ligands, a major pathway is *polymer transfer to Al centres*; in exchange a methyl group is transferred to the catalyst centres. New chains started there thus contain an extra CH_3 group, while the polymer product accumulates as Al-, mostly Me_2Al-capped chains. Upon hydrolysis of these polymerization systems, completely saturated polymer chains are obtained. In principle, the Al-bound polymer chains represent a stable but rather reactive kind of organometallic reagent and might be used for interesting purposes, such as the introduction of polar chain ends, or for transfer to a different catalyst with the aim of obtaining polymers with distinctly structured chain segments [C. Przybyla, G. Fink, *Acta Polym.* 1999, **50**, 77; S. Lieber, H.-H. Brintzinger, *Macromolecules* 2000, **33**, 9192; D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* 2006, **312**, 714].

Discussion Point DP6: *Alternative reaction sequences for the release of unsaturated chain ends from a catalyst centre are represented in Figure 20. Determine for each of these sequences how the termination rate* v_t *depends on the monomer concentration. Write reaction equations for several alternative chain-release and re-start reactions mentioned in Section 7.4.4. Can you think of polymerization systems for which increased ethylene concentrations might lead to polymers with reduced molar mass?*

For typical homogeneous polymerization catalysts the rates of chain growth by olefin insertion and of chain termination, by some combination of the processes discussed above, is likely to be rather independent of the length of the metal-bound polymer chain, except for the very first insertion steps. When a catalyst system meets this condition, its polymer product will have a relatively narrow, so-called Schulz-Flory molar mass distribution and its *polydispersity index* PDI, defined as the ratio of the weight average and the number average of its molar mass, M_W/M_N, will have a value close to 2. PDI values, experimentally determined e.g. by size-sensitive gel exclusion chromatography, are thus often used to test whether a given catalyst system is to be considered a *single-site catalyst* with uniform catalyst centres. In contrast to these mostly soluble polymerization catalysts the "classical" solid-state catalysts usually have rather broad molar mass distributions with PDI values of 5 15, due to the non-uniformity of their catalyst centres.

Polymers with even narrower mass distributions, e.g. with PDI values close to 1, arise in *living polymerization* systems, in which no chain termination processes can occur at all, such that all chains remain bound to the metal centre from which they have started to grow at the same time. Living polymerizations, which offer useful opportunities, *e.g.* with regard to the production of block copolymers by exchange of one monomer for another, occur in *anionic polymerizations* of styrenes or butadienes such as are induced by simple lithium alkyls. For α-olefin polymerization catalysts of the type discussed above, living polymerizations are rare. These more elaborate catalysts can thus release a newly formed polymer chain within a time interval of typically less than one second, such that each catalyst centre can on average produce many thousand polymer chains during its lifetime.

7.5 Supported Metallocene Catalysts

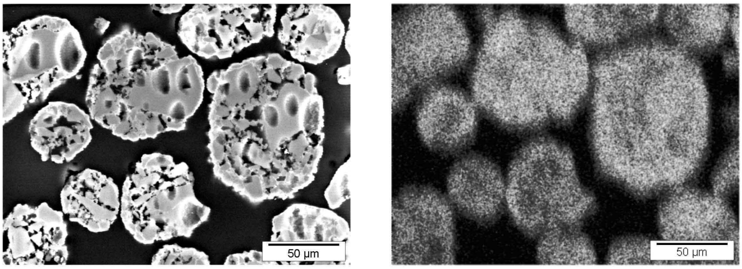
Metallocenes immobilized on solid support materials have been successfully introduced in industry as polymerization catalysts for the production of new application-oriented polymer materials. Industrial polymerizations, which are carried out either as a slurry process in liquid propylene or as a gas-phase process (Section 7.2.3), require that catalysts are in the form of solid grains or pellets; soluble metallocene catalysts thus have to be supported on a solid carrier.

These catalyst carriers have to be mechanically stable to avoid the formation of polymer fines (dust); on the other hand, they have to be sufficiently fragile to permit fragmentation into *primary particles* of sub-micrometer size by the hydraulic forces exerted by the growing polymer. At present amorphous, porous SiO_2 gels appear to be best suited as support for MAO-activated metallocene catalysts, since they possess high surface area and porosity, good mechanical properties, as well as stability and inertness under reaction and processing conditions.

For use as catalyst supports, silica gels are calcined at temperatures of 400 500°C so as to remove surface-bound water as well as most geminal and vicinal Si-OH groups. The remaining, mostly isolated Si-OH groups, are then deactivated by reaction with MAO and/or an aluminium alkyl. Upon contact with such a pretreated support the zirconocene catalyst precursor becomes immobilized, i.e. firmly attached to the support grains. Spectral studies show that ion pairs of the type discussed in Section 7.4.1 are then present. Properly chosen contact conditions leave the zirconocene deposited rather evenly throughout the interior of the porous SiO_2 grains.

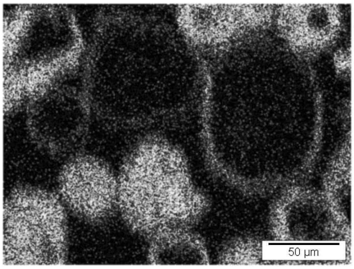
As a result of this immobilization the $[Al]_{MAO}/[Zr]$ ratio required for full activation of the catalyst can be decreased by about two orders of magnitude compared to homogeneous systems. In certain cases an $[Al]_{MAO}/[Zr]$ ratio of 40 is sufficient to obtain reasonable activities. Such a high polymerization activity requires however that all catalyst components are uniformly distributed throughout the volume of the support particles. The shell-like deposit of the MAO cocatalyst on the particle surface and its absence in the interior of a particle (Figure 22; Al mapping) has the consequence that polymerization takes place only in this outer shell, such that an unfragmented SiO_2 core remains in the product and hinders later polymer processing.

Initiation of polymerization and individual phases of polymer growth on SiO_2-supported catalyst particles can be followed by a combination of kinetic and microscopic methods. A few minutes after exposure to propylene the polymerization rate reaches an initial maximum, which is followed by a period of low activity (Figure 23). In a third phase the polymerization rate rises again and in a final, fourth phase, a broad maximum of activity is reached. This



SEM micrograph

Si mapping



Al mapping

Figure 22 *SiO_2-supported, MAO-activated zirconocene catalyst grains, Scanning Electron Microscopy (SEM) micrograph and element mapping by Energy-Dispersive X-ray Microanalysis.*

activity profile differs from that of the $MgCl_2$-supported solid-state catalysts described in Section 7.3, where high activities are immediately reached and continuously maintained.

Electron microscopy shows that polymerization starts at active centres on the surface of the particle. During this initial stage, a thin polymer cover is formed on and just below the outer surface of the silica support. This thin cover consists of highly crystalline polypropylene, which acts as a diffusion barrier for the monomer. Diffusion of propylene through this layer thus becomes rate-limiting for polymer formation; consequently the high initial polymerization activity decreases sharply after a few minutes and a period of relatively low activity is reached.

During this period, the length of which depends on temperature, monomer concentration and particle diameter, polymer is growing towards the centre of the carrier, thus breaking down increasing portions of the latter (Figure 23, bottom). As more and more active centres in the interior of the particle become exposed to monomer, the polymerization activity increases again and the silica particle is progressively fragmented by the hydraulic forces of the growing polymer. This process continues towards the centre of the particle, which is finally broken down into fragments with diameters of about 50 nm or less, evenly distributed in the polymer matrix. Since most active sites are now accessible to monomer, polymerization activity reaches its maximum and a further,

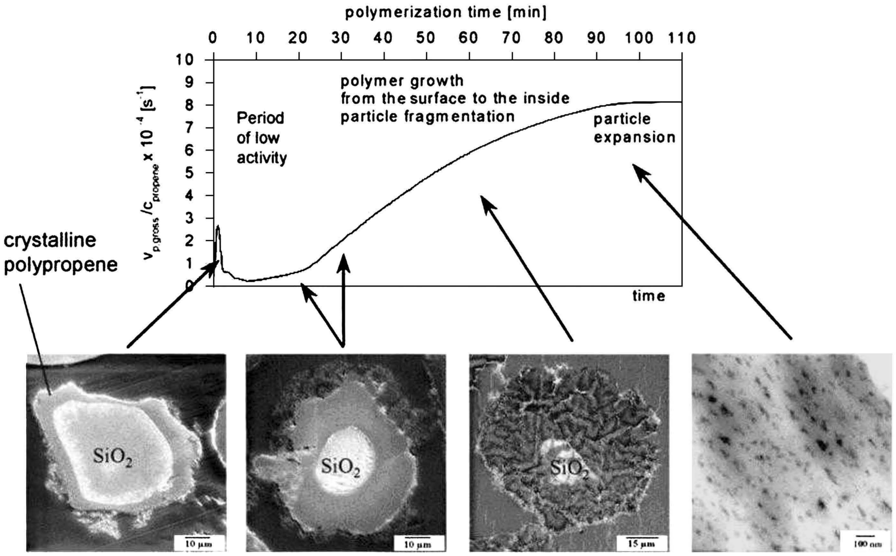


Figure 23 *Polymerization rate profile (top) and electron-micrographs of* SiO_2*-supported zirconocene catalyst grains (bottom) at successive stages of particle growth. (Reflection scanning-electron micrographs of embedded-block cross sections;* SiO_2 *light, polymer dark grey; last picture: high-resolution transmission electron micrograph of a microtomed thin Section;* SiO_2 *dark, polymer light grey).*

continuous particle expansion takes place, similar to that observed immediately after addition of monomer to Ziegler-Natta catalysts on more easily fragmented $MgCl_2$ supports.

Based on these kinetic and microscopic observations, olefin polymerization by supported catalysts can be described by a "shell by shell" fragmentation, which progresses concentrically from the outside to the centre of the support particles, each of which can thus be considered as a discrete *microreactor*. A comprehensive mathematical model for this complex polymerization process, which includes rate constants for all relevant activation, propagation, transfer and termination steps, serves as the basis for an adequate control of large-scale industrial polymerizations with SiO_2-supported metallocene catalysts [A. Alexiadis, C. Andes, D. Ferrari, F. Korber, K. Hauschild, M. Bochmann, G. Fink, *Macromol. Mater. Eng*. 2004, **289**, 457].

7.6 Copolymerization of Linear and Cyclic Olefins

Copolymers of ethylene with α-olefins, such as the short-chain branched LLDPE (linear low-density polyethylene) "impact" materials or the EPD (ethylene-propylene-diene copolymer) rubbers represent major percentages of the total polyolefin production, due to their desirable mechanical properties. Solid-state $MgCl_2$-supported Ziegler-Natta catalysts however, have unfavourable reactivity ratios for α-olefin comonomers. As these catalysts strongly prefer ethylene, a large excess of the α-olefin the longer the side chain the higher the excess has to be fed to these systems to achieve sufficient comonomer incorporation.

Metallocene-based catalysts, on the other hand, have rather comparable reactivity ratios for ethylene and even for the higher α-olefins. Accordingly, high comonomer incorporation (uniform in each polymer chain and independent of its molar-mass) can be achieved with these single-site catalysts. This is of great advantage with regard to polymer processability and application.

Single-site metallocene catalysts are also highly reactive vis-à-vis *cycloolefins* such as cyclobutene, cyclopentene or norbornene. While homopolymers of these cycloolefins have melting temperatures (>380°C), much too high for technical processability, ethylene-cycloolefin copolymers (COC's) e.g. ethylene-norbornene copolymers are amorphous materials with glass transition temperatures, above which they become soft and processable [W. Kaminsky, *J. Polym. Sci. A, Polym. Chem.*, 2004, **42**, 3911].

Metallocene catalysts insert norbornene into metal-polymer bonds stereoselectively with *cis*-2,3-*exo* orientation and without any ring opening (Figure 24). Different micro-structures of the copolymers result from various possible concatenation patterns e.g. from alternating or norbornene-norbornene diad and triad block structures and from alternative relative configurations of neighboring norbornene units (Figure 25). Accordingly, the macroscopic properties of a copolymer product depend on the selectivity of the particular metallocene catalyst used for its generation [D. Ruchatz, G. Fink, *Macromolecules* 1998, **31**, 4669, 4674, 4682, 4684; M. Arndt, I. Beulich, *Macromol. Chem. Phys.* 1998, **199**, 1221].

Ethylene-norbornene copolymers, which have thermoplastic properties when heated above their glass transition temperatures of *ca.* 200 250°C, have been commercialized by Ticona GmbH under the trade name TOPAS (*T*hermoplastic *O*lefin *P*olymer of *A*morphous *S*tructure). Their properties exceptional transparency, low double refraction, high stiffnes and hardness, low permeability for moisture and excellent biocompatibility make these ethylene-norbornene copolymers particularly valuable as engineering polymers, for optical applications and as materials for food and medical packaging.

Discussion Point DP7: *While ethylene and norbornene give essentially alternating, amorphous copolymers, attempts to copolymerize ethylene and cyclohexene give only crystalline polyethylene. Which factors might contribute to these observations? Unsaturated norbornenyl chain ends cannot arise by β-H transfer*

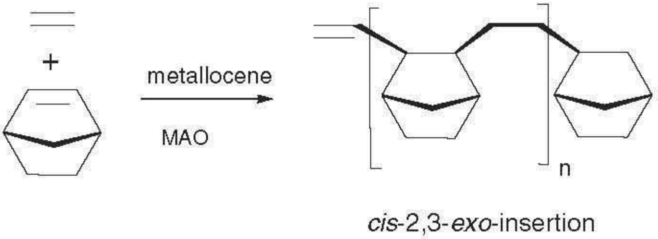
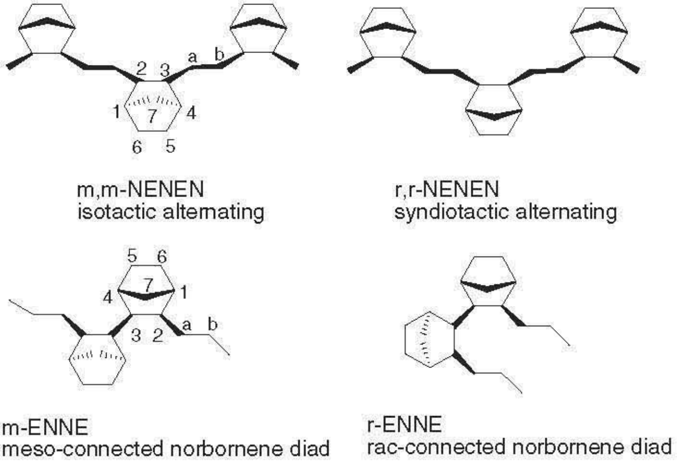


Figure 24 *Stereochemistry of ethylene-norbornene enchainment.*



m,m-NENEN
isotactic alternating

r,r-NENEN
syndiotactic alternating

m-ENNE
meso-connected norbornene diad

r-ENNE
rac-connected norbornene diad

Figure 25 *Alternative concatenation microstructures in ethylene-norbornene copolymers.*

from a metal-bound norbornyl unit. Try to verify this postulate by considering the stereochemistry of norbornene insertion and the consequences of Bredt's rule. Delineate how unsaturated norbornenyl chain starts arise by σ-bond metathesis.

7.7 Copolymerisation of Olefins with Polar Monomers and with CO

Despite many attempts, copolymers of olefins with polar monomers, such as vinyl or acrylic esters, which would combine the low price, toughness and easy processability of polyolefins with desirable surface properties of polar polymers e.g. with the possibility to glue these polymers to other materials have so far not been obtained using any of the catalysts based on group 4 transition metals, since these oxophilic catalysts are deactivated by oxygen-containing substrates. Soluble catalysts based on one of the less oxophilic group 10 transition metals nickel or palladium, however incorporate finite fractions of polar monomers, albeit at the expense of diminished activity [A. Sen, M. Kang, in *Late Transition Metal Polymerization Catalysis*, eds. B. Rieger, L. Saunders Baugh, S. Kacker, S. Striegler, Wiley-VCH, Weinheim, 2003, p. 307].

Another interesting example of the tolerance of group 10 transition metal catalysts toward oxygen functionality is the copolymerization of olefins with carbon monoxide. Exposure of an acidified methanol solution of a Pd(II) di-phosphine chelate to an olefin-CO mixture leads to the formation of polymers, which contain these monomers concatenated in strictly alternating fashion, with carboxylate ester groups occupying the chain ends [E. Drent, P. H. M. Budzelaar, *Chem. Rev.* 1996, **96**, 663; G. Consiglio, in *Late Transition Metal Polymerization Catalysis*, eds. B. Rieger, L. Saunders Baugh, S. Kacker, S. Striegler, Wiley-VCH, Weinheim, 2003, p. 279.

This reaction may proceed by a sequence of steps such as are represented in Figure 26: CO inserts into a Pd-OCH_3 unit, present in equilibrium with the starting compounds, to form a cationic carboxylate complex, which takes up an olefin to form, by insertion of the latter into the Pd-carboxylate bond, a rather stable five-ring chelate, containing a Pd-bound C═O group. This stable chelate can be broken up only by CO, which then inserts with formation of a ketyl species. In turn the latter reacts selectively with olefin to form a new, stable five-ring chelate, rather than with CO to some unstable species containing adjacent C═O groups. Repetition of this sequence leads to polymer growth until it is terminated, e.g. by attack of CH_3OH at the cationic ketyl centre. Interesting background to this and the relationship to the Pd(II) catalyzed carbonylation of ethylene to methyl propionate is in Chapter 4, Section 4.3.1.

The resulting polyketone, which has remarkable mechanical and thermal resistance, has been commercialized as a valuable engineering plastic, but general applications have so far been hindered by its sensitivity to photo-degradation.

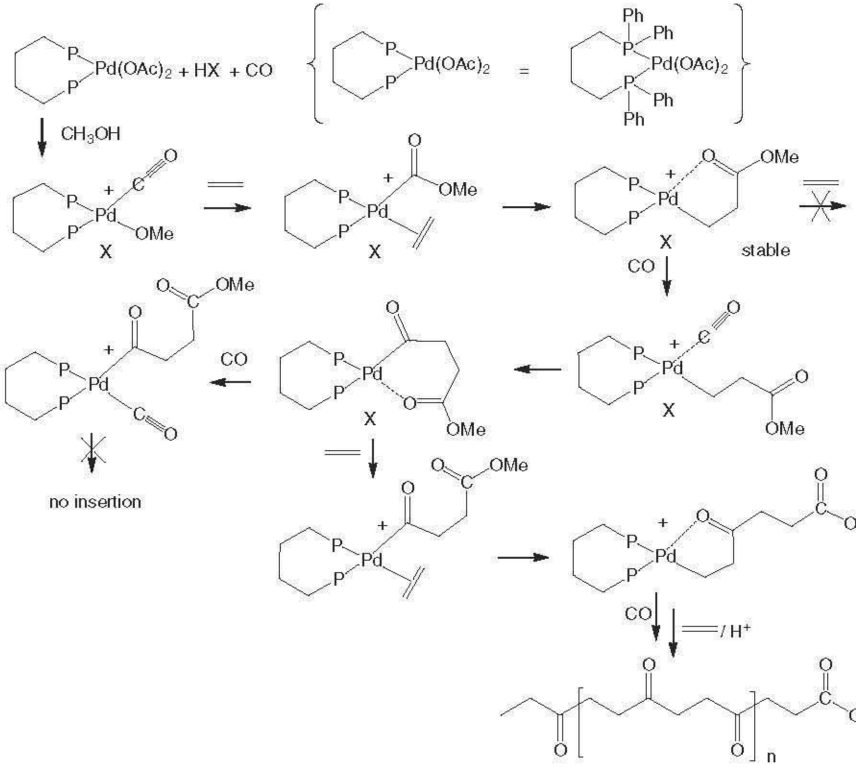


Figure 26 *Proposed steps in Pd(II)-catalyzed polyketone formation from ethylene and CO in MeOH.*

Annex 1 Polymer Stereochemistry Studied by ^{13}C NMR Spectroscopy

The *microstructures* of polyolefin materials are most effectively studied by ^{13}C NMR spectroscopy in solution. In particular C atoms at branching positions and at the ends of chains and branches are easily distinguished from those inside a chain. In this way, the numbers and mean lengths of branches, e.g. in polyethylene chains, can be determined rather reliably.

Another important practical application concerns the *microstructure* of polypropylene [V. Busico, R. Cipullo, *Progr. Polym. Sci.* 2001, **26**, 443]. The chemical shift of each CH_3 substituent in a polypropylene chain depends on the orientations of neighbouring substituents, i.e. on the relative configurations of the adjacent $-C(CH_3)CH_2-$ units. Pairs of adjacent CH_3 substituents are called *meso* or *m dyads* if their orientations are identical, while two CH_3 neighbors with opposite orientations form a *racemo* or *r dyad*. Together with its two neighbouring CH_3 groups, a given CH_3 group can form a mm *triad*, a rr triad or a mr = rm triad. Present standard spectrometer resolution distinguishes CH_3 resonances at the *pentad* level, where the position of each CH_3 signal is influenced by two adjacent units on each side. For atactic polymers with statistical distribution of relative configurations (such as are obtained by the simple system $(C_5H_5)_2ZrCl_2$/MAO) this resolution yields, instead of the three triad signals mm, rm and rr, nine pentad signals, the mm-centred set mmmm, mmmr and rmmr, the mr-centred set, mmrr, mmrm = rmrr and rmrm, and the rr-centred set rrrr, rrrm and mrrm (Figure 27). Completely isotactic polypropylene, on the other hand, would give rise only to the mmmm pentad signal, while a completely syndiotactic one would yield only the signal of the rrrr pentad.

In practice, however, ^{13}C NMR spectra of polymers produced with a particular catalyst always reveal finite proportions of various types of *stereoerrors*. Even highly isotactic polypropylene gives rise, in addition to its main mmmm signal, to small mmmr, mmrr and mrrm pentad signals. These signals indicate that a tertiary C atom will occasionally occur with the "wrong" configuration, its CH_3 substituent being oriented in a sense opposite to its neighbors.

The stereoselectivity of C_2-symmetric ansa-zirconocene catalysts, such as those discussed in Section 7.4 can be shown to have its origin in the chirality of the catalysts and not in the chirality of the last-inserted CH_2CHMe-unit (J. A. Ewen, *J. Am. Chem. Soc.* 1984, **106**, 6355). If such a *chain-end control* would be operative, an occasional stereoerror would be expected to perpetuate itself in the configuration of the following insertions, thus giving rise in addition to a mmmr signal to a stereoerror signal of the type mmrm. Instead, the actually observed signals of the double-r type, mmrr and mrrm, indicate that insertions return, after each stereoerror, to their previous enantiofacial preference, due to the *catalytic-site control* exerted by the chiral catalyst (Figure 28, p 252).

Discussion Point DP8: *Typical stereoerror patterns occurring in isotactic polypropylene are represented in Figures 27 and 28. Try to delineate the stereoerror patterns and the associated ^{13}C pentad signals which are to be expected for*

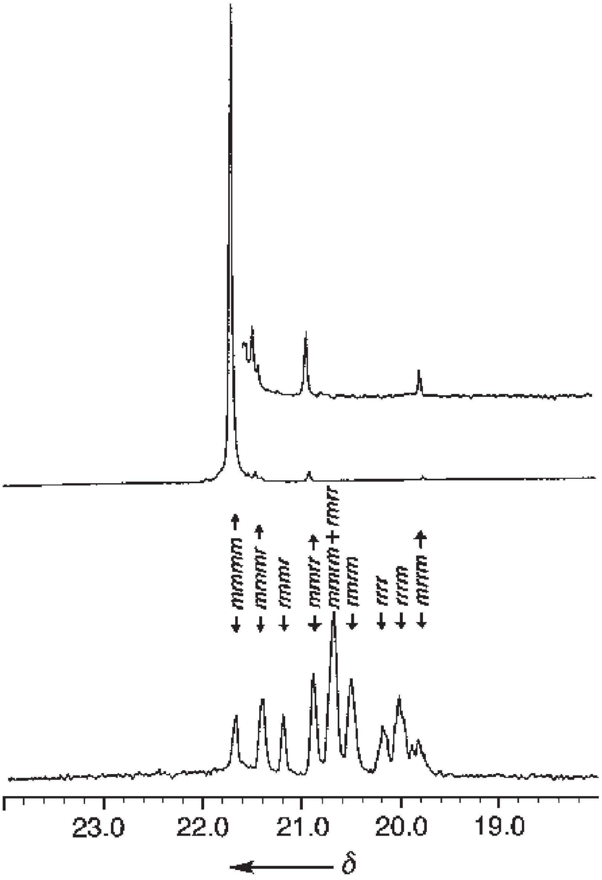


Figure 27 *Pentad ^{13}C NMR signals of essentially isotactic polypropylene (top) and of atactic polypropylene (bottom).*

syndiotactic polypropylene generated i) under chain-end control ii) under catalytic site control, and iii) under catalytic site control with occasional skipped insertions (i.e. change of coordination sites without insertion). Which effects might a change in monomer concentration have on the relative sizes of each of these error signals?

Annex 2 Stereospecific Polymerization of Conjugated Diolefins: Butadiene and Isoprene

For reasons of space diolefin polymerization has not been included in this Chapter. Some information and pertinent references are summarized here. 1,3-Dienes can be polymerized by lithium alkyls or by Ziegler-Natta type catalysts, containing titanium or cobalt, nickel, and neodymium. Industrially important products are 1,4-cis-polybutadiene (>2 Mt/a) and 1,4-cis-polyisoprene (>1 Mt/a). They are

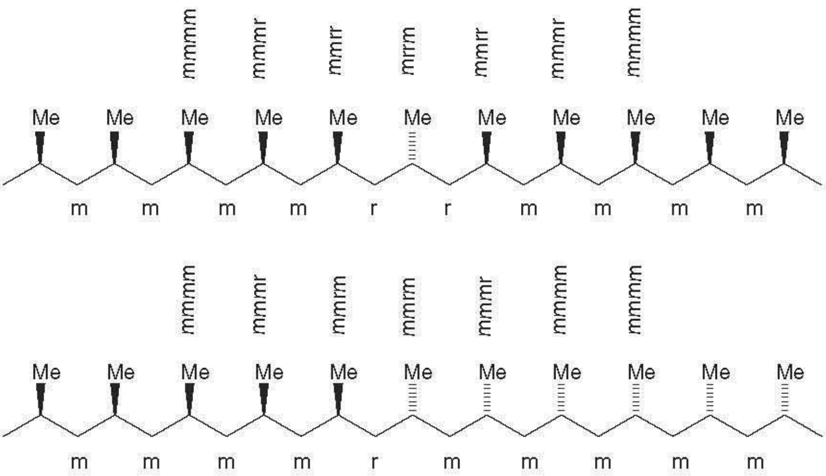


Figure 28 *Stereoerror pentads expected for essentially isotactic polypropylenes, generated under catalytic-site control (top) and under chain-end control (bottom).*

used as elastomers; that derived from isoprene corresponds to natural rubber. The chemistry of their polymerizations is based on multiple insertions, as in the case of the simple olefins discussed above. The intermediates are allylmetal complexes, see Chapter 5, Section 5.4. Detailed discussions can be found in the following reviews: R. Taube and G. Sylvester in *Applied Homogeneous Catalysis*, 2nd ed, vol.1; ed. B. Cornils and W. Herrmann, Wiley-VCH, Weinheim 2002, p. 285; L. Porri and A. Giarrusso in *Comprehensive Polymer Science*, vol. 4, part II, ed. G.C. Eastmond, A. Ledwith, S. Russo, and B. Sigwalt, Pergamon, Oxford, 1989, p. 53; W. Kaminsky and B. Hinrichs, *Plastics Engineering*, 2005, **70** (*Handbook of Polymer Science*, 2nd ed. Marcel Dekker), 333.

Annex 3 Some Hints to Help Start the Discussions

DP 1 Using suitable terms look up methods for the production of olefins from alternative sources in the internet or in one of the encylopedias of technical/industrial chemistry.

DP 2 For heats of polymerization assume *ca.* 100 kJ per mol of ethylene or propylene (disregard finer details). Consult e.g. Section 7.2 and references given at its end for heat removal aspects.

DP 3 Consider qualities such as "Lewis-acidic" and "weakly coordinating" with regard to the B- and Al-containing activators mentioned in Section 7.4.1. Consider also single-component catalysts.

DP 4 Find the species responsible for the respective rate-limiting steps: In which way might their concentrations depend on olefin concentrations and (if applicable) on the type of anion present?

DP 5 Let the metal freely migrate along the polymer chain attached to it and determine which site of renewed monomer insertion will lead to formation of the products specified in (i), (ii) and (iii).

DP 6 How are the species responsible for chain growth (Figure 14) and its termination (Figure 20) affected by monomer concentrations? Consider also Figure 16 for effects of monomer concentration.

DP 7 Consider structural and enthalpic differences between cyclohexene and norbornene and consult a text on organometallic reactions for causes and possible courses of "σ-bond metathesis".

DP 8 How would exchanging "m" and "r" in the last paragraph of Annex1 answer questions (i) and (ii)? For (iii), consider that "skipped insertions" are competing with normal olefin insertions.

Acknowledgements

Helpful suggestions for this Chapter from the editors and from Professor Ludwig Böhm, Professor Paolo Corradini and Dr. David Fischer are gratefully acknowledged. Figures 5-7 have been reproduced from an article by K. S. Whiteley and et al. in *Ullmann's Encyclopedia of Industrial Chemistry*, Figures 8 and 9 (with modifications) from an article by L. Böhm in *Angewandte Chemie*, Figure 23 from an article by G. Fink and collaborators in *Macromol. Chem. Phys.* 2003, **204**, 607, and Figures 27 and 28 from an article by H. H. Brintzinger et al. in *Angewandte Chemie* (all cited below). We thank the publishers for their consent to reproduce these figures, and BASELL GmbH for providing Figure 18 and data for Figure 4.

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