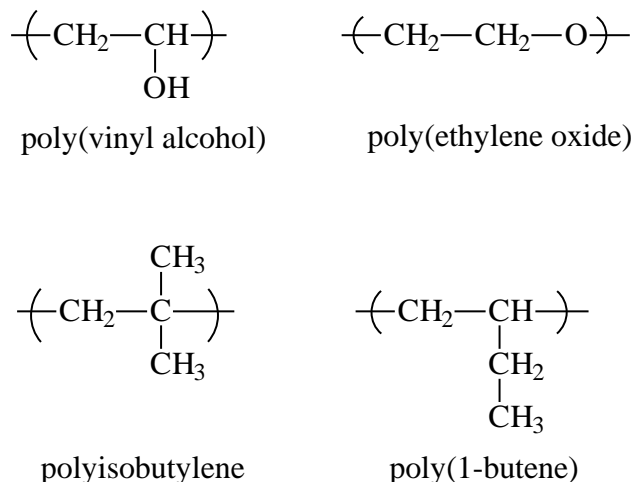


IX. STEREOREGULAR POLYMERIZATION VIA HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

A. Types of Stereoisomerism in Polymers

Constitutional isomerism (as opposed to stereoisomerism) occurs when polymers have the same overall chemical composition (elemental composition) but the elements are connected differently. Two examples are shown in Figure IX-1. In the bottom example, the isomeric polymers are derived from isomeric monomers; whereas in the top example, they are not. Constitutional isomerism can arise from a single monomer, for example, 1,4 vs. 1,2 enchainment of diene monomers, rearrangement during carbocationic chain polymerization, and head-to-head vs. head-to-tail enchainments during vinyl polymerization.

Figure IX-1

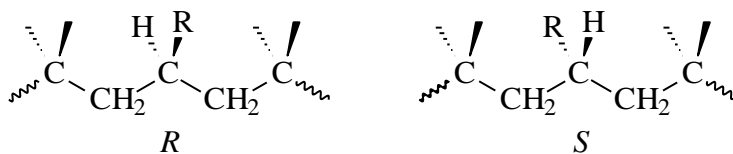


Stereoisomerism arises due to differences in configuration along the backbone of a polymer. These differences are usually directly attributable to the manner in which successive monomer units add to the growing chain during propagation. This is an important topic because of the profound effect that stereoisomerism has on the physical properties of the polymer, largely resulting from its effect on the tendency toward crystallization, and in some cases, on the crystal structure itself.

1. Monosubstituted Ethylenes (and $\text{CH}_2=\text{CRR}'$)

Polymerization of a monosubstituted ethylene results in a polymer in which every other carbon atom is a stereocenter. Each stereocenter can exhibit either of two different configurations. As in small-molecule enantiomers, the hypothetical exchange of any two substituents around the stereocenter converts its configuration to the opposite configuration. If the polymer is depicted in the fully extended, planar zig-zag conformation, the two configurations would correspond to placement of the substituent on one or the other side of the plane.

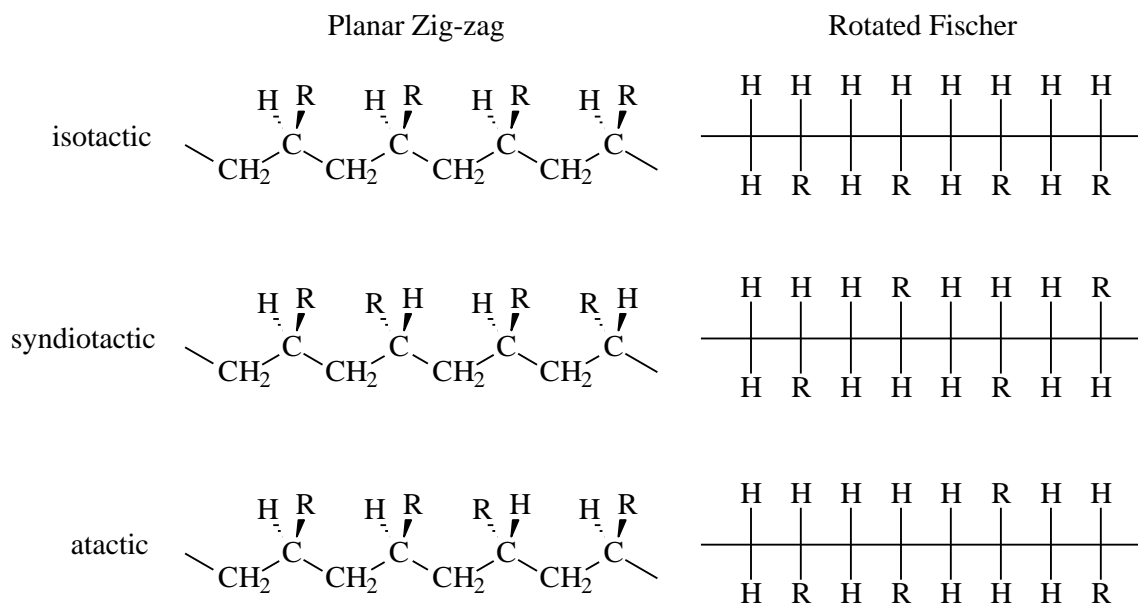
Figure IX-2



The *R* and *S* designations above are arbitrary since we do not have knowledge of the relative lengths (or the end groups) of the two chain segments attached to the stereocenter. In a related sense, a polymer chain containing solely *R* (or *S*) stereocenters would not exhibit optical activity (i.e., it would be achirotropic) because two of the groups bonded to the stereocenter are alike in the short range.

Tacticity refers to the overall or average relationship of the configurations of successive stereocenters along the backbone of a polymer derived from a monosubstituted ethylene. If the *R* groups on successive stereocenters are all the same configuration, the polymer is said to be isotactic. If the configurations of successive stereocenters alternate back and forth, the polymer is said to be syndiotactic. If the configurations of successive stereocenters are random, then the polymer is said to be atactic (Figure IX-3). A polymerization mechanism that leads to isotactic or syndiotactic polymer is said to be stereoselective, and the product is called a stereoregular polymer.

Figure IX-3

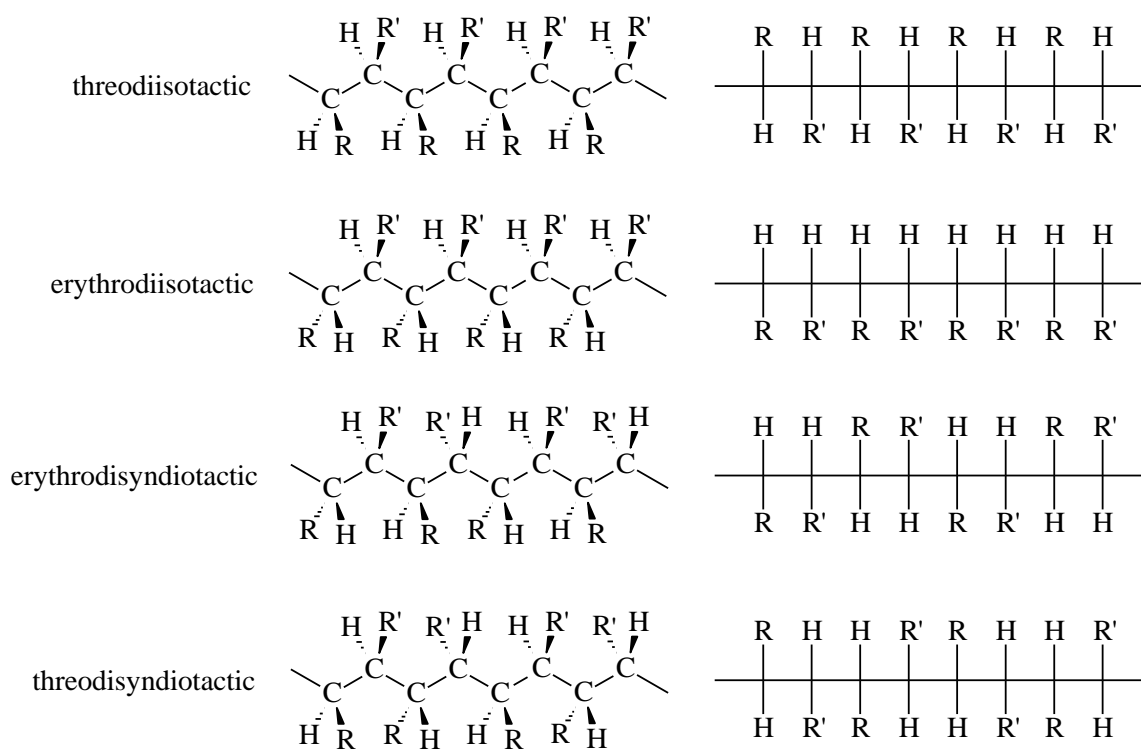


2. Disubstituted Ethylenes

Polymers from 1,1-disubstituted ethylenes, in which the two substituents are identical, do not display tacticity. If the two substituents are different, the situation is the same as for a 1-substituted ethylene.

In the case of a 1,2-disubstituted ethylene, four possibilities exist, as shown in Figure IX-4. The two diisotactic structures are unique and represent two different polymers with different properties; the two disyndiotactic structures are identical except for end groups and thus are the same polymer with the same properties.

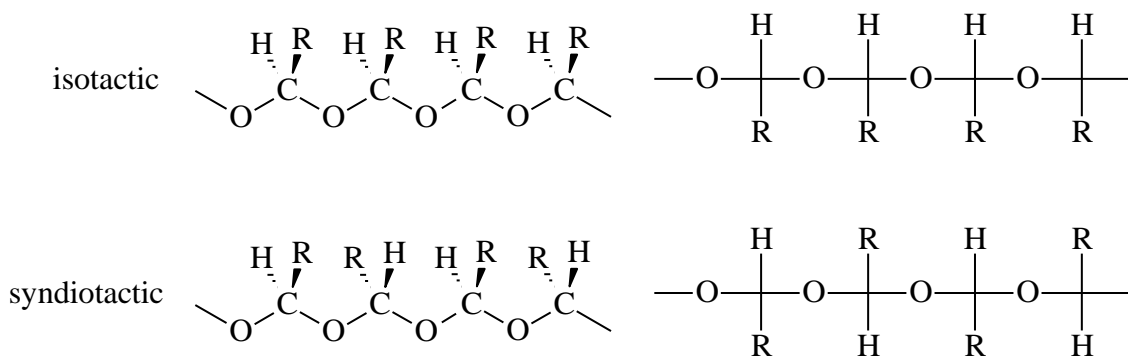
Figure IX-4



3. Carbonyl Monomers

Aldehydes and asymmetric ketones possess tacticities that are analogous to those of monosubstituted ethylenes. These polymers are achirotopic.

Figure IX-5



B. Properties of Stereoregular Polymers

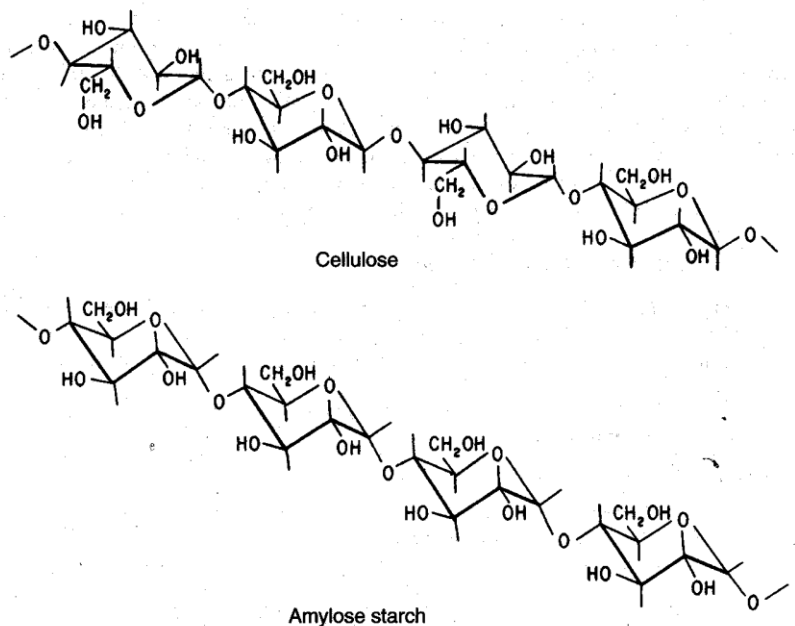
1. Significance of Stereoregularity

The occurrence of stereoregularity in polymers is of tremendous importance to their practical utilization. The main effect of stereoregularity is an increased tendency toward ordered structures and crystallinity in the solid state. In general, crystallinity dramatically enhances strength, toughness, and solvent resistance of polymers. Stereoregularity can also effect the properties of the amorphous state, such as the glass transition. Three examples illustrating these principles are discussed below.

Polypropylene can be obtained in the isotactic, syndiotactic, and atactic states. Isotactic polypropylene is a high-production volume, high melting (165°C), strong, semi-crystalline commercial polymer with many applications as a fiber and a molding plastic. In contrast, atactic polypropylene is an amorphous, soft, waxy material with very few commercial applications. It is used in asphalt blends and in formulations for lubricants, sealants, and adhesives, but the volume is insignificant compared to the isotactic variety. Syndiotactic polypropylene has only recently been developed as a result of advancements in catalyst technology. It is also crystalline, but its properties are not as good as isotactic polypropylene; it has a lower melting point (by about 20°C) and less solvent resistance.

Cellulose and amylose starch have identical structures except for the configuration about carbon 1 (Figure IX-6). The glucose units are incorporated into the cellulose chain in a trans (diequatorial) fashion; whereas they are cis (equatorial-axial) in amylose starch. This small change has a profound effect on the properties of these two polymers, and hence their utilization in nature. Cellulose organizes into an extended chain conformation, while starch exists as a random coil. The high organization of cellulose leads to denser chain packing and much greater intermolecular forces. Cellulose is a strong, insoluble polymer, with good resistance to hydrolysis, and is used as a structural material in nature. Starch is readily dissolved and hydrolyzed by water, and hence serves well as a food source and energy storage material.

Figure IX-6

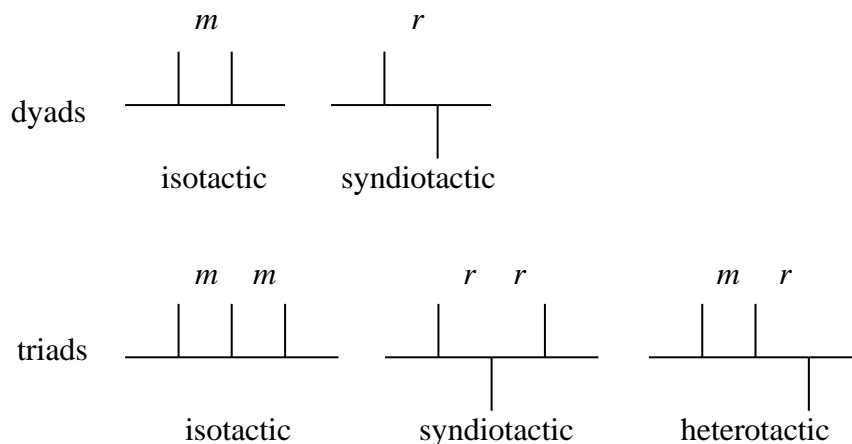


As the final illustration, cis- and trans-1,4-polyisoprene have dramatically different properties. The cis polymer (natural rubber) has very low crystallinity (essentially totally amorphous except under high-strain conditions) and low melting and glass transition temperatures, and is an excellent elastomer. The trans polymer is semi-crystalline due to the superior packing efficiency of the trans linkages. It is much harder and exhibits properties less like an elastomer and more like a plastic. It has relatively higher melting and glass transition temperatures.

2. Analysis of Stereoregularity

Analysis of stereoregularity in polymers is performed almost exclusively through the use of NMR. The process involves quantifying fractions of various stereoregular sequences, dyads, triads, tetrads, etc., along the polymer backbone. The more powerful the spectrometer, the longer are the sequences that can be detected and quantified. For example, in a polymer from a vinyl monomer (mono-substituted ethylene), the simplest and most easily detected sequence is the dyad, shown in Figure IX-7. It consists of two consecutive stereocenters, which can either have the same configuration (isotactic dyad designated “*m*” for meso) or different configurations (syndiotactic dyad designated “*r*” for racemic). The next higher sequence is the triad, consisting of three consecutive stereocenters. Triads are defined as isotactic *mm*, syndiotactic *rr*, or heterotactic *mr* or (*rm*). The fractions of isotactic and syndiotactic dyads are referred to as (*m*) and (*r*), and these two numbers are said to define the dyad tacticity of a polymer. The fractions of isotactic, syndiotactic, and heterotactic triads as (*mm*), (*rr*), and (*mr*), and these are said to define the triad tacticity of a polymer

Figure IX-7



By definition, the dyad and triads fractions each total unity.

$$\begin{aligned}(m) + (r) &= 1 \\ (mm) + (rr) + (mr) &= 1\end{aligned}\tag{IX-1}$$

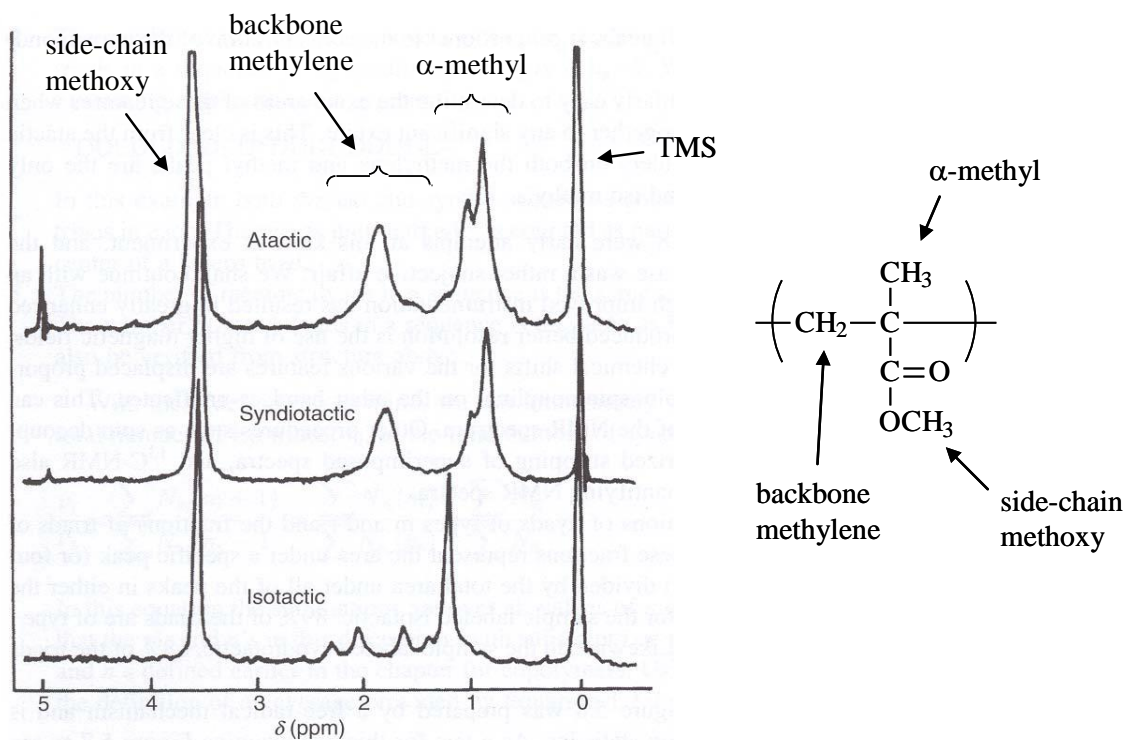
And dyads are related to triads as follows:

$$\begin{aligned}(m) &= (mm) + 0.5(mr) \\ (r) &= (rr) + 0.5(mr)\end{aligned}\tag{IX-2}$$

The determination of any two triad fractions allows a complete definition of both the dyad and triad tacticity of a polymer. A perfectly stereoregular isotactic polymer has $(m) = (mm) = 1$. A perfectly stereoregular syndiotactic polymer has $(r) = (rr) = 1$. A perfectly atactic polymer has $(m) = (r) = 0.5$ and $(mm) = (rr) = 0.25$, $(mr) = 0.5$, with a random distribution of dyads and triads. For random distributions that are not perfectly atactic, a polymer is said to tend toward isotacticity (to be predominantly isotactic) when $(m) > 0.5$ and $(mm) > 0.25$, or to tend toward syndiotacticity when $(r) > 0.5$ and $(rr) > 0.25$.

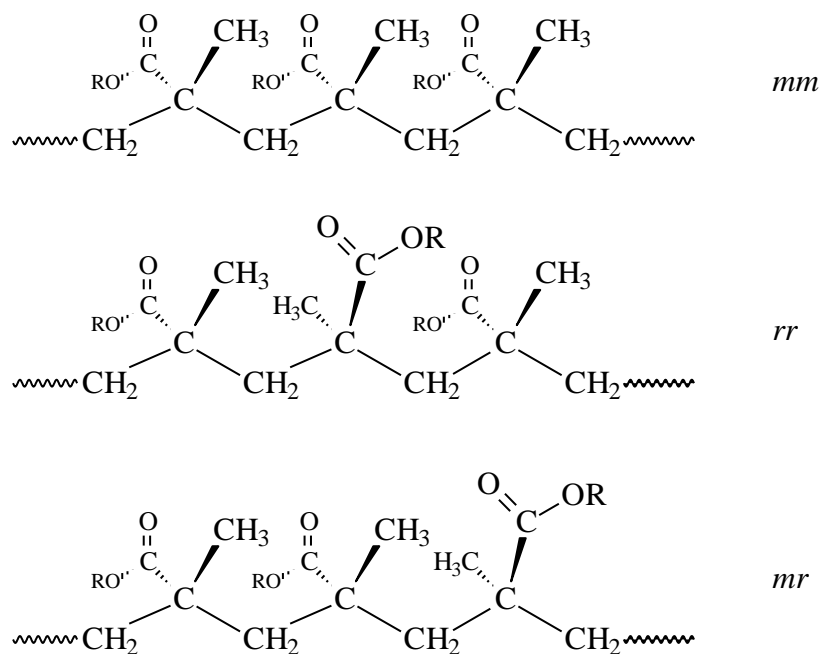
Figure IX-8 shows ^1H NMR spectra of three poly(methyl methacrylate) (PMMA) samples possessing different stereoregular configurations: isotactic (bottom), syndiotactic (middle), and atactic (top). Both the α -methyl and backbone methylene protons display significant chemical shift differences as a function of tacticity. The α -methyl protons display triad sensitivity. The signals for these protons appear around 1 ppm, but the exact position is dependent upon the tacticity. Figure IX-9 shows the backbone configuration for the three types of triads. The proton signal in the NMR spectrum corresponds to the α -methyl group of the center mer unit of the triad. For example, the signal appears about 1.2 ppm for an mm triad (isotactic), and about 0.8 ppm for an rr triad (syndiotactic). The mr or heterotactic triad appears at an intermediate position, about 1 ppm.

Figure IX-8



The methylene backbone protons display dyad sensitivity, and the signals for these protons appear in the range 1.3-2.3 ppm. For a meso dyad, the two methylene protons are non-equivalent, and hence they appear as a pair of doublets in the spectrum of the isotactic polymer. For a racemic dyad, the two protons are essentially equivalent, and they appear as a broad singlet centered about 1.8 ppm. The side-chain methoxy protons are not very sensitive to tacticity.

Figure IX-9



C. Forces of Stereoregulation in Alkene Polymerizations

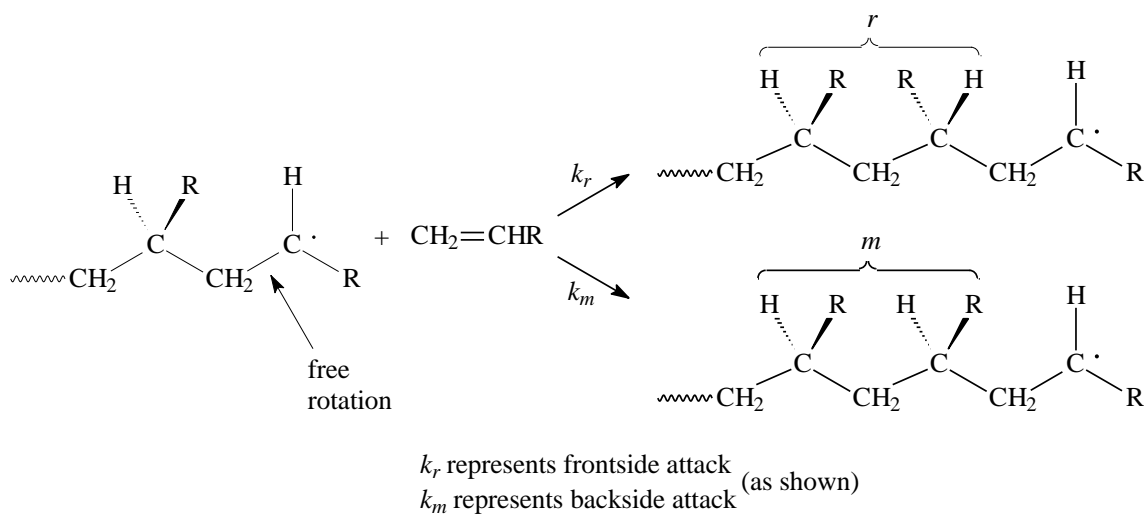
Type of tacticity (isotactic vs. syndiotactic) and degree of stereoregularity that result from chain addition polymerization of an alkene depend on the relative rate at which an incoming monomer adds to the chain with the same configuration as the preceding monomer unit, compared to the rate at which it adds with the opposite configuration. A critical factor effecting the outcome is whether the growing tip of the chain is free (as in a free radical polymerization) or strongly coordinated to another species such as a counterion (as in an ionic polymerization involving contact pairs) or a catalyst fragment (as in a coordination polymerization). If the chain end is free, both modes of addition are possible, and typically a low degree of stereoregularity is observed. However, one mode typically has lower activation energy than the other, and degree of stereoregularity will increase in that direction as temperature is lowered. If the chain end is coordinated, one or the other mode of addition may be strongly suppressed (or enhanced) resulting in a high degree of stereoregularity.

1. Free Radical Polymerization

Free radicals are representative of freely propagating species. As shown in Figure IX-10, because the carbon atom bearing the radical is trigonal planar, the configuration of this final monomer unit is not fixed until an incoming monomer adds to it. The incoming monomer can attack the radical from one side of the plane or the other, and it is this outcome that determines configuration of the final unit. As shown in Figure IX-10, frontside attack results in a racemic dyad and backside attack results in a meso dyad. However, frontside and backside attack are not equally favored; in general, due to steric interactions with the R group of the penultimate unit, k_r is slightly favored, leading to a slight tendency toward syndiotactic

placement. The degree of preference for syndiotacticity at a given temperature depends on the difference in activation energies between k_r and k_m . Equation IX-3 illustrates this in terms of the Arrhenius relationship. Thus, syndiotactic placement will become increasingly favored as temperature of polymerization is reduced. Moreover, the more bulky the R group, the greater will be the tendency toward syndiotacticity. This mechanism for syndioselectivity is referred to a polymer chain end control.

Figure IX-10



$$\frac{k_r}{k_m} = \frac{A_r}{A_m} e^{\frac{-(E_r - E_m)}{RT}} \quad \text{IX-3}$$

Table IX-1 gives activation energy differences ($E_r - E_m$) and frequency factor ratios (A_r/A_m) for methyl methacrylate (relatively bulky) and vinyl chloride (relatively non-bulky). For vinyl chloride, (r) changes from 0.51 to 0.67 as polymerization temperature decreases from 120 to -78°C . In contrast, for MMA, (r) changes from 0.64 to 0.87 as polymerization temperature decreases from 250 to -78°C . Since radical polymerizations are typically carried out at moderately elevated temperatures ($60\text{--}100^\circ\text{C}$), most polymers from radical polymerizations are highly atactic, but depending on the bulkiness of the monomer, some tendency toward syndiotacticity exists.

Table IX-1: Activation Energy Differences and Frequency Factor Ratios for Syndiotactic versus Isotactic Placement in Free Radical Polymerization

Monomer	$E_r - E_m$ (kJ/mol)	A_r/A_m
MMA	-4.5	0.60
vinyl chloride	-1.3	0.74

2. Ionic and Coordination Polymerizations

Ionic polymerizations involving free ions or solvent-separated ion pairs behave similarly to free radical polymerizations. Polymer chain end control operates and a slight-to-moderate tendency toward syndiotactic placement is increasingly favored as the temperature is lowered. However, for ionic polymerizations in poorly solvating media and/or those involving a strongly coordinating initiator fragment (counterion), a new type of control mechanism arises, termed catalyst site control. In this mechanism, strong coordination among propagating chain end, counterion (a.k.a. “initiator” or “initiator fragment”), and monomer occurs, and in the usual case, one of the two stereo modes of monomer addition is completely prevented, and the result is strongly isoselective polymerization. Table IX-2 lists some of the early stereoselective polymerizations. The isobutyl vinyl ether and MMA polymerizations (first two table entries) represent conventional ionic polymerizations in which the media are poorly solvating. The propylene polymerizations are examples of classical Ziegler-Natta polymerizations involving strongly coordinating transition metal catalysts. The titanium-based catalyst is a heterogeneous catalyst; whereas the vanadium catalyst is homogenous.

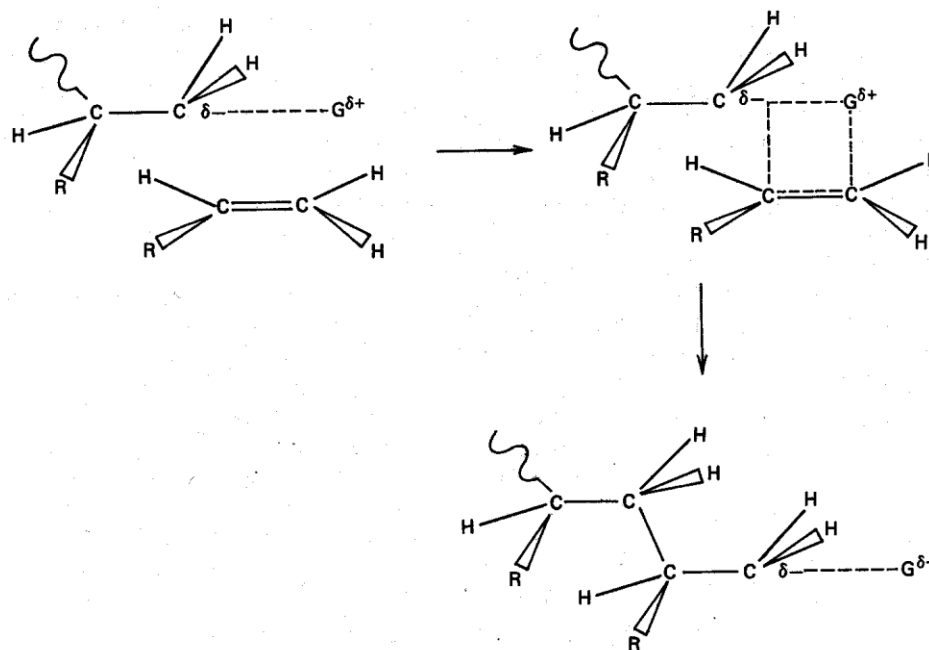
Table IX-2: Early Stereoselective Polymerizations

Monomer	Reaction Conditions	Tacticity	Year
Isobutyl vinyl ether	BF ₃ etherate in propene; -80 to -60°C	Isotactic	1947
MMA	φMgBr (30°C) or <i>n</i> -BuLi (-78 to 0°C) in toluene	Isotactic	1975
Propylene	TiCl ₄ /(Et) ₃ Al in <i>n</i> -heptane; 50°C	Isotactic	1958
Propylene	VCl ₄ /(Et) ₃ Al/anisole in toluene; -78°C	Syndiotactic	1963

The first recognized stereoselective polymerization was probably entry 1 above in 1947. Within the next 10-15 years, developments in the field occurred rapidly and led to a revolution in the engineering properties and applications of polyolefins including polyethylene and polypropylene. Much of the early, seminal work was performed by Ziegler in Germany, on ethylene polymerization, and Natta in Italy, on propylene polymerization. They jointly developed a large number of two-component catalyst systems, nowadays referred to as traditional Ziegler-Natta (ZN) initiators, that proved extremely effective at producing linear, high density polyethylene (HDPE), highly stereoregular isotactic polypropylene, and a number of polyolefin-based copolymers including ethylene-propylene (EPM) and ethylene-propylene-diene (EPDM) elastomers. In recognition of their work, they were jointly awarded the 1963 Nobel Prize in Chemistry.

The mechanism of catalyst site control, resulting usually in isotactic placement, is illustrated in Figure IX-11 for the general case of anionic coordination polymerization of an α -olefin (e.g. propylene).

Figure IX-11

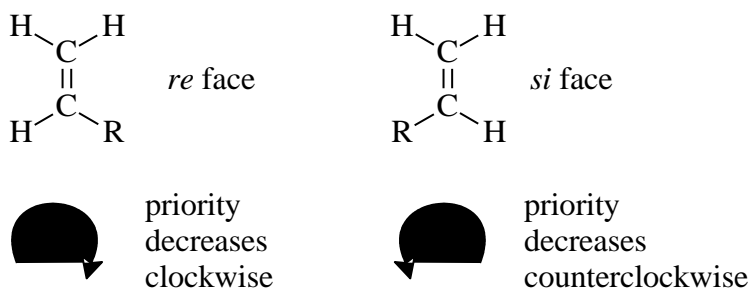


The chain end is partially negative, and hence addition to the double bond is 1,2 (termed primary insertion), which places the partial negative charge on the less-substituted carbon. The initiator fragment, G, is coordinated strongly to the chain end, and it is also capable of coordinating with the incoming monomer. In traditional ZN initiators, G is not a molecular species, but is rather a transition metal atom that is at the surface of an insoluble, coordination lattice. The nature of G is such that, due to severe steric/stereochemical constraints, it forces each monomer unit to approach the propagating center with the same face. A concerted, four-centered addition mechanism then ensues, as shown, and monomer is thereby inserted between the chain end and G. At this point, the new active center is ready to coordinate with the next incoming monomer unit. Successive coordinations occur identically, and the result is isotactic placement.

The two faces of monomer are identified as the *re* face and the *si* face. In Figure IX-11, the incoming monomer approaches with its *re* face directed toward G. As shown in Figure IX-12, when the *re* face is directed toward the viewer, the groups attached to the CHR carbon decrease in priority in a clockwise manner; when the *si* face is directed to the viewer, they decrease in a counterclockwise manner.

For most stereoselective initiators, G are chiral and consist of pairs of enantiomers. Left-handed G coordinate strictly with either the *re* or *si* face of monomer, and right-handed G coordinate strictly with the other face. The resulting polymers are generally not chiral, neglecting end groups. In ZN initiators, the chirality is attributable to the chiral crystal lattice in the vicinity of G. The newer, soluble metallocene initiators often possess “whole-molecule” chirality.

Figure IX-12



For certain soluble, traditional ZN initiators (vanadium-based) and some soluble metallocene initiators, catalyst site control produces syndiotactic polymers. In these cases, coordination accentuates the repulsive interactions between substituents on the polymer chain and incoming monomer. Syndiotacticity increases with decreasing temperature.

The ease of imposing catalyst site control for a given monomer increases with the ability of monomer to coordinate with G, and the latter increases with monomer polarity. Non-polar olefins such as ethylene, propylene, and styrene require strongly coordinating initiators. Heterogeneous initiators provide the severest restrictions on the approach of monomer; hence for traditional ZN initiators, only the heterogeneous initiators produce isotactic polymer.

D. Traditional Ziegler-Natta Polymerization of Nonpolar Alkene Monomers

Ziegler-Natta initiators are formed from two essential components (see Table IX-3):

- a Group IV-VIII transition metal halide or other derivative
- a Group I-III metal-based organometallic compound or hydride

The role of the transition metal is to form the polymerization-active bond at the tip of the growing chain. The Group I-III metal compound has two roles (two functions): 1) it reduces the transition metal to the proper oxidation state (typically, this involves reduction of TiCl_4 to TiCl_3), and 2) it provides the initiating moiety that resides at the head of the polymer chain, that is, it alkylates the transition metal-chloride bond (replaces the chlorine atom with an alkyl group, usually ethyl because triethylaluminum is the most commonly used Group I-III metal compound). The Group I-III metal also increases stereoselectivity and catalyst activity, but the mechanisms for these effects are more obscure. By far, the most common transition metal is titanium and the most common Group I-III metal is aluminum. The original initiator used by Ziegler was formed by reducing TiCl_4 with $(\text{C}_2\text{H}_5)_3\text{Al}$ in hydrocarbon solvent, producing the true catalyst, $\beta\text{-TiCl}_3$, as a precipitate. The entire mixture was then used directly as a polymerization catalyst. Later it was learned that other crystalline forms, α -, δ -, and γ -, provided higher stereoselectivity. Modern catalysts still employ TiCl_3 , but their preparation and usage are much more sophisticated. One major difference is that the active TiCl_3 crystals are dispersed onto an inexpensive solid support, typically MgCl_2 . This places a dramatically higher fraction of the more expensive transition metal at the surface of the catalyst.

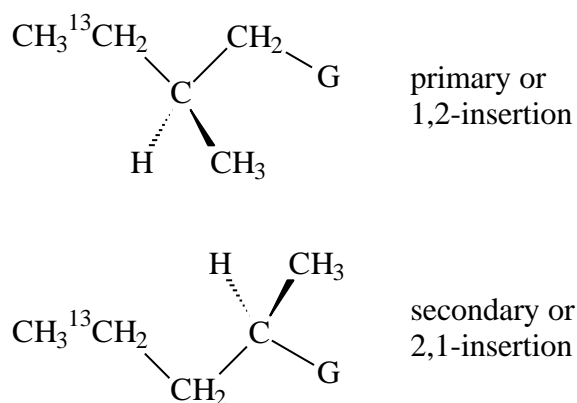
Table IX-3: Components of Ziegler-Natta Initiators

Group IV-VIII Transition Metal	Group I-III Metal
TiCl ₄	(C ₂ H ₅) ₃ Al
TiCl ₃	(C ₂ H ₅) ₂ AlCl
TiBr ₃	(C ₂ H ₅) ₂ AlBr
VCl ₄	(C ₂ H ₅)AlCl ₂
VCl ₃	(<i>i</i> -C ₄ H ₉) ₃ Al
(C ₂ H ₅) ₂ TiCl ₂	(C ₂ H ₅) ₂ Be
(CH ₃ COCHCOCH ₃) ₃ V	(C ₂ H ₅) ₂ Mg
Ti(OC ₄ H ₉) ₄	C ₄ H ₉ Li
Ti(OH) ₄	(C ₂ H ₅) ₂ Zn
MoCl ₅	(φ ₂ N) ₃ Al
NiO	φMgBr
CrCl ₃	(C ₂ H ₅) ₄ AlLi
ZrCl ₄	C ₅ H ₁₁ Na
WCl ₆	(C ₂ H ₅) ₂ Cd
MnCl ₂	(C ₂ H ₅) ₃ Ga

1. Primary vs. Secondary Insertion; Regioselectivity

In isoselective ZN polymerizations, the mode of monomer insertion is primary or 1,2-insertion (Figure IX-13). This is consistent with a growing chain end possessing anionic character, that is, the less substituted carbon is more stable. Primary insertion has been demonstrated conclusively using ¹³C NMR analysis of the end groups of polymers initiated from ¹³C-enriched (C₂H₅)₃Al. Moreover, isoselective polymerizations are highly regioselective; regioirregular placements, in which monomer enters the chain backwards to form an isolated head-to-head sequence are very low.

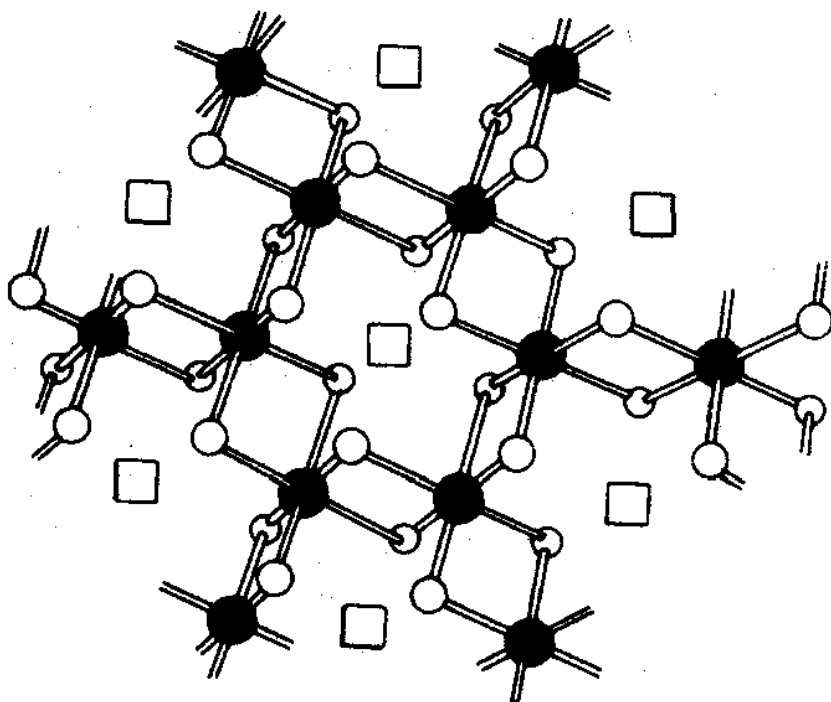
Figure IX-13



2. Mechanism of Isoselective Propagation

The crystalline structure of α -TiCl₃ is shown in Figure IX-14. It is a coordination lattice, characteristic of inorganic crystals such as NaCl, as opposed to a molecular crystalline lattice, characteristic of organic compounds such as sucrose. It is composed of elementary crystal sheets in which each octahedral (hexavalent) titanium atom (large black sphere) is bridged to each of three other titanium atoms via a pair of chlorine atoms (small open spheres). Every third titanium atom in the lattice is missing (indicated by an open square), which causes the overall crystal to possess electrical neutrality. Polymerization-active sites are formed at the terminal edges of truncated sheets. Titanium atoms at the edges can only form one bond where the pair of bridging chlorine atoms formerly resided. These titanium atoms are therefore only bonded to five chlorine atoms, which leaves one coordination site vacant. It is this vacant site that serves to coordinate monomer during polymerization. Of the five bonded chlorine atoms, four are directed into the crystal and are bridged to interior titanium atoms. The fifth, non-bridged chlorine is directed outward from the edge of the crystal, and it is this chlorine that is replaced by an ethyl group (or other alkyl group or hydride) by the Group I-III metal component and becomes the growing chain.

Figure IX-14

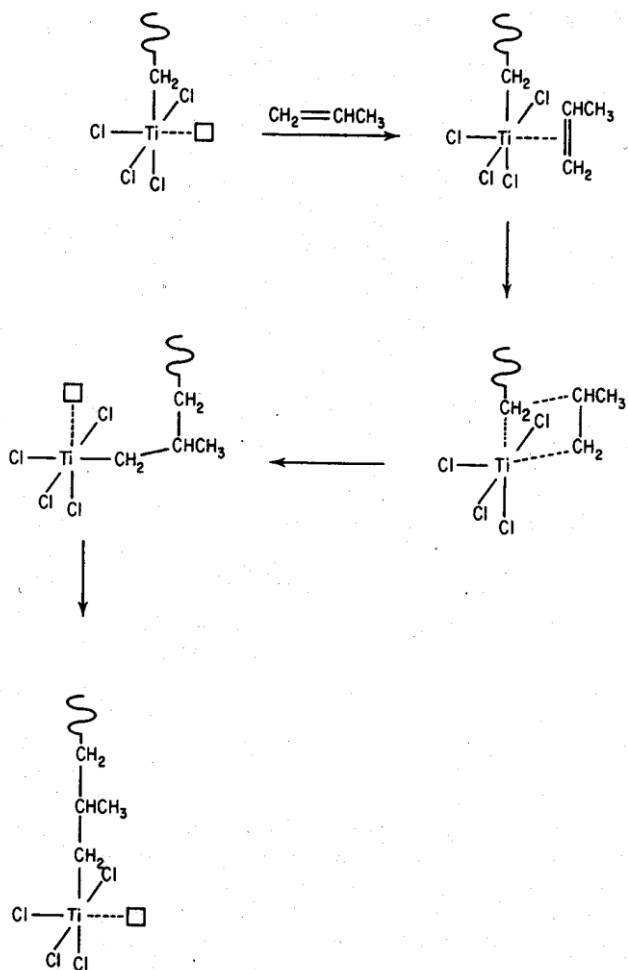


Because every third titanium atom is missing from the lattice, titanium atoms occur pairwise along any given plane in the lattice. The active polymerization sites described above likewise occur in pairs, and the two sites within a pair possess opposite chirality (they are mirror images and not superimposable). One site of the pair coordinates exclusively to the *re* face of monomer, and the other exclusively to the *si* face. Polymerization at each site results in isoselective polymerization via catalyst site control. One site of the pair creates polymer in

which the stereocenters have an absolute *R* configuration, and the other creates polymer with an absolute *S* configuration. For reasons already discussed, however, the two mirror-image polymers are indistinguishable since they are superimposable except for end groups.

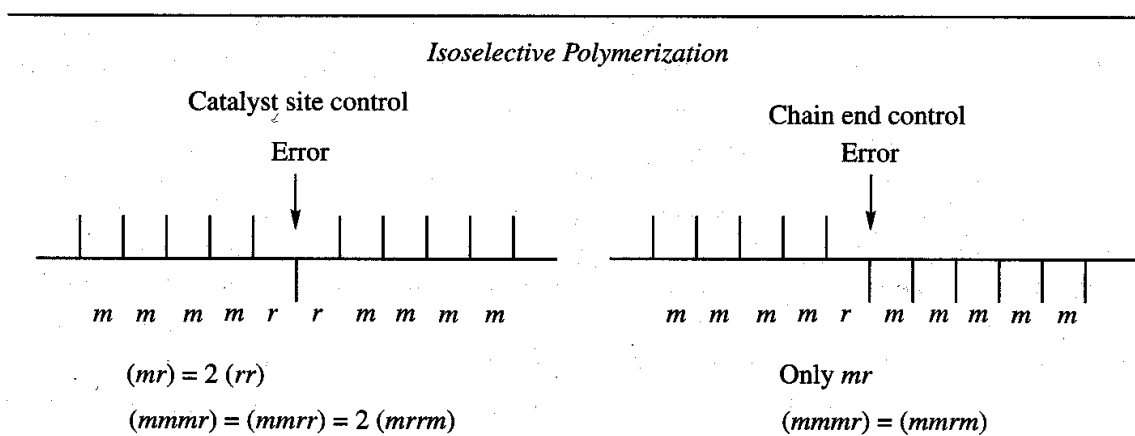
Figure IX-15 shows the catalyst site control mechanism for isoselective propagation of propylene from a TiCl_3 -based ZN catalyst. Keep in mind that the site of propagation pictured is not a molecular compound. Rather, the four chlorine atoms around the titanium atom are bridged to other titanium atoms below the surface of the coordination crystal lattice. However, these details are omitted from the diagram for clarity. Monomer approaches and coordinates to the vacant site (open square) on titanium in a stereospecific manner (either *re* or *si* face). A four-centered, 1,2-insertion reaction (primary insertion) takes place, after which the polymer chain is bonded to the formerly vacant site. This manner of insertion is referred to as migratory insertion. The polymer chain then migrates back to the original position in a process called back-skip or reset; at this point the site is ready to accept another incoming monomer. The evidence for back-skip is the observation of isoselective polymerization. If back-skip were not operable, the result might be syndioselective polymerization.

Figure IX-15



The catalyst site control mechanism is supported by the nature of occasional stereoerrors that are observed. ^{13}C NMR of isotactic polypropylene shows that the main error is pairs of racemic dyads rather than isolated racemic dyads (Figure IX-16). Immediate correction of the error is consistent with stereocontrol by the chiral catalyst site. A permanent “switchover” to the opposite site would be the expected outcome with stereocontrol by the chain end. Likewise, in ethylene-propylene copolymerization, ^{13}C NMR shows that the propylene units on either side of an ethylene unit have the same configuration. If chain end control were operating, the configuration of a propylene unit that followed an ethylene unit should be randomly determined, and hence the number of sequences in which the propylene units on either side of an ethylene unit have the same configuration would equal the number of sequences that have the opposite configuration.

Figure IX-16



3. Direction of Double Bond Opening

A syn or cis addition to the double bond is implied in the ZN mechanism. It is also consistent with the results of experiments performed using 1-deuteropropylenes. The experiments are based on the fact that the type of diisotacticity obtained from a 1,2-disubstituted ethylene depends on the mode of addition to the double bond and the configuration of the monomer. For example, syn addition to *cis*-1-deuteropropene would yield the erythrodiisotactic polymer (Figure IX-17); whereas anti addition to the same monomer would yield the threodiisotactic polymer.

4. Chain transfer

Ziegler-Natta propagations, in general, do not have an inherent termination step. They are not living, however, due to the occurrence of several types of chain transfer reactions as shown in Figure IX-18. Chain transfer to molecular hydrogen (bottom of figure) is used in the commercial process for molecular weight control.

Figure IX-17

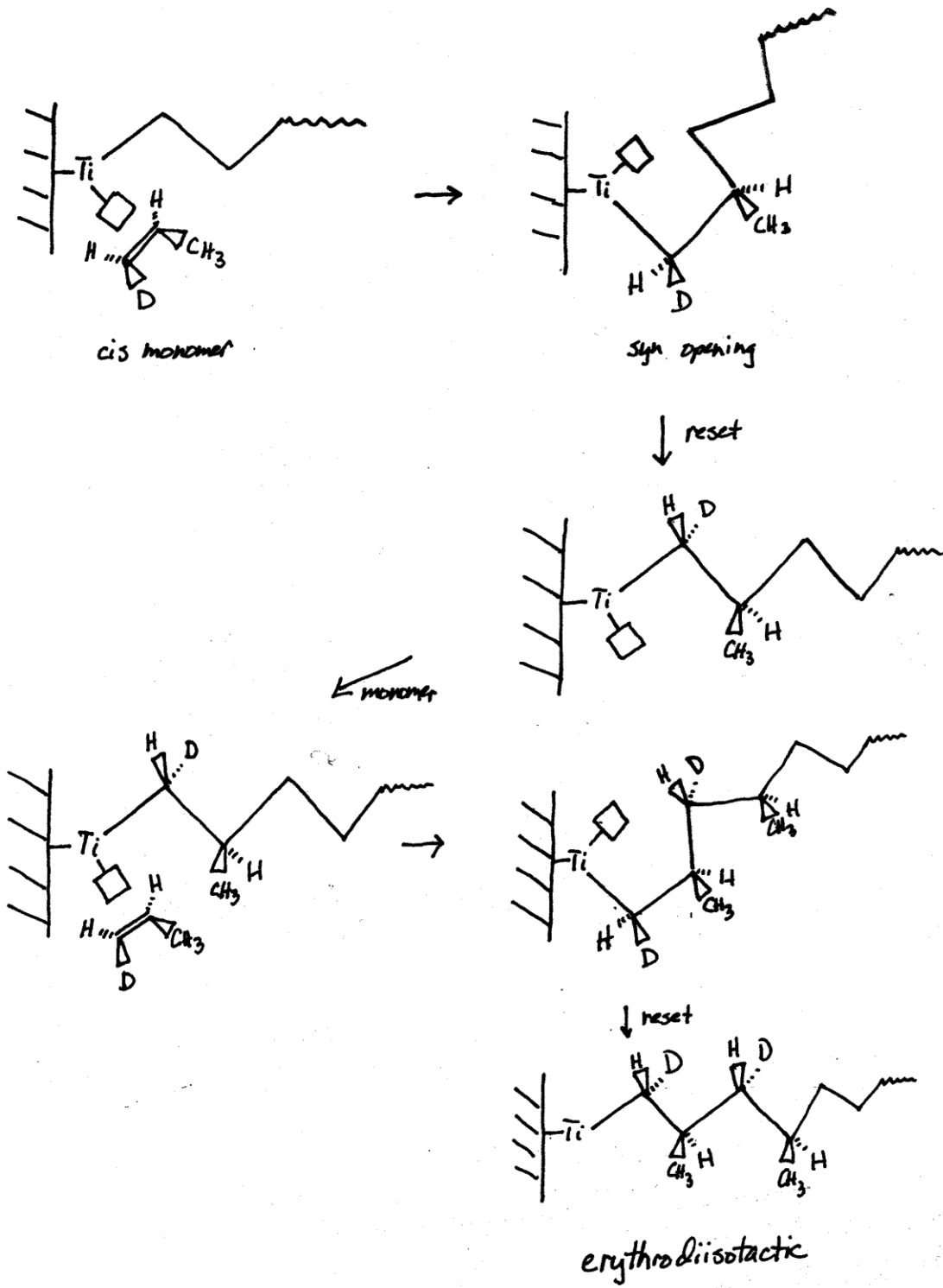
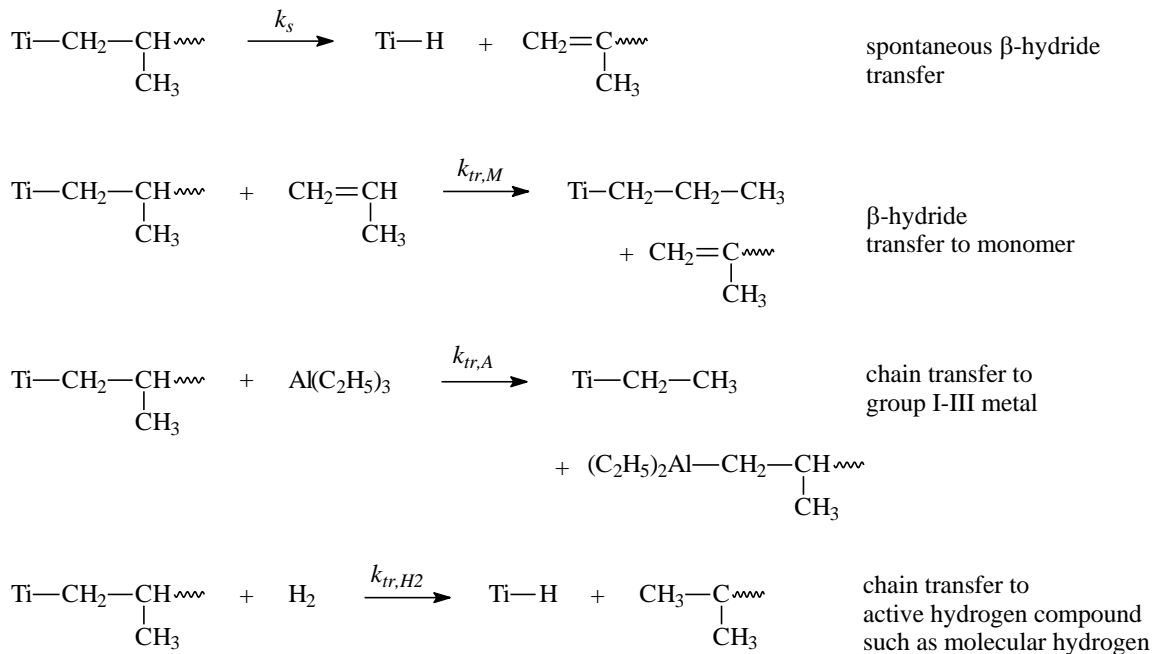


Figure IX-18

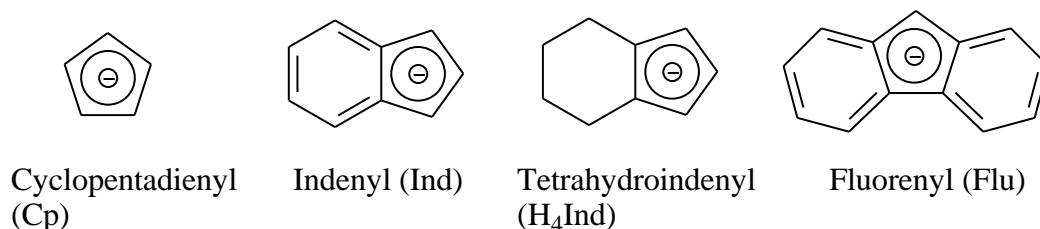


E. Metallocene Polymerization of Nonpolar Alkene Monomers

Metallocene initiators represent the most important development in stereo-controlled polymerization since the original discoveries of Ziegler and Natta. Metallocenes are a type of ZN initiator, but in comparison to traditional ZN initiators, metallocenes are well-defined, soluble, molecular compounds. Each metallocene molecule has a single catalytic site that is identical to the sites on all of the other molecules (hence the name *single-site* initiators). In comparison, traditional ZN initiators possess many, many sites on a single catalyst particle, and these sites exist in many slightly different steric and stereochemical environments.

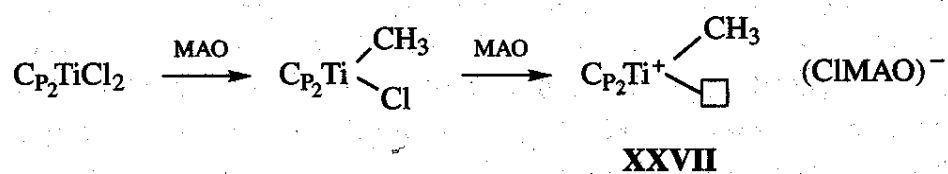
A metallocene catalyst has the formula $\text{LL}'\text{MtX}$, where L and L' are η^5 -cyclopentadienyl-type ligands such as cyclopentadienyl (Cp), alkyl-substituted Cp and various fused-ring cyclopentadienyls (Figure IX-19), which may be the same or different, Mt is a group IV transition metal, usually zirconium, but also titanium and to a lesser extent hafnium, and X is usually chloride or methyl.

Figure IX-19



The metallocenes, like traditional ZN initiators, require a second component in addition to the transition metal component. For metallocene catalysts, the compound of choice is almost universally methylaluminoxane (MAO), produced through controlled hydrolysis of trimethyl aluminum. MAO has two functions: 1) provides the initiating moiety that resides at the head of the polymer chain, that is, it alkylates one of a transition metal-chloride bonds (replaces the chlorine atom with a methyl group), and 2) removes the second chloride with its pair of electrons (acting as a Lewis acid) to yield a metallocenium cation with a vacant orbital site (Figure IX-20). Unlike traditional ZN initiators, in which the transition metal usually exists in oxidation state III, the transition metal in a metallocene is usually in oxidation state IV. Thus the active catalyst site possesses a positive charge, and MAO forms a negative counteranion.

Figure IX-20



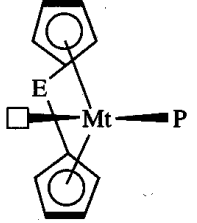
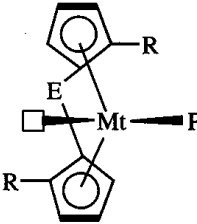
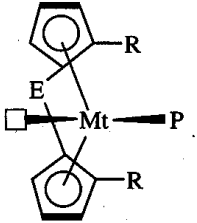
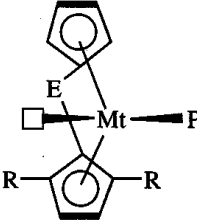
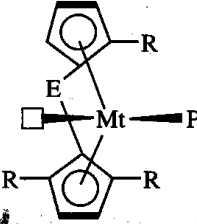
1. Metallocene Symmetry

Metallocenes must possess two characteristics in order to produce stereoselective polymerization with good reactivity: chirality and rigidity. These characteristics are realized through the use of substituted cyclopentadienyl ligands (as in Figure IX-19), and a bridging group that covalently connects the two Cp ligands. Bridged metallocenes are referred to as *ansa metallocenes*.

Table IX-4 shows the structures and properties of various ansa metallocenes with different types of molecular symmetry. The R group on the cyclopentadienyl ligands may represent an alkyl or aryl substituent or a fused aliphatic or aromatic ring such as found in Ind or Flu (Figure IX-19). E is the bridging group, usually $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-$, $-\text{Si}(\text{CH}_3)_2-$, or $-\text{C}(\text{CH}_3)_2-$. The transition metal (Mt) has two active sites. At any given moment, the growing chain occupies one site, and the other is available to coordinate monomer. After monomer coordination, migratory insertion occurs. Thus, the site at which the growing chain resides switches back and forth with each monomer propagation.

Table V-4 lists the types of symmetry possessed by each metallocene type. A C_2 axis of symmetry means that rotation of 180° about that axis yields a structure indistinguishable from the original structure. A symmetry plane indicates a mirror plane of symmetry in the molecule. The descriptions homotopic, diastereotopic, and enantiotopic indicate the mutual stereo relationship of the two active sites. In that same column, each site is described as non-selective (NS) or enantioselective (E) (i.e., the site directs either the *re* or *si* face of monomer). The final column indicates the polymer structure obtained with that type of metallocene and the controlling mechanism, either catalyst site control (CSC) or chain end control (CEC).

Table IX-4: Properties of Metallocene Initiators

Metallocene	Symmetry	Symmetry Elements		Coordination Sites ^a	Polymer Structure ^b
		Axis	Planes		
 <p>XXVIII</p>	C_{2v}	C_2	2	Homotopic NS, NS	Atactic (variable) CEC
 <p>XXIX</p>	C_2	C_2	None	Homotopic E, E	Isotactic CSC
 <p>XXX</p>	Meso C_s	None	1	Diastereotopic NS, NS	Atactic CEC
 <p>XXXI</p>	C_s	None	1	Enantiotopic E, E	Syndiotactic CSC
 <p>XXXII</p>	C_1	None	None	Diastereotopic E, NS or E, E	Variable CSC

^a E = enantioselective, NS = nonselective.

^b CEC = chain end control, CSC = catalyst site control.

The geometry of a group IV metallocene is shown in Figure IX-21. The molecule is bent by virtue of the bridging group, E. β is the so-called “bite angle,” which is in the range 60-75°. α is slightly larger than tetrahedral, in the range 115-125°. Ansa metallocenes are synthesized using the scheme shown in Figure IX-22.

Figure IX-21

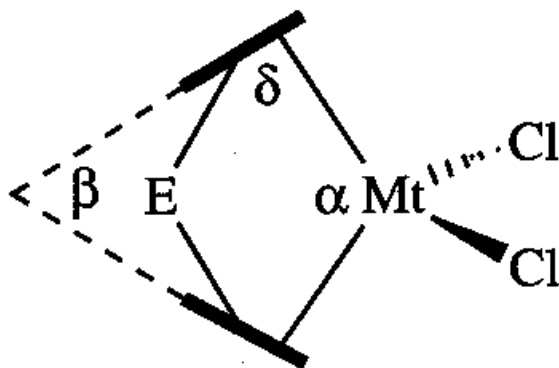
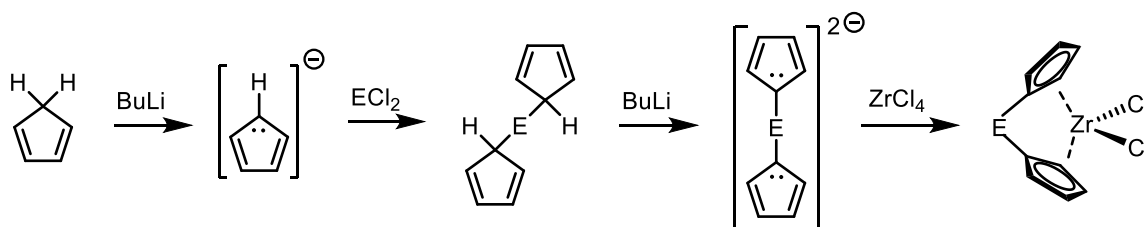


Figure IX-22



2. C_{2v} -Symmetric Metallocenes

Whether bridged or unbridged, these highly symmetrical catalysts contain two identical active sites (homotopic), which are nonselective. A modest tendency toward syndiotacticity is observed, increasing with decreasing temperature, due to chain end control.

3. C_2 -Symmetric Metallocenes

This class of initiator possesses a C_2 axis of symmetry and exists as a pair of enantiomers. In a given racemate, the two sites are chiral and homotopic (one enantiomer is R, R and the other is S, S) and selective for the same monomer face, i.e., both sites in the R, R enantiomer are selective for one monomer face (*re* or *si*) and both sites in the S, S enantiomer are selective for the other monomer face. The result is isoselective polymerization. (A racemic mixture of mirror-image polymer molecules is created, but neglecting end groups, all the polymer molecules are indistinguishable.) C_2 ansa metallocenes are one of two classes of initiators that produce highly isotactic polymer, the other class being the C_1 ansa metallocenes.

Isoselectivity occurs through catalyst site control. Monomer enters the chain through migratory insertion. Thus, in successive propagation steps, the propagating polymer chain

flips back and forth between the two coordination sites; however, isoselectivity is preserved because the two sites are homotopic and select for the same monomer face.

An example of a C_2 ansa metallocene is the pair of enantiomers, *rac*-(dimethylsilyl)bis(1-indenyl)zirconium, shown in Figure IX-23. During the synthesis shown in Figure IX-22, the racemic mixture is obtained, along with a meso compound. Since the stereoselectivity of the meso compound is very different from the enantiomeric pair, during workup, the former (meso C_s or “XXX” in Table IX-4) is separated from the latter by crystallization.

Figure IX-23

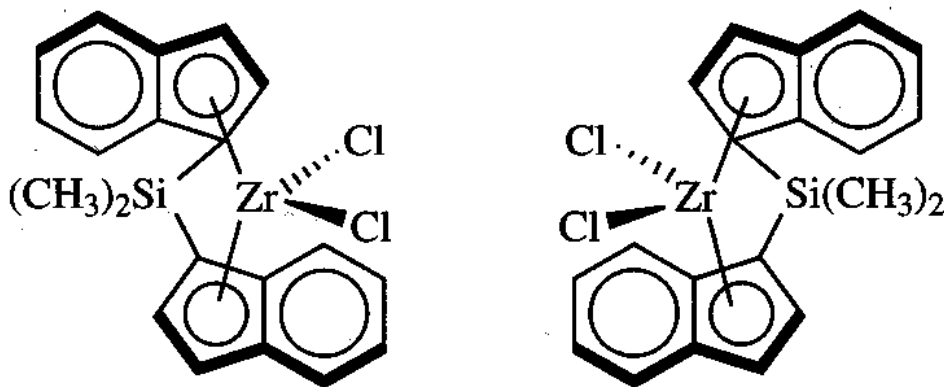


Table IX-5 lists a number of C_2 ansa metallocenes that yield highly isotactic polypropylene. The proper numbering of the carbon atoms in Cp and Ind ligands is shown in Figure IX-24.

Table IX-5: Propylene Polymerization with C_2 ansa Zirconocene/MAO

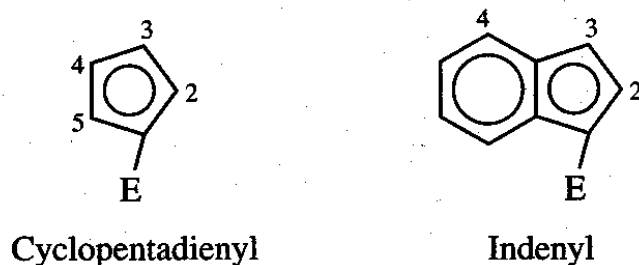
Initiator	T (°C)	A ^a	(<i>mmmm</i>)	M ^b ($\times 10^{-5}$)	PDI
Me ₂ Si(3-Me-Cp) ₂ ZrCl ₂	30	16.3	0.93	0.17	2.3
C ₂ H ₄ (3-Me-Cp) ₂ ZrCl ₂	40	5.8	0.92	0.20	2.3
Me ₂ Si(2,3,5-Me ₃ -Cp) ₂ ZrCl ₂	50	207	0.96	1.8	1.9
Me ₂ Si(2-Me-4-C ₆ H ₅ -Ind) ₂ ZrCl ₂	70	755	0.95	7.3	—
Me ₂ C(3- <i>t</i> -Bu-Ind) ₂ ZrCl ₂	50	125	0.95	0.89	—
CH ₂ (3- <i>t</i> -Bu-Ind) ₂ ZrCl ₂	50	37	0.97	2.4	—
Me ₂ Si(4-[1-naphthyl]-Ind) ₂ ZrCl ₂ ^c	50	875	0.99	9.2	—
Me ₂ C(Ind) ₂ ZrCl ₂	50	66	0.81	0.11	—
Me ₂ C(H ₄ Ind) ₂ ZrCl ₂	50	37	0.96	0.25	—

^a Activity in units of kg PP (mmol Zr)⁻¹ h⁻¹.

^b Either \bar{M}_w or \bar{M}_v .

^c Data from Coates [2000]. All other data from Resconi et al. [2000].

Figure IX-24

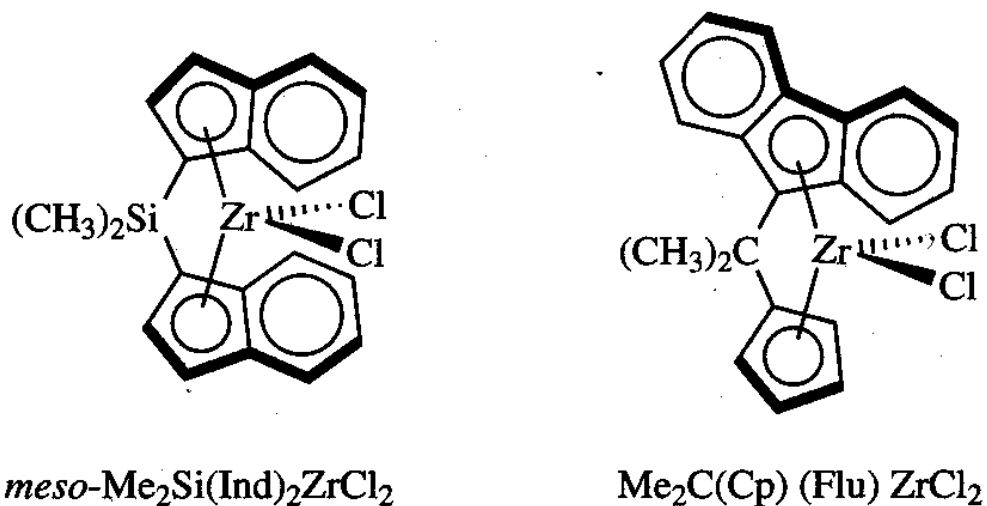


In general, increasing polymerization temperature increases rate of polymerization but decreases isoselectivity, regioselectivity, and molecular weight. Decreasing monomer concentration decreases isoselectivity. This suggests that stereo errors arise not through coordination of the wrong monomer face, but through epimerization (switching of the chirality) of the last monomer unit after it has entered the chain and is attached to the transition metal. Epimerization is unimolecular and unaffected by decreasing monomer concentration. However propagation is slowed by decreasing monomer concentration, and this allows more time for epimerization to occur.

4. C_s -Symmetric Metallocenes

C_s -symmetric metallocenes include C_s metallocenes (“XXXI” in Table IX-4), which possess a vertical mirror plane, and meso C_s referred to in the last section, which possess a horizontal mirror plane. Both are achiral molecules due to the symmetry plane. However, they yield very different stereoselectivity in polymerization; meso C_s produces atactic polymer, while C_s produces syndiotactic polymer. Figure IX-25 shows examples of a meso C_s (left) and a C_s (right).

Figure IX-25



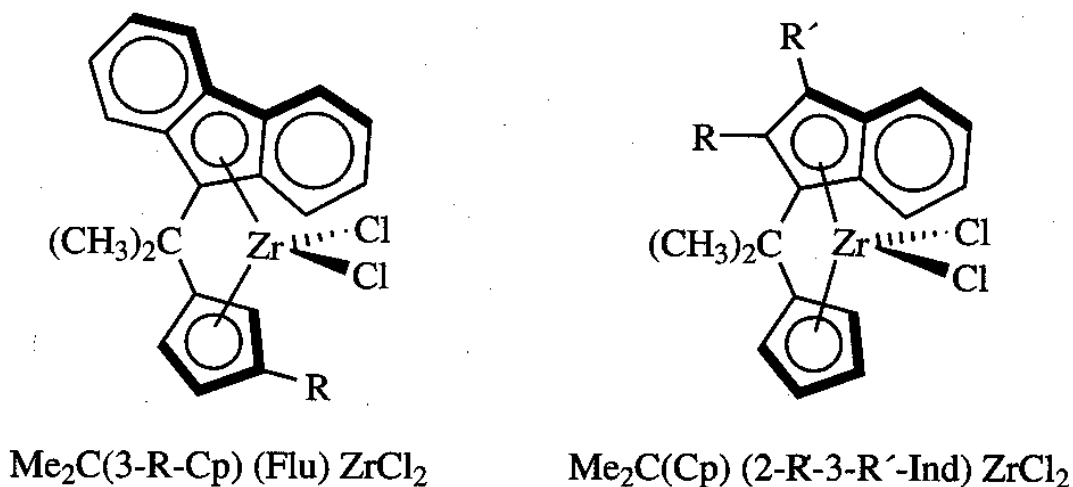
The two active sites in meso C_s are mutually non-equivalent (diastereotopic) but each is individually achirotopic due to local symmetry. Therefore, neither site is selective toward a particular monomer face, and the result is atactic polymer. However, regioselectivity is extremely good, better than most C_2 metallocenes.

The two active sites in a C_s metallocene are mirror images of each other and therefore mutually enantiotopic; each is locally asymmetric and therefore each is individually chirotopic. Thus one selects for the *re* face of monomer, and the other selects for the *si* face. With migratory insertion, the result is high syndioselectivity. Stereocontrol is via catalyst site control, which is supported by NMR analysis of stereoerrors. The highest syndiotacticity is obtained at low temperatures and high monomer concentrations, which conditions suppress epimerization. The best C_s initiators are not as stereoselective as the best C_2 initiators.

5. C_1 -Symmetric Metallocenes

C_1 -Symmetric metallocenes have neither a plane nor an axis of symmetry. A C_s metallocene is converted to a C_1 by producing asymmetry at one or the other cyclopentadienyl ligand. The two active sites in a C_1 metallocene are individually chirotopic and mutually non-equivalent (diastereotopic). Thus, each site has the potential to be more-or-less highly enantioselective, but not necessarily for the same monomer face. As a result, there is great variability in the polymer stereochemical outcome. For example, if both sites are highly selective to the same monomer face, the result is highly isotactic polymer. If the two sites happen to be each selective toward a different monomer face, the result is high syndioselectivity. Finally, if one site is highly enantioselective, and the other is not, the result is hemiisotacticity. C_1 metallocenes are often referred to as dual-site metallocenes since, to some extent, the two sites can be molecularly engineered independently of each other to give a wide range of behaviors. Many C_1 metallocenes have been studied, and two representative examples are shown in Figure IX-26.

Figure IX-26



$\text{Me}_2\text{C}(\text{3-R-Cp})(\text{Flu})\text{ZrCl}_2$ (Figure IX-26, left) yields highly hemiisotactic polypropylene when R is methyl, $T = -20^\circ\text{C}$, and $[\text{M}] = 1.8 \text{ mol/L}$. It is thought that the isoselective placements occur when the polymer chain is coordinated to the less hindered site (away from R) and monomer is forced to approach enantioselectively to the more sterically hindered site. Migratory insertion then causes the polymer chain to occupy the sterically hindered site, and in this arrangement, monomer undergoes a random (non-enantioselective) approach to the non-hindered site.

A trend toward greater isoselectivity is observed when the R group becomes larger (isopropyl, *tert*-butyl). Isotactic placement increasingly occurs because propagation increasingly occurs at only one site, namely when the polymer chain is coordinated to the less sterically hindered site and monomer coordinates at the more sterically hindered site. This does not come about by a departure from migratory insertion, but rather through the increasing occurrence of back-skip, as observed in traditional ZN catalysts. The degree of isotacticity also increases as the temperature is increased and/or as the monomer concentration is decreased. These conditions facilitate back-flip of the chain to the less hindered site.

$\text{Me}_2\text{C}(\text{Cp})(2\text{-R-3-R}'\text{-Ind})\text{ZrCl}_2$ (Figure IX-26, right) is an example of a C_1 metallocene that yields highly syndiotactic polymer. This occurs because the two sites each select a different monomer face, and migratory insertion occurs without back-flip.

6. Oscillating Metallocenes

Unbridged metallocenes generally yield atactic polymer because free rotation of the Cp ligands causes the two sites to become achirotopic. However, certain unbridged metallocenes with particularly large substituents, termed fluxional metallocenes, exhibit slow rotation due to the significant steric barrier (Figure IX-27). Stereoblock copolymers are theoretically possible with such initiators if different conformers impose different stereoselectivity and if interconversion of the conformers is sufficiently slow relative to propagation.

Figure IX-27

