

# Precise Control of Polyolefin Stereochemistry Using Single-Site Metal Catalysts

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Geoffrey W. Coates was born in 1966 in Evansville, IN. He received a B.A. degree in chemistry from Wabash College in 1989 working with Roy G. Miller and a Ph.D. in organic chemistry from Stanford University in 1994 with Robert M. Waymouth. After postdoctoral research with Robert H. Grubbs at the California Institute of Technology, he joined the faculty at Cornell University in 1997, where he is now Assistant Professor of Chemistry and Chemical Biology. His research interests include the development of single-site catalysts for synthesis and the preparation and characterization of well-defined polymer architectures.

has been actively pursued in both industrial and academic laboratories.

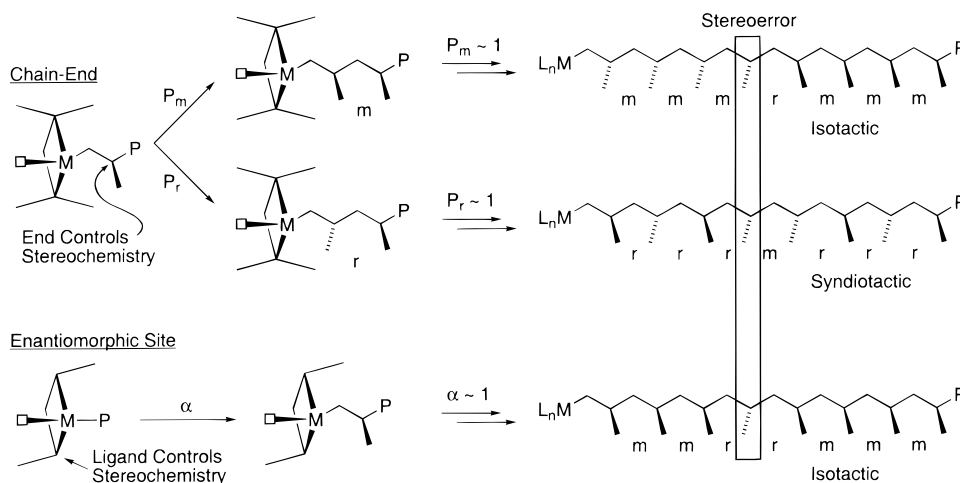
Historically, *heterogeneous* polymerization catalysts have been the workhorse of the polymer industry. Although these catalysts offer many important advantages over their *homogeneous* counterparts in commercial production, they also have a significant number of drawbacks. For example, heterogeneous catalysts typically have multiple active sites, each of which has its own rate constants for monomer enchainment, stereoselectivity, comonomer incorporation, and chain transfer.<sup>5</sup> Therefore a substantial amount of empirical optimization of these catalysts is necessary before polymers of relatively uniform molecular weights, composition, and stereochemistry can be produced.

During the last two decades, an extraordinary amount of research has been directed toward the development of homogeneous, single-site polymerization catalysts.<sup>6–12</sup> These molecular compounds have the general formula  $L_nMR$ , where  $L_n$  is an organic ligand set that remains bound to and thus modifies the reactivity of the active metal center (M) during the entire chemical reaction and R is the polymer or initiating group. By tailoring of the coordination environment of the metal center, single-site catalysts

## I. Introduction

### A. Background

Staudinger predicted a correlation between the physical properties of a polymer and its main-chain stereochemistry as early as 1929.<sup>1</sup> However it was not until 1947 that Schildknecht reported the first stereoregular synthetic polymer.<sup>2,3</sup> Amidst considerable controversy, he attributed the crystalline properties of a poly(isobutyl vinyl ether) to an ordered stereochemistry, or tacticity, of the polymer backbone. In 1954, research in the field of stereoregular polymers gained a tremendous amount of momentum when Natta discovered the synthesis of a crystalline “isotactic” polypropylene using a heterogeneous organometallic catalyst.<sup>4</sup> Since these initial discoveries, the synthesis of polymers of defined stereochemistry

**Scheme 1. Chain-End and Enantiomorphous Site Mechanisms of Stereocontrol**

are now available that can control the molecular weight, molecular weight distribution, comonomer incorporation, and both the relative and absolute stereochemistry of a polymer in a way that is often impossible using conventional heterogeneous catalysts. Although their commercial implementation in the solution phase is often impractical, they can be heterogenized for efficient gas-phase or flow-through reaction by attaching them to a solid support. Perhaps most importantly, these defined molecular-based systems allow detailed structural and mechanistic studies. Thus, through theoretical and empirical studies scientists can rapidly evolve new and improved generations of catalysts.

**B. Scope of Review**

This review covers the scientific literature from the mid-1980s to the present concerning stereoselective polymerization by single-site transition metal and f-block metal complexes. Strategies for controlling the relative configuration of main-chain stereogenic centers of chain-growth polyolefins are included; since the emphasis is on stereochemical control of polymerization by the homogeneous catalyst, the polymerization of optically active monomers will not be covered. The review will concentrate on examining state-of-the-art stereoselective polymerization catalysts and will focus on proposed mechanisms of stereocontrol. Although the emphasis will be on stereochemical control by the catalyst, other important characteristics such as polymerization activity and polymer properties will be included.

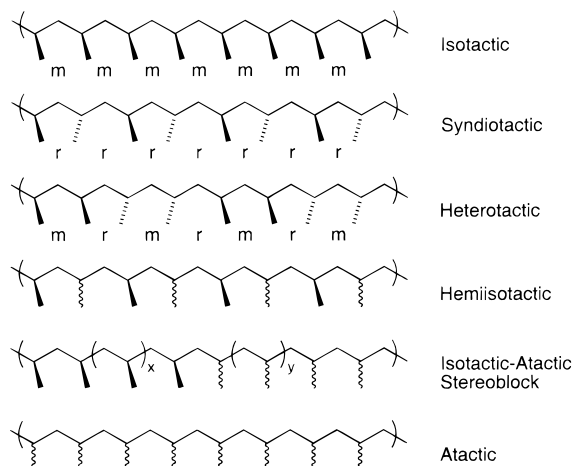
**C. Mechanisms, Nomenclature, and Quantification of Stereoregularity**

Both the ligand set of a single-site catalyst and the growing polymer chain influence the stereochemistry of the polymerization reaction.<sup>13</sup> It is interesting to note that, unlike the catalytic synthesis of small molecules, during a chain-growth polymerization reaction a polymer chain remains bound to the active metal center during monomer enchainment. Thus, the stereogenic center from the last enchainment monomer unit will have an influence on the stereochemistry of monomer addition; if this influence is signifi-

cant, the mode of stereochemical regulation is referred to as “polymer chain-end control”. It should be noted that in rare instances more than one stereogenic center of the polymer can play a significant role in stereoregulation. If the ligand set is chiral and overrides the influence of the polymer chain end, the mechanism of stereochemical direction is termed “enantiomorphous-site control” (Scheme 1). In the former mechanism, a stereochemical error is propagated, while in the latter a correction occurs since the ligands direct the stereochemical events.

Scheme 1 introduces the parameters that are used to describe the stereoselectivity of the monomer enchainment process. For chain-end control, the parameters  $P_m$  and  $P_r$  refer to the probability of *meso* and *racemic* placements, respectively (the Bovey formalism is a convenient way to describe polymer tacticity, with a small “*m*” for *meso*, and a small “*r*” for *racemic* relationships between adjacent stereogenic centers). A  $P_m$  equal to unity indicates isotacticity, while a  $P_r$  equal to unity signifies syndiotacticity. For site-control mechanisms, the parameter  $\alpha$  represents the degree of enantiotopic selectivity of the enchainment. When  $\alpha$  is either 1 or 0 an isotactic polymer forms, while an  $\alpha$  parameter of 0.5 produces an atactic polymer. Polymer architectures relevant to this review are shown in Figure 1.

There are several techniques for determining the type of tacticity and degree of stereoregularity of a polymer sample. Commonly used methods include solubility, X-ray diffraction, IR spectroscopy, and thermal properties (melting point and glass-transition temperature). In the case of chiral polymers, optical rotation can be used to determine the absolute configuration as well as degree of enantiomeric purity when the optically pure polymer is available. However the most useful method for determining a polymer's tacticity classification as well as quantifying its stereochemical purity is nuclear magnetic resonance (NMR).<sup>14,15</sup> In many cases the shifts for the various polymer nuclei are sensitive to adjacent stereogenic centers, resulting in fine structure that can provide quantitative information about the polymer microstructure once the shifts identities are assigned. For example, the methyl region of a high-resolution <sup>13</sup>C NMR spectrum of atactic polypropyl-



**Figure 1.** Common polymer tacticities, in order of decreasing stereoregularity.

ene displays 10 peaks, each of which represents a different set of five stereocenters (a pentad). Since the position of each pentad in the spectrum is known, a routine  $^{13}\text{C}$  NMR experiment can reveal both the tacticity as well as the degree of stereoregularity of a sample of polypropylene. Therefore, the degree of isotacticity or syndiotacticity of polypropylene is often reported as the fraction of *mmmm* and *rrrr* pentads, respectively. The ratio of the peaks can also be used to determine the mechanism of stereocontrol, since the spectra can be simulated using the statistical models presented above.<sup>16</sup> Scheme 1 shows that isospecific chain-end control mechanisms produce polymers with isolated *r*-dyad errors, while site-control mechanisms produce polymers with isolated *rr*-triad errors.

## II. Olefin Polymerization

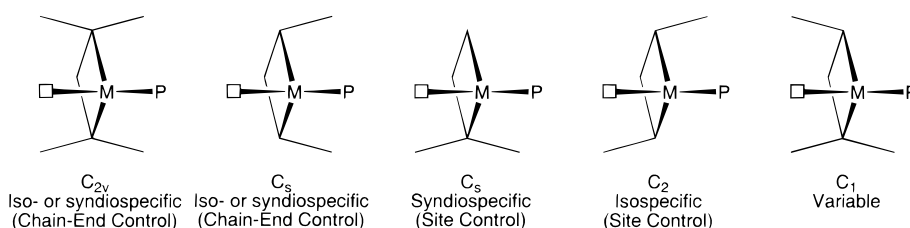
Soon after Ziegler and Natta discovered heterogeneous olefin polymerization catalysts in the mid-1950s, efforts were directed toward devising homogeneous catalyst model systems that would prove more amenable to study. In 1957, Natta and Breslow reported that the metallocene  $\text{Cp}_2\text{TiCl}_2$  ( $\text{Cp}$  = cyclopentadienyl) could be activated for olefin polymerization by  $\text{Et}_3\text{Al}$  or  $\text{Et}_2\text{AlCl}$ .<sup>17–19</sup> These soluble catalysts polymerized ethylene but were inactive for propylene and exhibited much lower activities than the heterogeneous systems. This situation changed dramatically in the early 1980s when Sinn and Kaminsky discovered that partially hydrolyzed  $\text{Me}_3\text{Al}$ , called methylaluminoxane (MAO), activated group IV metallocenes for the polymerization of both ethylene and  $\alpha$ -olefins.<sup>20,21</sup> This discovery has stimulated

a renaissance in single-site catalysis, with olefin polymerization clearly receiving the most attention. The development of well-defined polymerization catalysts has provided the opportunity to study the mechanisms of initiation, propagation, and termination steps of Ziegler–Natta polymerization reactions. These well-defined systems also provide extraordinary synthetic opportunities in the field of polymer science.

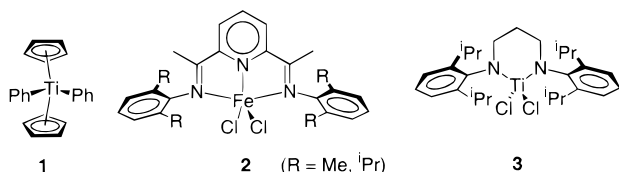
Concerning the organometallic chemistry of olefin insertion,<sup>22,23</sup> it is now clear that in most cases the active catalytic species for olefin polymerization are coordinatively unsaturated metal alkyls of the formula  $[\text{L}_n\text{M}-\text{P}]^+[\text{A}]^-$ , where P is a polymer chain, and A is a weakly coordinating anion. Many convenient methods for generating these species are now available; among the most used are reaction of a metal dihalide  $[\text{L}_n\text{MX}_2]$  with MAO or the reaction of a metal dialkyl  $[\text{L}_n\text{MR}_2]$  with either fluorinated boranes,<sup>24–28</sup> borate salts,<sup>29–34</sup> or aluminate salts.<sup>35</sup>

### A. Aliphatic $\alpha$ -Olefins

The polymerization of aliphatic olefins, in particular propylene, has received a tremendous amount of attention in the last 15 years. This topic is subject of a comprehensive review by Resconi et al. in this issue of *Chemical Reviews*; therefore, this review will focus on key advances concerning stereoselective olefin polymerization. After examination of the results of many separate investigations, a predictable relationship between complex symmetry and polymer tacticity is revealed.<sup>36–38</sup> Single-site polymerization catalysts can be divided into five main symmetry categories (Figure 2). It is assumed that the polymer rapidly equilibrates with the available coordination site for the purposes of assigning symmetry. Catalysts exhibiting  $\text{C}_{2v}$  symmetry typically produce atactic polymers or moderately stereoregular polymers by chain-end control mechanisms.  $\text{C}_s$ -symmetric catalysts that have mirror planes containing the two diastereotopic coordination sites behave similarly. However  $\text{C}_s$ -symmetric catalysts that have a mirror plane reflecting two enantiotopic coordination sites frequently produce syndiotactic polymers.  $\text{C}_2$ -symmetric complexes, both *racemic* mixtures and enantiomerically pure ones, typically produce isotactic polymers via a site-control mechanism. Stereoselectivities of asymmetric ( $\text{C}_1$ ) complexes are unpredictable and have been reported to produce polymer architectures ranging from highly isotactic, to atactic, including isotactic–atactic stereoblock and hemisotactic. Clearly there are important exceptions to these basic guidelines, and they will be highlighted. Al-



**Figure 2.** General symmetry classifications, based on ligand geometries, of catalysts and their stereoselectivities for polyolefin synthesis.



**Figure 3.**  $C_{2v}$ -symmetric catalyst precursors for the synthesis of isotactic polymers.

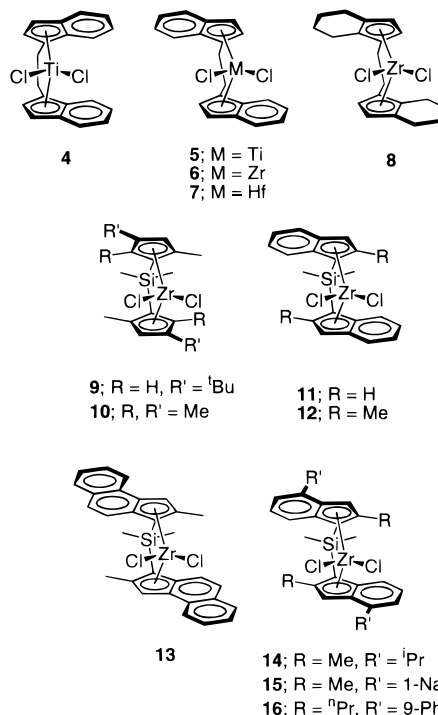
though the following section will emphasize propylene polymerization, these catalysts are generally applicable for the stereoselective polymerization of other  $\alpha$ -olefins as well.

### 1. Isotactic Polymers

In 1954, Natta's first experiments with propylene polymerization using heterogeneous catalysts yielded products that were mixtures of atactic and isotactic polymer chains. Shortly thereafter, Natta produced polymers that consisted primarily of isotactic chains by modifying the composition of the catalyst. The modification of group IV metallocenes to produce catalysts capable of isospecific polymerization has developed much more slowly but has recently seen dramatic success. These advances are outlined below.

**$C_{2v}$ -Symmetric Catalysts.** Prior to the mid-1980s, catalysts formed using achiral  $Cp_2MCl_2$  precursors were found to produce only atactic polypropylene (which, incidentally, cannot be obtained in the pure form directly from heterogeneous catalysts). In 1984, Ewen first reported the use of metallocene-based catalysts for the isospecific polymerization of propylene.<sup>39</sup> The polymerization of propylene at  $-45\text{ }^\circ\text{C}$  using a  $Cp_2TiPh_2$  (**1**)/MAO catalyst system produced a partially isotactic polymer with a *mmmm*-content of 52% ( $P_m = 0.85$ ) (Figure 3).  $^{13}\text{C}$  NMR analysis of the polymers formed using **1** as well as other achiral titanocenes have revealed stereochemical errors that are consistent with a chain-end control mechanism (*[mmmm]:[mmrm]* ratio of 1:1).<sup>39,40</sup> Interestingly, the related complex  $(^i\text{PrCp})_2TiCl_2$  produces either isotactic or syndiotactic polypropylene, depending on the temperature of the polymerization.<sup>41</sup> Using this catalyst, the tacticity of the polymer changed from slightly isotactic at  $-50\text{ }^\circ\text{C}$  ( $P_m = 0.8$ ) to atactic at  $-10\text{ }^\circ\text{C}$  ( $P_m = 0.5$ ) to slightly syndiotactic at  $+10\text{ }^\circ\text{C}$  ( $P_m = 0.4$ ). Brookhart has reported that iron complexes (**2**)<sup>42,43</sup> bearing bis(imino)pyridyl ligands activated by MAO produce isotactic polypropylene at  $-20\text{ }^\circ\text{C}$  with *mmmm*-contents as high as 67% ( $P_m = 0.90$ ).<sup>44</sup> Mechanistic studies revealed an unusual 2,1-insertion mechanism that likely plays an important role in stereoregulation. Soga has discovered that a titanium bis(amido) complex (**3**) originally reported by McConville<sup>45,46</sup> produces isotactic polypropylene (*[mmmm]* = 0.79;  $\alpha = 0.95$ ) via a site-control mechanism (*[mmmm]:[mmrr]:[mrrm]* = 2:2:1), suggesting the loss of  $C_{2v}$  symmetry.<sup>47</sup> The origin of the symmetry mutation is not currently clear. Activation of the complex with  $^i\text{Bu}_3\text{Al}[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  is essential for isotacticity; interestingly, other alkylaluminums investigated ( $\text{Me}_3\text{Al}$ ,  $\text{Et}_3\text{Al}$ ) only produced atactic polymer.

**$C_2$ -Symmetric Catalysts.** It is now clear that the most successful catalysts for isospecific olefin polym-



**Figure 4.** Bridged  $C_2$ -symmetric catalyst precursors for the synthesis of isotactic polymers.

erization are those with a bridging group, forming a rigid,  $C_2$ -symmetric chelating ligand structure. The explosion of research in this area can be traced to Ewen's 1984 publication that reported the synthesis of moderately isotactic polypropylene using the chiral *ansa*-metallocenes first prepared by Brintzinger<sup>48</sup> (Figure 4).<sup>39</sup> Using a mixture of MAO-activated *meso* (**4**) and *racemic* (**5**) *ansa*- (or "bridged") titanocenes, Ewen produced a mixture of atactic and isotactic polymer chains. In 1985, Kaminsky and Brintzinger confirmed Ewen's proposal that the chiral metallocene isomer was responsible for the formation of the isotactic polypropylene by using an isomerically pure tetrahydroindenyl zirconocene (**8**) to produce only isotactic polymer chains.  $^{13}\text{C}$  NMR spectroscopic analysis of the isotactic polymer formed using this catalyst revealed the anticipated enantiomeric site control mechanism. Ewen later explored the catalytic properties of the isostructural zirconium (**6**) and hafnium (**7**) complexes.<sup>49</sup> Even though the activities and stereoselectivities of **6** and **7** are nearly identical, the hafnium catalyst produces polymers of significantly higher molecular weights.

Although these chiral metallocenes stimulated an enormous amount of interest, their activities as well as the isotacticity and molecular weight of polymers produced were certainly inferior to their industrial heterogeneous counterparts. Nevertheless an attractive feature of Brintzinger's bridged metallocene system is that the ligands are easily modified, permitting an empirical yet rational optimization process. Brintzinger and Mise subsequently reported highly selective silyl-bridged Cp-based metallocenes for propylene polymerization (**9**, **10**).<sup>50-52</sup> These complexes display impressive isospecificity for propylene polymerization; however their activities are significantly lower than their indenyl-based counterparts



**Table 1. Polymerization of Propylene with Bridged,  $C_2$ -Symmetric Zirconocene Catalysts<sup>a</sup>**

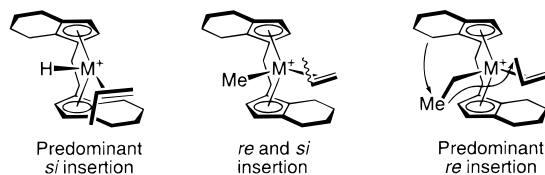
| metallocene                   | productivity <sup>b</sup> | $T_m$<br>(°C) | $M_w$   | [ <i>mmmm</i> ] | ref |
|-------------------------------|---------------------------|---------------|---------|-----------------|-----|
| <b>6</b>                      | 188                       | 132           | 24 000  | 0.78            | 58  |
| <b>9</b>                      | 5 <sup>c</sup>            | 149           | 4 000   | 0.97            | 51  |
| <b>10</b>                     | 1.6 <sup>d</sup>          | 162           | 134 000 | 0.977           | 50  |
| <b>11</b>                     | 190                       | 137           | 36 000  | 0.82            | 58  |
| <b>12</b>                     | 99                        | 145           | 195 000 | 0.88            | 58  |
| <b>13</b>                     | 403                       | 146           | 330 000 | 0.89            | 58  |
| <b>14</b>                     | 245                       | 150           | 213 000 | 0.89            | 58  |
| <b>15</b>                     | 875                       | 161           | 920 000 | 0.991           | 58  |
| <b>16</b>                     | 47                        | 160           | 400 000 | 0.992           | 62  |
| "4th generation" <sup>e</sup> | 20                        | 162           | 900 000 | >0.99           | 60  |

<sup>a</sup> Liquid propylene, 50 °C. <sup>b</sup> kg of PP/(mmol of M·h). <sup>c</sup> 28 psi propylene, 50 °C. <sup>d</sup> 42 psi propylene, 30 °C. <sup>e</sup> 4th generation heterogeneous Ziegler–Natta catalyst.

(Table 1). Bercaw and Yasuda have reported neutral ytrocene catalysts with a similar ligand design; although activities and molecular weights are low, stereoselectivities for propylene, butene, pentene, and hexene are very high ([*mmmm*] ~ 0.97).<sup>53–55</sup>

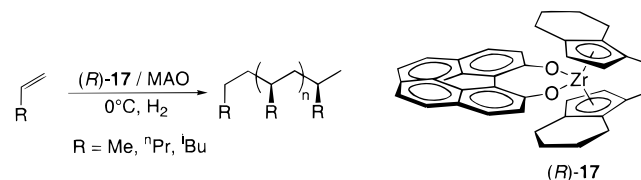
In the decade following the discovery of isospecific metallocene catalysts, scientists at Hoechst made significant progress at developing a new class of catalysts that rivaled their state-of-the-art heterogeneous competitors in virtually every respect.<sup>56–60</sup> Shown in Figure 4 are a progression of catalysts (**11**–**15**) that depict this evolution. Replacement of the ethane bridge of **6** with a shorter dimethylsilyl linker (**11**) increased the molecular weight and isotacticity of the polypropylene produced, thus also its melting point (Table 1).<sup>57</sup> Attachment of methyl groups in the 2-position of the indenyl ligand (**12**) halved activity versus **11** but increased molecular weight by a factor of 5.<sup>57</sup> The methyl group serves to significantly increase the regioselectivity for a 1,2-primary insertion of propylene, thereby reducing the formation of bulky secondary alkyl species ( $L_nM^+-CHMeP$ ) that favor chain-transfer relative to propagation. Spaleck and co-workers at Hoechst, as well as Brintzinger and co-workers, have reported that modification of the front rim (4-position) of the indenyl ligand results in dramatically improved performance.<sup>57,58,61</sup> Compounds **13**–**15** show significant enhancement in activity over compound **12**. Addition of 1-naphthyl groups in the 4-position of the indenyl produces a catalyst precursor (**15**) that is superior in virtually all respects to previously reported metallocenes. Recently, Kojoh has reported a metallocene with a 9-phenanthryl group in the 4-position of the indenyl ligand (**16**) that produces highly isotactic polypropylene.<sup>62</sup> Included in Table 1 for comparison are the specifications of a commercial "4th-generation" heterogeneous catalyst.<sup>60</sup>

One of the significant advantages of these homogeneous catalysts is that they permit detailed mechanistic studies. Elegant investigations have now revealed details about these homogeneous catalyst systems that not only permit the development of improved metallocene systems but also provide an insight into the heterogeneous catalysts that produce the vast majority of polypropylene today. Mechanistic studies concerning (1) enantiofacial selectivity, (2) origin of enantiomeric-site control, and (3)  $\alpha$ -ago-



**Figure 5.** Enantiofacial selectivity of insertion into M–H, M–Me, and M–Et bonds. Chirality of the ligand is relayed to the incoming monomer through the  $\beta$ -carbon of the metal–alkyl group.

### Scheme 2. Asymmetric Olefin Oligomerization Using Bridged, $C_2$ -Symmetric Catalysts

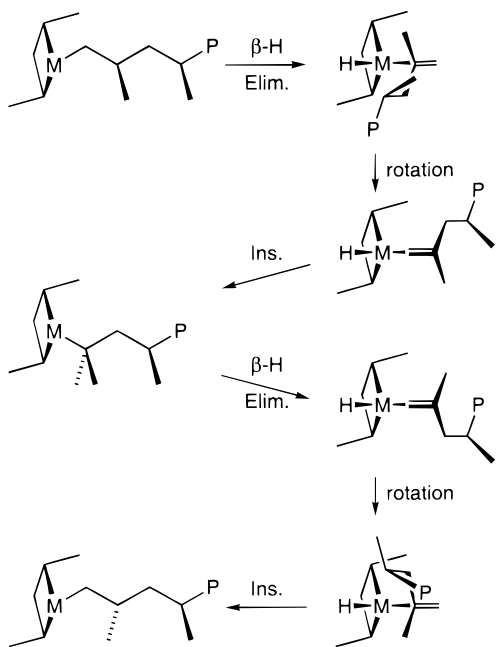


stic assisted olefin insertion and their relevance to stereocontrol are discussed below.

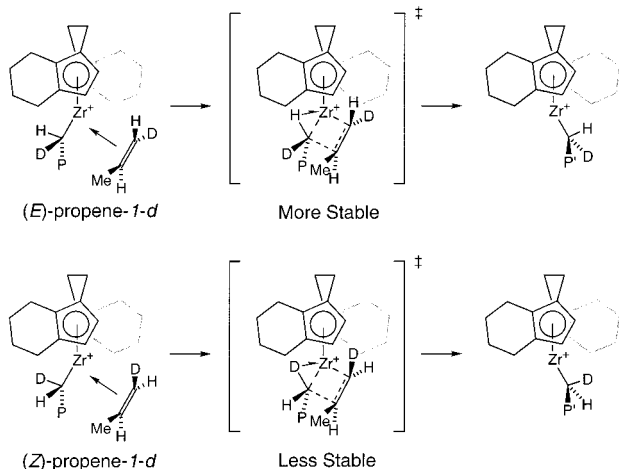
One of the beneficial features of homogeneous compounds over their insoluble counterparts is that they can be resolved into enantiomerically pure species. Pino first used this advantage to determine the enantiofacial preference of  $C_2$ -symmetric catalysts for olefin polymerization.<sup>63,64</sup> Reaction of propylene with **17**/MAO in the presence of hydrogen formed optically active oligomers (Scheme 2). Comparison of their optical rotations with those of known compounds allowed the assignment of the facial preference of olefin insertion (vide infra). Kaminsky also synthesized optically active olefin-terminated oligomers using a related chiral zirconocene and confirmed Pino's assignment.<sup>65</sup>

Zambelli has employed the chiral metallocene (**5**) to study the origin of enantiofacial selectivity of olefin insertion and discovered that the insertion of propylene into a M–Et bond proceeds with a high degree of enantiofacial selectivity, while the insertion into a M–Me bond occurs without selectivity (Figure 5).<sup>66,67</sup> Pino later reported that the insertion of propylene into a metal–polymer bond and a M–H bond occur with an opposite facial selectivity (Figure 5).<sup>68</sup> These results demonstrate that the high degree of stereoselectivity of these catalysts is contingent upon insertion into a M–R bond, where R is an alkyl group consisting of two or more carbon atoms. Conformational modeling studies by Corradini suggest that the polymer chain is forced into an open region of the metallocene, thereby relaying the chirality of the metallocene to the incoming monomer through the orientation of the  $\beta$ -carbon of the alkyl chain (Figure 5).<sup>69</sup> As these chiral metallocenes have  $C_2$  symmetry, both reaction sites are homotopic and therefore selective for the same olefin enantioface. The result is polymerization to yield an isotactic polyolefin. Interestingly, recent mechanistic studies by Busico,<sup>70–75</sup> Brintzinger,<sup>76,77</sup> and Resconi<sup>78</sup> have revealed that chain-end epimerization is often the source of stereoerrors in metallocene-formed polymers, not insertion of the incorrect enantioface (Scheme 3).

### Scheme 3. Chain-End Epimerization as a Source of Stereochemical Impurities

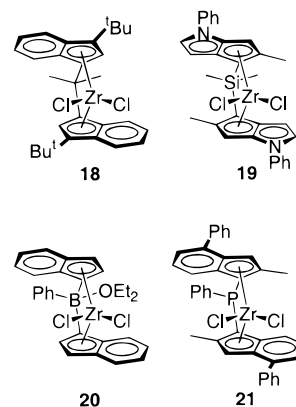


### Scheme 4. $\alpha$ -Agostic Assistance during Olefin Insertion Using Bridged, $C_2$ -Symmetric Catalysts



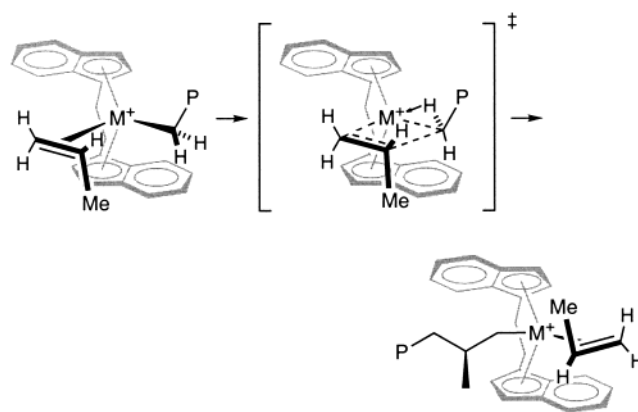
Elegant studies by Bercaw<sup>79,80</sup> and Brintzinger<sup>77,81</sup> using an isotopic labeling technique developed by Grubbs<sup>82,83</sup> have revealed that olefin insertion can be assisted by  $\alpha$ -agostic interactions<sup>84,85</sup> in many metallocene polymerization systems. Brintzinger used **8**/MAO to polymerize (*E*)-propene-1- $d_1$ ; the resultant polymer had a molecular weight about 1.3 times that made from the (*Z*)-isomer. This result implicates an  $\alpha$ -agostic effect that rigidifies the transition state for olefin insertion and thus increases the stereoselectivity (Scheme 4).<sup>77</sup> Together, these studies paint a detailed view of the mechanism of stereoselection using chiral metallocenes for olefin polymerization, as depicted in Scheme 5.

The effect of varying the bridged metallocene structure on the degree of stereoselectivity of the polymerization reaction has been the subject of intense investigation. Principally, the catalyst can be varied in three ways: (1) modification of the bridge; (2) modification of the  $\eta^5$ -ligand; (3) variation of the



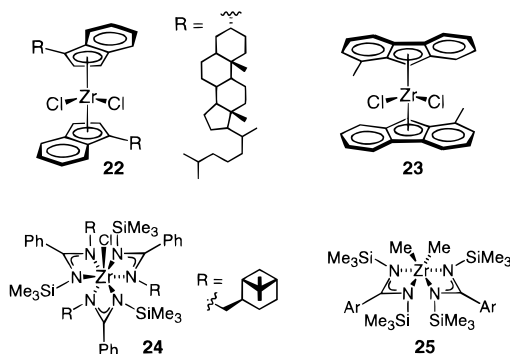
**Figure 6.** Modified  $C_2$ -symmetric catalyst precursors for isospecific olefin polymerization.

### Scheme 5. Proposed Mechanism of Isospecific Polymerization



activator (Figure 6). Resconi has reported that placement of *tert*-butyl groups in the 3-positions of  $\text{Me}_2\text{C}(\text{Ind})_2\text{ZrCl}_2$  (**18**; Ind = indenyl) dramatically improves the molecular weight and isotacticity of polymers produced, with *mmmm* contents as high as 97% at 20 °C.<sup>86</sup> Ewen has discovered that replacing the annulated benzene ring of **12** with an *N*-phenylpyrrole ring produces a catalyst (**19**) with isospecificity comparable to that of **18**.<sup>87</sup> Reetz<sup>88</sup> and Schaverien<sup>89</sup> have replaced the standard dimethylsilyl bridge of chiral metallocenes with phenyl-substituted boron (**20**) and phosphorus bridges (**21**). Polypropylenes produced with **20** at 20 °C<sup>88</sup> and **21** at 50 °C<sup>89</sup> had high molecular weights and *mmmm* contents of 96 and 98%, respectively. One appealing strategy for modifying the stereoselectivity of known metallocene systems has been reported by Marks, where activation of the dimethyl version of **11** with  $[\text{Ph}_3\text{C}][(\text{F}_9\text{-biphenyl})_3\text{AlF}]$  produces highly isotactic polypropylene ( $[\text{mmmm}] = 0.98$ ), in contrast to the MAO-activated **11**.<sup>35</sup>

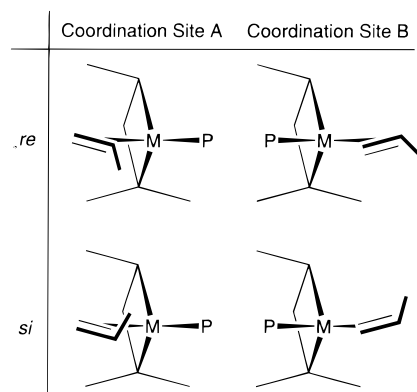
In retrospect, it is now clear that the most successful catalysts for isospecific olefin polymerization are those with rigid, chelating ligand structures. However a significant amount of research has been devoted to unbridged ligand sets, where carefully placed substituents can yield catalysts that display temporal  $C_2$  symmetry (Figure 7). In several cases, catalysts with impressive degrees of stereochemical control have been discovered despite the lack of a bridge that locks in axial symmetry.



**Figure 7.** Unbridged catalyst precursors for the synthesis of isotactic polymers.

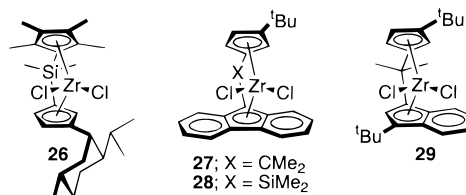
Erker and co-workers investigated a wide range of unbridged metallocenes for isospecific polymerization.<sup>90–100</sup> By placement of a 3- $\alpha$ -cholestanyl group on each 1-position of (Ind)<sub>2</sub>ZrCl<sub>2</sub>, a complex (**22**) was formed that, when activated by MAO, produced isotactic polypropylene via a site-control mechanism ( $-30\text{ }^\circ\text{C}$ ;  $[mmmm] = 0.80$ ).<sup>97</sup> In general, catalysts of this type only yield moderately isotactic polypropylene when reacted at room temperature or above. In addition, formation of isomerically pure zirconocenes from indenyl ligands with enantiomerically pure, chiral groups in the 1-position is challenging due to the possible formation of three diastereomers. Razavi has shown that metalation of the achiral ligand 1-methylfluorene forms the diastereomerically pure  $C_2$ -symmetric zirconocene **23**.<sup>101</sup> Activation of **23** with MAO and reaction with propylene at  $60\text{ }^\circ\text{C}$  forms isotactic polymer by a site-control mechanism ( $[mmmm] = 0.83$ ). Eisen recently reported that  $C_3$ -symmetric zirconium tris(benzamidinate) and  $C_2$ -symmetric zirconium bis(benzamidinate) complexes (**24**, **25**) form highly isotactic polypropylene when activated with MAO ( $[mmmm] = 0.95\text{--}0.99$ ).<sup>102,103</sup> Although the nature of the active species (especially in the case of **24**) has not been determined, generation of  $C_2$ -symmetric bis(benzamidinate)Zr<sup>+</sup>-R catalysts are proposed given that a site-control polymerization mechanism operates. Starzewski has synthesized an unbridged zirconocene where an interligand donor/acceptor interaction forms a rigid, chiral complex. Activation of the zirconocene with <sup>t</sup>Bu<sub>3</sub>Al in combination with [PhNHMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] produces isotactic polypropylene, with  $[mmmm] = 0.92$ .<sup>104</sup>

**Asymmetric Catalysts.** The control of polymer stereochemistry using asymmetric ( $C_1$  point group) catalysts is conceptually more complicated than using  $C_2$ -symmetric variants that contain homotopic coordination sites. Since  $C_1$  catalysts have inequivalent, diastereotopic sites (A, B) for olefin coordination, several stereochemical scenarios are possible (Figure 8). These processes will depend on the following: (1) the sequence and frequency of insertion at the two sites; (2) the enantiofacial selectivity at each site ( $P_{re,A}$ ,  $P_{re,B}$  = probability of insertion of *re*-face of monomer at sites A and B, respectively). Three pathways can yield isotactic polypropylene (pathways 1, 2, 4; Figure 8): (1) Insertion occurs at only one site, and the facial selectivity of this site is very high. (2) Insertion occurs randomly at two homotopic sites. (3) Insertion occurs in an alternated sequence at two



| Pathway | Insertion   | $P_{re,A}$ | $P_{re,B}$ | Outcome        |
|---------|---|------------|------------|----------------|
| 1       | Site A Only                                       | 1          | -          | Isotactic      |
| 2       | Random  | 1          | 1          | Isotactic      |
| 3       | Random  | $\geq 0.5$ | $\leq 0.5$ | Atactic        |
| 4       | (AB) <sub>x</sub>                                 | 1          | 1          | Isotactic      |
| 5       | (AB) <sub>x</sub>                                 | 1          | 0          | Syndiotactic   |
| 6       | (AB) <sub>x</sub>                                 | 1          | 0.5        | Hemioisotactic |
| 7       | [(A) <sub>n</sub> (B) <sub>m</sub> ] <sub>x</sub> | 1          | 0.5        | Stereoblock    |
| 8       | Random  | 1          | 0.5        | Stereoblock    |

**Figure 8.** Stereochemical pathways of  $C_1$  catalysts. (AB)<sub>x</sub> refers to the alternated insertion at sites A and B. [(A)<sub>n</sub>(B)<sub>m</sub>]<sub>x</sub> refers to the sequence of *n* insertions at site A, followed by *m* insertions at site B.  $P_{re,A}$  and  $P_{re,B}$  refer to the probabilities of insertion of the *re*-face when the monomer coordinates at sites A and B, respectively.

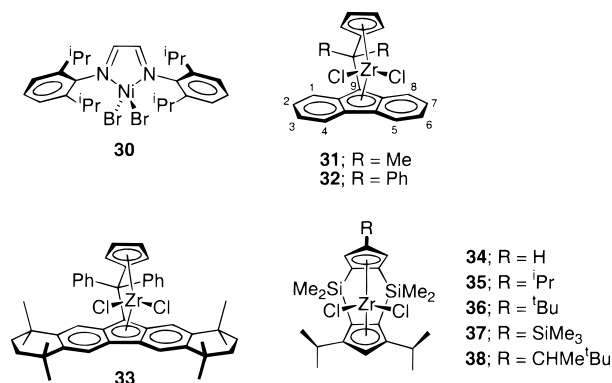


**Figure 9.** Asymmetric ( $C_1$ ) catalyst precursors for the synthesis of isotactic polymers.

homotopic sites. Since migratory insertion moves the polymer from one site to the other through a metal-cyclobutane transition state, pathway 1 requires a site epimerization (“insertionless migration”) where the polymer moves from one side to the other to allow repetitive insertions at the same site. All three pathways produce isotactic polymers by site-control mechanisms.

Highly isospecific  $C_1$  catalysts for propylene have been developed (Figure 9). Marks has synthesized a series of metallocenes of the formula Me<sub>2</sub>Si(Me<sub>4</sub>Cp)-(3-R<sup>\*</sup>Cp)ZrMe<sub>2</sub>, where R<sup>\*</sup> is a chiral substituent.<sup>105,106</sup> Activation of the complex with R<sup>\*</sup> = neomenthyl (**26**) using [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and reaction with propylene at  $0\text{ }^\circ\text{C}$  forms isotactic polymer ( $[mmmm] = 0.95$ ). Compounds of the formula X(3-<sup>t</sup>BuCp)(Fl)ZrCl<sub>2</sub> (**27**, X = Me<sub>2</sub>C; **28**, X = Me<sub>2</sub>Si; Fl = fluorenyl) form isospecific catalysts for propylene polymerization when activated with MAO.<sup>107–112</sup> Metallocene **27** is more selective, producing a polymer with  $[mmmm] = 0.95$  at  $30\text{ }^\circ\text{C}$ . Molecular modeling suggests that the polymer chain occupies the open quadrant of the active site, and the monomer inserts after coordination on the more crowded side, with the methyl pointed away from the *tert*-butyl group.<sup>111</sup> Miyake has discovered that *threo*-Me<sub>2</sub>C(3-<sup>t</sup>BuCp)(3-





**Figure 10.** Catalyst precursors for the synthesis of syndiotactic polymers.

$t$ BuInd)MCl<sub>2</sub>/MAO (M = Ti, Zr, Hf) all form highly isotactic polypropylene.<sup>113</sup> In the case when M = Zr (**29**), the polymers formed between 0 and 60 °C have a *mmmm*-pentad content of >98%, although molecular weights are low ( $M_w = 9000$ ) at the higher reaction temperature. Catalysts **26–29** form isotactic polymers via enantiomorphic site control. Although it is not clear in these four examples which pathway of Figure 8 is in operation, molecular modeling suggest that pathway 1 operates in the case of **27/28**.<sup>111</sup>

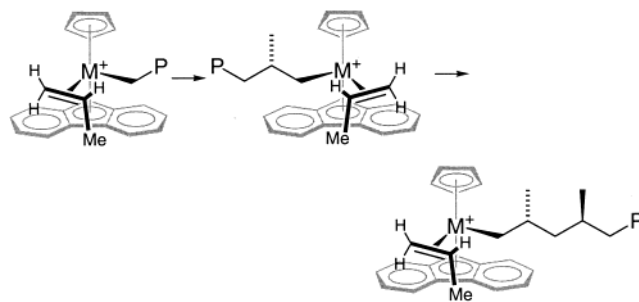
## 2. Syndiotactic Polymers

In 1962, Natta and Zambelli reported a heterogeneous, vanadium-based catalyst mixture which produced partially syndiotactic polypropylene at low polymerization temperatures.<sup>114</sup> The regiochemistry of the insertion was determined to be a 2,1-insertion of propylene, and a chain-end control mechanism determined the syndiospecificity of monomer insertion. This catalyst system suffered from both low activity and low stereoselectivity. Highly active single-site olefin polymerization catalysts have now been discovered that make syndiotactic polypropylene with nearly perfect stereochemistry. Catalysts of two different symmetry classes have been used to make the polymer, with  $C_s$ -symmetric catalysts typically outperforming their  $C_{2v}$ -symmetric counterparts due to different mechanisms of stereocontrol (Figure 10).

**$C_{2v}$ -Symmetric Catalysts.** Syndiotactic polymers have been formed using metallocene catalysts where the polymer chain end controls the syndiospecificity of olefin insertion. Resconi has shown that  $\text{Cp}^*_2\text{MCl}_2$  (M = Zr, Hf) derived catalysts produce predominantly syndiotactic poly(1-butene) with an approximate 2 kcal/mol preference for syndiotactic versus isotactic dyad formation.<sup>115</sup> At  $-20$  °C,  $\text{Cp}^*_2\text{HfCl}_2/\text{MAO}$  produces poly(1-butene) with 77% *rr* triads. Pellecchia had reported that the diimine-ligated nickel complex **30** forms moderately syndiotactic polypropylene at  $-78$  °C when activated with MAO ( $[rr] = 0.80$ ).<sup>116–118</sup> Olefin insertion was shown to proceed by a 1,2-addition mechanism,<sup>118</sup> in contrast to the related iron-based systems which insert propylene with 2,1-regiochemistry.<sup>44</sup>

**$C_s$ -Symmetric Catalysts.** Ewen has reported a metallocene catalyst precursor (**31**) that is highly active for the syndiospecific polymerization of propylene and

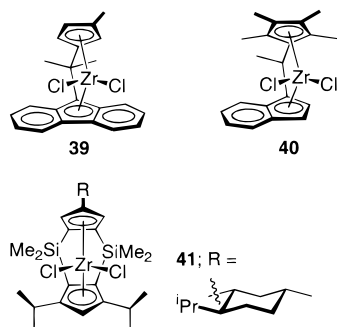
## Scheme 6. Proposed Mechanism of Syndiospecific Polymerization



higher aliphatic  $\alpha$ -olefins (Figure 10).<sup>119</sup> The <sup>13</sup>C NMR spectrum for polypropylene produced at 25 °C contains 86% *rrrr* pentads, indicative of a high degree of stereocontrol. It is now generally accepted that the mechanism of stereocontrol consists of the regularly alternating insertion of olefins at the enantiotopic sites of the  $C_s$ -symmetric complex (Scheme 6).<sup>120–122</sup> It is interesting that the related complex **27** undergoes site epimerization during polymerization, while such an isomerization does not appear to occur with **31**. Guerra has suggested that an  $\alpha$ -agostic structure in the active species of **31** restricts the polymer chain from undergoing isomerization.<sup>121</sup> Occasional misinsertion of the incorrect enantioface is proposed to be the predominant source of defects (*rmrr*), although chain end epimerization cannot be ruled out. Defects corresponding to chain migration without olefin insertion (*rmr*) have also been detected.<sup>123</sup> Hafnocenes are typically less syndiospecific than their zirconocene counterparts, although they make polymers of higher molecular weight.<sup>119,124</sup> A wide variety of modifications have been made to the ligand structure. Notably, a  $\text{Ph}_2\text{C}$  bridge<sup>125</sup> (**32**) slightly improves syndiospecificity, while catalysts  $(\text{CH}_2)_2$ <sup>110,126,127</sup> and  $\text{Me}_2\text{Si}$ <sup>128,129</sup> bridges produce polymer of decreased tacticity. Although substitution in the 2-, 3-, 6-, and 7-positions of the fluorenyl ring typically does little to the stereoselectivity of **31/32**,<sup>130,131</sup> Bercaw has reported that placing significant bulk in these positions remarkably improves the stereoselectivity.<sup>132</sup> Complex **33** produces syndiotactic polypropylene with a  $[rrrr] > 0.99$ , which is the most stereoregular syndiotactic polypropylene reported. Modification of **31** in the 4- and 5-positions has a detrimental effect on syndiospecificity.<sup>107</sup> Replacing the annulated benzene rings of **31** with thiophene rings produces a catalyst with lower activity and syndiospecificity.<sup>87</sup>

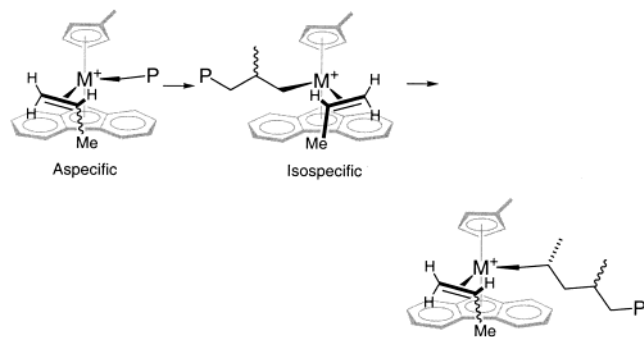
By taking into account the deleterious effects of substituents in the 4- and 5-positions of **31**, Bercaw has designed novel  $C_s$ -symmetric doubly bridged zirconocenes for the synthesis of syndiotactic polypropylene.<sup>133–136</sup> Compounds **34–37** when activated with MAO form polypropylene at 0 °C in liquid propylene with  $[rrrr]$  greater than 0.84; compound **35** is the most selective with an impressive  $[rrrr]$  content of 0.989. Converting the 3,5- $i$ -Pr groups of **35** to  $\text{SiMe}_3$  substituents results in a significant decrease in syndiotacticity of the polymer.<sup>134</sup> The syndiospecificities of these catalysts are strongly dependent upon monomer concentration; at low monomer pressures, site epimerization competes with insertion causing





**Figure 11.** Asymmetric ( $C_1$ ) catalyst precursors for the synthesis of hemiisotactic polymers.

### Scheme 7. Proposed Mechanism of Hemiispecific Polymerization



stereoerrors of the type *rmr* to occur. Stereoerrors of the type *rmmr* are attributed to chain-end isomerization on the basis of a deuterium labeling study; enantiofacial misinsertion is not a significant source of stereochemical impurities in these polymers.<sup>136</sup> As expected, complexes of type **34**–**37** are also highly syndiospecific for other  $\alpha$ -olefins. Interestingly, when R is a CHMe<sup>t</sup>Bu group (**38**) the catalyst's  $C_s$  symmetry is broken, and the polymer microstructure becomes predominantly isotactic when the reaction is run at lower concentrations of propylene at 25 °C. It is proposed that, under these reaction conditions, site epimerization can now compete with insertion, allowing pathway 1 of Figure 8 to operate.

### 3. Hemiisotactic Polymers

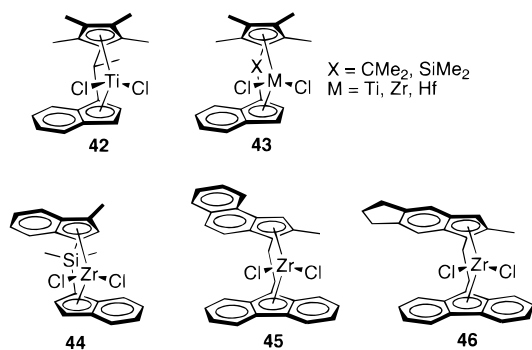
Hemiisotactic polymers are alternated polymers where isospecific monomer placements are separated by units of random stereochemistry. Ewen has developed a catalyst (**39**) which polymerizes propylene to hemiisotactic polypropylene (Figure 11).<sup>107</sup> Metallocene **39** has two different coordination sites—one which is isospecific and one which is aspecific. When used for propylene polymerization, the alternation between iso- and aspecific sites results in a hemiisotactic polymer (Scheme 7).<sup>137</sup> As with the related metallocene **31** which produces syndiotactic polypropylene, site epimerization is repressed during the reaction. Thus catalysts derived from **31**, **39**, and **27** represent an intriguing series where the addition of a group of increasing size to the cyclopentadienyl ligand causes a dramatic stereoselectivity change from syndiotactic, to hemiisotactic, and finally to isotactic. As with precatalysts **27** and **31**, the hafnium analogue of **39** also produces hemiisotactic polypropylene.<sup>125</sup>

The polymer made by Ewen using **39** was readily characterized since Farina had previously prepared this hemiisotactic material by an alternate route.<sup>138</sup> Microstructural analysis using <sup>13</sup>C NMR spectroscopy revealed the virtual absence of methyl shifts due to isolated *r* or *m* dyads (*mrmr*, *rmrr*, and *mrmm* pentads are absent) and the appropriate ratio of the remaining pentads<sup>139,140</sup> which is consistent with the hemiisotactic microstructure. Razavi has suggested the polymer might actually have an isotactic–syndiotactic stereoblock microstructure.<sup>125</sup> Such a polymer should have a  $[mmmr]:[mmrr]:[mrrr]$  ratio of 1:1:1, which was not experimentally verified. Alt has replaced the 3-methyl moiety of **39** with a 3-(3-butenyl) group, resulting in no significant change in catalytic behavior.<sup>141</sup> Chien and co-workers have claimed that the asymmetric zirconocene **40** produces hemiisotactic polypropylene, yet the pentad ratios reported in the paper do not agree with Ewen and Farina's reported values.<sup>142</sup> Bercaw has discovered that asymmetric zirconocenes **38** and **41** produce hemiisotactic-like polypropylene when the propylene concentration is carefully varied to yield 50% *m* dyads in the polymer.<sup>136</sup> Unlike **39**, catalysts formed using **38** and **41** show a strong microstructural dependence on monomer concentration (vide supra). Therefore highly hemiisotactic polymers are more challenging to prepare using these catalysts.

### 4. Stereoblock Polymers

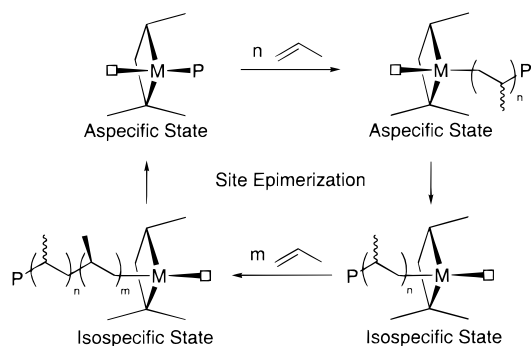
In the late 1950s, Natta reported that polypropylene formed from the heterogeneous catalyst TiCl<sub>4</sub>/Et<sub>3</sub>Al could be fractionated into three fractions: (1) an atactic portion soluble in acetone and ether; (2) a highly isotactic portion insoluble in refluxing heptane; (3) a partially crystalline portion of intermediate solubility.<sup>143,144</sup> This third fraction exhibited elastomeric properties, and on the basis of its solubility as well as thermal and mechanical properties, it was assigned an atactic–isotactic stereoblock microstructure. Such a polymer is of immense commercial interest due to its thermoplastic elastomeric properties.<sup>145–149</sup> There is general agreement today that Natta's block structure designation is indeed correct. Despite many detailed studies of this and related systems, the mechanism of formation of this unusual polymer is not known. Two reasonable mechanisms are (1) transfer of polymer chains between aspecific sites and isospecific sites of the multisited catalyst and (2) structural rearrangements of certain sites that temporarily decrease then restore stereoselectivity.<sup>150,151</sup> The advent of homogeneous, single-site catalysts has provided excellent mechanistic opportunities to model the nature of such systems, as well as to develop catalysts that produce novel and commercially important stereoblock polymers. These new systems can be divided into three main categories: (1) asymmetric ( $C_1$  point group) catalysts; (2) oscillating catalysts; (3) binary catalyst mixtures.

**Asymmetric Catalysts.** The first synthesis of a uniform elastic homopolymer of propylene was reported by Chien in 1990.<sup>152–161</sup> The polymer was made using an asymmetrically substituted *ansa*-titanocene complex **42** which was activated by MAO



**Figure 12.** Asymmetric ( $C_1$ ) catalyst precursors for the synthesis of stereoblock polymers.

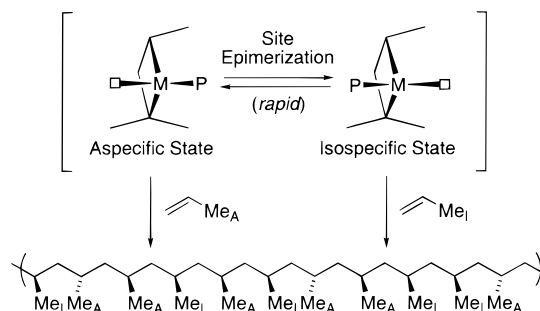
### Scheme 8. Site Epimerization Mechanism for Synthesizing Stereoblock Polymers



(Figure 12).<sup>153</sup> The catalyst exhibits high initial activity but undergoes rapid deactivation after short reaction times. Interestingly, the zirconium analogue has only a low activity for forming predominantly atactic polymer. The polymers synthesized at 25 and 50 °C using **42** are completely soluble in refluxing ether and exhibit narrow molecular weight distributions. Differential scanning calorimetry of the polymer formed at 50 °C revealed two low melting endotherms at approximately 51 and 66 °C. The <sup>13</sup>C NMR spectrum of the polymer revealed  $[mmmm] = 0.40$ . A microstructural analysis suggested the presence of 10 atactic blocks per chain, each of which contained 100 propylene units, while the isotactic blocks between have only 50 monomer units.<sup>158</sup> This structure was postulated to arise from an alternation of polymer growth between isospecific and aspecific sites, where site epimerization occurs on a time scale much slower than monomer enchainment (Scheme 8; Figure 8, pathway 7). This mechanism is a topic of considerable debate (vide infra).

Collins has reported the synthesis of a related class of metallocenes (**43**), some of which form elastomeric, stereoblock polypropylene when activated by MAO.<sup>162–164</sup> The elastomeric properties of the polymer formed using **43** (M = Hf, X = SiMe<sub>2</sub>;  $T_{rxn} = 25$  °C) were far superior to those formed by the other metallocenes in the study. The polymers made using **42** and **43** have similar microstructures, as well as physical and mechanical properties. However, after detailed microstructural analysis of the polymer the authors proposed an alternate mechanism of stereocontrol to Chien's site epimerization model (Scheme 9). This mechanism consists of random insertion at each of the two coordination sites of **43**, with one site

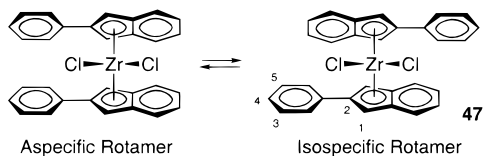
### Scheme 9. Random Site Epimerization Mechanism for Synthesizing Stereoblock Polymers



being perfectly isospecific and the other aspecific (Scheme 9; Figure 8, pathway 8). The resultant polymer will have an enrichment in isotactic runs in the polymer main chain, but block lengths will be relatively short since site epimerization is much faster than olefin insertion. Although this mechanism is consistent with the observed low melting points of the materials, Chien's model cannot be ruled out on the basis of the microstructural analysis of the NMR data alone.<sup>162–164</sup> It was proposed, however, that the polymers made using these and related  $C_1$  catalysts are substantially random in stereochemistry and that, if blocks are present, they must be on average relatively short. Collins has recently reported that **44** forms elastomeric polypropylene upon activation with MAO.<sup>165</sup> As with **42** and **43**, the microstructures of the polymers formed are sensitive to the reaction temperature as well as monomer concentration. Interestingly, the *syn*-diastereomer is comparatively less active and only makes very low molecular weight oligomers.

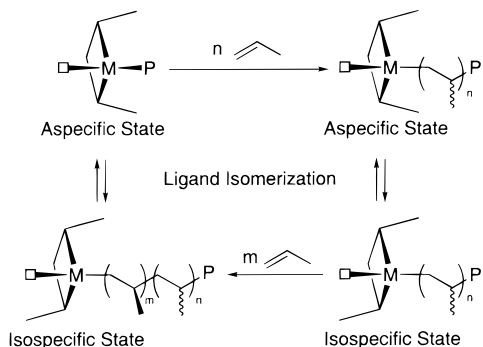
Rieger has recently reported another class of  $C_1$  catalysts (**45**) for the synthesis of stereoblock polypropylenes.<sup>166</sup> However unlike the polymers formed using **42–44**, polymers ranging from flexible plastics (with melting points as high as 134 °C) to thermoplastic elastomers are produced. Similar metallocenes (**46**) have been recently reported by Chien to produce polypropylenes ranging in microstructure from atactic to isotactic.<sup>167</sup> These polymers are presumably not elastomeric due to their low molecular weight.

*Oscillating Catalysts.* Waymouth and Coates have developed a conceptually different strategy for the synthesis of stereoblock polymers.<sup>168</sup> One of the disadvantages of using  $C_1$  catalysts (**42–46** with the exception of **45**) for the synthesis of elastomeric polymers is that the melting points of the materials are too low for commercial applications. The main reason for this is that the isotactic blocks of the polymers, which are responsible for physically linking the elastomeric network, are both short and stereochemically impure. By devising a ligand isomerization rather than site isomerization strategy (Scheme 10), it is possible to control block sizes and stereoregularity by rational ligand design as well as reaction conditions. In this system, the relative rates of propagation and ligand isomerization control block size; the relative energies of aspecific and isospecific states and their associated rate constants determine the overall amount of units in each tacticity domain.



**Figure 13.** Oscillating catalyst strategy for the synthesis of isotactic-atactic stereoblock polymers.

**Scheme 10. Ligand Isomerization Mechanism for Synthesizing Stereoblock Polymers**



Metallocene **47**, when activated by MAO, produces elastomeric polypropylene (Figure 13).<sup>168</sup> The microstructure of the polymer is sensitive to the reaction temperature, as well as monomer concentration (low temperatures and high monomer concentrations favor isotacticity). This experimental observation is consistent with an oscillation between achiral and chiral coordination geometries during propagation, which is proposed to produce the stereoblock microstructure.<sup>168,169</sup> X-ray analysis of **47** revealed both *racemic* and *meso* torsional isomers, suggesting that the two conformations are of similar energy. Bridged *meso* and *racemic* model compounds of **47** produced atactic and isotactic polypropylene, consistent with the proposed model of stereocontrol.<sup>170</sup> The polymer made at  $-18\text{ }^{\circ}\text{C}$  and 50 psi exhibited a broad melting transition between 125 and 145  $^{\circ}\text{C}$ , consistent with extended, highly isotactic blocks.

Waymouth has extensively investigated the effects of ligand and metal substitution of **47** on the stereochemistry of the polymer produced. Remarkably, the tacticity of polypropylene produced with **47**/MAO strongly depends on the *meta*- but not *para*-substituents of the 2-phenyl group.<sup>171,172</sup> With H in the 3,5-positions, the polymer produced at 25  $^{\circ}\text{C}$  and 75 psig is highly elastic with  $[mmmm] = 0.33$ . Modification with *meta*- $\text{CH}_3$  groups makes a less stereoregular polymer ( $[mmmm] = 0.23$ ), while  $\text{CF}_3$  groups results

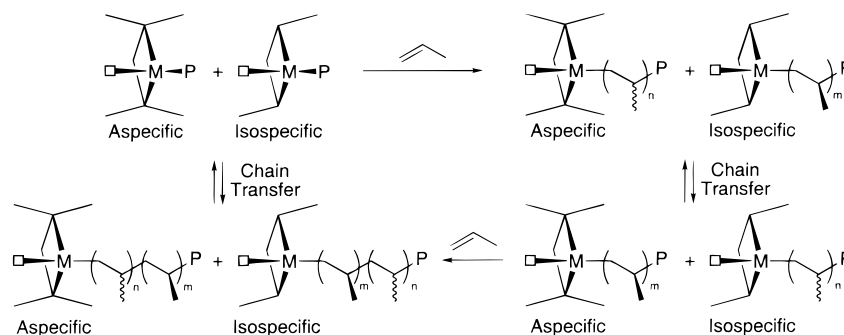
in a highly crystalline polymer with  $[mmmm] = 0.58$ . The corresponding hafnocenes make polypropylene that is nearly atactic; a less active isospecific site is proposed to be the source of the difference in stereochemistry.<sup>173</sup> Catalysts of type **47** bearing hydrogenated 2-phenyl groups and/or tetrahydroindenyl ligands produce predominantly atactic polymers,<sup>174</sup> supporting Rappé's proposal that aromatic-aromatic interactions are important stereocontrol elements in these systems.<sup>175</sup> Complexes with mixed ligand sets have been synthesized; their catalytic behavior is in general intermediate to those of their homoligated bis(indenyl) counterparts.<sup>176,177</sup> Zirconocene formation from 1-methyl-2-phenylindene produces *rac* and *meso* diastereomers; the purified compounds both make low molecular weight amorphous polypropylene.<sup>178</sup>

**Binary Catalyst Mixtures.** A third strategy for preparing stereoblock polymers consists of allowing chain transfer to occur between catalysts of differing stereoselectivities during chain formation (Scheme 11). The rates of chain transfer relative to the rates of monomer insertion will determine the size of each block domain, while the ligand structure of the two catalysts will determine the stereochemistry of each segment. Chien has simultaneously polymerized propylene employing aspecific and isospecific metallocene catalysts. Using the achiral complex  $\text{Et}(\text{Fl})_2\text{ZrCl}_2$  in combination with either  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  (**6**) or  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  (**11**) and activation using  $^i\text{Bu}_3\text{Al}$  in combination with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , polypropylene mixtures were formed.<sup>179</sup> Following extraction studies, it was concluded that the catalyst mixture formed pure atactic and isotactic polymer, along with a stereoblock copolymer that compatibilized the two homopolymers. Chien has also employed syndiospecific and isospecific catalysts using this same strategy to form mixtures of isotactic, syndiotactic, and isotactic-*block*-syndiotactic polypropylenes.<sup>180</sup> It is proposed that the  $^i\text{Bu}_3\text{Al}$  used to activate the catalyst acts as a crossover agent, transferring polymer chains between catalysts of different stereoselectivities. Fink has recently reported a similar preparation of this polymer by using a  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  (**11**)/ $\text{Me}_2\text{C}(\text{Cp})(\text{Fl})\text{ZrCl}_2$  (**31**) catalyst mixture on a solid support.<sup>181</sup>

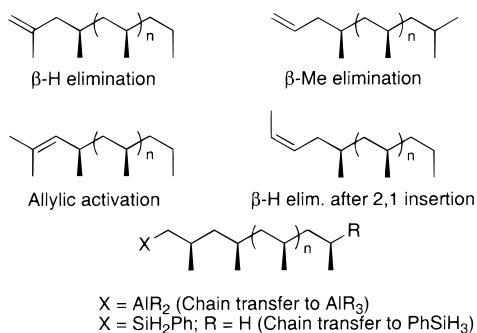
**B. Functional Olefins**

Single-site catalysts offer significant advantages over heterogeneous catalysts for the polymerization of functional olefins. One of the inherent liabilities of heterogeneous Ziegler-Natta catalysts is that they

**Scheme 11. Chain-Transfer Mechanism for Synthesizing Stereoblock Polymers**







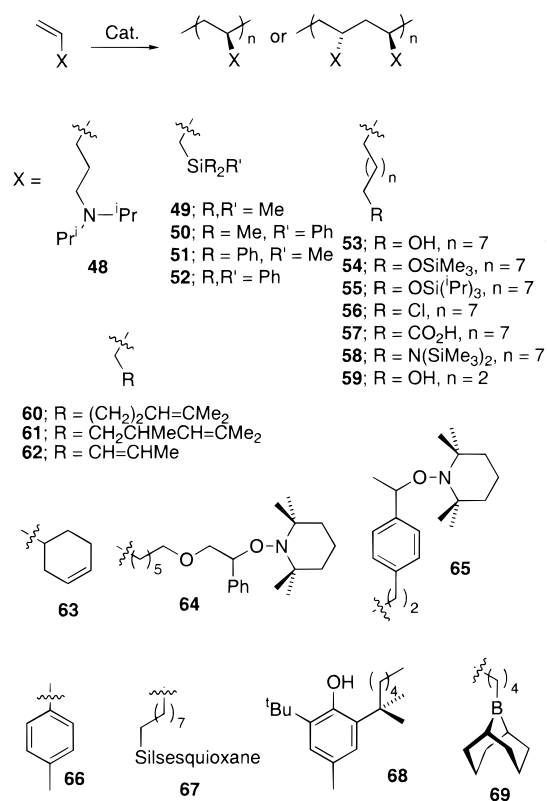
**Figure 14.** Functional end groups via chain-transfer mechanisms.

are highly electrophilic, rendering them vulnerable to poisoning by Lewis-base-containing monomers.<sup>182,183</sup> Molecular catalysts, in contrast, offer the potential for steric protection of the active site through careful ligand design. In contrast to multisited catalysts, chain-transfer mechanisms of these defined catalysts can also be tailored to allow functionality to be constructed into the polymers. There are three main techniques for the preparation of functionalized stereoregular polyolefins using single-site catalysts. First, postpolymerization modification of polymer end groups that arise from chain transfer reactions can be used to produce end-functionalized polymers. Second, functional monomers that are shielded with protecting groups (to avoid catalyst deactivation) can be directly polymerized. Third, monomers with catalyst-compatible groups can be polymerized. These latent groups, such as boranes and olefins, can be modified later if desired.<sup>184</sup>

There are six different types of end-functionalized polypropylenes that can be formed using metallocene catalysts (Figure 14).<sup>185</sup> Chain termination by  $\beta$ -hydrogen elimination forms vinylidene end groups, while  $\beta$ -methyl elimination forms allyl chain ends.<sup>6</sup> Polypropylene with isobutenyl groups has been proposed to come from allylic activation,<sup>186</sup> and  $\beta$ -hydrogen elimination after a 2,1-regioerror produces *cis*-2-butenyl end groups.<sup>187</sup> In the presence of alkyl-aluminum reagents<sup>188,189</sup> and silanes,<sup>190</sup> aluminum- and silane-terminated polymers have been produced. Olefin end groups of isotactic polypropylenes have been converted to anhydride, ester, amine, carboxylic acid, silane, borane, alcohol, and thiol groups in polymer analogous reactions.<sup>191–193</sup>

A wide range of functional monomers have been homopolymerized using isospecific and syndiospecific catalysts (Scheme 12). Waymouth reported the first stereoselective polymerization of functional monomers with metallocene catalysts.<sup>194</sup> Using the  $\text{B}(\text{C}_6\text{F}_5)_3$ -activated dimethylzirconium analogue of **17**, 5-(*N,N*-diisopropylamino)-1-pentene (**48**) was converted to the isotactic polymer. Waymouth later reported that the syndiotactic polymer could be formed as well using the borate-activated dimethyl version of **31**.<sup>195</sup> Workers at Mitsui Toatsu<sup>196</sup> have reported the syndiospecific polymerization of allyltrimethylsilane (**49**) using **31**/MAO. Zeigler and Guerra have synthesized isotactic and syndiotactic poly(allyltrimethylsilane) using **11**/MAO and **31**/MAO, respectively.<sup>197</sup> Okamoto has reported the asymmetric oligomerization of **49**–

## Scheme 12. Functional Monomers Polymerized by Stereospecific Catalysts



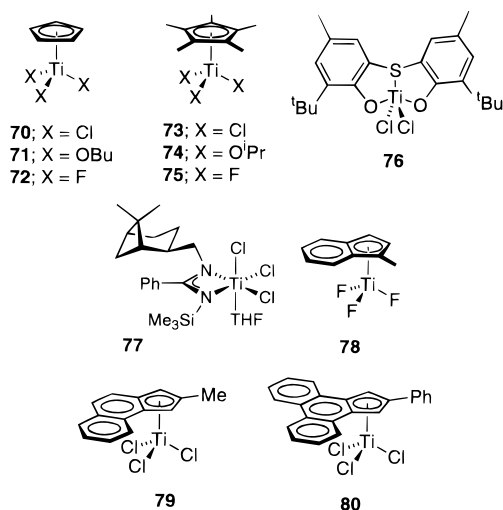
**52** using MAO-activated, optically pure binaphtholate and biphenolate derivatives of **8**, as well as the syndiospecific polymerization of the allylsilane monomers using **32**/MAO.<sup>198</sup> The isospecific polymerization of silyl ethers **54** and **55** has been accomplished using **11**/MAO,<sup>199</sup> while the chloride **56** has been polymerized using **6**/MAO.<sup>200</sup> Dienes with one polymerizable olefin and one inactive olefin can be polymerized, and then the latent olefin can be functionalized after the polymerization. Thus, Rieger has reported the homopolymerization of dienes **60** and **61** using **6**/MAO.<sup>201</sup>

The copolymerization of functional monomers with ethylene or propylene using isospecific catalysts has also been reported.<sup>202</sup> Although the materials formed are random copolymers, they presumably have a stereoregular microstructure when chiral catalysts such as **6**, **11**, or **17** are used. Monomers **48**,<sup>203</sup> **53**,<sup>203–205</sup> **54**,<sup>199</sup> **55**,<sup>199</sup> **56**,<sup>200</sup> **57**,<sup>204</sup> **58**,<sup>206</sup> **59**,<sup>204</sup> **62**,<sup>207</sup> **63**,<sup>208</sup> **67**,<sup>209</sup> and **69**<sup>184,210</sup> have been copolymerized with ethylene, while monomers **53**,<sup>204,205,211</sup> **56**,<sup>200</sup> **57**,<sup>204,211</sup> **59**,<sup>204</sup> **61**,<sup>201</sup> **64**,<sup>212</sup> **65**,<sup>213</sup> **66**,<sup>214</sup> **67**,<sup>209</sup> and **68**<sup>215</sup> have been copolymerized with propylene. Monomer **48** has been copolymerized with 1-hexene and 4-methyl-1-pentene,<sup>216</sup> while **56** has been copolymerized with 1-hexene.<sup>200</sup>

## C. Conjugated Olefins

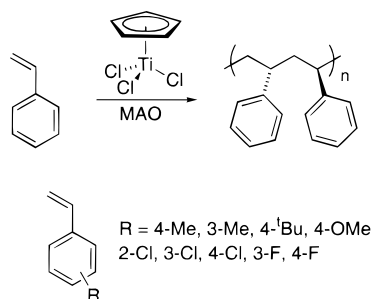
### 1. Styrenes

Syndiotactic polystyrene was first reported by Ishihara in 1986.<sup>217</sup> Using an undisclosed catalyst composed of titanium and aluminum components, polystyrene with a highly syndiotactic microstructure was synthesized. The polymer that was insoluble in



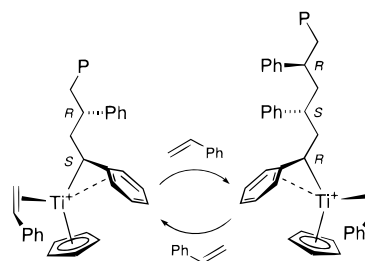
**Figure 15.** Catalyst precursors for the synthesis of syndiotactic polystyrene.

**Scheme 13. Synthesis of Syndiotactic Polystyrenes**



2-butanone (98% of total) had an *rrrr*-pentad content greater than 98%, a  $T_m$  of 270 °C, a high molecular weight, and a narrow distribution. Zambelli reported in the following year that tetrabenzyltitanium ( $\text{TiBz}_4$ ) could be activated by MAO to yield syndiotactic styrene with greater than 98% *rr* triads.<sup>218–221</sup> In 1988, Ishihara reported a range of titanium compounds that, when activated by MAO, formed the syndiotactic polymer.<sup>222</sup> Although  $\text{TiX}_4$  (X = Cl, Br, OMe, OEt) compounds with MAO form syndiotactic polystyrene, their activities are much lower than monocyclopentadienyltitanium compounds such as  $\text{Cp}^*\text{TiCl}_3$ ,  $\text{Cp}^*\text{TiCl}_2$ , and  $\text{Cp}^*\text{TiCl}$ .<sup>223,224</sup> Interestingly, group IV metallocenes give very low yields of syndiotactic or atactic polymer.<sup>222,225</sup> Using  $\text{Cp}^*\text{TiCl}_3$  (**70**)/MAO or  $\text{TiBz}_4$ /MAO a range of styrenes were polymerized (Figure 15; Scheme 13); monomers con-

**Scheme 14. Proposed Mechanism of Stereocontrol for Syndiospecific Polymerization of Styrene Using  $\text{Cp}^*\text{TiCl}_3$ /MAO**



taining halogen groups exhibited significantly slower reaction rates.<sup>222,226</sup>

Since the inception of syndiotactic polystyrene, a wide array of titanium complexes have been reported that are active for the formation of this polymer. Several reviews have been written on this topic.<sup>227–230</sup> In general, most ( $\eta^5\text{-Cp}'$ ) $\text{TiX}_3$  type compounds ( $\text{Cp}'$  = substituted Cp or indenyl) form active catalysts when combined with MAO. After fractionation using 2-butanone, the insoluble polymer typically contains >98% *rrrr* pentads. Alkylated titanium compounds ( $\eta^5\text{-Cp}'$ ) $\text{TiR}_3$  (R = hydrocarbyl) can be activated with  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  for styrene polymerization.<sup>231–233</sup> Shown in Figure 15 are some of the more active catalyst precursors of the type ( $\text{Cp}'$ ) $\text{TiX}_3$ , as well as some novel non-Cp complexes that form syndiotactic polystyrene. Data concerning their polymerization behavior are given in Table 2. For the  $\text{Cp}'\text{TiX}_3$  catalysts (**70–75**), fluorides are typically the most active,<sup>234</sup> followed by alkoxides<sup>224,235</sup> and then chlorides.<sup>236</sup> Compounds **76** and **77** are examples of non-Cp compounds that efficiently form highly syndiotactic polymer.<sup>102,237,238</sup> Compounds with sterically bulky indenyl ligands (**78–80**) form highly syndiotactic, high molecular weight polymer with the highest activities reported.<sup>239–241</sup>

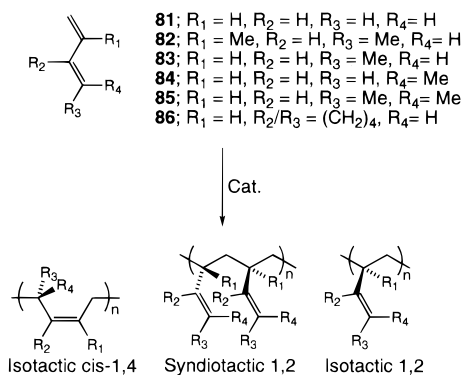
A significant amount of mechanistic information has been reported concerning this polymerization system.<sup>230</sup> The active species is thought to be a cationic titanium(III) complex which retains the Cp as a ligand, with the polymer chain serving as the other ligand.<sup>243–245</sup> As with metallocene catalysts for olefin polymerization, MAO serves as the anion (Scheme 14). In addition, Newman has suggested that the higher activity of  $\text{Cp}^*\text{Ti}(\text{OMe})_2$ /MAO versus  $\text{Cp}^*\text{Ti}(\text{OMe})_3$ /MAO is additional support for a Ti(III) species.<sup>246</sup> Elegant studies by Pellecchia have re-

**Table 2. Representative Polymerizations of Styrene Using Compounds 70–80/MAO**

| complex   | [Al]/[Ti] | $T_{\text{rxn}}$ | time (min)      | activity <sup>a</sup> | $M_w$   | SY (%) <sup>b</sup> | $T_m$ (°C) | ref |
|-----------|-----------|------------------|-----------------|-----------------------|---------|---------------------|------------|-----|
| <b>70</b> | 300       | 50               | NR <sup>c</sup> | 1100                  | 140 000 | NR                  | 258        | 236 |
| <b>71</b> | 1000      | 45               | 30              | 1589                  | 40 000  | 93                  | 258        | 224 |
| <b>72</b> | 300       | 50               | NR              | 3000                  | 100 000 | NR                  | 265        | 236 |
| <b>73</b> | 300       | 50               | NR              | 15                    | 169 000 | NR                  | 275        | 236 |
| <b>74</b> | 500       | 70               | 2               | 517                   | 545 000 | >95                 | 270        | 242 |
| <b>75</b> | 300       | 50               | NR              | 690                   | 660 000 | NR                  | 275        | 236 |
| <b>76</b> | 2267      | 80               | NR              | 2350                  | 87 000  | >98                 | NR         | 237 |
| <b>77</b> | 200       | 20               | NR              | 470                   | 15 200  | NR                  | 264, 270   | 102 |
| <b>78</b> | 300       | 50               | 10              | 17500                 | 140 000 | 94.2                | 268        | 239 |
| <b>79</b> | 4000      | 50               | NR              | 7920                  | 424 000 | 92.8                | 275        | 240 |
| <b>80</b> | 4000      | 75               | 10–20           | 33000                 | 130 000 | 92                  | 265        | 241 |

<sup>a</sup> kg of PS/(mol Ti·h). <sup>b</sup> Percentage insoluble in refluxing 2-butanone. <sup>c</sup> NR = not reported.

### Scheme 15. Stereoselective Polymerization of Conjugated Dienes



vealed that the styrene inserts into the growing chain in a secondary 2,1-fashion, where the phenyl group is on the carbon atom that becomes attached to the titanium center.<sup>231</sup> Isotopic labeling studies revealed that insertion using TiBz<sub>4</sub>/MAO occurs by *cis*-addition of the olefin to the metal-carbon bond.<sup>247</sup> Chain transfer is predominantly  $\beta$ -hydrogen elimination, although chain transfer to aluminum has been observed.<sup>220,248</sup> The mechanism of stereocontrol is a chain-end control process, and analysis of the polymer reveals Bernoullian statistics. Although little is known about the exact nature of the transition state leading to syndiotacticity, the coordinatively unsaturated nature of the titanium center (11 electron with the styrene coordinated  $\eta^2$  and an  $\eta^1$  polymer chain) suggests the possibility that the monomer coordinates in a *cis*- $\eta^4$  geometry, the  $\alpha$ -phenyl of the polymer chain end interacts with Ti in an agostic fashion, or the polymer chain is actually bound as an  $\eta^3$ -allyl species.<sup>249</sup> Such intermediates could impart stereochemical control as is suggested in Scheme 14.

Unlike syndiotactic polystyrene, isotactic polystyrene has been previously synthesized by heterogeneous catalysts. Although a range of soluble compounds have been reported to make predominantly isotactic styrene polymers and oligomers,<sup>250–255</sup> there are no examples of true single-site catalysts that form highly isotactic polymer.

### 2. Diolefins

A wide range of heterogeneous catalysts have been reported for the stereoselective polymerization of conjugated diolefins.<sup>256</sup> Although the tactic polymers produced have been structurally characterized in detail, the catalysts used to form them are typically poorly defined, hindering mechanistic studies. A notable exception is a cobalt complex first identified by Natta for the syndiospecific polymerization of 1,3-butadiene (**81**) (Scheme 15). By treatment of CoCl<sub>2</sub> with NaBH<sub>4</sub> in the presence of butadiene, a complex was isolated and crystallographically identified that consists of an  $\eta^5$ -butadienyl dimer and *cis*- $\eta^4$ -butadiene bound to a cobalt(I) center.<sup>257,258</sup> This complex has been used extensively for the syndiospecific polymerization of butadiene.<sup>259–261</sup> The catalyst is unusual since the polymer it forms actually serves as its ligand; unfortunately the modification of the ligand independently of the monomer polymerized is

**Table 3. Polymerization of Conjugated Dienes with Single-Site Catalysts**

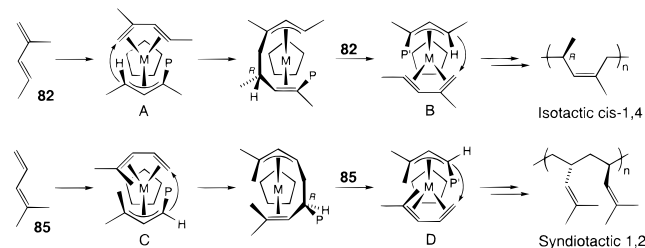
| mono-mer  | $T_{\text{rxn}}$ (°C) | catal (+MAO)  | polymer stereochem                           |
|-----------|-----------------------|---|--|
| <b>81</b> | 20                    | CpTiCl <sub>3</sub> ( <b>70</b> )                   | 81% <i>cis</i> -1,4; 19% <i>syn</i> -1,2     |
| <b>82</b> | 20                    | CpTiCl <sub>3</sub> ( <b>70</b> )                   | >98% <i>cis,iso</i> -1,4                     |
| <b>83</b> | 20                    | CpTiCl <sub>3</sub> ( <b>70</b> )                   | 56% <i>cis,iso</i> -1,4; 44% <i>syn</i> -1,2 |
| <b>84</b> | 20                    | CpTiCl <sub>3</sub> ( <b>70</b> )                   | >99% <i>cis,iso</i> -1,4                     |
| <b>84</b> | 0                     | CpTiCl <sub>3</sub> ( <b>70</b> )                   | 28% <i>cis,iso</i> -1,4; 72% <i>syn</i> -1,2 |
| <b>84</b> | -28                   | CpTiCl <sub>3</sub> ( <b>70</b> )                   | >99% <i>syn</i> -1,2                         |
| <b>85</b> | 20                    | CpTiCl <sub>3</sub> ( <b>70</b> )                   | 100% <i>syn</i> -1,2                         |
| <b>86</b> | 20                    | Et(Ind) <sub>2</sub> ZrCl <sub>2</sub> ( <b>6</b> ) | <i>iso</i> -1,2                              |

not possible. Related allylnickel and -lanthanide complexes have also been extensively explored for diene polymerization, where the addition of external donor ligands can modify the activity and selectivity of the catalysts.<sup>262</sup> Complex equilibria involving the donor ligands are common in these systems; thus, multiple mechanistic pathways hamper rational modification. In contrast, cyclopentadienyl-ligated complexes provide many opportunities concerning the stereoselective polymerization of dienes, since the strongly bound Cp ligand remains attached to, and thus modifies, the metal center throughout the entire reaction. In the following section, the use of single-site catalysts bearing permanent organic ligands to control polymer main-chain stereochemistry will be reviewed.

Immediately following the discovery of CpTiCl<sub>3</sub> and TiBz<sub>4</sub> with MAO as catalysts for syndiospecific styrene polymerization, the stereoselective polymerization of conjugated dienes was investigated. Zambelli investigated the use of TiBz<sub>4</sub>/MAO for diene polymerization and formed predominantly *cis*-1,4-polybutadiene and polyisoprene; in contrast 4-methyl-1,3-pentadiene (**85**) formed syndiotactic polymer by a 1,2-addition process (Scheme 15).<sup>263</sup> Oliva later investigated the polymerization of these dienes using CpTiCl<sub>3</sub>/MAO and obtained similar results.<sup>264</sup> The polymerization of monomers **81–85** with CpTiCl<sub>3</sub>/MAO has been studied in detail,<sup>265–270</sup> the results are summarized in Scheme 15 and Table 3. The general trend is that this catalyst at 20 °C produces isotactic, *cis*-1,4-units from monomers **82** and **84**, syndiotactic 1,2-units from monomer **85**, or a combination of the two from monomers **81** and **83**.<sup>270</sup> Interestingly, the microstructure and rate of polymerization of **84** vary as a function of temperature; the reaction rate increases as temperature is lowered, and the microstructure becomes highly syndiotactic via 1,2-enchainment.<sup>267</sup> The polymerization of 1-vinylcyclohexene has recently been studied; CpTiCl<sub>3</sub>/MAO yields *cis*-1,4-enchainment and Me<sub>2</sub>C(Fl)(Cp)ZrCl<sub>2</sub> (**31**)/MAO produces *trans*-1,4-linkages, while Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> (**6**) makes isotactic 1,2-polymer.<sup>271</sup> Monocyclopentadienylvanadium(III) complexes with MAO form diene polymers with low stereoselectivity.<sup>272</sup> The metallocenes Cp<sub>2</sub>TiCl<sub>2</sub> and Cp<sub>2</sub>TiCl with MAO give polymers with the same stereochemistry as CpTiCl<sub>3</sub> but with much lower activity.<sup>225</sup>

The mechanism of diene polymerization using catalysts such as CpTiCl<sub>3</sub>/MAO is not completely understood. It is reasonable that there are mechanistic similarities of this system with syndiospecific



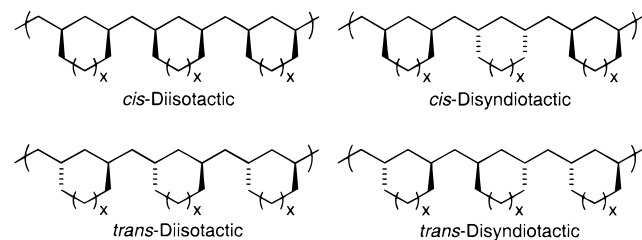
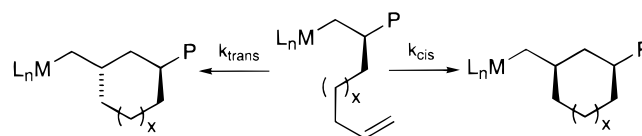
**Scheme 16. Proposed Mechanism of Stereocontrol in the Polymerization of Conjugated Dienes**

styrene polymerization and diene polymerization using allylnickel complexes. Guerra has performed a geometrical and nonbonded energy analysis on the system.<sup>273,274</sup> The proposed mechanism of enchainment is a Cp-titanium(III) center with an anti- $\eta^3$  coordinated polymer chain end and a *cis*- $\eta^4$ -coordinated diene (Scheme 16). These reactive organic groups can attain a relative *endo-endo* orientation. Attack by the polymer-substituted allyl carbon on the unsubstituted end of the coordinated diene produces a syndiotactic polymer with 1,2-linkages where the pendant olefin is temporarily coordinated to the metal center;<sup>269</sup> attack by the other external carbon of the allyl group produces an isotactic polymer with *cis*-1,4-units. Therefore, the monomer employed is largely responsible for determining the stereochemistry of the polymer formed since it ligates the active metal center after enchainment. These sequences are shown in Scheme 16. Note that intermediates A and B are equivalent and are related by a  $C_2$ -symmetry axis, while C and D are enantiomers related by a mirror plane.

Allylnickel compounds have been used extensively for the polymerization of dienes. Concerning main-chain stereochemistry, Grubbs has polymerized functionalized cyclohexadienes to highly regioregular (1,4) precursors to poly(*p*-phenylene) using bis[(allyl)-(trifluoroacetato)nickel(II)].<sup>275,276</sup> Although the polymers were clearly stereoregular on the basis of powder X-ray diffraction data, it is not clear whether they were isotactic or syndiotactic. In addition, catalysts derived from nickel(II) acetylacetonate/MAO,<sup>264</sup> neodymium carboxylates/MAO,<sup>277,278</sup> titanium tetraalkoxides/MAO,<sup>277,279</sup> and vanadium(III) acetylacetonate/MAO<sup>277</sup> have been explored for diene polymerization. In general, stereoselectivities of these catalysts are lower than the organotitanium-based catalysts, and since they fall outside the scope of the review, they will not be covered further here.

**D. Nonconjugated Diolefins**

Whereas poly( $\alpha$ -olefins) have only *two* microstructures of maximum order (isotactic, syndiotactic), cyclopolymers<sup>280</sup> have *four* microstructures due to the rings present in their main chain which can be either *cis* or *trans* in configuration (Scheme 17).<sup>13</sup> While the key issues concerning selectivity in the polymerization of  $\alpha$ -olefins are regioselectivity (head-to-tail monomer incorporation) and enantioface selectivity (tacticity), cyclopolymerization of  $\alpha,\omega$ -diolefins has added concerns. First, since the monomer has two olefins, either cyclization or cross-linking of the

**Scheme 17. Cyclopolymer Structures of Maximum Order ( $x = 0, 1, \text{ or } 2$ )****Scheme 18. Diastereoselectivity in Cyclopolymerization**

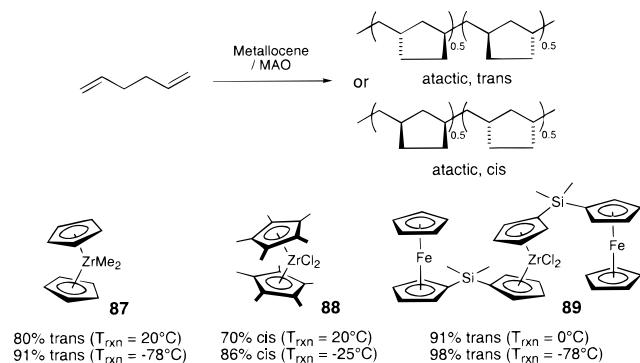
monomer can occur. In general, dienes with olefins that are linked by less than two or more than four atoms cannot undergo efficient cyclization and result in cross-linked materials. Second, since the rings can exhibit *cis* or *trans* stereochemistry, diastereoselectivity is an important facet of cyclopolymers that is not encountered in typical polyolefins. As a result, diene cyclopolymerization represents an ideal way to explore the degree to which metallocene-based catalysts can be used to control selectivity. Described below are studies concerning stereoselectivity (diastereo- and enantioselectivity) in the cyclopolymerization of dienes.

**1. Diastereoselectivity**

Metallocene-based catalysts exhibit extremely high cyclo- and regioselectivities for the cyclopolymerization of  $\alpha,\omega$ -dienes.<sup>281</sup> The cyclization step introduces an additional type of selectivity, diastereoselectivity, which concerns the formation of *cis* and *trans* rings (Scheme 18). Using heterogeneous catalysts, the diastereoselectivity for 1,5-hexadiene polymerization is extremely poor: the ratio of *cis:trans* rings is 1:1.<sup>282,283</sup> In contrast, the ease of tailoring the metallocene framework permits the rational design of catalysts capable of a high degree of diastereoselectivity. In the following sections, the factors which govern the diastereoselectivity of diene cyclopolymerization will be presented.

Cyclopolymerization studies of 1,5-hexadiene with a vast array of metallocene catalysts have revealed that the ligand structure of the metallocene catalyst is the main factor which determines the diastereoselectivity of the cyclization step. Waymouth reported that reactions carried out at 20 °C using MAO-activated  $\text{Cp}_2\text{ZrCl}_2$  (**87**) yielded poly(methylene-1,3-cyclopentane) (PMCP) with 80% *trans* rings, while the catalyst based on  $\text{Cp}^*\text{ZrCl}_2$  (**88**) yielded PMCP with 70% *cis* rings (Scheme 19).<sup>281</sup> At lower temperatures, the diastereoselectivity of the catalysts increases significantly: at -78 °C  $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$  gives 91% *trans* rings, and at -25 °C  $\text{Cp}^*\text{ZrCl}_2/\text{MAO}$  gives 86% *cis* rings. The physical properties of these materials are quite interesting, as PMCP with 81% *trans* has a  $T_m$  of 86 °C, while the polymer with 86%

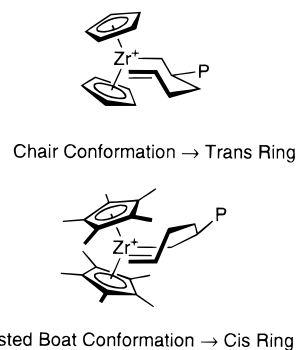
### Scheme 19. Metallocenes for the Diastereoselective Cyclopolymerization of 1,5-Hexadiene



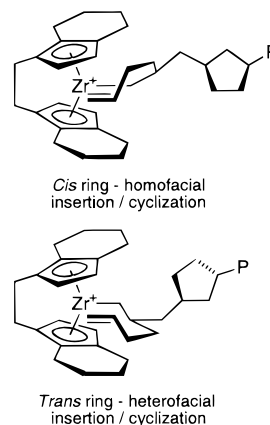
*cis* rings has a  $T_m$  of  $171^{\circ}\text{C}$ .<sup>283</sup> These polymers are essentially atactic. The diastereoselectivities of a multitude of other metallocenes have been determined; the best are shown in Scheme 19.<sup>284,285</sup> The following trends are revealed: (1) Metallocenes with unsubstituted Cp ligands give very high *trans* selectivities (80–91% *trans*). (2) Monatomic-bridged metallocenes give high *trans* selectivities (70–77% *trans*). (3) Chiral, diatomic-bridged metallocenes give moderate *trans* selectivities (65–69% *trans*). (4) Metallocenes with unbridged, highly substituted Cp ligands give moderate to high *cis* selectivities (56–86% *cis*). A recent paper by Mukaiyama has reported a bis(ferrocenyl) zirconocene complex (**89**) which exhibits an extremely high *trans* selectivity for ring formation in PMCP (Scheme 19).<sup>286</sup> At  $0^{\circ}\text{C}$ , the *trans* ring content is 91%; at  $-78^{\circ}\text{C}$  the selectivity increases to 98%. Waymouth has reported that  $\text{Cp}^*_2\text{ZrCl}_2$  (**88**)/MAO polymerized 2-methyl-1,5-hexadiene in a highly chemoselective and diastereoselective fashion, producing a polymer that only contains *trans* rings in head-to-tail arrangement.<sup>287</sup>

To determine the origin of this dramatic range of diastereoselectivities, a conformational modeling study was carried out by Cavallo et al.<sup>288</sup> In this study, noncovalent interactions between the incipient ring and the proposed catalytic sites of bis-Cp and bis-Cp\* zirconocenes were used to determine the lowest energy conformations of the cyclization intermediates. For the bis-Cp catalyst the lowest energy conformation is a chair structure with the growing polymer in a pseudoequatorial position, which yields a *trans* ring (Figure 16). Due to steric interactions with the methyl groups of the ligands, the minimum energy conformation for the bis-Cp\* complex appears to be a twisted-boat arrangement. With the polymer chain in a pseudoequatorial placement, this conformation results in the formation of a *cis* ring.

Predicting that Brintzinger's chiral bis(indenyl) metallocenes should be able to control the stereoselectivity of cyclopolymerization, Waymouth has investigated the use of **17**/MAO for the polymerization of a range of  $\alpha,\omega$ -diolefins.<sup>289–291</sup> It might be predicted that these highly stereoselective catalysts would effect a homofacial insertion/cyclization process in the polymerization of 1,5-hexadiene, yielding a cyclopolymer with predominantly *cis* rings (Figure 17). Remarkably, the polymers produced using these cata-



**Figure 16.** Lowest energy conformations for cyclization of 1,5-hexadiene with bis-Cp and bis-Cp\* catalysts. (Carbon atoms are gray, and hydrogens, white.)

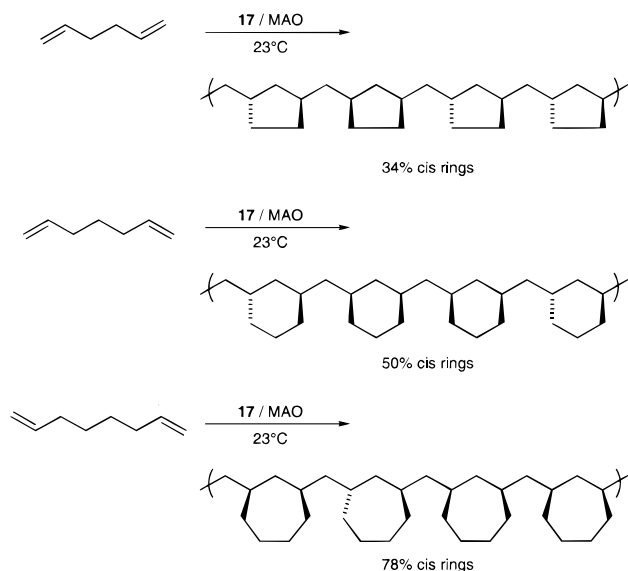


**Figure 17.** Proposed cyclization intermediates for *cis* and *trans* rings.

lysts contain predominantly *trans* rings. The formation of a *trans* ring requires a heterofacial insertion/cyclization sequence; i.e., the cyclization step must occur on a diastereoface of opposite topology to the enantioface selected for the initial insertion step (Figure 17). The *trans* selectivity in the presence of achiral  $\text{Cp}_2\text{ZrCl}_2$  derivatives has been interpreted in terms of a conformational preference of the incipient ring to adopt a chair transition state with the polymer chain occupying an equatorial position. If a similar situation applies to the more sterically hindered  $\text{Et}(\text{Ind-H}_4)_2\text{ZrBINOL}$  derivative (**17**), then the *trans* selectivity suggests that the conformational bias of the incipient ring may compete with the enantiofacial preference of the catalyst for the cyclization step.

The effect of length of the aliphatic diene linker on the *cis/trans* ratio of the polymer is a convenient probe of the competition between the developing ring and the chiral catalyst for diastereoselective control. Longer dienes result in a decrease in the conformational rigidity of the incipient ring during cyclization. The anticipated result is an increase in stereochemical control by the chiral catalyst. Since a homofacial insertion/cyclization sequence results in a *cis* ring, it is expected that an increase in diene length will result in an increase in the *cis* ring content of the polymer. Waymouth verified this anticipated trend, as the polymers formed from 1,5-hexadiene, 1,6-heptadiene, and 1,7-octadiene with a catalyst derived from **17** at room temperature exhibit *cis* ring contents of 28%, 50%, and 78%, respectively (Scheme 20).<sup>290</sup>

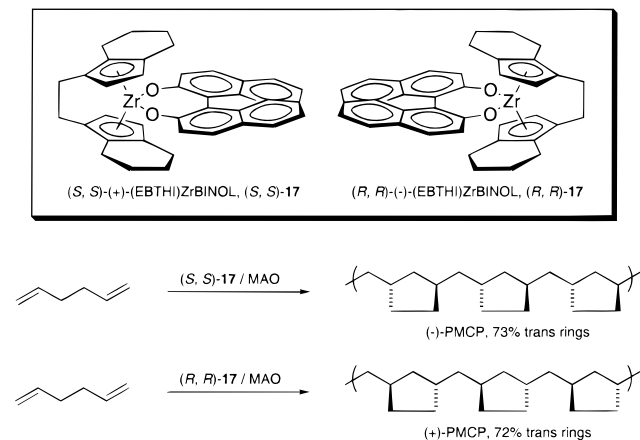
### Scheme 20. Effect of Diene Length on Diastereoselectivity of Cyclopolymerization Using 17/MAO



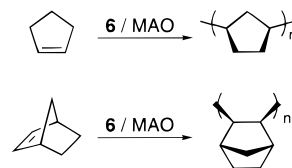
### 2. Enantioselectivity

Brintzinger has demonstrated the resolution of chiral metallocenes of type **8**,<sup>48,292</sup> opening many possible opportunities in the area of enantioselective catalysis.<sup>293</sup> One potential application of these complexes is the synthesis of optically active polymers, which are of interest for a variety of reasons.<sup>294</sup> Pino and Kaminsky were the first to utilize these optically pure compounds for the synthesis of optically active propylene oligomers; however the high molecular weight polymers do not exhibit optical activity since the chains contain pseudo mirror planes of symmetry perpendicular to the polymer backbones.<sup>63,65</sup> In general, the synthesis of optically active polymers from vinyl monomers requires complex architectures to circumvent the symmetry constraints of linear macromolecules. Waymouth noted that of the four structures of maximum order (Scheme 17), the *trans*-diisotactic configuration is chiral by virtue of its main-chain stereochemistry. Two necessary criteria for the chirality of this microstructure are a predominance of *trans* rings and isotacticity (same relative configuration of every other stereocenter). It had previously been determined that the chiral catalyst **17**/MAO exhibits *trans* selectivity for hexadiene polymerization. Since this catalyst is isospecific for olefin polymerization, Waymouth investigated the use of enantiomerically pure binaphtholate derived catalysts for diene polymerization. Cyclopolymerization of 1,5-hexadiene using (*R,R*)-(**17**)/MAO yielded a completely saturated polymer with 72% *trans* rings and a molar optical rotation of  $[\Phi]_{405}^{28} = +51.0^\circ$ .<sup>289,291</sup> As expected, the (*S,S*)-antipode gave a polymer with a similar fraction of *trans* rings (73%) but with a molar optical rotation of  $[\Phi]_{405}^{28} = -51.2^\circ$  (Scheme 21). The optical rotation of the polymer is temperature dependent ( $\Delta[\Phi]_D/\Delta T = -0.09^\circ/\text{C}$ ) and much larger than that of the model compound *trans*-(*R,R*)-1,3-dimethylcyclopentane ( $[\Phi]_{20}^{20} = +3.1^\circ$ ), consistent with the preference of one helical conformation in

### Scheme 21. Enantioselective Polymerization of 1,5-Hexadiene



### Scheme 22. Isospecific Polymerization of Cycloolefins



solution. The absolute stereochemistry shown in Scheme 21 was assigned on the basis of Pino's assignment for enantiofacial selectivity for propylene.<sup>291</sup>

## E. Cycloolefins

### 1. Ziegler–Natta Polymerization

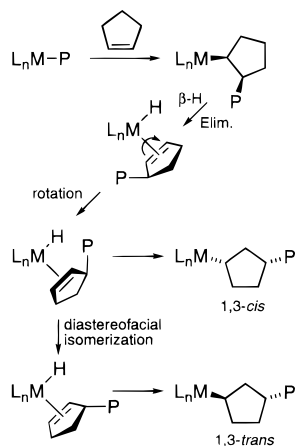
Metallocene-based Ziegler–Natta catalysts are capable of polymerizing cyclic monomers without ring-opening reactions that are characteristic of heterogeneous Ziegler–Natta catalysts. Kaminsky reported the homopolymerization of cyclic monomers such as cyclobutene, cyclopentene, norbornene, and dimethanonaphthalene (Scheme 22) with MAO-activated zirconocene catalysts.<sup>295–298</sup> Cyclobutene was approximately 5 times more reactive than cyclopentene, which was more reactive than norbornene.<sup>298</sup>

The polycycloalkenes produced with chiral, indenyl-ligated catalysts such as **6**/MAO are insoluble in common hydrocarbons and are highly crystalline. The melting points of polycyclobutene, polycyclopentene, and polynorbornene are around or above 400 °C, close to their decomposition temperatures, rendering the polymers difficult to melt process.<sup>10</sup>

The insolubility of these polymers makes their structural assignments difficult. Kaminsky proposed a 1,2-enchainment of cyclopentene to yield an isotactic microstructure with either *cis* or *trans* rings on the basis of IR, X-ray, and <sup>13</sup>C NMR chemical shifts of soluble oligomers produced at higher temperatures. A similar microstructure was proposed for polynorbornene with a *cis-exo*-1,2 configuration assigned on the basis of comparison with model compounds.<sup>298</sup>



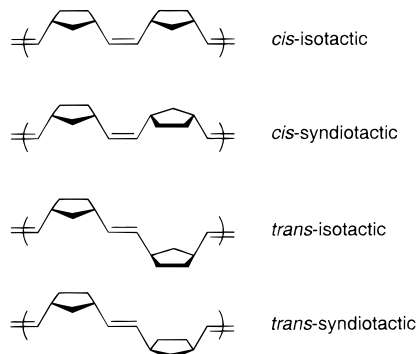
### Scheme 23. Mechanism of 1,3-Enchainment of Cyclopentene



A more recent assessment by Collins<sup>299–301</sup> and Kaminsky<sup>302,303</sup> proved the original assignment for polycyclopentene was incorrect. In an elegant series of experiments, Collins carried out the hydrooligomerization of cyclopentene to obtain a mixture of low molecular weight, hydrogenated oligomers. Collins found the <sup>13</sup>C NMR spectra to be inconsistent with a 1,2-enchainment of cyclopentene and proved, by the independent synthesis of the trimer, that cyclopentene homopolymerizes via a *cis*-1,3-enchainment of the monomer. Collins proposed a mechanism for the 1,3-polymerization of cyclopentene as outlined in Scheme 23. This mechanism involves a 1,2-insertion of cyclopentene followed by  $\beta$ -H elimination, olefin rotation, and reinsertion to afford a 1,3-enchainment of the monomer. This mechanism is similar to that proposed for the 1,3-enchainment of propylene, which has been observed as a minor process in the polymerization of propylene with similar catalysts. For cyclopentene, the intermediate derived from the 1,2-insertion of cyclopentene is apparently too sterically crowded to permit further insertion of another cyclopentene unit and isomerizes prior to subsequent olefin insertion. Insertion into the *cis*-1,3 unit species also appears to be sterically congested since chain-end stereocontrol effects are significant. For example, achiral metallocenes such as  $Cp_2ZrCl_2$  and *meso*- $Et(Ind)_2ZrCl_2$  also produce highly isotactic polymers. Interestingly, chiral metallocene  $Et(Ind-H_4)_2ZrCl_2$  (**8**)/MAO produces polycyclopentene with both *cis*- and *trans*-rings.<sup>300,301</sup> The mechanism of *trans* enchainment is proposed to be the intramolecular isomerization of the olefin hydride intermediate (Scheme 23) to the opposite olefin diastereoface via a  $\sigma$ -CH complex.<sup>301</sup>

McLain has recently reported the application of cationic nickel diiminate catalysts for the isospecific *cis*-1,3-polymerization of cyclopentene.<sup>304</sup> Although the catalysts exhibit a low activity for the reaction, polymers ranging from atactic to moderately isotactic can be selectively prepared depending on the catalyst precursor that is employed. As a result, the melting points of the polymers range from 241 °C (atactic) to 330 °C ( $[m] = 0.64$ ), rendering them melt processable. Given the propensity of these nickel complexes to

### Scheme 24. Microstructures of Maximum Order for ROMP Poly(norbornene)

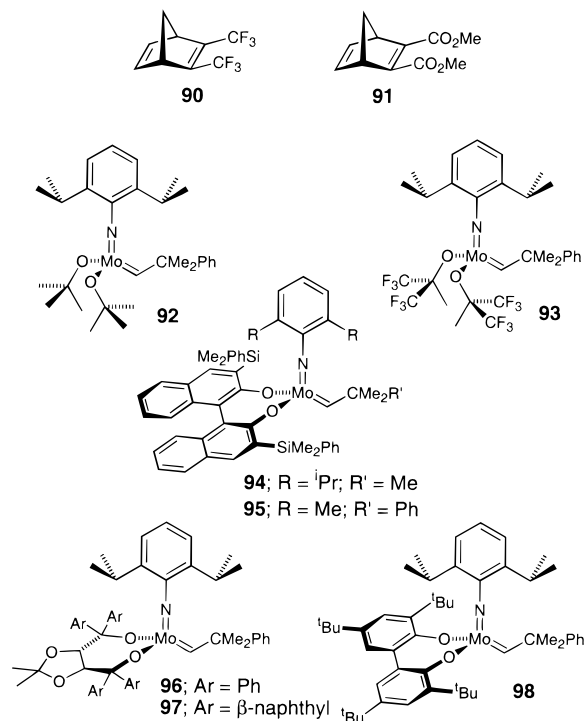


“chain-walk” via  $\beta$ -hydrogen elimination, it is likely that the mechanism of *cis*-1,3-enchainment is as depicted in Scheme 23 for cationic zirconocenes.

### 2. Ring-Opening Metathesis Polymerization

Beginning in the late 1950s, heterogeneous catalysts based on Mo, Ru, W, or Re oxides and halides were discovered that were capable of breaking open the double bond of a cyclic olefin and then converting the ring-opened molecule into a polymer with olefins in the main chain.<sup>305</sup> This process, called ring-opening metathesis polymerization (ROMP), has been studied in great deal since these initial discoveries. It is now known that olefin metathesis reactions are catalyzed by metal carbene complexes that are composed of a metal atom that is covalently bound to a  $CR_2$  group by a double bond. Reaction of this carbene with an olefin can effectively interchange the double-bond substituents of the two species via a metallacyclobutane transition state or intermediate.<sup>305</sup> Through careful empirical optimization, heterogeneous catalysts have been developed that are capable of impressive degrees of stereocontrol in the polymerization of cyclic olefins.<sup>306</sup> However, since these early heterogeneous catalysts were difficult to characterize and modify, a significant amount of research has been directed toward the development of single-site metal carbene complexes. These compounds, which have the general formula  $L_nM=CHR$ , allow the synthesis of new polymer microstructures with exceptional precision and, perhaps more importantly, allow the detailed study of the factors that dictate stereochemical control.

The ring-opening polymerization of a simple cyclic olefin such as cyclooctene yields two structures of maximum order, which are distinguished by the configuration (*cis* or *trans*) of their main-chain olefins. In contrast, polymers made from bicyclic olefins such as norbornene are inherently more complicated and have four structures of maximum order (Scheme 24). In addition to *cis*- and *trans*-olefins, the polymers can also be isotactic or syndiotactic. The stereochemistry of these polymers becomes even more complicated when the monomer is asymmetric, since head–head, head–tail, and tail–tail regioisomers are possible. Nevertheless, single-site metathesis catalysts have been developed that can control polymer stereochemistry to an impressive degree by both chain-end and site-control mechanisms.<sup>305,306</sup>

**Scheme 25. Monomers and Single-Site Molybdenum Catalysts for Stereoselective ROMP**


Grubbs has investigated the stereochemistry of ROMP using titanocene–metallacyclobutane complexes. These complexes offer little control over olefin stereochemistry or tacticity in the polymerization of norbornene.<sup>307</sup> However polymerization of *rac*-1-methylnorbornene yielded a polymer with 90–95% *trans*-olefins and a partially regioregular (head–tail) sequence of monomers (the tacticity of the polymer was not determined). Using a related Cp<sub>2</sub>Ti–metallacyclobutane complex, a polymer of *anti*-7-methylnorbornene was formed that was 80% *trans* in configuration and was partially syndiotactic (*lr* = 0.75).<sup>308</sup>

A major advance concerning the development of well-defined catalysts for ROMP was achieved in the late 1980s by Schrock and co-workers.<sup>309</sup> Molybdenum and tungsten carbene complexes have since been reported that exhibit high activities for ROMP and produce polymers with exceptional control of molecular weight and stereochemistry.<sup>310</sup> Using complex **92**, norbornadienes **90** and **91** were polymerized to give products that had 98% *trans*-olefins (Scheme 25; Table 4).<sup>311,312</sup> Although the polymers were predicted to be highly stereoregular due to exceptionally sharp <sup>13</sup>C NMR resonances, the tacticity was not determined until the mid-1990s when dielectric measurements suggested a syndiotactic microstructure.<sup>312,313</sup> Schrock later confirmed this microstruc-

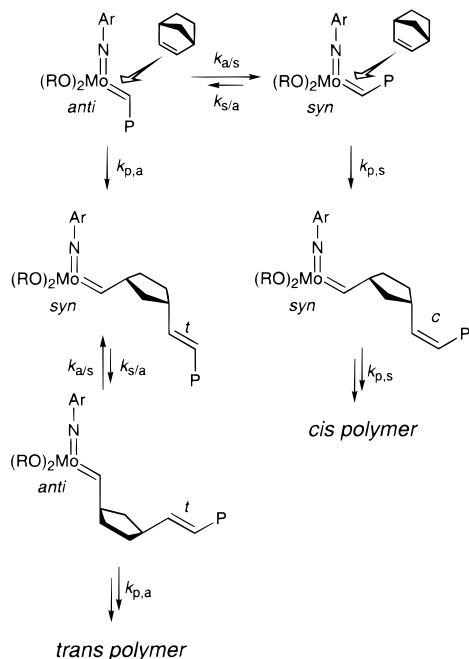
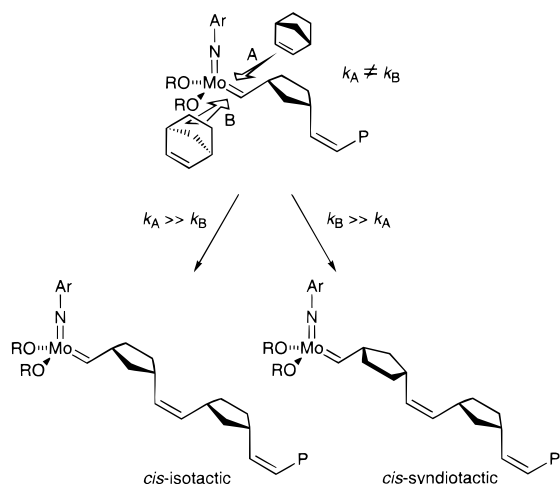
tural assignment by homonuclear H/H correlation spectroscopy and decoupling experiments on polymers made from related, enantiomerically pure norbornadienes using these catalysts.<sup>314,315</sup> In 1992, Gibson reported that the partially fluorinated molybdenum complex **93** forms polymers from **90** and **91** that are exclusively *cis* in configuration and highly stereoregular (Table 4).<sup>316</sup> Despite some contrasting reports concerning their tacticity, Schrock now has evidence that these polymers have isotactic microstructures.<sup>315</sup> Interestingly, Gibson has shown that the *cis/trans* content of polymers from **90** and **91** can be conveniently selected by employing varying ratios of **92** and **93**. Since alkoxide exchange is rapid relative to propagation in these complexes, a given polymer chain will experience a rapid equilibrium of *cis*-specific and *trans*-specific active sites during the reaction.<sup>316,317</sup> Schrock has also reported that the *cis/trans* ratios of polymers made from **90** and **91** can be controlled by reaction temperature and that tacticity can be varied by the choice of arylamido and alkoxide ligands.<sup>318</sup>

Since complexes **92** and **93** are achiral, it is likely that they form tactic polymers via a chain-end control process (vide infra). To increase the isospecificity of complex **93** for polymerization, Schrock replaced the achiral alkoxide groups with a range of C<sub>2</sub>-symmetric diols to create asymmetric complexes **94–98**.<sup>314,319</sup> These complexes, especially *rac*-**95**, exert an exceptionally high degree of stereochemical control in the polymerization of **90** and **91**, producing polymers that are >99% *cis* and have >99% isotactic (*mm*) triads. Even complex **98** that employs a conformationally flexible ligand produces highly isotactic, *cis* polymers.

A considerable amount of research has been directed toward understanding the mechanisms of stereocontrol in these molybdenum-based catalyst systems. Based on the results of a series of elegant studies by Schrock and co-workers a mechanistic scheme that explains the olefin configurations as well as main-chain tacticity in these polymers has been proposed.<sup>310,321</sup> The *cis/trans* content of the polymer is determined by the rate of isomerization of the *syn*- and *anti*-forms of the metal carbene complex and the associated rate constants for propagation of these isomers (Scheme 26). Regardless of the alkoxide ligand, the *syn* rotamer is approximately 3 orders of magnitude more stable than the *anti* isomer. Since the norbornene monomer approaches with its methylene bridgehead group directed toward the arylimido group, the *anti*-rotamer produces a *trans*-linkage, while the *syn*-rotamer yields a *cis*-olefin. When the alkoxide ligands are *tert*-butoxy groups, the rate of rotamer exchange is rapid relative to propagation, and since the *anti* rotamer is 4–5 orders of magni-

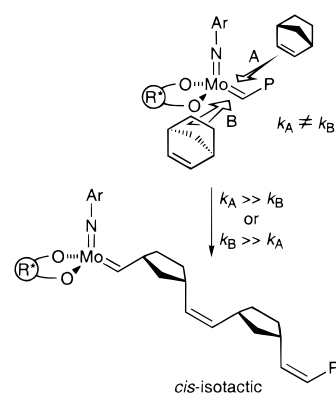
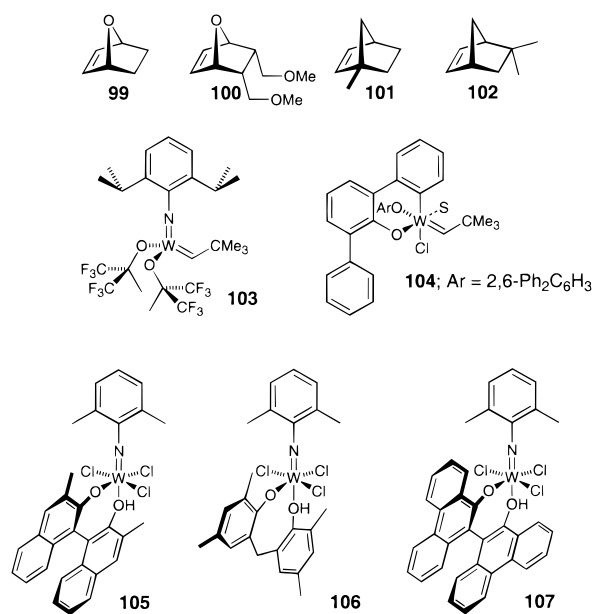
**Table 4. Polymerization of Monomers 90 and 91 with Molybdenum Complexes**

| monomer   | catal     | olefin config      | tacticity                         | ref           |
|-----------|-----------|--------------------|-----------------------------------|---------------|
| <b>90</b> | <b>92</b> | <i>trans</i> (98%) | syndiotactic ( <i>lrr</i> = 0.92) | 311, 312, 320 |
| <b>91</b> | <b>92</b> | <i>trans</i> (98%) | syndiotactic                      | 311, 312      |
| <b>90</b> | <b>93</b> | <i>cis</i> (97%)   | isotactic ( <i>lmm</i> = 0.74)    | 314           |
| <b>91</b> | <b>93</b> | <i>cis</i> (98%)   | isotactic ( <i>lmm</i> = 0.73)    | 314           |
| <b>90</b> | <b>95</b> | <i>cis</i> (>99%)  | isotactic ( <i>lmm</i> = >0.99)   | 314           |
| <b>91</b> | <b>95</b> | <i>cis</i> (>99%)  | isotactic ( <i>lmm</i> = >0.99)   | 314           |

**Scheme 26. Origin of *Cis/Trans*-Selectivity in ROMP Using Molybdenum Catalysts**

**Scheme 27. Chain-End Tacticity Control in ROMP**


tude more reactive than the *syn*, propagation occurs predominantly by the *anti* rotamer to give a *trans*-polymer. When the alkoxide ligands are fluorinated, carbene isomerization is slow relative to propagation; thus propagation occurs exclusively via the *syn* rotamer to give a *cis*-polymer. Concerning tacticity, the carbene faces of achiral catalysts **92** and **93** will be diastereotopic due to the last enchainment unit (Scheme 27). Therefore there will be a preference for either rear (A) or front (B) approach; if the difference is significant either isotactic or syndiotactic polymers will result. Scheme 27 shows the possibilities for the *syn* rotamer; this scenario can be extended to the *anti* rotamer as well. When the alkoxide ligand is chiral, there will be a preferential diastereofacial attack on the carbene regardless of the polymer's chain end configuration (Scheme 28). Again, if the barrier to enchainment at one face is significantly lower in energy, an isotactic polymer will form.

Although molybdenum complexes have in general been exploited more frequently for stereoselective

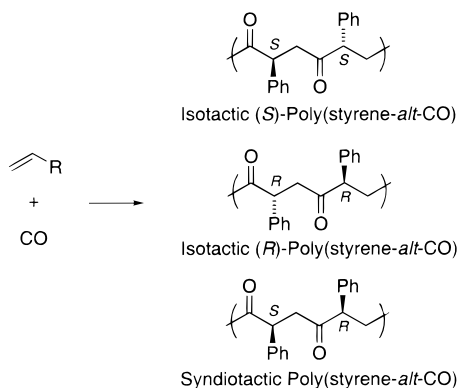
**Scheme 28. Enantiomorph-Site Tacticity Control in ROMP**

**Scheme 29. Monomers and Single-Site Tungsten Catalysts for Stereoselective ROMP**


ROMP, tungsten complexes have been investigated as well (Scheme 29). Interestingly, the polymers from norbornene derivatives are typically *cis* and syndiotactic in stereochemistry. Grubbs has reported the use of Schrock's tungsten-based carbene **103** for the *cis*-syndiospecific polymerization of 7-oxanorbornenes **99** and **100**.<sup>322</sup> Basset and Hamilton have reported that complex **104** produces a high *cis*-content, regular, partially syndiotactic polymer from *rac*-1-methylnorbornene (**101**).<sup>323,324</sup> Heppert has reported that chiral tungsten complexes **105**–**107** can be activated by Et<sub>2</sub>AlCl to form active catalysts for the syndiospecific polymerization of *rac*-5,5-dimethylnorbornene (**102**).<sup>325,326</sup> The resulting polymers contained greater than 95% *cis*-olefins.

**F. Alternated Copolymers**
**1. Olefin/Carbon Monoxide Copolymers**

The synthesis of alternating copolymers from carbon monoxide (CO) and olefins using palladium catalysts is currently an area of intense research interest. In cases where  $\alpha$ -olefins are used, the regiochemistry (head/tail orientations) and stereo-

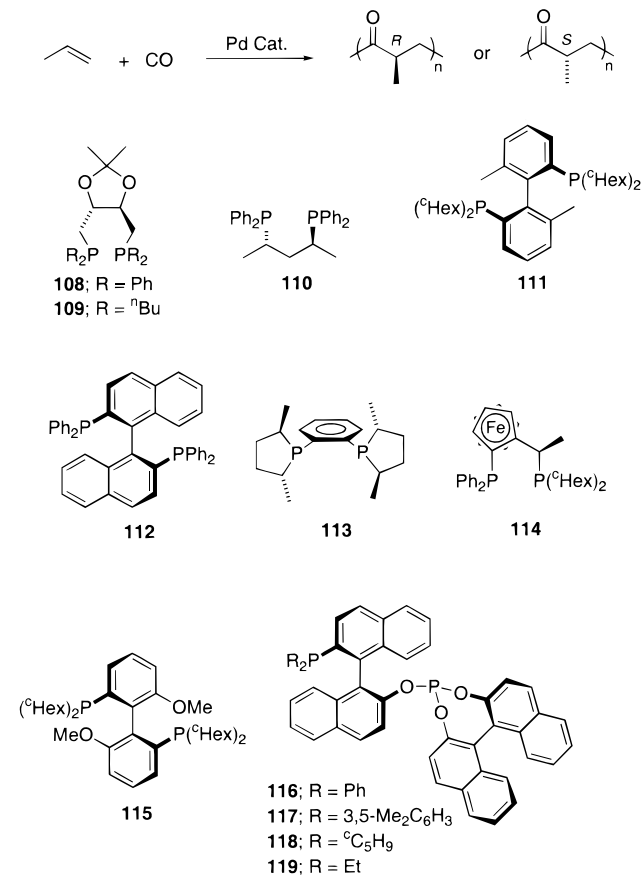


**Scheme 30. Isotactic and Syndiotactic Styrene/CO Polymers**

chemistry (tacticity) of olefin insertion have a strong influence on the physical and mechanical properties of the polymers. Unlike regioregular  $\alpha$ -olefin homopolymers, these copolymers have a directionality along the polymer backbone due to the incorporation of CO. Therefore isotactic, regioregular CO/olefin polymers are chiral by virtue of their main-chain stereochemistry; in contrast their syndiotactic counterparts are achiral (Scheme 30). Therefore the chiroptical properties of enantiomerically pure, isotactic polymers can be used in combination with NMR data to thoroughly analyze the stereochemical purity of the polymer main-chain.

In the early 1980s, it was discovered that cationic palladium catalysts with bidentate tertiary phosphines exhibited remarkable reaction rates for olefin/CO copolymerization.<sup>327,328</sup> Although initial studies using bidentate arylphosphines produced CO/propylene polymers with poor regioregularity, it was later revealed that bidentate alkylphosphines and/or chiral phosphines produced polymers with a much higher degree of regioregularity. In the early 1990s, the first reports concerning the use of enantiopure,  $C_2$ -symmetric ligated catalysts for the enantioselective, isospecific copolymerization of  $\alpha$ -olefins and CO began to appear (Schemes 31 and 32).<sup>329</sup>

In a 1990 patent, Wong briefly noted that palladium-based catalysts form optically active propylene/CO copolymers when enantiopure  $C_2$ -symmetric phosphine ligands **108** and **109** are employed (Scheme 31; Table 5).<sup>330</sup> In 1992, Consiglio and co-workers published several papers concerning the use of enantiopure bidentate phosphine ligands in CO/propylene copolymerization.<sup>331–333</sup> The copolymers formed using

**Scheme 31. Ligands Used in the Enantioselective, Isospecific Copolymerization of Propylene and Carbon Monoxide**

ligands **110** and **111** were highly regioregular, and due to the simplicity of the <sup>13</sup>C NMR spectra it was proposed that the polymers were isotactic. Proof of the isotactic microstructure (using ligand **111**) came when a circular dichroism spectrum of the copolymer revealed an intense band in the  $n$ - $\pi^*$  region (275 nm;  $\Delta\epsilon = -1.56 \text{ L mol}^{-1} \text{ cm}^{-1}$ ).<sup>333</sup> It was later shown that this polymer exhibits a specific optical rotation of  $[\alpha]_D^{20} = +26^\circ$ .<sup>334</sup> Such chiroptical properties are only possible with an isotactic microstructure, where an excess of propylene units are enchainned with the same absolute configuration. Interestingly, this polymer is isolated from the reaction in the spiroketal form but is converted to the polyketone by dissolution in hexafluoro-2-propanol (HFIP) followed by precipitation with methanol.<sup>335</sup>

**Table 5. Isospecific Copolymerization of Propylene and CO**

| catal <sup>a</sup> | yield <sup>b</sup> | comment  | ref      |
|--------------------|--------------------|--|----------|
| <b>108/A</b>       | 93                 | $[\alpha]_D^{25} = +6.6^\circ$ (HFIP)  | 330      |
| <b>109/A</b>       | 703                | $[\alpha]_D^{25} = +10.4^\circ$ (HFIP)   | 330      |
| <b>111/A</b>       | NR <sup>c</sup>    | highly regioregular; $\Delta\epsilon = -1.56 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; $[\alpha]_D^{20} = +26^\circ$ ; $T_m = 245^\circ \text{C}$                      | 333, 334 |
| <b>108/B</b>       | 500                | 78% H-T linkages; $[\alpha]_D^{20} = -7^\circ$ (CH <sub>2</sub> Cl <sub>2</sub> )  | 336      |
| <b>110/B</b>       | 630                | 76% H-T linkages; $[\alpha]_D^{20} = -29^\circ$ (CH <sub>2</sub> Cl <sub>2</sub> )   | 336      |
| <b>112/B</b>       | 300                | 66% H-T linkages; $[\alpha]_D^{20} = +36^\circ$ (CH <sub>2</sub> Cl <sub>2</sub> )   | 336      |
| <b>113/B</b>       | 1462               | $M_n = 36\,000$ ; $[\alpha]_D^{25} = -30^\circ$ (HFIP); $[\alpha]_D^{25} = +70^\circ$ (CHCl <sub>3</sub> )   | 342      |
| <b>114/A</b>       | 2975               | $M_n = 6300$ ; 99% H-T linkages; $\Delta\epsilon = +1.84 \text{ L mol}^{-1} \text{ cm}^{-1}$   | 340      |
| <b>115/A</b>       | 391                | $M_n = 6900$ ; 100% H-T linkages; $\Delta\epsilon = +1.73 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; $[\alpha]_D^{25} = -29.1^\circ$ (HFIP); $T_m = 237^\circ \text{C}$ | 343      |
| <b>116/C</b>       | 284                | $M_n = 65\,000$ ; 100% H-T linkages; $[\alpha]_D^{24} = +57.2^\circ$ (HFIP); $T_m = 164^\circ \text{C}$  | 338      |

<sup>a</sup> A = Pd(OAc)<sub>2</sub>, Ni(ClO<sub>4</sub>)<sub>2</sub>, naphthoquinine; B = [Pd(MeCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>; C = Pd(1,5-cyclooctadiene)(Cl)(Me), Na[B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>].  
<sup>b</sup> g<sub>polymer</sub>/g<sub>Pd</sub>. <sup>c</sup> Not reported.

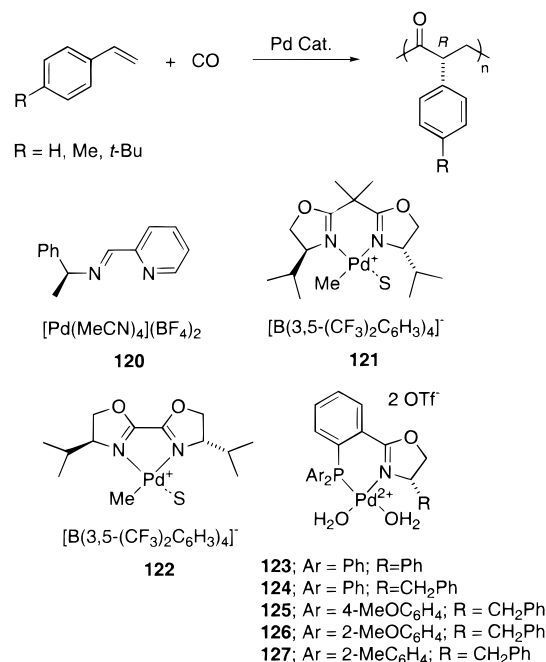
Sen has synthesized optically active propylene/CO copolymers using more traditional chiral phosphines (**108–110**).<sup>336</sup> Chien had previously carried out related polymerizations using **108** and **112** as ligands to produce modestly isotactic, semicrystalline polymers ( $[mm] = 0.5$ ; no chiroptical properties were reported).<sup>337</sup> Sen demonstrated that catalysts with ligands **108**, **110**, and **112** gave moderately regio-regular polymers with 66–78% head-to-tail linkages. The polymer formed using the atropisomeric binaphthyl ligand exhibited the highest optical rotation, although an enantioselectivity of the reaction was not reported.

In 1995, several new catalysts were reported to exhibit very high degrees of regioselectivity, stereoselectivity, and enantioselectivity for the synthesis of propylene/CO copolymers. From these studies, there is now good evidence that the regiochemistry results from a primary insertion of propylene into the Pd–acyl bond.<sup>334,338</sup> There is agreement concerning the absolute configuration of these polymers. On the basis of the sign of the CD band<sup>339</sup> and through the isolation of oligomers of known absolute configuration,<sup>338</sup> the copolymer that is dextrorotatory in HFIP is assigned the *S*-configuration. Note that the same polymer is *levorotatory* in chlorinated solvents.<sup>336</sup> Therefore it is difficult to measure and compare degrees of enantioselectivity since the specific optical rotations of these polyketones are also extremely sensitive to the sample concentration, temperature, and polymer molecular weight.<sup>336</sup> In addition, chiroptical values for the pure polymers are unknown. Nevertheless, it is clear that these catalysts exhibit excellent selectivities. Sen has reported a highly enantioselective copolymerization using a Duphos-ligated (**113**) catalyst.<sup>336</sup> By measurement of the <sup>13</sup>C NMR spectrum of the copolymer in the presence of chiral shift reagents, an enantioselectivity of greater than 90% was determined. Consiglio has exploited ferrocene-based mixed aliphatic/aromatic phosphines (**114**) to produce optically active copolymers with a proposed enantioface selectivity of 97%.<sup>340</sup> Aliphatic phosphine **115** can be used to produce polymers where the % ee of olefin insertion is as high as 98%.

Takaya has used a phosphine–phosphite bidentate ligand (**116**) to produce a copolymer with the highest reported specific optical rotation in HFIP ( $[\alpha]_D^{24} = +57.2^\circ$ ).<sup>338</sup> Nozaki has reported the effect of modifying the ligand of **116**. Replacement of the phenyl groups with 3,5-dimethylphenyl (**117**) substituents does not effect the enantioselectivity of the polymerization.<sup>341</sup> However addition of cyclopentyl groups (**118**) produces a highly isotactic polymer of *opposite* stereochemistry, and modification with ethyl groups (**119**) produces only atactic polymer. Mechanistic studies have determined that olefin insertion occurs with 1,2-regiochemistry where the acyl group is *trans* to the phosphine ligand. It is not currently clear why the enantioselectivity of the polymerization depends strongly on the type of groups present on the phosphorus atom of the ligand.

In addition to propylene, other nonconjugated olefins have been copolymerized with CO using enantiopure palladium catalysts. Allylbenzenes,

### Scheme 32. Catalysts Used for the Enantioselective, Isospecific Copolymerization of Styrene and Carbon Monoxide (S = solvent)



1-butene, 1-heptene, 4-methyl-1-pentene, cyclopentene, and *cis*-2-butene<sup>340,342</sup> as well as hydroxy- and carboxylic acid-functionalized monomers have been polymerized to give optically active polymers.<sup>344</sup> Consiglio has polymerized allylbenzenes using palladium complex ligated with **114**.<sup>345</sup> Waymouth, Takaya, and Nozaki have recently reported the enantioselective cyclocopolymerization of 1,5-hexadiene and CO,<sup>346,347</sup> and Nozaki has reported the asymmetric terpolymerization of propylene, styrenes, and CO using a catalyst derived from **116**.<sup>348</sup>

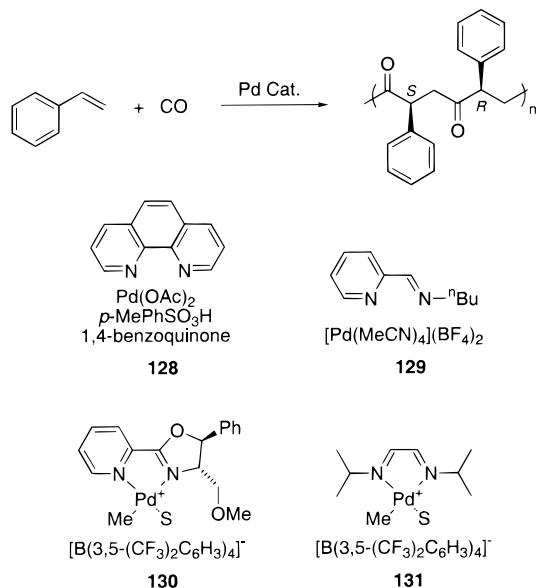
The enantioselective copolymerization of styrenes and CO has also been achieved (Scheme 32). Using bidentate pyridine–imine ligands (**120**), Sen synthesized optically active styrene and 4-methylstyrene copolymers.<sup>336</sup> On the basis of a microstructural analysis, a 36% ee for olefin insertion was reported.

Brookhart employed a *C*<sub>2</sub>-symmetrical bisoxazoline complex (**121**) to produce styrene-based copolymers that exhibited extremely high specific optical rotations.<sup>349</sup> After consideration of previous mechanistic studies and molecular models, it was proposed that propagation occurred by a 2,1-insertion mechanism to give an *R*-stereocenter (Scheme 32; Table 6). Polymerization using a *racemic* mixture of **121** also gives isotactic polymer; as expected, the product is not optically active and presumably consists of equal amounts of the poly-*R* and poly-*S* chains. Interestingly, addition of 1 equiv of the enantiomeric bisoxazoline ligand of **121** to the polymerization produces predominantly syndiotactic polymers.<sup>350</sup> It is proposed that a ligand change occurs on a time scale faster than polymerization, and the last stereocenter of the chain end dictates which ligand is present during the next olefin insertion. Thus for a syndiotactic polymer to form, enantiomeric ligands must alternate between monomer insertions. Musco<sup>351</sup> and Consiglio<sup>352</sup> have used palladium–oxazoline com-

**Table 6. Isospecific Copolymerization of Styrene and CO**

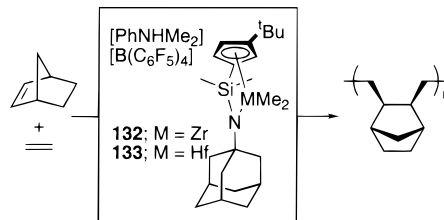
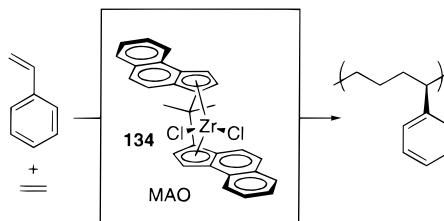
| catal <sup>a</sup> | R            | yield<br>(g <sub>poly</sub> gPd <sup>-1</sup> ) | comment  | ref |
|--------------------|--------------|---|--|-----|
| <b>120</b>         | H            | NR <sup>b</sup>                                 | [α] <sub>D</sub> <sup>20</sup> = -16° (CH <sub>2</sub> Cl <sub>2</sub> ); M <sub>n</sub> = 5600    | 336 |
| <b>120</b>         | Me           | NR  | [α] <sub>D</sub> <sup>20</sup> = -14° (CH <sub>2</sub> Cl <sub>2</sub> ); M <sub>n</sub> = 14000   | 336 |
| <b>121</b>         | <i>t</i> -Bu | 179   | [α] <sub>D</sub> <sup>25</sup> = -284° (CH <sub>2</sub> Cl <sub>2</sub> ); M <sub>n</sub> = 26 000 | 349 |
| <b>122</b>         | H            | 13  | [α] <sub>D</sub> <sup>25</sup> = -348° (Cl <sub>2</sub> HCCCHCl <sub>2</sub> )                     | 351 |
| <b>122</b>         | Me           | 66  | [α] <sub>D</sub> <sup>25</sup> = -350° (CH <sub>2</sub> Cl <sub>2</sub> )                          | 351 |
| <b>123</b>         | H            | NR  | [α] <sub>D</sub> <sup>25</sup> = -403° (HFIP/CHCl <sub>3</sub> )                                   | 352 |
| <b>119/A</b>       | <i>t</i> -Bu | 192   | [α] <sub>D</sub> <sup>23</sup> = -261° (CH <sub>2</sub> Cl <sub>2</sub> ); M <sub>n</sub> = 4300   | 338 |

<sup>a</sup> A = Pd(1,5-cyclooctadiene)(Cl)(Me), Na[B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]. <sup>b</sup> Not reported.

**Scheme 33. Catalysts Used for the Syndiospecific Copolymerization of Styrene and Carbon Monoxide (S = Solvent)**

plexes (**122**, **123**) to produce styrenic copolymers that exhibit high optical rotations. Upon modification of the diarylphosphine group from **124** to **127**, the stereoselectivities and regioselectivities of the catalysts rapidly decline.<sup>353</sup> Takaya has briefly noted the use of phosphine–phosphite bidentate ligands (**116**) for the enantioselective production of aromatic polyketones.<sup>338,354</sup>

Although syndiotactic propylene/CO polymers have not been reported, Corradini has reported the synthesis and crystal structure of a syndiotactic, alternating carbon monoxide/styrene polymer using a catalyst preparation reported by Drent (Scheme 33).<sup>355</sup> In the following year, Consiglio reported that a 1,10-phenanthroline-ligated palladium complex (**128**) could be activated to form syndiotactic polymer from CO and styrene that had 80% *rr* triads.<sup>356</sup> On the basis of stereoerrors present, it was reported that the mode of stereocontrol was chain end; on the basis of the polymer end groups, the styrene appears to insert into the Pd–acyl bond with 2,1-regiochemistry. Since these initial reports, a number of palladium complexes have been reported that form syndiotactic alternated copolymers from CO and styrene. A common feature of the catalysts is a bidentate ligand that binds to the metal center by two sp<sup>2</sup>-hybridized nitrogen atoms, where at least half of the ligand is a planar, achiral group such as a pyridine or imine. Thus, common examples of successful ligands are

**Scheme 34. Isotactic Poly(ethylene-*alt*-norbornene)****Scheme 35. Isotactic Poly(ethylene-*alt*-styrene)**

phenanthrolines (**128**),<sup>343,357–359</sup> bipyridines,<sup>343,350,358</sup> pyridine–imines (**129**),<sup>336</sup> pyridine–oxazolines (**130**),<sup>349</sup> and diimines (**131**) (Scheme 33).<sup>360</sup> Brookhart has also devised a clever ancillary ligand exchange, where the chiral bisoxazoline ligand of a cationic palladium complex (**121**) is replaced with an achiral bipyridine ligand during chain formation to create an optically active isotactic–syndiotactic stereoblock polymer.<sup>350</sup>

## 2. Other Copolymers

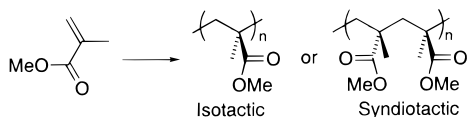
Crowther has reported the copolymerization of ethylene and norbornene using asymmetric cyclopentadienyl–amido complexes (**132**, **133**) to yield alternated polymers that melt at 250 °C (Scheme 34).<sup>361</sup> These materials have also been reported by Hoechst.<sup>362</sup> On the basis of their crystallinity and simple NMR spectra in comparison to other alternated polymers of this type, it is proposed that they are isotactic. A possible mechanism of stereocontrol is alternated insertion between isospecific (norbornene insertion) and aspecific sites (ethylene insertion). Arndt-Rosenau has used MAO-activated Me<sub>2</sub>C(3-<sup>i</sup>PrCp)(Fl)ZrCl<sub>2</sub> to form this polymer with a melting point as high as 320 °C.<sup>363</sup>

Waymouth has recently reported the alternated copolymerization of ethylene and propylene using **39**. Preliminary analysis of the polymers using <sup>13</sup>C NMR spectroscopy revealed that the alternated polymers are isotactic.<sup>364</sup>

Single-site catalysts offer many new opportunities for copolymerizing ethylene and styrene (Scheme 35). The alternating isospecific polymerization of these



### Scheme 36. Synthesis of Stereoregular Poly(methyl methacrylate)s



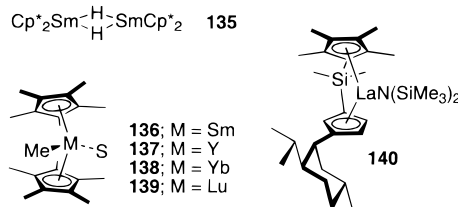
monomers has recently been accomplished, and the crystal structure of the polymer has been determined.<sup>365</sup> Kakugo has reported a titanium complex containing a thiobisphenoxy-based ligand (**76**) that forms the polymer when activated with MAO.<sup>237</sup> The chiral zirconocene (**6**) produces a polymer with 44 mol % styrene units and a melting point of 145 °C.<sup>366,367</sup> The complex  $[\text{Me}_2\text{Si}(\text{Fl})(\text{N}^t\text{Bu})\text{TiMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  forms a polymer with perfect alternation but lower melting point (118 °C) which is likely due to imperfect stereochemistry.<sup>368</sup> Arai has reported a isopropylidene-bridged zirconocene (**134**) that forms a highly alternated polymer with 50 mol % styrene units and a melting point of 154 °C.<sup>369</sup> It is proposed that the short  $\text{C}_1$  bridge is the key to high styrene incorporation.

### G. Methacrylate Polymers

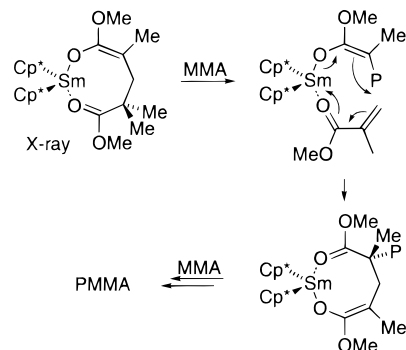
A wide range of highly stereoregular poly(methyl methacrylate) (PMMA) microstructures have been synthesized using anionic techniques. Polymerization of methyl methacrylate in toluene at  $-78$  °C using *tert*-butylmagnesium bromide as the initiator produces highly isotactic PMMA, while *tert*-butyllithium/trialkylaluminum produces the syndiotactic polymer. Addition of a bulky aluminum alkyl such as  $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_2\text{AlMe}$  to the syndiospecific reaction produces heterotactic PMMA.<sup>370</sup> Although the mechanisms of stereocontrol in these highly complex systems are not well-defined, they are at the current time the most selective methods for the synthesis of stereoregular PMMAs. Nevertheless, a range of metal-based single-site catalysts have recently been reported that exhibit impressive levels of stereocontrol in methacrylate polymerization. The two main classes of catalysts are (1) neutral lanthanocene hydrides and alkyls and (2) cationic zirconocene alkyls. For both classes, similar mechanisms of stereocontrol appear to operate. When the metallocene precursor exhibits  $C_{2v}$  symmetry, syndiotactic PMMA forms via a chain-end control mechanism. Chiral,  $C_2$ -symmetric metallocenes produce isotactic PMMA by a site-control mechanism (Scheme 36).

Yasuda has reported the use of organolanthanide metallocenes for the syndiospecific polymerization of methyl methacrylate (Scheme 37).<sup>55,371</sup> Using the dimer  $[\text{Cp}^*_2\text{SmH}]_2$  (**135**), syndiotactic PMMA was formed at  $-95$  °C with a *rr* triad content of 95.3%.<sup>372</sup> The polymerization is living in behavior up to 40 °C, producing polymers with narrow molecular weight distributions. An X-ray crystal structure of a complex formed by adding 2 equiv of monomer/Sm center revealed a cyclic adduct which is presumed to be a propagation intermediate (Scheme 38). Other lanthanocenes (**136–139**;  $\text{Cp}^*_2\text{LnMe}(\text{ether})$ ); Ln = Sm, Y, Yb, Lu) work in this reaction as well; the order of reactivity is  $\text{Sm} > \text{Y} > \text{Yb} > \text{Lu}$ . Several other studies

### Scheme 37. Lanthanide Complexes for the Stereospecific Polymerization of Methyl Methacrylate (S = Solvent)



### Scheme 38. Proposed Mechanism of Methyl Methacrylate Polymerization Using Samarocene Catalysts



have discovered achiral lanthanide complexes that form syndiotactic polymer as well.<sup>373–375</sup> Notably, Novak has developed a novel route to bimetallic initiators that form syndiotactic PMMA-containing block polymers.<sup>376,377</sup> Marks has reported the synthesis of isotactic PMMA using the asymmetric complex **140** as an initiator. At  $-35$  °C, the polymer formed had an *mm*-triad concentration of 94%.<sup>378</sup> The mechanism of stereocontrol in this case is not clear, since the monomer can in principle coordinate at two diastereomeric sites. Isomerization of the enolate at a rate faster than propagation to one side of the complex was proposed as a scenario for stereocontrol.

Collins first reported the use of cationic zirconocenes for acrylate polymerization.<sup>379</sup> Using the ionic complex  $[\text{Cp}_2\text{ZrMe}(\text{THF})][\text{BPh}_4]$  in combination with a  $\text{Cp}_2\text{ZrMe}_2$  initiator, partially syndiotactic PMMA ( $[r] = 0.8$ ) was formed. The mechanism was originally proposed to be related to that proposed for the lanthanide complexes; however, recent studies by Collins have suggested an alternate mechanism.<sup>380,381</sup> Collins has also reported the use of chiral zirconocenes for isospecific methyl methacrylate polymerization. Both the *racemic* and enantiomerically pure dimethylzirconium variants of  $\text{Et}(\text{Ind-H}_4)_2\text{ZrCl}_2$  (**8**) form isotactic PMMA by a site-control mechanism once activated by  $[\text{Bu}_3\text{NH}][\text{BPh}_4]$ .<sup>380</sup> Marks has recently reported the use of  $\{[\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}]_2(\mu\text{-Me})\}[\text{MeB}(\text{C}_{12}\text{F}_9)_3]$  to synthesize isotactic PMMA with  $[mm] = 0.93$ .<sup>26</sup> A bimetallic propagation mechanism similar to Collins'<sup>380,381</sup> is proposed to operate. Soga has extensively explored the activation of zirconocene dimethyl derivatives with  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  for methacrylate polymerization; only in the presence of excess  $\text{ZnEt}_2$  does the reaction take place. Using  $\text{Cp}_2\text{ZrMe}_2$ , mostly syndiotactic polymer is formed with approximately 50% *rrrr* pen-

tads.<sup>382,383</sup> However, using the chiral zirconocene  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  (**6**), highly isotactic PMMA with 94% *mmmm* pentads is synthesized.<sup>384,385</sup>

### III. Conclusions

It is now clear that the advent of single-site catalysts for the stereoselective polymerization of olefins has initiated a revolution in polymer synthesis. Although the vast majority of homogeneous polymerization catalysts are designed for olefin polymerization, the extension of this area of catalysis for the polymerization of other monomers, such as lactones and epoxides, is already in progress.<sup>386–388</sup>

There are a variety of strategies for the synthesis of new high-performance polymers from cheap starting materials. For example, the copolymerization of two or more monomers to yield novel materials, and the blending of two separate homopolymers (usually with a compatibilizer), are routes to new polymeric materials using currently existing monomers. However, the synthesis of homopolymers of unprecedented stereochemistry from common monomers using specifically tailored single-site catalysts is a technique that holds great potential for the synthesis of commercially valuable polymers. For example, well-defined catalysts are now available for the synthesis of highly syndiotactic polystyrene—a polymer that had not been synthesized before using heterogeneous catalysts—resulting in a new engineering resin with many potential applications. Single-site catalysts have now been disclosed that produce a wide range of polypropylene tacticities that also cannot be precisely synthesized using conventional heterogeneous catalysts, including atactic, syndiotactic, hemiisotactic, and isotactic–atactic stereoblock microstructures. There are many examples of polymerizations where homogeneous catalysts have significant advantages over their heterogeneous counterparts, including cycloolefin polymerization (via both ROMP and insertion mechanisms), CO/olefin copolymerization, and the polymerization of conjugated dienes and functional monomers.

Despite many successes, advances in the area of stereoselective polymerization do not come easily. Notwithstanding the rational appearance of homogeneous catalyst development, often the most successful catalysts are not those developed during the initial stages of a research project. Typically, a significant amount of empirical optimization is required to refine the catalyst to a point where it can efficiently and selectively enchain the monomers in the fashion desired. Therefore an easily modified ligand structure is essential for rapid catalyst evolution. An archetypal example is the development of isospecific catalysts for propylene polymerization. Over more than a decade, countless laboratory experiments were required to modify the metallocene framework in order to produce commercially viable polymers. Thus, new techniques are clearly necessary to allow the rapid discovery and optimization of new catalysts—not only stereoselective polymerization catalysts but catalysts in general. Such potential methods include molecular modeling and high-throughput (combinatorial) strategies. These tech-

niques are currently most valuable for developing and understanding catalyst systems once one has been discovered and have unfortunately been unsuccessful at either predicting or discovering radically different or outstanding systems. Given the substantial efforts devoted toward advancing each of these techniques, it should be clear soon whether these or other strategies will permit more rapid catalyst discovery and development.

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