

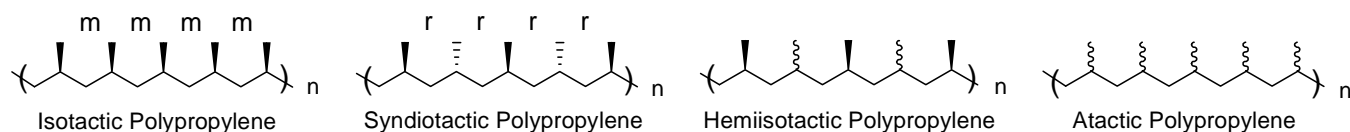
# FINE-TUNING ZIEGLER-NATTA POLYMERIZATIONS: STEREOCONTROL OF POLYPROPYLENE FORMATION

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## INTRODUCTION

Polyolefins, such as polypropylene, have found applications in many facets of our lives including clothing, food packaging, appliances, toys, foams, and films.<sup>1</sup> Because of the diversity of properties of polyolefins, they are used for many applications. Various polymer properties can be obtained through the control of the microstructure of polymer backbones, which have a strong influence on the morphology and macroscale physical properties of the material. Polymers with stereoregular backbones possess a crystalline morphology, whereas stereoirregular polymers are amorphous and have low melting temperatures that limit their applicability.<sup>1a</sup> Polymers that have consecutive monomer units with the same configuration relative to the backbone (*m*, meso) are classified as isotactic and polymers that have consecutive monomer units with opposite configuration relative to the backbone (*r*, racemic) are classified as syndiotactic (Figure 1).<sup>1a</sup> Polymers that have a random order of configurations in the monomer units are called atactic. A dyad (*x*) is the relative configuration between two monomer units, a triad (*xx*) is the relative configuration between three monomer units and a pentad (*xxxx*) is the relative configuration between a series of five monomer units ( $x = r/m$ ).<sup>1a</sup> It should be noted that pentad contents of stereoisomeric polymers are reported because this gives a more accurate description of the microstructure than dyad or triad contents.



**Figure 1.** Polypropylene pentad microstructures and configurational nomenclature.

Polypropylene was the first synthetic polymer with a stereoregular backbone to be synthesized and characterized.<sup>1</sup> The broad scope of applications of polypropylene has focused researchers' attention on controlling its properties through stereocontrolled syntheses. This report will discuss the most recent advances in catalyst design as well as mechanistic insight into the polymerization processes of propylene.

## POLYPROPYLENE

“The average yearly consumption of polymers of propylene is about 4 kg per inhabitant of the Earth!”<sup>2</sup> Currently, petroleum serves as the main source of olefins for polymerization. However, the

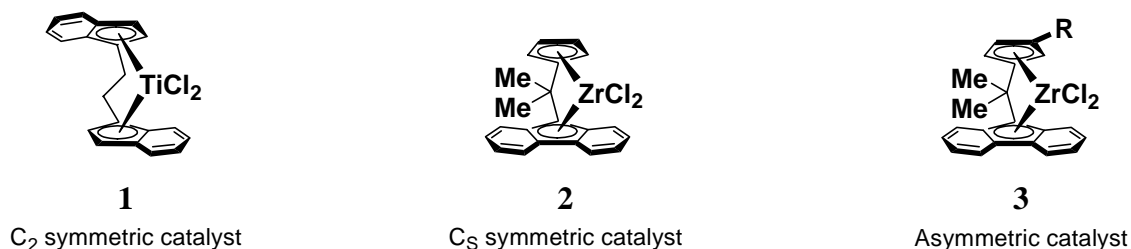
desire to reduce the consumption of fossil fuels makes it advantageous to create polymeric architectures that can be easily recycled. To address this goal, chemists have developed methods to control the tacticity of polypropylene, ultimately affecting the physical characteristics of the polymer, which can make the recycling process more facile.

## HISTORICAL BACKGROUND

The initial synthesis and characterization of stereoregular polypropylene has been attributed to the efforts of Ziegler and Natta in the early 1950s.<sup>3</sup> In the labs of Ziegler, heterogeneous titanium catalysts were developed that allowed for the polymerization of ethylene and propylene at low pressures and temperatures.<sup>3</sup> Natta and coworkers, however, elucidated the microstructure of the isotactic polypropylene (iPP) produced with Ziegler's catalyst.<sup>4</sup> Syndiotactic polypropylene (sPP) was synthesized with a heterogeneous vanadium catalyst developed by Ziegler and Zambelli shortly after the initial characterization of isotactic polypropylene.<sup>5</sup>

The next important set of results followed the discovery by Kaminsky and coworkers, in 1980, that hydrated trimethylaluminum (methyl aluminoxane, MAO) is a potent cocatalyst with homogeneous Group 4 metallocenes for the polymerization of olefins.<sup>6</sup> A new field of research was opened and many homogeneous catalysts were developed for this catalytic process. The pioneering work of Kaminsky and Ewen demonstrated a general trend that  $C_2$ -symmetric metallocene catalysts (**1**) produced iPP<sup>7</sup> and  $C_S$ -symmetric metallocene catalysts (**2**) produced sPP (Chart 1).<sup>8</sup> Asymmetric metallocene catalysts (**3**) have been developed to produce a variety of microstructures.<sup>9</sup>

Chart 1

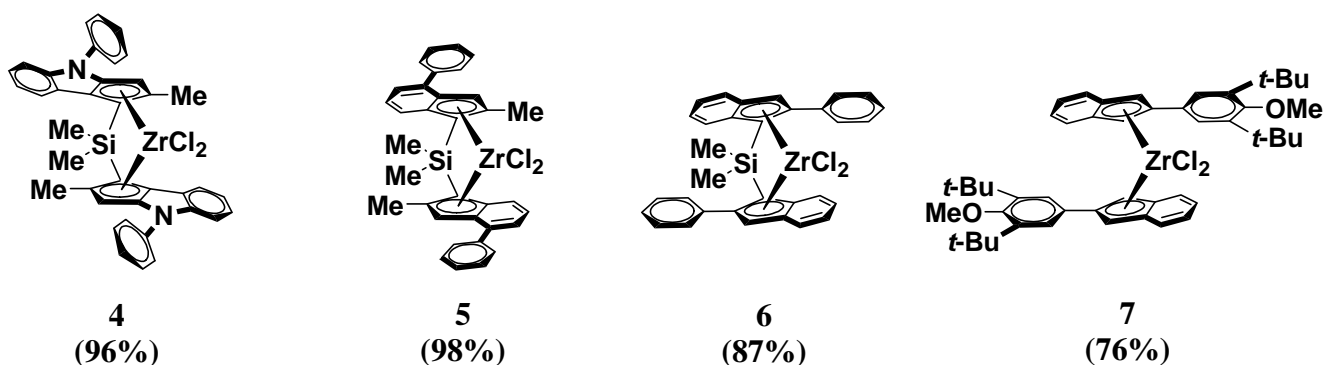


## Isotactic Polypropylene

Isotactic polypropylene is a rigid plastic that has a crystalline morphology with a melting temperature in the range of 155-165 °C.<sup>1a</sup> It is defined as a thermoplastic because iPP can be melted down and recycled without any appreciable change to its chemical structure. For these reasons, iPP has found many applications. Ewen's  $C_2$ -symmetric ansa-bis(indenyl) titanocene **1** gave moderately isotactic PP with a 56% "mmmm" pentad content (for five monomer units, there are four stereochemical

relationships).<sup>7</sup> Following Ewen's groundbreaking work in homogeneous catalysis, researchers examined other  $C_2$ -symmetric zirconocene catalyst structures that led to highly isotactic catalysts (Chart 2). In general, higher isotacticity can be achieved by increasing steric bulk in strategic positions and locking the structural conformations of the ligand with a bridging moiety. The effect of increasing the rigidity of the catalyst structure on stereoselectivity can be observed by examining the pentad contents of polypropylene synthesized with catalysts **1** (56%),<sup>7</sup> **4** (96%),<sup>10</sup> **5** (98%),<sup>11</sup> and **6** (87%).<sup>11</sup> The  $C_2$ -symmetric conformation of the catalyst structure can be induced by steric and/or electronic interactions in an unbridged ligand structure with free rotation (**7**, 76% "mmmm" pentad content).<sup>12</sup>

**Chart 2. Highly isotactic metallocene catalysts, (% mmmm content).**



There are also select examples of asymmetric catalysts that lead to isotactic polymers.<sup>13</sup>

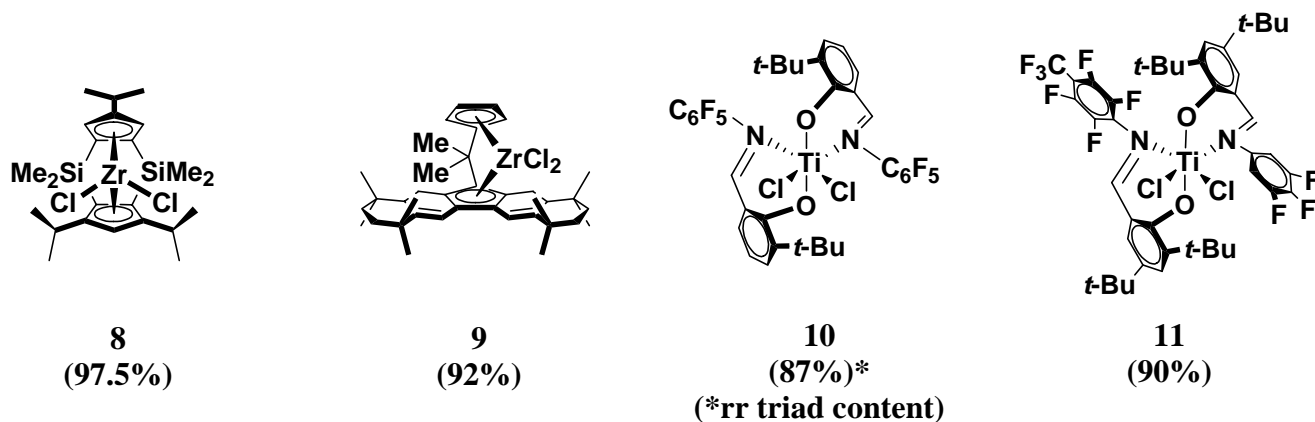
### Syndiotactic Polypropylene

In addition to the catalysts developed for the production of isotactic polypropylene, researchers have also designed catalysts that produce polymers with syndiotactic microstructures. Extending the work initiated by Ewen, Bercaw and coworkers have developed new  $C_5$ -symmetric ligand classes (Chart 3).<sup>14,15</sup> Doubly bridged zirconocene **8**<sup>14</sup> was developed to increase the stability of the catalyst and ansa-cyclopentadienyl/fluorenyl zirconocene **9**<sup>15</sup> was designed to provide increased steric interactions with the polymer chain, which directs facial binding of propylene (Chart 3). Both catalysts provided impressive selectivities for syndiotactic polymerizations; 97.5% and 92% "rrrr" contents were observed with catalysts **8** and **9**, respectively.<sup>14,15</sup>

Although metallocenes have proven to be a robust and diverse class of catalysts and have received much attention in propylene polymerizations, recent developments using phenoxyimine (PHI) ligands (**10** and **11**) have provided promising results for achieving highly syndiotactic polypropylene structures (Chart 3). Following Fujita's demonstration that bis(PHI) catalysts are highly active for ethylene polymerizations,<sup>16</sup> Coates applied these  $C_2$ -symmetric catalysts to propylene polymerizations. Coates and coworkers used combinatorial methods to screen for highly active and highly stereoselective

bis(PHI) catalysts<sup>17,18</sup> and identified heteroligated bis(PHI) **11** as one of the best catalysts,<sup>18</sup> giving 90% “rrrr” pentad content. Catalyst **10** gives 87% of “rr” triad content.<sup>19</sup>

**Chart 3. Highly syndiotactic catalysts, (% rrrr content).**



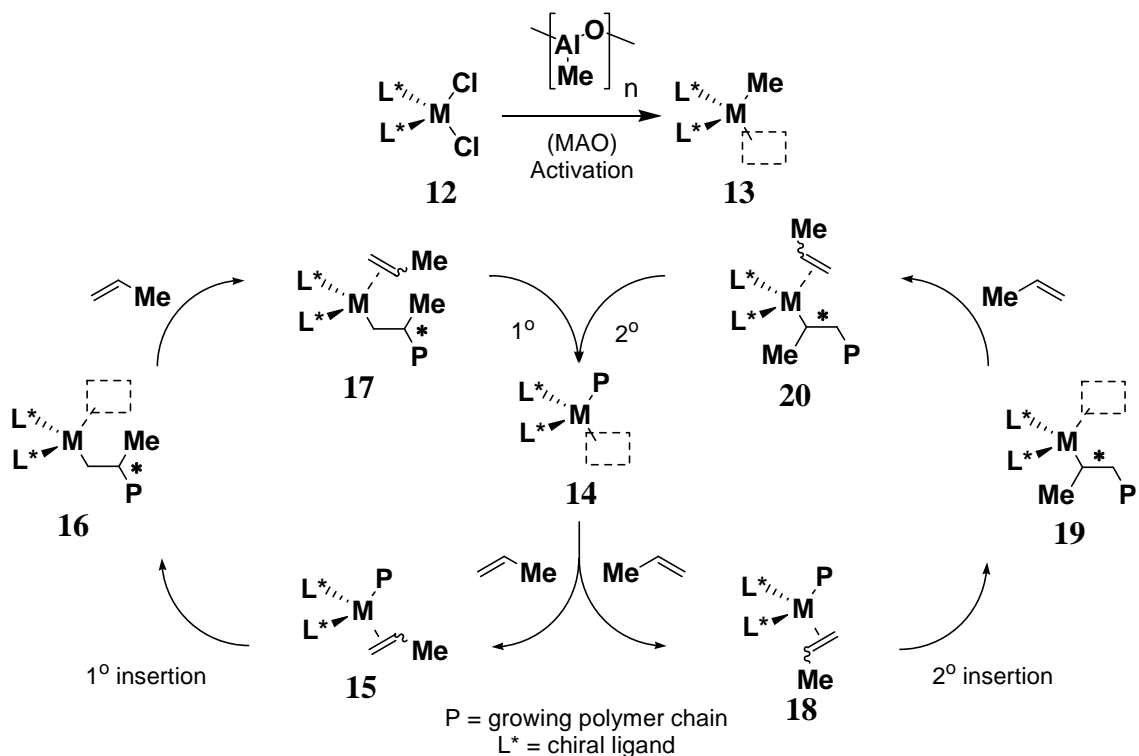
### Mechanistic Rationale

The general trends that relate catalyst symmetry and stereospecificity in propylene polymerizations can be explained by a detailed examination of the reaction mechanism. The mechanistic components of stereoselectivity for propylene polymerization have been determined by using computational and theoretical calculations,<sup>20</sup> as well as by examining the relative percentages and types of stereodefects<sup>7</sup> that exist in the polymer structures. Analysis of chain end groups gives insight into the initiation, propagation, and termination processes of polymerization.<sup>1b, 16b, 21</sup>

The catalytic cycle for propylene polymerization begins with activation of precatalyst **12** (generally a metal dihalide) by MAO or one of several other cocatalysts such as fluorinated boranes, borate salts, or aluminate salts (Scheme 1).<sup>22</sup> Upon activation, the Group 4 transition metal complex (comprised of ligands and an initiating alkyl group) presents a vacant coordination site to bind propylene (**13**). After coordination of propylene (**14**→**15** or **18**), the new complex undergoes a cis migratory insertion into the metal polymer bond. When 1-alkenes undergo polymerization, there is not only an issue of stereoselectivity, but also regioselectivity. Traditional metallocene catalysts, regardless of symmetry ( $C_2$  or  $C_S$ ) tend to react via a primary insertion pathway (**15**→**16**→**17**).<sup>22</sup> By contrast bis(PHI) catalysts have been observed to follow a secondary insertion mechanistic pathway (**18**→**19**→**20**).<sup>21</sup>

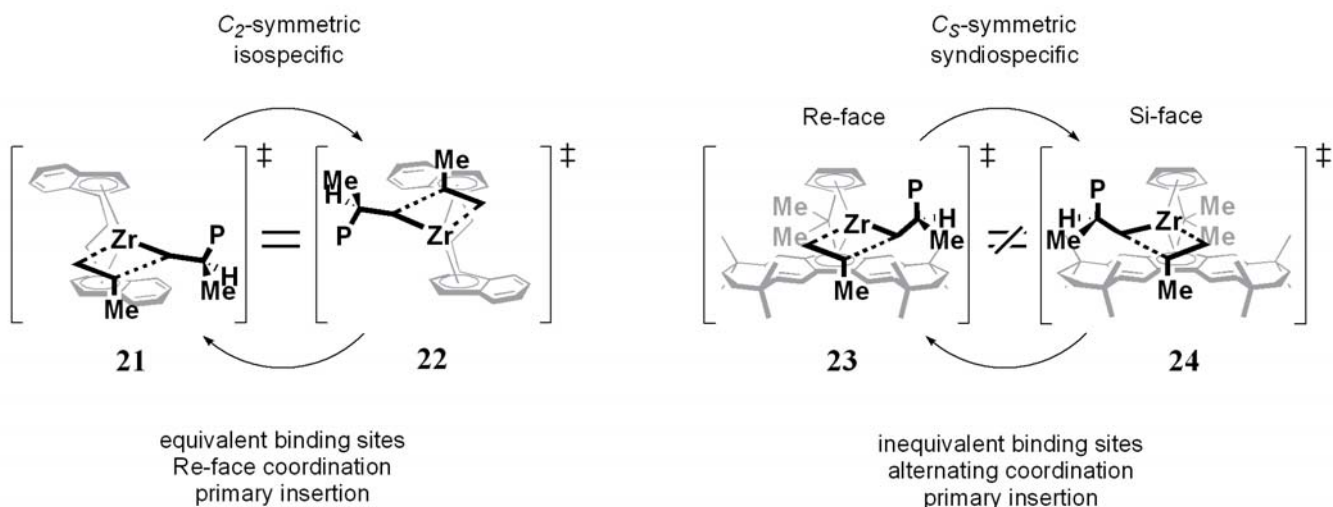
For metallocenes, which undergo primary insertion, the stereochemical outcome is controlled by the active site geometry (chiral-site stereocontrol).<sup>20</sup> Thus, for  $C_2$ -symmetric metallocenes (**21** and **22**), in which the binding sites are equivalent due to symmetry, each successive monomer coordinates with the same facial selectivity to minimize steric interactions, leading to isotactic polypropylene<sup>18</sup> (Scheme 2). For  $C_S$ -symmetric catalysts, each addition occurs at opposite faces of the propylene monomer (**23**

**Scheme 1. Mechanism for propylene polymerization.**



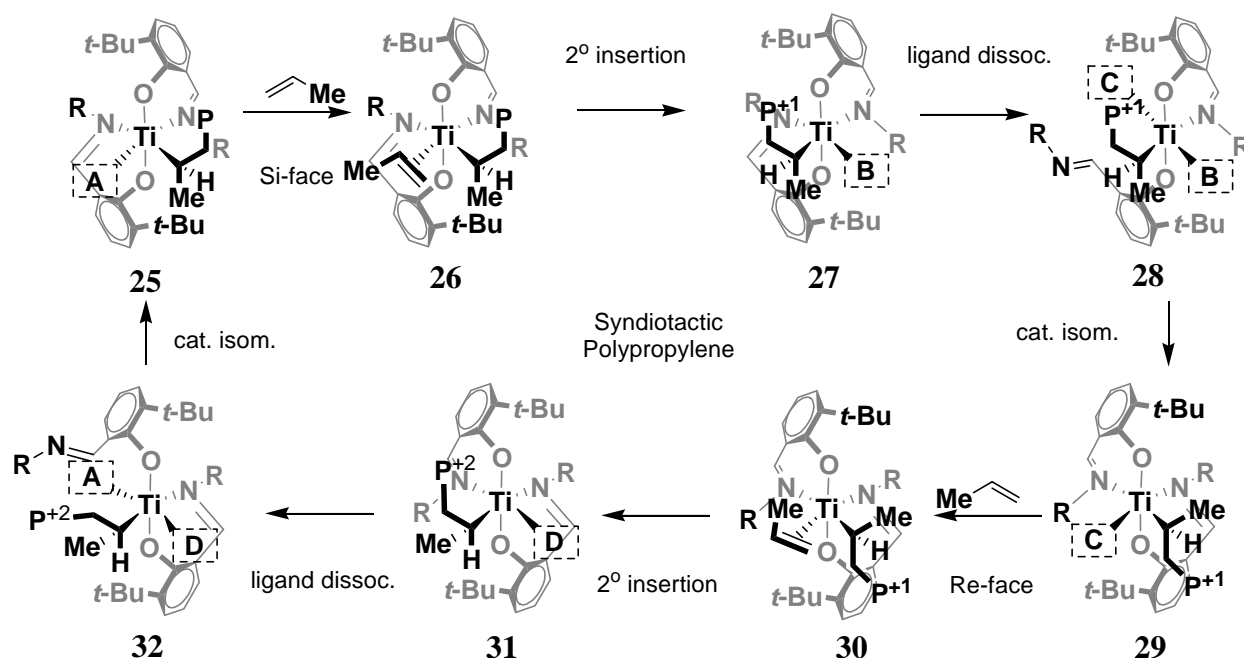
and **24**), leading to syndiotactic polypropylene<sup>14,15</sup> (Scheme 2). The steric bulk of the catalyst structure directs the growing polymer chain away from the ligand in order to minimize steric interactions. The polymer chain then directs binding through steric repulsion of the methyl group on the propylene monomer for subsequent coordination and insertion.

**Scheme 2. Metallocene transition state structures,  $C_2$ - and  $C_S$ -Symmetric.**



With the bis(PHI) catalyst systems, which undergo secondary insertion, stereocontrol is based on the last monomer unit inserted (chain-end control) (Scheme 3).<sup>20</sup> The surprising result that these  $C_2$ -symmetric catalysts produce syndiotactic polypropylene can be explained by the dynamic nature of the ligand metal complex. When both ligands are bound to the catalyst, there is a defined  $C_2$ -symmetry (**25**) with a vacant coordination site (site A) that binds the Si-face of propylene (**26**); the N-aryl group directs the methyl of the propylene away. After secondary insertion (**27**), the imine nitrogen coordinated cis to the polymer chain dissociates from its coordination site (**28**). The last monomer of the polymer chain directs the recoordination (site B) of the ligand to minimize steric interactions (**29**), leading to the enantiomeric catalyst structure of **25**. Catalyst structure **29** then binds the Re-face of propylene (**30**). Continuing this process (**31**→**32**→**25**) leads to an alternating configuration along the polymer backbone (syndiotactic polypropylene).

**Scheme 3. PHI ligand catalytic cycle and site isomerization.**

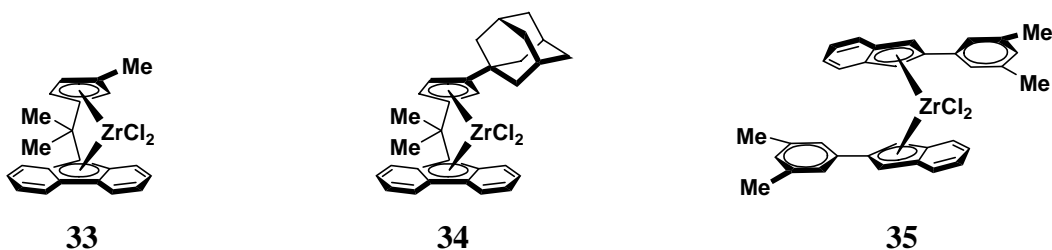


### Elastomeric Polypropylene

Polypropylene microstructures that have elastomeric characteristics are stereoblock isotactic-atactic or isotactic-hemiisotactic polymers.<sup>1a</sup> The atactic or hemiisotactic segments of stereoblock polypropylene form amorphous regions that are connected by isotactic segments that form crystalline regions.<sup>1a</sup> These non-covalent interactions give the material a rubbery consistency at ambient temperatures, but can be melted at higher temperatures and therefore can be recycled without chemical modification. Natta and coworkers were the first to report elastomeric polypropylene and proposed that the properties arise from the alternating crystalline and amorphous microstructures.<sup>23</sup> Many researchers

have developed catalysts that can produce these microstructures in a controlled fashion.<sup>23, 24, 25</sup> Bercaw explored the consequences of increasing the steric bulk at C(3) of the cyclopentadienyl ring of Ewen and Razavi's asymmetric catalyst **33**, which produced highly hemiisotactic polypropylene,<sup>9</sup> and found that catalyst **34** gives desirable stereoblock microstructures (Chart 4).<sup>24</sup>

**Chart 4. Hemiisotactic and stereoblock catalysts.**



Fixed catalyst structures such as bridged asymmetric catalysts produce elastomeric microstructures by control of site epimerization. Another method for producing elastomeric microstructures is by using a catalyst that can undergo ligand isomerization.<sup>23</sup> Waymouth and coworkers developed a catalytic system that is dynamic in its structural conformations. The rotational freedom that exists in bis(2-aryindenyl) metallocenes (**35**)<sup>25</sup> allows it to oscillate between a chiral  $C_2$ -symmetric isospecific conformation and an achiral  $C_{2v}$  nonspecific conformation (Chart 4). By varying the steric and electronic interactions, isotacticities ranging from only 5 % up to 87 % “mmmm” pentad content can be obtained.<sup>25</sup> With these advances in catalyst design, the production of elastomeric polypropylene can be accomplished in a controlled fashion.

## CONCLUSION

Since the pioneering work of Ziegler and Natta, there has been a growing interest in polyolefin chemistry. Development of homogeneous catalytic systems, from the discovery that MAO is a potent cocatalyst with homogeneous Group 4 metallocenes, sparked a renaissance in catalyst design and a better mechanistic understanding of propylene polymerization. Strategic construction of various ligands has enabled chemists to precisely control the microstructure and morphology of polypropylene and numerous other polyolefins. These advances are leading to the development of robust, highly active, highly stereospecific, and controlled polymerizations, which in turn allow the development of environmentally friendly recyclable polymer architectures. Currently the challenge for chemists is to transition these viable materials being produced in research laboratories to a full-scale industrial production.

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