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Development of a Diversity-Based Approach for the Discovery of Stereoselective Polymerization Catalysts: Identification of a Catalyst for the Synthesis of Syndiotactic Polypropylene**

Jun Tian and Geoffrey W. Coates*

The discovery of efficient and selective catalysts for organic and polymer synthesis will be a crucial requirement for the sustained growth of the chemical industry as economic and environmental constraints become more restrictive in the new millennium. Increasingly important will be the stereoselective catalysts that provide key enantiomerically pure building blocks to the pharmaceutical industry[1] as well as stereoregular macromolecules to the polymer industry.[2] Due to the complicated mechanistic nature of many transition metal based catalysts, structure–activity relationships are often unpredictable leaving empirical exploration and serendipity the most common routes to discovery. Although impressive catalyst breakthroughs have been made, more efficient strategies clearly must be implemented to aid the pursuit of new catalysts. Perhaps the most widely heralded approach that is proposed to influence the discovery and optimization of new catalysts is combinatorial chemistry.[3–5] Combinatorial methods have significantly hastened the discovery of new drugs through the rapid synthesis and efficient screening of diverse sets (libraries) of organic molecules.[6–8] It seems reasonable that a similar strategy might impact catalyst discovery and optimization if metal complex libraries can be rapidly synthesized and their desired properties tested.[9] Although the combinatorial approach is often viewed by some with skepticism, it should be stressed that the more rapidly new classes of highly selective catalysts are discovered, the faster traditional chemists can initiate studies to elucidate their detailed mechanisms of operation. Large collections of structure–activity data will not only provide a solid information base upon which mechanistic hypotheses can be proposed and supported, but will also facilitate the development of new catalyst systems. Herein we report a combinatorial approach for the discovery of stereoselective polymerization catalysts. Using this method, we identified a new catalyst system for the syndiospecific polymerization of propylene.

The development of new polymerization catalysts can be subdivided into three main steps: ligand preparation, complex synthesis, and screening of the behavior of these complexes for a specific reaction. Depending on the catalyst system under investigation, any one of these can be the rate-determining step that limits improvement. The synthesis and testing of catalyst libraries can occur primarily in two formats, parallel (spatially separate reaction vessels) and pooled (combined in one reaction vessel) libraries.[10, 11] Although each format has its advantages, the use of combinatorial methods for developing enantioselective catalysts for small-molecule transformations has thus far relied on the parallel synthesis of ligands and complexes, followed by the serial screening for enantioselectivity using chiral chromatography.[12, 13] Due to the time-consuming nature of sequentially screening the enantioselectivities of the products of a parallel library, one might wonder why the screening of a pooled, bead-bound stereoselective catalyst library has not been reported. Exchange of products between different beads and/or the reaction solution occurs, therefore only an average stereoselectivity of the library can be determined (Scheme 1).[14]

Interestingly, the situation changes in the case of stereoselective polymerization catalysts (Scheme 1). Unlike the asymmetric transformation of small molecules where the stereochemical events of the reaction are unconnected, the polymer itself serves as a stereochemical recording of the events of the polymerization catalyst. Assuming that the catalyst species do not interact with one another, then a group of complexes for stereoselective polymerization can be

[*] Prof. G. W. Coates, Dr. J. Tian
Department of Chemistry and Chemical Biology
Baker Laboratory
Cornell University
Ithaca, NY 14853-1301 (USA)
Fax: (+1) 607-255-4137
E-mail: gc39@cornell.edu

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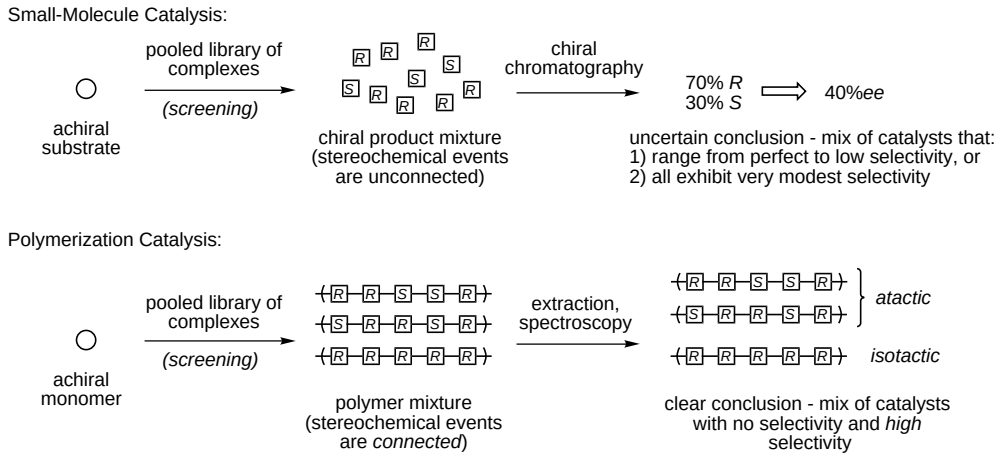


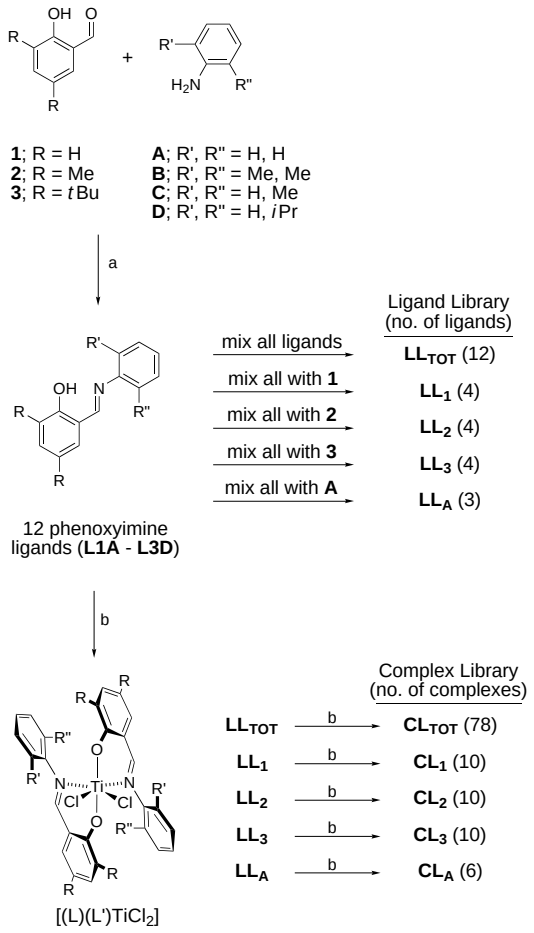
Scheme 1. Pooled screening of stereoselective catalysis: small-molecule catalysts and polymerization catalysts.

simultaneously screened. For example, a simple solvent extraction can identify the presence of a stereoregular polymer due to its lower solubility than the atactic form. Once a hit catalyst is detected, the library can be systematically narrowed and the new catalyst easily identified.[15]

There are several additional benefits of this pooled polymerization catalyst discovery strategy. Since the catalysts all exist in the same reaction vessel, they can be simultaneously synthesized from a ligand library if high-yield complex preparations are available. Complex synthesis and storage often requires an inert atmosphere, therefore this feature saves considerable time and expense. The approach can also be used to detect catalysts which produce polymer of high molecular weight by analysis of the crude polymer product using gel permeation chromatography. If high molecular polymer is present, the catalyst responsible for it can in theory be ascertained from the catalyst library. Likewise, incorporation of unreactive comonomers can be screened if there is a spectroscopic method to reveal its incorporation into the polymer chain. Similarly, carefully constructed sublibraries of the main catalyst collection can rapidly reveal the catalyst(s) that are capable of comonomer incorporation. Herein we demonstrate the feasibility of such a discovery process by identifying a new catalyst for the synthesis of syndiotactic polypropylene.[16–19]

To demonstrate the feasibility of this pooled polymerization catalyst discovery strategy, we designed a catalyst system after consideration of the following criteria. First, we reasoned that the ligands should be efficiently synthesized from commercially available starting materials. Second, complex synthesis must also be high yielding; bis-ligated complexes are favored over mono-ligated complexes since the former increase the diversity of the library (n ligands will form n mono-ligated species while $(n^2+n)/2$ bis-ligated complexes are formed). Third, ligand–metal bond strengths should be significant enough to ensure that a statistical library of the complexes is generated. Based on these considerations, we chose to investigate titanium complexes bearing salicylaldiminato ligands (Scheme 2). These ligands are readily synthesized by the condensation of a wide range of amines and salicylaldehydes. Although several recent reports have described the polymerization of ethylene using these complexes,[20–24] to our knowledge their behavior for propylene polymerization is unreported. Due to their C_2 symmetry, we anticipated that they might be isospecific catalysts for propylene polymerization.

To investigate a wide range of steric effects yet keep the library size manageable, we designed a 12-component ligand library made from three salicylaldehydes (**1**–**3**) and four anilines (**A**–**D**) (Scheme 2). The salicylaldimines were separately made and extensively purified by recrystallization. Equimolar amounts of the ligands were combined to make a 12-ligand library ($\mathbf{LL_{TOT}}$). Deprotonation of $\mathbf{LL_{TOT}}$ with nBuLi at $-60\,^{\circ}C$ followed by reaction with 0.5 equivalents of $TiCl_4$ yielded complex library $\mathbf{CL_{TOT}}$ (78 possible species). To investigate whether a statistical mixture



Scheme 2. Synthesis of the library of complexes. a) parallel synthesis; MeOH, reflux, 12 h, >95%; b) pooled synthesis; nBuLi, $-60\,^{\circ}C$ to $20\,^{\circ}C$, 4 h (1 equiv); $TiCl_4$, $-60\,^{\circ}C$ to $20\,^{\circ}C$, 16 h (0.5 equiv), >90%.

of complexes is formed, we reacted equal amounts of deprotonated **L1A** and **L3A** with $TiCl_4$. ^1H NMR spectroscopy of the product revealed the complexes $[(\mathbf{L1A})_2TiCl_2]$, $[(\mathbf{L1A})(\mathbf{L3A})TiCl_2]$, and $[(\mathbf{L3A})_2TiCl_2]$ in an approximate 1:2:1 ratio. Although we have not been able to collect acceptable mass spectrometry data on $\mathbf{CL_{TOT}}$, we believe this experiment is strong evidence that at least an appreciable amount of each complex exists in the library.

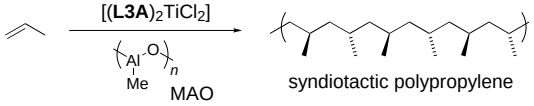
The complex library $\mathbf{CL_{TOT}}$ was activated with methylaluminoxane (MAO; [Al]/[Ti] = 100) in toluene and the resultant catalyst solution was exposed to propylene (2.7 atm) at 20 °C. Polypropylene (PP) was slowly formed with an activity of 480 g PP per mol Ti per hour. Although 90% of the resultant polymer was soluble in refluxing diethyl ether (atactic polypropylene), the remaining 10% was insoluble and unexpectedly was found to be *syndiotactic polypropylene* by ^{13}C NMR microstructural analysis.[25] To ascertain the identity of the catalyst(s) responsible for the formation of this stereoregular polymer, we investigated the polymerization behavior of four sub-libraries of $\mathbf{CL_{TOT}}$ (see Table 1). $\mathbf{CL_1}$ and $\mathbf{CL_2}$ produced only atactic polymer. However $\mathbf{CL_3}$ and $\mathbf{CL_A}$

Table 1. Propylene polymerization using MAO activated bis(salicylaldiminato)titanium complexes.

Complex/Library[a]	Activity[b]	% Et_2O soluble	% Et_2O insoluble
$\mathbf{CL_{TOT}}$	0.480	90	10
$\mathbf{CL_1}$	0.310	100	0
$\mathbf{CL_2}$	0.610	100	0
$\mathbf{CL_3}$	4.00	81	19
$\mathbf{CL_A}$	3.10	68	32
$[(\mathbf{L3A})_2TiCl_2]$	8.80	0	100

[a] Polymerization reactions were performed in toluene solution at 20 °C and 2.7 atm propylene for 6 h. [b] kg PP per mol Ti per h.

produced 19% and 32%, respectively, of polymer that was insoluble in diethyl ether. We have synthesized $[(\mathbf{L3A})_2TiCl_2]$, the common species of $\mathbf{CL_3}$ and $\mathbf{CL_A}$, and found that it forms monodisperse, highly syndiotactic polypropylene (Scheme 3).[26] Microstructural analysis using ^{13}C NMR



Scheme 3. Polymerization of propylene using $[(\mathbf{L3A})_2TiCl_2]$/MAO yields syndiotactic polypropylene with errors consistent with a chain-end control mechanism.

spectroscopy reveals that a chain-end control mechanism appears to operate.[25] Aside from the syndiotactic [*rrrr*] pentad, only the [*rrrm*], and [*rmrr*] pentads are present (1:1 ratio). Analysis of the peak intensities using a Bernoullian statistical model reveals that the probability of an *r*-dyad placement in the polymer chain is 92%. To our knowledge, this is the highest reported degree of chain-end control in a propylene polymerization.[27] When the polymerization is carried out at 0 °C, a polymer with 94% *r*-dyads is formed; Figure 1 shows the ^{13}C NMR spectrum of the methyl region of this polymer. This semicrystalline polymer exhibits a peak melting temperature of 108 °C.

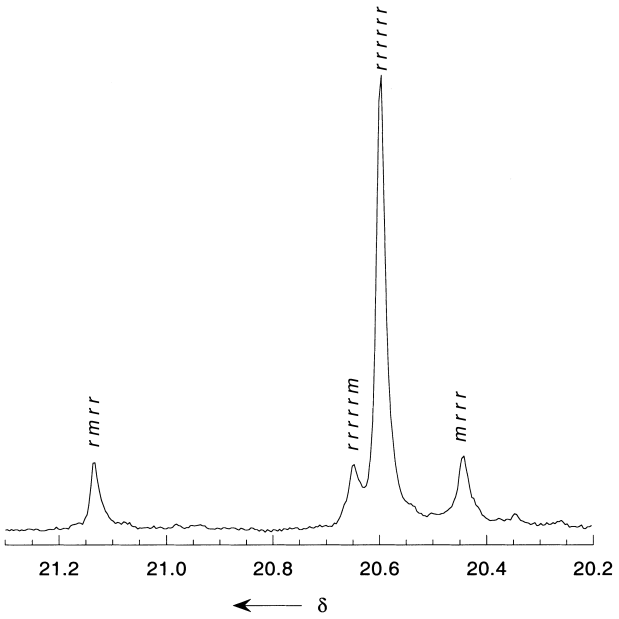


Figure 1. Quantitative proton-decoupled ^{13}C NMR spectrum of the methyl region of polypropylene prepared with $[(\mathbf{L3A})_2TiCl_2]$/MAO at 0 °C (100 MHz, C_6D_6).

At the current time, the detailed mechanism of polymerization is unknown. One unusual aspect of the reaction is that a chain-end mechanism apparently overrides the chiral C_2 symmetry of the catalyst precursor. Two intriguing mechanistic possibilities are currently being investigated. The first prospect is that the olefin is enchained by a secondary (2,1) mechanism, placing the last stereogenic center of the polymer chain on the carbon bound to the titanium center. Second is a ligand isomerization pathway, in which the catalyst site undergoes site inversion between olefin insertions due to the chain-end geometry of the polymer.[28]

In conclusion, we report a valuable strategy for the rapid screening of polymerization catalyst libraries. When a desired polymer product has distinguishing chemical or physical properties, techniques such as solubility, spectroscopy, or chromatography can be used to quickly probe the crude product of a pooled polymerization reaction to see if a noteworthy catalyst is present. Then the systematic synthesis of catalyst sub-libraries can be used to rapidly identify the desired catalyst. The viability of this strategy was successfully demonstrated by using a library of bis(salicylaldiminato)titanium complexes, where a syndiospecific catalyst for propylene polymerization was identified. To our knowledge, this is the first time that combinatorial methods have been reported to identify a new polymerization catalyst with unexpected, yet desirable properties.

Experimental Section

Complex library ($\mathbf{CL_{TOT}}$) synthesis: Twelve ligands (**L1A** – **L3D**, 0.500 mmol each) were carefully weighed and then codissolved in diethyl ether (40 mL) in a predried Schlenk tube under nitrogen. At −60 °C, the ligand library solution was treated dropwise with *n*BuLi (3.75 mL, 1.6 M in hexanes, 6.00 mmol) by using a gas-tight syringe. After the temperature of the reaction mixture had been allowed to rise to room temperature, the reaction was stirred for another 4 h. Half of the ligand solution was

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cannulated into a solution of $TiCl_4$ (0.569 g, 3.00 mmol) in Et_2O (20 mL) at $-60\,^{\circ}C$; after stirring at $-60\,^{\circ}C$ for 30 min, the other half of the ligand solution was added. The resultant solution was stirred while it was allowed to warm to room temperature. After 16 h, solvent was removed in vacuo and the complex was dissolved in dichloromethane. The mixture was filtered through Celite and was then dried in vacuo to yield a deep red powder.

Polymer synthesis: Polymerizations were conducted in a 6 ounce Lab-Crest pressure reaction vessel equipped with a magnetic stir bar. After drying in vacuo, the reactor was charged with dry MAO (1.80 g, 31 mmol) and toluene (150 mL) under N_2. At this point the atmosphere of the reactor was exchanged with propylene gas three times, and then adjusted to the desired pressure and temperature. Complex library $\mathbf{CL_{TOT}}$ (200 mg, 0.31 mmol) was dissolved in toluene (6 mL) at room temperature under nitrogen. The solution was then added to the reactor by using a gas-tight syringe to initiate the polymerization. After the desired period of time, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, washed with methanol, and then dried to constant weight.

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