Angewandte Chemie International Edition

Stereoselective Polymerization

DOI: 10.1002/anie.201101913

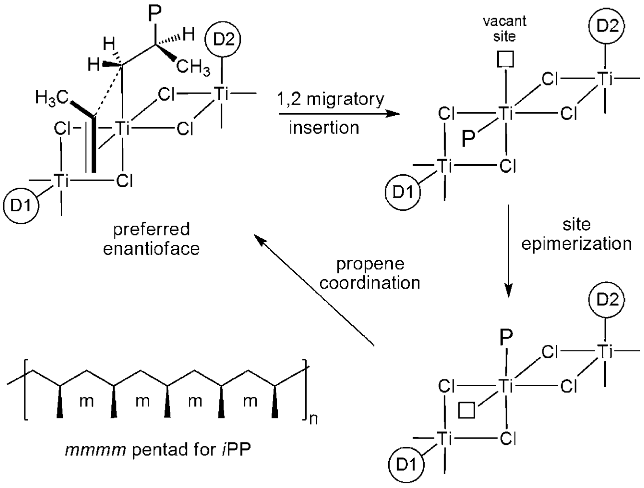
Duality in Catalyst Design: The Synergistic Coupling of Steric and Stereoelectronic Control over Polyolefin Microstructure**

*Lawrence R. Sita**

catalyst design · coordination modes · polymerization · polyolefins · stereoselectivity

With an annual global production of over 140 million metric tons—which is projected to increase to over 200 million metric tons by 2020—humankind will continue to be dependent upon commodity "plastics" based on polyethene (PE) and polypropene (PP) for the foreseeable future.[1] This sustained growth and the unrelenting demand for new fundamental forms of PE and PP materials, which are produced through the transition-metal-catalyzed coordination polymerization of ethene and propene monomers along with a supporting cast of longer-chain α-olefins as comonomers, is driven by the continually evolving societal and technological needs of a rapidly expanding world population that has just passed 7 billion people. With available feedstocks of commercially viable monomers limited to a relatively small number, however, new forms of PE- and PP-based materials can only be developed through the introduction of new classes of transition-metal catalysts that are themselves the product of new design strategies, discoveries, and a mix of Edisonian innovation and hypothesis-driven optimization.[2] On the other hand, the de novo design of a new coordination-polymerization catalyst that can provide a PE or PP material with superior physical and technological properties to those of currently available polymers is an exceedingly difficult task, and indeed, quite a rare event in the broader field of polyolefin research. In this regard, the recent study reported by Kol and co-workers[3] is significant, as it introduces the design of a new class of transition-metal catalyst in which a combination of steric and stereoelectronic differentiation is used to provide one of the highest degrees of control over the stereochemical microstructure of PP ever observed. The future extrapolation and implementation of this catalyst-design strategy for stereochemical control over polymer structure could potentially further increase the range of polyolefin products that are available to support new technological innovations.

The most commercially relevant form of PP is that with an isotactic stereochemical microstructure in which all the pendant methyl groups have the same relative configuration, as depicted in the idealized structure shown in Scheme 1. This particular stereoregular arrangement for isotactic PP (*i*PP) gives rise to a highly crystalline, rigid thermoplastic material with a melting temperature that is amenable to the production of, amongst other items, serviceware and containers that will not deform under the conditions required for microwave use or autoclave sterilization.



Scheme 1. Modified Cossee–Arlman mechanism for the production of isotactic polypropene. Stereoregular polymerization depends on the existence of a single propene coordination site for a C_1-symmetric active center and site epimerization when D1 and D2 are different. *m* denotes a *meso* dyad; P is the growing polymer chain; D1 and D2 represent donor molecule additives that are included in latest generation hetereogeneous Ziegler–Natta catalyst formulations.

Importantly, irrespective of mechanistic differences that may be operative for different classes of coordination-polymerization catalysts, the only way in which an isotactic microstructure can arise is through a chain-growth process in which the same prochiral (enantio-) face of propene is coordinated to the active transition-metal center prior to enchainment through insertion into the metal–carbon bond of

---

[*] Prof. L. R. Sita
Department of Chemistry and Biochemistry, University of Maryland
College Park, MD 20742 (USA)
Fax: (+1) 301-314-9121
E-mail: lsita@umd.edu

[**] Support for L.R.S. was provided by the NSF (0848293).

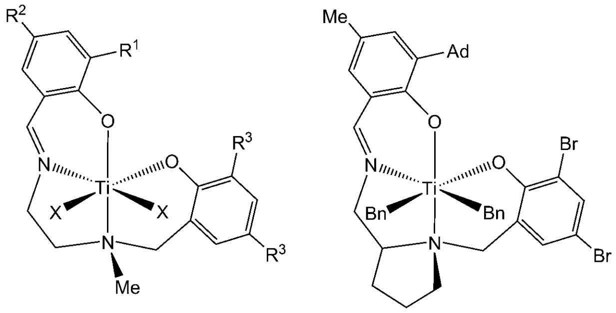
the nascent polymer chain. Stereoerrors that occur within a predominately isotactic microstructure can arise from coordination and enchainment of the “wrong”, or opposite, enantioface of the monomer, and for *i*PP, an increase in the frequency of these stereoerrors results in a decrease in the melting temperature (T_m) of the final product. A physical measure of stereoregularity for *i*PP can be obtained through ^{13}C NMR spectroscopy at the stereochemical-pentad level of analysis, whereby a higher %*mmmm* value indicates a greater degree of isotacticity (see Scheme 1).[2,4] Existing commercial grades of *i*PP have a T_m value of 165 °C, which is associated with a finite, but very low, level of stereoerror incorporation (e.g., %*mmmm* ≈ 99 %); thus, by extension, higher T_m values are theoretically possible if catalyst improvements can be made to increase the degree of isotactic stereoregularity of *i*PP even further.

Regarding the use of different catalyst designs to achieve an isotactic microstructure, it is speculated that *i*PP production with the latest generation of industrial heterogeneous Ziegler–Natta catalysts proceeds according to the modified Cossee–Arlman mechanism depicted in Scheme 1 in which D1 and D2 represent donor molecule additives that are included in the catalyst formulations to enhance isoselectivity.[5] When D1 and D2 are different, an intrinsically chiral, C_1-symmetric ligand geometry about the active transition-metal center provides a single stereodifferentiating vacant coordination site to which one enantioface of the monomer is preferentially coordinated prior to migratory 1,2-insertion.[5b,c] To maintain isotactic propagation through this single coordination site, however, the growing polymer chain must relocate back to its original position through a “site-epimerization” process prior to coordination of the next monomer unit.[5b,c,6] Thus, one source of stereoerror incorporation is the failure of the rate of site epimerization to be competitive with the rate of monomer coordination.

The heterogeneous nature of Ziegler–Natta catalysts has long impeded structural and mechanistic interrogations of the origins of stereocontrol in polymerization. However, the development of well-characterized, solution-soluble transition-metal complexes that can serve as active species for the coordination polymerization of propene upon cocatalyst “activation” has provided the opportunity to firmly establish the C_1 symmetry/isotactic microstructure relationship for propagation that occurs with a single monomer-coordination site and rapid site epimerization.[2,6] Strategies for the attainment of a high degree of isotactic stereoregularity have invariably relied on the judicious introduction of nonbonding steric interactions within the ligand sphere of the active transition-metal center to create a highly stereodifferentiating environment for monomer enantioface coordination, and to enforce propagation through a single coordination site by enhancing the rate of site epimerization of the polymer chain after migratory insertion.

On the one hand, reliance on the time-proven strategy of “steric control” for catalyst design is comforting, since it is relatively easy to establish an intuitive feel for how to employ an increase in steric “pressure” at one spatial location to (re)direct a molecular fragment to a different, desired spatial position. On the other hand, sole reliance on steric interactions to achieve positional control within a metal-coordination environment often leads to the crafting of elaborately designed ligand frameworks of increasing structural complexity that are also synthetically challenging in practice. Furthermore, when only steric control is involved in catalyst design, there exists the risk of introducing “steric overload” about the metal center that can negatively impact other desirable parameters, such as catalyst activity, as expressed by turnover frequency or the optimum operating temperature of the catalyst.

The novel approach to catalyst design taken by Kol and co-workers is to overlay steric control that is imparted by the ligand substituents to enable enantiofacial selectivity for monomer coordination with stereoelectronic control over site epimerization that is provided by intrinsic differences in the strength and nature of bonding interactions between the transition metal and the ligand framework. The tetradentate “salalen” ligand preferentially adopts a *fac–mer* coordination geometry about the metal center in a series of [(salalen)TiX$_2$] (X = O*i*Pr or Bn) complexes **I** (Scheme 2) that can serve as catalysts for the coordination polymerization of olefins upon activation with either a stoichiometric amount of the borane B(C$_6$F$_5$)$_3$ or an excess amount of methylaluminoxane (MAO) as a cocatalyst. The separate roles played by nonbonding steric interactions and stereoelectronic differences imparted by the *fac–mer* coordination of the salalen framework in controlling the degree of stereoregularity for *i*PP production were firmly established and optimized through evaluation of the relationship between ligand structure and PP microstructure for a family of substitutionally related derivatives. Further enhancement of the rate of site epimerization during propagation through use of MAO as the cocatalyst led to a higher level of isotacticity. These efforts culminated in the construction of the salalen-based precatalyst **Ia**, which in combination with MAO provided an extremely high degree of stereoregularity for *i*PP (%*mmmm* > 99.6 %). This level of stereoregularity translates into a T_m value of 169.9 °C, which is now the highest melting temperature ever recorded for *i*PP produced by either heterogeneous or homogeneous coordination-polymerization catalysts. Significantly, this high degree of stereocontrol did not come with a sacrifice in terms of



I (X = O*i*Pr or Bn)   **Ia**

Scheme 2. Salalen-based titanium complexes as precatalysts for the highly stereoselective production of *i*PP through the coordination polymerization of propene. Ad = adamantyl, Bn = benzyl.

catalyst activity, which for the **Ia**/MAO system was 10000 g (*i*PP) per mmol (catalyst) per hour.

As with any new design strategy, the generality of using steric control coupled with stereoelectronic differentiation within the ligand framework to direct stereoregularity of polyolefin microstructure will depend upon proof of its versatility. In contrast to the use of steric control to fine-tune catalyst properties through subtle variations in nonbonding interactions, it is not yet obvious how a similar level of finesse might be reached on the basis of stereoelectronic differences in metal—ligand bonding interactions alone. On the other hand, the beauty of the approach taken by Kol and co-workers is to not forsake one control mechanism in favor of the other, but rather, to exploit the synergism that emerges when the two are coupled. This duality in design should serve to greatly increase the structural range of available coordination-polymerization catalysts and thus the scope of polyolefin materials and products that can be created to support new technological advances, which will in turn lead to improvements in the quality of life.

Received: March 17, 2011

---

[1] a) A. Peacock, *Handbook of Polyethylene: Structures, Properties, and Applications*, Marcel Dekker, Basel, **2000**; b) *Polypropylene Handbook*, 2nd ed. (Ed.: N. Pasquini), Carl Hanser Verlag, Munich, **2005**; c) H. Knuuttila, A. Lehtinen, A. Nummila-Pakarinen, *Adv. Polym. Sci.* **2004**, *169*, 13–27; d) J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, *105*, 4073–4147; e) V. Busico, *Macromol. Chem. Phys.* **2007**, *208*, 26–29; f) V. Busico, *Dalton Trans.* **2009**, 8794–8802; g) P. D. Hustad, *Science* **2009**, *325*, 704–707.

[2] a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255–1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170; b) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; c) "Frontiers of Metal-Catalyzed Polymerization" (Ed.: J. A. Gladyz), special issue: *Chem. Rev.* **2000**, *100*; d) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315; e) *Stereoselective Polymerization with Single-Site Catalysts* (Eds.: L. S. Baugh, J. M. Canich), CRC, New York, **2008**; f) L. R. Sita, *Angew. Chem.* **2009**, *121*, 2500–2508; *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472.

[3] K. Press, A. Cohen, I. Goldberg, V. Venditto, M. Mazzeo, M. Kol, *Angew. Chem.* **2011**, *123*, 3591–3594; *Angew. Chem. Int. Ed.* **2011**, *50*, 3529–3532.

[4] V. Busico, R. Cipullo, *Prog. Polym. Sci.* **2001**, *26*, 443–533.

[5] a) E. J. Arlman, P. Cossee, *J. Catal.* **1964**, *3*, 99–104; b) V. Busico, R. Cipullo, G. Talarico, A. L. Segre, J. C. Chadwick, *Macromolecules* **1997**, *30*, 4786–4790; c) V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromolecules*, **1999**, *32*, 4173–4182.

[6] a) J. A. Ewen, M. J. Elder, R. L. Jones, L. Haspeslagh, J. L. Atwood, S. G. Bott, K. Robinson, *Makromol. Chem. Macromol. Symp.* **1991**, *48–9*, 253–295; b) Y. Obora, C. L. Stern, T. J. Marks, P. N. Nickias, *Organometallics* **1997**, *16*, 2503–2505; c) S. A. Miller, J. E. Bercaw, *Organometallics* **2006**, *25*, 3576–3592; d) A. Razavi, U. Thewalt, *Coord. Chem. Rev.* **2006**, *250*, 155–169.