Optically Active Polymers

DOI: 10.1002/anie.200701664

When Single-Site Polymerization Catalysis Meets Chirality: Optical Activity of Stereoregular Polyolefins

*Jean-François Carpentier**

Keywords:
chirality · optical activity · polymerization · single-site catalysis

In a recent, provocative paper Prof. Vincenzo Busico raised the question of the maturity of the field of Ziegler–Natta olefin polymerizations.[1] For most neutral observers in the chemical community, that is, academic and industrial scientists not directly involved in this research area, the question might appear futile. Indeed, as pointed out by our colleague, some may state that the efficient syntheses of commodity polymers, including quite sophisticated ones such as perfectly isotactic polypropylene, and even some "new" emerging materials, for example pure syndiotactic polystyrene, were devised several decades ago and have not changed fundamentally since then. Along this line, the new generations of olefin polymerization catalysts—the so-called "post-metallocenes"[2]—may appear as continuing efforts to revive the fading research area of metallocene catalysis with peripheral contributions.[3]

In fact, the reality of the olefin polymerization catalysis area is quite different. The development of tailor-made single-site catalysts, with significant and unique contributions of both metallocene and post-metallocene systems, has made it possible to manipulate the polyolefin architectures in their most intimate details.[2,3] Fine control of intrinsic (co)polymerization parameters (such as regio- and stereochemistry, and branching) has resulted in a large spectrum of materials, with sometimes dramatically different properties and, as a consequence, applications. Important breakthroughs in this area include, for instance, the recent chain shuttling polymerization (CSP), which provides access to unprecedented multiblock copolymers with outstanding thermoplastic–elastomeric properties.[4] Such progress in single-site polymerization catalysis undoubtedly results from modern techniques, in particular high-throughput screening of precatalyst/cocatalyst systems. Nevertheless, beyond technological tools that speed up but rarely initiate discovery (except in serendipitous cases), olefin polymerization catalysis benefits above all from the extraordinary fundamental understanding gained over the past decades. Comprehensive mechanistic and kinetic studies have identified virtually all elementary steps of the catalytic polymerization process, and the corresponding critical parameters that enable manipulation of the latter in a rational manner. In this sense Ziegler–Natta olefin polymerization can be considered a mature field. Full understanding of the polymerization mechanism provides the seeds for chemists to prepare at will precisely designed chain microstructures and develop more complex processes.

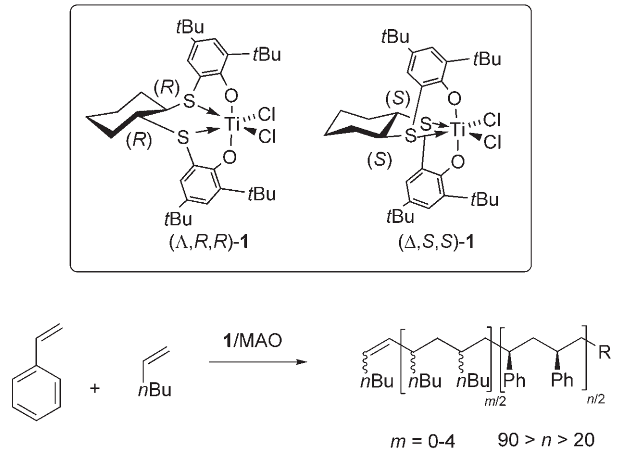
In this regard, Prof. Jun Okuda and his co-workers reported recently an elegant demonstration of how the subdisciplines of coordination chemistry, stereoselective catalysis, and chain-transfer polymerization can be cleverly combined to address an old physico-chemical issue.[5] They set out ultimately to determine at which degree of polymerization the optical activity of stereoregular, enantiomerically pure polyolefins is observable. As a matter of fact, most high-molecular-weight stereoregular vinyl polymers with configurationally controlled stereocenters in the main chain prepared from prochiral olefins cannot be optically active, because they feature C_s symmetry (mirror plane) if one does not consider chain-end groups.[6,7] On the other hand, low-molecular-weight (oligomers) polyolefins can be optically active, provided significant asymmetric induction is achieved in the main chain. Pioneering work in this field was conducted by Pino et al. for the asymmetric hydro-oligomerization of propylene using a resolved chiral metallocene catalyst of the Brintzinger type.[8] It is this border between "cryptochirality" and "active chirality" that Okuda and his co-workers have explored by preparing in a highly controlled manner isotactic "homochiral" polystyrenes with a range of molecular weights.[5]

Unlike isotactic polymers of classical olefins such as propylene and 1-hexene, which have been prepared by a variety of single-site catalysts,[2,3] isotactic polystyrene (iPS) has been best produced for almost half a century by heterogeneous Ziegler–Natta catalysis.[9] Okuda et al. recently implemented a family of structurally well-characterized catalyst precursors, namely 1,4-dithiabutane-bridged bis(phenolato)titanium complexes, that are capable of efficiently polymerizing styrene isospecifically (> 95 % *mm*) upon activation with methylaluminoxane (MAO).[10] Such [Ti(O-S-S-O)Cl_2]complexes adopt chiral C_2-symmetric structures, with a helical arrangement of the tetradentate ligand around the

---

[*] Prof. Dr. J.-F. Carpentier
Organométalliques et Catalyse
Institut de Chimie de Rennes
Université de Rennes 1
35042 Rennes (France)
Fax: (+33) 2-2323-6939
E-mail: jean-francois.carpentier@univ-rennes1.fr

octahedral titanium center. Most importantly, the 1,4-dithiabutane bridge imposes configurational stability on the complex, provided bulky *ortho* substituents are present on the phenolato rings; in other words, no interconversion of the helical Λ/Δ isomers takes place at temperatures up to 100 °C. Stereorigidity is a prerequisite for the preparation of diastereo(enantio)merically pure catalyst precursors, and stereorigidity was demonstrated to persist in the corresponding catalytically active alkyl cationic species [Ti(O-S-S-O)R]$^+$,[10c] which is of course mandatory for the targeted production of optically active polymers. Based on this model, the authors have achieved the synthesis of enantiomerically pure, stereorigid [Ti(O-S-S-O)X_2] catalyst precursors by introducing a *trans*-1,2-cyclohexanediyl backbone for the S-C-C-S bridge.[5] The chiral backbone leads to the formation of a single configuration (helicity) at the titanium center, with one enantiomeric pair of the diastereomeric complex (Λ,*R*,*R*)-**1** and (Δ,*S*,*S*)-**1** (Scheme 1).



Scheme 1. Chiral catalyst precursors **1** for the synthesis of isotactic polystyrene oligomers.

After the synthesis of these chiral precatalysts, the question arose how to prepare a set of isotactic polystyrenes with on-demand defined degrees of polymerization. Related Ti(OSSO)X_2/activator systems based on non-chiral ligands have been shown previously to exert a significant degree of control over the polymerization, characteristic of single-site catalysts; this includes relatively narrow molecular-weight-distributions ($M_w/M_n < 2$) and linear growth of the polymers' molecular weight with monomer conversion.[10] However, overall the catalysis cannot qualify as living because it is plagued by moderate initiation efficiencies (ca. 30–60 %); in other words, not all Ti centers are active in polymerization. This hampers the preparation of oligomers with controlled degree of polymerization. To tackle this issue, the authors first explored chain-transfer polymerization with traditional agents such as dihydrogen and metal alkyls,[11] but these routes were found inoperative. They finally took advantage of what would appear at first glance to be undesirable preference of their post-metallocene catalyst. In contrast to the vast majority of Group 4 metallocenes, [Ti(O-S-S-O)X_2]/MAO catalyst systems actually prefer vinyl-aromatic monomers over α-olefins (e.g. propylene) and, under copolymerization conditions, the latter α-olefins act as an "interrupter" of isotactic polystyrene chains.[12] This behavior was readily rationalized by an opposite regioselectivity of monomer insertion and termination by β-H elimination or β-methyl transfer of a primary inserted propylene unit. Thus, by adjusting the styrene/α-olefin (1-hexene) ratio, a series of isotactic oligostyrenes terminated by few hexene units was readily prepared with the (Λ,*R*,*R*)-**1** and (Δ,*S*,*S*)-**1** complexes (Scheme 1), and the dependence of the specific rotation values on the molecular weight of the iPS further studied.

As anticipated, measurable optical activity in solution was detected only for low-molecular-weight materials, with a threshold corresponding to ca. 45 styrene units (Figure 1). A steady evolution of the optical activity was found, which substantially complements the few discrete data available thus far. Also, the sign of optical rotation of oligomers depends on the configuration of the enantiomeric titanium catalyst used, confirming that prochiral monomer insertion into the titanium–alkyl bond is controlled by the chirality within the helical coordination sphere; in other words, enantiomorphic site control is operative mechanistically speaking. This elegant study provides another outstanding demonstration of the power and conceptual maturity that macromolecular engineering by single-site Ziegler–Natta catalysis has reached over the past decades.

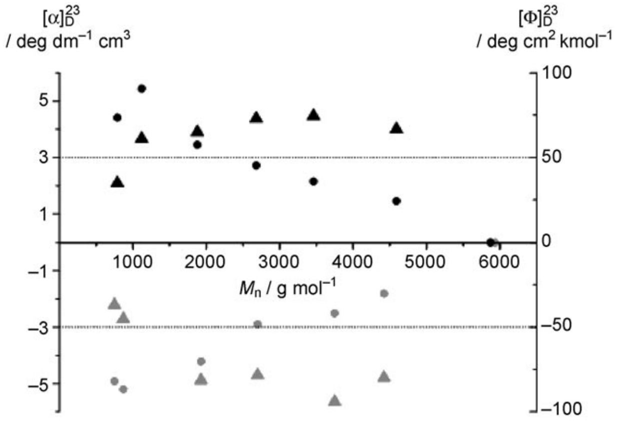


Figure 1. Dependence of the specific rotation $[\alpha]_D^{23}$ and molar rotation $[\Phi]_D^{23}$ on the number-averaged molecular weight of isotactic oligostyrene terminated by 1-hexene. Specific rotation (●) and molar rotation (▲) of samples prepared with the complex (−)-(Λ,*R*,*R*)-**1** (bottom); (●) optical rotation and molar rotation (▲) of samples prepared with the complex (+)-(Δ,*S*,*S*)-**1**) (top)

[1] V. Busico, *Macromol. Chem. Phys.* **2007**, *208*, 26–29.

[2] Reviews: a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315.

[3] Reviews: 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) H. G. Alt, A. Köppl, *Chem. Rev.* **2000**, *100*, 1205 – 1222; c) G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223 – 1252; d) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253 – 1345; e) "Metallocene Complexes as Catalysts for Olefin Polymerization": *Coord. Chem. Rev.* **2006**, *250* (Special Issue, Ed.: H. G. Alt).

[4] a) D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714 – 719; b) cf. M. Zintl, B. Rieger, *Angew. Chem.* **2007**, *119*, 337 – 339; *Angew. Chem. Int. Ed.* **2007**, *46*, 333 – 335.

[5] K. Beckerle, R. Manivannan, B. Lian, G.-J. M. Meppelder, G. Raabe, T. P. Spaniol, H. Ebeling, F. Pelascini, R. Mülhaupt, J. Okuda, *Angew. Chem.* **2007**, *119*, 4874 – 4877; *Angew. Chem. Int. Ed.* **2007**, *46*, 4790 – 4793.

[6] Reviews: a) M. Farina, *Top. Stereochem.* **1987**, *17*, 1 – 111; b) Y. Okamoto, T. Nakano, *Chem. Rev.* **1994**, *94*, 349 – 372.

[7] Waymouth and Coates have prepared optically active diisotactic poly(methyl-1,3-cyclopentane) (which does not contain mirror-plane symmetry) by enantioselective cyclopolymerization of 1,5-hexadiene using a chiral Brintzinger-type catalyst. G. W. Coates, R. M. Waymouth, *J. Am. Chem. Soc.* **1993**, *115*, 91 – 98; cf. J. Okuda, *Angew. Chem.* **1992**, *104*, 49 – 50; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 47 – 48.

[8] a) P. Pino, *J. Am. Chem. Soc.* **1987**, *109*, 6189 – 6191; b) P. Pino, M. Galimberti, P. Prada, G. Consiligio, *Makromol. Chem.* **1990**, *191*, 1677 – 1688.

[9] a) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* **1955**, *77*, 1708 – 1710; b) G. Natta, P. Corradini, *Makromol. Chem.* **1955**, *16*, 77 – 80; c) C. Overberger, H. Mark, *J. Polym. Sci.* **1959**, *35*, 381 – 389; d) R. J. Kern, H. G. Hurst, W. J. Richard, *J. Polym. Sci.* **1960**, *45*, 195 – 204.

[10] a) C. Capacchione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moller, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2003**, *125*, 4964 – 4965; b) C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T. P. Spaniol, J. Okuda, *Organometallics* **2005**, *24*, 2971 – 2982; c) K. Beckerle, R. Manivannan, T. P. Spaniol, J. Okuda, *Organometallics* **2006**, *25*, 3019 – 3026.

[11] Review: R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764 – 2773.

[12] C. Capacchione, F. De Carlo, C. Zannoni, J. Okuda, A. Proto, *Macromolecules* **2004**, *37*, 8918 – 8922.