

2-Arylindene Metallocenes: Conformationally Dynamic Catalysts To Control the Structure and Properties of Polypropylenes

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ABSTRACT

Polymerization of propylene with catalysts derived from unbridged 2-arylindene metallocenes leads to elastomeric, low-tacticity polypropylenes. The polymerization behavior of these conformationally dynamic catalyst systems is interpreted in terms of a multistate mechanism where the catalyst enchains the monomer from both stereoselective and nonstereoselective conformations during the lifetime of a single polymer chain. The structure and properties of the polypropylenes depend sensitively on the metallocene and the polymerization conditions (temperature, pressure, monomer concentration); samples of low to intermediate isotacticity ([mmmm] = 20–40%) are elastomeric, with low densities and broad melting ranges that extend to 150 °C. Samples of higher tacticity ([mmmm] = 40–70%) behave as softened thermoplastics.

Introduction

Polyolefin manufacture is among the most atom-economical¹ industrial processes.² The catalytic polymerization of olefins in modern gas-phase commercial units is a remarkably efficient process, converting gaseous monomers (propylene or ethylene) to valuable commercial products with little or no solvents, no waste, and high energy efficiencies.³ The development of new catalyst systems that are adaptable to these manufacturing processes has led to an enhanced level of control over the structure and properties of polyolefins. An important goal of these efforts is to tailor polyolefin properties to minimize the need for additives and plasticizers.

In this Account, we summarize recent progress from our laboratories on the development of catalyst systems for the synthesis of low-crystallinity polypropylenes. In particular, we focus on efforts to control the structure, crystallinity, and properties of this versatile material.

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Historical Background

Giulio Natta's discovery of stereoselective polymerization of α -olefins⁴ with Ziegler catalysts⁵ helped lay the foundation for an entire field of science and establish the polypropylene industry. Natta demonstrated that the crystallinity of polypropylene was a consequence of a regular arrangement of adjacent methyl groups of the same relative configuration (an "m" relationship⁶), a structure he termed isotactic (Figure 1a). Atactic polypropylene (aPP) is an amorphous material due to a stereorandom arrangement of methyl groups (both "m" and "r" relationships, Figure 1b). Natta's early investigations of Ziegler's catalysts produced mixtures of polymers; from some of these mixtures, a fraction exhibiting elastomeric properties was isolated.^{7,8} Natta proposed a structure consisting of alternating isotactic and atactic stereosequences within the same polymer chain (Figure 1c); elastomeric properties were proposed to arise from cocrystallization of isotactic segments to create a physically cross-linked network of amorphous chains. Natta's rubbery polymer had desirable mechanical properties; the hypothesis of a stereoblock structure implied that the properties could be influenced by controlling the length and distribution of the stereorandom sequences within the polymer chains.

Following Natta's pioneering studies, progress in the controlled synthesis of lower crystallinity polypropylenes continued,^{9–13} albeit more slowly than that of highly crystalline isotactic polypropylene.³ The advent of metallocene catalysts¹⁴ stimulated renewed interest in developing well-defined catalysts for lower crystallinity elastomeric polypropylenes^{15–21} (metallocenes **1–3**) and offered the prospect of controlling and systematically studying factors which determine the length and distribution of isotactic and atactic stereosequences.

The synthesis of a stereoblock polymer presents an unusual synthetic challenge: the catalyst must change its stereoselectivity with time. In systems exhibiting chain transfer, this change must occur on the time scale of the growth of a single polymer chain. For Natta's heterogeneous system²² and metallocenes **1–3**,^{15,17–21,23} migration of the polymer chain between different catalyst environments or coordination sites exhibiting different stereoselectivities was proposed (Scheme 1). In these cases, the lengths of the isotactic and atactic blocks, structural features expected to have a significant impact on material properties, are influenced by the relative rate and stereospecificity of monomer enchainment and the rate of the process modulating the stereoselectivity.

We were intrigued with the idea that conformationally dynamic metallocenes^{24–26} might prove viable candidates for generating elastomeric polypropylenes, particularly because the rate of monomer insertion should be kinetically decoupled from the rate of isomerization. Investigations by Kaminsky²⁷ (metallocene **4**, Figure 2) and Erker^{28–31}

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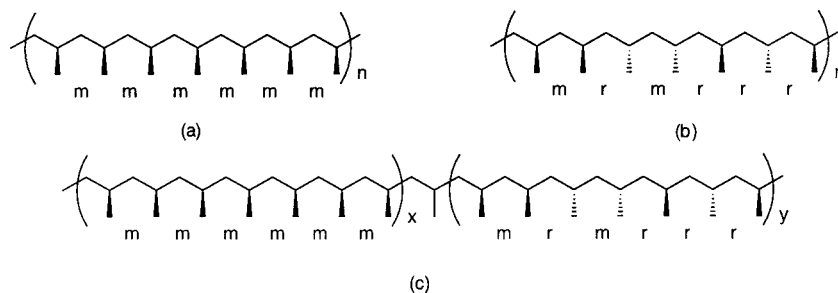


FIGURE 1. (a) Isotactic polypropylene, (b) atactic polypropylene, and (c) isotactic–atactic stereoblock polypropylene.

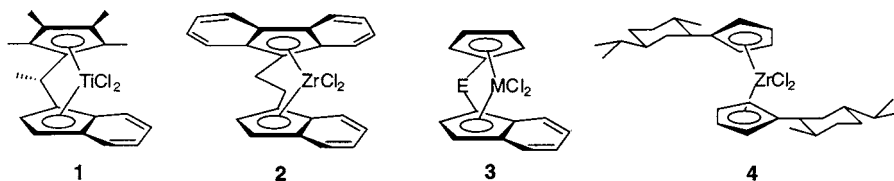
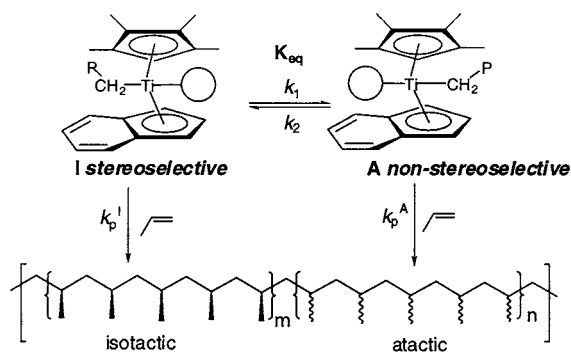


FIGURE 2. Representative metallocenes for the synthesis of low-tacticity polypropylenes (3, M = Zr, Hf; E = SiMe₂, CMe₂).

Scheme 1. Proposed Enchainment Mechanisms for the Synthesis of Elastomeric Polypropylene with Bridged Metallocenes



suggested that polypropylenes of intermediate tacticity could be generated with unbridged metallocenes. In 1995, we reported that bis(2-phenylindenyl)ZrCl₂ ((2-PhInd)₂ZrCl₂, **5**) (Figure 3) in the presence of methyl aluminoxanes (MAO) yielded an elastomeric polypropylene (ePP).^{32,33} The interconversion of the metallocene between stereoselective conformations and nonstereoselective conformations can account for the intermediate tacticities of these polypropylenes (Scheme 2).^{32–34} A stereoblock structure for these polymers was inferred from the analysis of the microstructure by ¹³C NMR and from the elastomeric properties; however, elastomeric properties are insufficient evidence for a blocky structure (vide infra). Information on the microstructure is obtained by ¹³C NMR analysis³⁵ (Figure 4): Atactic polypropylene (Figure 4a) yields a statistical distribution of all possible stereochemical pentads,³⁶ whereas isotactic polypropylene exhibits only one resonance, corresponding to the isotactic pentad [mmmm] (Figure 4b). The ¹³C NMR spectrum of a representative ePP prepared from (2-PhInd)₂ZrCl₂/MAO is shown in Figure 4c. Analysis of this pentad distribution^{19,36–38} is consistent with either a stereoblock structure or a mixture of isotactic and atactic chains.

In the following discussion, we describe our investigations on the scope and limitations of unbridged metallocenes for the synthesis of ePP. While we are far from

a complete understanding of these complicated systems, the experimental results are summarized in light of our current hypotheses about the behavior of these conformationally dynamic catalysts and the structure and properties of the resultant polymers.

Mechanism of Enchainment: Kinetic Models

The basic kinetic principles for the formation of stereoblock vinyl polymers were delineated by Coleman and Fox in 1963, in their seminal paper on the formation of stereoblock polyacrylates with anionic initiators.³⁴ A key prediction of their kinetic model was that the length of the stereoblock sequences should depend on the relative rate of enchainment versus isomerization, and thus depend on monomer concentration. Coates showed that the tacticity of the polypropylenes produced with the (2-PhInd)₂ZrCl₂/MAO catalyst system depended quite sensitively on monomer concentration: the isotactic pentad [mmmm] increased with increasing monomer concentration.³² A change in the stereospecificity of a reaction with substrate concentration is a signature for a mechanism involving a kinetic step that competes with the stereodifferentiating step;³⁹ we proposed that the rotation of the indenyl ligands was a likely candidate for this kinetic step (Scheme 2).

Bruce and Mark^{40,41} attempted to define the relationship between the block lengths of an isotactic–atactic stereoblock polypropylene and the resulting pentad distributions using computer simulations. A series of isotactic–atactic stereoblock copolymers were simulated where the isotactic block length (BL_i), atactic block length (BL_a), BL_i/BL_a, and the number of stereoerrors in each block were varied (Figure 5a). Experimental data by Lin⁴² closely followed the simulations by Bruce (Figure 5b), implicating that the increase in monomer concentration resulted in an increase in BL_i and BL_a, as predicted. A more sophisticated kinetic model was developed by Nele and Collins⁴³ and provided estimates for some of the key kinetic parameters. A fit of this model to Lin's data was

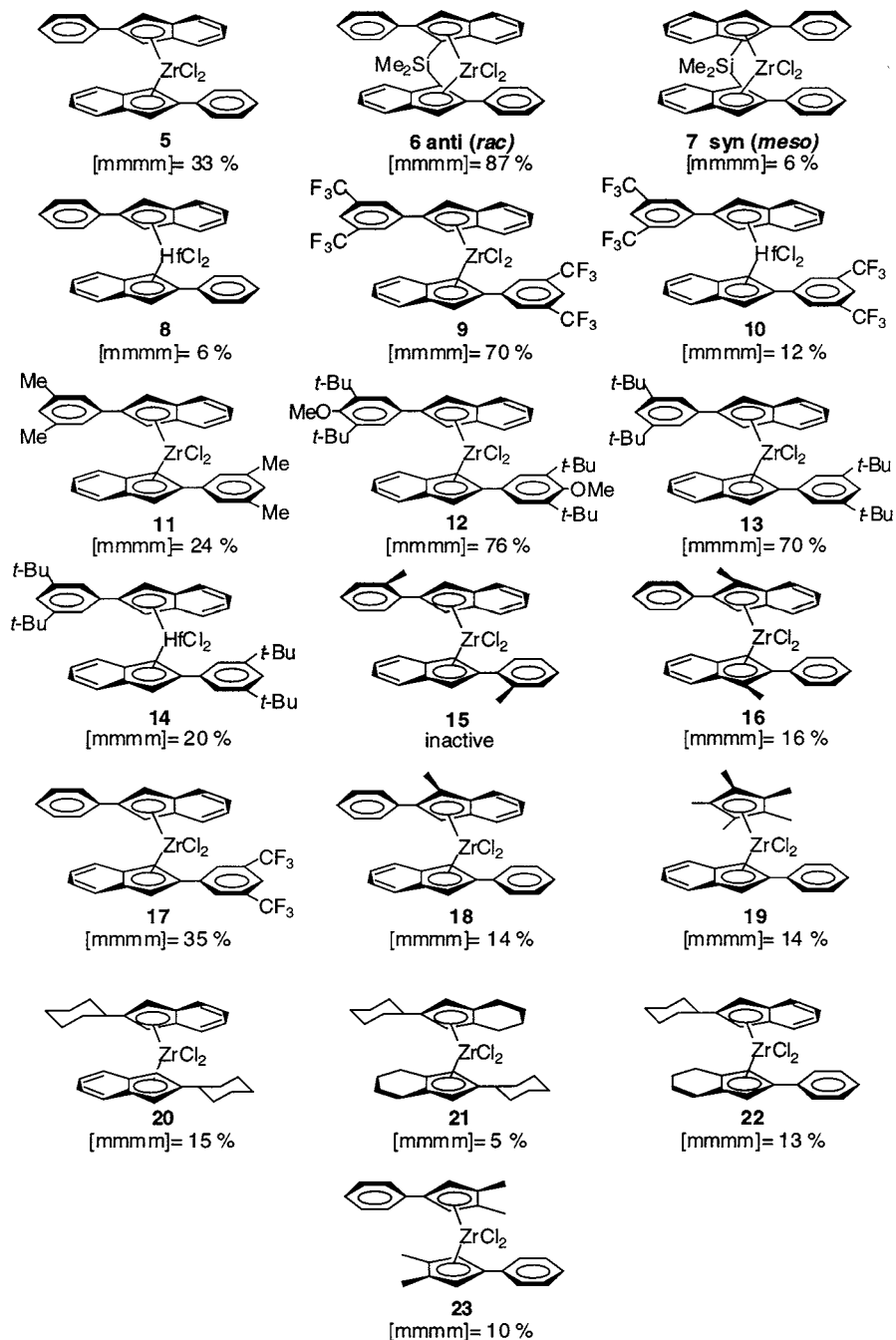


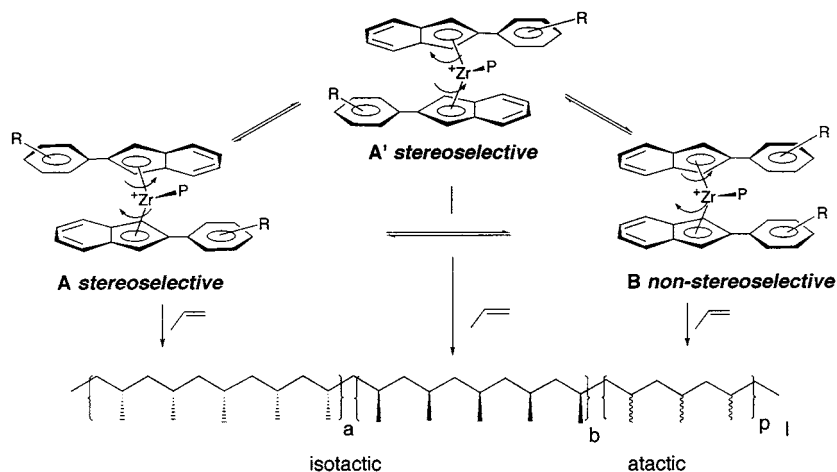
FIGURE 3. Relationship of metallocene structure and isotactic pentad content of polypropylenes prepared in liquid propylene at 20 °C.

consistent with the contribution of a highly stereoselective state A ($\alpha = 0.97$) and a less stereoselective state B ($\beta = 0.44$). State A was calculated to be 0.6 times as stable/reactive as state B. The parameters calculated from the kinetic model were consistent with those derived from analysis of the polymer microstructure^{37,38,44} and suggested that the lengths of the isotactic and atactic sequences are significantly shorter than the chain length, an indication that multiple blocks exist in a given chain.⁴³

Mechanistic and Model Studies

The kinetic model of Collins assumed both stereoselective and nonstereoselective states. Reasonable candidates for these states were provided by the X-ray crystal structure

of **5**, which exhibited two conformations in the solid state: a chiral (*rac*) *anti* conformation and an achiral (*meso*) *syn* conformation.³² Theoretical calculations^{45–47} identify these two conformations as being among the lowest energy rotameric forms with a relatively low barrier to interconversion. Of course, there are two enantiomers for the *anti* conformation which are equal in energy (Scheme 2). The *anti* (*rac*) and *syn* (*meso*) isomers of the bridged metallocene $\text{Me}_2\text{Si}(\text{2PhInd})_2\text{ZrCl}_2$ (**6** and **7**) (Figure 3) were prepared, and their polymerization behavior was investigated^{48,49} to estimate the relative contribution of these two conformations to the performance of unbridged **5**. The *rac*-**6** and *meso*-**7** model compounds produced iPP and aPP, respectively; a 3:2 mixture of *rac*-**6** to *meso*-**7**

Scheme 2. Proposed Mechanism for Propylene Enchainment by (2-Arylindenyl)₂ZrCl₂ Metallocenes

produced a mixture of iPP and aPP with a pentad distribution matching that of ePP made by **5** under identical conditions. This experiment provided an independent estimate of the relative reactivities of the stereoselective and nonstereoselective conformations ($k_p^A/k_p^B \approx 0.5$) and their relative abundance ($B/(A + A') \approx 0.7$). While we cannot be sure that these stereorigid complexes mimic the behavior of the corresponding unbridged conformers,⁵⁰ these values agree with those extracted from the kinetic model of Collins. This analysis implies that the high mole fraction of atactic sequences originates from a higher rate of enchainment from the *meso* isomer.

Dynamics of Unbridged Metallocenes

NMR studies of a variety of 2-arylindenyl metallocenes were conducted to measure the rate of interconversion

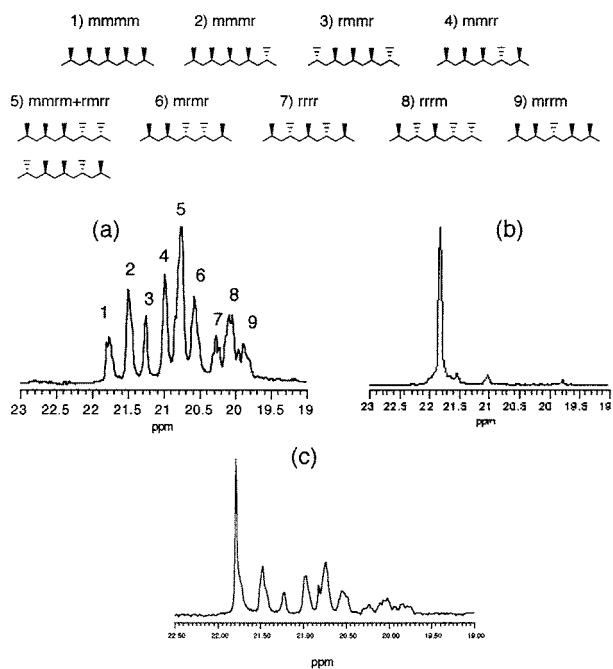


FIGURE 4. Polypropylene pentads and ¹³C NMR spectra of the methyl region in (a) atactic polypropylene, (b) isotactic polypropylene, and (c) elastomeric polypropylene synthesized by **5**/MAO.

among the torsional isomers. Dynamic NMR investigations of the dibenzyl derivatives L₂Zr(CH₂Ph)₂ by Bruce⁵¹ (L = 2PhInd) and Brintzinger⁵² (L = 2-phenylcyclopenta[1]phenanthrene) yielded activation barriers $\Delta G^\ddagger = 12.1 \pm 0.2$ kcal/mol at 273 K for interconversion of the two racemic isomers in solution. The *meso* isomers were not observed; similarly, only *anti* (*rac*) rotamers were observed for bis(2-aminoindenyl)ZrCl₂ complexes.³¹ These results are nominally at odds with the mechanism of Scheme 2,

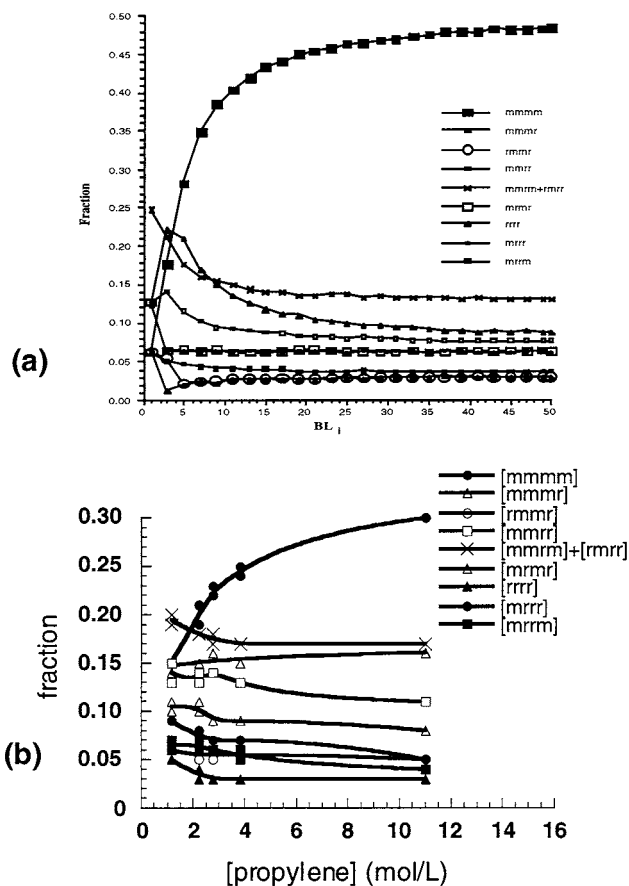


FIGURE 5. (a) Simulated dependence of pentad fraction on increasing isotactic block length. (b) Experimentally observed dependence of pentad fraction on increasing monomer concentration.

since the rate of ligand rotation for the dibenzyl derivatives at room temperature (6700 s^{-1} at $20 \text{ }^\circ\text{C}$) is too fast to account for the formation of blocks of isotactic and atactic stereosequences if the rate of propylene insertion of approximately 30 s^{-1} (calculated from average productivities)⁴⁸ is assumed.^{51,52} Several explanations might account for this discrepancy: (1) the kinetic model of Scheme 2 is incorrect, (2) the rate of interconversion of the dibenzyl derivatives is not representative of the rate of interconversion of the active species,⁵¹ or (3) the rate of insertion is actually several orders of magnitude higher than that calculated from the productivities.⁵² We suspect that both (2) and (3) may play a role, but further studies are needed to provide better estimates for k_p^A , k_p^B , k_i , and k_2 . Investigation of the bulk kinetics of propylene polymerization with **5**⁴² did not yield reliable estimates for k_p^A and k_p^B due to the difficulty in counting the active site concentrations.⁵³ Nevertheless, these studies revealed that the low productivities for these metallocenes may not necessarily originate from low rates of monomer insertion but rather from the formation of "dormant states"⁵⁴ that can be reactivated by H_2 or ethylene.^{55,56}

Influence of Catalyst and Conditions on Stereoselectivity

The stereoselectivity of this class of catalysts is highly sensitive to polymerization conditions (temperature, pressure, monomer concentration) as well as the nature of the ligands, the transition metal, and the cocatalyst. This behavior is a mark of versatility of these catalysts since the structure and properties of the polypropylenes produced can be varied over a wide range. The hypothesis that the conformational dynamics competes with insertion (Scheme 2) has proven useful in interpreting the influence of these parameters on the stereoselectivity. The stereoselectivities of the hafnium derivatives of these metallocenes are much lower than those of the zirconium complexes (Figure 3),⁵¹ even though they are structurally similar by X-ray analysis. Moreover, the dibenzyl derivatives have identical barriers to indene rotation.⁵¹ We have proposed that the lower stereoselectivity of the Hf analogues might be a consequence of a slower rate of monomer insertion for Hf versus Zr, leading to similar relative rates of insertion and isomerization (Scheme 2), shorter isotactic sequence lengths, and more stereorandom microstructures.

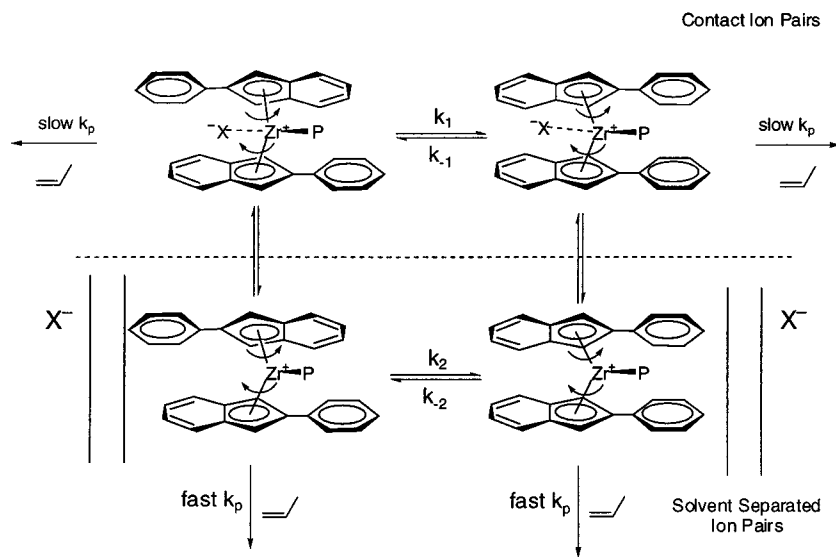
The structure and substitution pattern of the ligands also has a dramatic influence on the stereoselectivity of these metallocenes (Figure 3). The nature of the substituents at the 3,5-positions of the 2-phenyl substituent has a large influence on the stereoselectivity,^{33,51,57,58} whereas variations on the para-position have a more modest influence.^{36,58,59} One strategy that we have employed is to introduce ligand substitutions on the 2-phenylindene ligand of **5** that might bias the conformational equilibria to disfavor the achiral *meso* conformations. Electronically biased ($\text{R} = \text{CF}_3$, **9**)^{33,51} or sterically biased ($\text{R} = t\text{-Bu}$, **12**, **13**)^{57,58} metallocenes were prepared to perturb the steady-

state equilibria toward the more stereospecific conformations to generate more highly tactic polypropylenes. This proved a useful prediction, as introduction of trifluoromethyl (**9**) or *tert*-butyl groups (**12**, **13**) at the 3,5-positions of the aryl ring yielded more highly stereoselective catalysts ($[\text{mmmm}] = 70\text{--}76\%$, Figure 3) than **5**.^{33,51,57,58} Analysis of lower tacticity polypropylenes prepared with **13** at low monomer concentrations revealed only isolated $[\text{mrmm}]$ stereoerrors rather than blocks of stereoerrors, implying that isomerization takes place primarily between the two enantiomeric *anti* (*rac*) conformations for these sterically hindered metallocenes (Scheme 2, $p = 0$). Similar conclusions were recently reached by Busico from high-resolution ^{13}C NMR analysis of polymers derived from **12**.^{60,61} These results suggest that the accessibility of various conformations can be manipulated by careful choice of the ligand structure.⁵⁷

Replacement of the phenyl ring at the 2-position of the indene with a methyl or cyclohexyl ring (**20**), hydrogenation of the six-membered part of the indene ring (**21**, **22**), or replacement of the indenyl ligand with dimethylcyclopentadienyl ligand (**23**) resulted in much lower tacticity polypropylenes than those obtained from **5** ($[\text{mmmm}] = 6\text{--}15\%$).^{33,36,51,58,59,62} Unsymmetrical metallocenes containing two different 2-arylindenes exhibit unique behavior, with stereoselectivities intermediate to those of the symmetrically substituted metallocenes (compare **17** with **9** and **5**).⁶³

The nature of the cocatalyst also influences the polymerization behavior of the 2-arylindene metallocenes. The type of MAO and the presence of isobutylaluminum species affect the $[\text{mmmm}]$ content of the polymer; more isotactic polypropylenes are obtained in the presence of isobutylaluminum-containing cocatalysts or scavengers.^{49,64,65} Even larger differences are observed with catalysts derived from $5/\text{B}(\text{C}_6\text{F}_5)_3$, which yield atactic polypropylene under conditions where catalysts derived from MAO, $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, or $[\text{PhN}(\text{Me})_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ yield elastomeric polypropylenes ($[\text{mmmm}] = 20\text{--}40\%$). These results suggest that the nature and dynamics of the ion pair can influence the stereoselectivity (Scheme 3), perhaps through strong anion coordination which inhibits insertion.^{65,66}

While we are unable to predict catalyst stereoselectivity for a particular ligand environment under a given set of conditions, experimental and theoretical investigations have enabled us to optimize these catalysts. The first-generation metallocene **5** yields an attractive material of intermediate tacticity and appropriate molecular weight when polymerizations are carried out at room temperature in liquid monomer, but attempts to utilize this catalyst at higher temperatures led to a low-molecular-weight aPP. Studies on the influence of the metal ion and the ligands resulted in the development of the bis(2-(3,5-*tert*-butyl)phenylindenyl)hafnium metallocene (**14**) as a catalyst system that can generate an ePP at $50 \text{ }^\circ\text{C}$ with tacticity and molecular weight similar to those produced by **5** at $20 \text{ }^\circ\text{C}$.^{67,68}

Scheme 3. Possible Ion-Pairing Effects for Polypropylene Polymerization by (2-Arylindenyl)₂ZrCl₂ Metallocenes (Only One Stereoselective *anti* Isomer Shown for Clarity)Table 1. Representative Tensile Properties of Polypropylenes (Figure 6)⁷⁰

	polymer					
	1	2	3	4	5	6
[mmmm] (%)	29	33	36	37	44	56
M_w (g/mol)	261 000	214 000	185 000	386 000	233 000	228 000
M_n (g/mol)	101 000	79 000	60 000	136 000	69 000	68 000
density		0.866	0.866	0.866	0.868	0.875
T_m (DSC)	150	151	150	148	151	144
modulus (MPa)	3.0	6.3	6.9	8.9	16.5	40
elongation to break (%)	920	910	960	830	880	610
strength (break) (MPa)	5.1	8.1	8.5	12.3	15.9	16.7
tensile set, 100% elong.	12	10	12	7	12	40

Structure and Properties of Polypropylenes Derived from (2-ArInd)₂ZrCl₂/MAO

Catalysts derived from 2-arylidene metallocenes yield an extraordinary range of polypropylene microstructures with properties that range from gum elastomers to high-melting thermoplastics.^{44,69,70} Samples of lower tacticity exhibit relatively low initial tensile moduli (slope of the stress–strain curve, Figure 6, Table 1) and retain their shape, with good recovery of elongation upon removal of strain (measured by tensile set, which is the residual elongation upon removal of the tensile strain, Table 1), whereas those of higher tacticities (generally above [mmmm] = 40%) begin to show yielding and deformation behavior more typical of thermoplastics. In general, polypropylenes made with this family of catalysts with isotacticities in the range of [mmmm] = 20–50% have properties typical of a thermoplastic elastomer.

The elastomeric properties of these polypropylenes are due to the presence of stereodefects in the chains which lower the crystallinity and provide amorphous sequences that can be oriented under application of a deformation. The distribution of these stereodefects has been the subject of considerable study,^{44,69,71} but quantitative determinations of the length of isotactic and atactic stereosequences are difficult to establish since ¹³C NMR provides only average estimates of these quantities.³⁵ Attempts to infer information about the microstructure from the

physical properties⁷¹ are compromised by the paucity of studies in the literature on the properties of random versus blocky polypropylenes.^{72–74} Nevertheless, results from fractionation experiments, thermal analysis, NMR characterization,^{44,67,69,75–77} and morphological studies by tapping-mode atomic force microscopy^{68,78} indicate that these polypropylenes are mixtures of stereoblock polymers with a broad distribution of isotactic sequence lengths.

A characteristic feature of the polypropylenes prepared with the 2-arylidene catalysts is a broad melting range from approximately 40 to 160 °C, with melting peaks centered at 40 and 150 °C (Figure 7). This behavior is different from that observed for polypropylenes obtained from catalysts **1–3**^{15–21} and is likely a consequence of both crystallization kinetics⁷⁴ and a broad distribution of crystallite sizes and stabilities;^{44,78} the latter is indicative of a distribution of crystallizable isotactic sequence lengths in the polymer. Direct comparison of **5** and the mixed-ring metallocene (2-PhInd)(Me₅Cp)ZrCl₂ (**19**) revealed that, while both catalysts produced ePPs with very similar ¹³C NMR spectra (at pentad resolution), the melting points of the polypropylene produced by **19** were below 90 °C, whereas those from **5** were much broader and extended up to 150 °C (Figure 7),⁷⁹ an indication that the polymer derived from **5** has longer isotactic sequence lengths than that from **19**.

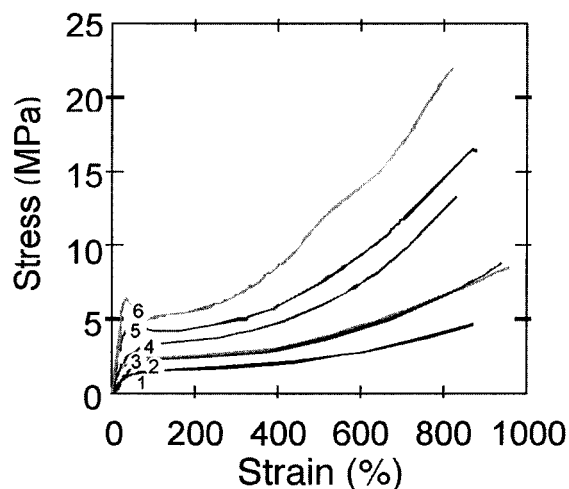


FIGURE 6. Tensile properties of representative polypropylenes (Table 1).

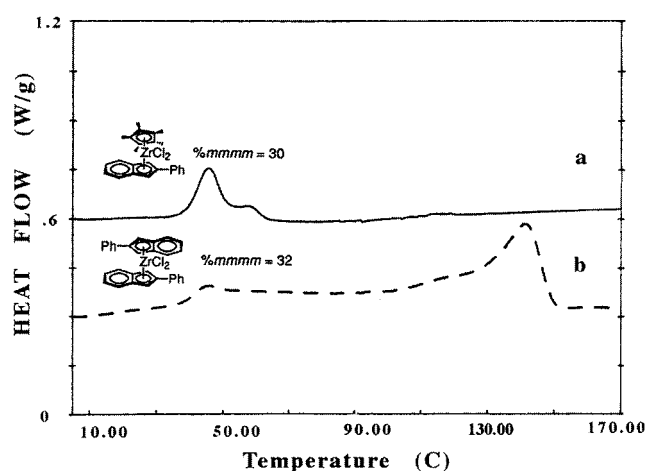


FIGURE 7. Comparative DSC thermograms of polypropylenes obtained from **19** and **5**.

Elastomeric polypropylenes prepared with 2-arylidene catalysts are more heterogeneous than those made by stereorigid metallocenes based on C_1 -symmetric metallocenes.^{15,17–21,23,80} Fractionation experiments reveal that these polypropylenes are a mixture of polymer chains with a distribution of isotacticities.^{36,44,67,69,75–77} These results suggest that the distribution of sequence lengths, implied by the broad melting range, is intramolecular (within the polymer chains), intermolecular (existing in mixtures of chains), or both. Analysis of PP10-HS ([m m m m] = 44%, $M_w/M_n = 2.4$), an ether-insoluble, heptane-soluble fraction of PP10 ([m m m m] = 34, $M_w/M_n = 2.6$), by thermal fractionation differential scanning calorimetry (DSC)⁷⁸ revealed a broad melting transition from 40 to 158 °C, with a series of melting peaks from 50 to 150 °C (Figure 8).⁶⁷ The presence of high-melting peaks provides indirect evidence for long isotactic sequences, while the heptane solubility implies that these long isotactic sequences are chemically attached to amorphous sequences. Analysis of the microstructure of PP10-HS by ¹³C NMR at pentad resolution is more consistent with a polymer containing blocks of atactic stereosequences rather than isolated stereoerrors, but experiments at higher resolution³⁵ are

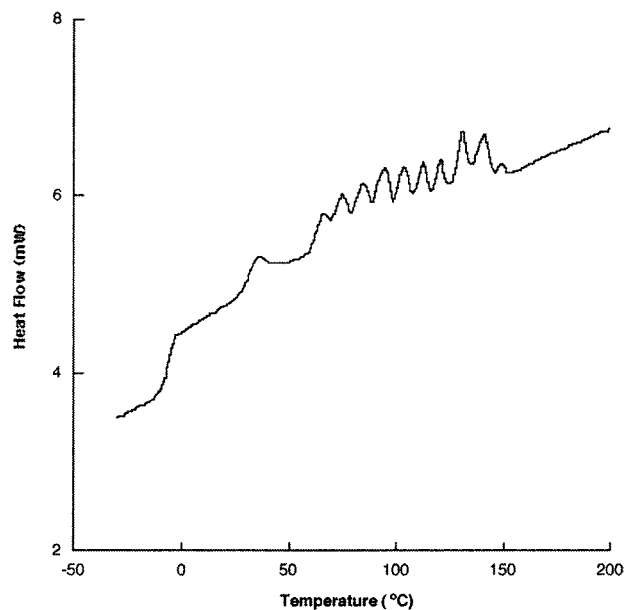


FIGURE 8. Thermal fractionation DSC of PP10-HS.

warranted. The unusual properties of these materials underscore the need for further studies to establish the contributions of the number and distribution of stereo-defects in polypropylene chains to the solid-state structure, morphology, and physical properties of polypropylene materials.

Green Context and Future Directions

Polyolefin manufacturing embodies many of the principles of Green Chemistry;⁸¹ these processes represent some of the largest scale applications of catalysis and generate products that have remarkable properties for their weight and cost. The negative environmental reputation of polyolefin plastics is, in some sense, correlated to these manufacturing efficiencies; the low cost of these materials provides little economic incentive for recycling or recovery.^{82,83} Nevertheless, two important trends illustrate the role of scientific and technological advances in mitigating the environmental impact of polyolefins.² The dramatic improvement in properties enabled by modern catalysts has led to significant “down-gauging” of finished articles,⁸⁴ meaning that less polymer is needed for a given application (the steady decrease in the thickness of plastic garbage bags is an example). In addition, our evolving ability to tailor the structure and properties of polyolefins is allowing these materials to displace less environmentally friendly alternatives, such as plasticized poly(vinyl chloride) (PVC).⁸⁵ Plasticized PVC is a remarkable material, but it owes much of its properties to the presence of small-molecule additives and plasticizers that can leach from the product. In this Account, we have attempted to outline our own efforts to control the properties of polypropylene by tailoring the chemical structure rather than using plasticizers or other additives. Some of these materials have been shown to have properties that might make them suitable as replacements for plasticized PVC.^{85,86} Nevertheless, before such displacements can be realized,

we need a better understanding of how catalyst performance can be tamed to control polymer architecture and, in turn, to control the properties of the final product.

We are indebted to our many colleagues whose names are given in the references and who were responsible for the intellectual and experimental advances outlined in this account. We are also grateful to our collaborators at Amoco (now BP Chemical Company) for their many contributions in what has proved a fruitful industrial/academic collaborative project: Dr. Eric Moore, Dr. Charley Myers, Dr. Andrew Ernst, Dr. Roger Quan, Larry Bendig, Hussam Naim, Dr. Larry Satek, Dr. Joseph Golab, Dr. George Kwiatkowski, Dr. Ruth Montag, Dr. Kim Neuberg, Scott Grimmer, Kent Alexander, Roman Salij, Heidi Wolfe, Dr. Liang Tee, Dr. Ada Nielsen, Ron Courtney, and Wally Oliver, Esq. Funding for this project was provided by the NSF, BP Chemical Company, and the ATP program administered by NIST.

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