Enantioselective Cyclopolymerization of 1,5-Hexadiene Catalyzed by Chiral Zirconocenes: A Novel Strategy for the Synthesis of Optically Active Polymers with Chirality in the Main Chain

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Abstract: Enantioselective cyclopolymerization represents a novel strategy for the synthesis of optically active main-chain chiral polymers. Cyclopolymerization of 1,5-hexadiene using the optically active catalyst precursor, (*R*,*R*)-(EBTHI)ZrBINOL ((*R*,*R*)-**1**) [EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl); BINOL = 1,1′-bi-2-naphtholate], yields optically active poly(methylene-1,3-cyclopentane) (PMCP) with a molar optical rotation of $[\Phi]^{28}_{405}$ +51.0° (*c* = 0.80, $CHCl_3$). Cyclopolymerization with (*S*,*S*)-**1** affords the enantiomeric polymer with a molar optical rotation of $[\Phi]^{28}_{405}$ −51.2° (*c* = 0.80, $CHCl_3$). The molar optical rotation for the polymer derived from (*R*,*R*)-**1** is higher than that of the model compound *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane and is also temperature dependent, suggesting that the polymer adopts chiral conformations which contribute to the observed optical rotation. The microstructure of the polymer was interpreted by ^{13}C NMR at tetrad resolution. A statistical model for the microstructure based on an enantiomorphic site control mechanism provided good agreement with the experimental data. On the basis of this model, the enantioface selectivity for the cyclopolymerization of 1,5-hexadiene in the presence of catalysts derived from (*R*,*R*)-**1** is 91% at 23 °C, indicative of a highly isotactic microstructure. The molar optical rotation of poly(methylene-1,3-cyclopentane) is independent of molecular weight, which provides experimental support for an enantiomorphic site control mechanism. The absolute configuration of PMCP was tentatively assigned on the basis of the sign of the optical rotation of the model compound *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane and the known enantioface selectivity of **1** with similar α-olefins.

Introduction

Almost all naturally occurring polymers are chiral.[1] Historically, interest in chiral synthetic polymers has focused on modeling natural polymers, interpreting the conformational properties of macromolecules in solution,[2] and investigating the mechanism of polymerization reactions.[3] Chiral polymers have also been utilized as chromatographic supports,[4] polymeric reagents, and catalysts.[5] More recently, the proposal that chirality can be used as a means of influencing the two- or three-dimensional order of macromolecules[6] has focused efforts on the application of chiral macromolecules for piezoelectric, ferroelectric, and nonlinear optical applications.[7]

Nature takes advantage of the ready availability of chiral monomers such as amino acids and sugars to construct proteins, nucleic acids, and polysaccharides. For synthetic macromolecules, the strategy of polymerizing chiral monomers has enjoyed considerable success,[8] but suffers from the limited availability and/or high expense of enantiomerically enriched monomers. Enantioselective polymerization of achiral monomers constitutes a far more efficient synthesis of chiral polymers. However, the intrinsic symmetry properties of macromolecules impose severe constraints on the types of monomers and polymerization reactions which yield chiral polymers.

Macromolecular chirality is intriguing because it involves molecules which are best modeled as infinitely long chains. The criteria for chirality in polymers include (1) the absence of reflection elements of symmetry (mirror planes) as well as (2) the absence of glide reflection elements (mirror–glide planes). The synthesis of optically active polymers whose chirality derives from configurational asymmetry in the main chain constitutes a formidable synthetic problem since most stereoregular vinyl polymers contain mirror planes of symmetry and are thus achiral[9] (Figure 1). Synthesis of chiral polymers from vinyl monomers requires complex architectures in order to circumvent the symmetry properties of simple vinyl polymers;[10] the repetitive nature of most polymerization reactions leads to macromolecular structures that have mirror planes of symmetry.

Recently, the polymerization of sterically demanding achiral monomers with chiral initiators has led to conformationally restricted polymers which are chiral due to their helicity. Notable examples include poly(triarylmethyl methacrylate)s,[11] polychloral,[12] polyisocyanates,[13] and polyisocyanides.[14] These fas-

Scheme I

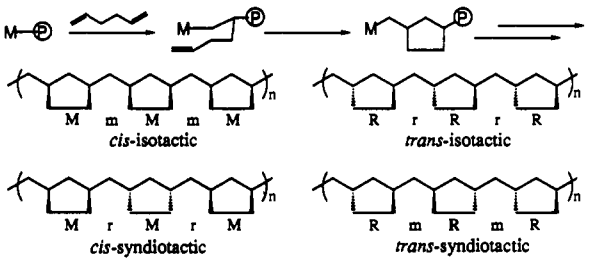

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Table I. Homogeneous Cyclopolymerization of 1,5-Hexadiene in Toluene

	metallocene	[cat] (× 10^4 M)	[Al]/[Zr]	$[diene]_i$ (M)	T (°C)	time (min)	conv (%)	trans[a] (%)	cyclization[b] (%)	M_w[c] (× 10^{-3})	M_n[c] (× 10^{-3})
1	Cp_2ZrCl_2	0.5	2300	0.21	21	60	11.1	80	>99	27	13
2	Cp_2ZrMe_2	0.6	2500	0.20	0	270	56.0	84	>99	26.5	12
3	Cp_2ZrMe_2	2.6	1300	0.37	-78	420	0.6	91	>99	nd	nd
4	Cp_2TiCl_2	7.1	2600	5.2	20	1200	17	63	>99	41	12
5	$Cp^*_2ZrCl_2$	7.0	2500	4.21	20	180	46.0	30	>99	1.1	nd
6	$Cp^*_2ZrCl_2$	4.4	1000	1.03	-25	330	65.0	14	>99	3.5	1.5
7	**2**	0.5	2400	0.20	25	60	81.4	64	99	48.5	16
8	**2**	0.3	3000	0.20	55	60	98.0	61	>99	40.0	23
9	**1**	1.9	800	0.27	0	360	79.8	64	94	260	17
10	**1**	1.9	980	0.27	25	360	93.0	67	96	36	3
11	**1**	1.9	880	0.27	50	360	86.3	65	97	18	0.3
12	**1**	1.9	880	0.27	80	360	79.6	58	97	3	nd

[a] Determined by ^{13}C NMR. [b] Determined by ^1H NMR. [c] Determined by GPC versus polystyrene.

Table II. Homogeneous Cyclopolymerization of 1,5-Hexadiene in Toluene Using Optically Active Metallocene Precursors

	metallocene	[cat] (× 10^4 M)	[Al]/[Zr]	$[diene]_i$ (M)	T (°C)	time (min)	conv (%)	trans[a] (%)	cyclization[b] (%)	M_w[c] (× 10^{-3})	M_n[c] (× 10^{-3})	$[\Phi]^T_\lambda$ (deg) 405 nm	589 nm
1	(*R,R*)-**1**[d]	0.9	1100	0.12	23	210	85	72	>99	180	30	+51.0[e]	
2	(*S,S*)-**1**[f]	0.9	1100	0.12	23	210	55	73	>99	204	36	-51.2[e]	
3	(*R,R*)-**1**[g]	2.2	1265	0.42	-25	540	47	63	82	111	38		+17.6[h]
4	(*S,S*)-**1**[f]	0.7	1200	0.24	23	233	79	72	99	70	18	-44.0[i]	
5	(*R,R*)-**1**[d]	0.8	950	0.09	23	180	90	70	>99	82	23		+20.3[j]
6	(*R,R*)-**1**[k]	0.8	950	0.09	23	180	96	67	>99	48	16		+11.1[j]

[a] Determined by ^{13}C NMR. [b] Determined by ^1H NMR. [c] Determined by GPC versus polystyrene. [d] Catalyst-specific optical rotation $[\alpha]^{24}_{435}$ -1685° (*c* = 0.20, benzene). [e] *T* = 28 °C, *c* = 0.80 ($CHCl_3$). [f] Catalyst-specific optical rotation $[\alpha]^{24}_{435}$ +1848° (*c* = 0.05, $CHCl_3$). [g] Catalyst-specific optical rotation $[\alpha]^{28}_{435}$ -1431° (*c* = 0.12, $CHCl_3$). [h] *T* = 28 °C, *c* = 0.60 (1,1,2,2-tetrachloroethane). [i] *T* = 26 °C, *c* = 0.76 ($CHCl_3$). [j] *T* = 20 °C, *c* = 0.80 ($CHCl_3$). [k] Deliberately mixed with racemic **1** (47%); specific optical rotation $[\alpha]^{24}_{435}$ -902° (*c* = 0.19, benzene).

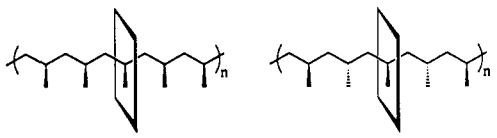

Figure 1. Most stereoregular vinyl polymers contain mirror planes of symmetry.

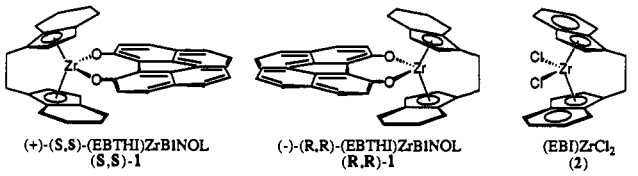

Figure 2. Chiral metallocene catalyst precursors.

cinating materials are configurationally achiral and owe their chirality exclusively to restricted conformational states.

The configurational symmetry constraints of vinyl polymers were recognized long ago by Natta and Farina, who pioneered enantioselective polymerization of pentadienes[15] and benzofuran.[16] We have recently developed an exciting and general synthetic strategy for the enantioselective synthesis of chiral polymers of well-defined microstructure[17] based on the cyclopolymerization[18] of nonconjugated dienes using stereospecific, homogeneous Ziegler–Natta catalysts.[19] Cyclopolymerization of 1,5-hexadiene with homogeneous Ziegler–Natta catalysts[20] yields poly(methylene-1,3-cyclopentane) (PMCP), a polymer for which four microstructures of maximum order are possible (Scheme I). Of these, only the trans-isotactic microstructure contains no mirror planes of symmetry and is thus chiral by virtue of its main-chain stereochemistry. Because the structures of the catalyst precursors are well-defined, homogeneous Ziegler–Natta catalysts provide a unique opportunity to study the factors which govern the en-

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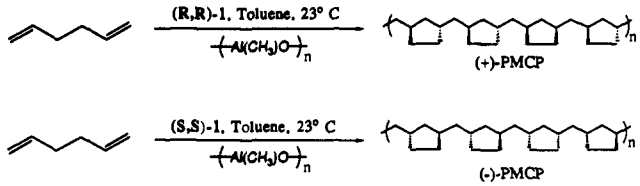
Scheme II



antioface and diastereoface selectivity of cyclopolymerization. In this article we present our results on the enantioselective cyclopolymerization of 1,5-hexadiene to optically active poly(methylene-1,3-cyclopentane). We also describe the chiroptical properties of these materials and present a description of the microstructure of these novel chiral polymers.

Results

Cyclopolymerization of 1,5-hexadiene in the presence of the achiral catalyst precursors Cp_2MX_2 (M = Ti, Zr; X = Cl, Me) and methylaluminoxane at room temperature affords PMCP where approximately 80% of the rings are trans, as determined by ^{13}C NMR.[21] With these catalyst precursors, a decrease in the polymerization temperature leads to a higher trans selectivity; cyclopolymerization at −78 °C afforded a polymer with 90% trans rings. In contrast, cyclopolymerization of 1,5-hexadiene with the more sterically hindered $Cp^*_2MX_2$ precursors (Cp^* = pentamethylcyclopentadienyl) yields predominantly *cis*-PMCP; at a polymerization temperature of −25 °C a polymer with 86% cis cyclopentane rings could be prepared (Table I). Significantly, the melting points of these polymers are sensitive to the cis/trans ratio of the carbocyclic rings. The trans polymers are waxes with melting points ≤70 °C; polymers containing >90% cis rings are crystalline and melt at 189 °C!

In the presence of the chiral racemic catalysts (EBTHI)ZrBINOL (**1**) and (EBI)$ZrCl_2$ (**2**) [EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl); BINOL = 1,1′-bi-2-naphtholate; EBI = ethylene-1,2-bis(η^5-1-indenyl)], cyclopolymerization of 1,5-hexadiene yields PMCP where approximately 70% of the cyclopentane rings are trans. With these catalysts, the cis/trans stereochemistry is relatively insensitive to the temperature of polymerization, in contrast to results obtained with the achiral metallocene derivatives (Table I).

Polymerization of 1,5-hexadiene in the presence of the tetrahydroindenyl precursor **1** results in a lower selectivity for cyclization than that observed with the Cp_2ZrCl_2, $Cp^*_2ZrCl_2$, or (EBI)$ZrCl_2$ precursors. Cyclopolymerization of 0.42 M solution of 1,5-hexadiene in toluene with (*R,R*)-**1** at −25 °C yielded a polymer where 18% of the monomer units did not cyclize[22] (Table II, entry 3). The selectivity for cyclization with **1** is temperature dependent and increases with increasing temperature;[17b,23] for example, 99% cyclization was observed at 23 °C at an initial monomer concentration of 0.12 M. (Table II, entry 1).

The ^{13}C NMR spectra for polymers obtained from the achiral catalyst precursors are slightly different from those obtained from the chiral catalysts, suggesting that the latter polymers are tactic. Since trans-isotactic polymers are chiral, the successful enantioselective cyclopolymerization of 1,5-hexadiene was accomplished in the presence of the optically active catalyst precursor (*R,R*)-**1** and a methylaluminoxane (MAO) cocatalyst. This catalyst system yielded PMCP (Scheme II), which exhibited a molar optical rotation[24] of $[\Phi]^{28}_{405}$ +51.0° (*c* = 0.80, $CHCl_3$). Cyclopolymerization with (*S,S*)-**1** afforded the enantiomeric polymer with a molar optical rotation of $[\Phi]^{28}_{405}$ −51.2° (*c* = 0.80, $CHCl_3$) (Table II, entries 1 and 2).[25]

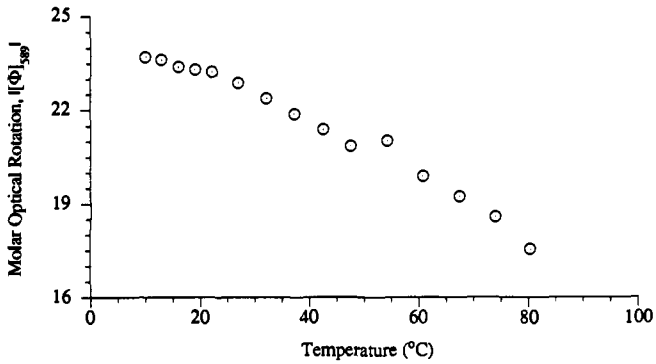


Figure 3. Absolute value of the molar optical rotation as a function of temperature for (−)-PMCP. Determined in toluene (*c* = 0.53, toluene) and corrected for change in solvent density.

Several experiments were carried out to insure that the observed optical rotations were not due to catalyst residues. Subjection of (*S,S*)-**1** to the workup conditions of the polymerization reaction resulted in destruction of the zirconocene complex; the specific rotation of the metallocene decreased from $[\alpha]^{26}_{435}$ +1843° to $[\alpha]^{26}_{435}$ +306° (*c* = 0.05, benzene) for the residue. Since the reaction only uses 0.03 mol % catalyst, the contribution of the catalyst residues to the observed polymer optical rotation should be minimal. In another control experiment, propylene was polymerized with (*S,S*)-**1** and isolated under conditions identical to those employed when polymerizing 1,5-hexadiene. Within the limits of the polarimeter used, we could detect no optical rotation in the polypropylene prepared under these conditions.

Cyclopolymerization of 1,5-hexadiene in the presence of (*R,R*)-**1** of lower enantiomeric purity afforded optically active PMCP with a lower optical rotation (Table II, entry 6). A plot of the molar optical rotation of the polymer versus the specific optical rotation of the catalyst yields a straight line, indicating that there is no chiral amplification[26] in the enantioselective cyclopolymerization of 1,5-hexadiene with chiral metallocenes.

Chiroptical Properties of PMCP. Shown in Figure 3 is a plot of the molar optical rotation of a sample of optically active PMCP as a function of temperature. The slope of the temperature dependence, $\Delta[\Phi]_{589}/\Delta T$ = −0.09°/°C, is lower than that reported for optically active poly((*S*)-3-methyl-1-pentene), $\Delta[\Phi]/\Delta T$ = −0.36°/°C ($[\Phi]^{25}_{589}$ +161°),[2] but is in the range for optically active polyolefins adopting helical conformations in solution. This temperature dependence is reversible.

Microstructure: Tacticity. The microstructure of cyclopolymers is considerably more complicated than that of simple vinyl polymers since it includes both the cis/trans stereochemistry of the rings and the relative stereochemistry between rings. Of the various ways to describe the structure of these materials, we find that one based on the reaction mechanism is most useful. Here we assume a two-step mechanism for cyclopolymerization involving olefin insertion followed by cyclization. According to this formalism, we describe the tacticity as the relative stereochemistry of the first stereocenter of every ring, independent of the cis/trans stereochemistry. This structural description facilitates mechanistic interpretations since the tacticity is determined by the level of enantioface discrimination for the olefin insertion step and the cis/trans ratio is determined by the diastereoselectivity of the cyclization step.

It is impossible to establish the degree of enantioface discrimination from the magnitude of the optical rotations, since the pure

(21) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953–4954.

(22) If polymerization reactions are run to high conversion of monomer under these conditions, a significant fraction of the isolated material is insoluble in refluxing toluene, suggesting that cross-linking has occurred.

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(24) The optical cavity of a polymer is most often reported in terms of a molar optical rotation, $[\Phi]^T_\lambda = [\alpha]^T_\lambda(M/100)$, where *M* is the molecular weight of the repeating polymer unit.[3a]

(25) For these experiments, the catalyst precursors did not show equal and opposite signs for the specific optical rotation (λ = 435 nm), but these complexes were diastereomerically pure by ^1H NMR.

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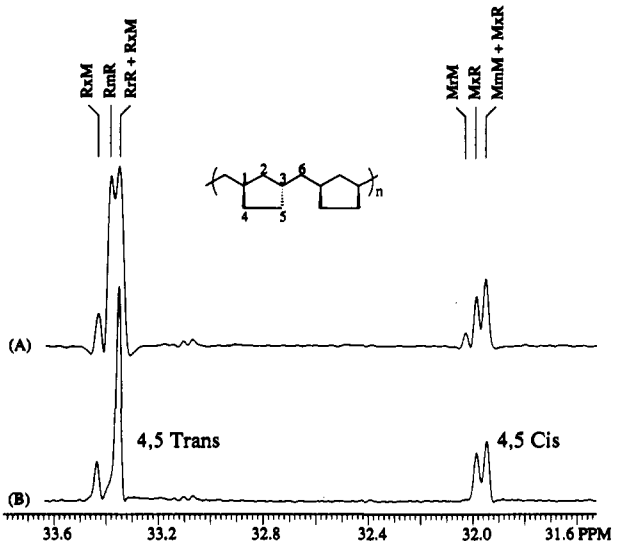

Figure 4. Resolution-enhanced ^{13}C NMR spectra (100 MHz, $CDCl_3$) of $C_{4,5}$ for PMCP prepared with (A) Cp_2ZrCl_2 and (B) (*S,S*)-(EBTHI)ZrBINOL ((*S,S*)-**1**).

enantiomeric polymers are unavailable and there appears to be a strong conformational contribution to the optical rotation (vide infra). A unique advantage of polymerization catalysis is that the polymer microstructure provides a stereochemical record of the catalytic reaction. Analysis of the relative stereochemistry of the polymer provides a means of determining the degree of enantioface discrimination.[27] As there have been few previous efforts to elucidate the microstructure of cyclopolymers,[28] we have carried out a series of studies to characterize the microstructures of these materials.

The mr stereochemical notation developed by Bovey[29] has proven extraordinarily powerful in describing and analyzing the microstructures of vinyl polymers. For cyclopolymers, a modified mr formalism is convenient, where capital letters (M for meso, R for racemic) denote relative stereochemistry within the rings and lower case letters (m and r) refer to relative stereochemistry between rings (Scheme I). This notation provides an unambiguous description of any possible microstructure for PMCP.

To assign the microstructure, we carried out the cyclopolymerization of 1,5-hexadiene in the presence of the achiral precursor Cp_2ZrCl_2 and the chiral precursor (EBTHI)ZrBINOL (**1**) under conditions where the cis/trans ratios of the two polymers were similar. For assignment of the microstructure, resonances corresponding to carbons C_4 and C_5 of the cis and trans repeating units (at 32.0 and 33.4 ppm, respectively)[21,30] proved most informative. Shown in Figure 4 are the resolution-enhanced ^{13}C NMR spectra for carbons C_4 and C_5 of the repeating units of polymers produced from the achiral precursor (Figure 4A) and the chiral precursor (Figure 4B). The fine structure in these resonances suggests that the NMR is sensitive to relative stereochemistry between the rings (i.e., tacticity). The multiplicity of peaks for the ^{13}C NMR resonances at 32.0 and 33.4 ppm in Figure 4 is indicative of tetrad resolution (i.e., RmR, RmM, etc.), where two of the four possible tetrad peaks for each set of resonances exhibit chemical shift equivalence.

(27) Similar investigations of the microstructure of polypropylene have yielded an extraordinary amount of mechanistic information about the polymerization mechanism. (a) Cheng, H. N. In *Modern Methods of Polymer Characterization*; Barth, H. G., Mays, J. W., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp 409–493. (b) Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH Publishers: New York, 1989; pp 1–252. (c) Randall, J. C. *Polymer Sequence Determinations: Carbon-13 NMR Method*; Academic Press: New York, 1977; pp 1–155.

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(29) Frisch, H. L.; Mallows, C. L.; Bovey, F. A. *J. Chem. Phys.* **1966**, *45*, 1565–1577.

(30) Cheng, H. N.; Khasat, N. P. *J. Appl. Polym. Sci.* **1988**, *35*, 825–829.

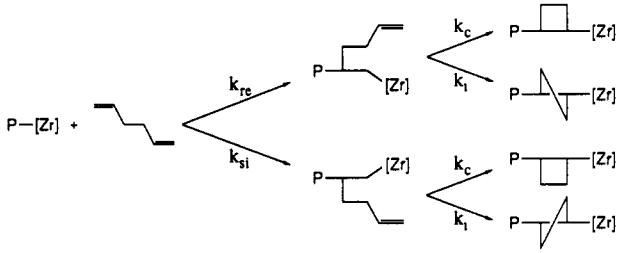


Figure 5. Stereoselectivity parameters: $\alpha = k_{re}/(k_{re} + k_{si})$; $\sigma = k_c/(k_c + k_t)$.

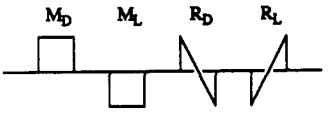


Figure 6. Four possible rings in cyclopolymers.

One very important consequence of the enantioselective cyclopolymerization is that the observation of optical activity *provides unambiguous proof that the microstructure of the polymer represented in Figure 4B is isotactic.* Thus, resonances absent in the spectrum of Figure 4B were assigned to atactic tetrads (RmR and MrM). The assignments for the isotactic tetrads between similar rings (RrR and MmM) were straightforward, but it was not possible to unambiguously assign the tetrads between dissimilar rings (RmM, RrM, MrR, and MmR).

To further substantiate the tetrad assignments and to attempt to extract mechanistic information from the polymer microstructure, we have derived a statistical model for the microstructure based on kinetically relevant reaction parameters. We have based our statistical model on a modified enantiomorphic site control model[31] where we make the following simplifying assumptions: (1) the enantioface selectivity of olefin insertion is independent of previous stereochemical events and is only determined by the stereochemistry of the catalyst; and (2) the diastereoselectivity of cyclization is independent of both previous stereochemical events and catalyst stereochemistry. Thus, our model assumes that the olefin insertion step is under enantiomorphic site control, whereas the cyclization step is controlled exclusively by the conformational preferences of the incipient ring. The first assumption is consistent with a number of previous studies for olefin polymerization with chiral Brintzinger metallocenes.[19] The second assumption, that the cis/trans selectivity is independent of the catalyst stereochemistry, is probably less reasonable and may introduce some error into the calculated tetrad distributions. Nevertheless, as a first approximation this model allows us to make reasonable predictions of the polymer microstructure based on a minimal number of adjustable parameters.

We base our statistical analysis on two reaction parameters, α and σ. To describe the tacticity, we define a parameter $\alpha = k_{re}/(k_{si} + k_{re})$, where k_{re} and k_{si} are rate constants for insertion of the *re* and *si* enantiofaces, respectively. For the cis/trans diastereoselectivity, we assume a single probability $\sigma = k_c/(k_c + k_t)$, where k_c and k_t are rate constant for formation of cis and trans rings, respectively. In this case, σ is also equal to the mole fraction of cis rings in the polymer and can be determined directly from the relative ratio of the $C_{4,5}$ resonances at 32.0 and 33.4 ppm in the ^{13}C NMR spectrum.

Because we have not unambiguously assigned the absolute stereochemistry of the polymer (vide infra), we cannot correlate the enantioface selectivity with the absolute stereochemistry of the rings. Therefore, we will denote the ring stereochemistry arbitrarily, where in the Fischer projection if the first stereocenter (reading left to right) of the ring is up, we assign a subscript D, and if the first stereocenter is down, we assign a subscript L (Figure 6).

(31) (a) Sheldon, R. A.; Fueno, T.; Tsunstsugu, T.; Furukawa, J. *J. Polym. Sci., Part B* **1965**, *3*, 23–26. (b) Sheldon, R. A.; Fueno, T.; Tsunstsugu, T.; Furukawa, J. *J. Polym. Sci., Part B* **1969**, *7*, 763–773.

Table III. Tetrad Probabilities

tetrad	probability
RrR	$(1-\sigma)^2(\alpha)^2 + (1-\sigma)^2(1-\alpha)^2$
RmR	$2(1-\sigma)^2(1-\alpha)\alpha$
MrM	$2\sigma^2(1-\alpha)\alpha$
MmM	$\sigma^2\alpha^2 + \sigma^2(1-\alpha)^2$
RrM + MrR	$\sigma(1-\sigma)^a$
RmM + MmR	$\sigma(1-\sigma)^a$

[a] RrM = MrR = RmM = MmR = $\sigma(1-\sigma)/2$.

Table IV. Calculated and Experimental Tetrad Distributions for Polymers Obtained with Cp_2ZrCl_2

		intensities	
chemical shift	tetrad	exptl	calcd[a]
31.94	MmM + MxR	10.1	9.5
31.98	MxR	7.1	7.7
32.01	MrM	1.8	1.8
33.35	RrR + RxM	41.9	40.7
33.38	RmR	34.0	32.6
33.43	RxM	5.1	7.7

[a] $\sigma = 0.19$, $\alpha = 0.54$.

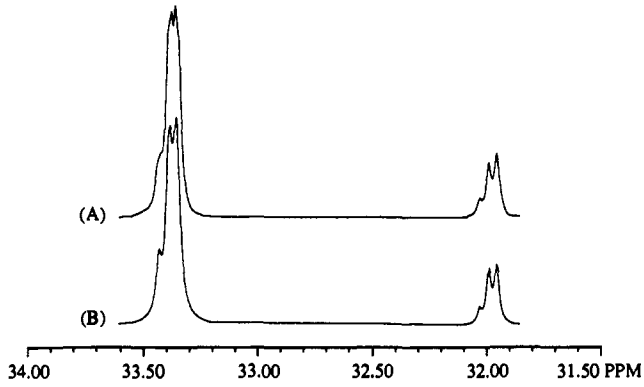


Figure 7. Actual (A) and simulated (B; $\sigma = 0.19$, $\alpha = 0.54$) ^{13}C NMR spectra for $C_{4,5}$ (Cp_2ZrCl_2 precursor).

The mole fraction of the four possible rings, M_D, M_L, R_D, and R_L, in the polymer can be expressed in terms of σ and α:

$$\begin{aligned} M_D &= \sigma(\alpha) \\ M_L &= \sigma(1-\alpha) \\ R_D &= (1-\sigma)\alpha \\ R_L &= (1-\sigma)(1-\alpha) \end{aligned} \quad (1)$$

and the probabilities for the various tetrads are then described by

$$F_D(x)(y) + F_L(1-x)(y) \quad (2)$$

where F_D or F_L is the mole fraction of the initial ring, x equals the conditional probability α or $1-\alpha$, and y equals the unconditional probability σ or $1-\sigma$. The tetrad probabilities are listed in Table III.

Because of the close overlap of the ^{13}C NMR resonances for the various tetrads, the experimental tetrad distribution was evaluated by fitting the ^{13}C NMR spectra to Lorentzian line shapes. The calculated tetrad distributions were then determined by measuring σ from the spectra and then varying α until an optimum fit was obtained.

The experimental and calculated tetrad distributions for the polymers obtained from hexadiene in the presence of the achiral precursor Cp_2ZrCl_2[32] are represented in Figure 7 and listed in Table IV. From the table, it is shown that the best fit to the data occurs for $\sigma = 0.19$ and $\alpha = 0.54$, which corresponds to an atactic microstructure, as expected. The fact that the calculated tetrads match closely with the experimental data provides strong support that our tetrad assignments are correct and establish the validity of the simple statistical model.

(32) See Table I, entry 1 for polymerization conditions.

Table V. Calculated and Experimental Tetrad Distributions for Polymers Obtained with (+)-(*S,S*)-(EBTHI)ZrBINOL ((*S,S*)-**1**)

		intensities	
chemical shift	tetrad	exptl	calcd[a]
31.94	MmM + MxR	15.1	16.7
31.98	MxR	12.9	10.1
32.01	MrM	0.0	1.2
33.35	RrR + RxM	53.6	53.8
33.38	RmR	6.6	8.1
33.43	RxM	11.8	10.1

[a] $\sigma = 0.28$, $\alpha = 0.91$.

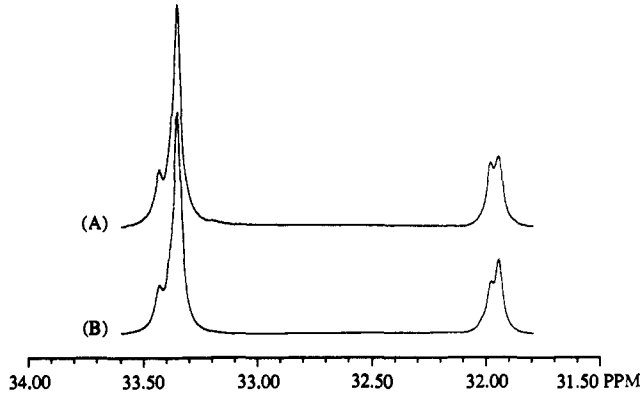


Figure 8. Actual (A) and simulated (B; $\sigma = 0.28$, $\alpha = 0.91$) ^{13}C NMR spectra for $C_{4,5}$ ((*S,S*)-(EBTHI)ZrBINOL ((*S,S*)-**1**) precursor).

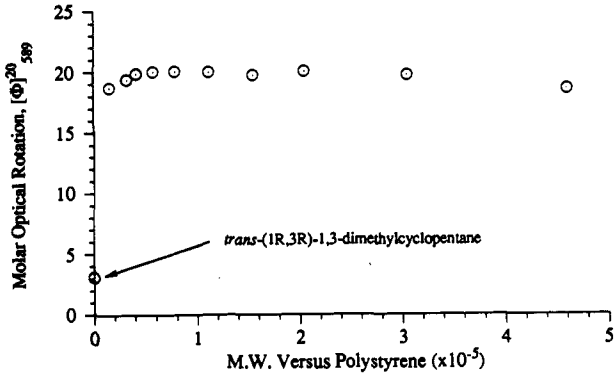


Figure 9. Molar optical rotation ($c = 1.0$, $CHCl_3$) as a function of molecular weight for (+)-PMCP.

The experimental and calculated tetrad distributions for the polymers obtained with the chiral (EBTHI)ZrBINOL (**1**)[33] catalyst are represented in Figure 8 and listed in Table V. Using our statistical model for these polymers, the best fit to the data occurs for $\sigma = 0.28$ and $\alpha = 0.91$, which corresponds to a highly isotactic microstructure and an impressive (91%) enantioface selectivity.

To compare the level of enantioface selectivity calculated for hexadiene ($\alpha = 0.91$) with that of propylene, propylene was polymerized under identical conditions with *rac*-**1**, and the microstructure of the isolated polypropylene was analyzed by ^{13}C NMR. The microstructural analysis of polypropylene revealed an mmmm pentad content of 85%, which corresponds to an enantioface selectivity as defined by the enantioface copolymerization parameter $\alpha = 0.97$.

Molecular Weight Dependence of Optical Rotations. The dependence of the molar optical rotation on molecular weight was determined on a single sample of PMCP obtained from (*R,R*)-**1**. For these experiments, 1,5-hexadiene was polymerized to 90% conversion (Table II, entry 5) to obtain a broad molecular weight distribution. Individual molecular weight fractions were isolated by preparative gel permeation chromatography (GPC), and the

(33) See Table II, entry 4 for polymerization conditions.

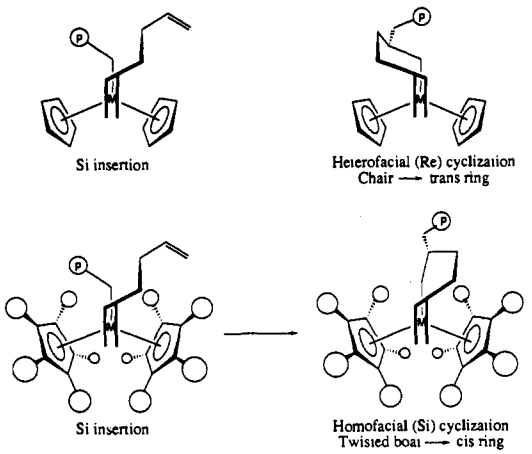


Figure 10. Conformational model for diastereoselectivity of cyclopolymerization.

optical rotations for the various fractions were measured. The data represented in Figure 9 indicate that the molar optical rotations are relatively insensitive to molecular weight.

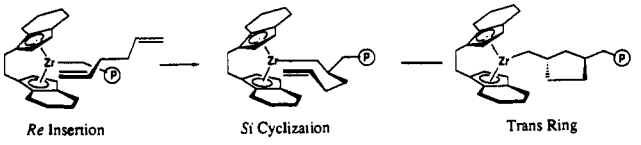
Discussion

Cyclopolymerization is a fascinating polymerization process which leads to an array of architecturally rich polymer microstructures. For poly(methylene-1,3-cyclopentane), there are two criteria for chirality: isotacticity and the presence of trans rings.[34] The tacticity of the polymer is influenced by the enantioface selectivity of the first insertion step; the cis/trans selectivity is influenced by the diastereoselectivity of the cyclization step.

As part of our systematic investigations of the stereochemistry of cyclopolymerization, our first series of studies[21] was carried out with achiral catalysts in an effort to investigate the diastereoselectivity of the cyclization step in the absence of chirality at the metal center. It was discovered that the nature of the cyclopentadienyl ligand had a strong effect on the diastereoselectivity of ring formation, leading to the first examples of atactic *cis*-PMCP and *trans*-PMCP. We have proposed that the trans selectivity with the Cp_2ZrX_2 precursors is due to a preference of the growing chain to adopt an equatorial position in a pseudo-chair transition state.[35,36] However, a chair-type transition state does not appear to be readily accommodated in the presence of the more sterically hindered $Cp^*_2ZrX_2$ precursors. A twist-boat conformation could be accommodated, but placement of the chain in an equatorial position in this case leads to a cis ring (Figure 10). More sophisticated conformational calculations have been carried out by Guerra et al. and will be reported elsewhere.[37]

Studies with the achiral catalysts suggested that the diastereoselectivity of the cyclopolymerization reaction is influenced by the conformational preferences of the incipient ring and the interaction of that ring with the cyclopentadienyl ligands at the transition metal. The enantioface selectivity of olefin insertion can be controlled with chiral catalysts of the Brintzinger type. Since these catalysts also produce polymers with a predominance of trans rings, we recognized that this catalyst system was capable of an enantioselective polymerization reaction. In fact, the enantioselective cyclopolymerization of 1,5-hexadiene yields cyclopolymers which exhibit significant optical rotations in solution. Either enantiomer of the polymer can be prepared with the appropriate choice of catalyst precursor, and control experiments

Scheme III



established that the observed optical rotations are not due to catalyst residues.

Cyclopolymers of 1,5-hexadiene obtained from the Brintzinger catalysts contain a mixture of cis and trans rings. Despite the presence of cis rings, the molar optical rotations of optically active PMCP are considerably higher than the model compound *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane ($[\Phi]^{20}_D$ +3.1°).[38] The most reasonable explanation[2] for this observation is that the polymer adopts two diastereomeric helical conformations in solution, where one of the helices is thermodynamically preferred. Thus, the observed optical rotations are due both to contributions from the main-chain chirality and to a predominance in solution of one helical conformation. The observed temperature dependence of the optical rotations is consistent with a conformational contribution to the optical activity.[2]

Absolute Stereochemistry. Because of the large difference in the optical rotations between the model compound dimethylcyclopentane and PMCP, the assignment indicated in Scheme II for the absolute stereochemistry of the polymer must be regarded as tentative. This assignment assumes that the absolute configuration of the polymer derived from hexadiene and (*R*,*R*)-**1** is the same as that of the model compound *trans*-(1*R*,3*R*)-(+)-1,3-dimethylcyclopentane having the same sign of optical rotation. While this is not a very good assumption, it is consistent with that predicted if the enantioface selectivity for the initial insertion of hexadiene is *the same* as that established for the enantioselective oligomerization of 1-pentene, 1-butene, and propylene (Scheme III).[39]

The formation of a trans ring requires a heterofacial insertion/cyclization sequence, i.e., the cyclization step must occur on a diastereoface of opposite topicity to the enantioface selected for the initial insertion step. The trans selectivity in the presence of achiral Cp_2ZrCl_2 derivatives has been interpreted in terms of a conformational preference of the incipient ring to adopt a chair transition state with the polymer chain occupying an equatorial position. If a similar situation applies to the more sterically hindered (EBTHI)ZrBINOL derivative (**1**), then the trans selectivity suggests that the conformational bias of the incipient ring may compete with the enantiofacial preference of the catalyst for the cyclization step.[40] This competition between the diastereoselectivity and the enantioface preference of the catalyst could be responsible for the lower cyclization selectivity for **1**.

Microstructure. Detailed analysis of the microstructure provided the only means of establishing the degree of enantioface selectivity. On the basis of ^{13}C NMR analysis, we can unambiguously assign four of the possible eight tetrads (RrR, RmR, MmM, and MrM), but it was not possible to unambiguously assign the tetrads between dissimilar signs (RmM, RrM, MrR, and MmR).

The ^{13}C NMR spectra for the polymers matched those calculated from a statistical model based on a modified enantiomorphic site control mechanism. These results represent the first detailed assignment of the microstructure of a cyclopolymer. On the basis of our statistical analysis, we were able to derive an enantioface

(34) These are two necessary but insufficient criteria: the polymers must also possess an excess of stereocenters of one absolute configuration.

(35) Recent observations by Stille in the stoichiometric cyclization of substituted hexenyl titanium reagents were interpreted in terms of a similar model. (a) Young, J. R.; Stille, J. R. *Organometallics* **1990**, *9*, 3022–3025. (b) Young, J. R.; Stille, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 4936–4937.

(36) (a) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123–3125. (b) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294.

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(38) Richter, J. R.; Richter, B. *Isr. J. Chem.* **1976**, *15*, 57–62.

(39) (a) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189–6191. (b) Pino, P.; Galimberti, M.; Prada, P.; Consiglio, G. *Makromol. Chem.* **1990**, *191*, 1677–1688. (c) Pino, P.; Galimberti, M. *J. Organomet. Chem.* **1989**, *370*, 1–7. (d) Kaminsky, W.; Ahlers, A.; Möller-Lindenhof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216–1218.

(40) Alternatively, the trans selectivity could be explained in terms of a frontal coordination of the olefin in the cyclization step, as has been proposed for olefin hydrogenation with these catalysts. (a) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911–4914. (b) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501–1505 and references therein.

Figure 11. Limiting microstructures of polypropylene.

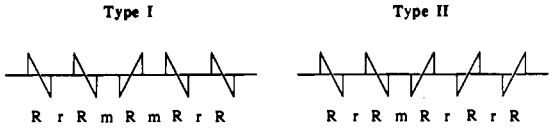

Figure 12. Limiting microstructures of PMCP.

selectivity of 91% for the cyclopolymerization of 1,5-hexadiene in the presence of the chiral (EBTHI)ZrBINOL (1) derivatives. This high enantioface selectivity is similar to that observed for propylene polymerization (97%) under similar conditions.

Because a trans ring is required for main-chain chirality, enantioselective cyclopolymerization requires a subtle interplay between enantioface selectivity of olefin insertion and diastereoselectivity for cyclization. A detailed understanding of the factors which influence these two steps is critical for the molecular design of main-chain chiral polymers. We have demonstrated the utility of homogeneous Ziegler–Natta catalysts in studying and controlling these important stereochemical parameters. Further stereochemical modeling of these reactions is being carried out in collaboration with the Guerra group in order to provide the necessary design criteria for developing catalysts which should exhibit improved diastereoselectivity of these cyclopolymerizations while maintaining the high enantioface selectivity. Our ability to interpret the microstructure of these polymers will prove critical to these efforts.

Enantiomorphic Site Control versus Chain-End Control. There are two limiting mechanisms that have been proposed to account for the origin of tacticity in vinyl polymers. An enantiomorphic site control mechanism[31a,41] implies that the catalyst site is responsible for differentiating the olefin enantiofaces, whereas a chain-end control mechanism[42] implies that the penultimate stereocenter of the polymer chain influences the stereochemistry of subsequent olefin insertions. For polypropylene, a number of statistical models have been devised to interpret the ^{13}C NMR spectra and distinguish between these two limiting mechanisms.[19b,27,29] The limiting microstructures for polypropylene derived from enantiomorphic site control and chain-end control have been described as type I and type II polypropylene, respectively, and are presented in Figure 11. Type I polypropylene is indicative of enantiomorphic site control since stereoinversions are isolated mistakes that are immediately corrected. In contrast, type II polypropylene is indicative of chain-end control since stereomistakes are propagated in the polymer.

The corresponding limiting structures for trans-isotactic PMCP are presented in Figure 12. Inspection of these two limiting microstructures reveals that following a stereocenter inversion, the only difference in the two cases is one additional RmR tetrad for the type I polymer (enantiomorphic site control).

The statistical model that we have presented for the microstructure of PMCP is based on an enantiomorphic site control model and provides reasonable agreement with the experimental data. Nevertheless, while this statistical model is useful for obtaining an estimate of the degree of tacticity, the NMR data are not sufficiently unambiguous to distinguish between type I and type II PMCP. Thus, we cannot rule out a chain-end control mechanism on the basis of the NMR analysis.

The chirality of the PMCP provides a means of distinguishing between site control and chain-end control. If a chain-end control mechanism were responsible for the enantioface selectivity, then a single mistake in a polymer chain would have a significant effect on the molar optical rotation of the polymer. The probability of a mistake for a given chain would be expected to increase with molecular weight; thus, there would be a strong molecular weight dependence of the molar optical rotation for a chain-end control mechanism.[43] The fact that we observe no dependence of the optical rotation on molecular weight provides strong evidence that the enantioselective cyclopolymerization of 1,5-hexadiene with chiral metallocenes is governed by an enantiomorphic site control mechanism.

Conclusions

In conclusion, we report a novel strategy for the synthesis of main-chain chiral polymers. We have delineated several mechanistic principles for enantioselective cyclopolymerization in the context of our work with homogeneous Ziegler–Natta catalysts. The molecular design of main-chain chiral polymers requires a detailed understanding of the factors which control both the ring stereochemistry and the tacticity. The advent of well-defined organometallic catalyst precursors has provided a unique opportunity for the systematic investigation of the important stereochemical control elements necessary to influence stereodifferentiation. Our efforts to date have provided chiral polymers of 1,5-hexadiene which contain a mixture of cis and trans 5-membered rings. Further efforts are directed at designing new catalyst systems which will exhibit better control over the cis/trans selectivity while maintaining the high enantioface selectivity. Our ability to interpret the microstructure of poly(methylene-1,3-cyclopentane) will prove critical for these efforts.

One of the most exciting features of enantioselective cyclopolymerization is the potential generality of the method as a rational strategy for preparing chiral macromolecules. We are intrigued by the prospect that these principles can be generalized to other polymerization processes.

Enantioselective polymerization processes should facilitate investigations on the influence of chirality on polymer properties. An enantioselective polymerization provides ready access to either the racemic or enantiomerically enriched materials, allowed for detailed studies of the influence of enantiomeric purity on the properties of polymers.[44] In addition, enantioselective cyclopolymerization should provide a general strategy for the synthesis of a wide range of new chiral macromolecules.

Experimental Section

General Considerations. All reactions with organometallic compounds were carried out under dry nitrogen using a Vacuum Atmospheres drybox or standard vacuum line techniques. Hydrocarbon solvents were vacuum transferred from sodium benzophenone ketyl; chlorinated solvents were vacuum transferred from activated 4-Å molecular sieves.

Propylene (Matheson) was used as received. 1,5-Hexadiene (Wiley) was vacuum transferred from CaH_2. Methylaluminoxane (MAO) was obtained as a 30% toluene solution (Sherex) and was used after removing all volatiles in vacuo (6 h, 0.02 Torr). Cp_2ZrCl_2 (Boulder Scientific), $Cp^*_2ZrCl_2$ (Strem), and Cp_2TiCl_2 (Aldrich) were used as received. BINOL (1,1′-bi-2-naphthol) was purchased from Aldrich (99%). The complexes *rac*-(EBI)$ZrCl_2$ (2), *rac*-(EBTHI)$ZrCl_2$, *rac*-(EBTHI)$ZrMe_2$, *rac*-(EBTHI)ZrBINOL (1), (+)-(*S,S*)-(EBTHI)ZrBINOL ((*S,S*)-1), and (−)-(*R,R*)-(EBTHI)ZrBINOL ((*R,R*)-1) were prepared according to literature preparations[19a,45] and were recrystallized until pure by ^1H NMR.

NMR spectra were recorded on a Varian XL-400 (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer. Quantitative ^{13}C NMR polymer spectra were obtained at 50 °C in $CDCl_3$ solvent (150 mg/mL; pulse width = 90°; sweep width = 60 ppm; delay time ≥3.5 s; inverse gated decoupling).[46] Line shape analysis was carried out on a Macintosh computer using KaleidaGraph software. Optical rotations were obtained using a JASCO DIP-360 or Rudolph Research Autopol III polarimeter. Gel permeation chromatography (GPC) analyses were carried out with a Waters 510 instrument equipped with a Waters 410 differential refractometer and

(41) Inoue, Y.; Itabashi, Y.; Chûjô, R.; Doi, Y. *Polymer* **1984**, *25*, 1640–1644.

(42) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173–182.

(43) Frisch, H. L.; Schuerch, C.; Szwarc, M. *J. Polym. Sci.* **1953**, *11*, 559–566.

(44) For some examples, see: (a) Zawadzke, L. E.; Berg, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 4002–4003. (b) Tsuji, H.; Hyon, S.-H.; Ikada, Y. *Macromolecules* **1992**, *25*, 2940–2946.

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Waters Ultrastyragel 10^3 Å, 500 Å, and linear columns in series. The GPC columns were eluted with tetrahydrofuran at 35 °C and were calibrated using Shodex SM-105 polystyrene standards. Preparative GPC was conducted with a Waters UK6 instrument equipped with a Waters R-404 differential refractometer and Polymer Laboratories PLgel (10 mm) mixed preparative column. Samples (100 mg of polymer in 2 mL of toluene) were eluted with toluene at ambient temperature. DSC measurements were obtained with a Perkin-Elmer DSC 7 thermal analyzer at a heating rate of 10 °C/min from −50 to 200 °C.

General Polymerization Procedure. In the drybox, (EBTHI)ZrBINOL (**1**) (5 mg, 7.8×10^{-6} mol), MAO (500 mg, 8.6×10^{-3} mol), and a magnetic stir bar were placed in a 100-mL Schlenk tube. After it was sealed with a rubber septum, the flask was removed from the drybox and connected to a vacuum line. Toluene (100 mL) was added to the flask via cannula needle, and after the homogeneous solution was stirred for 5 min, 1,5-hexadiene (5 mL) was added via syringe. After allowing the solution to react at room temperature for 3 h, polymerization was stopped by carefully adding 10 mL of methanol. After the reaction was stirred for 8 h, all volatiles were removed in vacuo. The resulting solid was washed with 4 M HCl/methanol (1/1) and then methanol. After drying, the solid was extracted with boiling toluene (4 × 25 mL), filtered over a medium glass frit prepared with a Celite filtering agent, and dried in vacuo to constant weight.

Polymerization of Propylene with (*S*,*S*)-1. In a 100-mL Schlenk tube equipped with a rubber septum and magnetic stirring bar were placed 4 mg of (*S*,*S*)-**1**, 940 mg of dry MAO, and 100 mL of toluene. After aging for 5 min at room temperature, the rapidly stirred solution was cooled to 0 °C and was saturated with propylene (800 mmHg). The mixture was allowed to stir for 1.5 h under a constant pressure of propylene and then quenched with 10 mL of methanol and 10 mL of 4 M HCl. After the resulting mixture was stirred overnight, volatiles were removed in vacuo. The remaining white solid was extracted with boiling toluene and dried in vacuo to yield 200 mg of a white, powdery solid. ^{1}H NMR was consistent with isotactic polypropylene. The polymer showed no observable optical rotation (c = 0.64, 1,1,2,2-tetrachloroethane).

Polymerization of Propylene with *rac*-1. In a 100-mL Schlenk tube equipped with a rubber septum and magnetic stirring bar were placed 3 mg of *rac*-**1**, 247 mg of dry MAO, and 36 mL of toluene. After aging for 5 min at room temperature, the rapidly stirred solution was saturated with propylene (800 mmHg). The mixture was allowed to stir at 23 °C for 40 min under a constant pressure of propylene and then quenched with 10 mL of methanol and 10 mL of 4 M HCl. After the resulting mixture was stirred overnight, volatiles were removed in vacuo. The remaining white solid was extracted with boiling toluene and dried in vacuo to yield 6.95 g of a white, powdery solid. Using ^{13}C NMR, the mmmm pentad content was determined to be 85%, which corresponds to an enantioface selectivity of 97%.

Temperature Dependence of Molar Optical Rotation. A 53.1-mg sample of (−)-PMCP (Table II, entry 4) was dissolved in 10.0 mL of toluene at 20 °C. (Note: Turbid solutions were observed in chloroform at temperatures lower than 20 °C.) A 10-cm sample polarimetry cell and a 10-cm blank polarimetry cell containing toluene were connected in series to a thermostated ethylene glycol bath. A thermometer was placed in-line between the two cells to provide accurate temperature readings. After the bath was cooled to 10 °C, three blank and three sample readings were taken after the temperature had become stable for 5 min. Readings were taken at approximately 5 °C intervals until the temperature of 80.5 °C was reached. After change in solvent density was corrected for using published values of the density of toluene at various temperatures, molar optical rotations were calculated for each temperature.

Molecular Weight Dependence of Molar Optical Rotation. A 100-mg sample of (+)-PMCP (Table II, entry 5) was dissolved in 2.0 mL of toluene and was injected into a preparative GPC column. After 23 min, elution of the polymer from the column commenced, and 36 fractions were collected at 0.5-min intervals. This procedure was repeated for three more 100-mg samples. Solutions of the same retention time for the four runs were combined. Starting with the highest molecular weight fraction, solvent was removed in vacuo in a tared 100-mL flask. One by one, the next highest weight samples were added and solvent was removed until 20 mg of dry polymer were in the flask. At this point, the polymer was scraped out of the flask and dried in vacuo at 0.001 mmHg overnight. Ten such samples of differing molecular weights were obtained in this way. After obtaining a molecular weight for each polymer, a weighed sample (ca. 10 mg) was dissolved at 20 °C in a weighed amount of dry chloroform (ca. 1.5 g). Rotations for each solution were obtained using 589-nm polarized light at 20.0 °C.

Catalyst Enantiomeric Purity Dependence of Molar Optical Rotation. In a drybox, 0.0132 g of (*R*,*R*)-**1** ($[\alpha]^{24}_{435}$ −1685° (c = 0.20, benzene)) and 0.0117 g of *rac*-**1** were placed in a 100-mL Schlenk tube. After they were dissolved in ca. 3 mL of benzene, the solvent was removed in vacuo to give a sample of (*R*,*R*)-**1** with a specific optical rotation of $[\alpha]^{24}_{435}$ −902° (c = 0.19, benzene). In two 100-mL Schlenk tubes, 6 mg of the optically pure and of the enantiomerically enriched metallocene **1** were separately placed, one sample in each tube. After MAO (525 mg) and toluene (114 mL) were added to each flask, the solutions were allowed to stir for 15 min. Over a period of 2 min, 1,5-hexadiene (2.5 mL) was added to each catalyst solution at 23 °C. After stirring for 3 h, each polymerization was stopped by carefully adding methanol (ca. 10 mL) to the flask. After the mixtures were stirred overnight, all volatiles were removed in vacuo. By gas chromatography it was determined that each reaction went to approximately 90% conversion. The resulting solid was washed with 4 M HCl/methanol (1/1) and then methanol. After drying, the solid was extracted with boiling toluene (4 × 25 mL), passed over a paper filter prepared from a Celite filtering agent, and dried in vacuo to constant weight. A weighed sample (ca. 40 mg) of each polymer was then dissolved with chloroform in a 5-mL volumetric flask. Rotations for both solutions were obtained using a 589-nm polarized light at 20.0 °C. Molar optical rotations of $[\Phi]^{20}_{589}$ +20.3° (c = 0.80, $CHCl_3$) and $[\Phi]^{20}_{589}$ +11.1° (c = 0.80, $CHCl_3$) were obtained for the polymers made using optically pure and enantiomerically enriched samples of **1**, respectively (Table II, entries 5 and 6).

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