Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Dr. W. Nugent for helpful discussions and Professor Negishi for sharing results prior to publication.

Registry No. 1,7-Octadiene, 3710-30-3; 1,6-heptadiene, 3070-53-9; 1-octene, 111-66-0; ethenylbenzene, 100-42-5; *cis*-1,2-dimethylcyclohexane, 2207-01-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,4-cyclohexanedimethanol, 3236-47-3; *trans*-1,4-cyclohexanedimethanol, 3236-48-4; *cis*-1,2-dimethylcyclopentane, 1192-18-3; *trans*-1,1-dimethylcyclopentane, 822-50-4; 3-methylnonane, 5911-04-6; 2-hexyl-1,4-butanediol, 18755-31-2; *n*-butylbenzene, 104-51-8; (1-methylpropyl)benzene, 135-98-8; 1-deuterio-2-(deuteriomethyl)nonane, 122348-19-0; *cis*-1,2-bis(deuteriomethyl)cyclohexane, 133816-67-8; *trans*-1,2-bis(deteriomethyl)cyclohexane, 133816-68-9; dibutylmagnesium, 1191-47-5; butylmagnesium chloride, 693-04-9; diethylmagnesium, 557-18-6; ethylmagnesium bromide, 925-90-6; zirconocene dichloride, 1291-32-3.

Supplementary Material Available: Experimental details and spectral data (3 pages). Ordering information is given on any current masthead page.

Enantioselective Cyclopolymerization: Optically Active Poly(methylene-1,3-cyclopentane)

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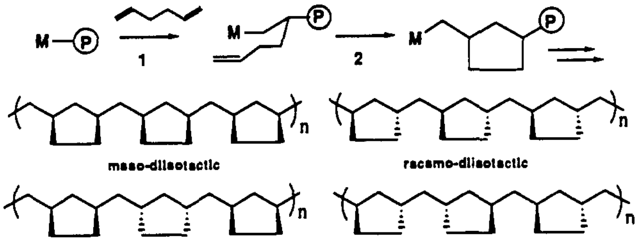
The impressive stereoselectivity of homogeneous Ziegler–Natta catalysts[1] presents an unprecedented opportunity for the molecular design of polymers that are difficult or impossible to prepare with conventional heterogeneous catalysts. The availability of chiral metallocene precursors[2] provides an opportunity to prepare new chiral polymers.[3,4] However, the symmetry of high molecular weight stereoregular vinyl polymers is such that they generally contain mirror planes of symmetry and thus are achiral.[5-8] Herein we report a synthetic route to polymers that do not have this fundamental symmetry limitation. The enantioselective cyclopolymerization of 1,5-hexadiene yields a novel example of an optically active polyolefin whose chirality derives from configurational main-chain stereochemistry.[6,7,9]

Figure 1. Resolution-enhanced ^{13}C NMR spectra (100 MHz, $CDCl_3$, 40 °C) of $C_{4,5}$ for PMCP prepared with (a) Cp_2TiCl_2 and (b) *rac*-(EBTHI)ZrBINOL.

Scheme I



Cyclopolymerization[10] of 1,5-hexadiene with homogeneous[11] Ziegler–Natta catalysts yields poly(methylenecyclopentane) (PMCP), a polymer for which four structures of maximum order[8] are possible (Scheme I). Of these, only the racemo diisotactic polymer contains no mirror planes of symmetry and is thus chiral by virtue of its main-chain stereochemistry. There are two criteria for chirality in these materials: (1) the polymer must be predominantly isotactic, and (2) the polymer must contain predominantly trans rings. The enantioface selectivity of olefin insertion determines the tacticity of the polymer (the relative stereochemistry of every other stereocenter), and the diastereoselectivity of the cyclization step determines whether cis or trans rings are formed. We have previously shown that the cis/trans diastereoselectivity is influenced by the size of the catalyst precursor, leading to the first examples of *trans*-PMCP and *cis*-PMCP.[12,13] In an effort to control the enantioface selectivity of olefin insertion (and therefore the tacticity), we investigated chiral metallocenes of the Brintzinger type[2] $(EBI)ZrX_2$ and $(EBTHI)ZrX_2$ (EBI = ethylenebis(1-indenyl), EBTHI = ethylenebis(tetrahydro-1-indenyl). Shown in Figure 1 are the ^{13}C NMR resonances of carbons C_4 and C_5 of the repeating unit of polymers produced at 25 °C from (a) Cp_2TiCl_2 and (b) the chiral precursor *rac*-(EBTHI)ZrBINOL (BINOL = 1,1′-bi-2-naphtholate). The ratio of resonances at 33.3 and 31.9 ppm indicates[12,14] that both catalysts exhibit a trans ring selectivity (between 63 and 68%). Closer analysis reveals fine structure in these resonances: the differences in the two spectra imply that the ^{13}C chemical shifts of these carbons are sensitive to stereochemistry between rings (i.e., tacticity), but do not provide unambiguous information about the microstructure.

Cyclopolymerization of 1,5-hexadiene in the presence of the optically active catalyst precursor (−)-(*R*)-ethylenebis(tetra-

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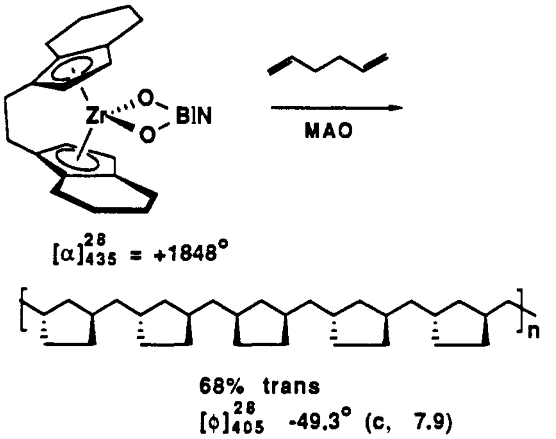
hydroindenyl)zirconium (*R*)-binaphtholate ($[\alpha]_{435}$ −1431° (*c* 1.2, $CHCl_3$))[2] and a methylaluminoxane (MAO) cocatalyst yields *optically active* poly(methylene-1,3-cyclopentane).[15] Following acidic workup, extraction of the polymer into chloroform, and precipitation with acetone, this polymer showed the molar optical rotation (per monomer unit) $[\Phi]^{28}_{405}$ +50.1° (*c* 7.8, $CHCl_3$).[16] Cyclopolymerization with (+)-(*S*)-ethylenebis(tetrahydroindenyl)zirconium (*S*)-binaphtholate ($[\alpha]_{435}$ +1848° (*c* 0.52, $CHCl_3$)) afforded the enantiomeric polymer (eq 1) with the molar optical rotation $[\Phi]^{28}_{405}$ −49.3° (*c* 7.9, $CHCl_3$).



(1)

The optically active polymers contain approximately 68% trans rings and have ^{13}C NMR spectra identical with those obtained with the racemic catalyst. Since isotacticity is a requirement for chirality (for this polymer), the observation of optical activity provides an unambiguous proof for an isotactic microstructure.[17] Because of incomplete diastereoselectivity in the cyclization, the polymer obtained with chiral catalysts of the Brintzinger type is essentially an isotactic copolymer of *cis*- and *trans*-poly(methylene-1,3-cyclopentane).

Despite the presence of cis rings, the molar optical rotations (per monomer unit, $|[\Phi]^{20}_D|$ 22.8° (*c* 7.8, $CHCl_3$)) of the polymers are considerably higher than that of the model compound *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane, $[\Phi]^{20}_D$ +3.1°.[18] This suggests that the polymer adopts conformations in solution that contribute to the observed optical rotation.[5,7,8] The temperature dependence of the molar optical rotation for the polymer is consistent with this interpretation: the molar optical rotations $[\Phi]^T_D$ decrease from 26.2° at 2.5 °C to 19.5° at 51.1 °C with a slope $\Delta[\Phi]/\Delta T = -0.14°/°C$.[19]

In summary, we report the first *enantioselective cyclopolymerization to give a main-chain chiral polymer.* Because there is no requirement for chirality in the monomer, enantioselective polymerization is the most efficient means of preparing chiral polymers.[20-23] Further studies are underway to assign the absolute configuration of the polymer and to study the chiroptical and physical properties of these novel materials.

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Registry No. Cp_2TiCl_2, 1271-19-8; (±)-(EBTHI)ZrBINOL, 133868-91-4; (−)-(*R*)-(EBTHI)ZrBINOL, 123236-85-1; (+)-(*S*)-(EBTHI)-ZrBINOL, 132881-66-4; 1,5-hexadiene (homopolymer), 25067-96-3; *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane, 1759-58-6.

Supplementary Material Available: Polymerization procedures and ^{13}C NMR spectra (3 pages). Ordering information is given on any current masthead page.

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(15) M_w = 35 000; M_w/M_n = 1.9 (GPC vs polystyrene).

(16) Rotations due to residual catalyst would be opposite in sign to that of the isolated polymer. Nevertheless, to rule out contributions from residual catalyst, propylene was polymerized and isolated under identical conditions with the same optically active catalyst. Residual optical activity in this sample due to the catalyst was virtually undetectable (see supplementary material).

(17) Preliminary microstructural analysis by ^{13}C NMR spectroscopy is consistent with a high degree of tacticity. Coates, G. W.; Waymouth, R. M., unpublished results.

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(19) Similar measurements on poly((*S*)-3-methyl-1-pentene) ($[\Phi]_D$ = +161° at 25 °C) showed temperature-dependent optical rotations with slope $\Delta[\Phi]/\Delta T = -0.36°/°C$. Pino, ref 5.

(20) Previous examples include the enantioselective cationic polymerization of benzofuran,[21] the enantioselective polymerization of pentadienes,[22,23] and the asymmetric polymerization of trityl methacrylates and chloral.[6]

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An Unsymmetrical 1,1,3,3-Tetramethylallyl Cation

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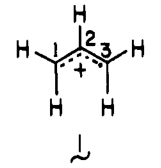
Theoreticians tell us that the allyl cation (**1**) is symmetrical.[2,3] Recent studies in our laboratory[4] have prompted us to question this concept and to carry out a detailed study of the 1,1,3,3-tetramethylallyl cation (**2**). In principle, treatment of **3** with XH



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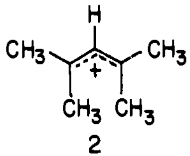

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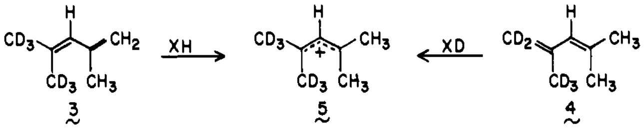
and of **4** with XD should yield the same allyl cation, **5**. We now present experimental evidence that unequivocally establishes that **3** and **4** do not yield the same allyl cation on protonation and deuteration, respectively.



Treatment of 2,4-dimethyl-1,3-pentadiene (**6**) with protic acid produces an allyl cation, which rapidly adds to **6** to produce the ionic Diels–Alder product **7**.[5] Thus, addition of **5** to **3**[6] and to

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(1) National Science Foundation Fellow, 1983–1986.

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(3) The rotational barrier for the allyl cation (**1**) is proposed to be approximately 35 kcal/mol in the gas phase.[2] This suggests that the planar form of **1** is about 35 kcal/mol more stable than the perpendicular form, which should represent the transition state for rotation. Alkyl substitution on the allyl cation is predicted to reduce this barrier (vide post).

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