Stereoselective Polymerization of α-Olefins by Heterogeneous Chiral Ziegler–Natta Catalysts[1]

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ABSTRACT: $MgCl_2$-supported $TiCl_3$ catalysts were synthesized to contain either chiral (racemic or optically active) or nonchiral Lewis basic esters. They were compared along with ordinary $TiCl_3$ in the stereospecific polymerization of propylene and in the stereoselective and stereoelective polymerizations of chiral 3- and 4-methyl-substituted olefins. The number and type of active sites, kinetic parameters, stereoregularity and optical purity of the polyolefins produced, and optical purity of unpolymerized monomer have been determined. The results suggest that active sites differing in steric constraints are responsible for the polymerizations of various monomers. The catalyst modified with the optically active Lewis base possesses several times more active centers of both stereospecific as well as nonstereospecific kinds than the catalyst modified with the corresponding racemic Lewis base in both propylene and racemic 4-methyl-1-hexene polymerizations. The results indicate a mechanism of site stereoselection by the chiral Lewis base. Polymerization of racemic 4-methyl-1-hexene, 3-methyl-1-hexene, and 3,7-dimethyl-1-octene by an optically active catalyst preferentially consumes one antipode showing stereoelectivity for the process.

Introduction

One of the important scientific and technological advances in the stereospecific polymerization of α-olefins was the discovery of $MgCl_2$-supported $TiCl_3$ catalysts. This family of catalysts possesses 2–3 orders of magnitude higher productivities and significantly greater yield of isotactic polymer (IY) than the traditional δ-$TiCl_3$/AlR_2Cl catalyst and offers other advantages such as control of polymer morphology and elimination of deashing and pelletization processes. The material obtained simply by ball-milling $MgCl_2$ with $TiCl_4$ and activated with AlR_3 exhibits low stereospecificity (IY ~ 50%), which is not much better than the original Ziegler's mixed $TiCl_4$/AlR_3 catalytic system. The significant discovery was that the judicious usage of Lewis basic modifiers, such as esters and silanes, can elevate IY to 98% or more. All high-activity $MgCl_2$-supported catalysts employed modifiers both during the preparation of the support (internal Lewis base denoted by B_i) and for the activation (external Lewis base abbreviated as B_e). These Edisonian findings led to major changes in the industrial production of isotactic polypropylene; new plants were constructed and old facilities have been retrofitted to use the supported high-activity catalysts. More than 2 decades have transpired since the first patent application of the $MgCl_2$-supported catalysts. In spite of intensive research in this field, as evidenced by frequent international symposia dealing with this topic,[3] our basic knowledge about the nature of the catalytic titanium species and the function of the ubiquitous Lewis base is still unsatisfactory.

It is common knowledge that the Lewis base greatly reduces the overall productivity of a $MgCl_2$-supported catalyst but increases its stereospecificity. Pino et al.[4] said that "the Lewis base either selectively poisons the catalytic centers producing polymers with low stereoregularity or it modifies the non-stereospecific centers by increasing their stereospecificity and decreasing their productivity, or it acts in both ways". We have put the effect of Lewis base on a quantitative level by radiotagging techniques[5] to count separately the numbers of stereospecific sites (C_i) and nonstereospecific sites (C_a) in catalysts with and/or without B_i and/or B_e. The results showed that the function of B_i is to create active centers of both kinds while B_e acts to preferentially inhibit the nonstereospecific ones. All the catalytic centers for propylene polymerization were found to be Ti(III) ions by redox titrations.[6] The stereospecific sites were observable by EPR, but the nonstereospecific centers were EPR silent.[7]

Polymerizations of racemic and optically active α-olefins were used to establish that the catalytic sites in Ziegler–Natta catalysts are chiral centers.[8] In the case of the $MgCl_2$-supported catalysts, the use of an optically active Lewis base in its preparation offers a means to investigate the stereoelective process of the chiral catalytic centers.[4,9] The $MgCl_2$/(−)-MA/$TiCl_4$/TBA/(−)-MA catalyst ((−)-MA = (−)-menthyl anisate, TBA = tri-*iso*-butylaluminum) was shown to possess centers polymerizing the *S*-antipode of 3,7-dimethyl-1-octene ((*S*)-DMO) from the racemic mixture to PDMO (poly(DMO)) with positive optical rotation, others consuming the (*R*)-DMO to PDMO with negative optical rotation, and finally nonchiral centers producing stereoirregular polymers without optical rotation. The same was observed for 4-methyl-1-hexene (4MH).[9c] Pino et al.[4] proposed six types of catalytic centers of different Lewis acidity. The most Lewis acidic centers are coordinatively highly unsaturated, sterically accessible, nonchiral, and nonstereospecific. The least Lewis acidic centers are less coordinatively unsaturated, sterically restrictive, chiral, and stereospecific. But the relationship between these catalytic centers and the Lewis basic modifiers is at best uncertain (vide supra).

In this work we synthesized two types of $MgCl_2$-supported catalysts either with optically active B_i* or with the corresponding racemic B_i and also one with nonchiral Lewis bases. A "third generation" CW type catalyst was prepared from crystalline magnesium chloride (c-$MgCl_2$), and a "fourth generation" CH type catalyst was obtained from a soluble $MgCl_2$·3ROH adduct (s-$MgCl_2$). The stereoselective and stereoelective polymerizations of nonchiral and racemic 3- and 4-methyl-substituted olefins as well as propylene were compared. The results demonstrate the principal role of chiral Lewis base to be active-site stereoselection. The population of different types of active centers and their kinetic parameters were quantitatively determined. The steric and optical purities of the polyolefins were measured to find a relationship between the

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steric accessibility of a catalytic site and its stereoselectivity. Detailed differences between the "third" and "fourth" generation Ziegler–Natta (ZN) catalysts were revealed by this study.

Experimental Section

All chemicals were purchased from Aldrich unless stated otherwise.

Procatalysts. CH((*R,S*)-2MBP) and CH*((*S*)-2MBP). This is our version of the super-high-activity (fourth-generation) ZN catalyst. It was prepared from a $MgCl_2$·alcohol adduct. We have described the preparation of the CH(EH,BP) catalyst[10] (EH = 2-ethylhexanol, BP = butyl phthalate) and its catalysis of stereospecific polymerizations. This procedure was adapted for the synthesis of the racemic CH((*R,S*)-2MBP) and optically active CH*((*S*)-2MBP) catalysts using racemic 2-methylbutanol and (*S*)-2-methylbutanol ($[\alpha]^{25}_D = -5.8°$ (neat)), respectively, to form the soluble $MgCl_2$·alcohol adducts. Bis(2-methylbutyl) phthalate (2MBP) and bis[(*S*)-2-methylbutyl] phthalate ($[\alpha]^{25}_D = +4.8°$ (cyclohexane)) were synthesized from the respective alcohols and phthaloyl dichloride in pyridine. Elem anal. Found (calcd for bis(2-methylbutyl) phthalate): C, 70.9 (70.6); H, 8.31 (8.57); O, 21.0 (20.9). Found for bis[(*S*)-2-methylbutyl] phthalate: C, 70.5; H, 8.39; O, 21.0.

All the catalyst synthesis was performed under dry argon. Anhydrous $MgCl_2$ (1.40 g, 14.7 mmol; Toho Titanium) was mixed with 2-methylbutanol (9.60 mL, 88.0 mmol) and heated to 105 °C in 10 mL of toluene for 2 h. Phthalic anhydride (0.235 g, 2.25 mmol) was introduced and heating continued for 2 h. The solution was then cooled to room temperature, forming a gel. The gel was heated to 50 °C to solubilize it and added dropwise via syringe into neat $TiCl_4$ (70 mL, 0.638 mol) at −20 °C over a period of 1 h. The mixture was heated gradually to 110 °C over a period of 4 h, and phthalic diester (1.13 g, 3.68 mmol) was added to it. The mixture was stirred for 2 h, hot filtered, resuspended in 70 mL of fresh $TiCl_4$, and reacted for a further 2 h at 120 °C. The product was hot filtered, washed twice with 100 mL of decene, and thrice with 100 mL of heptane. This CH catalyst was slurried in 100 mL of heptane and stored under argon. The percents of Ti in the racemic and the optically active catalysts were 3.76 and 3.60, respectively.

The CH*((*S*)-2MBP) catalyst was more extensively characterized. It was found by Galbraith Laboratories to have the following elemental compositions (in wt %): Ti = 3.60, Mg = 13.10, Cl = 55.84, C = 16.72, H = 2.19, and O = 6.90. The organic components were analyzed by hydrolysis–GC. A catalyst sample (0.1–0.2 g) was dissolved in 3 mL of 1 N HCl, stirred for either 4 or 24 h, and then extracted twice with diethyl ether. The extract was analyzed by GC for 2-methylbutanol (2MB) and 2MBP with *n*-hexanol added as internal standard. Extraction efficiencies were determined by extracting known amounts of 2MB or 2MBP; they were found to be quantitative (99.3% for 2MB and 100.2% for 2MBP). The analysis showed the catalyst to contain 0.811 mmol of 2MBP/g, 0.062 mmol of MB/g, and 0.752 mmol of Ti/g, which are the same for the 4- and 24-h hydrolyzates. The mole ratio of 2MBP/Ti is 1.08. The previous CH(EH,BP) catalyst also contained equimolar amounts of phthalate ester and Ti. The amount of 2MB found was only 8% of 2MBP.

CW*((−)MBz) Catalyst. This is our version of the high-activity (third-generation) Ziegler–Natta catalyst, which is less active and less stereospecific than the fourth-generation catalyst above. We have described in detail the preparation and characterization of the $MgCl_2$/ethyl benzoate (EB)/*p*-cresol/TEA/$TiCl_4$/TEA/methyl *p*-toluate (MPT) catalyst, CW(EB,MPT), and its stereospecific polymerizations.[1a] This procedure was adapted for the preparation of CW*((−)-MBz) ((−)-MBz = (−)-menthyl benzoate). Anhydrous $MgCl_2$ (10 g, 0.105 mol) was mixed with (−)-MBz (3.30 g, 16.2 mmol), prepared from (−)-menthol and benzoyl chloride, in a ceramic jar under argon. The mixture was ball-milled for 72 h and then transferred under argon into a Schlenk tube containing 40 mL of *n*-heptane. *p*-Cresol (3.44 mL, 32.9 mmol) was added dropwise, and the mixture was stirred for 1 h at 50 °C. Triethylaluminum (2.25 mL, 16.4 mmol; Ethyl Corp.) was added dropwise, and the mixture was stirred for 1 h at room temperature. Finally, $TiCl_4$ (40.4 mL, 0.368 mol) was added, reacted for 1 h at 100 °C, cooled to room temperature, filtered, washed thrice with 100 mL of *n*-heptane, and stored in 100 mL of *n*-heptane under argon. The percent of Ti in the catalyst was 3.92.

α-$TiCl_3$. It was used as received from Aldrich.

Cocatalysts. Both TEA and TBA were used as received from Ethyl Corp. Phenyltriethoxysilane (PES) was dried over molecular sieves and stored under argon. Methyl *p*-toluate (MPT) was fractionally distilled and stored under argon.

Monomers. Propylene (Linde) was purified by passing it through 13X molecular sieves and then through Cu/CuO (BASF) columns into the polymerization reactor. 4-Methyl-1-hexene (4MH) and (*S*)-3,7-dimethyl-1-octene ((*S*)-DMO) were purchased from Fluka; 3-methyl-1-hexene (3MH) and 4-methyl-1-pentene (4MP) were supplied by Aldrich. The monomers were distilled over Na/K alloy under argon prior to use. Racemic DMO was synthesized by published procedures.

Polymerizations. Polymerization was performed in dry Schlenk tubes under argon with magnetic stirring. The catalytic productivity was affected by the order of mixing the reactants. The best results were obtained with the mixing order of diluent, monomer, aluminum alkyl, external Lewis base, and finally the catalyst. *n*-Heptane was used to adjust the concentrations of all the reactants. However, in the case of α-$TiCl_3$ polymerizations, $TiCl_3$ was introduced first, followed by monomer and then TBA.

The catalyst compositions employed in polymerizations were as follows. The CH catalysts used [TEA]/[PES]/[Ti] = 167/8.35/1, and [M]/[Ti] ([M] = monomer concentration) ranged from 3600 to 300 depending upon the monomer. In the case of the CW catalyst the ratios were [TBA]/[MPT]/[Ti] = 167/55.7/1. It was simply a 3/1 ratio for the TBA/$TiCl_3$ system.

Polymerization temperature was 50 °C for the $MgCl_2$-supported catalysts and 70 °C for $TiCl_3$. The polymerization times were 1 h for propylene and 4MP, 5–12 h for 4MH, and 72 h for 3MH and DMO. The polymerization was quenched by either normal methanol or isotopic methanol. In the case of the branched monomer polymerizations, the mixture was first cooled to 0 °C and then quenched with methanol. Polyolefin was filtered, catalyst residues in it were removed by treatment with a 1% HCl/methanol solution, and the resulting solution was washed several times with normal methanol and dried in vacuo. The unpolymerized monomer was recovered as the dibromide derivative followed by regeneration with Zn in boiling methanol as previously described.[11]

Polymer Characterization. Polymers were fractionated with boiling solvents in a Kumagawa extractor. Optical rotation measurement was made at 25 °C in cyclohexane and 589-nm light using a Perkin-Elmer Model 141 spectrometer having a sensitivity of 0.003. IR measurement was made with a Perkin-Elmer 1600 FTIR spectrometer on film cast upon KBr plates. A GPC chromatograph was obtained for polymer dissolved in 1,2,4-trichlorobenzene at 135 °C using a Waters 150C ALC/GPC instrument. The melting transition was measured on a Du Pont 2000 DSC instrument.

IR Spectroregularity Index (I_s). The IR assignments for isotacticity for P4MH and PDMO were given by Pino.[12] In the case of P4MH, the base line was drawn between the absorbances at 1060 and 935 cm^{-1}; the value of I_s was the ratio of the absorbances $D_{997}/D_{964} \times 100$. In the case of PDMO, the base line was drawn between 1186 and 954 cm^{-1} and the absorption ratio $D_{1217}/D_{1168} \times 100$ was used as I_s. The determination of I_s for P3MH cannot be found in the literature. We have separated P3MH into fractions by solvent extraction. The IR spectra of the fractions exhibited no systematic change of the intensity of the bending vibrations with their solubility. Therefore, no I_s measurements could be made for this polymer by IR spectroscopy.

Active-Site Counting. The procedures used to determine the active-site concentration, [C], and the kinetic isotope effect had been described elsewhere.[13] The [C] was determined by quenching six polymerizations after time periods of 5, 10, 15, 20, 25, and 30 min with 3-fold excess of tritiated methanol (22.73 mCi/mol). One equivalent of methanol was assumed to be 4[Ti] + 3[Al]. The polymerization mixture, cooled to 0 °C, was stirred for 4.5 h and then treated with 120 mL of 2% HCl/methanol. After filtration, washing, and vacuum drying, the polymer was radioassayed with a Beckman Model 1800 scintillation counter.

Table I
Polymerization of α-Olefins by Various Ziegler–Natta Catalysts[a,b]

	activity, (g of polymer)/(g of Ti·[M]·h)		
monomer	CH*((*S*)-2MBP)	CW*((−)-MBz)	α-TiCl$_3$[c]
C_3H_6	22000 (1.0)[d]	15000 (1.0)[d]	7.4 (1.0)[d]
4MP	3800 (0.17)	2500 (0.17)	5.0 (0.61)
4MH	55 (0.0025)	230 (0.015)	0.1 (0.014)
DMO	0.60 (2.7 × 10^{-5})	38 (0.0025)	0.0081 (0.0011)
3MH	0.60 (2.7 × 10^{-5})		

[a] $MgCl_2$/(*S*)-2MBP/$TiCl_4$/$AlEt_3$/PTES [Al]/[Ti] = 167, [Al]/[PTES] = 20. [b] Ball-milled $MgCl_2$/(−)-MBz/*p*-cresol/TEA/$TiCl_4$/TBA/(−)-MBz; [Al]/[Ti] = 167, [Al]/[(−)-MBz] = 3. [c] α-$TiCl_3$/TBA = 1/3. [d] Activities normalized to propylene in parentheses.

A value of 1.60 for the kinetic isotope effect[13] was used to convert the specific radioactivity to [MPB] ([MPB] = [Ti–P] + [Al–P] = metal–polymer bond concentration).

Optical Purity Determinations. Optical rotation at the sodium D line (α_{ob}) was measured for cyclohexane solution at 25 °C. The specific rotation is

$$[\alpha]^{25}_{D} = \alpha_{ob}/cI \quad \text{or} \quad [\alpha]^{25}_{D} = \alpha_{ob}/\rho I \qquad (1)$$

where c is the concentration of polymer solution in g mL^{-1}, ρ is the density for neat monomer, and I is the path length. The two quantities of interest are the optical purity of the monomer remaining after a polymerization (P_m) and the optical purity of the polymerized monomer in the polymer (P_p). The former is given by

$$([\alpha]_m/[\alpha]_m^\circ) \times 100 = 100 - \frac{[\alpha]_m^\circ - [\alpha]_m}{[\alpha]_m^\circ} \times 100 \qquad (2)$$

where $[\alpha_m]$ is the molar optical rotation and $[\alpha]_m^\circ$ is that for the neat optically pure monomer. The values of $[\alpha]_m^\circ$ are +3.03°, +28.9°, and +16.3° for (*R*)-4MH, (*S*)-3MH, and (*S*)-DMO, respectively.[4,14] For example, in polymerization of 4MH the unpolymerized monomer had $[\alpha_m] = +0.02$; the value of $P_m = (0.02/3.03) \times 100 = 0.66\%$. The purity of the polymerized monomer was determined with knowledge of P_m and percent conversion (Y) of the polymerization

$$P_p = ((100 - Y)/Y)P_m \qquad (3)$$

In the above 4MH polymerization at 37% conversion, $P_p = ((100 - 37)/37) \times 0.66 = 1.1\%$.

The stereoelective efficiency (E) is determined by the relation

$$E = \frac{P_p}{[B^*]/[Ti]} (\%) \qquad (4)$$

where [B*] is the concentration of optically active Lewis base. In the case of the 4MH polymerization above, $E = (1.1/1.08) = 1.02\%$.

Results

Polymerization Activities of Linear and Branched α-Olefins. Both linear and branched α-olefin were polymerized by the optically active CH*((*S*)-2MBP) and CW*((−)-MBz) catalysts and compared with the α-$TiCl_3$ catalyst. The results are summarized in Table I. The CH* catalyst is slightly more active than the CW* catalyst for propylene polymerization. Previously, a CH(EH,BP) was determined to have an activity of 25 kg of PP/(g of Ti·[M]·h); it was 6.2 kg of PP/(g of Ti·[M]·h) for a CW-(EB, MPT) catalyst. The structure of the Lewis base has been shown to have a significant effect on the activity of the catalyst.[15] The activity of 4MP polymerization is about one-sixth of that of propylene for both the CH*((*S*)-2MBP) and CW*((−)-MBz) catalysts.

Previously we have polymerized decene-1 with the CW-(EB,MPT) catalyst;[16] the activity was 1 kg of polydecene/(g of Ti·[M]·h). The total amount of catalytic centers was 12% of Ti; the overall rate constant of propagation (k_p) was 24 (M s)$^{-1}$. Recently, we found that hexene-1 was polymerized by this catalyst with an activity of 1.7 kg of polyhexene/(g of Ti·[M]·h). Therefore, the CW(EB,MPT) catalyst polymerizes decene and hexene with comparable activity, number of active centers, and k_p.

The $MgCl_2$-supported catalysts behaved grossly different in the polymerizations of other branched olefins. 4MH was polymerized 400 times slower than 4MP by the CH* catalyst; it was 50-fold slower by the CW* catalyst. The polymerization activities of the 3-methyl-substituted olefins are 2 orders of magnitude smaller than 4MH for the CH* catalyst, the difference is only a factor of 6–13 for the CW* catalyst. Therefore, the CH* catalyst is much more sensitive to the steric structure of the monomer than the CW* catalyst. The latter behaves similar to the $TiCl_3$ catalyst in these regards. These large activity differences observed for the three kinds of catalysts need to be understood.

The P4MH was fractionated, and the molecular weights of the fractions were determined by GPC (Table II). All the fractions of P4MH obtained with the CW*((−)-MBz) and the α-$TiCl_3$ catalysts have comparable $\bar{M}_n$, $\bar{M}_w$, and polydispersity (PD = $\bar{M}_w/\bar{M}_n$). The corresponding polymers produced by CH*((*S*)-2MBP) have 5–7 times smaller number-average molecular weights. We showed that the catalyst possesses fewer active sites for branched olefins.

It is worthy to note that the PD of the P4MH fractions ranges from 3 to 11. Efficient fractionation by molecular weight should produce polymer fractions of narrow distributions. Therefore, this fractionation by solubility is primarily the separation of polymers according to microstructures.

The most stereoregular fraction (cyclohexane) of PDMO's produced by the $MgCl_2$-supported catalysts had lower $\bar{M}_n$ than the cyclohexane fraction of P4MH. Furthermore, the polymer produced by the CW*((−)-MBz) catalyst has 30 times greater $\bar{M}_w$ than the product of CH*((*S*)-2MBP) catalyst. The former is 60 times more active than the latter for DMO polymerization.

The catalytic centers in the CH*((*S*)-2MBP) catalyst are more stereospecific than they are in the other two catalysts. This is evidenced by the DSC data on the P4MH fractions (Table III). The fractions of polymers produced by the CH* catalyst have either the same or higher T_m (melting transition temperature) and appreciable greater ΔH_m (enthapy of fusion) in spite of their lower molecular weights (compare Tables II and III). However, a possibility remains that the polymers produced by the CH* and CW* catalysts may have similar stereoregularity, but the former exhibit more crystallinity because of their lower molecular weights facilitating crystallization.

Kinetics of 4MP Polymerization. The branched α-olefins with asymmetric carbons are quite expensive chemicals, and the polymerization yields are low. For practical reasons we conducted polymerizations of the inexpensive 4MP, instead of 4MH, to count the various kinds of catalytic centers for comparison with propylene polymerizations. CW catalysts containing EB for B_i, with or without MPT as B_e, were used for the polymerizations.

4MP (5 mL, 36 mmol) was introduced into a glass reactor (190 mL in volume, argon filled) containing 50 mL of *n*-heptane kept at 50 °C. TEA (2.0 mmol in heptane) was added to initiate the polymerization. In the case of CW(+B_e) catalyst, 0.67 mmol of MPT was also added along with TEA. Figure 1 shows the polymerization profiles. The experimental yield versus time data is given in open symbols, circles for CW(+B_e) and triangles for CW(−B_e).

Table II
GPC Molecular Weights for P(4MH) and P(DMO)

		catalyst								
		CH*((*S*)-2MBP)			CW*((−)-MBz)			α-TiCl$_3$		
polymer	fraction	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	PD	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	PD	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	PD
P4MH	acetone	0.18	0.75	4.1						
P4MH	ethyl acetate	0.525	1.72	3.3	2.55	9.20	3.6	2.39	14.1	5.9
P4MH	diethyl ether	0.99	2.77	3.0	7.13	29.9	4.2	6.39	31.7	5.0
P4MH	cyclohexane	1.12	5.26	4.9	7.27	82.3	11.3	7.81	72.3	9.3
PDMO	cyclohexane	0.72	5.76	8.0	6.66	152	22.9	12.6	176	14.0

Table III
Thermal Transition Data of P(4MH) Obtained by Different Catalysts

	CH*((*S*)-2MBP)		CW*((−)-MBz)		α-TiCl$_3$	
fractions	T_m, °C	ΔH_m, cal g^{-1}	T_m, °C	ΔH_m, cal g^{-1}	T_m, °C	ΔH_m, cal g^{-1}
ethyl acetate	97–121	1.02				
diethyl ether	186–191	2.37	186–194	0.54	191–196	0.25
cyclohexane	209–214	7.29	194–208	2.72	205–213	3.25

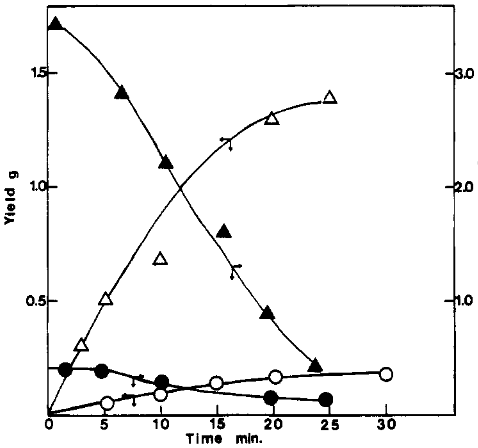


Figure 1. Polymerizations of 4MP by CW catalyst at 50 °C, [Ti] = 0.22 mM, and [4MP] = 0.65 M: with MPT (○) yield and (●) R_p versus time; without MPT (△) yield and (▲) R_p versus time.

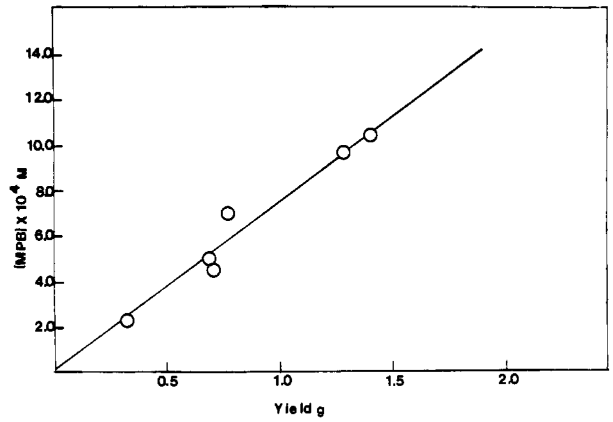


Figure 2. Variation of [MPB] versus yield of total t-P[4MP] obtained with the CW(−B$_e$) catalyst. Experimental conditions are as in Figure 1.

The R_p was calculated from the tangent of the Y vs t plot and given in corresponding filled symbols. The R_p was reduced greatly by the presence of B$_e$, and it decays during the first 30 min of polymerization. Both these characteristics are similar to the corresponding propylene polymerizations.[5] The average productivity of P4MP is 1.3 and 9.7 kg/(g of Ti·[4MP]·h)$^{-1}$ with and without MPT, respectively.

The concentration of metal–polymer bonds was determined as described above. Figures 2 and 3 illustrate typical data of the variation of [MPB] versus Y for total P4MP obtained with the CW(−B$_e$) and CW(+B$_e$) catalyst, respectively. The intercept at $Y = 0$ gave the values of total active sites [C*$_t$]. The radiolabeled P4MP was subjected to extraction with refluxing *n*-pentane for 6 h. The insoluble stereoregular P4MP samples were also radioassayed to give [C*$_i$]. The rate constant of chain transfer to TEA ($k^A{}_{tr}$) was calculated from the slope of the [MPB] vs Y plot.[13] Table IV summarizes the kinetic parameters for 4MP polymerizations by the CW catalysts (columns 2 and 5). Also given are the results of propylene polymerizations[13c] (columns 3 and 6). The relative effects of B$_e$ on the polymerization of these two monomers can be seen by comparing column 7 with column 4. They agree within a factor of 2 except for R_p and $k_{p,a}$. MPT appears

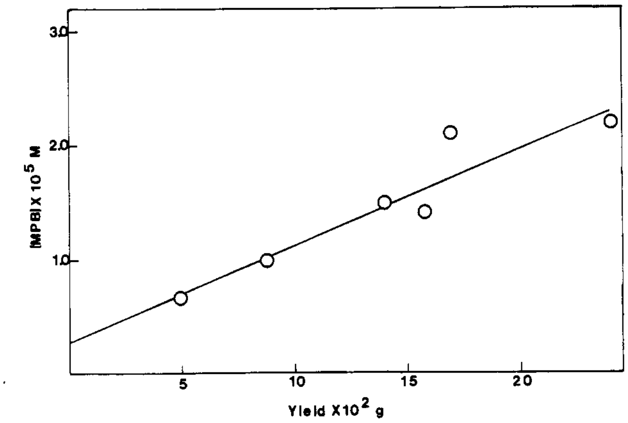


Figure 3. Variation of [MPB] versus yield of total t-P[4MP], obtained with the CW(+B$_e$) catalyst. Experimental conditions are as in Figure 1.

Table IV
Kinetic Parameters for 4MP and Propylene Polymerizations by CW Catalyst

monomer	4MP	C$_3$H$_6$	C$_3$H$_6$^{a} / 4MP	4MP	C$_3$H$_6$	C$_3$H$_6$^{a} / 4MP
B$_e$	none	none	none	MPT	MPT	MPT
$R_p \times 10^4$, M s^{-1}	3.6	15.0	4.2	0.40	4.6	11.5
IY, %	59^b	55^c	0.93	91^b	94^c	1.0
[C$_i$], %	1.7	15	8.8	0.46	6.7	14.6
[C$_a$], %	5.4	55	10	0.74	6.5	8.8
[C$_t$], %	7.1	70	9.9	1.2	13	11
$k_{p,i}$, (M s)$^{-1}$	68	209	3.1	46	200	4.3
$k_{p,a}$, (M s)$^{-1}$	17	27	1.6	2.4	11	4.6
$k^A{}_{tr,i} \times 10^3$, s^{-1}	73	1.5	0.02	12	0.17	0.01
$k^A{}_{tr,a} \times 10^3$, s^{-1}	90	3.1	0.03	14	0.26	0.02

^{a} Ratio of kinetic parameters for propylene to 4MP. ^{b} *n*-Pentane insoluble. ^{c} *n*-Heptane insoluble.

Table V
Stereoelective Polymerizations of Racemic α-Olefins

				recovered monomer			total polymer				
catalyst	monomer	[M]/[Ti][a]	convn, %	$[\alpha]^b$	P_m	prev[c] chir	$[\alpha]^d$	P_p	prev[c] chir	eff,[e] %	$R_p(R)/R_p(S)$
CH*((*S*)-2MBP)	4MH	3600	37	+0.020	0.66	*R*	+4.8	1.1	*S*	1.02	0.98
CW*((−)-MBz)[b]	4MH	3600	27.4	+0.010	0.32	*R*	+3.7	0.85	*S*	0.03	0.98
CH*((*S*)-2MBP)	3MH	1200	6.4	+0.066	0.33	*S*	*g*	4.8	*R*	4.4	1.10
CH*((*S*)-2MBP)	DMO	300	9.4	+0.157	0.76	*S*	−3.2	9.3	*R*	8.6	1.21
CH*((*S*)-2MBP)	DMO	1200	8.4	+0.086	0.52	*S*	−4.3	5.6	*R*	5.2	1.12
CW*((−)-MBz)[b]	DMO	3600	20.8	+0.13	1.10	*S*	−3.4	4.0	*R*	0.14	1.08

[a] [M] is monomer concentration. [b] At 25 °C, sodium D line, neat. [c] Prevailing chirality. [d] In cyclohexane. [e] Efficiency according to eq 4. [f] Reference 8. [g] P3MH is incompletely soluble in cyclohexane at 25 °C.

Table VI
Microstructure of Stereoelectively Polymerized P4MH and PDMO Catalyzed by CH*((*S*)-2MBP)

			fraction												
			acetone			ethyl acetate			diethyl ether			cyclohexane			
monomer	[M]/[Ti][a]	convn, %	%	$[\alpha]^b$	I_s	%	$[\alpha]^b$	I_s	%	$[\alpha]^b$	I_s	%	$[\alpha]^b$	I_s	insol, %
4MH	1200	37	11	+6.2		19	+10		8.9	21		59	+9.8		0
4MH	3600	35	9.0	+5.4	44[c]	12	+10	73	10	+15	80	67	+9.9	85	0
DMO	1200	8.2	20	−2.3		29	−3.7		24	−6.3		27	−4.6		0
DMO	300	9.1	36	−1.2	28[d]	41	−5.1	46	16	−4.2	59	6.4	−0.71	67	0
85% (*S*)-DMO	1200	4.6	9.2	+28	29	20	+59	47	25	+71	59	41	+75	74	0
3MH	1200	6.4	22	−3.7		14	−8.1		6.9	−16		13	(−)[e]		47
3MH/85% (*S*)-DMO	300	12	40	+7.8	170[g] (48)[i]	34	23	63 (28)	6.1	+22	76 (30)	7.0	(−)[h] (19)	20	14

[a] [M] is monomer concentration. [b] In cyclohexane $d = 1$, $c = 1.0$ g/dL. [c] $D_{997}/D_{964} \times 100$ base line drawn between 1060 and 935 cm^{-1}. [e] Insoluble at 25 °C in cyclohexane. [f] [3MH]/[(*S*)-DMO] = 2.9, racemic catalyst used. [g] $D_{918}/D_{896} \times 100$ base line drawn through points 923 and 886 cm^{-1}, indicative of [3MH]/[(*S*)-DMO] ratio. [h] Not very soluble but in dilute solution shows (−)-rotation. [i] Percent DMO content determined by comparison with mixtures of two homopolymers.

to influence similarly the active sites for propylene and 4MP polymerizations.

Stereoelective Polymerizations. Stereoelective polymerizations of racemic 4MH, 3MH, and DMO were performed using the CH*((*S*)-2MBP) catalyst. The results in Table V on the total polymers showed that all poly(*S*)-olefins have positive [α]. Thus, it is the *S*-antipode in the cases of 4MH that is preferentially polymerized, and the recovered monomer is enriched in the *R*-antipode. On the other hand, the preferentially polymerized enantiomers of 3MH and DMO are the *R*-antipodes. The same overall preference for the opposite antipodes of 4- and 3-methyl-substituted olefins was reported before.[4,9] The optical purities of polymerized monomer were 4–9 times greater for the 3-methyl-substituted olefins than 4MH. The chiral catalytic centers can discriminate the antipodes more effectively when the asymmetric carbon is situated closer to the double bond. We have previously reported the stereoelective polymerizations by the CW*((−)-MBz), catalysts.[9] The efficiency of stereoelection for DMO is about 5 times greater than it is for 4MH. The absolute magnitudes of stereoelective efficiencies cannot be compared for different systems, i.e., the CW* and the CH* catalysts, because the former uses about 30 times more optically active Lewis base, internal plus external, than in the case of the CH* catalyst.

P4MH and PDMO were fractionated to investigate in detail the relationship between stereoelection ([α] by optical rotation) and stereoselection (I_s by IR). ^{13}C NMR is not as useful in measuring the stereoregularity of microstructure in these branched higher α-olefins as it is a really powerful technique for polypropylene. The results of [α] and I_s are summarized in Table VI.

Let us first describe the properties of polyolefin fractions derived from racemic monomers. The P4MH fractions have isotactic stereoregularity which increases in the order acetone < ethyl acetate < diethyl ether < cyclohexane. The fact that this is also the order of increase in molecular weights has been discussed above. The PDMO fractions exhibit stereoregularity increases in the same order as the P4MH fractions. The optical rotations of the fractions of P4MH, PDMO, and P3MH obtained from stereoselective polymerization of racemic monomers increase in the order acetone < ethyl acetate < diethyl ether. However, the cyclohexane-soluble fractions have smaller optical rotations than the diethyl ether fractions (in absolute values).

The stereoelective polymerization of racemic 4MH is much more stereospecific than that of racemic DMO. The former (Table VI) produces more than 60% of cyclohexane-soluble, ether-insoluble polymers. This fraction was only 6–27% in the case of PDMO and 13% for P3MH. The latter, however, gives also 47% cyclohexane-insoluble polymer due to low solubility of stereoregular P3MH.

In the case of polymerization of (*S*)-DMO, having 85% optical purity (*S*/*R* = 12/1), by CH*((*S*)-2MBP), the polymer fractions have positive rotations. Therefore, it is the *S*-antipode that is preferentially polymerized, in contrast to the preferred polymerization of the *R*-antipode from racemic DMO (Table V). This is obviously due to the larger concentration of the *S*-antipode. The optical rotation increases steadily with the increase of solvent power; the cyclohexane fraction has the highest rotation. The stereoregularity of the fraction also increases monotonically in the same manner. This polymerization is more stereospecific than the polymerization of the racemic DMO, producing 41% of the cyclohexane fraction.

3MH was copolymerized with 85% (*S*)-DMO to study site stereoselection.[17] The copolymer was found to be more soluble than P3MH. Only 14% of the copolymer was insoluble in cyclohexane while 47% of the P3MH was insoluble. About 80% of the copolymer was soluble in diethyl ether while 43% of the P3MH was soluble. The IR absorbance ratio (D_{918}/D_{896}) was indicative of the [DMO]/[3MH] ratio in the copolymer. Comparison to IR absorbance ratios of standard mixtures of the homopolymers showed that the content of (*S*)-DMO units

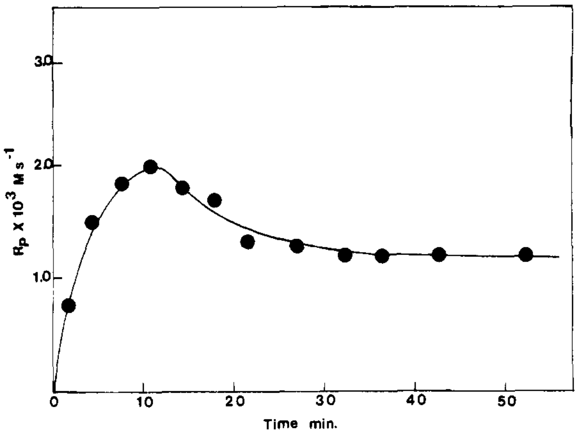


Figure 4. Variation of R_p versus time of propylene polymerization catalyzed by CH((*R*,*S*)-2MBP).

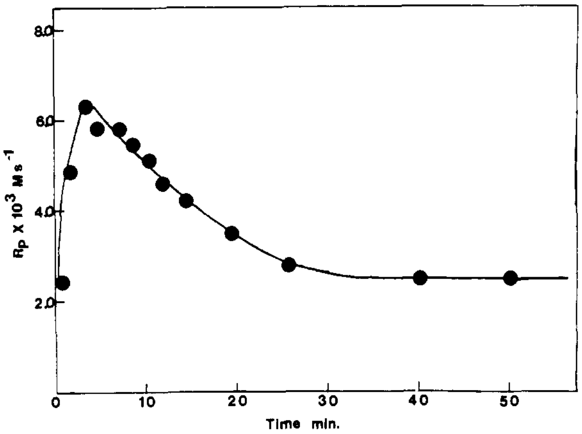


Figure 5. Variation of R_p versus time of propylene polymerization catalyzed by CH*((*S*)-2MBP).

in the copolymer is 48% in the least stereoregular fraction, 30% in the next two fractions, and only 19% in the most stereoregular fraction.

Effect of Optically Active and Racemic Lewis Bases. CH catalyst was also prepared with racemic 2-methylbutanol. The resulting CH((*R*,*S*)-2MBP) catalyst was less active than the CH*((*S*)-2MBP) catalyst in olefin polymerizations. For instance, the former has an activity for propylene polymerization ($[C_3H_6]$ = 0.73 M, $[C_3H_6]/[Ti]$ = 3000, time = 1 h, temp = 50 °C) of 24 kg of PP/(g of Ti·M·h) as compared to an activity of 49 kg of PP/(g of Ti·M·h) for the latter. The two catalysts have the same stereospecificity (IY = 98% for PP). The difference in activity is even greater for the polymerization of 4MH; the values are 9.3 and 70 g of P4MH/(g of Ti·M·h) for CH((*R*,*S*)-2MBP) and CH*((*S*)-2MBP) catalysts, respectively.

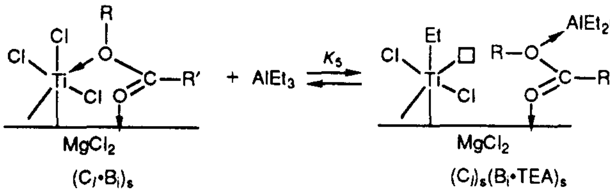
Those unexpected differences between the optically active and racemic catalysts prompted a detailed comparison of their kinetics of propylene polymerization. Figure 4 showed that the CH((*R*,*S*)-2MBP)-catalyzed polymerization was slow to initiate. The rate of polymerization increased gradually during the first 11 min to a maximum rate of 2×10^{-3} M s^{-1} followed by a modest 50% rate decay. In contrast, the CH*((*S*)-2MBP)-catalyzed polymerization reaches a maximum R_p of 6.4×10^{-3} M s^{-1} within a couple of minutes after activation (Figure 5) which decayed to about 40% of the maximum rate. These behaviors suggest that the number of active sites present initially is smaller in the racemic CH catalyst than in the optically active CH* catalyst. The kinetic parameters were determined and listed in Table VII. The main differences between the two catalysts are the numbers of stereospecific and nonstereospecific active centers determined by radiolabeling which are 3.4 and 9.5 times greater, respectively, in the CH*((*S*)-2MBP) than they are in the racemic system. The stereospecific sites in the two catalysts have identical $k_{p,i}$ and k^A_{tr} values. It is the nonstereospecific sites in the CH((*R*,*S*)-2MBP) catalyst which propagate 8 times faster than in the CH*((*S*)-2MBP) catalyst. Previously, we have determined the kinetic parameters for the nonchiral CH(EH or BP) catalyst.[13d] The values included in Table VII (column 4) showed a close similarity between this catalyst and the CH*((*S*)-2MBP) catalyst, except for differences in the chain-transfer rate constants.

Table VII
Kinetic Parameters of Propylene Polymerizations by Various CH Type Catalysts

catalyst	CH((*R*,*S*)-2MBP)	CH*((*S*)-2MBP)	CH(EH,BP)[9]
$[C_t]$, mol % of Ti	7.2	38	40
$[C_i]$, mol % of Ti	5.0	17	25
$[C_a]$, mol % of Ti	2.2	21	15
$k_{p,t}$, (M s)$^{-1}$	158	96	126
$k_{p,i}$, (M s)$^{-1}$	217	213	206
$k_{p,a}$, (M s)$^{-1}$	28	3.5	11
$k^A_{tr,i} \times 10^3$, s^{-1}	1.4	2.2	25
$k^A_{tr,a} \times 10^3$, s^{-1}	3.1	3.6	23

Discussion of Results

The principal concern of this work is the nature of the catalytic sites for the stereospecific and nonstereospecific[18] polymerizations of various α-olefins. Propylene is the reference monomer because most studies were made on it. The stereospecific $MgCl_2$-supported catalysts were comprised of 1–2 mol of internal Lewis base/mol of Ti. Bonding interactions between B_i and $MgCl_2$ were observed by FTIR[19] and solid ^{13}C NMR;[20] evidences for bonding between B_i and Ti(III) were provided by EPR[7] and ^{13}C NMR.[20] The structure of B_i has pronounced influence on the activity and stereospecificity of the CH type catalysts prepared from it.[15] The most stereospecific sites are chiral, designated as $(C_l{\cdot}B_i)_s$ and $(C_d{\cdot}B_i)_s$ by Pino et al.[4] and coordinatively saturated. Activation of TEA frees a vacant coordination position (□) as depicted in eq 5. The amount of active centers depends upon the concentration of monomeric TEA in equilibrium with the dimeric TEA and the $TEA{\cdot}B_e$ complex. It is characterized by large k_p (the values of k_p are about the same for the CW and CH type catalysts) and small k^A_{tr} values.[21] Isotactic polypropylene produced by it has a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \sim 2.0$).[22] These active centers are sterically restrictive and inaccessible to higher α-olefins.



(5)

The differences between the optically active and racemic CH(2MBP) catalysts in olefin polymerizations may be explained by the relative stability of the diastereomeric complexes of C_l or C_d with either antipode of B^*_i

$$\mathrm{C}^*_l\text{·}(S)\text{-B}^* \overset{K_6(l,S)}{\rightleftarrows} \mathrm{C}^*_l + (S)\text{-B}^* \tag{6}$$

$$\mathrm{C}^*_d\text{·}(R)\text{-B}^* \overset{K'_6(d,R)}{\rightleftarrows} \mathrm{C}^*_d + (R)\text{-B}^* \tag{6'}$$

$$\mathrm{C}^*_l\text{·}(R)\text{-B}^* \overset{K_7(l,R)}{\rightleftarrows} \mathrm{C}^*_l + (R)\text{-B}^* \tag{7}$$

$$\mathrm{C}^*_d\text{·}(S)\text{-B}^* \overset{K'_7(d,S)}{\rightleftarrows} \mathrm{C}^*_d + (S)\text{-B}^* \tag{7'}$$

The equilibria may involve TEA, and all the species are attached to the $MgCl_2$ surface as in eq 5. The C*-B* species on the left-hand side of the equilibria are in the resting states; the C* species on the right-hand side of the equilibria are catalytically active. One set of diastereomers is more stable than the other set; we can assume $K_6 \gg K_7$ without loss of generality. In the CH*((S)-2MBP) system, the C^*_l is present largely in the dissociated state which is catalytically active, while the stable C^*_d·(S)-B* is not. In the racemic system both C^*_l and C^*_d form stable complexes with the preferred antipode (R)-B* and (S)-B*, respectively. Dissociation of these stable complexes has to occur before they can initiate polymerization (Figure 4). The racemic catalyst has only one-eighth of the 4MH polymerization activity as CH*((S)-2MBP). The latter also has 3 times more active sites for propylene polymerization than the CH((R,S)-2MPB) catalyst (Table VII). It seems that racemic B_i complexes with both C^*_d and C^*_l, whereas the optically active B^*_i complexes probably and preferentially with one enantiomorphic site.

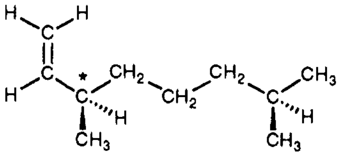
The *n*-heptane-soluble polypropylenes are formed by several kinds of active centers. They probably differ in the number of coordinative bonds between a Ti(III) ion and the support, or in coordinate alkylaluminum if any, or in the number of Lewis base molecules either in the inner coordination sphere as depicted by $(C_l\text{·}B_i)_s$ and/or in the outer coordination sphere as represented by $(C_l)_s(B_i\text{·}TEA)$ in eq 5. The ability of a site to polymerize a monomer with more steric bulk at the double bond increases with coordination vacancy with a concomitant decrease in stereochemical control. In propylene polymerizations the nonstereospecific centers have high Lewis acidity, associate with B_i more strongly, and exist mostly in the resting state. The apparent $k_{p,a}$ is 1/10 to 1/60 as large as $k_{p,i}$ for the stereospecific sites, suggesting a correspondingly larger ratio of the resting state to the active state (refs 5b and 13d; Table VII).

In CW(EB,MPT) catalyst there are about 1.2% of Ti which catalyze polymerization of 4MP, which is about one-fifth the amount of low stereospecific sites for propylene polymerization. The former has $k^A{}_{tr}$ values 30–100 times larger than the latter. This means the 4MP polymerization sites have low steric constraints and are accessible to TEA. In the case of P4MH, even the most stereoregular polymer was soluble in cyclohexane and has an IR I_s of only 85%. More than a third of the P4MH is soluble in diethyl ether. The catalytic centers for the polymerization of 3-methyl-α-olefins have the lowest activity and stereospecificity. Table VI showed that less than one-fifth of the PDMO was insoluble in diethyl ether which has a low I_s of 67%. As much as one-fifth to one-third of the PDMO is soluble in acetone and has an I_s value of only 28%. These active centers have very little steric hindrance and stereochemical control, yet they show high stereoelective efficiencies (Table V).

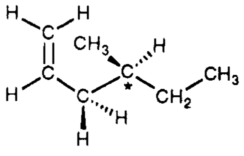
The CH* catalyst polymerizes 4MH and 3-methyl-α-olefins with 0.25% and 2.7×10^{-3}% of the propylene polymerization activity; they are 1.5% and 0.2%, respectively, for the CW* and α-$TiCl_3$ catalysts. The former produces polymer of much lower molecular weights (Table II). The differences indicate that the most stereospecific CH catalyst contains very few active centers capable of polymerizing bulky monomers, and they do so at relatively lower propagation rates.

We have previously compared[9a,b] the CW type catalyst prepared with nonchiral B_i (ethyl benzoate) and chiral B_e. When the latter is (−)-dimenthyl terephthalate, the catalyst is 7.5 times more stereoelective in the polymerization of racemic DMO than the catalyst with (−)-menthyl benzoate as the B_e. The diester is expected to be more strongly complexed with the chiral center resulting in more effective site stereoelection.

In all polymerizations carried to less than 30% conversion, the polymers of 4MH and DMO produced and the monomers recovered exhibit opposite chirality (Table V; refs 4 and 9) as expected for the stereoelective process. With the same enantiomer of the Lewis base for either the CW* or CH* type catalyst, the (S)-4MH is preferentially polymerized to produce P4MH having positive optical rotation. The converse is true for DMO and 3MH; polymerization of the R-antipode was preferred to give polymer with negative optical rotation. This suggests that the active site possesses very strict steric requirements which may involve a precise conformation of the side chain of the monomer. The corresponding minimum energy conformations for the 4MH and DMO are



(R)-DMO



(S)-4MH

The propagation preference of one antipode over another is best expressed by the ratio of the rates of polymerization $R_p(S)/R_p(R)$ which can be calculated with the knowledge of P_p, which is the percent content of the prevalent enantiomer in the polymer

$$\frac{R_p(S)}{R_p(R)} = \frac{50 + 0.5P_p}{50 - 0.5P_p} \tag{8}$$

At low conversion this is also equal to $k_p(S)/k_p(R)$. Changing monomer composition will affect the $k_p(S)$ or $k_p(R)$ calculation. The results of $R_p(S)/R_p(R)$ given in the last column of Table V showed that the stereoelective efficiency is lower for 4MH than DMO. This is as expected, because the methyl branch is further removed from the double bond in the former. Polymerization of five-substituted olefins is nonstereoelective.[23] This difference is diminished for active centers which are less sterically hindered. For instance, low stereospecificity sites produce P4MH and PDMO of low stereoregularity with the same handedness.[9]

When 85% (S)-DMO was used as the monomer, the PDMO produced exhibited large positive rotation regardless of the stereoregularity of the polymer (Table VI). Therefore, the (S)-DMO was polymerized in this case even though the opposite antipode was favored for stereoelective polymerization of the racemic monomer. This may be explained by a small energy difference between the coordination of one enantiomer over another.[24] An alternative explanation is that the active centers have two vacant coordinative positions[4] and that a Ti(III) ion of either chirality can complex with (S)-2MBP molecules.

The results observed with 85% (*S*)-DMO would mean that it is the chirality of the titanium which determines the stereoelection process and that the chiral influence of the Lewis base is weak.

Finally, the stereospecificity and stereoelectivity are not associated phenomena. The optical rotation of the polymer increases with increasing stereoregularity for the acetone, ethyl acetate, and diethyl ether fractions (Table V); however, the most stereoregular cyclohexane fraction has a smaller optical rotation than the ether fraction. In the case of the copolymer of 3MH with 85% (*S*)-DMO, this rotation changes sign. In other words, the low and high stereospecific active centers seem to prefer the opposite antipodes. This was also found to be the case for P4MH obtained with CW catalysts containing either chiral B_i or B_e or both.[9] The fractions with intermediate stereoregularity possess the highest optical purity. The PDMO produced by these catalysts exhibit the opposite optical rotation for the stereoregular and stereoirregular fractions. Using the catalyst $MgCl_2$/(−)-menthyl anisate/$TiCl_4$/TBA, Pino et al.[4] found the stereoirregular and stereoregular P4MH to contain monomers with prevalent *S* and *R* chirality, respectively. These observations cannot be attributed to polymerization of the prevailing antipode in the unpolymerized monomer. In fact, when the amount of Lewis base is small, [(−)-menthyl anisate]/([Ti] + [Al]) = 0.13, the catalyst polymerized the (*S*)-DMO preferentially in both stereoirregular and stereoregular products;[4] also the optical purity of the DMO polymerized to the stereoirregular polymer is larger than that of the unpolymerized monomer.[2] Therefore, the synthesis of stereoirregular ethyl acetate soluble PDMO is also stereoelective. Pino et al.[4] had suggested that the active center for the polymerization of branched α-olefins should have two free coordination sites, one of which is occupied by the optically active Lewis base, as is also proposed above. The stability of the complexed B* would depend upon the chirality of the Ti ion, i.e., C_l·(*S*)-2MBP and C_d·(*S*)-2MBP. The former complex is unstable; the site is stereospecific and polymerizes one antipode stereoelectively. The latter complex is more stable; the Lewis base can dissociate and reassociate. The site will polymerize the opposite antipode with lower stereoregularity.

References and Notes

(1) This paper is part 30 of the series on *Magnesium Chloride Supported High Mileage Olefin Polymerization Catalysts*. Part 1: (a) Chien, J. C. W.; Wu, J. C.; Kuo, C. I. Chemical Composition and Oxidation States of Titanium. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2445. Part 29: (b) Chien, J. C. W.; Nozaki, T. Molecular Basis of Hydrogen Activation. *J. Polym. Sci., Part A* **1991**, *24*, 505.

(2) Dipartimento di Chimica e Chimica Industriale, Macromolecole Stereordinate Officamente Attive, Universita di Pisa, 56100 Pisa, Italy.

(3) There have been many international symposia on olefin polymerizations which had significant portions dealing with $MgCl_2$-supported heterogeneous Ziegler–Natta catalysts. Those symposia, the proceedings of which were published, are the following: (a) *Transition Metal Catalyzed Polymerizations*; Quirk, R. P., Ed.; Harwood: New York, 1983. (b) *Catalytic Polymerizations of Olefins*; Keii, T., Soga, K., Eds.; Elsevier Science Publishers: Amsterdam, The Netherlands, and Kodansha, Tokyo, 1986. (c) *Transition Metal Catalyzed Polymerizations: Ziegler–Natta and Metathesis Polymerizations*; Quirk, R. P., Ed.; Cambridge University Press: Cambridge, U.K., 1988. (d) *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988. (e) *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Elsevier Science Publishers: Amsterdam, The Netherlands, and Kodansha, Tokyo, 1990.

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(18) The nonstereospecific sites, sometimes referred to as atatic sites, are in fact sites possessing low stereochemical controls. Even though the polyolefins produced by them, such as polypropylene, have been called stereoirregular or atactic, they are in fact low in stereoregularity and can be separated into fractions differing in molecular weights and stereoirregularities. Most of the polymer fractions were semicrystalline, albeit of very low crystallinity, and contain appreciable [mmmm] homosteric sequences by ^{13}C NMR. Ideal atactic polymer, characterized by [mm] = [rr] = 0.5[mr], is seldom produced, if at all, by catalysts designed to be highly stereospecific.

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