Latent Bimodal Polymerization of 1-Hexene by a Titanium-Based Diastereomeric Catalyst Containing a *rac*/*meso*-Aminodiol Ligand

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ABSTRACT: A New titanium catalyst bearing an aminodiol ligand was synthesized as *racemic* (C_2), as *meso*, and as a diastereomeric mixture. The *racemic* catalyst (**rac**) produced isotactic polymer by enantiomorphic-site control mechanism whereas *meso* catalyst (**meso**) produced atactic oligomers. The **rac** and the diastereomeric catalyst (**mix**) produced polymers with single-site catalyst behavior at ambient temperatures. When the polymerization temperature was lowered, **rac** gave high molecular weight polyhexene with polydispersity value approaching close to a living system whereas the **mix** exhibited a latent bimodal behavior. **meso** produced just oligomers and did not show any change in behavior with polymerization temperature. Deliberate mixing of **rac** and **meso** produced two polyhexene fractions: high molecular weight polymer and oligomers indicating an independent behavior of the mixed catalyst.

Introduction

After the discovery of methylaluminoxane (MAO) and the chiral *ansa*-metallocene catalyst, the metallocenes containing cyclopentadienyl, indenyl, fluorenyl, and bridged amidocyclopentadienyl ligand containing complexes have received a lot of attention because of their ability to produce polymers with high stereoregularity, narrow molecular weight distribution and good thermal properties.[1] It has been observed in the synthesis of large number of group III or group IV metallocene catalysts, complexation of a pure *racemic* ligand results in auto-isomerization and produces a mixture of *racemic and meso* catalysts.[2] Pure *racemic* catalysts have been prepared by repeated crystallization and the extent of isomerization has been controlled by face selection of the Cp ring attachment to the metal[3a] or by amine elimination mode of catalyst synthesis[3b,c] or by racemoselective synthesis.[3d] The group IVB *ansa*-metallocenes also undergo photoisomerization on exposure to light or UV radiation to give mixture of *racemic* and *meso* isomers.[4]

In recent years, select *non*-metallocene complexes have also been effectively used for the polymerization of ethylene and propylene.[5a] Notably, bulky diimine ligand based late transition metal catalysts for the polymerization of ethylene with narrow molecular weight distribution and long chain branching by chain walking phenomenon created a renewed interest toward designing novel nonmetallocene single-site catalysts.[5b] Dialkoxide,[5c,d] benzamidine,[5e−g] diamide,[5h−l] amidoalkoxy,[5m] ketiminato,[5n] bisphenoxy,[5o] and phenoxyimine[5p−r] based catalysts, employing early transition metals for olefin polymerization, have also drawn more attention toward the synthesis of new catalysts. These catalysts have been found to polymerize ethylene, α-olefins, and higher α-olefins like 1-hexene in a living manner.[6]

The effect of two different catalyst mixtures for polymerization of ethylene and propylene has started gaining considerable attention in industrial laboratories because these binary mixtures produce polymers with bimodal molecular weight distribution, providing superior mechanical properties with good processability.[7] Combinations of two different metallocenes or nonmetallocene catalysts and in some instances, highly active nonmetallocene catalysts capable of producing higher 1-alkenes, in combination with active ethylene polymerization metallocene catalyst, have been used for tailor-made polyolefin synthesis.[8] The *racemic* and *meso* catalyst mixtures usually produce polyolefins with bimodal molecular weight distribution and/or low stereoregularity. For instance, when a mixture of *meso*- and *rac*-ethylenebis(4,7dimethyl-1-indenyl)$ZrCl_2$ was employed for propene polymerization, it was found that the *meso* produced low molecular weight atactic polypropylene.[9] Nickel-based diimine catalyst bearing different ortho substituents on the same aromatic ring, which exists in *racemic* and *meso* forms, has been used for the polymerization of propylene.[10] Recently, diastereomeric amido fuctionalized *ansa*-half sandwich complexes of titanium and zirconium employed for ethylene polymerization have been found to produce polymers with bimodal distribution.[11] However, the effect of *racemic* or *meso* catalyst and possibly of a deliberate mix of the two species, on the polymerization of higher α-olefin has not been reported so far. In this connection, we have synthesized a new titanium dialkoxide catalyst containing an aminodiol ligand in C_2 symmetric *racemic* (**rac**), in *meso* (**meso**), and as a diastereomeric mixture (**mix)**. Herein we report the activity of pure **rac** and **meso** isomers and the effect of deliberate mixing of **rac** and **meso** (mixed catalysts) and the unusual latent bimodal behavior of diastereomeric catalyst (**mix**) with change in temperature, for the polymerization of 1-hexene with MAO as cocatalyst.

Results and Discussion

The required aminodiol was obtained as a diastereomeric mixture (containing *racemic* and *meso* forms) by refluxing 1 equiv of benzylamine with 2 equiv of (±)-styreneoxide in ethanol after separating the unsymmetrical aminodiol (minor isomer) by silica gel column chromatography. The two-methylene protons of N−C$\mathbf{H_2}$−C−OH appeared at 2.73 and 2.80 ppm as a doublet of

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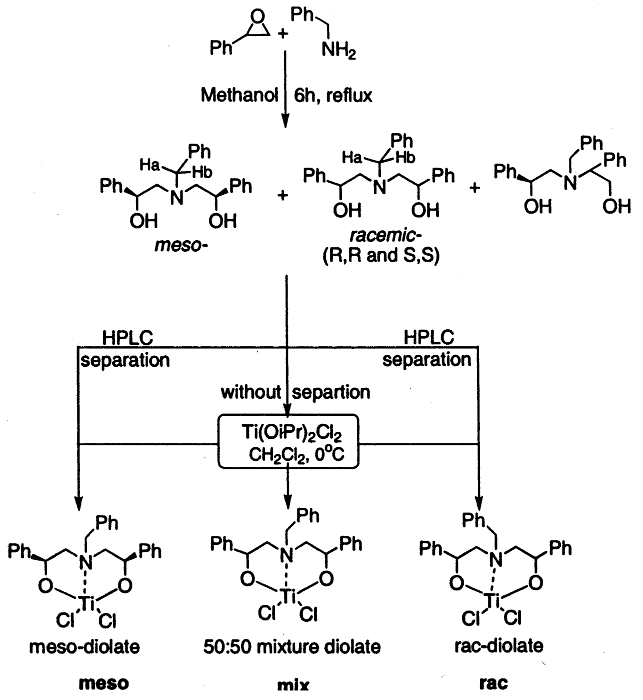
Table 1. Polymerization of 1-Hexene[a]

catalyst	temp (°C)	solvent	activity [b]	M_n[c]	pdi	tacticity[d] (mmmm %)
meso	50	chlorobenzene	520[e]	700	1.2	atactic
	28	chlorobenzene	580[e]	900	1.07	atactic
	28	CH_2Cl_2	410[e]	1050	1.1	atactic
	28	toluene	380[e]	nd	nd	atactic
	28	neat	390[e]	<500	nd	atactic
rac	50	chlorobenzene	520	3600	2.9	isotactic (62)
	28	chlorobenzene	700	6600	2.4	isotactic (65)
	4	chlorobenzene	28	320 000	1.9	isotactic (70)
	−10	chlorobenzene	<20	386 000	1.4	isotactic (80)
mix	50	chlorobenzene	590	6100	2.4	isotactic (47)
	28	chlorobenzene	760	18 300	2.1	isotactic (45)
	4	chlorobenzene	40	20 100	4.3	isotactic (49)
	−10	chlorobenzene	24	152 300	5.8	isotactic (51)

[a] Reaction conditions: catalyst = 0.5 mmol; MAO = 100 mmol; chlorobenzene = 20 mL; 1-hexene = 3 mL; polymerization time = 50 h (72 h for low temperatures). [b] Activity in (g of PH/mol of catalyst)/h. [c] Determined from GPC in THF using narrow polystyrene standards [d] Determined by ^{13}C NMR. [e] Activity in (g of oligohexene/mol of catalyst)/h.

Scheme 1. Synthesis of Titanium Diolated Catalyst



doublet. The methine proton of O−C**H**-Ph appeared as a doublet of doublet at 4.75 ppm. The benzylic protons, which appeared at 3.70 and 3.96 ppm as two doublets and also as a additional singlet at 3.83 ppm were the used to determine the diastereomeric ratio. ^1H NMR and HPLC analysis of the diol indicated that the *racemic* and the *meso* aminodiol were present in 1:1 ratio. The ligands were then separated by semipreparative HPLC. ^1H NMR of the separated ligands showed a doublet of doublet pattern around 4.70 ppm and two doublet of doublet around 2.80 ppm as expected but the benzylic protons of the *racemic* ligand were diastereotopic in nature and the two hydrogens (H_a and H_b, see Scheme 1) appeared as two doublets at 3.40 and 3.60 ppm whereas the *meso* ligand showed a singlet at 3.83 ppm. The structure of the *racemic* ligand was unequivocally confirmed by synthesizing the corresponding chiral aminodiol[12a] and whose crystal structure was reported elsewhere. The separated aminodiol or the diastereomeric ligands were used as such for the synthesis of catalyst by exchanging the alkoxide ligand in $Ti(O^iPr)_2Cl_2$ with the required diol[12a] (Scheme 1).

All the protons in the aminodiol shifted downfield after complexation. The two-methylene protons of N−C**H**$_2$−C−OH which appeared at 2.73 and 2.80 ppm as a doublet of doublet shifted to 3.30 and 3.50 ppm and the methine protons of O−C**H**−Ph which appeared at 4.75 ppm moved downfield to 5.46 ppm. The benzylic protons of the **meso** showed a singlet at 4.48 ppm (the same proton appeared at 3.83 ppm in the *meso* ligand).

Polymerizations were carried out with all the catalysts in toluene at different Al/Ti ratio, low temperatures and at high monomer-to-catalyst ratio (80/1, in contrast to the usual ratio of 48/1), but none of the reactions yielded polymer. Increase in polymerization activity was observed by others when polymerizations carried out in CH_2Cl_2[13] but with our titanium catalysts the reaction mixture turned red in color upon adding MAO leaving a red pasty material on the sides of the flask. Addition of monomer to this solution did not result in polymer even after a week. With chlorobenzene as solvent, we could observe tangible polymerization activities, attributable possibly to the high dielectric constant of the medium.

Table 1 collates the change in activity, variation in molecular weight with temperature and microstructures of the polymers produced with the **meso**, **rac**, and **mix** after optimizing the reaction conditions. It could be seen in all the polymerization reactions, upon addition of MAO, the reaction mixture immediately turned to pale brown in color and black within 10−20 min. The polymers were isolated as colorless sticky mass by pouring the reaction mixture in acidified ice-cold methanol and were highly soluble in $CHCl_3$ and THF.

The activity of **rac** decreased slightly when the polymerization temperature was increased to 50 °C from ambient temperature (28 °C), but the activity decreased drastically when the temperature was lowered to 4 °C and dipped a little more when the temperature was lowered to −10 °C. The changes in the activity of the **mix** also showed similar behavior. The similarity in behavior of these catalysts was evident from the activation energies calculated for the polymerization of hexene. (E_a(**rac**) = 40 kJ/mol and E_a(**mix**) = 38 kJ/mol[14]). The slight decrease in activity at high temperatures observed could be due to the deactivation of the active species and the drastic decrease at low temperatures could be due to the slow activation of catalyst to generate the necessary active species (the color change of the solution could be observed only after 6−7 h).

In contrast, but as could be expected, the molecular weight of the polymers obtained with **rac** increased 50-fold from 6600 for room-temperature polymerization to 320 000 when the temperature was lowered to 4 °C and

Table 2. Polymerization of 1-Hexene^a with Different Catalyst Ratios

		fraction 1				fraction 2^g		
no.	% rac/meso	activity^b	M_n ^{c}	pdi	tacticity^d (% mmmm)	activity^e	M_n ^{c}	pdi
1	100/0	700	6600	2.3	isotactic (65)			
2	75/25	320	7100	2.1	isotactic (58)	420	700	1.2
3	50/50	410	11 700	2.1	isotactic (41)	390	800	1.1
4	50/50^f	640	18 300	1.8	isotactic (47)			
5	25/75	<20	5600	2.4	isotactic (42)	405	1100	1.2
6	0/100					540	900	1.1

[a] Al/Ti = 200; 1-hexene = 3 mL; reaction time = 72 h; chlorobenzene = 20 mL; temperature = 28 °C. [b] (g of PH/mol of catalyst)/h. [c] Determined from GPC in THF using narrow polystyrene standards. [d] Determined by ^{13}C NMR. [e] (g of oligohexene/mol of catalyst)/h. [f] 50/50 mixture as generated. [g] Oligomers were atactic in nature.

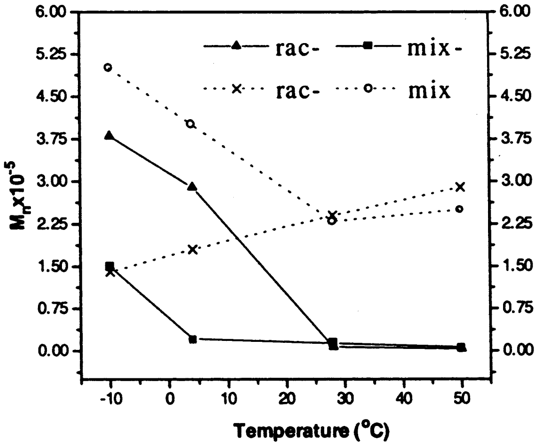


Figure 1. Variation of molecular weight and polydispersity index with temperature (Hollow spheres with broken lines indicate polydispersity index).

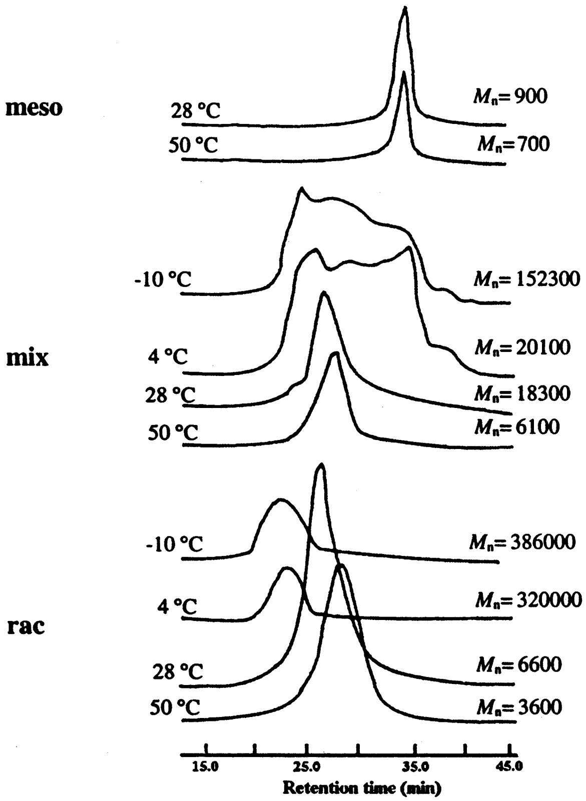


Figure 2. GPC curves of polyhexene obtained with **meso**, **rac**, and **mix** at different temperatures.

further to 380 000 when the temperature of polymerization was brought down to −10 °C (Table 1). In comparison, the changes in the molecular weight of the polyhexenes obtained with the **mix** were not as striking up to 4 °C (Figure 1, Table 1), *but* when the polymerization temperature was decreased to −10 °C, the molecular weight increased 8-fold but was still three times lower than the molecular weight of the polyhexene obtained with **rac** at −10 °C. It was also seen that as the polymerization temperature was increased, the molecular weights of the polymers decreased, suggesting a high rate of chain termination at elevated temperatures.

The molecular weight and the dispersity values of the polyhexenes obtained with various catalysts are plotted in Figure 1. With **rac**, the pdi of polyhexene was 2.4 for room-temperature polymerization, and it decreased to 1.4 when the reaction temperature was brought down to −10 °C, indicating a tendency to approach living polymerization. In contrast, the **mix** produced polymers with broad molecular weight distribution, with pdi greater than 5, a typical behavior of a classical Ziegler−Natta system (Figure 2). We could reason such observation presuming that the **meso** component in the **mix** also gets activated at low temperatures to produce polymers with broad molecular weight distribution. But to our surprise, the **meso**, when employed alone for polymerization of 1-hexene, gave only liquid samples with molecular weights (M_n) in the region of 700−1100 with moderate yields at all temperatures. This might then suggest that the oligomers discarded by the **meso** are consumed by the **rac** to give high pdi value for the polymers obtained from the **mix**. To verify this postulate, 1-hexene was polymerized by mixing equimolar concentration of **meso** and **rac** (mixed catalysts). While the **mix** gave rise to polyhexenes with bimodal distribution, the deliberately mixed catalyst system gave rise to two fractions, pasty high molecular weight polymer (Fraction 1) and liquid low molecular weight sample (Fraction 2) indicating that the two catalysts acted independently retaining their individual identities (see Table 2).

In all polymerizations performed by mixing two different catalysts, polymers with bimodal distribution and a good increase in activity have been observed by synergistic effect.[15] In contrast, our mixed catalysts gave rise to two fractions as anticipated because the pure **meso** had no polymerization activity but the increase in activity normally observed could not be seen with our mixed system. Although, the expected increase in activity was not observed, the possibility of a synergistic effect could not be ignored because an increase in molecular weight of the polymer was seen for the Fraction1 (contribution from the **rac** in the mixed catalysts) when compared to the molecular weight of the polymer obtained from pure **rac**. It could also be seen that as the percentage of the **meso** in the mixed catalysts increased the molecular weights of the polymer

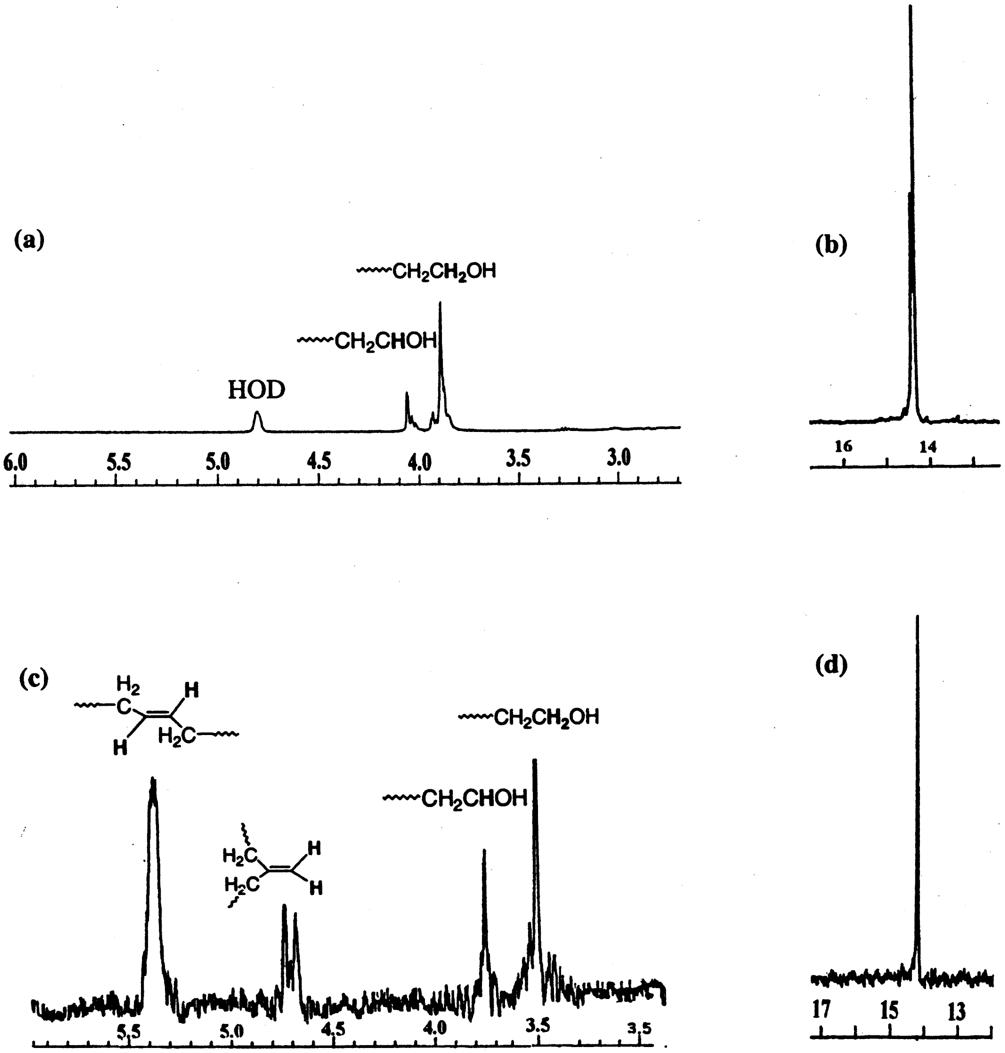


Figure 3. ^{1}H NMR (3.0−6.0 ppm) of polyhexene from (a) **rac** and (c) **meso** and ^{13}C NMR of methyl region of polyhexene from (b) **meso** and (d) **rac** indicating various chain termination reactions.

obtained decreased (fraction 1, Table 2). The pdi values for the high and the low molecular weight polyhexene fraction was almost same as the polymer or oligomers from the individual catalysts and was found to be true if the polymerizations were carried out by mixing **rac** and **meso** at different ratios (Table 2 and Figure 6).

The reason for the oligomers formed along with the high molecular weight fraction and not taken up by the **rac** when mixed catalyst systems were employed for polymerization became clear when we examined the chain termination reactions of the polymers and the oligomers obtained with these catalysts. The ^{1}H NMR spectrum of polyhexenes showed, apart from the expected signals, weak resonances in the 3.0−6.0 ppm region, which could be ascribed to various chain termination reactions like β-hydride elimination and chain transfer to aluminum that occur during the polymerization (Figure 3).[16] In the case of **rac**, a multiplet appeared at 5.4 ppm indicating the formation of an RCH=CHR′ olefin moiety, which occurs due to β-hydride elimination after a 2,1-insertion of 1-hexene. Two signals at 4.6 and 4.7 ppm are due to the olefinic protons of the vinylidene end (RR′C=CH$_2$), which arise by β-hydride elimination after a 1,2-insertion of the monomer (Figure 3c). With **meso**, however, the oligomers produced showed no olefinic signals indicating the absence of β-hydride elimination (Figure 3a). The ^{13}C NMR of the oligomers indicated an additional overlapping signal at 14.3 ppm (Figure 3b). Unlike isotactic polypropylene, where the backbone methyl carbons appear at 21.0 ppm and the end-methyl group (generated after transfer to aluminum, followed by hydrolysis) appears at 14.3 ppm, both the methyl carbon signals of polyhexene appeared around 14.3 ppm. Thus, the additional signal observed along with the regular methyl carbon of 1-hexene indicates that the oligomers produced underwent chain transfer to aluminum. In addition to these signals, **rac** showed two weak signals at 3.4 and 3.7 ppm, and the **meso** showed two multiplets at 3.7 ppm and at 4.1 ppm. These signals could be assigned to oligomers with hydroxyl end group (−CH−OH and −CH$_2$OH),[16] and is felt that these signals can result from transfer of active metal center to aluminum of MAO after 2,1- and 1,2-insertion, which on exposure to oxygen during polymer precipitation produces a hydroxyl end group as pointed out by Chien.[16] The oligomers of **meso** when exchanged with D$_2$O and was found to decrease the complexity of the muliplet at 3.7 ppm and at 4.1 ppm and did not have any pronounced effect on the NMR spectrum of the oligomers, suggesting the possible coupling of the OH hydrogen with the neighboring methylene or methine protons of hexene units.

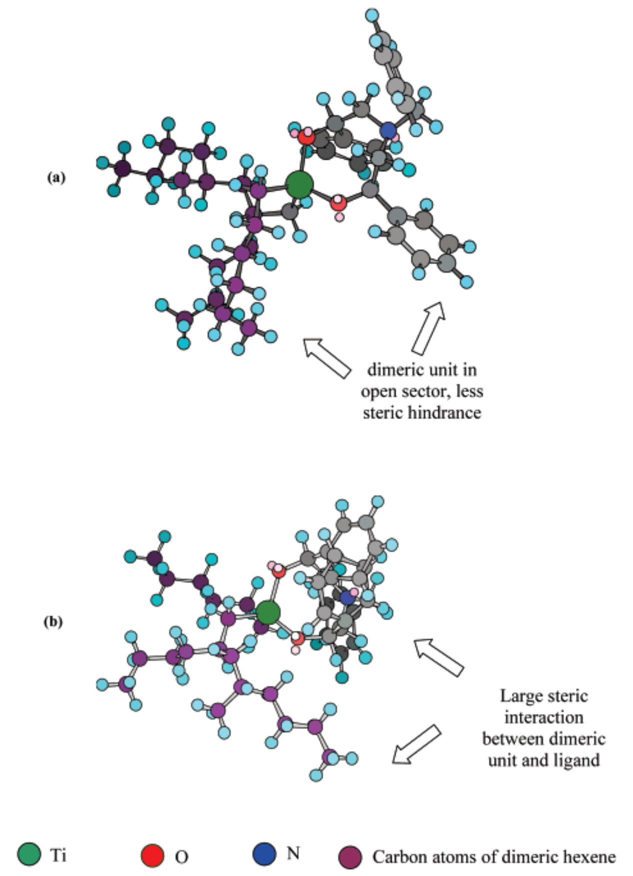


Figure 4. MM2 energy minimized structure of (a) **rac** and (b) **meso** catalyst after two 1,2-insertions of hexene.

It is known that catalysts of meso form produce atactic polymers with low or sometimes good activity, but the **meso** did not produce any polymer. A rudimentary MM2 energy minimization done for both the **rac** and **meso** with dimeric hexene unit attached to the active center suggested a high steric interaction of the ligand with the alkyl chain for the **meso**, and hence possibly the chain gets terminated at oligomeric stage. For the **rac**, the minimization studies show that the polymer chain occupies the open sector environment and can easily take up more monomers to produce high molecular weight polymers (Figure 4).

The ^{13}C NMR of the all the polymers obtained with the **rac** and **mix** under quantitative conditions showed a signal at 34.6 ppm (C-3 carbon, Figure 5) indicating that the polymers obtained are isotactic in nature. It could be seen that the percentage isotacticity was higher for polymers obtained from **rac** than the **mix** whereas the **meso** produced atactic oligomers.[17]

For both the catalysts, the percentage isotacticity increased with a decrease in temperature of the reaction. The increase in stereoregularity of the polymer obtained at low temperature is because the polymer chain gains the required conformational stability at low temperature.[18] Similar behavior observed by Odian[19] for hexene polymerization was rationalized by suggesting that the tight coordination of the propagating center, catalyst counterion, and monomer loosens at high temperatures to allow some misinsertions, thereby decreasing the stereoregularity of the polyhexene. Brull et al.[20] observed a 30−40% stereoregularity between 20 and 100 °C and an unexpected increase in isotacticity at 55 °C. To have an insight of the mechanism of polymerization, the other pentads in the polyhexene spectrum obtained with **rac** were assigned as per literature reports,[21] and the triad/pentad analysis indicated that the **rac** produced isotactic polymer by enantiomorphic site control mechanism.[22] In the case of polymers from mixed catalysts, where both the catalysts retain their individual identities, a decrease

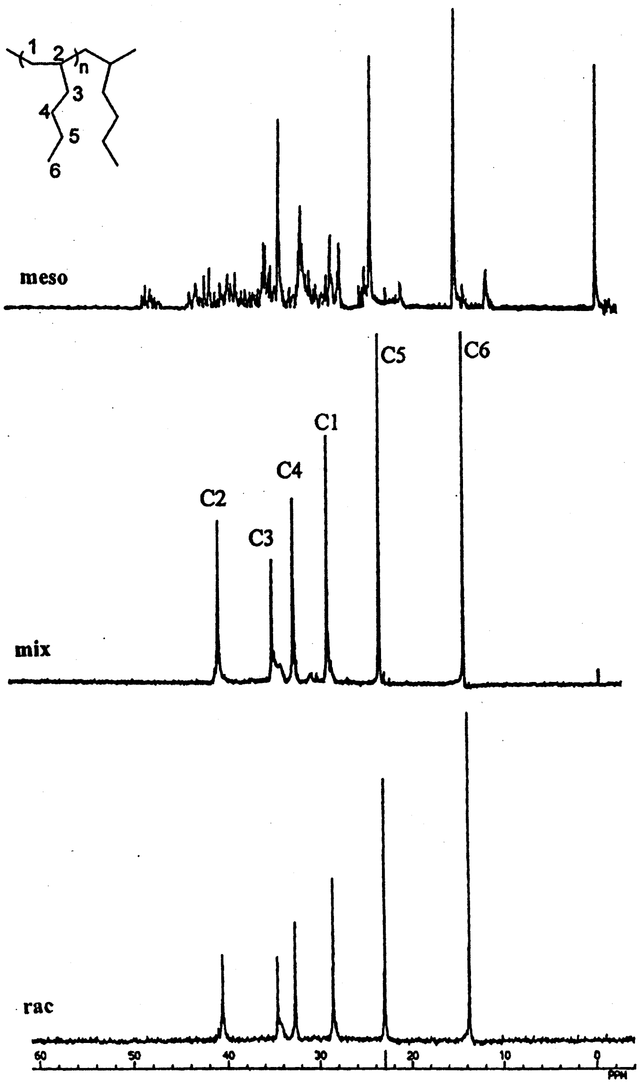


Figure 5. ^{13}C NMR of polyhexene obtained at −10 °C with (a) **meso**, (b) **mix**, and (c) **rac**.

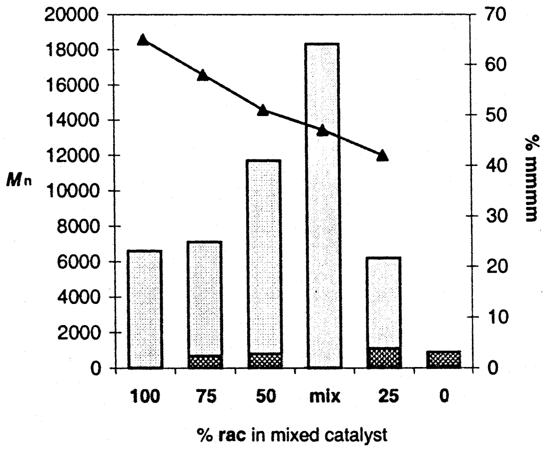


Figure 6. Molecular weight and stereoregularity of polyhexene with different ratio of mixed catalysts.

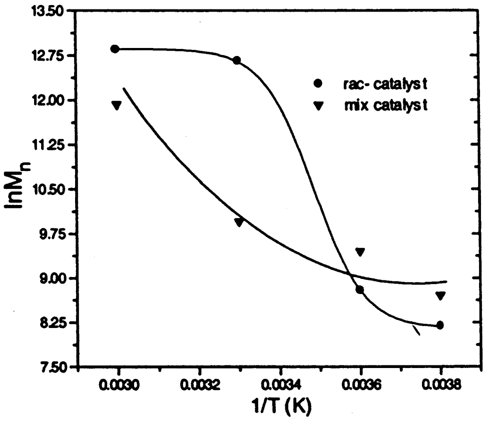


Figure 7. Modified Arrhenius plot (ln M_n vs $1/T$) for **rac** and **mix** catalysts.

in the percentage *mmmm* value of fraction 1 was seen (Figure 6, Table 2). It is felt that the atactic oligomers with its active end transferred to the Al of MAO, act as a source of chain transfer for the isotactic polymer produced by the **rac** catalyst.[23]

Since our initial suggestion that the discarded oligomers are used by the **rac** was vitiated by the fact that **meso** produced oligomers without any olefinic residues and two molecular weight fractions were obtained with mixed catalysts, we felt that the observed broad distribution with **mix** is more complicated to explain. In other words, **mix**, being a diastereomeric catalyst, is also expected to show a broad molecular weight distribution, but this was observed only when the polymerization temperature was lowered. At ambient and higher temperatures **mix** catalyst gave polymers with unimodal distribution. Vathauer and Kaminsky[24] have calculated the activity of the *meso* catalyst from the combined activity of the mixture of *rac*/*meso* catalysts (obtained after exposure of pure racemic catalyst to light) and the percentage of the isomer from NMR. When activity calculations for the **mix** were applied along the same line, the suggested activity of the **meso** was 60 (g of PH/mol of catalyst)/h at room temperature, but the **meso** gave oligomers. Also, the modified Arrhenius plot (ln M_n vs $1/T$) for the **rac** showed a sigmoidal behavior indicating the existence two active species, one producing high molecular weight polymer at low temperature and another producing low molecular weight polymer at high temperature (Figure 7). In strict contrast, with the **mix**, similar plot revealed an exponential increase over the temperature region studied.

Höcker[25] reported such a sigmoidal behavior and has pointed toward the existence of two active species. Kristen and Jutzi and co-workers[26] have also suggested the existence of two catalytically active species, which produce high and low molecular weight polymers with change in temperature. These facts lead us to propose tentatively that the racemic and meso ligands should form aggregates during the **mix** formation and can exist as two or three aggregated species, each of them getting activated at low temperature, thereby producing a broad molecular weight distribution. This type of aggregation phenomenon has been observed in asymmetric synthesis.[27]

Conclusion

We were able to synthesize a new catalyst in *racemic* and *meso* forms and as a diastereomeric mixture in an easy way and have used it for the polymerization of 1-hexene, each having a different behavior toward polymerization. We have tentatively proposed aggregate formation to explain the latent bimodal behavior of **mix**.

Experimental Section

General Procedures. Catalyst preparation and polymerizations were carried out under dry and oxygen free argon atmosphere. Transfers were performed in argon-filled glovebag or by standard syringe techniques. MAO was purchased as a 10 wt % solution from Witco GmbH and was used after estimating the aluminum content. 1-Hexene purchased from Aldrich was dried over calcium hydride and used. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.5 MHz) spectra were recorded using JEOL GSX400 spectrometer in $CDCl_3$ at ambient temperature. ^{13}C NMR spectra for polyhexenes were recorded with pulse angle = 25°, pulse width = 2.8 μs, acquisition time = 0.655 s, relaxation time = 6 s, and number of scans = 3000. Molecular weights of the polymer were determined by Waters GPC instrument with Styragel columns (10^6, 10^5, and 10^3 Å columns connected in series) equipped with an RI detector using THF as solvent at a flow rate of 1.0 mL/min. Calibration was done using narrow polystyrene standards. Analytical HPLC was performed with Waters HPLC instrument equipped with UV detector at 254 nm and C-18 column using MeOH:H_2O = 80:20 solvent system at a flow rate of 1.0 mL/min. Semipreparative separation was done in a Schimadzu (LC-8) HPLC instrument equipped with UV detector at 254 nm and ODS column using MeOH:H_2O = 80:20 solvent system at a flow rate of 10 mL/min. Energy minimization was done using CHEM 3D software available from the Cambridge Soft Corporation.

Synthesis and Characterization of Aminodiol (3-Aza-3-benzyl-1,5-dihydroxy-1,5-dipheynylpentane). To a cooled solution of benzylamine (1.07 g, 9.98 mmol) in ethanol (2 mL) was added styrene epoxide (2.4 g, 19.997 mmol), in ethanol (4 mL), at 0 °C and stirred for an hour. The contents were then refluxed for 6 h. The product was obtained as a colorless syrupy liquid. The product was then purified by silica gel (60−120 mesh) column chromatography using and 80:20 hexane:ethyl acetate mixture. The major isomer was isolated as a colorless syrupy liquid. Yield: 85%. The obtained aminodiol was dissolved in 80:20 = methanol:water (solubility 200 mg in 2 mL) and used for semipreparative HPLC. The separated *racemic* and *meso* aminodiols were extracted in CH_2Cl_2 after removing methanol and were further characterized.

50/50 Aminodiol. Nature: colorless syrupy liquid: ^{1}H NMR (400 MHz, $CDCl_3$): 2.73 (dd, J = 13.7, 3.4, 1H), 2.80 (dd, J = 13.7, 3.4, 1H), 3.62 (s, 2H, OH), 3.70 (d, J = 13.7, N−CH_2Ph, 1H), 3.83 (s, 2H, N−CH_2Ph), 3.96 (d, J = 13.7, N−CH_2Ph, 1H), 4.75 (dd, J = 9.5, 3.4, 1H), 7.1−7.3 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 59.15, 59.81, 62.15, 63.0, 70.54 (−C−OH), 71.65 (−C−OH), 125.70, 125.81, 127.91, 128.10, 128.12, 128.16, 128.25, 128.70, 137.94 (s), 138.11 (s), 142.13 (s), 142.21 (s). Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03; Found: C, 79.47; H, 7.21; N, 4.10.

***meso*-Aminodiol.** Nature: colorless syrupy liquid ^{1}H NMR (400 MHz, $CDCl_3$): 2.79 (dd, J = 13.4, 3.9, 1H), 2.87 (dd, J = 8.7, 13.4, 1H), 3.83 (s, 2H, N−CH_2Ph), 4.25 (s, 2H, OH), 4.71 (dd, J = 8.7, 3.9, 1H, −CH−OH), 7.2−7.4 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 59.16, 62.15, 70.54, 125.78, 126.98, 128.32, 128.93, 137.90 (s), 142.2 (s) Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03; Found: C, 79.58; H, 7.18; N, 3.97.

***racemic*-Aminodiol.** Nature: colorless solid: Mp: 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 2.73 (dd, J = 13.67, 3.4, 1H), 2.80 (dd, J = 13.67, 3.4, 1H), 3.62 (s, 2H, OH), 3.70 (d, 13.7, N−CH_2Ph, 1H), 3.96 (d, J = 13.7, N−CH_2Ph, 1H), 4.75 (dd, J = 9.5, 3.4, 1H), 7.1−7.3 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 59.72, 62.50, 70.77 (−C−OH), 125.86, 127.36, 127.48, 128.30, 128.45, 129.11, 138.11(s), 142.13 (s). Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03; Found: C, 79.43; H, 7.18; N, 4.13.

Synthesis of the Titanium Catalyst. $TiCl_4$ (2 g, 10.5 mmol) in 10 mL of dry hexane was cooled to 0 °C. $Ti(O^iPr)_4$ (2.9 g, 10.54 mmol) was added and stirred for 1 h. $Ti(O^iPr)_2Cl_2$

settled at the bottom of the flask. Hexane was removed by cannula, and the white solid was dried in a vacuum and redissolved in 10 mL of CH_2Cl_2; to this was added the required amino diol (4.74 g, 13.66 mmol) in 5 mL of CH_2Cl_2, and the mixture was stirred at room temperature for 2 h to give a clear yellow solution. The solvent was removed under reduced pressure. The resulting compound was dissolved in dichloromethane and reprecipitated in hexane, to give a white powder.

50/50 Diolate Catalyst (mix). ^1H NMR (400 MHz, $CDCl_3$): 3.2−3.9 (m, 4H), 4.2−4.7 (m, 2H), 5.1−5.5 (m, 2H), 7.3−7.6 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 58.3, 58.7, 60.48, 67.27, 125.8, 127.3, 127.9, 128.3, 128.7, 129.1, 129.7, 130.9, 131.2, 131.6, 131.8, 139.3, 141.84. Anal. Calcd for $C_{23}H_{23}NO_2TiCl_2$ C, 59.51; H, 4.99; N, 3.09. Found C, 59.6; H, 4.91; N, 3.01.

***meso*-Diolate Catalyst (meso).** ^1H NMR (400 MHz, $CDCl_3$): 3.2−3.41 (m, 4H), 4.45 (s, 2H), 5.46 (m, 2H), 7.3−7.6 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 58.7, 60.48, 67.27, 125.81, 127.33, 127.90, 128.31, 128.72, 129.71, 130.94, 131.88, 139.32. Anal. Calcd for $C_{23}H_{23}NO_2TiCl_2$ C, 59.51; H, 4.99; N, 3.09. Found C, 59.6; H, 4.91; N, 3.01.

***rac*-Diolate Catalyst (rac).** ^1H NMR (400 MHz, $CDCl_3$): 3.41 (m, 4H), 4.60 (m, 2H), 5.45 (d, 1H), 5.5 (d, 1H), 7.2−7.9 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): 60.8, 63.17, 69.40, 125.8, 127.8, 128.3, 129.37, 130.31, 131.63, 140.12. Anal. Calcd for $C_{23}H_{23}NO_2TiCl_2$ C, 59.51; H, 4.99; N, 3.09. Found C, 59.6; H, 4.91; N, 3.01.

Polymerization Procedure. To dry deaerated chlorobenzene (20 mL) were added the catalyst (1 mL, 70 μmol) in CH_2Cl_2 and MAO in toluene (0.9 mL, 1.4 mmol) by syringe to a clean, dry, argon-filled 100 mL round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and a septum. The mixture was stirred for about 10 min, and then 1-hexene (3 mL) was added and stirring was continued for 2 days. The polymerization was quenched by pouring the mixture into an acidified cold methanol solution, the polymers were dried under vacuum and weighed to calculate the activity of catalyst. Polymers were obtained as a pasty material. Polymerizations were carried out with the mixed catalysts by adopting the same procedure as described earlier with the sum of catalyst concentration kept at 70 μmol. After precipitation, two fractions were obtained—a pasty material sticking to the magnetic stir bar and the other an oily liquid sample.

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