

STEREOCHEMICAL CONTROL IN PROPYLENE POLYMERIZATION CATALYZED BY UNBRIDGED METALLOCENE CATALYSTS*

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Abstract Two unbridged metallocene catalysts, bis(2,4,7-trimethylindenyl)zirconium dichloride (met-I) and bis(2,4,6-trimethylindenyl)zirconium dichloride (met-II), which are different in the position of substituents on the six-membered ring of the indenyl ligands were synthesized. The effect of substituents in the two metallocenes on the propylene polymerization was studied in the presence of methylaluminoxane (MAO) and triisobutylaluminum (TIBA). From the analysis of microstructure determined by ^{13}C -NMR, it was demonstrated that the polymers produced by met-II have higher [mmmm] isotactic sequences than that of met-I. Using a mechanism based on model statistical analysis, it was found that chain-end model was dominant for met-I. However, met-II obeys the concurrent two-sites model during polymerization, which can be attributed to the existence of "racemic-like" conformer in its system.

Keywords Unbridged metallocene, Propylene polymerization, Elastomeric polypropylene, Stereochemical mechanism

INTRODUCTION

Since the discovery of homogeneous metallocene catalysts, it has been possible to tailor the structure and properties of polyolefin through the design of catalyst ligand structures^[1]. For polypropylene (PP), isotactic, syndiotactic, heterotactic and stereoblock microstructures can be prepared using metallocene catalysts^[2-5]. Recently, researchers have also paid attention to the production of elastomeric PP. As early as 1957, Natta^[6] discovered that one of the fractions of PP based on traditional Ziegler-Natta catalysts possessed elastomeric properties and proposed a stereoblock structure for the materials. Two decades later, Collette^[7] and co-workers developed the supported tetraalkyl group IVB catalysts for the production of elastomeric PP without being fractionated to be a useful elastomer. Chien^[8] and co-workers were the first to prepare elastomeric PP by means of ansa-titanocene complex and explained that polymerization occurred alternatively at α -specific and *iso*-specific coordination sites, which were interconvertible, due to the facile rotation of indenyl ligand about the metal-ligand bond axis during polymerization. Collins^[9] also reported a 3-methyl substituted ansa-zirconocene that produces elastomeric PP which is a high molecular weight atactic PP or a stereoblock PP. However, unbridged metallocene catalysts lately have played an important role in the synthesis of elastomeric PP. Erker^[10] and Naga^[11] investigated the effect of substituents in bis-cyclopentadienyl metallocene for the production of PP at appropriate temperature. Waymouth^[12] developed a theory that ligand rotation occurs during propylene polymerization with $(2\text{-PhInd})_2\text{ZrCl}_2$ to give stereoblock PP. Lee^[13] and Yoon^[14] synthesized the bis(2-R-Ind)zirconium dichloride complex to investigate the effect of alkyl substituents at the 2-position of indene on the rotational conversion rate between rotamers (racemic and meso) and the catalytic activities toward olefin polymerization.

In our previous work^[15], the two metallocenes, $(2,4,7\text{-Me}_3)_2\text{ZrCl}_2$ (met-I) and $(2\text{-Me-4,7-Et}_2)_2\text{ZrCl}_2$ were

* This project was supported by the National Natural Science Foundation of China and the Petrochemical Incorporation of China (Grant number: 29734144).

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Received August 21, 2000; Revised October 10, 2000; Accepted October 18, 2000

synthesized to compare the effect of the size of alkyl groups substituted at positions 4 and 7 in the six membered ring of the indenyl ligand on propylene polymerization. In this paper, we prepared the unbridged metallocene catalysts, $(2,4,7\text{-Me}_3)_2\text{ZrCl}_2$ (met-I) and $(2,4,6\text{-Me}_3)_2\text{ZrCl}_2$ (met-II), which have the same substituents but their position in the six-membered ring of the indenyl group is different. Their catalytic activity in the propylene polymerization, and especially the microstructure of resulting PP were studied.

EXPERIMENTAL

Materials

All operations were carried out under dry nitrogen atmosphere using the standard Schlenk techniques. All chemicals used were of analytical grade and were further purified. Toluene was purified by refluxing over Na-benzophenone ketyl under nitrogen atmosphere and distilled before use. Methylaluminoxane (10% *W/W* toluene solution, Albemarle Co.) was used as received. Triisobutylaluminum (TIBA, Fluka Co.) was vacuum distilled before use. Propylene was further purified by passing through activated 4A molecular sieves.

Catalyst Preparation

The zirconium complexes, met-I and met-II were prepared according to the procedures reported previously^[15, 16]. They were characterized by $^1\text{H-NMR}$ (90 MHz, CDCl_3 , 25°C) and elemental analysis.

Polymerization Procedure

Polymerization was carried out in toluene at atmospheric pressure in a 250 mL Schlenk glass flask equipped with a propylene inlet and a magnetic stirrer. Toluene (100 mL) was introduced into the reactor at controlled temperature and was saturated with propylene of 0.1 MPa pressure. Calculated amounts of TIBA, MAO and metallocene in toluene were added respectively. The propylene pressure was kept constant at 0.1 MPa and the flow rate was recorded by a computer, which monitored the electromagnetic gas inlet valve. Polymerization was stopped after 1 h by acidified ethanol and the product was poured into an excess amount of ethanol. The resulting polymer was separated by filtration, washed and dried in vacuum to constant weight.

Polymer Characterization

The molecular weight and molecular weight distribution of the polymers were measured by GPC (Waters-208) at 25°C using tetrahydrofuran as the eluent and calibrated with polystyrene standards. $^{13}\text{C-NMR}$ spectra of the polymers were recorded on a Bruker AMX-500 spectrometer at 90°C. The polymer solutions were prepared by dissolving ca. 100 mg of polymer in 0.5 mL *o*-dichlorobenzene- D_4 . The peak of *o*-dichlorobenzene- D_4 was used as the internal standard.

RESULTS AND DISCUSSION

Results of Propylene Polymerization

The effects of temperature on propylene polymerization at -15, 0, and 25°C are illustrated in Table 1. The activity of met-II increases and then decreases as the polymerization temperature (T_p) rises from -15 to 25°C. On the contrary, the activity of met-I increases with decrease of T_p . The different electronic and steric effects, attributed to varied position of two methyl substituents on the six-member of the indenyl ligand, should account for this. The molecular weights of PP produced with both catalysts are higher at lower temperature and increase with decrease of temperature. The molecular weight distribution is narrow ($M_w/M_n = 1.8\text{--}2.6$) which is typical of the metallocene-catalyzed polymerization. However, at lower T_p (-15°C), the polydispersity of the PP obtained with met-II is broader, which is another peculiar feature for this catalyst. During the polymerization at 0°C for both metallocenes, samples were taken at 10, 30 and 60 min intervals to determine the effects of polymerization time on the activity and polymer structure. It was found that the molecular weight of polymers based on met-I and met-II changed differently with polymerization time.

Table 1. Results of propylene polymerization using met-I and met-II^a

Run No.	Catalyst	T_p (°C)	Polym. time (min)	Activity ^b ($\times 10^{-6}$)	M_n^c ($\times 10^{-4}$)	M_w^c ($\times 10^{-4}$)	M_w/M_n^c
1	met-I	-15	60	3.38	25.8	54.2	2.10
2		0	10	—	6.35	11.68	1.84
3			30	—	5.40	11.77	2.18
4			60	1.78	5.79	14.06	2.43
5		25	60	0.13	0.53	1.36	2.55
6	met-II	-15	60	0.56	5.31	19.96	3.76
7		0	10	—	4.47	8.32	1.86
8			30	—	5.48	12.17	2.22
9			60	1.33	4.62	10.18	2.20
10		25	60	0.88	0.59	1.31	2.21

^a Polymerization conditions: [Zr] = 20 μ mol/l; Zr:MAO:TIBA=1:1000:600^b Activity unit: g PP/mole Zr $\cdot$ h^c Determined by GPC

Microstructure Analysis

The ^{13}C -NMR spectra of the PP produced by the two metallocenes are given in Fig. 1, while the methyl pentad sequence distributions are listed in Table 2. It can be found that the intensity of [mmmm] isotactic sequence of polymer based on met-II is stronger than that of met-I. This can be explained by comparing the stability of “racemic-like” conformers formed by rotating the indenyl group around the Ind-Zr axis as illustrated in Fig. 2. For met-I, the methyl group at position 2 of one indenyl group may “face to” the methyl group at position 4 or 7 of the other indenyl group, thus the stability of “racemic-like” conformer will be lowered. As regards met-II, the indenyl ligand with the methyl groups substituted at 4 and 6 position experiences less hindrance and the racemic isomers becomes more stable than met-I, hence the content of isotactic pentad sequence is somewhat higher. At -15°C , the met-II based PP possesses a [mmmm] isotactic pentad sequence content as high as 15.9%. For both metallocenes, the [mmmm] of PP decreases with the increase of temperature. This phenomenon has also been observed in other metallocene catalyzed propylene polymerization. The [mmmm] isotactic pentad sequence of met-II based PP decreases with the extension of polymerization time. On the contrary, for met-I, there is only a slight change in [mmmm] with polymerization time.

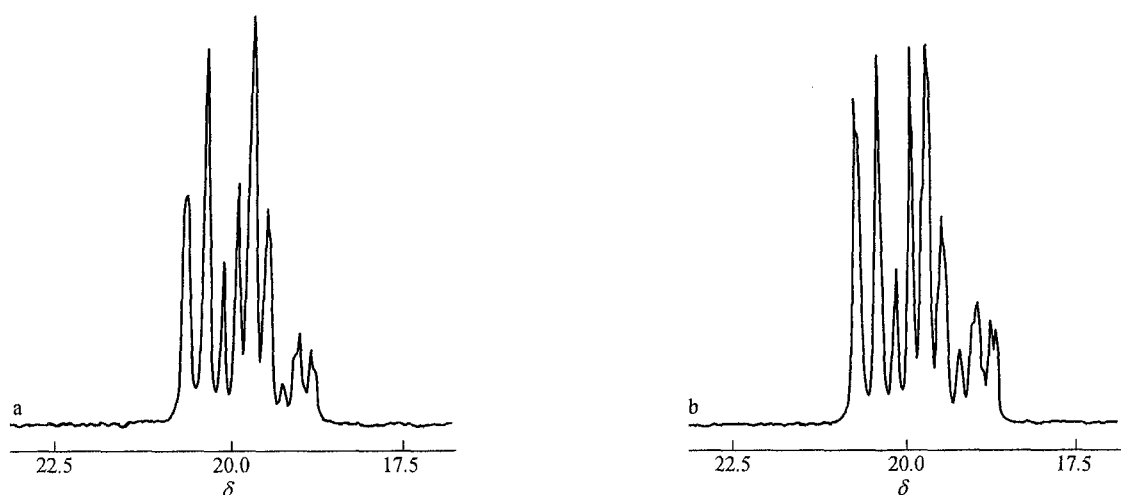


Fig. 1 Methyl region of the ^{13}C -NMR spectra of polypropylene obtained with different metallocenes. Polymerization conditions are same as Table 1, $T_p = 0^\circ\text{C}$, $t_p = 1$ h
a) met-I; b) met-II

Table 2. Results of pentad distributions of PP observed by ^{13}C -NMR and calculated according to concurrent two-sites model fitting

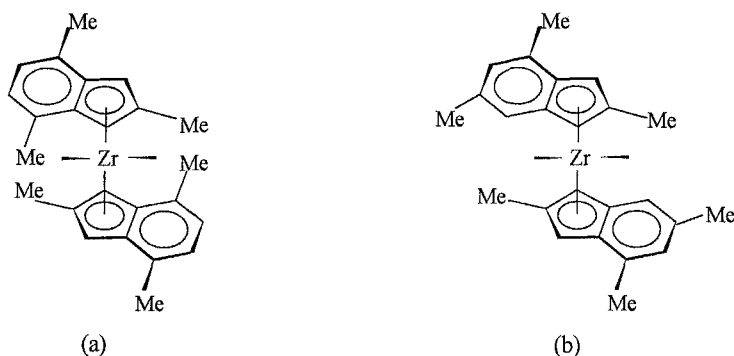
Catalyst Run no T_p ($^{\circ}\text{C}$) t_p (min)	met-I				met-II			
	1	2	3	4	6	7	8	9
	-15 60	0 10	30	60	-15 60	0 10	30	60
m m m m ^a	0.150	0.145	0.149	0.147	0.159	0.168	0.164	0.154
	0.151	0.145	0.148	0.150	0.161	0.170	0.165	0.155
m m m r	0.180	0.180	0.180	0.184	0.158	0.160	0.162	0.164
	0.182	0.179	0.181	0.182	0.156	0.156	0.158	0.162
r m m r	0.068	0.063	0.066	0.062	0.065	0.059	0.058	0.058
	0.055	0.056	0.055	0.055	0.051	0.049	0.051	0.053
m m r r	0.105	0.104	0.103	0.105	0.129	0.135	0.130	0.131
	0.110	0.112	0.111	0.111	0.132	0.138	0.132	0.131
x m r x ^b	0.248	0.247	0.247	0.254	0.196	0.188	0.202	0.209
	0.249	0.249	0.249	0.249	0.211	0.200	0.210	0.216
r m m r	0.122	0.128	0.127	0.120	0.119	0.110	0.108	0.113
	0.110	0.112	0.111	0.111	0.103	0.098	0.102	0.104
r r r r	0.021	0.020	0.019	0.022	0.032	0.034	0.034	0.031
	0.020	0.022	0.021	0.020	0.035	0.036	0.033	0.032
m r r r	0.060	0.068	0.063	0.060	0.081	0.084	0.085	0.082
	0.067	0.070	0.068	0.067	0.084	0.084	0.082	0.082
m r r m	0.045	0.044	0.046	0.046	0.061	0.062	0.058	0.058
	0.055	0.056	0.055	0.055	0.066	0.069	0.066	0.065
α ^d	—	0.878	0.893	—	0.815	0.790	0.816	0.792
σ	0.623	0.616	0.620	0.622	0.557	0.552	0.561	0.571
ω	0	0.001	0.001	0	0.247	0.357	0.250	0.237
ee^* ^b	0	0.001	0.001	0	0.156	0.207	0.158	0.138
RSS ^c ($\times 10^4$)	4.9	5.3	5.6	3.4	7.2	4.6	2.4	2.3

^a Relative intensity of ^{13}C -NMR methyl pentad observed, and the data below is calculated from concurrent two-sites model.

^b $xmrx = m m r m + r m r r$, $ee^* = (2\alpha - 1) \omega$

^c RSS = residual sum of squares

^d For definitions of α , σ , ω and ee^* see text

**Fig. 2** Proposed “racemic-like” conformer structure of unbridged metallocenes during polymerization

a) met-I, b) met-II

For the purpose of elucidating the stereocontrol mechanism of propylene polymerization catalyzed by these unbridged metallocenes, we try to use statistical analysis methods. The stereochemical dyad and triad

distributions are shown in Table 3. It's well known that statistical models for stereochemical control can be classified into two types, one is the chain-end growing dependent model^[17]. The simplest model of this type is the symmetric one-parameter model (Bernoullian model). According to this model, the equation, $4[\text{mm}][\text{rr}]/[\text{mr}]^2 = 1$, exists between the triad tacticities. The other type is the catalyst-dependent model. A well-known model of this type is the enantiomorphic-site model^[18]. According to this model, the following relation must exist between the triad tacticities, $2[\text{rr}]/[\text{mr}] = 1$. It has been reported that racemic bridged metallocene produces isotactic polypropylene according to the enantiomorphic-site stereochemical control mechanism, and only the enantiomorphic-site model can produce high isotactic polypropylene^[2]. Judging from the calculated values tabulated in Table 3, the triad sequences test results show that chain-end control is predominant for met-I. However, for met-II the results of triad tests on PP are not conformable to any type of models. This means that the application of a single active center model is inadequate for met-II.

Table 3. Simple statistical analysis of PP microstructure obtained with met-I and met-II

Run No.	Catalyst	T_p (°C)	t_p (min)	Dyads ^a		Triads ^a			Triad test ^a		$\langle n_1 \rangle^a$	$\langle n_2 \rangle^a$	$\langle m \rangle_{n,\sigma}^b$	$\langle m \rangle_{n,\alpha}^b$
				m	r	mm	mr	rr	$2[\text{rr}]/[\text{mr}]$	$4[\text{mm}]/[\text{rr}][\text{mr}]^2$				
1	met-I	-15	60	0.635	0.365	0.398	0.475	0.125	0.53	0.89	2.67	1.54	2.65	—
2		0	10	0.629	0.371	0.389	0.479	0.132	0.55	0.895	2.62	1.55	2.60	—
3			30	0.633	0.367	0.395	0.476	0.129	0.542	0.899	2.66	1.54	2.63	—
4			60	0.632	0.368	0.393	0.479	0.128	0.534	0.877	2.64	1.53	2.65	—
6	met-II	-15	60	0.604	0.396	0.382	0.444	0.174	0.783	1.349	2.72	1.78	2.26	4.63
7		0	10	0.604	0.396	0.387	0.433	0.180	0.830	1.486	2.79	1.83	2.23	4.03
8			30	0.603	0.397	0.383	0.440	0.177	0.804	1.401	2.74	1.80	2.28	4.66
9			60	0.602	0.398	0.376	0.453	0.171	0.755	1.250	2.66	1.76	2.33	4.06

^a Calculated directly from the observed ¹³C-NMR data, $\langle n_1 \rangle = ([\text{mm}] + 0.5[\text{mr}])/0.5[\text{mr}]$, $\langle n_2 \rangle = ([\text{rr}] + 0.5[\text{mr}])/0.5[\text{mr}]$

^b Calculated from the data in Table 2, $\langle m \rangle_{n,\sigma} = 1/(1 - \sigma)$, $\langle m \rangle_{n,\alpha} = [1 - 2\alpha(1 - \alpha)]/[\alpha(1 - \alpha)]$

All these parameters were defined in the text.

Table 4. Triad and pentad proportions for the concurrent two-sites models^{a,b}

Triad	Weight fraction	
	ω	$1 - \omega$
[mm]	$1 - 3\beta$	σ^2
[mr]	2β	$2\sigma(1 - \sigma)$
[rr]	β	$(1 - \sigma)^2$
Pentad		
[mmmm]	$1 - 5\beta + 5\beta^2$	σ^4
[mmmr]	$2\beta - 6\beta^2$	$2\sigma^3(1 - \sigma)$
[rmmr]	β^2	$\sigma^2(1 - \sigma)^2$
[mmrr]	$2\beta - 6\beta^2$	$2\sigma^2(1 - \sigma)^2$
[mmrm]	$2\beta^2$	$2\sigma^3(1 - \sigma)$
[rmrr]	$2\beta^2$	$2\sigma(1 - \sigma)^3$
[rmm]	$2\beta^2$	$2\sigma^2(1 - \sigma)^2$
[rrrr]	β^2	$(1 - \sigma)^4$
[mrrr]	$2\beta^2$	$2\sigma(1 - \sigma)^3$
[mrrm]	$\beta - 3\beta^2$	$\sigma^2(1 - \sigma)^2$

^a $\beta = \alpha(1 - \alpha)$

^b For definitions of α , σ and ω see text

To rationally explain the microstructure of samples from met-I and met-II, a concurrent two-site model^[19] was proposed. This model assumes that there are two different coexisting stereocontrol mechanisms, one obeys the chain-end growing dependent model, and the other follows the enantiomorphic-site model. According to this

model, the triad and pentad tacticities of the polymer can be described with three parameters, σ , α , and ω (summarized in Table 4). Here, σ is the probability of selection of an m configuration at a chain-end control site, α is the probability of selection of a d-preferring enantiomorphous sites, and the third parameter ω is the mole fraction of the polymer produced at the enantiomorphous sites. And here we cite the fourth parameter $ee^{*[20]}$, which is a combination of α and ω in the equation, $ee^* = (2\alpha - 1)\omega$. The ee^* value so defined could be termed as "relative enantioselectivity" and is a useful parameter for describing the effective transfer of chirality from the chiral active catalytic site.

The optimized values of the four parameters for all the samples, which have been obtained by an iterative fitting calculation, are shown in Table 2. The calculated values of the pentad distribution based on these parameters are also listed in Table 2. For all the samples concerned, we can find that the calculated values of pentad distribution are reasonably consistent with the observed ones. But in the case of met-I, the value of ω is very small (for Run 1, 2, 3 and 4, ω is 0, 0.001, 0.001 and 0, respectively) and approaches zero. This indicates that there is almost no enantiomorphous-sites control during polymerization, which is in good agreement with the chain-end control mechanism. This fact also means that in the met-I system the stability of "racemic-like" conformer is so low that it can not act as the active center. In the case of met-II, one can notice that the pentad distribution fits the concurrent two-sites model well. The fraction of enantiomorphous control, ω is 24.7% (Run 6, $T_p = -15^\circ\text{C}$), and there are many "mistakes" along the polymer chain produced by enantiomorphous site ($\alpha = 81.5\%$), thereby the overall effective chirality transfer, ee^* is 15.6%. This means that some active centers based on "racemic-like" conformer, which follow the enantiomorphous control mechanism, truly exist in met-II catalyzed polymerization system. The polymerization temperature and reaction time do not influence the mechanism of both metallocenes systems, except that some parameters are changed for met-II. For met-I, the parameters have no obvious difference when reaction temperature and time are changed. For met-II, given the same polymerization time ($t_p = 1$ h), the relative enantiomorphous control ee^* increases as the temperature decreases, but it decreases when t_p extends from 10 min to 1 h. By this fact it may be deduced that the "racemic-like" conformer of met-II is more stable at lower temperature. High temperature can speed up the rotation of ligand, and thus reduces the lifetime of the "racemic-like" conformer. On the other hand, it can also be deduced that the "racemic-like" conformer more readily undergoes deactivation or transformation into other conformers during polymerization. This can explain the decrease of the content of [mmmm] sequence with reaction time in the met-II system.

To characterize the microstructure of the polymer chain, the four parameters, $\langle n_1 \rangle$, $\langle n_2 \rangle$, $\langle m \rangle_{n, \alpha}$ and $\langle m \rangle_{n, \sigma}$ are introduced and are shown in Table 3. $\langle n_1 \rangle$, $\langle n_2 \rangle$ represent respectively the number averaged sequence length of meso and racemic dyad of the polymers based on observed data^[21], and $\langle m \rangle_{n, \alpha}$, $\langle m \rangle_{n, \sigma}$ mean the number averaged sequence length of meso dyad of the polymers generated at the enantiomorphous site and the Bernoullian site, respectively^[22]. The latter two parameters are calculated from statistical data. From Table 3, one can notice that $\langle n_1 \rangle$ and $\langle n_2 \rangle$ values of all samples obtained with met-II are slightly higher than that of met-I. But the $\langle m \rangle_{n, \sigma}$ values of met-II is somewhat lower than those of met-I. For met-II, $\langle m \rangle_{n, \alpha}$ values are larger than $\langle m \rangle_{n, \sigma}$ values under the same conditions, and $\langle m \rangle_{n, \alpha}$ values increase with the decrease of T_p . For all the samples produced by the two metallocenes, $\langle n_1 \rangle$ is longer than $\langle n_2 \rangle$. This shows that the polymer has stereoblock structure with many short isotactic blocks interrupted by atactic blocks along the chain.

CONCLUSION

By changing the position of the two methyl groups on the six-membered ring of the indenyl ligand from 4, 7 to 4, 6, the stability of "racemic-like" conformer of the unbridged zirconocenes can be sensibly changed. The differences in the microstructure of polypropylene synthesized by using catalyst met-I and met-II can be explained by the difference in the mechanism of stereochemical control between the two metallocenes. In the case of met-I, steric hindrance between the ligands makes the "racemic-like" conformer unstable, thus the number of active centers acting in the enantiomorphous-site mechanism is reduced. Only one type of active site, the chain-end control site, can explain its stereochemical control. However, in the case of met-II, lower steric hindrance

between the ligands favors the presence of active centers in “racemic-like” conformer, which produce polypropylene of high isotacticity in the enantiomorphic-site mechanism. The microstructure of polypropylene prepared by met-II can be well explained by a concurrent two-sites model, in which one site follows the enantiomorphic-site model and the other follows the chain-end control model.

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