

Ethylene/Propylene Copolymerization Over Three Conventional C_2 -Symmetric Metallocene Catalysts: Correlation Between Catalyst Configuration and Copolymer Microstructure

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ABSTRACT: This work reports on a correlation between catalyst configuration and copolymer microstructure for ethylene/propylene (E/P) copolymerization using three conventional C_2 -symmetric metallocene catalysts, namely, *rac*-Et(Ind)₂ZrCl₂ (EBI), *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ (SiPh), and *rac*-CH₂(3-*t*Bu-Ind)₂ZrCl₂ (MBu), with MAO as a common cocatalyst. Copolymerization reactions were conducted in toluene at three different temperatures with varied E/P ratios. Some typically obtained copolymers were characterized in detail using ¹³C-NMR spectroscopy, by which triad distribution data were elaborated in a statistical method to determine the reactivity ratios (r_E and r_P) of the comonomers, which were also obtained by Fineman-Rose estimation. The production of alternating-like

copolymers from EBI is attributed to the rapid interconversion between two conformation states of the active site, one of which favors the incorporation of propylene but the other one does not. Both SiPh and MBu are structurally more rigid and of larger dihedral angles than EBI; however, SiPh which owns open active site conformation tend to produce random copolymers at all studied temperatures, and for MBu, sterically hindered catalyst, block-like copolymers were obtained. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3218–3226, 2010

Key words: ethylene/propylene copolymerization; copolymer microstructure; metallocene catalyst; catalyst configuration; association

INTRODUCTION

Ethylene/propylene (E/P) rubbery copolymers are important commercial products, especially as a rapidly growing class of elastomers, the so-called polyolefin elastomers (POE).^{1,2} One important application of these E/P copolymers is to be used as impact-strength modifiers in blends with isotactic polypropylene (iPP).^{3,4} Blending iPP with E/P copolymers will greatly widen iPP's properties envelopes and applications, because of the diversified compositions and microstructures of E/P copoly-

mers. The comonomer content, in particular, the comonomer distribution within and between single polymer chains determines the properties and performance of an E/P copolymer. So the synthesis of E/P copolymers with tailored structures, consequently designed properties becomes extremely significant.

Commercial polyolefins and their copolymers are usually produced by heterogeneous Ti-based and homogeneous V-based catalysts.⁵ For Ti-based heterogeneous catalysts, it is difficult to obtain E/P copolymers with uniform microstructure, because of the multiplicity of the catalytic centers. Some catalytic sites produce E/P copolymers with long crystallized ethylene segments affecting rubber performance. Certain active sites can conduct amorphous copolymers, however, the molecular weight is very low.⁶ So most of the commercial E/P copolymers are conducted with V-based catalysts, which are somewhat more suited than Ti-based catalysts.^{5,7–9} The open active site brings random E/P copolymers with high propylene content, a large number of inverted propylene units, and meso and racemic pairs, which prevent the formation of long crystallized ethylene or propylene sequences. So

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amorphous E/P copolymers are produced.^{10,11} Moreover, the single center nature of V-based catalytic systems allows the preparation of E/P copolymers with homogeneous copolymer structure.¹² However, for V-based catalysts, it is still of great difficulty to obtain E/P copolymers with tailored and varied structures due to the monotonous nature of the catalytic centers. Metallocenes, like traditional homogeneous V-based catalysts, can also produce E/P copolymers with narrow molecular weight distribution, high comonomer incorporation, and uniform compositional sequence.¹³ In addition, with respect to V-based catalysts metallocenes mark a dramatic change in the nature of the catalytic center, characterized not only by high homogeneous but also by diverse coordination environments defined by ligands.² This brings the opportunity to steer the behavior of the copolymerization and the characteristics of the copolymers by designing the structures of ligands. Therefore, a well understanding of the relationship between the structure or configuration of metallocene catalysts and their copolymerization behaviors is crucial for both industrial and academic researches.

Microstructures of ethylene/ α -olefin copolymers made by metallocene catalysts have been roughly studied as functions of central metal, ligand substitution pattern, and inter-annular bridge group.^{1,14–18} One common observation from these studies is that ansa-metallocenes with one- or two-membered bridge between the ligands have stronger ability to incorporate α -olefin comonomers than unbridged metallocenes. Other studies have shown that benzannelation of bridged indenyl ligands increases reactivity toward α -olefins.

This work reports on a specific correlation between catalyst structure and copolymer microstructure for E/P copolymerization using three conventional C_2 -symmetric metallocene catalysts, namely, [*rac*-Et(Ind)₂ZrCl₂] (EBI), [*rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂] (SiPh), and [*rac*-CH₂(3-*t*Bu-Ind)₂ZrCl₂] (MBu), with MAO as a common cocatalyst. These three catalysts are typical iPP-affording metallocene catalysts, which are expectable to be used in heterophasic PP copolymer production, for which E/P copolymerization is an essential step to build the dispersed E/P elastomeric phase. As such, a detailed investigation of correlation between catalyst structure and E/P copolymer microstructure is both necessary and interesting.

EXPERIMENTAL SECTION

Materials and instrumentation

All O₂ and moisture-sensitive manipulations were carried out inside an argon filled vacuum atmos-

phere dry-box equipped with a dry train. Chemical pure (CP) grade toluene was deoxygenated by argon purge before refluxing for 48 h and distilling over sodium. MAO (10 wt % in toluene) was purchased from Albermarle and used as received. The catalysts were either purchased from Aldrich (EBI) or synthesized according to published procedures (SiPh and MBu).^{19,20} Polymerization grade ethylene and propylene gasses were supplied by Yanshan Petrochemical Co. of China.

All ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AM-300 instrument in *o*-dichlorobenzene-d₄ at 110°C. The melting temperatures (T_m), heat of fusions (ΔH), and glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) using a PerkinElmer DSC-7 instrument controller. The DSC curves were recorded during the second heating cycle from –100 to 180°C with a heating rate of 10°C/min. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of u-Styragel HT columns of 10⁶, 10⁵, 10⁴, and 10³ pore size in series. The measurement was performed at 150°C with 1,2,4-trichlorobenzene as the eluent with a flow rate of 1.0 mL/min. Narrow molecular weight PS samples were used as standards for calibration. The molar proportion of ethylene and propylene units in E/P copolymers were determined by Nicolet 6700 FTIR spectrometer.²¹ The sample films were cast from their toluene solutions (~ 4 wt %) on the plates of KBr at a temperature of 100°C and were made sufficiently thin to obey the Beer-Lambert Law. The residual solvent was removed in a vacuum oven. Ethylene contents were calculated from the IR spectra by the following equation calibrated by some composition-known E/P copolymer standards: E mol% = 1.263–1.575 (A_{1379}/A_{1460}), where A_{1379} is the absorbance at 1379 cm^{–1} representing methyl groups from propylene units, and A_{1460} the sum of the absorbances of C–H bonds at 1460 cm^{–1} owing to both methylene and methyl groups from ethylene and propylene units together.

Copolymerization of ethylene with propylene

In a typical copolymerization reaction, a 250 mL glass reactor equipped with a magnetic stirrer was vacuumed for 30 min at 100°C and then charged with 50 mL anhydrous toluene and 2.83 mL (4.2 mmol) MAO/toluene solution under mixture of E/P, which was premixed in a 2-L gasholder. The gas was introduced first at 1 atm. After thermal equilibration of the reactor system at the preset reaction temperature, 1 mL toluene solution of the catalyst (2

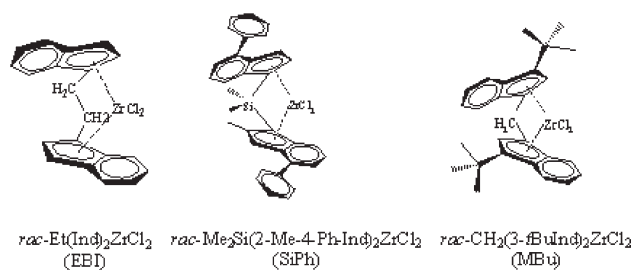


Figure 1 Structures of the catalysts.

μmol , MAO/Zr = 2120) was added into the reaction system. During the reaction, the mixture of ethylene and propylene was continuously supplied. The copolymerization was terminated after 15 min by adding acidic ethanol into the reactor. The precipitated product was isolated and washed with ethanol several times, then dried under vacuum at 50°C .

RESULTS AND DISCUSSION

In this study, three single-site metallocene catalysts with different ligand structures^{17,18} were chosen to perform E/P copolymerizations. The structures were shown in Figure 1. To study the association between the geometrical configurations of the metallocene catalysts and microstructures of the obtained E/P copolymers, a series of E/P copolymerizations were conducted over a wide range of temperatures and feed ratios.

As far as we know, polymerization temperature plays an important role in copolymerization by affecting the relative reactivities of comonomers as well as their intramolecular distributions. However,

systematic studies on the effect of temperature on E/P copolymerizations are rare in the literature.²² So in this article, behaviors of E/P copolymerization at 40, 60, and 80°C over a wide range of comonomer feed ratios with three metallocenes were concentrated on. Some typical copolymers were characterized in detail through ^{13}C -NMR spectra analysis. The investigation of particular temperature effect on E/P copolymerization and copolymer microstructures leads us to discover the correlation between catalyst configuration and copolymer microstructure and understand the mechanism of the copolymerization more deeply.

E/P copolymerization and copolymer characterization

E/P copolymerization reactions were performed with EBI, SiPh, and MBu catalysts at varied temperatures and E/P ratios. The polymerization results are summarized in Tables I–III, respectively. In each reaction, to keep a constant ratio of E/P in the course of the reaction, a reported technique was followed to keep the conversion of both monomers lower than 5%.^{17,23} E/P copolymers with ethylene contents ranging from 33 to about 95 mol %, calculated using FTIR spectra, were prepared.

The results of E/P copolymerizations with EBI/MAO were shown in Table I. At each temperature, the propylene molar content in copolymer increases with the decrease of E/P ratio in feed. In the same E/P ratios, copolymers produced at higher temperature have higher propylene content. The same results are obtained for E/P copolymerizations with

TABLE I
E/P Copolymerization with EBI/MAO^a

Run no.	Reaction temperature ($^\circ\text{C}$)	[E] in comonomer feed (mol/L)	E/P ^b (mol/mol) in liquid	Catalyst activity ($10^6\text{g/mol Zr}\cdot\text{h}$)	E ^c mol % in copolymer	P ^c mol % in copolymer	T_m ($^\circ\text{C}$)	ΔH (J/g)	T_g ($^\circ\text{C}$)
E1	40	0.090	1.8	2.50	0.942	0.058	84.2/102.8	188.5	-35.3
E2		0.083	1.0	3.68	0.889	0.111	55.9/95.6	109.9	-41.9
E3		0.075	0.60	2.51	0.850	0.15	42.0	55.1	-47.5
E4		0.060	0.30	2.60	0.681	0.319	–	–	-59.7
E5		0.043	0.15	2.95	0.599	0.401	–	–	-64.2
E6	60	0.087	1.8	1.74	0.878	0.122	47.4/101.1	110.2	-37.0
E7		0.078	1.0	1.28	0.809	0.191	20.5	52.4	-43.1
E8		0.067	0.60	2.17	0.730	0.27	–	–	-45.9
E9		0.050	0.30	3.63	0.592	0.408	–	–	-64.4
E10		0.034	0.15	2.54	0.508	0.492	–	–	-57.0
E11	80	0.082	1.8	2.89	0.827	0.173	24.5/97.4	104.7	-52.0
E12		0.071	1.0	3.79	0.705	0.295	10.0	43.1	-67.2
E13		0.059	0.60	4.12	0.612	0.388	–	–	-68.9
E14		0.041	0.30	3.39	0.507	0.493	–	–	-63.3
E15		0.027	0.15	2.11	0.421	0.579	–	–	-58.4

^a Polymerization conditions: toluene = 50 mL, Al/Mt = 2120 (mol/mol), [catalyst] = 2 μmol , total pressure = 1.0 atm, and polymerization time = 15 min.

^b E/P feed ratio (mol/mol) in liquid phase.

^c From FTIR analysis.

TABLE II
E/P Copolymerization with SiPh/MAO^a

Run no.	Reaction temperature (°C)	[E] in comonomer feed (mol/L)	E/P ^b (mol/mol) in liquid	Catalyst activity (10 ⁻⁶ g/mol Zr.h)	E ^c mol % in copolymer	P ^c mol % in copolymer	T _m (°C)	ΔH (J/g)	T _g (°C)
S1	40	0.090	1.8	4.12	0.937	0.063	89.5	109.5	-34.7
S2		0.083	1.0	4.64	0.847	0.153	44.8	80.0	-41.8
S3		0.075	0.60	2.92	0.754	0.246	30.0	27.1	-49.2
S4		0.060	0.30	4.88	0.599	0.401	-	-	-58.3
S5		0.043	0.15	3.44	0.460	0.54	-	-	-48.5
S6	60	0.087	1.8	3.32	0.879	0.121	69.7	100.9	-36.1
S7		0.078	1.0	3.5	0.744	0.256	41.1	29.7	-39.7
S8		0.067	0.60	2.96	0.660	0.34	-	-	-52.7
S9		0.050	0.30	1.18	0.530	0.47	-	-	-55.6
S10		0.034	0.15	0.92	0.402	0.598	-	-	-41.8
S11	80	0.082	1.8	4.46	0.792	0.208	32.6	43.3	-48.7
S12		0.071	1.0	2.96	0.663	0.337	-	-	-53.2
S13		0.059	0.60	4.38	0.578	0.422	-	-	-59.9
S14		0.041	0.30	4.08	0.454	0.546	-	-	-49.5
S15		0.027	0.15	2.94	0.336	0.664	-	-	-40.1

^a Polymerization conditions: toluene = 50 mL, Al/Mt = 2120 (mol/mol), [catalyst] = 2 μmol, total pressure = 1.0 atm, and polymerization time = 15 min.

^b E/P feed ratio (mol/mol) in liquid phase.

^c From FTIR analysis.

SiPh/MAO, as shown in Table II. When the E/P copolymerization is catalyzed by MBu/MAO, the results are not exactly the same and more complicated, shown in Table III. In the same E/P ratio higher than 0.15 in feed, copolymers with the highest propylene contents are obtained at 60°C, not 80°C like the others. When E/P ratio is 0.15, the propylene molar content of copolymer prepared at 60°C is no longer the highest, and the effect of reaction temperature on propylene content weakens. In other

words, when the propylene concentration in feed is not much higher than that of ethylene, there is an optimal temperature for the propylene insertion. Comparing the copolymerization performance of the three catalysts, we find that E/P copolymers produced by SiPh have the highest propylene content, while MBu prepares the copolymers with lowest propylene content in the same conditions.

DSC was used to study the thermal performance of E/P copolymers, and the results were also

TABLE III
E/P Copolymerization with MBu/MAO^a

Run no.	Reaction temperature (°C)	[E] in comonomer feed (mol/L)	E/P ^b (mol/mol) in liquid	Catalyst activity (10 ⁻⁶ g/mol Zr.h)	E ^c mol % in copolymer	P ^c mol % in copolymer	T _m (°C)	ΔH (J/g)	T _g (°C)
M1	40	0.090	1.8	2.00	0.952	0.048	96.5/110.1	104.8	-22.2
M2		0.083	1.0	3.24	0.917	0.083	69.6/105.8	97.4	-30.2
M3		0.075	0.60	3.08	0.854	0.146	51.3/101.2	60.4	-40.4
M4		0.060	0.30	2.10	0.749	0.251	82.9	15.1	-46.7
M5		0.043	0.15	1.56	0.577	0.423	56.9	1.1	-56.2
M6	60	0.087	1.8	2.18	0.908	0.092	69.9/107.7/112.4	85.0	-
M7		0.078	1.0	3.74	0.812	0.188	57.5/105.8	45.4	-11.8
M8		0.067	0.60	2.46	0.771	0.229	96.1	22.5	-49.7
M9		0.050	0.30	2.46	0.645	0.355	-	-	-62.2
M10		0.034	0.15	1.14	0.604	0.396	-	-	-58.0
M11	80	0.082	1.8	1.82	0.944	0.056	86.9/115.1	110.8	-
M12		0.071	1.0	1.48	0.898	0.102	66.6/107.4	67.6	-24.3
M13		0.059	0.60	0.80	0.845	0.155	58.6/94.6	46.8	-30.3
M14		0.041	0.30	0.38	0.731	0.269	37.4/71.8	20.1	-60.4
M15		0.027	0.15	0.30	0.650	0.350	-	-	-72.2

^a Polymerization conditions: toluene = 50 mL, Al/Zr = 2120 (mol/mol), [catalyst] = 2 μmol, total pressure = 1.0 atm, and polymerization time = 15 min.

^b E/P feed ratio (mol/mol) in liquid phase.

^c From FTIR analysis.

TABLE IV
Molar Mass and Polydispersity Index (PDI) of Some
Typical E/P Copolymers Obtained from GPC
Measurements

Run no.	Catalyst	Reaction temperature (°C)	M_n^a (10 ⁴ g.mol ⁻¹)	M_w^b (10 ⁴ g.mol ⁻¹)	PDI
E1	EBl	40	9.28	24.14	2.60
E6		60	6.09	11.02	2.42
E11		80	1.98	3.85	1.94
S1	SiPh	40	7.60	16.26	2.14
S6		60	5.16	10.79	2.09
S11		80	1.92	3.99	2.07
M1	MBu	40	13.67	40.01	2.93
M6		60	2.08	5.57	2.67
M11		80	1.66	3.33	2.00

^a Number average molar mass, calculated according to polystyrene.

^b Weight average molar mass, calculated according to polystyrene.

summarized in the three tables above. The increase of propylene contents within the scope of our study results in a sustained reduction of T_m and ΔH , and when the propylene content is low enough, there is no crystallization and the glass transition becomes visible. The E/P copolymers containing approximately 40 mol % propylene have the lowest T_g , which is consistent with Ref. 24.

Table IV shows the molar mass and polydispersity index (PDI) of some typical copolymers obtained at the same E/P ratio (1.8) in feed. For all of the catalysts, the increase of temperature leads to the decrease of molar mass and PDI. These can be attributed to the increase of chain transfer rate and the faster monomer diffusion at higher temperature, respectively.

Determination of reactivity ratios of comonomers

¹³C-NMR spectra was used to investigate the detailed microstructures of the typical copolymers, and in Figure 2, a ¹³C-NMR spectrum of sample-E8, selected as a representative copolymer, is shown. The assignment of all peaks was carried out according to the literatures.^{10,11,25-27} The terminology of Carman et al.²⁵ and Cheng¹¹ was used, where P, S, and T denoted primary (methyl), secondary (methylene), and tertiary (methine) carbons, respectively. The letters *m* and *r* referred to meso and racemic, respectively, in defining tacticity.¹¹ The position of a carbon relative to its nearest methine carbon bearing a methyl group was expressed by two Greek subscripts.

The ¹³C-NMR analyzes show that there are no significant head-to-head and tail-to-tail structures (inverted propylene sequences); therefore, the quantitative evaluation of the comonomer distribution at a triad level from ¹³C-NMR spectra is allowed. The results of the ¹³C-NMR characterization of typical

copolymers are collected in Table V. To eliminate the effect of comonomer content, the relative concentrations of the P and E centered triads, plotted as a function of the propylene and ethylene content, respectively, are reported. The number average sequence length (\bar{n}_E) of ethylene and the number average sequence length (\bar{n}_P) of propylene are also listed in Table V. A method, already reported in previous literature,²⁸ was used to elaborate these triads. The method allows one to identify the statistical model suitable for describing the copolymerizations and derive the reactivity ratios between the comonomers summarized in Table VI.

Herein, a first-order Markovian statistical model is adopted to determine the reactivity ratios of ethylene and propylene in E/P copolymerization with the three metallocene catalysts. This approach has been extensively applied to characterize the kinetics of olefin copolymerization.²⁹ According to this model, the insertion rate of a monomer is influenced by the last inserted monomer unit. So the reactivity ratios are derived: $r_E = k_{EE}/k_{EP}$, $r_P = k_{PP}/k_{PE}$, the ratio of the rate constant for the homopropagation reaction (k_{ii}) to the rate constant for the cross-propagation reaction (k_{ij}). r_E and r_P indicate the copolymerization capability, and the product $r_E r_P$ is an indicator of the comonomer sequence distribution. Reactivity ratios for each catalyst at different reaction temperatures were summarized in Table VI, which had been calculated experimentally from the triad distributions determined by ¹³C-NMR spectra according to the following two equations³⁰:

$$r_E = (2[\text{EEE}] + [\text{EEP}]) / ([2[\text{EPE}] + [\text{PPE}]](X_E/X_P))$$

$$r_P = (2[\text{PPP}] + [\text{PPE}]) (X_E/X_P) / (2[\text{EPE}] + [\text{PPE}])$$

Because of not being affected dramatically by the relative concentration of the comonomers, reactivity ratios at different temperatures were obtained from ¹³C-NMR spectra of only one copolymer of a typical composition. Meanwhile, Fineman-Ross method was

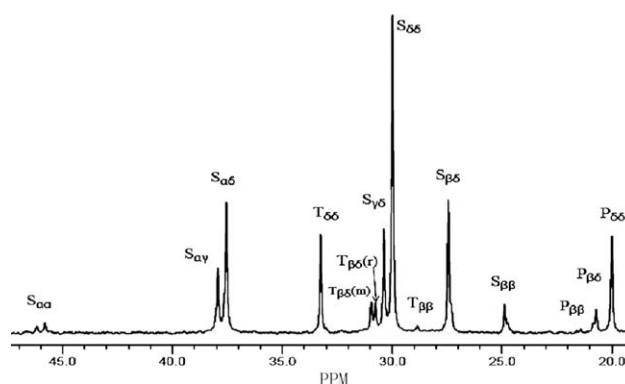


Figure 2 ¹³C-NMR spectra of sample-E8 produced by EBl.

TABLE V
¹³C-NMR Characterization of Typical E/P Copolymers Prepared with Different Metallocene Catalysts at Different Polymerization Temperatures

Run no.	Catalyst	Reaction temperature (°C)	E ^a	P ^a	PPP/P	PPE/P	EPE/P	EEE/E	EEP/E	PEP/E	\bar{n}_E	\bar{n}_P
E5	EBl	40	0.6151	0.3849	0.161	0.379	0.500	0.312	0.409	0.246	2.22	1.39
E9		60	0.5924	0.4076	0.140	0.380	0.480	0.308	0.455	0.246	2.11	1.45
E13		80	0.6202	0.3798	0.136	0.359	0.506	0.341	0.473	0.189	2.35	1.44
S4	SiPh	40	0.6239	0.3761	0.229	0.468	0.303	0.439	0.408	0.142	2.89	1.74
S8		60	0.6581	0.3489	0.219	0.462	0.319	0.496	0.403	0.110	3.21	1.70
S14		80	0.4322	0.4678	0.447	0.460	0.093	0.294	0.420	0.253	2.16	2.34
M5	MBu	40	0.6249	0.3751	0.289	0.433	0.278	0.501	0.399	0.085	3.51	2.11
M8		60	0.7707	0.2293	0.188	0.507	0.279	0.684	0.272	0.041	5.64	1.68
M13		80	0.8485	0.1515	0.125	0.426	0.450	0.745	0.204	0.025	7.84	1.40

^a Calculated according to Ref. 28.

also applied to calculate the monomers' reactivity ratios r_E and r_P .³¹ The results are also shown in Table VI. $F(f-1)/f$ and F^2/f have a reasonably good linear relationship, $F(f-1)/f = r_E(F^2/f) - r_P$, where F and f represent the molar concentration ratio of ethylene (E) to propylene (P) in the feed and copolymer, respectively. The slope and intercept are r_E and r_P , respectively. Comparing the results obtained from different methods, there is a gap between the two sets of r_E and r_P , especially the SiPh and MBu systems, even though they have the similar trend. According to the literature,² the results afforded by statistical method are more reliable with respect to the Fineman-Ross approach, which is based on the assumption of the validity of the ultimate effect. So the gap between the two sets of r_E and r_P indicates that there is a strong "penultimate effect" in the SiPh and MBu systems, which is referred by some authors for E/P copolymerizations.^{2,23,32-37} In this case, with respect to first-order Markovian statistical model, the second-order model allows a better fitting with experiment data. On the basis of literature,³²⁻³⁷ model selection seems not to affect the interpretation of experimental data; therefore, the results from first-order Markovian model are still analyzed in detail.

In general, $r_E > r_P$, this indicates that ethylene insertion is preferred when either ethylene or propylene is the last inserted unit. According to the reactivity ratio product $r_E r_P$, it can be considered that EBl, SiPh, and MBu conduct alternating-like, nearly random, block-like E/P copolymers, respectively. In E/P copolymers produced by EBl, EPE/P is nearly closed to 0.5, the PEP/E is relatively higher than the other two catalysts, and the value of \bar{n}_P is the lowest. These all indicate that propylene exits mainly in the form of single insertion at all reaction temperatures studied. These polymers are the so-called alternating-like E/P copolymers. With regard to the distribution of the propylene units in E/P copolymers, propylene mostly presented itself in the form of PPE for both SiPh and MBu, but about ethylene distribution, EEE is the predominant form for copolymers produced by MBu, which can be considered as block-like copolymers. In addition, random copolymers were formed by SiPh.

About temperature effect on reactivity ratios and copolymer microstructure, it is different from each other for three catalysts. For EBl, the increase of copolymerization temperature causes a decrease of r_E and an increase of r_P , as a consequence, an almost

TABLE VI
 Reactivity Ratios Determined by ¹³C-NMR and Fineman-Rose Method for E/P Copolymerizations with Different metallocene Catalysts at Varied Temperatures

Catalyst	Reaction temperature (°C)	Determined by ¹³ C-NMR			Determined by Fineman-Ross method		
		r_E	r_P	$r_E r_P$	r_E	r_P	$r_E r_P$
EBl	40	8.03	0.08	0.64	7.76	0.08	0.62
	60	4.09	0.19	0.78	3.68	0.10	0.37
	80	2.31	0.27	0.62	2.41	0.29	0.70
SiPh	40	6.66	0.26	1.73	5.53	0.21	1.16
	60	4.09	0.49	2.00	2.35	0.15	0.35
	80	3.82	0.55	2.10	1.87	0.27	0.50
MBu	40	15.8	0.15	2.37	11.5	0.16	1.84
	60	7.8	0.41	3.20	5.21	0.28	1.46
	80	12.0	0.30	3.60	8.60	0.09	0.77

constant value of $r_E r_P$ product is obtained. Meanwhile, the triad distributions are affected a little. For SiPh, a decrease of r_E and an increase of r_P also occur with the increase of copolymerization temperature, meanwhile the increase of reaction temperature has a great effect on E/P copolymers microstructure. At 80°C, PPP/P increases rapidly to 0.447 from 0.219 at 60°C. A different behavior by increasing polymerization temperature was observed with MBu. At 60°C, r_E and r_P achieve minimum and maximum, respectively, indicating that 60°C is the optimal temperature for propylene to incorporate during the temperatures studied, neither the highest nor the lowest. This was already concluded above. Higher temperature brings out the reduction of PPP/P and PEP/E and the addition of EEE/E and EPE/P, indicating that the increase of temperature is not conducive to the incorporation of propylene in some ways and decreases the blockiness of propylene. The decrease of \bar{n}_P as the rise of copolymerization temperature also proves the above conclusions.

Correlation between catalyst configuration and copolymer microstructure

Obviously, under the adopted conditions, SiPh gives the highest incorporation of propylene, and MBu gives the lowest. In addition, although all of the three metallocenes are isospecific catalysts for propylene polymerization, the style of E/P copolymerization is different from each other, corresponding to alternating-like, random and block-like E/P copolymers, respectively. However, why does this occur? The analysis is as follows one by one.

For EBI, propylene mostly presents itself in the form of EPE whatever the reaction temperature was, but higher reaction temperatures gives rise to higher propylene contents, which is indicated by smaller r_E and larger r_P at higher temperatures. These results are attributed to the flexibility of the ethylene bridge in EBI. Ziegler³⁸ has proved that, in solution, there is a rapid (NMR time scale) interconversion between the Π (indenyl-forward) and Y (indenyl-backward) conformations of the active site as shown in Figure 3. Conformation Y leads to an opened active site in favor of the insertion of propylene; however, the structural-congested Π much favors ethylene insertion than propylene. Obviously, this interconversion is the cause of the alternating-like sequence of the copolymer. When the conformation of active site is Y, a propylene molecule inserts into the copolymer chain. Following that, the active site turns to conformation Π , which makes it difficult for propylene to insert continuously but easy for ethylene, therefore, alternating-like E/P copolymers are obtained. At higher polymerization temperatures, this equilibrium shifts toward higher energy conformation Y; hence

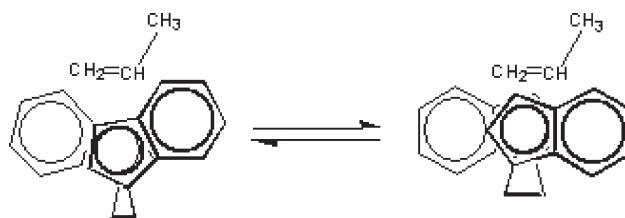


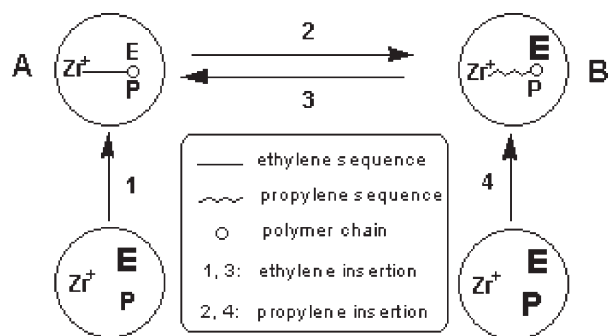
Figure 3 Π and Y conformations of active site formed by EBI.

under those conditions conformation Y is predominant, which leads more propylene to insert. As a result, E/P copolymers with highest propylene content are produced. Meanwhile, the higher temperature makes the interconversion faster; however, the interconversion between the Π (indenyl-forward) and Y (indenyl-backward) conformations is still going. Therefore, EBI produces alternating-like E/P copolymers at any given temperatures.

For MBu, propylene contents are generally low in the products and ethylene exists mainly in a sequence of homotriad EEE, implying that propylene is difficult to insert. As viewed from the openness of the large dihedral angle between the indenyl planes, these results seem difficult to understand. The dihedral angle between the indenyl planes of MBu (76.4°)²⁰ is larger than those of EBI (48.6°)³⁸ and SiPh (59.2°),¹⁹ which should favor the insertion of propylene. Eventually, it is the bulky substituent group of *tert*-butyl of MBu that makes active site much congested for larger monomer like propylene to insert.¹⁷

In addition, we also found that in MBu system, propylene units in the copolymers, even in small amounts, tend to arrange in a consecutive way to form mini-blocks within polymer chains, and there is a strong penultimate effect, which is widespread for many metallocenes and is reported by some authors.^{32–37} Losio et al.³³ consider the “penultimate effect” as the influence of penultimate unit on the insertion rate of a monomer. In comparison with “ultimate effect,” “penultimate effect” should be so smaller that it can be ignored, because the distance between penultimate unit and active site is much longer. So we attribute “penultimate effect” to comonomer concentration fluctuation around the catalytic center, which is caused by comonomer insertion and diffusion which decreases and increases the instantaneous comonomer concentration, respectively. When continuous insertion of a certain comonomer is done, its concentration around active site decreases due to that reduced concentration by consumption is greater than increased concentration by diffusion.

Taking E/P copolymerization as an example, the comonomer concentration fluctuation around the catalytic center during copolymerization is shown in Scheme 1. As shown for any E/P copolymerization, apart from the very beginning Process 1 or 4,



Scheme 1 The comonomer concentration fluctuation around the catalytic center during E/P copolymerization.

copolymerization almost is the circulatory reaction of Process 2 and 3. In Process 3, during the insertion reaction of ethylene, its concentration around active site becomes lower and lower until propylene begins to insert, indicating entering Process 2. In Process 2, because of the insertion of propylene and the diffusion of ethylene, each propylene insertion reaction is carried out in environments of different comonomers concentration until the insertion of ethylene begins. The cyclical process is repeated up to the end of reaction. So the insertions of adjacent unite at different monomer concentrations cause the “penultimate effect.” In analogy, there may be antepenultimate effect and so on. The more difficult it is for propylene to insert, the larger the amplitude of concentration fluctuation is. Consequently, “penultimate effect” is more obvious and the E/P copolymer is blockier, as a result of the higher propylene concentration around active site with respect to ethylene at some moment. Herein, among the three catalysts, the propylene copolymerization ability of MBu is worst, attributed to the bulky substituent group of *tert*-butyl of MBu making active site crowded for propylene to insert. Therefore, the “penultimate effect” for MBu is strongest and block-like E/P copolymers are obtained.

In addition, the model of comonomer concentration fluctuation can also explain that the change of E/P ratio in feed and solvent have few effect on reactivity ratios intramolecular distribution, over a broad range of monomer concentrations, which makes it possible to obtain the same comonomer distribution exploring different polymerization bath conditions in industry.³⁴

Generally, the activation energy of propylene insertion is higher than that of ethylene insertion,³⁹ therefore, propylene content in the copolymer should increase with the increasing of polymerization temperature. However, as outlined in Figure 4, there is also a conformation diversification while increasing temperature. The *tert*-butyl group rotates faster at higher temperatures, which will occupy more space around the quaternary carbon and hence hinders propylene insertion. Combining both the activation energy and steric

effect arguments, we explained the polymerization results that there is an optimal temperature for maximum propylene incorporation when E/P ratio is higher than 0.15 and in this article it is 60°C. As temperature rises from 40°C to 80°C with MBu, the faster rotation of *tert*-butyl group makes the active center more congest and increases the difficulty of propylene insertion, especially continuous insertion, so PP blocks tend to be shorter, and activity of MBu at 80°C decreases dramatically as E/P ratio decreases. In addition, such a large steric hindrance causes the lowest molar mass at 80°C.

When the E/P ratio is lower than 0.15, the propylene content of copolymer conducted at 60°C no longer maintains the highest, and the temperature effect on propylene content in copolymer is weakened. These are explained as follows: At 40°C, the lowest rotation of *tert*-butyl group makes it easiest for propylene to coordinate, and 80°C is most conducive to the propagation of propylene, as a result, these prominent advantages for propylene insertion display significantly when propylene concentration is much higher than ethylene concentration.

For SiPh, as a whole, the comonomer distribution in polymer chain is in a more random fashion relative to those from other two catalysts. In addition, higher temperature favors the insertion of propylene. As for copolymers microstructures, temperature effect is obvious: at 40 and 60°C, PPE is the primary form for propylene existing in copolymer; however, at 80°C, PPP becomes predominant. The rigid and open structure of active site formed by SiPh, resulting from the large dihedral angle between the indenyl planes and no substitute group at 3-position of the indene ligands, is proposed to explain these. The active site is so open that there is no obstructive for propylene to coordinate and then propagate like ethylene, besides, the chance of coordination to site is random, so propylene units exit in E/P copolymers in a more random form.

In fact, insertion of propylene requires two steps: propylene coordination and propagation. As long as catalyst is active for propylene polymerization, it allows an easy propylene propagation to have the formation of propylene sequences, and an increase of temperature favors propylene propagation because the activation energy of propylene insertion is higher than that of ethylene insertion. So in combination with the findings reported in the literature and in this article, the first step-propylene

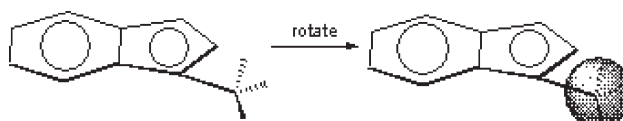


Figure 4 Rotation of *tert*-butyl group in MBu.

coordination is considered the key to determine the type of copolymers. Based on this, we have tried to find the correlation between catalyst configuration and copolymer microstructure. If metallocene has two kinds of active sites, one of which favored the coordination of propylene but the other one did not, the catalyst favors to conduct alternating-like copolymers like EBI and *meso*-(EBDMI)ZrCl₂.^{32–37} For catalysts with open active site conformation, the coordination capacity of propylene is similar to ethylene, so the probabilities of ethylene and propylene coordination are mainly determined by comonomer concentration. In consequence, the catalysts as SiPh and the so-called “constrained geometry” half-sandwich complex tend to produce random copolymers.⁴⁰ Block-like copolymers are obtained by sterically hindered catalyst such as MBu and *rac*-CH₂(3-*t*Bu-Cp)₂ZrCl₂.² For these catalysts, the coordination of propylene is difficult. Only when ethylene instantaneous concentration around active site is very low with respect to propylene, propylene begins to insert continuously until ethylene concentration is sufficiently high as a result of its diffusion, consequently ethylene starts reaction.

CONCLUSIONS

In this work, a correlation between catalyst configuration and copolymer microstructure was investigated through ethylene/propylene (E/P) copolymerization using three conventional C₂-symmetric metallocene catalysts, namely, *rac*-Et(Ind)₂ZrCl₂ (EBI), *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ (SiPh), and *rac*-CH₂(3-*t*Bu-Ind)₂ZrCl₂ (MBu). For each catalyst, E/P copolymerization was studied by varying both polymerization temperatures and E/P molar ratios. It was found that EBI turned to produce alternating-like E/P copolymers, which was attributed to the rapid interconversion between two conformation states of the active site, one of which favored the incorporation of propylene but the other one did not. And both SiPh and MBu were structurally more rigid and of larger dihedral angles than EBI; however, SiPh which owns open active site conformation tended to produce random copolymers at all studied temperatures, and for MBu, sterically hindered catalyst, block-like copolymers were obtained.

References

- Fan, W.; Leclerc, M. K.; Waymouth, R. M. *J Am Chem Soc* 2001, 123, 9555.
- Galimberti, M.; Piemontesi, F.; Fusco, O.; Camurati, I.; Destro, M. *Macromolecules* 1998, 31, 3409.
- Mirabella, J. F. M. *Polymer* 1993, 34, 1729.
- D’Orazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G.; Masari, P. *Polymer* 1993, 34, 3671.
- Natta, G.; Pasquon, I.; Zambelli, A. *J Am Chem Soc* 1962, 84, 1488.
- Dy, H. *Polypropylene: Principle, Process and Technology*; China Petrochemical Press: Beijing, 2002.
- Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J Am Chem Soc* 1962, 84, 1688.
- Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* 1975, 8, 687.
- Zambelli, A.; Sessa, I.; Grisi, F.; Fusco, R.; Accomazzi, P. *Macromol Rapid Commun* 2001, 22, 297.
- Randall, J. C. *Macromolecules* 1978, 11, 33.
- Cheng, H. N. *Macromolecules* 1984, 17, 1950.
- Zucchini, U. D. O. T.; Resconi, L. *Indian J Technol* 1993, 31, 247.
- Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew Chem Int Ed* 1995, 34, 1143.
- Chien, J. C. W.; He, D. W. *J Polym Sci A Polym Chem* 1991, 29, 1585.
- Lehtinen, C.; Löfgren, B. *Eur Polym J* 1997, 33, 115.
- Kravchenko, R.; Waymouth, R. M. *Macromolecules* 1998, 31, 1.
- Galimberti, M.; Piemontesi, F.; Mascellani, N.; Camurati, I.; Fusco, O.; Destro, M. *Macromolecules* 1999, 32, 7968.
- Reyback, S. E.; Meyer, A.; Waymouth, R. M. *Macromolecules* 2002, 35, 637.
- Spaleck, W.; Kueber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* 1994, 13, 954.
- Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S.; Mercandelli, P.; Sironi, A. *Organometallics* 2000, 19, 420.
- ASTM 3900–05³.
- Yoon, J. S.; Lee, D. H.; Park, E. S.; Lee, I. M.; Park, D. K.; Jung, S. O. *J Appl Polym Sci* 2000, 75, 928.
- Galimberti, M.; Destro, M.; Fusco, O.; Piemontesi, F.; Camurati, I. *Macromolecules* 1999, 32, 258.
- Dong, J. Y.; Hong, H.; Chung, T. C.; Wang, H. C.; Datta, S. *Macromolecules* 2003, 36, 6000.
- Carman, C. J.; Harrington, R. A.; Wilkes, C. E. *Macromolecules* 1977, 10, 536.
- Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatake, T. *Macromolecules* 1982, 15, 1150.
- Wang, W. J.; Zhu, S. *Macromolecules* 2000, 33, 1157.
- Sun, Z.; Yu, F.; Qi, Y. *Polymer* 1991, 32, 1059.
- Odian, G. *Principles of Polymerization*; Wiley: New York, 1991.
- Fink, G. R. W. In *Polymer Handbook (Copolymerization Parameters of Metallocene-catalyzed Copolymerizations)*; Wiley: New York, 1999.
- Kelen, T.; Tüdös, F. *React Kinet Catal Lett* 1974, 1, 487.
- Herfert, N.; Montag, P.; Fink, G. *Makromol Chem* 1993, 194, 3167.
- Losio, S.; Piemontesi, F.; Forlini, F.; Sacchi, M. C.; Tritto, I.; Stagnaro, P.; Zecchi, G.; Galimberti, M. *Macromolecules* 2006, 39, 8223.
- Galimberti, M.; Piemontesi, F.; Baruzzi, G.; Mascellani, N.; Camurati, I.; Fusco, O. *Macromol Chem Phys* 2001, 202, 2029.
- Busico, V.; Cipullo, R.; Segre, A. L. *Macromol Chem Phys* 2002, 203, 1403.
- Karssenber, F. G.; Piel, C.; Hopf, A.; Mathot, V. B. F.; Kaminsky, W. *J Polym Sci B Polym Phys* 2005, 44, 747.
- Karssenber, F. G.; Wang, B.; Friederichs, N.; Mathot, V. B. F. *Macromol Chem Phys* 2005, 206, 1675.
- Piemontesi, F.; Camurati, I.; Resconi, L.; Balboni, D.; Sironi, A.; Moret, M.; Zeigler, R.; Piccolrovazzi, N. *Organometallics* 1995, 14, 1256.
- Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem Rev* 2000, 100, 1253.
- Maurizio, G.; Nicoletta, M.; Fabrizio, P.; Isabella, C.; Galimberti, M.; Mascellani, N.; Piemontesi, F.; Camurati, I. *Macromol Rapid Commun* 1999, 20, 214.