

Effect of Polymerization Temperature on Propylene Polymerization with C_s -symmetric Metallocene Catalyst

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Abstract: A novel highly active C_s -symmetric metallocene catalyst namely: *meso*-dimethylsilylbis(2,4,6-trimethyl-1-indenyl)zirconium dichloride is presented. The effect of polymerization temperature (0–70 °C) on the catalyst performance for propylene polymerization has been investigated. This catalyst shows very high activity at 50 °C which is higher than the activity of the racemic analogue, and the resulted polypropylene is amorphous in nature with isotactic pentad content [mmmm] of 12 %.

Keywords: Polymerization, metallocene catalyst, propylene.

The synthesis of bridged *ansa* metallocenes usually gives a diastereomeric mixture of racemic and *meso* metallocene isomers and in many cases the *meso* form is about 50 % of the product of metallocene synthesis^{1,2}. The amount of desired racemic isomer is rather poor and can be separated from the *meso* isomer by fractional crystallization³. The racemic *ansa*-metallocene isomer acts as catalyst for propylene polymerization to produce isotactic polypropylene (PP) while the corresponding *meso* isomer gives atactic PP due to its lack of stereoselectivity⁴. The *meso* isomer is considered as unwanted product due to its low activity and low molecular weight of the polymer. Collins *et al.* separated the racemic and *meso* isomer of ethylene bis(tetrahydroindenyl)zirconium dichloride⁵. The pure *meso* isomer of this complex, when activated with MAO, produced atactic PP at 40 °C with molecular weight (M_w) of about 2400, at activity of 630 kg-PP/mol-Zr⁵.

We synthesized a novel bridged *ansa*-metallocene catalyst, namely, dimethylsilylbis(2,4,6-trimethyl-1-indenyl) zirconium dichloride and separated its *meso* and racemic forms by fractional crystallization. The influence of T_p on the *meso* isomer of this catalyst for propylene polymerization is reported.

Experimental

Methylaluminoxane (10 wt.-% toluene solution, Albemarle Co.) was used as received. Toluene was refluxed over Na-benzophenone ketyl under nitrogen atmosphere before use. All procedures in the synthesis, purification of zirconocenes and polymerization process were carried out in argon atmosphere using the Schlenk techniques. Ligand of the zirconocene was synthesized by the method reported in our previous work⁶.

Polymerization grade propylene was further purified by passing it through a column containing supported MnO and over activated 4A molecular sieve column.

The polymerization of propylene was carried out in a 250 mL glass reactor equipped with propylene inlet and magnetic stirrer. After the reactor was flushed with argon, toluene (100 mL) was injected into the reactor with a syringe at required temperature followed by introducing propylene gas to saturate the solvent and maintain at constant pressure of 0.1 MPa. Appropriate amount of MAO was added to the reactor and polymerization was initiated by adding the solution of metallocene in toluene.

¹³C NMR spectra of the polymer were recorded on a Bruker dmx-500 spectrometer at 120°C. The polymer solution (15 wt.-%) was prepared in *o*-dichlorobenzene-*d*₄. The intrinsic viscosity of the polymer was determined in decalin as solvent at 135 °C using Ubbelohde viscometer and the molecular weight (M_w) were calculated by the following equation ⁷: $[\eta] = 1.1 \times 10^{-4} [M_w]^{0.8}$.

Results and Discussion

A mixture of racemic and meso forms of the bridged π -ligand substituted zirconocene was obtained from the reaction of dilithio salt of the ligand (I) with ZrCl₄ in CH₂Cl₂ (Scheme 1). The pure meso form (*meso*-II) and pure racemic form (*rac*-II) was obtained by fractional crystallization from toluene ⁸.

The effect of polymerization temperature T_p on the polymerization behaviors of *meso*-II is shown in **Table 1**. The catalyst activity was very sensitive to the change of T_p . It increases as the T_p increases and the maximum activity is obtained at 50 °C. The activity is higher than the activity obtained by the corresponding racemic isomer. In the study of similar zirconocenes for propylene polymerization, Kaminsky *et al* ⁹. and Spaleck *et al* ¹. reported that the *meso*-zirconocene showed much lower activity than the corresponding racemic isomer. For example, propylene polymerization activity by *meso*-Me₂Si(2-Me-4,6-*i*-Pr₂Ind)₂ZrCl₂ was only 6.4 % of the activity by the racemic zirconocene ⁹. The molecular weight of PP by the *meso* catalyst was also found to be much lower than PP by the racemic one. Other zirconocenes which show such differences between the *meso*- and *rac*-isomer include: Me₂Si(Ind)₂ZrCl₂, Me₂Si(2-MeInd)₂ZrCl₂, Me₂Si(2-Me-4-*i*-PrInd)₂ZrCl₂ and Me₂Si(2-Me-4-NaphInd)₂ ZrCl₂. Therefore, the relatively high polymerization activity and polymer molecular weight observed for the *meso*-II is quite unusual. This phenomenon may be the result of the basically symmetrical spacial arrangement of the methyl groups at 2- and 6-positions of the ligand around the central metal. A detailed molecular mechanics analysis of the catalysis may provide more definite evidences. As indicated by Spaleck *et al.* ¹, the behaviors of *ansa*-metallocene as polymerization catalyst can not be rationally explained in many cases. This may mean that we need to find out those more subtle factors in the structure of metallocene and in the catalysis process, which play important role in special cases. Such work may result in surprising improvement of the catalysts.

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Table 1. Effect of polymerization temperature T_p on catalytic activity and polymer properties

Cat	T_p (°C)	[Zr] μmol/L	Yield (g)	Activity ^{a)}	M_w ($\times 10^{-3}$)	T_m ^{b)} (°C)	mmmm ^{c)}
meso- II	0	40	0.20	50.0	48.1	amorphous	- ^{d)}
meso- II	20	40	1.01	252.5	45.1	amorphous	- ^{d)}
meso- II	30	40	1.61	402.5	25.3	amorphous	8.9
meso- II	50	40	17.32	4330.0	17.9	amorphous	13.2
meso- II	70	40	12.18	3045.0	10.6	amorphous	12.1
rac- II	50	20	6.28	3141.0	20.2	146	91.0
rac- II	70	20	8.20	4100.0	12.8	128	71.3

Polymerization conditions: toluene = 100 mL; Al/Zr = 2000; time = 1 h;

a) in kg-PP/mol-Zr.h ; b) measured by DSC; c) determined by ^{13}C NMR spectroscopy; d) not measured.

Polypropylene obtained by *meso-**II*** is basically stereorandom at all T_p . The methyl pentad distribution of PP produced by *meso-**II*** is summarized in **Table 2**. It can be concluded from the pentad intensities at 50 °C that the polymer propagation is controlled by the chain-end control model ($4[\text{mm}][\text{rr}]/[\text{mr}]^2 = 1.07$) than to the enantiomeric-site control model ($2[\text{rr}]/[\text{mr}] = 0.78$). The heterotactic triad population is $[\text{mr}] = \sim 0.50$, for perfectly random statistics.

Table 2. Methyl pentad distribution of polypropylene

catalyst	T_p (°C)	mmmm	mmmr	rmmr	mmrr	xmrx	mrrr	rrrr	mrrr	mrrm
meso- II	30	8.9	13.0	7.8	11.6	23.7	14.2	4.3	10.5	6.0
meso- II	50	13.2	12.8	7.0	10.9	23.6	13.6	4.2	8.6	6.0
meso- II	70	12.1	12.1	6.5	12.2	23.5	12.6	5.2	9.8	6.1
rac- II	50	91	3.6	0	2.5	1.6	0.7	0	0	0.5

Polymerization conditions are the same as in table 1, $\text{xmrx} = \text{mrrm} + \text{rmmr}$

The polymer obtained at 50 °C was extracted by refluxing diethyl ether and 18.8 wt % of the polymer was insoluble. The ^{13}C NMR spectrum of the diethyl ether insoluble fraction has the methyl pentad distributions $[\text{mmmm}] = 42.6$, $[\text{mmmr}] = 11.0$, $[\text{rmmr}] = 4.5$, $[\text{mmrr}] = 7.9$, $[\text{mrrm}] + [\text{rmrr}] = 13.9$, $[\text{mrrr}] = 7.8$, $[\text{rrrr}] = 2.8$, $[\text{mrrr}] = 6.3$, $[\text{mrrm}] = 3.1$, the triad population of $[\text{mm}] = 58.1$, $[\text{mr}] = 29.6$ and $[\text{rr}] = 21.2$ while the M_w is 31.9×10^{-3} and T_m is 137.9 °C. The polymer obtained at $T_p = 50$ °C was also extracted with boiling heptane and gave 98.4 % heptane soluble fraction and only 1.6 % heptane insoluble fraction.

Moreover, all the samples obtained by *meso-**II*** at different T_p contained no regioirregularity due to 2,1- or 1,3-insertion as compared to the polymer obtained with its corresponding *rac-**II*** isomer which contains 0.42 % 2,1-insertion and 0.17 % 1,3-insertion.

In conclusion, the activity of *meso-**II*** for propylene polymerization has been found to be very sensitive to polymerization temperature. Very high activity was observed at 50 °C and higher temperature, which is even higher than the activity of the corresponding *rac-**II*** analogue. The polymer molecular weight by *meso-**II*** was also not much different from that by *rac-**II***. This is a novel phenomenon different from similar systems reported in

literature. High activity and polymer molecular weight make the *meso*-**II** a potentially practical catalyst for producing atactic-PP.

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References and notes

- 1 W. Spaleck, M. Aulbach, B. Bachmann, F. Kuber and A. Winter, *Macromol. Symp.* **1995**, *89*, 237.
- 2 H. Wiesenfedt, A Reinmuth, E. Barsties, K. Evertz and H.H. Brintzinger, *J. Organomet. Chem.*, **1989**, *369*, 359.
- 3 W. Kaminsky, O. Rabe, A.M. Schauwienold, G.U. Schupfner, J. Hanss and J. Kopf, *J. Organomet. Chem.*, **1995**, *497*, 181.
- 4 H.H. Brintzinger, D. Fischer, R. Muhlhaupt B. Rieger and R. M. Waymouth, *Angew. Chem.Int. Ed. Engl.*, **1995**, *34*, 1142, and references therein.
- 5 S. Collins, W.J. Gauthier, D.A. Holden, B.A. Kuntz, N.J. Taylor, and D.G. Ward, *Organometallics*, **1991**, *10*, 2061.
- 6 T. Yasin, Z.Q. Fan, L.X. Feng, *Chemical Res. Chinese Univ.*, **1999**, *15*(3), 281.
- 7 Kinsinger, J.B. and Hugres, R.E, *J. Physico Chemistry*, **1959**, *63*, 2001.
- 8 ¹H NMR of *meso*-dimethylsilylbis (2,4,6-trimethyl-1-indenyl)ZrCl₂ (CDCl₃, 25 °C) δ = 7.25 (s, 2H), 6.68 (s, 2H), 6.55 (s, 2H), 2.42 (s, 6H), 2.28 (s, 6H), 2.16 (s, 6H), 1.42 (s, 3H), 1.19 (s,3H).
- 9 W. Kaminsky, A.M. Schauwienold, F. Freidanck, *J. Mol. Catal. A: Chemical*, **1996**, *112*, 37.

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