

METALLOCENE POLYETHYLENES WITH BROAD OR BIMODAL MOLECULAR WEIGHT DISTRIBUTION*

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Abstract Seven new binuclear titanocenes with different linking bridges, unsubstituted or substituted on the Cp rings, were synthesized and tested for their effect on ethylene polymerization in the presence of MAO. The polyethylenes thus obtained had broad MWD or even bimodal GPC curves, as compared with that from two reference mononuclear titanocenes. This is explained by the difference in degree of steric hindrance around the active center sites imposed by the bulky substituted ligands assuming different configurations in the rotation of the catalyst molecules. Lower polymerization temperatures alleviate the effect of these configuration differences, as reflected in change in MW and $\overline{M}_w/\overline{M}_n$. This effect is not caused by decomposition or disproportionation of the binuclear titanocenes as evidenced by the stability of the catalyst.

Keywords Metallocene polyethylene; Binuclear titanocenes

INTRODUCTION

An outstanding feature of polyolefins synthesized with metallocene catalysts is their narrow molecular weight distribution (MWD) as a result of their single-sited active-centers. This feature, though unique in distinguishing them from other polyolefins with usual Ziegler-Natta catalysts, is undesirable and even detrimental to polymer processing. Efforts have been made in industrial circles to modify this molecular parameter to maximize polymer processibility.

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Organometallic chemistry has given enormous impetus in each phase of the development of metallocene catalysts, and it is also greatly benefited by the expeditious advance in the fastest growing phase of polymer materials science. Numerous new metallocenes have been synthesized and tested in correlating molecular structure and polymerizability. We noticed bridged binuclear metallocenes^[1~4], few of which are that of Group IV elements (e.g. $[X(C_5H_4)_2][(C_5R_5)ZrCl_2]_2$ ($X=CH_2$ or $SiMe_2$ and $R=H$ or Me)^[5], $(C_5H_4SiMe_2C_5H_4)(C_5H_4XMe_2C_5H_4)(TiCl_2)_2$ ($X=C$, Si)^[6], $[CpTiCl_2(C_5H_4)]_2XMe_2$ ($X=C$, Si)^[6]), but information on their behavior in olefin polymerization is unavailable. In this paper we report the syntheses of binuclear metallocenes and their unique effect on MWD of the polyethylenes, either broad MWD or bimodal MWD are obtained.

EXPERIMENTAL

Preparation of bridged ligands

Seven binuclear titanocenes (Fig. 1) were prepared as follows in the traditional

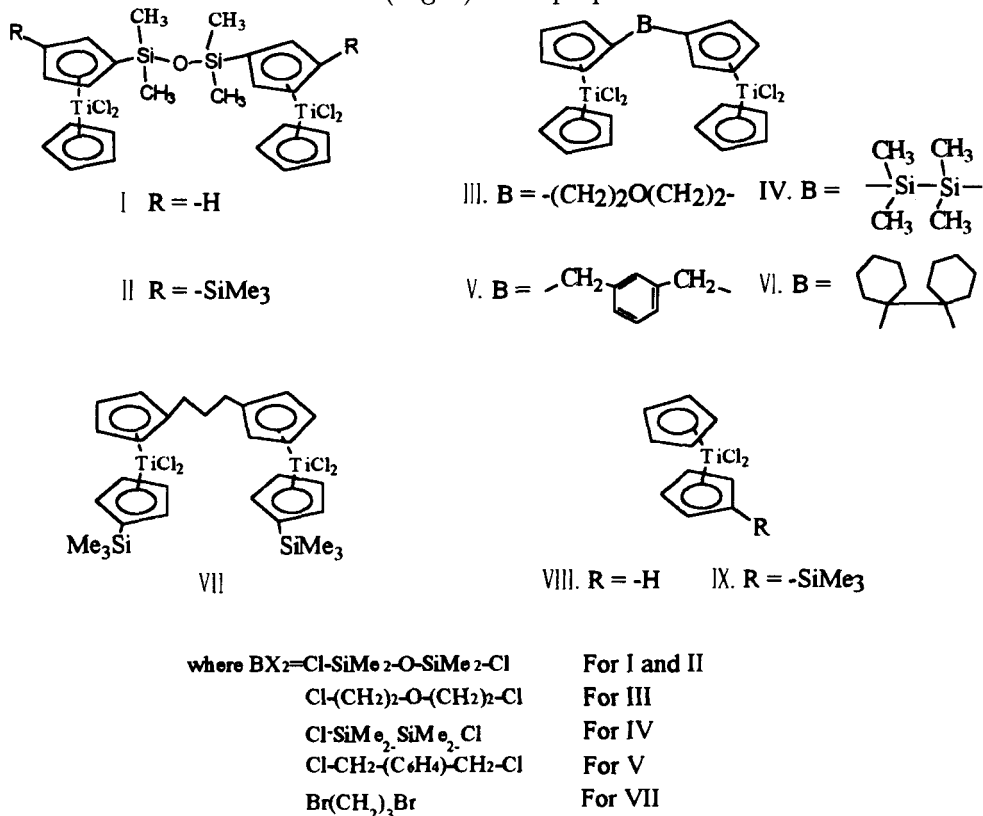


Fig. 1 Binuclear titanocenes I-VII for ethylene polymerization (VIII and IX are reference mononuclear titanocenes)

manner (Fig. 2). For I and II, see literature^[7].

These α, ω -dihalo compounds were (vacuum) distilled before use. Compounds CpTiCl_3 ^[8], CpSiMe_3 ^[9], Cp_2TiCl_2 ^[10], $\text{C}_5\text{H}_4\text{SiMe}_3\text{TiCl}_3$ ^[8], and $\text{Cp}(\text{C}_5\text{H}_4\text{SiMe}_3)\text{TiCl}_2$ ^[9] were synthesized according to literature. The intermediate for VI was synthesized as described in the literature^[11].

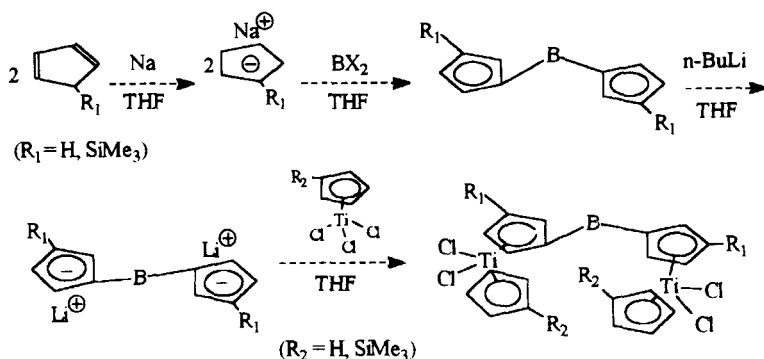


Fig. 2 Scheme of binuclear titanocene syntheses

Preparation of lithium salts of the ligands

The precursor dilithium salts were synthesized, as exemplified for unsubstituted (VII), in the following manner.

Forty mL of a tetrahydrofuran solution of cyclopentadienylsodium (CpNa) were put in a 100 mL three-necked round-bottom flask equipped with a dropping funnel and a bulb condenser. To the ice-cooled solution were added dropwise 7.13 mL (0.07 mol) of 1,3-dibromopropane. The resulting light pink solution after being reacted for 3 h at room temperature was hydrolyzed with a saturated aq. NH_4Cl solution. The organic layer was separated and dried with Na_2SO_4 and CaH_2 . After removal of the solvent at room temperature the residue was extracted into 100 mL of petroleum ether. A 10.3 g light yellow viscous liquid was obtained after removal of the solvent under vacuum at room-temperature.

Preparation of the binuclear titanocenes

The syntheses of the binuclear metallocenes I-VII (Fig. 2) from the above bridged dicyclopentadienyls were performed by reacting their dilithium salts with CpTiCl_3 in tetrahydrofuran, as exemplified by the synthesis of (I).

The dilithium salt $\text{Li}_2^+[\text{C}_5\text{H}_4\text{-SiMe}_2\text{-O-SiMe}_2\text{-C}_5\text{H}_4]^{2-}$ was prepared by adding dropwise under stirring 6.4 mL (11.4 mmol) 1.77 N hexane solution of $n\text{-BuLi}$, into a 50 mL Schlenk flask containing 1.50 g (5.7 mmol) $\text{C}_5\text{H}_5\text{-SiMe}_2\text{-O-SiMe}_2\text{-C}_5\text{H}_5$ and 15 mL tetrahydrofuran.

To the yellowish solution of the dilithium salt, transferred through a stainless steel tubing to a 100 mL three-necked flask fitted with a dropping funnel and a bulb condenser, were added under stirring at ice-water temperature 2.5 g (11.14 mmol) CpTiCl_3 and 15 mL THF. The color of solution in the reaction flask turned instantaneously to red. After stirring at room temperature overnight and stripped off the solvent at room temperature, the reddish solid residue was taken up in 30 mL of chloroform. To the dark red filtrate after concentration was added anhydrous ether and the solution cooled in a refrigerator. The solid separated was filtered and washed twice with ether. The red solid after recrystallization with dichloromethane weighed 1.49 g (41.6%).

All the end-products were characterized by elemental analysis (Table 1), infrared and ^1H -NMR spectroscopy (data not shown).

Table 1 Characterization of compounds I-VII

Compound	Melting point (°C)	Elemental analysis, found (calculated)		
		C	H	Cl
I	163~165	45.50 (45.51)	4.81 (4.82)	
II	196~198	46.68 (46.64)	5.89 (5.96)	
III	56 (soften)	50.75 (50.75)	5.07 (4.57)	24.56 (24.98)
IV	212~215	46.98 (47.07)	4.88 (4.90)	
V	158~160 (soften)	56.17 (56.04)	4.51 (4.71)	23.91 (23.63)
VI	207~209	58.08 (58.20)	5.68 (5.76)	21.46 (21.52)
VII	200~201	50.84 (51.04)	5.90 (5.91)	51.46 (20.78)

Ethylene polymerization runs and molecular weight distribution determinations on the PE samples (GPC) were the same as described before^[12].

RESULTS AND DISCUSSION

Earlier work has shown that substitution on metallocene greatly reduces its activity in polymerization.^[12,13] This is seen in the comparison of ethylene polymerization using the reference mononuclear metallocene (VIII, activity 11.0×10^5 g PE/molTi·h) with that substituted with Me_3Si -(IX, 4.69×10^5 g PE/molTi·h) under the same catalyst concentration (Table 2).

The binuclear metallocenes, in which each metallocene entity is substituted with another metallocene entity linked through a bridge, suffer from severe steric hindrance.

In the rapid rotation of groups around the active-center sites in a binuclear

metallocene in solution, there must be various modes of disposition of steric groups around the active centers, the thermodynamically most probable assuming the least hindered configuration for monomer coordination, activation and insertion in the polymerization process. This variation in configuration constitutes a circumstance as manifested in the broad or even bimodal MWD curves by GPC (Fig. 3). This is different from the case of unhindered mononuclear metallocenes (Fig. 4), where the single-sitedness of the active centers is characterized by narrow MWD.

Table 2 Ethylene polymerization with binuclear titanocene/MAO*

Complex	[Ti] (mmol)	Time (min)	Catal. effcy. ($10^5 \text{ gPE/mol Ti}\cdot\text{h}$)	$\overline{M}_w/\overline{M}_n$	T_m ($^{\circ}$)	χ_c (%)
I	0.010	30	2.92	38.0	129.9	55.4
II	0.010	30	1.88	9.38	130.8	52.4
III	0.010	30	3.08	28.8	131.2	51.4
IV	0.010	60	1.30	18.6	129.8	49.1
V	0.010	30	1.67	13.8	130.7	51.1
VI	0.010	30	1.45	6.79	131.6	53.5
VII	0.010	60	1.28	12.7	130.6	49.0

* Polymerization conditions: $[\text{Al}]/[\text{Ti}]=500$; in 100 mL toluene; $50 \pm 0.1^{\circ}\text{C}$; pressure of ethylene $1.51 \times 10^5 \text{ Pa}$; χ_c : crystallinity of PE

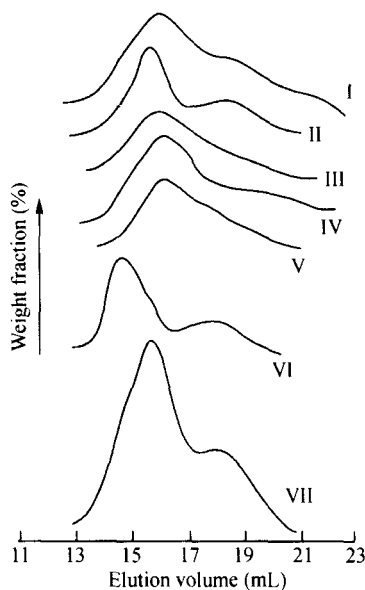


Fig. 3 GPC profiles of PE with binuclear titanocenes

For titanocenes structures see Fig. 1

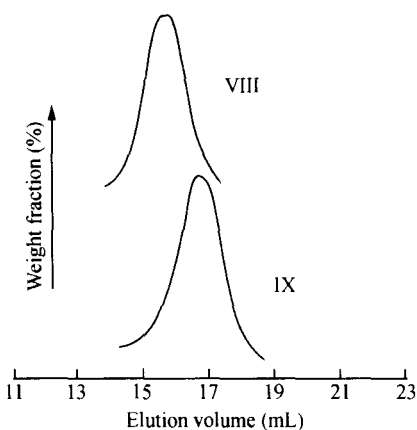


Fig. 4 GPC profiles of the reference mononuclear titanocenes

From Table 3, we see that the MWD of PE from the two reference mononuclear titanocenes (VIII, IX) shows $\overline{M}_w/\overline{M}_n$ values of 1.7~2.3, characteristic of single-sited metallocene polymerization. On this experimental basis, the polymerization results of the binuclear titanocenes can be evaluated. All the binuclear titanocenes show much lower polymerization activity than the usual metallocenes.

Thus, the length and size of the bridge linking the two metallocene entities will dictate the polymer parameters, such as MW, MWD, χ_c , etc.. Of the limited number of binuclear metallocenes studied in this work, though the polymer parameters and catalyst structures are not to be correlated directly because of divergence in structural factors, the following phenomenological differences are to be noted:

Table 3 Ethylene polymerization with mononuclear titanocenes/MAO*

Complex	[Ti] (mmol)	Time (min)	Catal. efficy. (10 ⁵ gPE/mol Ti·h)	$\overline{M}_w/\overline{M}_n$	T_m (°C)	χ_c (%)
XIII	0.005	30	19.6	1.92	132.9	67.9
XIII	0.010	30	11.0	2.32	132.8	63.9
XIII	0.050	10	8.94	2.18	131.6	64.6
IX	0.010	30	4.69	1.67	132.6	66.1

* Polymerization conditions same as that in Table 2

(1) Long, flexible bridges (I, III) favor higher activity and broader $\overline{M}_w/\overline{M}_n$, while shorter bridges (IV, I) lower the activity.

(2) Bulky spiroalkyl ring on the bridge (VI) and stiff benzene ring (V) lowers the activity.

(3) Ring substitution (II, VII) is disadvantageous to activity and favors a lower $\overline{M}_w/\overline{M}_n$.

(4) The later two types (VI, II, VII) give bimodal GPC curves.

Lowering of polymerization temperature should effectively reduce the speed of rotation in a binuclear metallocene and thus an increase in active-centers corresponding to the thermodynamically stable configurations. Polymerization of ethylene with VII/MAO at different temperatures (−50 ~ 50°C) are shown in Table 4 and Fig. 5. The activity decreases with lowering of temperature. Lowering in M_w is not observed due to higher dosage fo MAO used at lower tem-

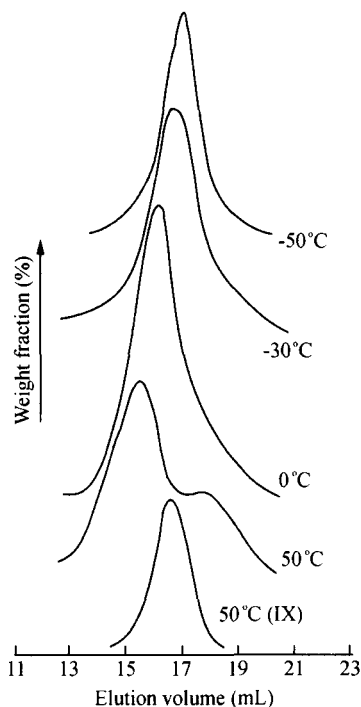


Fig. 5 Effect of temperature on GPC of PE polymerized with VII

peratures. Bimodality disappeared at lower temperatures and $\overline{M}_w/\overline{M}_n$ decreased abruptly from 12.7 for 50°C polymer to 3.8 ~ 1.9 for 0 ~ -50°C polymers.

Table 4 Influence of temperature upon ethylene polymerization of binuclear titanocene VII/MAO

T (°C)	Catalyst (mmol)		Time (min)	Catal. efficy. (10 ⁵ gPE/mol Ti·h)	$\overline{M}_w/\overline{M}_n$	T_m (°C)	χ_c (%)
	Ti	Al					
50	0.010	5.0	60	12.83	12.7	130.6	48.0
0	0.020	10.0	60	9.920	3.81	134.0	76.9
-30	0.028	13.0	140	2.081	2.68	132.4	66.1
-50	0.030	15.0	180	0.477	1.85	131.9	76.0

It is to be noted that the binuclear metallocenes studied in this work are stable and not subject to decomposition and disproportionation. Compound VII in chloroform standing for one week or being heated for a couple of hours at 50°C showed no decomposition on 2D ¹H-NMR. A presumed share of higher M_w from much more reactive mononuclear metallocenes (e.g. Cp₂TiCl₂ or (Me₃SiCp)₂TiCl₂), should the decomposition of the binuclear metallocenes have taken place, did not appear on the GPC curves. Besides, VII after long standing at room temperature in toluene still gave a narrow MWD PE similar to that shown in Table 4 and Fig. 5.

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