

Syndiospecific polymerization of styrene catalyzed by half-titanocene catalysts

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Abstract

Those effective catalyst precursors for syndiotactic styrene polymerization, Cp*Ti(OCH₂-CH=CH₂)₃ (I), Cp*Ti(OCH₂-CH=CHC₆H₄)₃ (II), Cp*Ti(OCH₂C₆H₅)₃ (III), Cp*Ti(OCH₂C₆H₄OCH₃)₃ (IV) were synthesized, and the influence of catalyst ligands on the catalytic activity and properties of polymer were investigated. The polymer thus obtained coupled with higher molecular weight and higher syndiotacticity determined by GPC and ¹³C NMR as well as solvent extraction manners, respectively. Those catalysts promoted by methylaluminoxane (MAO) as cocatalyst exhibited higher catalytic activity. Of all catalysts mentioned foregoing, Cp*Ti(OCH₂-CH=CHC₆H₄)₃ (II), Cp*Ti(OCH₂C₆H₅)₃/MAO (III) and Cp*Ti(OCH₂C₆H₄OCH₃)₃ (IV) catalysts showed higher activity and stability even at fairly low Al/Ti ratio of 600, and possessed excellent control of the stereoregular insertion of monomer, exhibited a significant increase of the ratio of the propagation rates to chain transfer termination. The kinetic and titration results also indicated that those metallocene catalysts (II), (III), and (IV) showed higher catalytic activity and produced polymer with higher molecular weight, because of a great number of active species, and lower ratio of K_{tr}/K_p , higher ratio of K_{tr}/K_{tr} which indicate that β-H elimination was predominant.

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1. Introduction

Ishihara [1] first reported the syndiotactic polymerization of styrene catalyzed with organotitanium compounds using methylaluminoxane (MAO) as cocatalyst. After that, extensive research has been embarked on it [2]. The catalytic activities for styrene polymerization increased in this order, TiBr₄ < TiCl₄ < Ti(OMe)₄ < Ti(OEt)₄ ~ CpTiCl₂H < Cp*TiCl₃ (Cp* = η⁵-pentamethylcyclopentadienyl) ~ CpTiCl₃ (Cp = cyclopentadienyl), and half-titanocenes exhibited good stereocontrol in the syndiotactic polymerization of styrene. However, the activities of those catalysts for styrene polymerization were much lower than that for polymerization of olefins. So much research had been embarked on improving catalytic activity, stereospecificity and properties of polymer. Recently, Chien, Rausch and Brintzinger [2], [3] had demonstrated that even

subtle structural modifications of a given ligand framework led to greatly increased catalytic activity, syndiotacticity, and molecular weight, in contrast to Cp'TiCl₃ (Cp' = η⁵-C₅H₅, η⁵-C₅Me₅), IndTiCl₃ and its likes. Campbell and Chien [3c–e] also found that the catalyst CpTiCl₃ was converted into CpTi(OMe)₃, CpTi(OEt)₃, and CpTi(OBu)₃, their catalytic activity and polymerization behaviors showed considerable changes. So any change of substituents around the Ti atom could result in dramatically difference in catalytic activity and polymerization performances. However, very little work on it has been reported in the open literature. In order to understand the influence of catalyst ligands around the Ti atom on the catalyst behaviors for further perfect design in styrene syndiotactic polymerization, we have now synthesized four novel half-titanocenes (I–IV) as catalytic precursors. The performances of those catalysts in the presence of MAO (solid) and the properties of polymers obtained were investigated in comparison with previously reported half-titanocenes [2–4]. On the other hand, the oxidation state of titanium by redox titration and the polymerization kinetics were studied to provide more information about polymerization behavior of the active species.

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2. Experimental section

2.1. Materials

All operations of air- and moisture-sensitive materials were performed using the rigorous repellency of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line under a nitrogen atmosphere. Toluene, benzene and *n*-hexane were further purified by refluxing over metal sodium under nitrogen for 48 h and distilled before use. Triethylamine was dried using molecular sieve. Styrene was purchased from market and was treated over calcium hydride (CaH_2) for 48 h, and stirred in the presence of $\text{Al}(i\text{-Bu})_3$ solution (2.6 M in *n*-hexane) for 24 h, then distilled under reduced pressure. Trimethylchlorosilane (Aldrich) was distilled after treated by CaH_2 and degassed before use. TiCl_4 was freshly distilled from Cu turnings. Methylaluminoxane (MAO) with 25 mol% of AlMe_3 was prepared according to the literature [5]. 1,2,3,4,5-pentamethylcyclopentadiene, cinnamyl alcohol, *p*-methoxy-1-benzyl alcohol, benzyl alcohol, and allyl alcohol were purchased from Aldrich, they were treated with molecular sieve for a week, and further purified before use.

2.2. Titanium oxidation states

The manipulations for the determination of titanium oxidation states (Ti(II), Ti(III), and Ti(IV)), were according to the literature [6]. Two redox titration, A and B were carried out. The Ti(II) ion was titrated as two electron-redoxing species in 'A', the titer was equal to $2[\text{Ti(II)}] + [\text{Ti(III)}]$. And in 'B' the Ti(II) ion was first oxidized to the Ti(III) ion by proton and subsequently titrated as a one electron-reducing species. So the titer B was the sum of $\{[\text{Ti(II)}] + [\text{Ti(III)}]\}$. The total Ti concentration was determined by atomic absorption. Sodium diphenylamine sulfonate was used as the indicator, the titrimetric end point showed a sharp color change from purple to green within ± 2 drops of 0.1000 N $\text{K}_2\text{Cr}_2\text{O}_7$.

2.3. Polymerization procedure

All polymerization were carried out in a 150 ml glass reactor equipped with a magnetic stirrer. After purging out all moisture and oxygen by a high-vacuum pump, the reactor was sealed under a nitrogen atmosphere. Freshly distilled toluene (20 ml), styrene (20 ml), and the desired amounts of methylaluminoxane (MAO solid) were added in this order. The reactor was put in an oil bath at selected temperature and stirred. Finally the preactivated half-titanocene catalyst (15–20 μmol) with MAO ($\text{Al/Ti}=200$) (preactivated time about 10 min) in toluene was syringed. After a selected reaction time, the polymerization was terminated with 150 ml of 10 wt% HCl in alcohol. The polymer obtained was filtered, and washed with alcohol for three times, then dried overnight in a vacuum oven at 80 °C. The polymer was extracted with 2-butanone at boiling temperature for 24 h in a Soxhlet extractor to remove atactic polystyrene. The syndiotactic polystyrene was determined as the amount of polymer insoluble in 2-butanone.

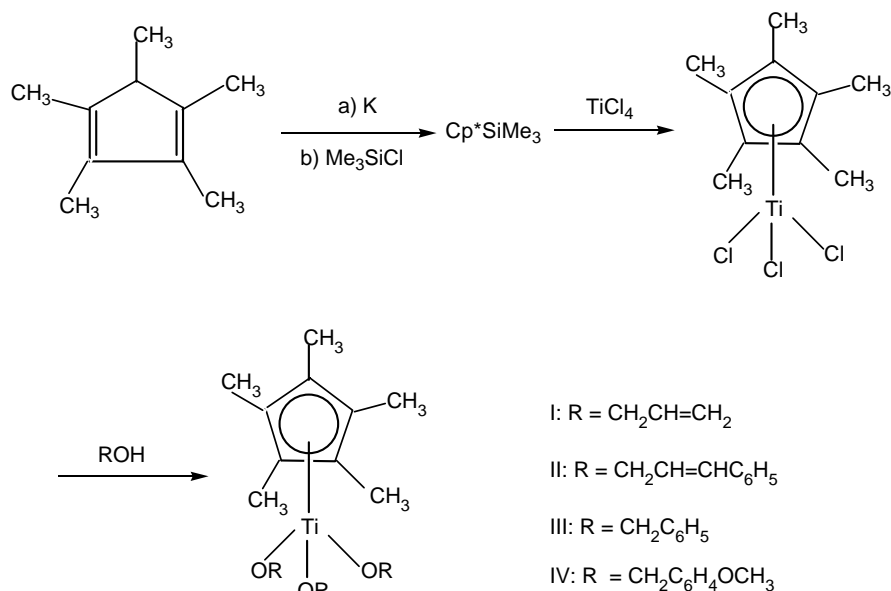
2.4. Characterization procedure

The average molecular weight and molecular weight distribution was measured by PL-GPC200 instrument using standard polystyrene as reference and 1,2,4-trichlorobenzene as solvent at 150 °C. ^{13}C NMR spectra were determined with INOVA500 in 1,2,4-trichlorobenzene (d_3) solvent at 130 °C. Chemical shifts were referenced using internal solvent resonance and reported related to tetramethylsilane. DSC thermograms were recorded with a Perkin–Elmer DSC-7 instrument at 10 K/min. The melting temperature of the syndiotactic polystyrene was determined as the second heating scanning. Elemental analyses were performed on a PE-2400 spectrometer. The concentration of active species C^* was calculated according to the literatures [7].

3. Results and discussion

3.1. Synthesis of catalyst precursors

1,2,3,4,5-Pentamethylcyclopentadiene (12.4 ml, 79.4 mmol) was treated with metal K (3.1 g, 79.5 mmol), then with trimethylchlorosilane (10.1 ml, 80.0 mmol) to form trimethylsilyl derivative according to convenient method. 1,2,3,4,5-pentamethylcyclopentadienyltrichlorotitanium (Cp^*TiCl_3) was prepared by the reaction of trimethylsilyl derivative with TiCl_4 in hexane solution. The crude product was sublimated at 115–120 °C under vacuum to get red needle crystal, Cp^*TiCl_3 (15.5 g, 68.0%, mp 199.5 °C, ^1H NMR: $\delta = 2.06$, s 15H, Cp^*). Anal. Calcd: C, 41.59; H, 5.19. Found: C, 41.81; H, 5.32). Cp^*TiCl_3 (0.81 g, 28 mmol) was esterified with allyl alcohol (5.8 ml, 84.5 mmol), cinnamyl alcohol (11.26 g, 84.5 mmol), benzyl alcohol (8.8 ml, 84.5 mmol), and *p*-methoxy-1-benzyl alcohol (11.65 g, 84.5 mmol) in benzene (20 ml) solution in the presence of triethylamine (1.2 ml, 84.5 mmol) at ambient temperature for 24 h to obtain metallocene catalysts (I), (II), (III) and (IV), respectively. 1,2,3,4,5-pentamethylcyclopentadienyltriallyloxidititanium (I), yellow liquid, 0.97 g, 98.1%, ^1H NMR (CDCl_3): δ 4.05 (s; 6H, $\text{O}-\text{CH}_2$), 2.05 (s; 15H, Cp^*), 5.89 (m; 3H, $-\text{CH}=\text{}$), 5.08 ~ 5.22 (m; 6H, $=\text{CH}_2$). Anal. Calcd for $\text{Cp}^*\text{Ti}(\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2)_3$ (I): C, 64.40; H, 8.53. Found: C, 64.47; H, 8.59. 1,2,3,4,5-pentamethylcyclopentadienyltricinmyloxidititanium (II), yellow liquid, 1.60 g, 98.0%, ^1H NMR (CDCl_3): δ 7.25 (s, 15H, ph_3), 6.54 (s, 3H, phenyl- CH), 6.37 (t, 3H, $=\text{CH}-\text{CH}_2$), 4.46 (d, 6H, CH_2-O), 1.99 (s, 15H, Cp^*). Anal. Calcd for $\text{Cp}^*\text{Ti}(\text{O}-\text{CH}_2\text{CH}=\text{CH}-\text{ph})_3$ (II): C, 76.42; H, 7.23. Found: C, 76.85; H, 7.45. 1,2,3,4,5-pentamethylcyclopentadienyltribenzoyloxidititanium (III), yellow liquid, 1.38 g, 98.0%, ^1H NMR (CDCl_3): δ 7.21 (s, 15H, ph_3), 4.54 (s, 6H, $\text{O}-\text{CH}_2$), 1.88 (s, 15H, Cp^*). Anal. Calcd for $\text{Cp}^*\text{Ti}(\text{O}-\text{CH}_2-\text{ph})_3$ (III): C, 73.81; H, 7.14. Found: C, 73.40, H, 7.25. And 1,2,3,4,5-pentamethylcyclopentadienyltri(4-methyl-1-benzoyloxide)titanium (IV), yellow liquid, 1.63 g, 98.0%, ^1H NMR (CDCl_3): δ 6.73 ~ 7.19 (s, 12H, ph_3), 3.70 (s, 9H, $\text{O}-\text{CH}_3$), 4.46 (s, 6H, $\text{O}-\text{CH}_2$), Anal. Calcd for $\text{Cp}^*\text{Ti}(\text{OCH}_2\text{C}_6\text{H}_4\text{OCH}_3)_3$ (IV): C,



Scheme 1.

68.46; H, 7.55; Found: C, 68.71; H, 7.72. The reaction course was listed in Scheme 1.

3.2. Polymerization of styrene

Four newly synthesized half-titanocene catalysts (I–IV) were investigated using methylaluminoxane (MAO solid) as cocatalyst for syndiotactic polymerization of styrene to demonstrate their catalytic behaviors. Catalytic activities of those catalysts and the properties of polymer obtained were compiled in Table 1, compared with those of CpTiCl₃ and Cp*TiCl₃ catalysts previously employed. The stereostructure of polymer insoluble in 2-butanone was determined by ¹³C NMR (Fig. 1). The presence of a single resonance for the quaternary C carbon in phenyl ring at $\delta = 145.2$ ppm showed that the polymer was highly syndiotactic [2a]. The other two signals of phenyl ring were at $\delta = 125.6$ and 127.8 ppm. Two

sharp peaks at $\delta = 43.93$ and 40.62 ppm were attributed to methylene and methine carbon in backbone chain, respectively. Those values were in agreement with the results reported in the literatures [1].

From Table 1 one can notice that each of the four catalyst systems examined (I–IV) were exhibited high activity and high stability during the polymerization even at fairly low Al/Ti ratio of 600, as compared with those of CpTiCl₃ and Cp*TiCl₃. The activities of catalysts II, III, and IV except for I, for example, maintained nearly constant over 2 h at polymerization temperature 60 °C even at fairly low Ti concentration, such as 1.0 μ M. Thus a low rate of deactivation of those catalysts might be attributable to the enhanced steric hindrance of those ligands [8]. The complexes (II–IV) exhibited much higher catalytic activity than those of no phenyl ring ligands complexes in our laboratory. The discovery indicated that the presence of a phenyl ring ligand moiety met the electronic

Table 1
Syndiotactic polymerization of styrene promoted by half-titanocene catalysts

Catalysts	A ^a × 10 ⁻⁷	S.I. ^b (%)	M _w ^c × 10 ⁻⁵	M _w /M _n	T _m ^d
CpTiCl ₃	0.61	75.3	0.56	2.3	266
Cp*TiCl ₃	0.82	94.0	0.96	2.0	267
Cp*Ti(OCH ₂ CH=CH ₂) ₃ (I)	5.92	95.1	1.81	2.1	269
	0.13 ^e	93.2	2.62	2.8	271
Cp*Ti(OCH ₂ CH=CHC ₆ H ₅) ₃ (II)	7.73	97.0	3.32	1.9	272
	3.19 ^e	96.5	4.21	2.2	272
Cp*Ti(OCH ₂ C ₆ H ₅) ₃ (III)	8.12	97.1	3.61	2.0	273
	3.45 ^e	96.8	4.30	2.3	273
Cp*Ti(OCH ₂ C ₆ H ₄ OCH ₃) ₃ (IV)	7.57	97.0	3.55	2.2	273
	3.33 ^e	96.5	4.30	2.3	273

Polymerization conditions: [Ti] = 83 μ M; Al/Ti = 600 mol/mol; styrene = 20 ml; toluene = 20 ml; polymerization temperature = 60 °C, polymerization time = 20 min.

^a A (activity) = g of sPS/[mol of Ti](h).

^b S.I.(%) = (g of polymer insoluble in boiling 2-butanone)/(g of total polymer) × 100%.

^c Determined with GPC.

^d Melting temperature determined by DSC.

^e Performed at polymerization time = 2 h and [Ti] = 1.0 μ M.

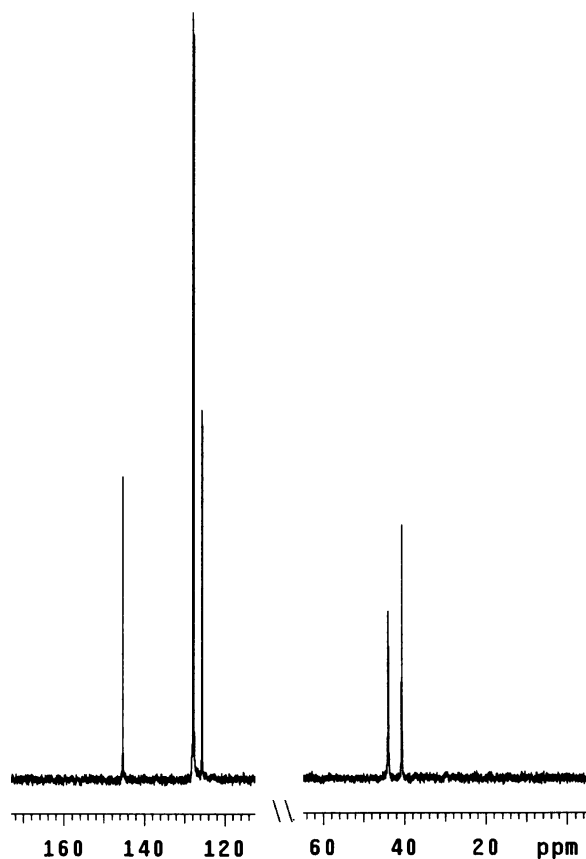


Fig. 1. ^{13}C NMR spectrum of syndiotactic polystyrene obtained with $\text{Cp}^*\text{Ti}(\text{OBz})_3/\text{MAO}$ under $[\text{Ti}] = 83 \mu\text{M}$; $\text{Al}/\text{Ti} = 600 \text{ mol/mol}$; polymerization temperature = 90°C , and time = 20 min.

coordination requirements for high activity. In addition, due to the charge of active site of complex (II, III and IV) could be effectively delocalized over all the phenyl ring, the electron donation and the resonance stabilization increased from phenyl ring substituent would stabilize the active species and make the monomer styrene with high order to access the coordination site more ease, which enlarged the number of active species or made it have longer life. Therefore, the overall activity was enhanced. The high molecular weight of syndiotactic polystyrene thus obtained could be mainly due to the electron effect caused by the presence of the electron-releasing Cp^* and phenyl ring moiety, resulting in an increase in electron density

Table 2

The effect of Al/Ti molar ratio on the catalytic activity and molecular weight of sPS catalyzed by half-titanocene catalysts

Titanocenes	$A^a \times 10^{-7}$					$M_w^b \times 10^{-5}$	
	$\text{Al}/\text{Ti} = 400$	$\text{Al}/\text{Ti} = 600$	$\text{Al}/\text{Ti} = 1000$	$\text{Al}/\text{Ti} = 2000$	$\text{Al}/\text{Ti} = 4000$	$\text{Al}/\text{Ti} = 600$	$\text{Al}/\text{Ti} = 4000$
CpTiCl_3	0.23	0.61	0.86	1.22	1.53	0.56	0.41
Cp^*TiCl_3	0.46	0.82	1.16	1.36	1.78	0.96	0.78
$\text{Cp}^*\text{Ti}(\text{OCH}_2\text{CH}=\text{CH}_2)_3$ (I)	5.13	5.92	7.87	9.11	12.1	1.81	1.21
$\text{Cp}^*\text{Ti}(\text{OCH}_2\text{CH}=\text{CHC}_6\text{H}_5)_3$ (II)	5.41	7.73	10.58	12.77	15.5	3.32	2.89
$\text{Cp}^*\text{Ti}(\text{OCH}_2\text{C}_6\text{H}_5)_3$ (III)	6.15	8.12	11.36	13.73	16.13	3.61	3.43
$\text{Cp}^*\text{Ti}(\text{OCH}_2\text{C}_6\text{H}_4\text{OCH}_3)_3$ (IV)	5.92	7.57	11.61	13.79	16.94	3.55	3.27

Polymerization conditions: $[\text{Ti}] = 83 \mu\text{M}$; $\text{Al}/\text{Ti} = 600 \text{ mol/mol}$; styrene = 20 ml; toluene = 20 ml; polymerization temperature = 60°C , polymerization time = 20 min.

^a A (activity) = g of sPS/[(mol of Ti)(h)].

^b Determined by GPC.

at the metal center and also at the β -carbon. Consequently, the β -hydrogen elimination and chain transfer to monomer reactions would be diminished during the polymerization course [9]. On the other hand, the phenyl ring substituent in the complex (II, III and IV) made the titanium center might diminish detrimental β -agostic interaction during the propagation [10]. This steric advantage made monomer styrene insertion relative to chain termination mainly by β -hydrogen elimination or sterically stabilized the active species. In fact, complex (I) was more sensitive to moisture.

The relationship between polymerization behavior and the details of ligand structure of titanocenes was also observed in the melting temperature and molecular weight of polymers thus obtained, which revealed the stereospecificities and typical chain propagation/chain termination ratios of those titanocenes (Table 1). One can notice that from Table 1 the melting points or the syndiotacticities of the polymers obtained with titanocenes (II, III, and IV) except for (I) were all very similar, melting points ranged in 272 – 273°C , and syndiotacticities in 96.7 – 97.1% , respectively, which suggested that aromatic ring substituent titanocene catalysts didn't bring about the regioerrors or stereoerrors of monomer insertion. On the other hand, for those titanocenes (I–IV), a high rate of propagation was almost associated with an increased molar mass of the polymers thus obtained. It seemed that an improved control over the rates of both chain propagation (R_p) and chain termination or chain transfer (R_T or R_{tr}) could be come true by designing the ligand structure of metallocene catalysts.

From Table 2 one can notice that the catalytic activity depended upon the concentration of MAO as associating with previous reports [1,11]. However, high activity was shown even at fairly low Al/Ti ratio of 600 for those complexes (I–IV). For industrial uses, it was interested in these complexes (I–IV) because of possessing a high activity at a fairly low Al/Ti ratio of 600 to result in lower productive cost. But the molecular weight of all polymers thus obtained had minor change as increasing Al/Ti ratio. The result suggested that MAO acted as a chain transfer agent to some extent.

The relationship between the activities of those half-titanocene catalysts, resultant properties and the polymerization temperature were also investigated. As showed by Table 3, the catalytic activities increased with the

Table 3
The effect of polymerization temperature on catalytic activity and properties of sPS

Catalysts	T_p (°C)	$A^a \times 10^{-7}$	S.I. ^b (%)	$M_w^c \times 10^{-5}$	T_m^d (°C)
Cp*TiCl ₃	40	0.38	94.3	1.35	267
	60	0.82	94.0	0.96	267
	90	1.36	93.5	0.73	266
	110	1.11	93.0	0.56	266
Cp*Ti(OCH ₂ CH=CH ₂) ₃ (I)	40	4.31	96.5	2.11	270
	60	5.92	96.1	1.81	268
	90	7.56	96.0	1.78	268
	110	6.17	93.8	1.22	267
Cp*Ti(OCH ₂ CH=CHC ₆ H ₅) ₃ (II)	40	5.54	97.0	3.21	272
	60	7.73	96.7	3.52	272
	90	12.01	96.0	3.40	270
	110	11.36	95.0	2.88	270
Cp*Ti(OCH ₂ C ₆ H ₅) ₃ (III)	40	5.91	97.0	4.23	273
	60	8.12	97.1	3.61	273
	90	12.33	96.9	3.36	272
	110	11.10	95.0	3.00	271
Cp*Ti(OCH ₂ C ₆ H ₄ OCH ₃) ₃ (IV)	40	5.03	97.1	3.76	273
	60	7.57	96.8	3.55	273
	90	11.55	96.2	3.31	271
	110	10.76	95.3	3.02	271

Polymerization conditions: [Ti]=83 μM; Al/Ti=600 mol/mol; styrene=20 ml; toluene=20 ml; polymerization time=20 min.

^a A (activity)=g of sPS/(mol of Ti)(h).

^b S.I.(%)=(g of polymer insoluble in boiling 2-butanone)/(g of total polymer)×100%.

^c Determined with GPC.

^d Melting temperature determined by DSC.

polymerization temperature T_p rising up to 90 °C for those catalysts (I–IV). Further enhancing T_p to 110 °C, small reduction of activity and syndiotacticity was observed for catalyst (I)/MAO system. However, catalytic activities of those catalysts (II, III, and IV), melting points T_m and syndiotacticities of the polymers thus obtained were nearly invariable in the polymerization temperature T_p range examined. In contrast, many homogenous metallocene catalysts exhibited the decreasing of syndiotacticity and melting temperature T_m as increasing polymerization temperature T_p [12]. On the other hand, the molecular weight (M_w) of the polymers obtained decreased with increasing polymerization temperature for all of these catalysts investigated. This was because of the fact that the average molecular weight of polymers were predominantly decided by the K_p/K_{tr} ratio, where K_p increased with temperature slower than K_{tr} , which resulted in the decreasing of M_w as increasing temperature. This was very remarkable that those complexes (II, III, and IV) resulted in high molecular weight even at temperature as high as 110 °C, which indicated that complexes (II, III, and IV) were extremely stable.

The relationship between the catalytic activity and polymerization time of Cp*Ti(OBz)₃/MAO (III) catalyst was showed in Fig. 2. From Fig. 2 one can notice that the catalytic activity Cp*Ti(OBz)₃/MAO (III) catalyst system was relative to the polymerization time. At higher temperatures (over 50 °C), a maximum value of catalytic activity was gotten after a short time (less 10 min), then it was become down. But at low temperature (30 °C), the polymerization rate nearly maintained constant over the polymerization time (1 h).

To further understand the effect of the ligands in titanocenes on the polymerization behaviors, we investigated the

concentration of active species C* according to the kinetic methods [7]. The results (Table 4) were the average molar concentrations of active species C* on the basis of yield and M_n values at polymerization temperature of 60 °C. Under low conversion of monomer and short polymerization time conditions, the ratio of the yields of polymer thus obtained to M_n gave the values of active species C* in the text. We can notice that a consequence of termination and transfer reactions could result in the values of C* calculated following this method being larger than the real ones. The C* of Cp*Ti(OBz)₃/MAO (III) catalyst system was 3.12×10^{-6} mol (corresponding to about 94% of the total Ti (3.32×10^{-6} mol)) at the Al/Ti ratio of 600. The C* for Cp*Ti(OCH₂CH=CH₂)₃/MAO (I), Cp*Ti(OCH₂CH=CHC₆H₅)₃/MAO (II),

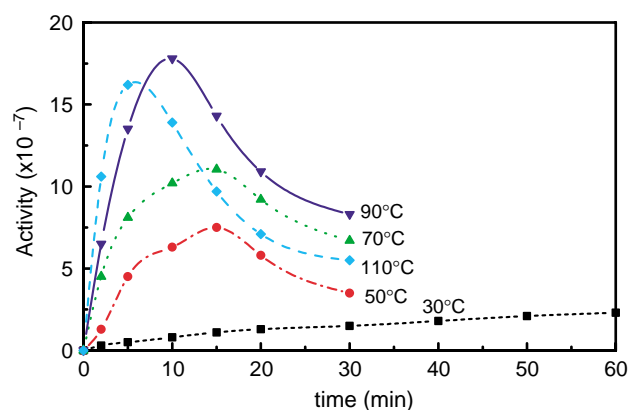


Fig. 2. Curves of catalytic activity vs. time for Cp*Ti(OBz)₃/MAO (III) catalyst system in the polymerization of styrene at different polymerization temperature. [Ti]=50 μM, Al/Ti=600.

Table 4
Concentration of active species and Ti oxidation state of half-titanocenes activated by MAO

Catalyst	Al/Ti (mol/mol)	C* ^a (%)	[Ti(III)] ^b (%)
Cp*Ti(OCH ₂ CH=CH ₂) ₃ (I)	600	68	43.3
	2000	81	50.4
Cp*Ti(OCH ₂ CH=CHC ₆ H ₅) ₃ (II)	600	89.5	55.5
	2000	90.8	58.7
Cp*Ti(OCH ₂ C ₆ H ₅) ₃ (III)	600	94	60.7
	2000	98	63.2
Cp*Ti(OCH ₂ C ₆ H ₄ OCH ₃) ₃ (IV)	600	87.6	60.1
	2000	98.1	62.5

[Ti]=83 μM, mixed for 10 min after adding styrene.

^a Calculated by kinetic method.

^b Determined by titration.

and Cp*Ti(OCH₂C₆H₅OCH₃)₃/MAO (IV) catalyst systems were 2.25 mol (about 68% of the total Ti), 3.00 mol (about 89.5% of the total Ti), and 2.87 mol (about 87.6% of total Ti), respectively, under the same conditions. These discoveries were coincident with the results listed in Tables 1 and 2. It indicated that the higher activities of those complexes were due to have a greater number of active species.

The results were listed in Table 4, one cannot correlate [Ti(III)] values thus obtained with kinetic method, and redox titration. However, at [Ti]=83 μM, i.e. concentration of Ti was fairly low, those values followed this order: C* > [Ti] determined by titration. The findings were similar to the result reported by Chien [4a].

From already investigated, the ligand structure of half-titanocenes showed observable effects on the properties of polymers obtained, especially in polymer molecular weight. It was indicated that the ratio of chain propagation rate to chain termination rate or the chain transfer rate determined the polymer molecular weight. We studied the kinetics of styrene polymerization catalyzed by half-titanocenes examined, it was found that in all cases the relationship between the yield of syndiotactic polystyrene and styrene concentration followed Eq. (1). Which indicated that the chain propagation rate with respect to styrene concentration was a first-order.

$$R_p = K_p C^* [S] \quad (1)$$

Where R_p was the chain propagation rate, C^* was active species global molar concentration, $[S]$ was styrene molar concentration, K_p was the specific constant of the propagation reaction. The number average degree of polymerization DP_n (DP_n = R_p/R_{tr} , R_{tr} was of the global rates of all chain transfer or chain termination) results [3e].

$$\frac{1}{DP_n} = \frac{K_{tr}}{K_p} + \frac{K_{trm} + K_{tr\beta}}{K_p [S]} \quad (2)$$

Where K_p , K_{tr} , K_{trm} , and $K_{tr\beta}$ were the chain propagation constant, the chain transfer constant with monomer (styrene), the chain transfer constant with MAO, and the chain transfer constant with β-hydrido abstraction, respectively. Many results demonstrated that only Ti(III) was the active species for syndiotactic polymerization of styrene. So the K_p and K_{tr}

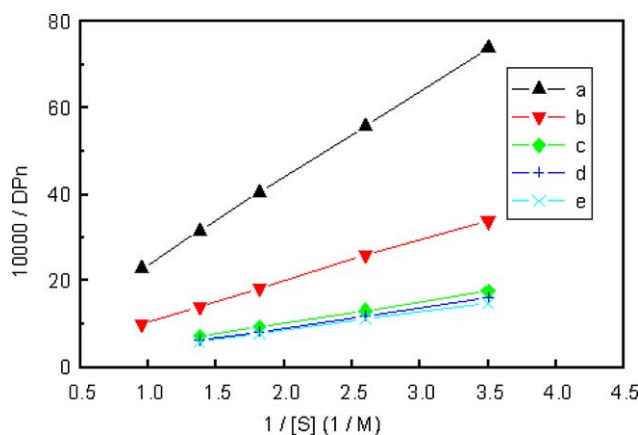


Fig. 3. Curves of 1/DP_n vs. 1/[S] for syndiotactic polymerization of styrene performed by half-titanocene catalysts activated with MAO at 60 °C: (a) Cp*TiCl₃; (b) Cp*Ti(OCH₂CH=CH₂)₃ (I); (c) Cp*Ti(OCH₂CH=CHC₆H₅)₃ (II); (d) Cp*Ti(OCH₂C₆H₅)₃ (III); (e) Cp*Ti(OCH₂C₆H₄OCH₃)₃ (IV).

values in the Eqs. (1) and (2) were only characteristic of the Ti(III) oxidation state. On the other hand, the concentration of MAO was weak influence on the molecular weight of syndiotactic polystyrene in this investigation (Table 2). So Eq. (2) was changed into Eq. (3):

$$\frac{1}{DP_n} = \frac{K_{tr}}{K_p} + \left(\frac{K_{tr\beta}}{K_p} \right) \left(\frac{1}{[S]} \right) \quad (3)$$

DP_n was given according to Eq. (4):

$$DP_n = \frac{M_n}{\text{styrene molecular weight}} \quad (4)$$

The number-average degree of polymerization, DP_n, was calculated according to Eq. (4). The intercept and the slope of curves of 1/DP_n vs. 1/[S] were the K_{tr}/K_p , $K_{tr\beta}/K_p$ ratio, respectively (Fig. 3). These results were compiled in Table 5. From the results one can notice that, comparison with Cp*TiCl₃/MAO catalyst system, the complexes (I–IV), especially in complex (II, III, and IV), had fairly low tendency of chain termination or chain transfer, and high tendency of chain propagation, which resulted in high molecular weight polymers for styrene polymerization. It was in agreement with the experimental results (Table 1). On the other hand, the ratio of $K_{tr\beta}/K_{tr}$ for titanocene (II)/MAO, (III)/MAO and titanocene (IV)/MAO system were no less than 12, which suggest that

Table 5
Kinetics constants of polymerization reaction in styrene polymerization catalyzed by half-titanocene catalysts

Titanocenes	$K_{tr\beta}/K_p \times 10^{-4}$	$K_{tr}/K_p \times 10^{-4}$	$K_{tr\beta}/K_{tr}$
Cp*TiCl ₃	20.0	3.6	5.5
Cp*Ti(OCH ₂ CH=CH ₂) ₃ (I)	9.3	1.2	7.7
Cp*Ti(OCH ₂ CH=CHC ₆ H ₅) ₃ (II)	4.9	0.36	13.6
Cp*Ti(OCH ₂ C ₆ H ₅) ₃ (III)	4.3	0.3	14.3
Cp*Ti(OCH ₂ C ₆ H ₄ OCH ₃) ₃ (IV)	4.1	0.32	12.8

Polymerization conditions: [Ti]=83 μM; Al/Ti=600 mol/mol; polymerization temperature=60 °C.

the β -H elimination was the main termination manner, and the hydrogen transfer to monomer could be neglectable. But the ratio of K_{trp}/K_{trs} for titanocene (I)/MAO was 7.7, which indicated that the β -H elimination was main termination manner.

4. Conclusions

The effects of ligands of half-titanocenes on catalytic activity and polymer properties were observable. Comparison with the Cp^*TiCl_3/MAO catalyst system, those catalysts, $Cp^*Ti(OCH_2CH=CH_2)_3$ (I), $Cp^*Ti(OCH_2CH=CHC_6H_5)_3$ (II), $Cp^*Ti(OBz)_3$ (III), and $Cp^*Ti(OCH_2C_6H_4OCH_3)_3$ (IV), activated by MAO, exhibited higher catalytic activity and better polymerization behaviors, the polymers thus obtained had higher molecular weight, higher syndiotacticity and melting temperature. Complexes (II), (III) and (IV) with ligands of phenyl ring substituents, however, showed more stable and higher catalytic activity than complex (I).

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