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Syndiospecific Polymerization of Styrene with Half-Sandwich Titanocene Catalysts. Influence of Ligand Pattern on Polymerization Behavior

Guangxue Xu*,† and Danling Cheng

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, P. R. China

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ABSTRACT: As modifications of the effective catalyst precursor for syndiospecific styrene polymerization, namely [2-Me-thBenz[*e*]Ind]$TiCl_3$ (**Ic**), [2,3-Me_2-thBenz[*e*]Ind]$TiCl_3$ (**IIc**), [1,2,3-Me_3-thBenz[*e*]Ind]$TiCl_3$ (**IIIc**), and [2-Me-3-Ph-thBenz[*e*]Ind]$TiCl_3$ (**IVc**) have been synthesized to examine the influence of ligand pattern on the catalyst activity and polymer properties. These complexes, activated by methylaluminoxane (MAO), showed high activities compared with previously employed titanocene catalysts. Of all titanocenes examined, [2-Me-3-Ph-thBenz[*e*]Ind]$TiCl_3$ (**IVc**)/MAO showed the highest activity and stability at an even fairly low Al/Ti ratio of 1000, revealed the excellent control over the stereoregular insertion of monomer, and exhibited a significant increase of the ratio of the propagation rates to chain transfer termination as evidenced by the kinetic results, thus producing polymers with the highest syndiotacticity and molecular weight. The kinetic investigations, combined with the EPR spectrum and polymerization experiments, showed that the higher activity of tetrahydrobenz[*e*]indenyl-based systems is due to a great number of active species.

Introduction

The discovery of syndiotactic polystyrene (sPS) by Ishihara at Idemitsu Kodan Co.[1] opened a new field in stereospecific polymerization to develop new polymers or tailor-make new polymer materials from easily available monomers. In contrast to the well-known isotactic polystyrene (iPS), which has a very low crystallization rate and is therefore useless for most industrial applications,[2] the syndiotactic polystyrene (sPS) shows a fast crystallization rate (more than an order of magnitude higher than that of iPS), a high crystallinity, a high melting point (275 °C) compared to 230 °C, superior heat and chemical resistance, high modulus of elasticity, and unique mechanical and/or electrical properties. These new properties, which are similar to those of some expensive engineering plastics, are the main reason for the interest in sPS as electronic and/or low-cost engineering plastics.[3]

Half-sandwich titanocenes exercise stereocontrol in the syndiospecific polymerization of styrene.[1,3,4] Extensive investigation of the substituent effect has resulted in highly active, highly syndiospecific homogeneous catalysts for styrene polymerization. These contain cyclopentadienyl, substituted cyclopentadienyl, indenyl, and substituted indenyl derivatives of titanium.[4] However, compared to the polymerization of olefins, the activity for styrene polymerization was much lower. Therefore, intensive research has been aimed at improving catalyst activities and stereospecificities and polymer properties. Recently, Chien and Rausch[4i−j] and Brintzinger et al.[5] have shown that even minor structural modifications of a given ligand framework can lead to significantly enhanced catalyst activities, polymer syndiotacticities, and molecular weights, as compared with $Cp'TiCl_3$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$), $IndTiCl_3$, and its analogue. To understand the effect of ligand pattern on the catalyst performances for further catalyst design in styrene syndiospecific polymerization, we have now prepared four new half-sandwich titanocenes (**Ic**−**IVc**) as catalyst precursors, derived from the tetrahydrobenz[*e*]indenyl and its substituted derivatives. The behavior of these complexes as catalysts in the presence of MAO and the properties of polymers thus obtained were studied in comparison with previously described titanocenes.[1,4,5] Additionally, the titanium oxidation state of active species and the polymerization kinetics were investigated in order to provide some more information on polymerization behavior of the active species.

Experimental Section

Materials. All manipulations of air- and moisture-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high-vacuum (10^{-6} Torr) line or in a argon-filled vacuum atmosphere glovebox with a high-capacity recirculator (<1 ppm of O_2). Anhydrous hexane, tetrahydrofuran (THF), methylene chloride, pentane, diethyl ether, and toluene were further purified by refluxing over Na−K alloy/benzophenone ketyl under nitrogen for at least a week followed by distillation. Styrene was purchased from Aldrich and dried over calcium hydride for a week at room temperature and distilled in the presence of $Al(i\text{-}Bu)_3$ solution (2.5 M) under reduced pressure. Trimethylsilyl chloride (Aldrich) was redistilled from CaH_2 and degassed by pump−thaw cycles before use. $Cp'TiCl_3$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$), $IndTiCl_3$, and all other reagents were purchased from Aldrich and used without further purification. $TiCl_4$ (Aldrich) was freshly distilled from Cu turnings. Methylaluminoxane (MAO) with about 28 mol % of $AlMe_3$,[4l] $MeCpTiCl_3$,[4m] (benz[*e*]indenyl)trichlorotitanium ([Benz[*e*]Ind]$TiCl_3$),[4i] (2-methylbenz[*e*]indenyl)trichlorotitanium ([2-MeBenz[*e*]Ind]$TiCl_3$),[4i] (1,2,3-trimethylbenz[*e*]-indenyl)trichlorotitanium ([1,2,3-Me_3Benz[*e*]Ind]$TiCl_3$),[4i] (2-methylindenyl)trichlorotitanium ([2-MeInd]$TiCl_3$),[4j] 2-methyltetrahydrobenz[*e*]indanone,[6a] (2-methylcyclopenta[*l*]-phenanthryl)trichlorotitanium ([2-MeCp[*l*]Phen]$TiCl_3$),[5] and (2-phenylcyclopenta[*l*]-phenanthryl)trichlorotitanium ([2-Ph-Cp[*l*]Phen]$TiCl_3$)[5] were prepared according to literature procedures. The compounds were

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* To whom correspondence should be addressed. E-mail: gxx5@psu.edu.

† Present address: Department of Material Science and Engineering, Penn State University, University Park, PA 16802.

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characterized by a ^{1}H NMR spectrometer (Bruker PX-300 MHz) and by an elemental analyses spectrometer (PE-2400).

2-Methyl-1-(trimethylsilyl)tetrahydrobenz[*e*]indene (Ib). 2-Methyltetrahydrobenz[*e*]indene (**Ia**) (5.53 g, 30 mmol), prepared by the procedure of Brintzinger et al.,[6a] was dissolved in 100 mL of anhydrous THF. The solution was cooled to 0 °C and treated dropwise with 18.8 mL (30 mmol) of a 1.6 M solution of butyllithium in hexane. The resulting solution was warmed to room temperature and stirred for 8 h. The solvent was removed in vacuo. The solid residue was stirred in 50 mL of pentane for 30 min, collected by filtration, and washed with 20 mL of pentane. The solid was then dissolved in 100 mL of THF, chlorotrimethylsilane (3.48 g, 32 mmol) was added at room temperature, and the mixture was stirred overnight. The THF was removed in vacuo, the residue was extracted with 80 mL of pentane, and then the mixture was filtered. The solvent was removed in vacuo to give **Ib** (6.85 g, 89%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.01 (2d, 2H), 6.58 (broad s, Cp-H), 3.45 (s, Cp-H), 2.85 (t, 2H), 2.73 (t, 2H), 2.20 (s, 3H), 1.86 (m, 4H), −0.02 (s, 9H). MS (EI): *m/z* 256 (M^+), 183 ($M^+ - SiMe_3$). Anal. Calcd for $C_{17}H_{24}Si$: C, 79.62; H, 9.43. Found: C, 79.48; H, 9.45.

(2-Methyltetrahydrobenz[*e*]indenyl)trichlorotitanium (Ic). To a solution of **Ib** (5.0 g, 19.5 mmol) in 100 mL of CH_2Cl_2 was added redistilled $TiCl_4$ (3.70 g, 19.5 mmol) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solvent was removed and the residue extracted with 50 mL of dry toluene. After the toluene was removed under vacuum, the residue was washed with pentane and then filtered. The solid residue was dissolved in 50 mL of fresh CH_2Cl_2 and cooled to −20 °C to give **Ic** (4.42 g, 67%) as red crystals. ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 1H), 7.30 (m, 1H), 7.12 (s, 1H), 6.89 (s, 1H), 2.85 (t, 2H), 2.71 (s, 3H), 1.85 (m, 4H). MS (EI): *m/z* 338 (M^+). Anal. Calcd for $C_{14}H_{16}TiCl_3$: C, 49.68; H, 4.76. Found: C, 49.21; H, 4.73.

2,3-Dimethyltetrahydrobenz[*e*]indene (IIa). To a suspension of Mg (4.1 g, 0.17 mol) in 50 mL of diethyl ether was slowly added CH_3I (23.7 g, 0.17 mol) at 0 °C; the mixture was warmed to room temperature and stirred for 2 h. 2-Methyltetrahydrobenz[*e*]indanone[6a] (34.1 g, 0.17 mol) in 20 mL of ether was added dropwise at 0 °C, and the solution was warmed to room temperature and then stirred for 10 h. The mixture was hydrolyzed with aqueous NH_4Cl (18 g in 100 mL of H_2O), and the organic layer was separated. The layer was dried (Na_2SO_4) and filtered, and the solvent was removed. The residue was dissolved in 200 mL of toluene, and 40 g of oxalic acid was added. The mixture was refluxed, using a Dean−Stark trap, until the formation of water subsided. The mixture was washed with 250 mL of 10% $NaHCO_3$ (pH ≈ 7) and dried with $MgSO_4$. After filtration, the solution was mixed with 50 g of silica gel and evaporated to dryness. The residue was chromatographed over 150 g of silica gel with hexane/ethyl acetate (49:1) eluent mixture to give **IIa** (25.6 g, 70%) as a colorless solid. ^{1}H NMR ($CDCl_3$): 7.05−7.31 (m, 2H), 3.40 (s, 2Cp-H), 2.85 (t, 2H), 2.73 (t, 2H), 2.50 (d, 3H), 2.18 (s, 3H), 1.87 (m, 4H). MS (EI): *m/z* 198 (M^+), 183 ($M^+ - CH_3$), 168 ($M^+ - 2CH_3$). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.83; H, 9.10.

1,2,3-Trimethyltetrahydrobenz[*e*]indene (IIIa). To a solution of **IIa** (12.5 g, 63 mmol) in 100 mL of THF was slowly added 1.6 M butyllithium (40 mL, 64 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 10 h. The solvent was removed, and the solid was washed with pentane. The residue was then dissolved in 100 mL of THF, CH_3I (9.0 g, 63 mmol) was added, and the mixture was stirred for 4 h. The solvent was removed, and the solid was extracted with 60 mL of pentane. The extracts were filtered, and the solvent was removed. The residue was chromatographed over a short silica gel column using a hexane/ethyl acetate (49:1) eluent mixture to give **IIIa** (6.7 g, 50%) as colorless needles. ^{1}H NMR ($CDCl_3$): δ 7.05−7.25 (m, 2H), 3.51 (bs, Cp-H), 2.85 (m, 4H), 2.15 (br s, 6H), 1.86 (m, 4H), 1.45 (m, 3H). MS (EI): *m/z* 211 (M^+), 196 ($M^+ - CH_3$), 181 ($M^+ - 2CH_3$), 166 ($M^+ - 3CH_3$). Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.47; H, 9.51.

2,3-Dimethyl-1-(trimethylsilyl)tetrahydrobenz[*e*]indene (IIb). Following the procedure described for **Ib**, **IIa** (11.5 g, 58 mmol), 1.6 M butyllithium (36.3 mL, 58 mmol), and chlorotrimethylsilane (6.6 g, 60 mmol) gave **IIb** (13.4 g, 85%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.18−7.35 (m, 2H), 3.50 (s, Cp-H), 2.86 (m, 2H), 2.58 (s, 3H), 2.20 (s, 3H), 1.86 (m, 4H), −0.15 (s, 9TMS−H). MS (EI): *m/z* 270 (M^+), 197 ($M^+ - SiMe_3$). Anal. Calcd for $C_{18}H_{26}Si$: C, 79.93; H, 9.96. Found: C, 79.85; 9.62.

(2,3-Dimethyltetrahydrobenz[*e*]indenyl)trichlorotitanium (IIc). Following the procedure described for **Ic**, **IIb** (6.5 g, 24 mmol) and $TiCl_4$ (4.5 g, 24 mmol) gave **IIc** (3.4 g, 40%) as brown/red crystals. ^{1}H NMR ($CDCl_3$): δ 7.75 (m, 2H), 6.85 (s, 1H), 3.40 (s, 3H), 2.98 (s, 3H), 2.85 (m, 4H), 1.87 (m, 4H). MS (EI): *m/z* 352 (M^+). Anal. Calcd for $C_{15}H_{18}TiCl_3$: C, 51.11; H, 5.15. Found: C, 51.15; H, 5.17.

1,2,3-Trimethyl-1-(trimethylsilyl)tetrahydrobenz[*e*]indene (IIIb). Following the procedure described for **Ib, IIIa** (6.3 g, 30 mmol), 1.6 M butyllithium (18.8 mL, 30 mmol), and chlorotrimethylsilane (3.3 g, 30 mmol) gave **IIIb** (4.95 g, 58%) as an orange oil. ^{1}H NMR ($CDCl_3$): δ 7.15−7.30 (m, 2H), 2.88 (m, 2H), 2.57 (s, 3H), 2.15 (s, 3H), 1.87 (m, 4H), 1.60 (s, 3H), −0.21 (s, 9H). MS (EI): *m/z* 284 (M^+), 211 ($M^+ - SiMe_3$). Anal. Calcd for $C_{19}H_{28}Si$: C, 80.21; H, 9.92. Found: C, 80.18; 9.90.

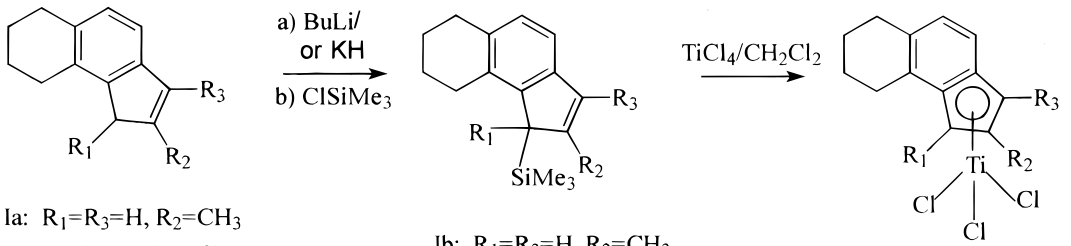
1,2,3-Trimethyltetrahydrobenz[*e*]indenyl)trichlorotitanium (IIIc). Following the procedure described for **Ic**, **IIIb** (4.8 g, 17 mmol) and $TiCl_4$ (3.2 g, 17 mmol) produced **IIIc** (2.8 g, 45%) as red/purple crystals. ^{1}H NMR ($CDCl_3$): δ 7.52−7.71 (m, 2H), 3.35 (s, 3H), 3.14 (s, 3H), 2.92 (s, 3H), 2.85 (m, 2H), 1.88 (m, 4H). MS (EI): *m/z* 366 (M^+). Anal. Calcd for $C_{16}H_{20}TiCl_3$: C, 52.43; H, 5.50. Found: C, 52.40; H, 5.47.

2-Methyl-3-phenyl-tetrahydrobenz[*e*]indene (IVa). To a solution of 2-methyltetrahydrobenz[*e*]indanone (3.0 g, 15.1 mmol) in 100 mL of toluene was added dropwise 3 M phenylmagnesium bromide in ether (6 mL, 18 mmol) at 0 °C. After warming to room temperature, the reaction mixture was stirred for 2 h and then hydrolyzed with 100 mL of a saturated aqueous solution of NH_4Cl and extracted with 350 mL of ether. The organic layers were extracted again with 150 mL of brine, dried over $MgSO_4$, and evaporated to dryness. The solid thus obtained was dissolved in 150 mL of toluene and stirred with 200 mg of *p*-toluenesulfonic acid under reflux for 3 h. After addition of 100 mL of a saturated aqueous solution of $NaHCO_3$ (pH ≈ 7) and extraction with 350 mL of ether, the organic layers were dried over $MgSO_4$ and evaporated to dryness. Further purification by adsorptive filtration over flash silica gel with pentane/ethyl acetate (50:1) as an eluent yielded 3.69 g of pure 2-methyl-3-phenyl-tetrahydrobenz[*e*]indene (**IVa**) as a colorless solid (94% yield). ^{1}H NMR ($CDCl_3$): δ 7.25 (d, 1H), 7.05 (d, 1H), 3.15 (s, 2H), 2.84 (t, 2H), 2.75 (t, 2H), 2.18 (s, 3H), 1.86 (m, 4H), 7.75 (d, 2 orthoPh-H), 7.42 (t, 2 metaPh-H), 7.29 (t, paraPh-H). MS (EI): *m/z* 260 (M^+), 245 ($M^+ - CH_3$), 183 ($M^+ - Ph$). Anal. Calcd for $C_{20}H_{20}$: C, 92.31; H, 7.69. Found: C, 92.40; H, 7.72.

2-Methyl-3-phenyl-1-(trimethylsilyl)tetrahydrobenz[*e*]indene (IVb). A solution of 3.50 g of 2-methyl-3-phenyltetrahydrobenz[*e*]indene (**IVa**) (13.46 mmol) in 100 mL of THF was added at 0 °C to a suspension of 3 equiv of KH (1.80 g, 45.0 mmol) in THF. After the mixture was stirred for 30 h, the deep red solution was filtered to remove the unreacted KH. Me_3SiCl (1.50 g, 13.8 mmol) was then added dropwise at room temperature, and the reaction mixture was stirred overnight. After solvent was removed under reduced pressure, the resulting solid was extracted with toluene (2 × 150 mL). The toluene solution was evaporated to dryness and the residue washed with pentane, yielding **IVb** as a sightly yellow oil (4.02 g, 90%). ^{1}H NMR ($CDCl_3$): δ 7.68−7.50 (m, 2Ph-H), 7.45−7.36 (m, 2Ph-H), 7.27−7.05 (m, 1H + 1Ph-H), 6.95 (d, 1H), 3.78 (bs, Cp-H), 2.83 (m, 4H), 2.20 (s, 3H), 1.84 (m, 4H), −0.29 (s, 9TMS−H). MS (EI): *m/z* 332 (M^+), 259 ($M^+ - SiCH_3$). Anal. Calcd for $C_{23}H_{28}Si$: C, 83.13; H, 6.87. Found: C, 83.18; H, 6.95.

(2-Methyl-3-phenyltetrahydrobenz[*e*]indenyl)trichlorotitanium (IVc). To a solution of **IVb** (4.00 g, 12.05 mmol) in 100 mL of dry toluene was added dropwise redistilled fresh $TiCl_4$ (2.30 g, 12.10 mmol) at 0 °C. The mixture was

Scheme 1



Ia: $R_1=R_3=H, R_2=CH_3$
IIa: $R_1=H, R_2=R_3=CH_3$
IIIa: $R_1=R_2=R_3=CH_3$
IVa: $R_1=H, R_2=Me, R_3=Ph$

Ib: $R_1=R_3=H, R_2=CH_3$
IIb: $R_1=H, R_2=R_3=CH_3$
IIIb: $R_1=R_2=R_3=CH_3$
IVb: $R_1=H, R_2=Me, R_3=Ph$

Ic: $R_1=R_3=H, R_2=CH_3$
IIc: $R_1=H, R_2=R_3=CH_3$
IIIc: $R_1=R_2=R_3=CH_3$
IVc: $R_1=H, R_2=Me, R_3=Ph$

Table 1. Syndiospecific Polymerization of Styrene Using Methylaluminoxane-Activated Half-Sandwich Titanocene Catalysts[a]

titanocene	yield (g)	$10^{-7}A^b$	s-PS[c] (%)	$T_m{}^d$ (°C)	$10^{-5}M_w{}^e$	M_w/M_n
$CpTiCl_3$	0.8	1.45	67.5	256	0.65	2.2
Cp^*TiCl_3	0.4	0.73	98.5	275	4.85	2.1
[Me-Cp]$TiCl_3$	1.0	1.81	78.9	260	0.79	2.0
Ind$TiCl_3$	1.4	2.54	93.4	265	3.0	2.0
[2-Me-Ind]$TiCl_3$	2.2	3.99	95.5	270	3.27	2.1
Benz[*e*]Ind$TiCl_3$	1.8	3.27	95.7	270	3.01	1.9
[2-Me-Benz[*e*]Ind]$TiCl_3$	3.0	5.44	96.2	272	3.35	2.0
[1,2,3-Me_3-Benz[*e*]Ind]$TiCl_3$	1.2	2.18	97.8	275	4.68	2.3
[2-Me-thBenz[*e*]Ind]$TiCl_3$ (**Ic**)	7.5	13.61	95.2	270	0.95	2.1
[2,3-Me_2-thBenz[*e*]Ind]$TiCl_3$ (**IIc**)	7.0	12.70	96.1	272	1.79	2.0
[1,2,3-Me_3-thBenz[*e*]Ind]$TiCl_3$ (**IIIc**)	4.3	7.80	97.5	272	2.56	2.3
[2-Me-3-Ph-thBenz[*e*]Ind]$TiCl_3$ (**IVc**)	8.0[f]	21.77	98.1	275	6.57	2.0
[2-Me-3-Ph-thBenz[*e*]Ind]$TiCl_3$ (**IVc**)[g]	7.5	22.68	98.7	275	6.85	2.1
[2-Me-Cp[*l*]Phen]$TiCl_3$[g]	3.4	10.28	95.0	270	2.75	2.2
[2-Ph-Cp[*l*]Phen]$TiCl_3$[g]	4.2	12.69	96.2	269	5.03	2.0

[a] Polymerization conditions: [Ti] = 83.3 μM; Al/Ti = 1000 mol/mol; [styrene] = 2.94 M; polymerization time = 15 min; polymerization temperature = 60 °C; total volume (styrene + toluene) = 30 mL. [b] *A* (activity) = g of PS/[(mol of Ti)(mol of styrene) h]. [c] s-PS (%) = (g of polymer insoluble in 2-butanone)/(g of total polymer) × 100%. [d] Melting point determined by DSC. [e] Determined by GPC. [f] Polymerization time = 10 min. [g] [Ti] = 50 μM.

warmed to room temperature and stirred for 8 h. The solvent was removed under vacuum, washed with pentane, and then dried to leave a red solid of the compound **IVc**. Yield: 2.87 g (58%). ^{1}H NMR ($CDCl_3$): δ 7.60−7.45 (m, 2Ph-H), 7.35−7.30 (m, 2Ph-H), 7.25−7.10 (m, 2H + 1Ph-H), 7.01 (s, Cp-H), 2.85 (m, 4H), 2.73 (s, 3H), 1.85 (m, 4H). MS (EI): *m/z* 413 (M^+), 378 ($M^+ - Cl$), 342 ($M^+ - 2Cl$). Anal. Calcd for $C_{20}H_{19}TiCl_3$: C, 58.11; H, 4.60. Found: C, 58.23; H, 4.65.

Polymerization and Analytical Procedures. A 100 mL glass reactor equipped with a magnetic stirrer was attached to a high-vacuum line and then sealed under a nitrogen atmosphere. Freshly distilled toluene (20 mL) was introduced through a syringe, followed by addition of styrene (10 mL) and of the appropriate amount of methylaluminoxane(MAO). The bottle was placed in a bath at the desired temperature and stirred for 10 min. The preactivated titanocene compound (1.5−2.5 μmol) with MAO (Al/Ti = 500 mol/mol) in toluene was then added, and the mixture was stirred for selected reaction times. The reaction mixture was subsequently quenched with 10% HCl in methanol, filtered, and dried overnight in a vacuum oven at 85 °C. The polymer was then extracted with 2-butanone for 48 h in a Soxhlet extractor to remove any atactic polymer. The syndiotactic polymer was determined as the amount of polymer insoluble in 2-butanone.

The molecular weight was determined by GPC (Water 150C) using standard polystyrene as reference and 1,2,4-trichlorobenzene as eluent at 135 °C. DSC thermograms were recorded with a Perkin-Elmer DSC-7 system at a heating rate of 10 K/min. The melting temperature of the polymers was determined from the second heating scanning. EPR experiments were run at 60 °C on a Bruker B-R70 X-band EPR spectrometer at ~9.70 GHz with the field centered at ~3400 G; the magnetic field was calibrated with DPPH (*g* = 2.000), and standard solutions of TEMPO (1×10^{-3}−1×10^{-5} M) were used where appropriate for quantitative calculations[7] of the concentrations of titanium (III) species present. The concentration of active species *C** was determined according to the literature.[8]

Results and Discussion

Synthesis of Catalyst Precursors. 2-Methyltetrahydrobenz[*e*]indanone[6] and 2-methyltetrahydrobenz[*e*]indene (**Ia**)[6] were synthesized by literature procedures. 2,3-Dimethyltetrahydrobenz[*e*]indene (**IIa**), 1,2,3-trimethyltetrahydrobenz[*e*]indene (**IIIa**), and 2-methyl-3-phenyltetrahydrobenz[*e*]indene (**IVa**) were prepared by a convenient method as described in Experimental Section. The unsubstituted and/or substituted tetrahydrobenz[*e*]indene were converted into the trimethylsilyl derivatives by reaction with butyllithium or KH followed by chlorotrimethylsilane. The corresponding titanium complexes were obtained by reaction of the unsubstituted and substituted (trimethylsilyl)tetrahydrobenz[*e*]indene derivatives with $TiCl_4$ in a dichloromethane solution (Scheme 1).

Polymerization of Styrene. The newly synthesized complexes (**Ic**−**VIc**) were studied with methylaluminoxane (MAO) as cocatalyst in the syndiospecific polymerization of styrene to demonstrate their catalytic performance. Productivities of these catalysts and the properties of the resulting polystyrene are listed in Table 1, together with those of previously employed half-sandwich titanocenes.

Each of the four new catalyst systems examined were found to be highly active and very stable during the polymerization at the Al:Ti ratio of 1000, as compared with previously employed titanocene catalysts. The activity of compound **Ic**, for example, remained nearly constant over a period of 3.5 h.[9] This low rate of deactivation might be attributable to the increased steric hindrance of the ligand framework, which prevents the system from formation of inactive species by reduction,[4i,10] dimerization,[11] or reaction with oxygen and moisture as well as chain transfer. The tetrahydrobenz[*e*]indenyl-based titanocene complexes **Ic** and/or **IIIc** yield, with MAO, much more active catalysts than their unhydrogenated benz[*e*]indenyl counterparts; this contrasts with substantially reduced activities for the tetrahydroindenyltitanium complex as compared with its indenyl analogue.[4j] These findings, together with the results for MeCpTiCl$_3$, [2-Me-Ind]TiCl$_3$, [2-Me-Benz[*e*]Ind]TiCl$_3$, and [2-Me-thBenz[*e*]Ind]TiCl$_3$ (**Ic**), suggest that the presence of an indenyl (rather than a cyclopentadienyl) ligand moiety satisfies the electronic coordination requirements for high activity; further extension of the ligand framework appears to have mainly steric advantages, which are satisfied by a tetrahydro-C$_6$ ring better than by an aromatic one. From Table 1 one can notice that the methyl-substituted catalysts have substantially higher activities than their unsubstituted counterparts, probably attributable to the donating electronic effect of the methyl substituent. However, further methyl substitution in titanocenes examined, which appears to have mainly steric effects, results in reducing activity. Hindrance of monomer access to the coordination site by more steric substituents would slow down the propagation rate. Similar behavior was observed in CpTiCl$_3$/MAO and Cp*TiCl$_3$/MAO systems.[4]

The strong dependence of polymerization behavior on the details of structural pattern in titanocenes is also shown in the melting points and molecular weights of the polymers, which reflect the stereospecificities and typical chain propagation/chain termination ratios of the different metallocenes (Table 1). As revealved in Table 1, the melting points or the syndiotacticities of polymers obtained with the tetrahydrobenz[*e*]indenyl titanocenes and their unhydrogenated benz[*e*]indenyl counterparts are all very similar (270−275 °C), indicating that tetrahydrogenated benz[*e*]indenyl titanocene catalysts do not result in the regioerrors or stereoerrors of monomer insertion. However, tetrahydrobenz[*e*]indenyltitanocene **Ic, IIc**, **and IIIc** except for complex **IVc** produce polymers of lower molar mass than do their unhydrogenated benz[*e*]indenyl counterparts, despite their higher activity. The findings suggest that a high rate of insertion/propagation is not associated with an increased molar mass of the polymers. Similar behavior was observed in the cyclopentadienyl-, indenyl-, and benz[*e*]indenyl-based half-sandwich titanocene catalysts. These results indicate that the rates of propagation (V_P) and of chain termination (V_T), which determine the mean degree of polymerization, $P_N \approx V_P/V_T$, vary in a partially compensatory manner when the structure of the titanocene catalyst is changed. However, it is not case for the 2-methyl-3-phenyltetrahydrobenz[*e*]indenyl-based catalyst (**IVc**): a high rate of insertion is almost associated with an increased molar mass of the polymer. It seems that an improved control over the rates of both chain propagation (V_P) and chain termination or chain transfer (V_T or V_{tr}) can be fulfilled by designing the ligand structure of metallocene catalysts.

Table 2. Comparison of Activities of Titanocene Catalysts Based on Modified Benz[*e*]indenyl Ligands at Different MAO/Ti Ratio[a]

titanocene	$10^{-7}A$		
	Al/Ti = 500	Al/Ti = 1000	Al/Ti = 4000[c]
CpTiCl$_3$	1.01	1.48	2.82
Cp*TiCl$_3$	0.56	0.74	1.42
IndTiCl$_3$	nil	1.48	4.75
[2-Me-Ind]TiCl$_3$	nil	2.22	7.25
Benz[*e*]IndTiCl$_3$	nil	3.32	12.35
[2-Me-Benz[*e*]Ind]TiCl$_3$	nil	5.54	14.94
[1,2,3-Me$_3$-Benz[*e*]Ind]TiCl$_3$	nil	2.22	6.27
[2-Me-thBenz[*e*]Ind]TiCl$_3$ (**Ic**)	0.50	13.61	19.21
[2,3-Me$_2$-thBenz[*e*]Ind]TiCl$_3$ (**IIc**)	0.49	12.70	17.23
[1,2,3-Me$_3$-thBenz[*e*]Ind]TiCl$_3$ (**IIIc**)	0.15	7.80	10.52
[2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$ (**IVc**)[c]	4.52	21.77	26.45
[2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$ (**IVc**)[d]	4.78	22.68	27.10
[2-Me-Cp[*l*]Phen]TiCl$_3$[d]	2.75	10.28	19.53
[2-Ph-Cp[*l*]Phen]TiCl$_3$[d]	1.12	12.69	24.89

[a] Polymerization conditions: [Ti] = 83.3 μM; [styrene] = 2.94 M; polymerization time = 15 min; polymerization temperature = 60 °C; total volume (styrene + toluene) = 30 mL. [b] A (activity) = g of PS/[(mol of Ti)(mol of styrene) h]. [c] Polymerization time = 10 min. [d] [Ti] = 50 μM.

One can notice that the catalytic system **IVc**/MAO exhibits particularly high activities in the production of polystyrenes with high stereoregularity and molecular weight. It is interesting to note that, when the concentration of catalyst (**IV**) is reduced to 1.5 μmol, the **IV** complex still shows high catalytic activity. In contrast, other catalysts examined except for [2-Me-Cp[*l*]Phen]-TiCl$_3$ and [2-Ph-Cp[*l*]Phen]TiCl$_3$ complexes have no catalytic activity under the identical concentration of catalyst. These findings suggest that the **IVc/**MAO system is highly active and more stable. This is probably attributable to the both electric and steric effects of catalysts. On the one hand, the electron donation from methyl substituent and the increased resonance stabilization from phenyl substitution (the charge of active site can be effectively delocalized into the phenyl ring) would stabilize the active cationic species or facilitate its formation from the trichloro complex and thus enlarge the number of active sites or even make the coordination of the counterion less tight,[4] thus enhancing the overall activity. On the other hand, the variable conformation of the hydrogenated six-membered ring and phenyl substituent in the complex **IVc** makes the titanium center sterically rather inaccessible; this steric congestion at the titanium center could possibly suppress detrimental β-agostic interactions during the propagation.[5,12] As a result, this steric advantage promotes the olefin insertions relative to chain termination by β-H transfer or sterically stabilizes the active species.

The increase of the catalytic activity with an increase of MAO concentration is as expected in all titanocene catalysts examined (Table 2), but high activity was observed even at a fairly low Al/Ti ratio of 1000 for the tetrahydrobenz[*e*]indenyl-based catalytic systems (**Ic**−**IVc**). The benz[*e*]indenyl-, indenyl-, and cyclopenta[*l*]-phenanthryl-based titanocenes are more active only at the higher Al/Ti ratio of 4000. For industrial uses, it is important for thBenz[*e*]Ind-based titanocene catalysts to have both a high activity and a fairly low Al:Ti ratio, because of the resulting reduction in catalyst costs.

The polymerization activities of titanocene catalysts and polymer properties thus obtained are also dependent upon the polymerization temperature. As revealed by Table 3, the catalytic activities increase as the

Table 3. Polymerization of Styrene with Unsubstituted and Substituted [thBenz[*e*]Ind]TiCl$_3$ Compounds Activated with MAO

[thBenz[*e*]Ind]TiCl$_3$ compds								
no.	R$_1$	R$_2$	R$_3$	T_p, °C	$10^{-7}A$[b]	s-PS[c], %	T_m[d], °C	$10^{-5}M_w$[e]
Ic	H	Me	H	20	1.07	96.5	271	2.10
				60	13.61	96.0	270	0.75
				80	13.61	95.5	270	0.70
				100	8.63	90.0	265	0.49
IIc	H	Me	Me	20	1.74	96.8	272	4.69
				60	12.70	96.2	270	1.29
				80	13.53	95.7	270	1.05
				100	8.10	90.7	266	0.90
IIIc	Me	Me	Me	20	0.72	98.5	274	5.78
				60	7.80	97.2	272	2.16
				80	7.94	96.5	272	1.80
				100	7.90	96.2	272	1.23
IVc[f]	H	Me	Ph	20	2.13	99.0	280	7.40
				60	22.68	98.7	275	6.85
				80	23.35	98.5	275	5.96
				100	22.47	97.8	274	4.03

[a] Polymerization conditions: [Ti] = 83.3 μM; Al/Ti = 1000 mol/mol; [styrene] = 2.94 M; polymerization time = 15 min; polymerization temperature = 60 °C; total volume (styrene + toluene) = 30 mL. [b] *A* (activity) = g of PS/[(mol of Ti)(mol of styrene) h]. [c] s-PS (%) = (g of polymer insoluble in 2-butanone)/(g of total polymer) × 100%. [d] Melting point determined by DSC. [e] Determined by GPC. [f] [Ti] = 50.0 μM.

polymerization temperature T_p increases up to 80 °C for the complexes **Ic**−**IVc**. Increasing T_P to 100 °C causes only small reductions in activity and stereospecificity for the **Ic**/MAO and **IIc**/MAO systems. The most interesting catalyst precursors are **IIIc** and **IVc** because of the temperature invariance of their polymerization activity, the polymer melting temperature T_m, and polymer stereospecificity thus obtained in the T_P range investigated. In contrast, many homogeneous metallocene catalysts based on η^5 ligands lead to a precipitous lowering of stereospecificity and T_m value with increasing T_p.[13] On the other hand, one can also notice that the molecular weight (M_w) decreases with increasing polymerization temperature in all of the tetrahydrobenz[*e*]indenyl-based catalyst systems. This can be explained by the fact that the average molecular weights are mainly determined by the k_P/k_{tr} ratio, where k_{tr} increases with temperature faster than k_P with the following decrease of M_w with increasing temperature. It is very interesting that the [2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$ **IVc** leads to a high M_w ($M_w = 4.03 \times 10^5$) even at temperatures as high as 100 °C. These findings indicate that the **IVc**/MAO catalyst is extremely stable.

Figure 1 shows the relationship between the catalytic activity and polymerization time for the [2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$/MAO catalyst. It can be seen from Figure 1 that the activity of thBenz[*e*]Ind-based systems depends on the polymerization time. At higher temperatures, a maximum activity is reached after a short induction time (below 10 min) whereafter the activity decreases. Only at low temperature (20 °C) is the polymerization rate nearly constant over polymerization time.

To get some insight into the effect of the ligands in titanocenes on the polymerization activity, we examined the concentration of active species *C** according to kinetic methods (Table 4).[8] The molar concentrations of active species *C** reported in the text were the average values calculated at polymerization temperature of 60 °C on the basis of yield and M_n values. The ratio of the yields of polymers obtained at low conversion and at short polymerization time to M_n provides the upper limit of the concentration of the active species *C**. The experimental values calculated according to this method obviously could be equal to or larger than the real ones as a consequence of termination and/or transfer reactions. As shown in Table 4, the *C** calculated for [2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$/MAO system is 2.40×10^{-6} mol (corresponding to about 96% of the total Ti) at the Al/Ti ratio of 1000, while the *C** for [2-Me-Ind]TiCl$_3$/MAO and [(2-Me-Benz[*e*]Ind)]TiCl$_3$/MAO systems are respectively 0.70×10^{-6} mol (about 28% of the total Ti) and 0.90×10^{-6} mol (about 36% of the total Ti) under identical conditions. Only at higher Al/Ti ratio (Al/Ti = 4000) have the [2-Me-Ind]TiCl$_3$/MAO and [(2-Me-Benz[*e*]Ind)]TiCl$_3$/MAO systems increased the concentration of active species *C** (70% and 87% of the total Ti, respectively) comparable to other highly active catalysts, thus showing higher polymerization activity. These findings are coincident with the polymerization experiments (Tables 1 and 2). It is clear that the higher activity of thBenz[*e*]Ind-based catalytic systems is due to a greater number of active species.

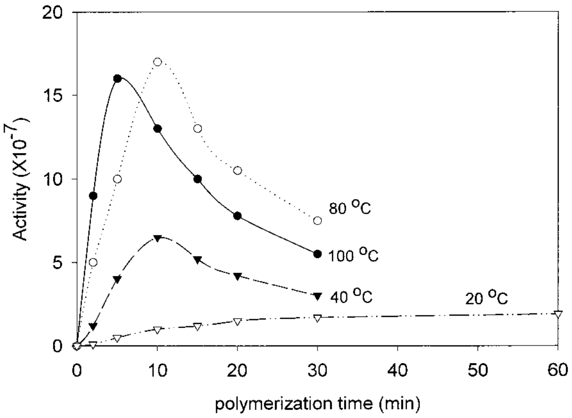


Figure 1. Dependence of polymerization activity on polymerization time with [2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$/MAO catalyst for the polymerization of styrene. [Ti] = 50 μM; Al/Ti = 1000.

It is notable that, under the identical polymerization temperature, these concentrations of active species *C** of titanocene catalysts examined are proportional to the molar concentrations of Ti(III) complexes determined in the presence of styrene by means of quantitative ESR spectroscopy (Table 4 and Figure 2). Figure 2 shows the EPR spectra of [2-Me-Ind]TiCl$_3$/MAO, [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO, and [2-Me-thBenz[*e*]Ind]TiCl$_3$/MAO catalysts. For the [2-Me-thBenz[*e*]Ind]TiCl$_3$/MAO system, the EPR shows a broad singlet at $g = 1.982$ with a hyperfine coupling constant $a = 7.5$ G, together with a shoulder at $g = 1.990$ (Figure 2c). The observed value of $g = 1.982$ and coupling constant lead to the reasonable assignment of this singlet to a Ti(III) hydride species similar to that reported previously for CpTi(OBu)$_3$/MAO system ($g = 1.989$, $a = 7$G).[4d] Hyperfine splitting for the ^{47}Ti ($I = ^5/_2$) and ^{49}Ti ($I = ^7/_2$) isotopes can also be seen. Integration of the spectrum in Figure 2c gives a [Ti(III)] of 85%. The main spectral feature of EPR for the [2-Me-Ind]TiCl$_3$/MAO and [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO (Figure 2a,b) is very similar to that observed in the [2-Me-thBenz[*e*]Ind]TiCl$_3$/MAO system (Figure 2c). However, the main EPR signal attibutable to Ti(III) species shifts toward high field in the [2-Me-Ind]TiCl$_3$/MAO ($g = 1.972$) and [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO systems ($g = 1.979$) and has a lower EPR spectral intensity or lower Ti(III) complex. One can also notice

Table 4. Comparison of Concentration of Active Species and Ti Oxidation State in the MAO-Activated Titanocene Catalysts ([Ti] = 83.3 μM)

titanocene	[MAO]/[Ti], mol/mol	C^* (%)[a]	[Ti(III)] (%)[b]	[Ti(II)] + Ti(IV)] (%)
[2-Me-Ind]TiCl$_3$	1000	28	24.2	75.8
	4000	70	65.1	34.9
[2-Me-Benz[*e*]Ind]TiCl$_3$	1000	36	29.9	70.1
	4000	87	75.1	24.9
[2-Me-thBenz[*e*]Ind]TiCl$_3$ (**Ic**)	1000	85	73.5	26.5
	4000	94	80.7	19.3
[2-Me-3-Ph-thBenz[*e*]Ind]TiCl$_3$ (**IVc**)	1000	96	82.5	17.5
	4000	98	86.3	13.7

[a] Determined by kinetic method in percentage of the total titanocene. [b] Determined in the presence of styrene by EPR spectra.

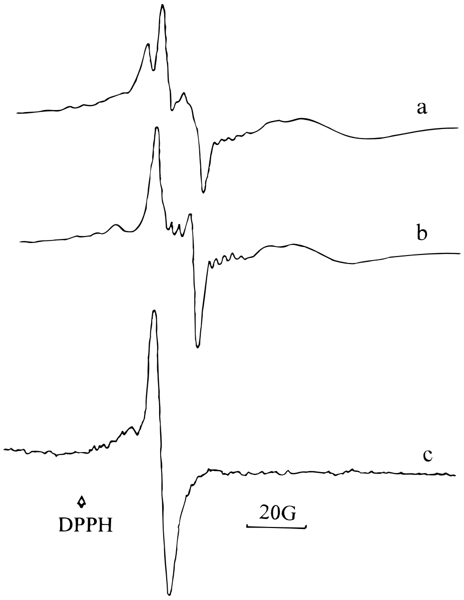


Figure 2. EPR spectra of (a) [2-Me-Ind]TiCl$_3$/MAO, [Ti] = 83.3 μM, Al/Ti = 1000; (b) [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO, [Ti] = 83.3 μM, Al/Ti = 1000; and (c) [2-Me-thBenz[*e*]Ind]TiCl$_3$/MAO, [Ti] = 83.3 μM, Al/Ti = 1000.

that there are additional three resonances between $g = 1.970$ and $g = 1.949$, and EPR shows excessive line broadening in the [2-Me-Ind]TiCl$_3$/MAO and [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO systems, which is probably caused by various types of interactions between paramagnetic ions (including ^{27}Al nuclei interactions)[4d,k] and/or the change of the Ti oxidation states to diamagnetic Ti(IV) or Ti(II).[4d] The EPR results are very reproducible in our experiments. These findings, combined with the polymerization experiments, further support the fact that the Ti(III) complexes constitute the major active species for syndiospecific polymerization of styrene;[4d,g,h,k,l,n−s] while Ti(IV)[14] and even Ti(II) complexes[15] as active species may not be ruled out. It must be pointed out that EPR spectroscopy is an exceedingly sensitive spectroscopic technique, and thus the traces of impurities far below concentration could cause the difficulty to calculate the precise Ti(III) concentrations. The sample preparation, aging time, and test temperature are also crucial in EPR experiments. Therefore, inconsistent results may be observed in some catalyst systems.[14]

As already discussed, the catalyst structure has a great influence on the polymer molecular weight. It is believed that the ratio of the rates of chain propagation to chain termination or chain transfer control the polymer molecular weights. Up to now, few investigations are carried out to quantitatively determine the relative ratio of these processes.[4c,n] To quantitatively evaluate the effect of ligands in titanocenes examined on the relative weight of these processes, we investigated the kinetics of styrene polymerization. We found that, in all cases of styrene polymerization with titanocene catalysts examined, the variation of yield of sPS with monomer concentration was linear, suggesting a first-order kinetics with respect to the monomer. Therefore, the kinetic equation for propagation reaction rate V_P is the following:[8]

$$V_P = k_p C^*[S] \tag{1}$$

where k_p, C^*, and S are the specific kinetic constant of the propagation reaction, the molar concentration of the active site, and the styrene molar concentration, respectively. The number-average degree of polymerization ($P_N = V_P/V_{tr}$, where V_{tr} is the sum of the rates of all chain transfer or chain termination) is given by[4]

$$1/P_N = k_{tr}^{M}/k_P + (k_{tr}^{\beta} + k_{tr}^{A})/k_P[S] \tag{2}$$

where k_P, k_{tr}^{M}, k_{tr}^{β}, and k_{tr}^{A} are propagation rate contant, the rate contant of chain transfer with monomer, of β-H elimination, and of chain transfer to MAO, respectively. To simplify the kinetic calculation for comparison, we only consider the kinetic contribution from the Ti(III) complex. In fact, the Ti(III) complex is the main active species in the syndiospecific polymerization of styrene, as suggested from the findings of the kinetic investigation, EPR spectrum, and polymerization experiments (vide supra). Ti(IV) and Ti(II) as active species, if any, are very minor in the system examined. Therefore, the k_p and k_{tr} values in the eqs 1 and 2 are only characteristic of the Ti(III) oxidation state.

In addition, we observed that the concentration of MAO did not affect the molecular weight of sPS. Similar behavior have been observed in previous investigations.[4] Therefore, it is reasonable that the chain transfer to MAO is negligible in the syndiospecific styrene polymerization. Equation 2 can be changed:

$$1/P_N = k_{tr}^{M}/k_P + (k_{tr}^{\beta}/k_p)1/[S] \tag{3}$$

The number-average degree of polymerization, P_N, can be calculated according to the relationship $P_N = M_n$/(monomer molecular weight). The intercept and the slope of a plot of $1/P_N$ versus $1/[S]$ provides the k_{tr}^{β}/k_p and k_{tr}^{M}/k_p ratio, respectively. We calculated $k_{tr}^{\beta}/k_p = 5.0 \times 10^{-4}$ and $k_{tr}^{M}/k_p = 0.4 \times 10^{-4}$ for styrene polymerizations carried out at 60 °C in the presence of the **IVc**/MAO system (Figure 3). Under identical conditions, we also calculated $k_{tr}^{\beta}/k_p = 1.3 \times 10^{-3}$ and $k_{tr}^{M}/k_p = 0.2 \times 10^{-3}$ for the [2-Me-Ind]TiCl$_3$/MAO system, $k_{tr}^{\beta}/k_p = 9.0 \times 10^{-4}$ and $k_{tr}^{M}/k_p = 1.5 \times 10^{-4}$ for the [(2-Me-Benz[*e*]Ind)]TiCl$_3$/MAO catalyst, $k_{tr}^{\beta}/k_p = 6.8 \times 10^{-4}$ and $k_{tr}^{M}/k_p = 0.5 \times 10^{-4}$ for the [(2-Ph-Cp[*l*]Phen)]TiCl$_3$/MAO catalyst, and $k_{tr}^{\beta}/k_p = 1.1 \times 10^{-2}$ and $k_{tr}^{M}/k_p = 0.15 \times 10^{-2}$ for the [(2-Me-thBenz[*e*]Ind)]TiCl$_3$/MAO

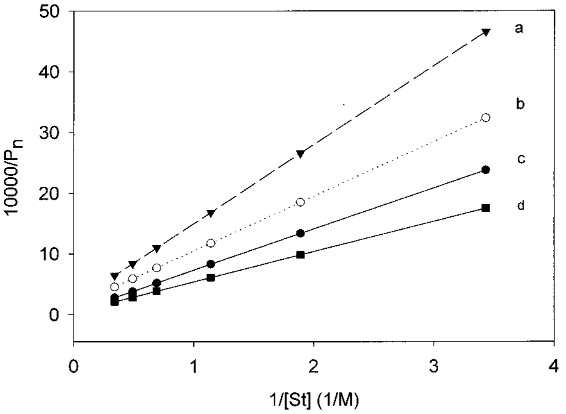


Figure 3. Plot of $1/P_N$ versus 1/[S] for the sPS polymerization carried out with MAO-activated titanocene catalysts at 60 °C: (a) [2-Me-Ind]TiCl$_3$/MAO; (b) [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO; (c) [2-Ph-Cp[*l*]Phen]TiCl$_3$/MAO; (d) [2-Me-3-Ph-thBenz[*e*]Ind]-TiCl$_3$(**IIIc**)/MAO.

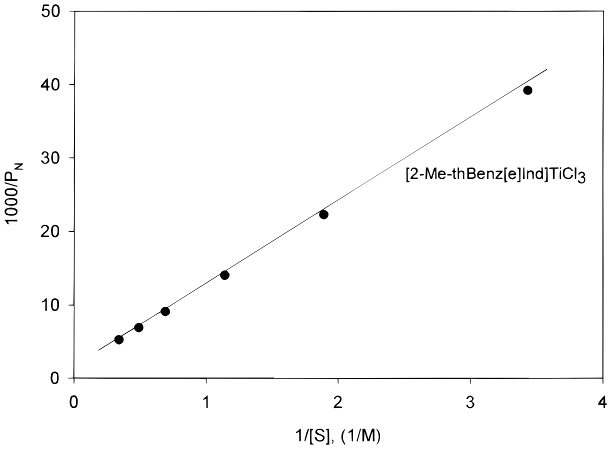


Figure 4. Plot of $1/P_N$ versus 1/[S] for the sPS polymerization by using MAO-activated complex [2-Me-thBenz[*e*]Ind]TiCl$_3$ (**Ic**) at 60 °C.

system (Figure 4). Similarly, Grassi et al.[4n] also observed $k_{tr}^{\beta}/k_p = 5.8 \times 10^{-3}$ and $k_{tr}^{M}/k_p = 1.3 \times 10^{-3}$ for styrene polymerizations carried out at 50 °C in the presence of the Cp*Ti(CH$_2$Ph)$_3$/B(C$_6$F$_5$)$_3$ system. From these results it can be seen that, by comparison with other catalyst systems examined, the [2-Me-3-Ph-th-Benz[*e*]Ind]TiCl$_3$/MAO system might apparently favor reducing their tendency for chain termination or chain transfer processes and enhancing their tendency for chain propagation, thus increasing the polymer molecular weight.

On the other hand, the ratio of the two chain transfer processes ($k_{tr}^{\beta}/k_{tr}^{M}$) inflects the information on the transfer mechanism of the active sites. The ratio of $k_{tr}^{\beta}/k_{tr}^{M}$ for **IVc**/MAO system is no less than 12, indicating that β-H migration from the polymer chain to the metal of the active sites (β-H elimination) is the main termination process and that hydrogen transfer to the monomer may be ruled out, if any. The ratio of $k_{tr}^{\beta}/k_{tr}^{M}$ for the [2-Me-Ind]TiCl$_3$/MAO, [2-Me-Benz[*e*]Ind]TiCl$_3$/MAO, [2-Ph-Cp[*l*]Phen]TiCl$_3$/MAO, and [2-Me-thBenz-[*e*]Ind]TiCl$_3$/MAO catalytic systems are 6.5, 6.0, 13.6, and 7.3, respectively. These findings indicate that β-H elimination is still the main termination process in these titanocene catalysts.

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