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(η^5-Indenyl)trichlorotitanium. An Improved Syndiotactic Polymerization Catalyst for Styrene

Thomas E. Ready, Roberta O. Day,
James C. W. Chien,* and Marvin D. Rausch*

Departments of Chemistry and of Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Organotitanium compounds activated with methylaluminoxane (MAO) were discovered to catalyze syndiospecific polymerization of styrene at ambient temperature.[1] (Monocyclopentadienyl)trialkoxytitanium, (monocyclopentadienyl)trichlorotitanium, and (pentamethylcyclopentadienyl)trichlorotitanium are among the most active catalysts,[1,2] but their activities (*A*) and stereospecificities are sensitive to various polymerization conditions such as temperature (T_p), [MAO]/[Ti] ratio, dielectric constant of media, and monomer concentration. We report here that (η^5-indenyl)trichlorotitanium ($IndTiCl_3$) activated with MAO is a catalyst exceedingly high in both *A* and specificity and which is relatively insensitive to polymerization conditions.

$CpTiCl_3$ was prepared by a literature procedure.[3] The synthetic method for $(C_5Me_5)TiCl_3$[4] was adapted to synthesize $IndTiCl_3$. 1-(Trimethylsilyl)indene[5] (25.0 g, 0.133 mol) was added dropwise to a solution of $TiCl_4$ (17.5 mL, 0.16 mol in 200 mL of CH_2Cl_2). After overnight reaction and storage at −20 °C for 24 h, the solvent was decanted. The remaining dark red crystals (34.2 g, 96.3% yield) were dried under vacuum and sublimed at 80 °C and 0.001 mmHg. The compound was characterized by its proton NMR spectrum,[7] elemental analysis,[8] and X-ray structure.[9]

$IndTiCl_3$ exists in the solid state as a monomer in which the indenyl group shows η^5 bonding. The bonding is not entirely symmetrical in that bonds from the Ti atom to C(8) and C(9) are about 0.1 Å longer than those to C(1), C(2), and C(3). This feature distinguishes the molecule from the related Cp[10] and $(Me_3Si)_2Cp$[11] compounds in which no hint of ring slippage is observed. However, bis(η^5-indenyl) compounds of Ti, Zr, and Hf do show a similar difference in the M–C(π) distances,[12,13] suggesting that this feature is characteristic of η^5 bonding to the indenyl group.

The geometry about the Ti atom, as defined by the centroid of the five-membered ring and the Cl atoms, is nearly tetrahedral, where the angles from the centroid to the Cl atoms are slightly larger (average 115.1 (1) Å) than the angles between the Cl atoms (average 103.42 (3) Å). The least-squares mean plane through the nine atoms of the indenyl group (coplanar to within ±0.042 (3) Å) is nearly parallel to the plane defined by the three Cl atoms (dihedral angle = 3.5 (3)°). The indenyl group is canted with respect to the latter plane so that atoms C(1), C(2), and C(3) are closest and atoms C(5), C(6), and C(7) are furthest away.

Polymerizations[14] of styrene produce a mixture of syndiotactic and atactic polystyrenes, *s*-PS and *a*-PS, respectively. A measure of syndiospecificity is the yield of the former (SY) in wt %. The results are summarized in Table I.

The functions of MAO are not well understood, however; the scavenging of impurities is certainly one of them.[15] In the present experiments, a concentration minimum of about 50 mM of MAO is required, below which there is little or no polymerization activity (runs 5 and 8). An increase of [MAO] increases the *A*, reaching the maximum values at [Al]/[Ti] of *ca.* 4000 (run 3). The decline of *A* at still higher amounts of MAO may be due to excessive alkylation or decomposition of the titanium compound. The $IndTiCl_3$/MAO catalyst system appears to be 50–100% more active than the corresponding $CpTiCl_3$/MAO system.

Previously we found by radio-quenching experiments that 75% of $CpTi(OR)_3$ was converted by MAO to active species.[2b] If this is true here, then the slightly greater *A* for $IndTiCl_3$ may be attributed to the higher propagation rate due to the greater electron-donating ability of the indenyl ring relative to the Cp moiety.[16] The SY is lower for $CpTiCl_3$/MAO catalysis which seems to increase from 63% at low Al/Ti ratio to 79.5% for [Al]/[Ti] = 6000. In contradistinction, the $IndTiCl_3$/MAO system exhibits very high stereospecificity of 95.8–96.6% over the entire [Al]/[Ti] range studied.

In runs 3, 6, and 7 with [Al]/[Ti] = 4000, both the *A* and SY of $IndTiCl_3$/MAO are not much affected by changes in [$IndTiCl_3$]. In comparison, a decrease of [$CpTiCl_3$] tends to lower SY and raise *A*.

Many homogeneous Ziegler–Natta catalysts based on pentahapto ligands lose stereospecificity precipitously with an increase of T_p.[17] This appears also to be the case for the $CpTiCl_3$/MAO system (last four entries on Table I).

Table I. Styrene Polymerization Catalyzed by $IndTiCl_3$ and $CpTiCl_3$ with MAO

					$CpTiCl_3$			$IndTiCl_3$		
run	[Ti] (μM)	[MAO] (M)	Al/Ti	T_p (°C)	total yield PS (g)	A^a ($\times 10^{-7}$)	s-PS^b (%)	total yield PS (g)	A^a ($\times 10^{-7}$)	s-PS^b (%)
1	50	0.4	8000	25				0.530	0.97	95.8
2	50	0.3	6000	25	0.289	0.53	79.5	0.651	1.2	96.1
3	50	0.2	4000	25	0.502	0.92	63.2	1.024	1.9	96.6
4	50	0.1	2000	25	0.356	0.67	63.4	0.525	0.96	96.6
5	50	0.05	1000	25				0.099	0.18	96.0
6	100	0.4	4000	25	0.703	0.64	86.3	1.381	1.3	94.1
3	50	0.2	4000	25	0.502	0.92	63.2	1.024	1.9	96.6
7	25	0.1	4000	25	0.305	1.1	59.1	0.451	1.7	92.2
8	12.5	0.05	4000	25				0.001	0.0017	
9	50	0.2	4000	100				0.600	1.1	89.6
10	50	0.2	4000	75	0.614	1.1	52.4	0.969	1.8	96.3
11	50	0.2	4000	50	0.749	1.4	67.4	2.039	3.7	98.2
3	50	0.2	4000	25	0.502	0.92	63.2	1.024	1.9	96.6
12	50	0.2	4000	0	0.308	0.57	89.3	0.293	0.54	95.6

[a] *A* (activity) = (g of bulk polymer)/(mol of Ti)(mol of monomer)(h). [b] % *s*-PS = (g of 2-butanone insoluble polymer)/(g of bulk polymer) × 100.

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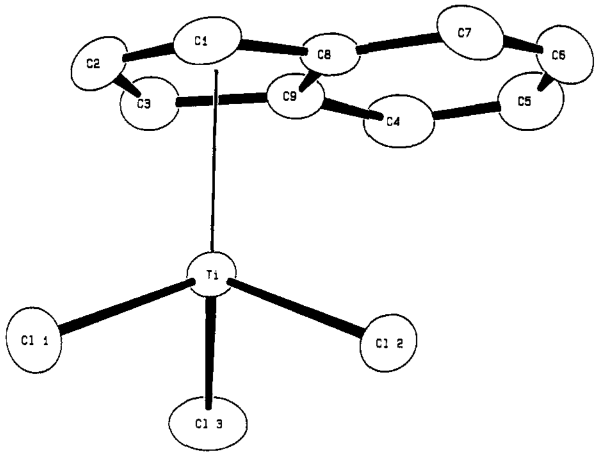

Figure 1. ORTEP plot of $IndTiCl_3$ with thermal ellipsoids at the 30% probability level. Distances (Å): Ti–Cl(1) = 2.2248 (8), Ti–Cl(2) = 2.2319 (8), Ti–Cl(3) = 2.2355 (8), Ti–CENT = 2.032 (3), Ti–C(1) = 2.333 (3), Ti–C(2) = 2.319 (3), Ti–C(3) = 2.304 (3), Ti–C(8) = 2.433 (2), Ti–C(9) = 2.404 (2). Angles (deg): CENT–Ti–Cl(1) = 116.45 (8), CENT–Ti–Cl(2) = 114.21 (8), CENT–Ti–Cl(3) = 114.69 (8), Cl(1)–Ti–Cl(2) = 102.44 (3), Cl(1)–Ti–Cl(3) = 103.32 (3), Cl(2)–Ti–Cl(3) = 104.09 (3). CENT = centroid of the five-membered ring.

In comparison, both the *A* and SY of $IndTiCl_3$/MAO remained high up to T_p = 75 °C. Nonbonded steric interactions have been shown to be responsible for the stereospecificities in propylene polymerization promoted by zirconocenium catalysts.[18] It seems plausible to attribute the observed differences in stereospecificity of the catalysts to the large steric interactions between the benzene ring of the indenyl ligand with the phenyl ring of the π-complexed and the 2,1-inserted[19] monomers. These interactions are diminished in the Cp case.

In conclusion, we have synthesized $IndTiCl_3$ in 96% yield, obtained its X-ray structure, and demonstrated that it possesses unusually high activity and syndioselectivity in styrene polymerizations which are relatively insensitive to T_p, catalyst concentration, and [Al]/[Ti]. These are exceedingly important attributes for a commercially viable polymerization catalyst.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, distances and angles, and selected mean planes (6 pages). Ordering information is given on any current masthead page.

References and Notes

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(5) 1-(Trimethylsilyl)indene was synthesized by a modification of a literature procedure:[6] bp 78–80 °C (0.3 mm), 78% yield. ^1H NMR ($CDCl_3$): δ 7.5–7.15 (m, 4H, ar), 6.95 (d, 1H, sp^2 3-position, $J_{3,2}$ = 3 Hz), 6.65 (d, 1H, sp^2 2-position, $J_{2,3}$ = 3 Hz), 3.55 (s, 1H, sp^3 1-position), 0.01 (s, 9H, TMS–CH_3).

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(7) ^1H NMR spectrum of $IndTiCl_3$ in $CDCl_3$: δ 7.81 (m, 2H, ar), 7.55 (m, 2H, ar), 7.19 (d, 2H, $J_{1,2} = J_{3,2}$ = 12 Hz), 7.16 (t, 1H, $J_{1,2} = J_{3,2}$ = 12 Hz).

(8) Analysis for $IndTiCl_3$. Calcd for $C_9H_7Cl_3Ti$: C, 42.38; H, 3.20. Found: C, 42.53; H, 3.35.

(9) Crystal data: $C_9H_7TiCl_3$, monoclinic space group $P2_1/n$ (No. 14), a = 7.042 (1) Å, b = 12.501 Å, c = 12.068 (1) Å, β = 97.52 (1) Å, V = 1053.2 (3) Å^3, Z = 4, and $\mu_{\mathrm{Mo}\ K\alpha}$ = 15.211 cm^{-1}. A total of 1851 independent reflections was measured (Enraf-Nonius CAD4 diffractometer, 23 ± 2 °C, graphite-monochromatized Mo radiation, $\lambda(K\alpha)$ = 0.710 73 Å, $2\theta_{\max}$ = 50°). An empirical absorption correction based on ψ scans was applied. Anisotropic refinement of non-hydrogen atoms with hydrogen atoms as fixed isotropic scatterers in ideal positions led to R = 0.029 and R_w = 0.055 for 1554 observed reflections ($I \geq 3\sigma_I$).

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