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Fluorinated Half-Sandwich Complexes as Catalysts in Syndiospecific Styrene Polymerization

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ABSTRACT: Fluorinated half-sandwich complexes of titanium, such as $CpTiF_3$, show an increase in activity of up to a factor of 50 compared to chlorinated compounds. In a temperature range of 10−70 °C the excess of methylaluminoxane (MAO) can be reduced to an Al:Ti ratio of 300. The highest melting point of 277 °C can be obtained using pentamethylcyclopentadienyltitanium trifluoride Cp^*TiF_3. This fluorinated complex affords polymers with a significantly higher molecular weight than with the chlorinated compound. Alkyl substitution of the cyclopentadienyl ligand can increase the activity.

Introduction

Polystyrene is an indispensable commodity plastic similar to polyolefins. The monomer is easily available. Since Ishihara at Idemitsu showed how to produce syndiotactic polystyrene by titanium/MAO catalysts, a great number of patents and papers for technical applications have been published.[1−9]

In contrast to the long known isotactic polystyrene, which shows a slow crystallization rate and is therefore useless for most industrial applications, the syndiotactic material shows a fast crystallization rate and a higher melting point of 275 °C compared to 240 °C, the melting point of the isotactic polymer, and compared to the glass transition temperature of 100 °C of the common atactic polymer. These new properties, which are similar to those of some expensive engineering plastics are the reason for the interest in syndiotactic polystyrene.

A variety of alkoxy, cyclopentadienyl, and pentamethylcyclopentadienyl complexes of titanium, zirconium, and hafnium have been investigated, e.g., by Ishihara,[10] Zambelli,[11] Chien,[12] Grassi,[13] and Soga[14] for the syndiospecific polymerization of styrene.

Table 1 compares some typical catalysts described in the literature for the production of syndiotactic polystyrene.

The highest activities are achieved with half-sandwich titanocenes of the type $CpTiCl_3$, $IndTiCl_3$, and substituted $IndTiCl_3$ with methylaluminoxane (MAO) as cocatalyst. $BMe(C_6F_5)_3$ and other borates can be used as precursors instead of MAO.

Zirconium complexes can also be activated by MAO for the polymerization of styrene. They are less active than the titanium compounds and show lower syndiospecificities and molecular masses for the polymers. The technical production of syndiotactic polystyrene is hindered by reactor fouling, which is caused by polymer precipitation during the polymerization.

In comparison to the polymerization of olefins, the activity for the polymerization of styrene is much lower. Because of this, an intensive search to find more active catalysts has begun.

First experiments show that fluorinated catalysts not only have much higher activities and produce polymers with higher molecular weights but also allow the reduction of the molar titanium/MAO ratio.[19,20]

It is difficult to compare the results presented in the literature (see Table 1) because the process parameters are different. Therefore, the polymerizations were carried out under identical conditions in this work and compared to catalysts from the literature.

Results and Discussion

The polymerizations were carried out in a temperature range of 10−70 °C. Figure 1 compares the average

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Table 1. Typical Catalysts for the Syndiospecific Polymerization of Styrene[a]

catalyst[b]	T (°C)	10^{-4}[M] (mol/L)	[S] (mol/L)	Al:M	A	10^{-3} M_W	lit
$TiCl_4$	50	4.07	1.63	800	8.5		10
$Ti(OEt)_4$	50	4.07	1.63	800	19.8		10
$TiBz_4$	50	6.25	3.26	100	18.3	153	11
$CpTiCl_3$	50	4.07	1.63	600	207		10
Cp^*TiCl_3	50	4.07	1.63	600	157		10
$IndTiCl_3$	30	1.00	4.3	1000	260		
$(1\text{-PhInd})TiCl_3$	50	0.5	0.88	4000	3400	424	6
(2-methylbenz[*e*]indenyl)$TiCl_3$	50	0.5	0.88	4000	8000	424	6
$CpTiCl_2$	50	4.07	1.63	600	92		10
Cp_2TiCl_2	50	4.07	1.63	600	2.1		10
$Ti(acac)_2$	50	6.25	3.26	100	6.4	327	11
$(\eta^6\text{-}C_6H_5Me)\ Ti(Cl_2AlCl_2)$	50	27	2.6	700	1.8	1190	15
$CpTiCl_3/(Bu_3Sn)_2$	25	1.8	1.74	1244	11.9		16
$Cp^*TiBz_3/\ B(C_6F_5)_3$	50	27.5	2.72		409		17
$ZrBz_4$	50	6.25	3.26	100	3.4	9	11
$Zr(OPr)_4$	50	0.09			1.8×10^{-5}	14	18

[a] T = polymerization temperature, [M] = concentration of the catalyst, [S] = styrene concentration, Al:M = molar ratio (cocatalyst MAO), A (activity) = (kg of sPS)/(mol of M h), M_W = molecular weight. [b] Et = ethyl, Bz = benzyl, Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl, Ind = indenyl, acac = acetylacetonato, Bu = butyl, Pr = propyl, Ph = phenyl.

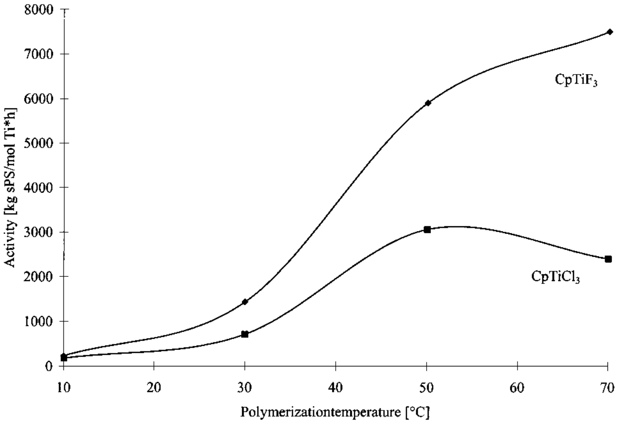

Figure 1. Activity of the polymerization of styrene with $CpTiX_3$/MAO with X = Cl and F at different polymerization temperatures. [Ti] = 6.25×10^{-5}, Al:Ti = 900.

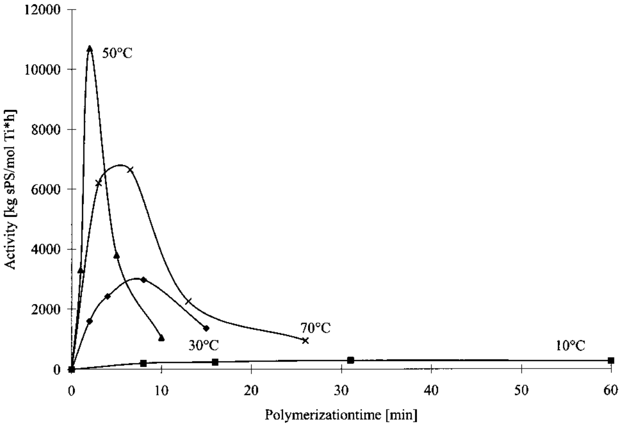

Figure 2. Dependence of polymerization activity on polymerization time with $CpTiF_3$/MAO for the polymerization of styrene. [Ti] = 6.25×10^{-5}, Al:Ti = 300.

polymerization activities of $CpTiCl_3$ and $CpTiF_3$. At all temperatures, the fluorinated compound is more active than its chlorinated counterpart. The chlorinated system is less stable, as can be seen by the decrease of the average activity at 70 °C. On the other hand, the activity for the fluorinated system is also dependent on the polymerization time (Figure 2). At higher temperatures (50 °C), a maximum activity is reached after a short induction time whereafter the activity decreases. Only at low temperatures (10 °C) is the polymerization rate nearly constant over time.

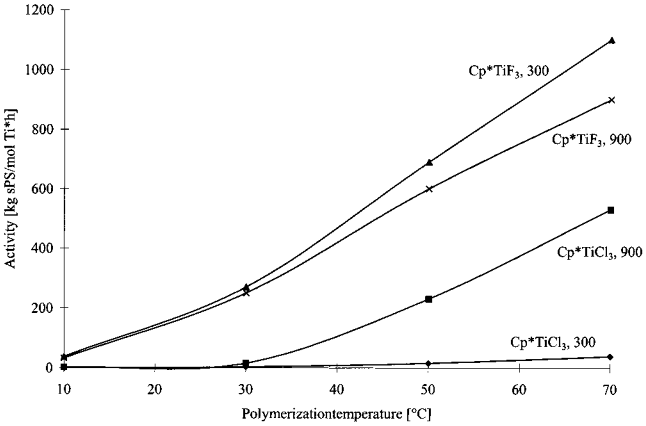

Figure 3. Dependence of polymerization activity on polymerization temperature for different Al:Ti ratios for the polymerization of styrene. Catalyst: Cp^*TiX_3 (X = Cl and F), Al:Ti = 300 and 900, [Ti] = 6.25×10^{-4}.

The melting points of the obtained polymers are 258 °C for the chlorinated system and 265 °C for the fluorinated catalyst at a polymerization temperature of 50 °C. Over the whole range of polymerization temperatures, the melting points of the polymers made with $CpTiF_3$ are 5−10 deg higher.

If the cyclopentadienyl ligand in the metallocene is changed to a pentamethylcyclopentadienyl ligand (Cp*), which is a stronger electron donor and exerts a greater sterical hindrance, the polymerization activity is lowered. On the other hand, hydrogen transfer reactions tend to occur less often, so that the molecular weight of the obtained polystyrene increases. The thermostability of this catalyst is high. If, again, the chlorine atoms are substituted by fluorine atoms, the activity rises drastically (Figure 3). At a molar ratio of Al:Ti = 300, the polymerization activity of the fluorinated catalyst is about 30 times higher than that of the chlorinated system. The main activity is reached at 70 °C. As known from the polymerization of olefins, the activity is influenced by the Al:Ti ratio. Higher activities for the fluorinated catalysts are reached at a fairly low Al:Ti ratio of 300, while the chlorinated system is more active at the higher Al:Ti ratio of 900. For industrial uses, it is important to have both a high activity and a low Al:Ti ratio, because of the resulting reduction in catalyst costs. The syndiotacticity of the polystyrene obtained is exceedingly high, as can be seen in the melting points of 275 °C.

Table 2. Polymerization of Styrene with $(MeCp)TiF_3$ at Different Temperatures[a]

T (°C)	t (min)	yield (mg)	A	mp	mol mass
10	10	93	220	271	
10	20	392	720	272	
10	40	768	450	272	1 420 000
10	90	1573	390	270	1 050 000
30	5	571	2750	271	520 000
50	5	2890	14000	269	140 000
70	5	1852	8900	264	42 000

[a] T = polymerization temperature, t = polymerization time, A (activity) = (kg of sPS)/(mol of Ti h), mp = melting point of the syndiotactic PS in °C, styrene concentration = 4.3 mol/L, Ti concentration = 6.25×10^{-5} mol/L; Al:Ti = 300.

Table 3. Comparison of the Activities (kg of sPS)/(mol of Ti h) of Chlorinated and Fluorinated $(RMe_4Cp)TiX_3$ of the Syndiospecific Polymerization of Styrene at 30 °C[a]

catalyst	X = Cl	X = F
$(Me_5Cp)TiX_3$/MAO	6.0	480
$(EtMe_4Cp)X_3$/MAO	3.1	160
(n-$PrMe_4Cp)X_3$/MAO	2.6	160
(n-$BuMe_4Cp)X_3$/MAO	2.8	180

[a] Ti concentration = 6.25×10^{-5} mol/L, Al:Ti = 500, styrene concentration = 4.3 mol/L.

The highest activity is reached by using methylcyclopentadienyltitanium trifluoride $(MeCp)TiF_3$ in combination with MAO (Table 2).

At a low Al:Ti ratio of 300, activities of up to 14 000 kg of syndiotactic polystyrene in 1 h can be achieved. These are values very close to activities obtained with metallocene catalysts in the polymerization of olefins. Up to 50 °C, the activity is very stable over time. An influence on the melting points of the obtained polystyrenes can also be observed. On average, the melting points of the polymers are 7 deg higher than those of the polymers obtained with $CpTiF_3$. This shows that the substitution of methyl not only has an influence on the activity caused by electronic effects but also has an effect on the syndiotacticity and the molecular mass.

Therefore, the influence of other higher substituted cyclopentadienyltitanium trichlorides and trifluorides such as $(EtMe_4)TiCl_3$, $(PrMe_4Cp)TiCl_3$, $(BuMe_4Cp)TiCl_3$, $(EtMe_4Cp)TiF_3$, and $(BuMe_4Cp)TiF_3$ was investigated (Table 3). Table 3 compares the activities of pentamethyl-, ethyltetramethyl-, propyltetramethyl-, and butyltetramethylcyclopentadienyltitanium trichlorides and trifluorides at a polymerization temperature of 30 °C.

It is apparent that the influence of the substitution from ethyl to butyl is not very strong. Only the pentamethylcyclopentadienyl compound has a significantly higher activity. In all cases the fluorinated catalysts are about 40 times more active than the chlorinated ones.

In Table 4 the results of the compounds discussed are summarized together with some other fluorinated titanium, zirconium, and hafnium compounds.

The catalyst Cp^*TiF_3 is highly active, producing syndiotactic polystyrene with a very high melting point of 277 °C and a high molecular weight (660 000 at 50 °C) and showing thermal stability up to polymerization temperatures of 70 °C, while the chlorinated analogue has a strongly reduced activity and causes a lower molecular weight in the resulting polymer.

The activity of fluorinated complexes decreases drastically when zirconium or hafnium compounds are used instead of titanium (Table 4). In comparison to the chlorinated compounds, the fluorinated systems are again much more active, but on a lower level. The same decrease in activity is found for substituted bis(cyclopentadienyl)titanium difluorides. Their activity is lower than that of the half sandwich complexes by a factor of 1000−5000. The two Cp rings hinder the polymerization and make a higher Al:Ti ratio necessary. The molecular weight distribution is about 2 for all catalysts.

Table 4. Synthesis of Syndiotactic Polystyrene with Different Titanium and Zirconium/MAO Complexes[a]

catalyst	T (°C)	A	mp (°C)	M_w	M_w/M_n
$CpTiCl_3$	50	1100	258	140 000	1.9
$CpTiF_3$	50	3000	265	100 000	2.0
Cp^*TiCl_3	30	3.5	277	186 000	2.3
Cp^*TiCl_3	50	15	275	169 000	3.6
Cp^*TiF_3	30	300	277	700 000	1.8
Cp^*TiF_3	50	690	275	660 000	2.0
Cp^*ZrCl_3	50	0.08	249	16 000	1.6
Cp^*ZrF_3	50	0.9	248	38 000	2.5
$(MeCp)_2TiF_2$	50	1.8	264	121 000	2.4
$(Me_3SiCp)_2TiF_2$	10	0.2	275	290 000	1.7

[a] T = polymerization temperature, A (activity) = (kg of PS)/(mol of Ti (Zr) h), mp = melting point, M_w = molecular weight, styrene concentration = 4.3 mol/L, [Ti] = 6.25×10^{-5} mol/L, [Zr] = 6.25×10^{-4} mol/L, Al:Ti = 300.

Substituted cyclopentadienyltitanium trifluoride compounds, such as $MeCpTiF_3$, show thermal stability up to 70 °C and activities of up to 14 000 (kg of syndiotactic polystyrene)/(mol of catalyst h). The melting points are between those of polymers obtained with Cp and Cp* systems. The Al:Ti ratio of 300 is acceptable for industrial scale production.

Work is in progress to find out whether the higher activity of the fluorinated catalysts is due to a greater number of active species or due to the active species having different oxidation states and thus propagation rate constants.

Experimental Section

Experiments were performed in an inert gas atmosphere using Schlenk techniques or a drybox.

Materials. Toluene that was used as solvent was purified by refluxing over sodium−potassium alloy for at least 1 week followed by distillation. Styrene was commercially obtained from Fluka and dried over calcium hydride for 5 days and distilled under reduced pressure. Methylaluminoxane was purchased from Witco.

$CpTiCl_3$, $CpTiF_3$, Cp^*TiCl_3, Cp^*TiF_3, $MeCpTiF_3$, Cp^*ZrCl_3, Cp^*ZrF_3, $(MeCp)_2TiF_2$, and $(Me_3SiCp)_2TiF_2$ were prepared according to the literature.[19,21]

The substituted cyclopentadienyl compounds $EtMe_4CpH$, n-$PrMe_4CpH$, and n-$BuMe_4CpH$ were prepared according to the literature:[22] 2-Lithio-2-butene was mixed with the corresponding ester, thus obtaining a carbinol, which was transformed into the Cp compound by acid-catalyzed dehydration. The catalytic compounds were prepared as described in the literature.[19] The yields ranged from 28 to 57%.

Physical Data of the Compounds. $(EtMe_4Cp)TiCl_3$: MS $m/z = 304$ (M^+); ^{1}H-NMR ($CDCl_3$) δ 2.88 (q, 2H), 2.38 (s, 12H), 1.09 (t, 3H). (n-$PrMe_4Cp)TiCl_3$: MS $m/z = 318$ (M^+); ^{1}H-NMR ($CDCl_3$) δ 2.61 (t, 2H), 1.97 (s, 6H), 1.90 (s, 6H), 1.03 (sx, 2H), 0.62 (t, 3H). (n-$BuMe_4Cp)TiCl_3$: MS: $m/z = 332$ (M^+); ^{1}H-NMR ($CDCl_3$) δ 2.67 (t, 2H), 1.99 (s, 6H), 1.92 (s, 6H), 1.04 (sx, 4H), 0.77 (t, 3H).

Compounds $(EtMe_4C_5)TiF_3$, (n-$PrMe_4C_5)TiF_3$, and (n-$BuMe_4C_5)TiF_3$, respectively, were prepared by adding 20 mmol of each chlorine compound in toluene (80 mL) to a suspension of Me_3SnF (60 mmol) in toluene (60 mL). The resulting mixture was stirred at room temperature overnight. The solvent and Me_3SnCl were removed in vacuo, and the residue was recrystallized from THF/hexane. The yields ranged from 90 to 98%.

Physical Data of the Compounds. $(EtMe_4Cp)TiF_3$: mp 139 °C; MS $m/z = 254$ (M^+); ^{1}H-NMR (C_6D_6) δ 2.63 (q, J_{HH} =

7.7 Hz), 2.01 (s, 6H), 1.95 (s, 6H), 0.71 (t, J_{HH} = 7.7 Hz); ^{19}F-NMR (C_6D_6) δ 121.3 (s). (n-PrMe$_4$Cp)TiF$_3$ mp 102 °C; MS m/z = 268 (M$^+$); ^{1}H-NMR (C_6D_6) δ 2.63 (t, J_{HH} = 7 Hz, 2H), 2.05 (s, 6H), 1.95 (s, 6H), 1.16 (sx, J = 7Hz, 2H), 0.67 (t, J = 7 Hz, 3H); ^{19}F-NMR (C_6D_6) δ 117.7 (s). (n-BuMe$_4$Cp)TiF$_3$: mp 70 °C; MS m/z = 282 (M$^+$); ^{1}H-NMR (C_6D_6) δ 2.65 (t, J_{HH} = 7.2 Hz, 2H), 1.99 (s, 6H), 1.91 (s, 6H), 1.05 (sx, 4H), 0.75 (t, J_{HH} = 7.2 Hz, 3H); ^{19}F-NMR (C_6D_6) δ 122.6 (s).

Polymerization and Analytical Procedures. Polymerization of styrene was carried out in a 0.1 dm^3 thermostated glass reactor equipped with a magnetic stirrer by introducing successively toluene, a solution of MAO in toluene, 20 mL of styrene, and the titanium or zirconium compound dissolved in toluene. The total volume of the polymerization mixture was 40 mL for every run. Polymerizations were terminated by adding a mixture of ethanol and hydrochloric acid. The product was filtered out, washed with ethanol, and dried in vacuo at 60 °C.

DSC thermograms were recorded with a Perkin-Elmer DSC-4 at a heating rate of 20 K/min. The melting temperatures of the polymers were determined from the second heating rate.

The molecular masses and molecular weight distributions were measured at 135 °C by GPC (Waters 150-CALC/GPC) using trichlorobenzene as solvent.

^{1}H- and ^{19}F-NMR spectra were recorded on a Bruker AM 250 spectrometer.

Mass spectra were obtained on a VG-70−250-VSE spectrometer.

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