New Fluorine-Containing Bissalicylidenimine–Titanium Complexes for Olefin Polymerization

S. C. Gagieva,[1] T. A. Sukhova,[2] D. V. Savinov,[3] V. A.Optov,[3] N. M. Bravaya,[2] Y. M. Belokon',[4] B. M.Bulychev[1]

[1]Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, Moscow, 119992 Russia
[2]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432 Russia
[3]Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow, 117977 Russia
[4]Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova 28, Moscow, 119991 Russia

ABSTRACT: Three new titanium complexes bearing salicylidenimine ligands—bis[(salicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (**1**), bis[(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (**2**), and bis[(3,5-di-*tert*-butylsalicylidene)-4-trifluoromethyl-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (**3**)—were synthesized. The catalytic activities of **1–3** for ethylene polymerization were studied with poly-(methylaluminoxane) (MAO) as a cocatalyst. Complex **1** was inactive in ethylene polymerization. Complex **2** at a molar ratio of cocatalyst to pre catalyst of $Al_{MAO}/Ti = 400–1600$ showed very high activity in ethylene polymerization comparable to that of the most efficient metallocene complexes and titanium compounds with phenoxy imine and indolide imine chelating ligands. It gave linear high-molecular-weight polyethylene [weight-average molecular weight $(M_w) \geq 1,700,000$. weight-average molecular weight/number-average molecular weight $(M_w/M_n) = 4–5$] with a melting point of 142°C. The ability of the **2**/MAO system to copolymerize ethylene with hexene-1 in toluene was analyzed. No measurable incorporation of the comonomer was observed at 1:1 and 2:1 hexene-1/ethylene molar ratios. However, the addition of hexene-1 had a considerable stabilizing effect on the ethylene consumption rate and lowered the melting point of the resultant polymer to 132°C. The **2**/MAO system exhibited low activity for propylene polymerization in a medium of the liquid monomer. The polymer that formed was high-molecular-weight atactic polypropylene ($M_w \sim 870,000$, $M_w/M_n = 9–10$) showing elastomeric behavior. The activity of **3**/MAO in ethylene polymerization was approximately 70 times lower than that of the **2**/MAO system. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1040–1049, 2005

Key words: catalysis; polyethylene (PE); poly(propylene) (PP)

INTRODUCTION

The considerable advances that have been made over the recent decade in the field of olefin polymerization with heterogeneous Ziegler–Natta catalysts,[1] homogeneous metallocene, and postmetallocene catalytic systems involving IVB group metals[2–8] have provided an opportunity to gain deeper insight into various mechanistic aspects of Ziegler catalysis and to develop high-performance technologies for the manufacture of polymeric materials[9] with tailored properties. The design of new catalysts for olefin polymerization remains an area of intense research. Among recent achievements, we should mention the discovery of phenoxyimine chelate complexes of the IVB group, the so-called FI series: $MCl_2\{\eta^2\text{-1-}[C(H)=NPh^R]\text{-2-}O\text{-}Ph^{R'}\}_2$.[10–15] In terms of activity in ethylene polymerization, the catalysts derived from these complexes are comparable to or surpass the most efficient metallocene catalysts. Varying the substituents in the ligands that serve as Schiff bases allows changes in both the catalytic properties and thermal stability of the complexes over a wide range and the synthesis of diverse polymeric products, including low-molecular-weight vinyl-terminated polyethylene (PE), extremely high-molecular-weight linear PE, isotactic, syndiotactic, and atactic polypropylenes (PPs), and olefin block copolymers.[10,11]

In this work, we report the synthesis of new complexes with phenoxyimine ligands as well as their catalytic behavior in the homopolymerization of ethylene and propylene and in the copolymerization of ethylene with hexene-1 under conditions somewhat different from those reported elsewhere.[10,11]

EXPERIMENTAL

Complexes were synthesized under a dry argon atmosphere with standard Schlenk techniques. Dichloromethane, toluene, hexane, and ethyl acetate (all reagent-grade) were purified before use according to a previously described procedure.[16] $TiCl_4$ and $Ti(OiPr)_4$ (Fluka, Switzerland) were distilled under argon. $TiCl_2(OiPr)_2$ was prepared according to a procedure described in the literature.[17] 2,4-*tert*-Butylphenol, paraform, 4-picoline, salicylic aldehyde, 2,3,5,6-tetrafluoroaniline, 4-trifluromethyl-2,3,5,6-tetrafluoroaniline, and 3,5-di-*tert*-butylsalicylic aldehyde (Fluka and Aldrich, Switzerland) were used as received. Special-purity-grade toluene and heptane were used in the catalytic polymerization of ethylene. The solvents were distilled over $LiAlH_4$ and stored over molecular sieves (5 Å) before use. Poly(methylaluminoxane) (MAO) as a 10% solution in toluene (Witco, Germany) was used as received. Special-purity-grade argon, ethylene, and propylene were dried by passage through a column packed with molecular sieves (5 Å) before use.

^{1}H NMR spectra, measured at 25°C, were recorded on a Bruker WP-200 or a Bruker AMX-400. IR spectra were measured on a Magna IR 750 spectrometer.

Synthesis of the ligands

Synthesis of salicylidene-2,3,5,6-tetrafluoroanilinate

2,3,5,6-Tetrafluoroaniline (0.85 mmol) and *para*-toluenesulfonic acid (0.01 mmol) were added to a toluene solution of salicylic aldehyde (0.85 mmol). The as-obtained mixture was refluxed under stirring for 20 h, filtered, evaporated, and purified by passage through a chromatographic column packed with silica gel (a 5:1 hexane/ethyl acetate mixture was used as an eluent) to afford a yellow oil in a yield of 67%.

ANAL. Calcd for $C_{13}H_7NOF_4$: C, 57.99%; H, 2.62%; N, 5.20%. Found: C, 57.31%; H, 2.51%; N, 5.28%. ^{1}H NMR (δ): 6.40 (m, 1H, aniline), 6.95 (2H, aromatic H), 7.55 (2H, aromatic H), 9.84 (s, 1H, CH=N), 11.79 (s, 1H, OH).

Other ligands of the series were obtained in an identical manner.

(3,5-Di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinate

ANAL. Calcd for $C_{21}H_{23}NOF_4$: C, 66.14%; H, 6.04%; N, 3.67%. Found: C, 66.98%; H, 6.58%; N, 3.08%. ^{1}H NMR (δ): 1.50 (s, 18H, *tert*-Bu), 6.70 (m, 1H, aniline), 6.82–7.42 (m, 2H, aromatic H), 8.64 (s, 1H, CH=N), 13.95 (s, 1H, OH).

(3,5-Di-*tert*-butylsalicylidene)-4-trifluoromethyl-2,3,5,6-tetrafluoroanilinate

ANAL. Calcd for $C_{22}H_{22}NOF_7$: C, 58.80%; H, 4.68%; N, 3.12%. Found: C, 58.64%; H, 4.58%; N, 3.15%. ^{1}H NMR

(δ): 1.31–1.45 (s, 18H, *tert*-Bu), 7.52–7.72 (m, 2H, aromatic H), 9.84 (s, 1H, CH=N), 11.61 (s, 1H, OH).

Synthesis of complexes 1–3

These were synthesized according to the common procedure.

Bis[(salicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (1)

A two-necked flask filled with argon was charged with salicylidene-2,3,5,6-tetrafluoroanilinate (0.10 mmol) dissolved in methylene chloride, and $TiCl_2(OiPr)_2$ (0.05 mmol) was added to the stirred solution. After 20 h, a red precipitate was filtered and washed successively with methylene chloride and toluene (85% yield).

ANAL. Calcd for $TiC_{26}H_{12}N_2O_2F_8Cl_2 \cdot CH_2Cl_2$: C, 43.82%; H, 1.91%; N, 3.79%. Found: C, 43.20%; H, 1.92%; N, 3.53%. IR (ν, cm^{-1}): 1610 (C=N), 520 (Ti—O), 450 (Ti—N).

Bis[(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (2)

ANAL. Calcd for $TiC_{42}H_{44}N_2O_2F_8Cl_2$: C, 57.34%; H, 5.04%; N, 3.18%. Found: C, 57.87%; H, 4.92%; N, 2.96%. IR (ν, cm^{-1}): 1618 (C=N), 570 (Ti—O), 440 (Ti—N). ^{1}H NMR (δ): 1.54 (s, 36H, *t*-Bu), 6.30 (m, 2H, aniline), 6.90–7.53 (m, 4H, aromatic H), 9.89 (s, 2H, CH=N).

Bis[(3,5-di-*tert*-butylsalicylidene)-4-trifluoromethyl-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (3)

ANAL. Calcd for $TiC_{44}H_{42}N_2O_2F_{14}Cl_2$: C, 52.02%; H, 4.14%; N, 4.72%. Found: C, 52.90%; H, 4.20%; N, 4.41%. IR (ν, cm^{-1}): 1610 (C=N), 560 (Ti—O), 470 (Ti—N). ^{1}H NMR (δ): 1.54 (s, 36H, *tert*-Bu), 6.90–7.53 (m, 4H, aromatic H), 9.89 (s, 2H, CH=N).

Polymerization of ethylene

All experimental details concerning the preparation of the polymerization unit, the techniques of introducing of ethylene and catalyst components into the reactor, and the procedure of kinetic measurements were analogous to those described in ref. 18. After ethylene was completely dissolved in toluene or heptane containing a desirable amount of an MAO solution, polymerization was initiated by the addition of the catalyst solution in toluene into the reactor. Polymerization was terminated by the treatment of the reaction mixture with a 10% solution of HCl in ethanol. The polymeric product was filtered, washed multiple times with ethanol and a water/ethanol mixture, and then dried *in vacuo* at 50–60°C to a constant weight.

	R_1	R_2
(1)	H	H
(2)	t-Bu	H
(3)	t-Bu	CF_3
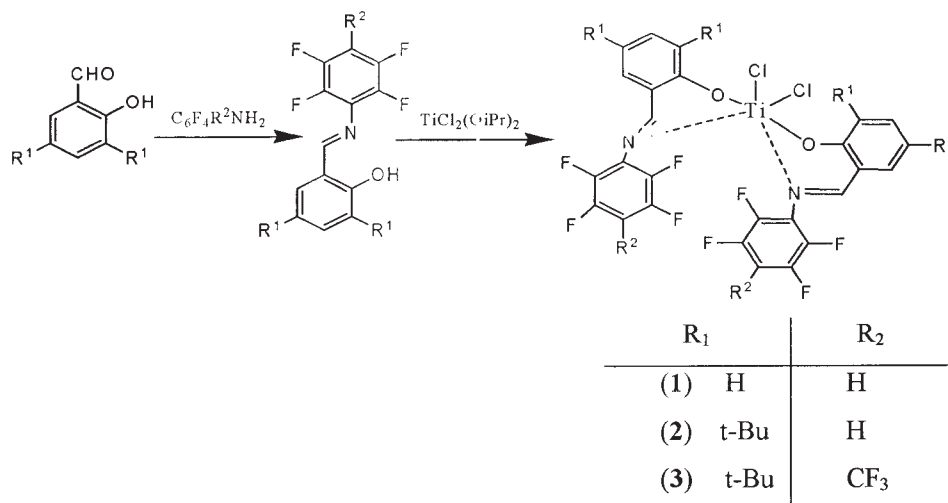
Scheme 1

Polymerization of propylene

The polymerizations were conducted with the reactor completely filled with liquefied propylene (C_3H_6 pressure $\approx$ 40 atm). The general experimental technique is described in ref. 19. In this work, the catalyst was introduced in one of the two ways. With the first one, the reactor containing the liquefied propylene was charged in portions with nearly three-fourths of the calculated amount of a 10% MAO solution in toluene. The remainder of the MAO solution was used for catalytic complex dissolution and then added to the stirred solution to start the polymerization. The second method involved the loading of a solid complex into the reactor after the entire amount of MAO was charged into the reactor. In both cases, the total molar ratio of Al to Ti was approximately 2000.

^{13}C-NMR spectra were recorded at 110°C on a Bruker AC-200 instrument with a PP solution in 1,1,2,2-tetrachloroethane-d_2; the concentration of the polymer in the solution was 7.5 wt %.

X-ray powder diffraction analysis of the PP samples was carried out on a DRON-2 diffractometer.

Mechanical testing was performed on an Instron 1122 machine as described in ref. 20.

The molecular mass characteristics [weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (MWD)] of PE and PP samples were measured at 135°C by gel permeation chromatography (GPC) with polymer solutions in 1,2-dichlorobenzene. The measurements were made with a Waters 150-C instrument equipped with a linear HT μ-Styragel column.

The melting points of PEs were determined with differential scanning calorimetry (DSC). The measurements were performed in air at a heating rate of 16°C/min.

RESULTS AND DISCUSSION

The general scheme for the synthesis of phenoxyimine complexes **1–3** is given in Scheme 1. When the interaction of salicylic aldehyde or its substituted analogues with 2,3,5,6-tetrafluoroaniline was conducted in the presence of *para*-toluenesulfonic acid used as a catalyst, salicylidene-2,3,5,6-tetrafluoroanilinates were isolated in yields of 65–68%. The reaction between 2 mol of the corresponding ligand and 1 mol of $TiCl_2(OiPr)_2$ in methylene chloride gave rise to the targeted titanium dichloride complexes in yields of 85–88%.

Basically, titanium complexes containing two asymmetric bidentate ligands may adopt five octahedral isomeric structures. However, as reported in refs. 21–25, only an octahedral structure with two ambidentate [O,N] ligands is usually realized in compounds, and so oxygen atoms are in trans positions to each other, with nitrogen and chlorine atoms taking cis positions. This situation seems also to be typical of complexes **1–3** in this work, as demonstrated by IR and NMR measurements. The ^{1}H NMR spectra of complexes **1–3** show a single signal due to an azomethine proton (—CH═N—) of a phenoxyimine ligand, and their IR spectra exhibit a low-frequency shift of a band at ν(C═N) by 10–18 cm^{-1} with respect to its position in the starting ligand; moreover, new absorption bands can be assigned to ν(Ti—N) and ν(Ti—O) stretching at 450–570 cm^{-1}.

Polymerization of ethylene

Upon the addition of a suspension of complex **1** in toluene to a reaction medium with dissolved MAO, a partial dissolution of the precipitate, accompanied by a rather rapid change of its color from red to dark

TABLE I
Polymerization of Ethylene with the 2/MAO Catalytic System (Ethylene Pressure = 0.98 atm)

Entry	$Ti \times 10^6$ (mol)	$[Ti] \times 10^5$ (mol/L)	Al_{MAO}/Ti (mol/mol)	T_p (°C)	Time (min)	Y (g)[a]	A[b]	M_n	M_w/M_n
1	3.80	18.8	1600	30	5	0.71	22.2	340,000	4.8
2	3.80	18.8	400	30	5	0.81	23.3	350,000	4.2
3	0.63	3.10	600	30	9	0.47	45.2	n.r.[c]	
4	0.13	0.63	600	30	17	0.32	79.0	n.r.[d]	
5[e]	0.82	4.10	460	30	12	0.55	31.8	n.r.[f]	
6[e]	0.82	4.10	460	70	14	0.30	27.2	520,000	11.0
7[g]	0.20	1.00	600	30	15	0.49	89.1	n.d.[h]	
8[i]	0.20	1.00	600	30	37	0.10	7.4	450,000	21.0

[a] Polymerization temperature.
[b] Polymer yield.
[c] Specific activity (kg of PE/mmol of Ti h [C_2H_4]).
[d] n.r. = not reliable GPC data (M_n = 1,580,000, M_w/M_n = 7.1).
[e] n.r. = not reliable GPC data (M_n = 2,500,000, M_w/M_n = 7.4).
[f] The polymerization was carried out in heptane.
[g] n.r. = not reliable GPC data (M_n = 660,000 M_w/M_n = 11.1.
[h] The polymerization was carried out in toluene in the presence of 1-hexene at a 1-hexene/ethylene molar ratio of 1.1.
[i] n.d. = not determined.
[j] The polymerization was carried out in toluene in the presence of 1-hexene at a 1-hexene/ethylene molar ratio of 2.2.

brown and concomitant gas evolution, took place. The gassing probably indicates the reduction of Ti(IV) to Ti(III). We suppose that both the titanium reduction and poor solubility of **1** in toluene are responsible for low polymerization activity of the catalyst.

The addition of a *tert*-butyl substituent at the ortho position to oxygen in the *O*-phenyl moiety appreciably improves the solubility of complex **2** in toluene. When mixed with MAO, **2** in toluene rapidly changes from bright dark red to yellow. No gas evolution was observed during the catalyst and cocatalyst mixing. These changes possibly indicate that the reduction stability of **2** is higher than that of **1** and that the alkylation of catalyst **2** under the action of MAO proceeds smoothly.

The **2**/MAO system exhibits very high activity in ethylene polymerization (Table I) comparable to the activity of the most efficient catalytic systems of the FI series.[10–15,21,24] At a rather high concentration of the complex and at a molar ratio of cocatalyst to precatalyst of Al_{MAO}/Ti = 1600, the specific activity of the catalyst was 22.2 kg of PE/(mmol of Ti h [C_2H_4]) (entry 1). A fourfold decrease in the concentration of the cocatalyst did not lead to an appreciable change in the specific activity of the catalyst (entry 2). The activity of metallocene systems, as a rule, increases with a rise in the MAO/catalyst molar ratio,[26] and the maximum activities are achieved at high or very high molar ratios (up to 10^3–10^4 mol/mol).[27] Thus, the specific feature of the catalytic system of interest is that the high activity of complex **2** in the homogeneous polymerization of ethylene may be achieved with a small molar excess of the cocatalyst to the catalyst.

When the concentration of **2** was reduced by 6 or 30 times at a molar ratio of Al_{MAO}/Ti = 600, the specific

activity of the catalyst increased by or and 3.4 times, respectively (entries 3 and 4). The lower specific activities of the catalyst at its higher concentrations (entries 1 and 2) are associated with the rapid formation of a great amount of a polymer in the reaction medium and, as a result, mass-transfer limitations.

Complex **2** exhibits rather good solubility in heptane. When ethylene was polymerized in this solvent (all other conditions being equal), about twice the reduced specific activity, compared with that in toluene, was observed (cf. entries 4 and 5, Table I). This finding can be attributed to both a reduction of the polarity of the medium and a partial heterogenization of the polymerization reaction resulting from the insolubility of MAO in heptane.

When comparing the catalytic behavior of the **2**/MAO system in heptane at 30 and 70°C (entries 5 and 6), we see that the specific activities of the system are approximately equal, taking into consideration a change in the ethylene solubility with the temperature. The initial rates of ethylene consumption are also low-temperature-dependent (Fig. 1). The lower value of the reduced integral activity of the system at 70°C, with respect to that at 30°C, is connected to the slightly more distinct deactivation of the catalyst. However, the thermal stability of the **2**/MAO catalyst is as high as that of unsubstituted[21,24,27] and other fluorine-containing titanium complexes of the FI series,[10,12] being considerably higher than that of the corresponding fluorine-free zirconium analogues.[23,28,29] Interestingly, the kinetic profiles of polymerization reactions carried out in toluene and heptane are similar (cf. curves 4 and curves 5 and 6 in Fig. 1). This possibly attests to the fact that deactivation reactions in both solvents follow similar mechanisms. The rather high thermal stability
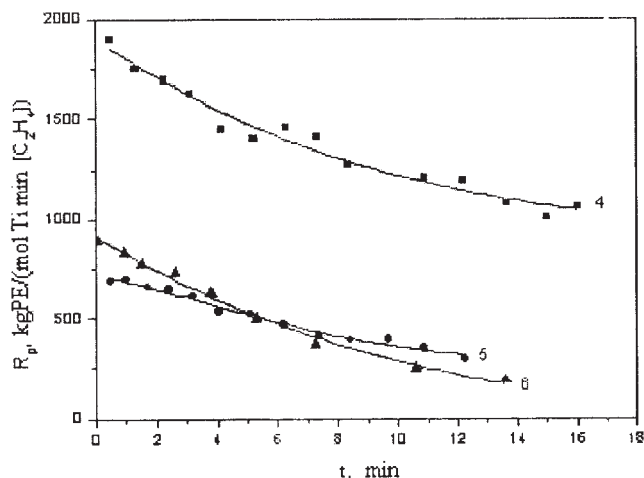
Figure 1 Ethylene-consumption-rate/time-resolved profiles for ethylene polymerization with the **2**/MAO catalytic system in (4) toluene and (5,6) heptane at reaction temperatures of (4,5) 30 and (6) 70°C (R_p = ethylene consumption rate; t = time). The numbering of the curves corresponds to the numbering of the experiments in Table I.

of the catalyst when polymerization is carried out in aliphatic solvents is essential for the practical application of this catalytic system.

The melting points (DSC data) of PE samples prepared in toluene and heptane (entries 3, 5, and 6) were very high (142°C), and this suggested that linear (polymethylene-like) high-molecular-weight PE was generated with the **2**/MAO system under the examined conditions. PE of a very high molecular weight was generated by this catalytic system even at a low polymerization time (entries 1 and 2). An increase in the Al_{MAO}/Ti molar ratio from 400 to 1600 was not accompanied by changes in the molecular weight characteristics of the resulting polymer (entries 1 and 2). Hence, it follows that neither MAO nor $AlMe_3$ contained in MAO acted as a chain-transfer reagent. A considerable increase in the molecular mass of the produced PE was observed at a longer polymerization time at a lower catalyst concentration in both toluene and heptane (entries 3–5). Very high-molecular-weight PE was generated with **2**/MAO even at 70°C (entry 6), and so its molecular mass could not be reliably determined by GPC according to polystyrene standards ($M_n = 520,000$, $M_w > 3$–4×10^6 g/mol). This indicates that chain-transfer reactions by β-H elimination are strongly restricted for complex **2**, just as for series of FI catalysts bearing fluorine ligands at the ortho position of the =N—Ph function[10,11] because of ortho-fluorine interaction with β-hydrogen of growing polymer chain. The distinctive feature of this catalytic system, with respect to the other titanium catalysts of the FI series reported earlier,[10–12] is that despite the similar increase in the PE molecular weight with the polymerization time (living-like process), the

2/MAO system yields PEs with a wide MWD ($M_w/M_n \gtrsim 4$–5) at all examined polymerization times. A possible explanation is not detectable in the ^{1}H-NMR scale admixture of other stereoisomers in synthesized complex **2** also with cis-located chlorine ligands but showing quite different reactivity toward ethylene coordination and insertion. The formation of bimodal and trimodal PE with an FI zirconium catalyst bearing cumyl substituents at the 3,5-positions of the phenoxy ligand was reported recently.[29] The authors attributed the effect to the dynamic structures of different stereoisomers being in equilibrium, as detected by variable-temperature ^{15}N NMR analysis for starting zirconium dichloride. In this case, the high values of M_w/M_n for PEs generated with the **2**/MAO system were due to the presence of different stereoisomers of **2** that strongly differed in their catalytic properties. This effect may be used for synthesis of high-molecular-weight PEs with tunable M_w/M_n values and should be further analyzed.

According to refs. 10–14, the most fascinating feature of titanium catalysts of the FI series is that their activity can be significantly raised if electron-withdrawing substituents F or CF_3 are added to the para and meta positions of phenoxyimine fragments of complexes. Upon the addition of fluorine substituents to the ortho positions of substituents, the activity of the catalyst noticeably decreases, but simultaneously the chain-transfer reaction involving a β-hydrogen atom becomes blocked. The effect of electron-acceptor substituents can be explained by a reduction in the energy of the highest occupied molecular orbitals of an imine ligand and, as a result, by the rise in the electrophilicity of the central metal atom in an active site.[12] However, the ambiguity of the role of an electron-accepting substituent within the model advanced in ref. 12 can be illustrated by a change in the catalytic behavior of complex **3**, which differs from complex **2** by the presence of a CF_3 substituent in the para position of a phenyl ring. The activity of the **3**/MAO catalytic system is approximately 70 times lower than that of the **2**/MAO system (Fig. 2), all other conditions being the same. The stability of catalytic system **3**/MAO is considerably lower than that of the **2**/MAO system.

Table II demonstrates the catalytic behavior of the **2**/MAO system in the liquid monomer polymerization of propylene at 50°C. The activities of the system are nearly three orders of magnitude lower than those in ethylene polymerization. An analogous difference in the catalytic activity of a series of titanium complexes of the FI type was observed in a comparison of their behavior in the polymerizations of ethylene and propylene.[10,11]
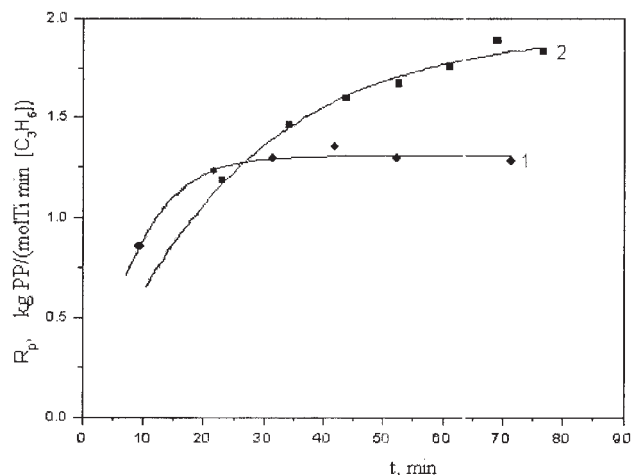
The technique of adding the catalyst affects the catalytic properties of the system and, to some extent, the physicomechanical properties of the resulting PPs.
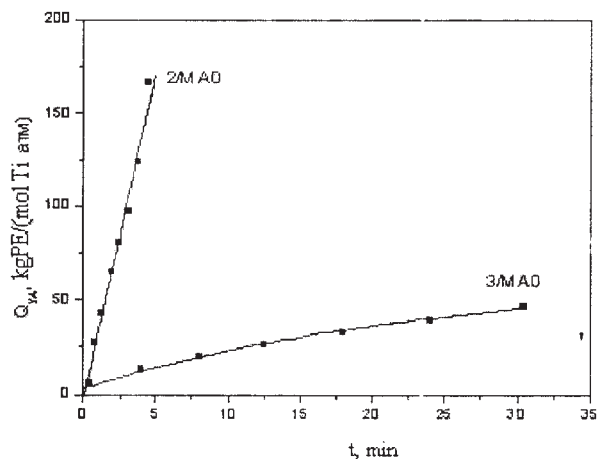
Figure 2 Comparison of the catalytic activity of the 2/MAO and 3/MAO systems in ethylene polymerization (t = time) (Q = specific polyethylene yield in kg of PE per mol of catalyst per atm). The ethylene pressure was 0.98 atm. The conditions for the 2/MAO system were [Ti] = 1.88×10^{-4} mol/L and Al_{MAO}/Ti = 400; the conditions for the 3/MAO system were [Ti] = 1.53×10^{-4} mol/L and Al_{MAO}/Ti = 500.

Figure 3 Propylene-consumption-rate/time-resolved profiles for propylene polymerization in bulk with catalyst 2 added as (1) a 10% MAO solution in toluene or (2) a solid (R_p = ethylene consumption rate; t = time). The numbering of the curves and polymerization conditions correspond to the numbering of the experiments in Table II.

Upon the preliminary dissolution of 2 in MAO (the first technique), the activity of the catalytic system is somewhat lower than that when the catalyst components are added to the reactor at once (the second technique; Table II). Figure 3 shows that, in both cases, the polymerization rate gradually increases over the course of polymerization until a constant value is achieved. For the catalyst prepared with the first technique, the steady-state rate of polymerization is attained earlier, but its value is approximately 1.5 times lower than that of the catalyst prepared according to the second technique. The catalyst shows considerably higher stability in bulk propylene polymerization than in ethylene polymerization in both toluene and heptane.

PP of a high molecular weight was generated with the 2/MAO system in bulk (Table II). The GPC curve of a PP sample obtained under the conditions of entry 1 is presented in Figure 4. The total curve has a wide polydispersity index (M_w/M_n = 5.6). However, 80% of the curve may be represented by the sum of two peaks

showing different M_w and M_n values but very low M_w/M_n values. The third peak (~20%) is the peak of very high-molecular-weight PP with an M_w/M_n value of 2.5. Therefore, at least three types of active species may be detected in the examined catalytic system. However, the main portion of PP is generated by a single type of active species operating in a living-like manner.

X-ray diffraction data and ^{13}C NMR measurements of PP produced with the 2/MAO system in liquid monomer surprisingly indicated the formation of atactic PP (Table III). The distribution of methyl pentads in the ^{13}C NMR spectrum (Fig. 5) of this polymer is close to that in ideally atactic PP. PP macromolecules contain many inverted propylene units (~5 mol %), which are marked by an asterisk in Figure 5. The effect is in line with the tendency of other fluorinated titanium complexes of the FI series to produce regiomistakes.[25] The formation of atactic PP in bulk with catalytic system 2/MAO is in contrast to other data on the formation of highly syndiotactic PP (with an *rr* triad concentration of up to 90%)

TABLE II
Bulk Polymerization of Propylene with the 2/MAO Catalytic System

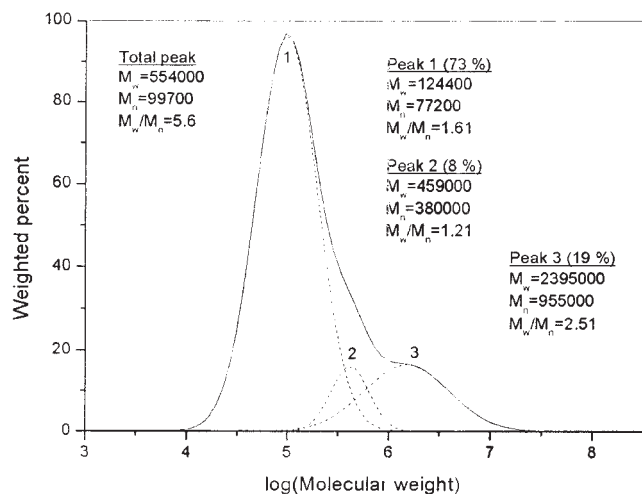| Entry	Ti × 10⁶ (mol)	[Ti] × 10⁵ (mol/L)	Al_MAO/Ti (mol/mol)	Y (g)	Aᵃ	M_w	M_w/M_n
1ᵇ	4.47	2.23	2300ᶜ	5.0	0.07	872,200	8.8
2ᵈ	4.72	2.36	2000	6.9	0.09	952,300	10.1

Reaction temperature = 50°C; reaction time = 1.5 h. Y = polymer yield.
ᵃ Activity (kg of PE per mmol of Ti h [C_3H_6]).
ᵇ The catalyst was added to the reactor as a 10% MAO solution in toluene.
ᶜ Total ratio.
ᵈ The catalyst was added to the reactor as a solid.

Figure 4 GPC curve of atactic PP obtained with catalytic system **2**/MAO.

with structurally related perfluorinated titanium complexes of the FI series when propylene is polymerized in toluene even at high polymerization temperatures (up to 50°C).[10,11,13,15,25,30–32]

It is difficult to explain the formation of atactic PP with catalyst **2**. An analysis of the microstructure of syndiotactic PPs obtained in toluene and end-group analysis have allowed us to conclude that chain-end control with prevailingly 2,1-propylene insertions is predominant over the course of syndiotactic propylene formation with structurally related catalysts.[11,25,31,32] Ethylene and propylene copolymerization experiments have shown a loss of steric control after ethylene insertion.[31] The model assuming rapid site inversion in comparison with propylene insertion with energetically favored *re*-chain/Λ-site/*si*-propylene or *si*-chain/Δ-site/*re*-propylene isomers was shown to explain the formation of syndiotactic PP on these catalysts of C_2 symmetry.[33] However, the model does not consider the effect of any substrate capable of coordination to active species, such as toluene, the counterion effect, and so forth. At the same time, it has been demonstrated[31] that the replacement of toluene for heptane leads to a significant increase in the catalyst productivity with a simultaneous decrease in the stereoregularity of PP formed under other similar conditions (*rr* = 87% in toluene vs 62% in heptane). As shown for the catalyst based on the $TiCl_2\{\eta^2$-1-

$[C(H){=}NC_6H_5]$-2-*O*-(3-*t*BuC$_6$H$_4$)$\}_2$ complex,[34] a high-molecular-mass polyhexene appears only if the reaction is conducted in heptane, whereas in toluene, this catalyst proves to be inactive. An analogous trend was observed in the polymerization of α olefins initiated with chelate diamine complexes of titanium.[35] With the use of chelate acetylacetonate complexes of zirconium in toluene, a highly isotactic (*mmmm* = 99%) PP was prepared, whereas an elastomeric stereoblock PP (*mmmm* = 19%) was synthesized in methylene chloride.[36] Therefore, the coordinating ability of a solvent and/or counterion competitive with the α olefin should probably be taken into consideration in terms of activity and stereoselectivity.

The atactic PP formed with the **2**/MAO system possessed elastomeric properties: the residual strain after 300% elongation did not exceed 21% (Table IV). Moreover, the samples did not rupture even after almost 20-fold elongation (Table IV).

Only a few catalytic systems are efficient for the synthesis of high-molecular-mass atactic PP. Among these systems are catalysts based on half-sandwich titanium complexes [Cp*Ti(—O—CH$_2$—CH=CH$_2$)$_3$/MAO[37] or Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$[38]], a system based on ansa complexes of zirconium [Me$_2$Si(9-Flu)$_2$ZrX$_2$/MAO (X = Cl or Me)],[39] and catalysts of the FI series {TiCl$_2\{\eta^2$-1-[C(H)=NPh]-2-*O*-3-*t*Bu—C$_6$H$_3\}_2$/*i*Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4^{11}$}. However, the chain microstructure close to the structure of ideally atactic PP was achieved only with the Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$ system and FI catalyst. For all other catalysts, the elastomeric atactic PP was characterized by an increased content of syndiotactic fragments (*rr* > *mm*). In terms of the activity and molecular weight of the PP formed, the **2**/MAO system ranks below the aforementioned catalytic systems.

We now demonstrate an interesting stabilizing effect of the α olefin on the catalytic behavior of the **2**/MAO system. The pattern of the curves in Figure 1 demonstrates that the polymerization of ethylene, if not limited by mass transfer, proceeds at the maximum initial rate; that is, the catalytic active sites form rather rapidly. However, they also deactivate rather rapidly. On the contrary, a gradual rise in the rate of propylene polymerization in bulk indicates that the rate of formation of active sites is low even under the preactivation of complex **2** with an MAO solution, and a long period of the steady-

TABLE III
Comparison of the Pentad Content (%) of PP Prepared with the 2/MAO Catalytic System in Liquid Propylene with that of Ideally Atactic PP

Polymer	mmmm	mmmr	rmmr	mmrr	mmrm + rmmr	rmrm	rrrr	mrrr	mrrm
PP (entry 1)	8.9	12.3	4.7	11.2	25.6	10.5	3.7	15.9	7.1
Atactic PP	6.25	12.50	6.25	12.50	25.00	12.50	6.25	12.50	6.25
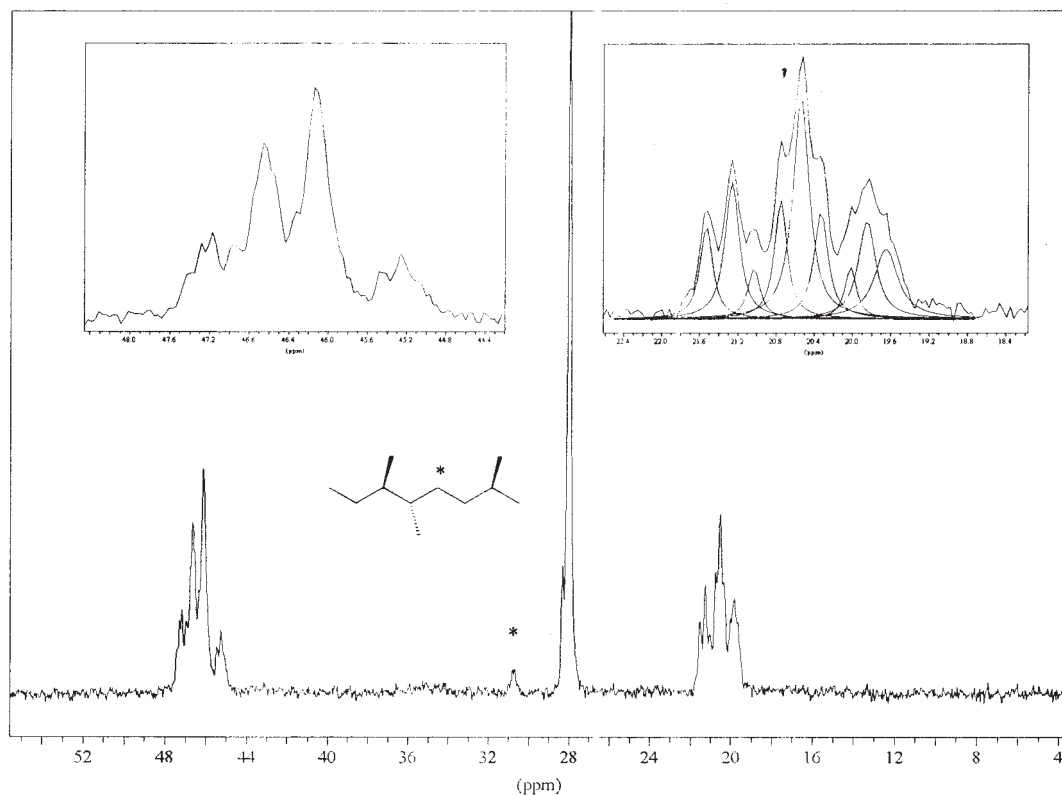
Figure 5 Fragment of the ^{13}C NMR spectrum of atactic PP prepared with the **2**/MAO catalytic system (experiment 1, Table II). The signal due to methylene carbons of regiomistakes (2,1-additions) is asterisked. The fragments of the signals of carbon atoms of methylene and methyl sequences are shown at the upper left and right, respectively. The deconvolution results are given in Table III.

state rate of polymerization attests to a certain stabilization of these sites in the medium of propylene. The nature of this phenomenon remains unclear, even though this tendency can be illustrated by the data on the copolymerization of ethylene with a bulky 1-hexene. In the latter case, testing the catalyst (experiments 7 and 8 in Table I) showed that only ethylene was mainly consumed from a mixture of comonomers. Figure 6 depicts the IR spectrum of the polymer prepared at a molar ratio of 1-hexene/ethylene = 1.1 mol/mol (entry 7). This is the spectrum of mainly linear PE, as is evident from the absence of an absorption band due to the bending

TABLE IV
Physicomechanical Properties of Atactic PP Prepared with the 2/MAO Catalytic System

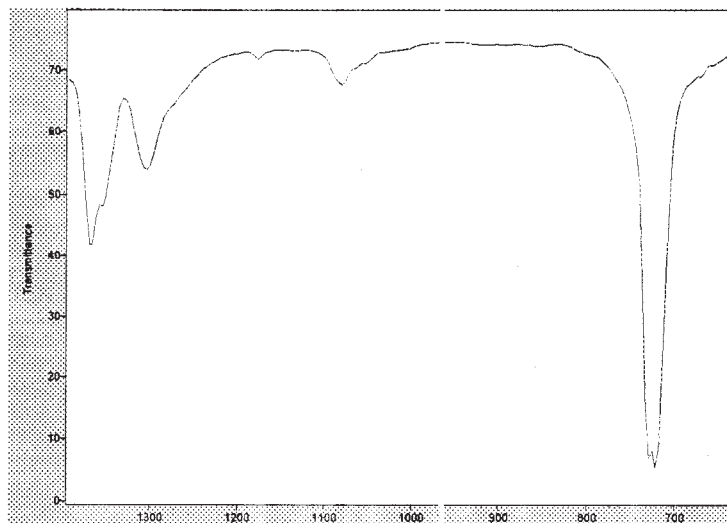| Entry	E (MPa)[a]	ε_{300} (%)[b]	σ_b (MPa)[c]	ε_b (%)[d]
1	2.9	19.2	>0.6	>1800
2	4.3	20.1	>0.8	>1800

[a] Elastic modulus.
[b] Residual strain after 300% elongation.
[c] Breaking strength.
[d] Elongation at break. The samples actually did not break so far as the machine crosshead running was not enough.

vibrations of methyl groups in branches (1378 cm^{-1}). At the same time, the melting temperature of this polymer is as low as 132°C, which is 10°C below that of PE produced by ethylene homopolymerization. This finding indicates that branches are nevertheless formed but are probably located in macromolecules very rarely. This implies that 1-hexene shows an extremely low competing ability with enchainment in comparison with ethylene. Nevertheless, 1-hexene has a considerable effect on the polymerization process. This can be validated by the data shown in Figure 7. A comparison of the ethylene-consumption/time-resolved profiles taken with approximately equal concentrations of the complex (entries 4 and 7 in Table I) when the reaction mixture contained only ethylene (curve 5, Fig. 7) or an equimolar ethylene/1-hexene mixture (curve 7) reveals that the presence of 1-hexene does not reduce the activity of the catalyst but significantly stabilizes working active sites. An increase in the relative fraction of 1-hexene in the comonomer mixture markedly suppresses the activity of the catalytic system; however, a steady-state rate of ethylene uptake was again observed within 40 min (curve 8, Fig. 7). Therefore, the coordination of the α olefin
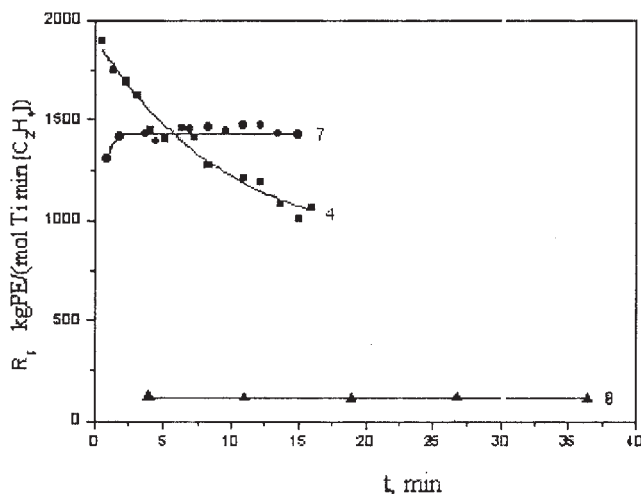
Figure 6 Fragment of the IR spectrum of PE prepared with the **2**/MAO catalytic system at a 1-hexene/ethylene molar ratio of 1.1 (experiment 7, Table I).

(here both propylene and 1-hexene) markedly reduces the turnover number of active species but makes them more resistant to deactivation. Thus, the evidence leads us to infer that higher α-olefins can be used as stabilizers of the catalytic action of the **2**/MAO system in the polymerization of ethylene. This may be essential for the implementation of this process at elevated temperatures.

Figure 7 Ethylene-consumption-rate/time-resolved profiles for (4) ethylene homopolymerization and (7,8) ethylene/1-hexene copolymerizations with the **2**/MAO catalytic system in toluene (R_p = ethylene consumption rate; t = time). The 1-hexene/ethylene molar ratios in the feed were (7) 1.1 and (8) 2.2 mol/mol. The numbering of the curves corresponds to the numbering of the experiments in Table I.

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