

A New Catalytic System $(2\text{-PhInd})_2\text{ZrMe}_2/\text{Al}(\text{iso-Bu})_3$ for the Synthesis of Stereoblock Polypropylene

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Received November 30, 2000

Abstract—A new efficient two-component homogeneous system consisting of $(2\text{-PhInd})_2\text{ZrMe}_2$ and $\text{Al}(\text{iso-Bu})_3$ cocatalyst was developed for the synthesis of elastomeric stereoblock polypropylene. The catalytic behavior of this system was studied in toluene and liquid propylene. It was shown that a change in the Al/Zr molar ratio enables one to vary the system activity, the kinetic characteristics of the polymerization process, and the properties of polypropylene over wide ranges. For example, an increase in the Al/Zr ratio from 50 to 300 mol/mol is accompanied by an increase in the activity by a factor of 4, an increase in the molecular weight from 80000 to 220000, and a decrease in isotactic pentad content from 39 to 16%. It was found that the polymerization rate is proportional to the concentration of $\text{Al}(\text{iso-Bu})_3$ and to the square of the monomer concentration. Some assumptions about the nature of active centers and about reactions leading to the formation of these centers were made. A model for the formation of sequences of isotactic and atactic blocks was proposed. This model takes into account the multiple inversion of the active center (fast dynamic equilibrium) from the iso-specific to the nonspecific state during chain growth. This inversion is due to the coordination of an additional $\text{Al}(\text{iso-Bu})_3$ molecule. This model satisfactorily describes the pentad composition of polypropylene samples as a function of the Al/Zr ratio.

INTRODUCTION

Metallocene complexes of IVb group cations are very efficient catalysts of homo- and copolymerization of olefins. The extremely high activity of these systems and the correlation of the structure of these complexes and their stereoregulating activity in α -olefins polymerization have drawn interest from both fundamental science and industry. These catalytic systems open wide opportunities for the preparation of polymeric materials with unique properties. Stereoblock elastomeric polypropylene is one of these polymers.

Polymethylalumoxane (MAO) or strong Lewis acids without nucleophilic fragments, for example, perfluorophenyl borates or borates [1–5], are known as efficient activators of metallocene complexes of IVb group metals. Although in the early 1960s A.E. Shilov and co-workers [6–8] studied the homogeneous catalytic system $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_2\text{Cl}$ and suggested and proved a hypothesis that the active center of polymerization is the cationic metal–alkyl species, there are still few examples of the efficient activation of metallocene precursors of organoaluminum compounds. Perfluorophenylaluminates [9–11] and the combination of aluminum–alkyls $\text{AlMe}_3/\text{AlMe}_2\text{F}$ [12] are among these rare examples.

Recently, we have found unique homogeneous catalytic systems based on dimethylated bisindenyl zirconocenes with alkyl and aryl substituents in the second position, where triisobutylaluminum (TIBA) acts as an efficient cocatalyst [13]. This system provides the

activity, stereospecific action, and stability of the catalyst at the level of the respective zirconocene dichlorides activated by MAO.

The dichloride complexes $2\text{-PhInd}_2\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Hf}$) were the first nonbridge metallocene complexes [14–20], which led to the formation of stereoblock elastomeric polypropylene with activation by MAO. X-ray diffraction studies have shown [14, 21–23] that these complexes exist as two rotational isomers with the rotation about the bond of metal with the η -bonded ligand (two independent molecules in one elementary crystal cell). This demonstrates that both isomers are energetically equivalent. These observations formed the basis for the “oscillating active center” model [14], which explained the formation of alternating stereoblocks and the dependence of the length of isotactic sequences on the monomer concentration.

Because dimethylated “oscillating” catalysts are metallocenes, which are activated efficiently by TIBA, it was interesting to study the features of stereoblock propylene polymerization catalyzed by the $2\text{-2-PhInd}_2\text{ZrMe}_2/\text{Al}(\text{iso-Bu})_3$ system. In this work, we analyzed how the Al/Zr ratio and the monomer concentration affect the system activity, the kinetic characteristics of polymerization, and the properties of polypropylene.

EXPERIMENTAL

The dimethylation of zirconocene $2\text{-PhInd}_2\text{ZrCl}_2$ was carried out using the known procedure [24]. In

these experiments, we used spectroscopically pure toluene, which was additionally dried over molecular sieves 5 Å and distilled immediately before the experiment over LiAlH_4 . TIBA (25% solution in toluene, Aldrich) was used without any additional treatment. Argon and propylene were dried using a column filled with molecular sieves 5 Å. All operations of catalyst preparation were carried out in a dry box filled with helium.

Propylene polymerization in toluene solution was carried out in a 250-cm³ stainless steel reactor. The reactor was evacuated at 70°C for 1 h and was cooled to the temperature of the experiment with evacuation. Toluene (65 ml) and the calculated amount of TIBA were introduced into the reactor. The solution was saturated with propylene at the desired pressure for 5–10 min. Propylene polymerization in the liquid monomer was carried out in a reactor fully filled with liquid propylene containing the calculated amount of TIBA. Propylene polymerization was initiated by the addition of a certain amount of the catalyst as a solution in toluene. Polymerization in toluene was carried out at constant propylene pressure. Polymerization was interrupted by the addition of a monomer supply and by the addition of ethyl alcohol containing 10% of HCl. Polypropylene (PP) was thoroughly stirred, separated from the reaction medium after precipitation, and washed several times with ethyl alcohol and water. The washed polymer was dried until constant weight at 60°C in a vacuum.

Because the activity of the catalytic system was measured in this work as the specific polymerization rate (w_{sp}) divided by the monomer concentration, we measured the solubility of propylene in toluene at the reaction temperature. The Henry constant was equal to 0.63 mol/l at 30°C and at a propylene pressure of 1 atm. In calculations, we assumed that the monomer concentration is proportional to the pressure in the studied range.

The molecular weight of polypropylene was determined by the measurement of the viscosity of polymer solution in decalin at 135°C using the Mark–Houwink equation with constants equal to $K_\eta = 1.6 \times 10^{-4}$ and $\alpha = 0.77$. In some cases, the molecular weight parameters of polypropylene (M_w , M_n , and MMP) were measured for a polymer solution in 1,2-dichlorobenzene at 135°C by gel-permeation chromatography (GPC) using a Waters 150-C instrument equipped with a linear HT- μ -styragel column.

The IR spectra of polypropylene films were recorded using a PE FTIR-1600 instrument. The microtacticity was determined using the ratio of absorbances D_{998}/D_{973} [25, 26]. The microstructure of stereoblock polypropylene was determined by the analysis of ¹³C NMR spectra of a polymer solution in dideuterotetrachloroethane (10 wt %) at 130°C using a Bruker AC-200 instrument.

RESULTS AND DISCUSSION

The study of two-component systems (2- $\text{RInd}_2\text{ZrMe}_2$)/TIBA showed that they are efficient catalysts for olefin polymerization [13]. This result is unusual for homogeneous metallocene catalysis. The study of the catalytic behavior of “oscillating” zirconocene 2- $\text{PhInd}_2\text{ZrMe}_2$ in propylene polymerization under the action of TIBA attracts particular interest. First, this catalytic system is “homogeneous” because in this reaction solid particles of the polymer are not formed. This enables the study of the kinetic characteristics of the reaction, when these characteristics are not complicated by the formation of the solid phase of the polymeric product. Second, it was interesting to study the stereospecific action of this catalytic system in the synthesis of polypropylene. Analysis of the polymerization rate as a function of monomer and TIBA concentrations and reaction temperature, as well as the analysis of the microstructure of polypropylene formed in the reaction, provides information on reactions leading to the formation of active centers and on the mechanism of catalytic and stereospecific action. The main experimental results are presented in Table 1.

It is possible to illustrate the efficiency of the catalytic system (2- $\text{PhInd}_2\text{ZrMe}_2/\text{Al}(\text{iso-Bu})_3$ (II) by comparing it with the known catalytic system (2- $\text{PhInd}_2\text{ZrCl}_2/\text{MAO}$ (I). Results presented in Table 1 show that the activity w_{sp} of system II measured in units (kg PP) (mol Zr)⁻¹ h⁻¹ [C_3H_6]⁻¹ is comparable with, or even higher than, the activity of the complex activated by MAO at Al/Zr = 1000 and 4000 (experiments 1 and 2). The molecular weight of polypropylene under certain conditions is also higher than the molecular weight of polypropylene formed in the presence of MAO.

To analyze the catalytic behavior of the system depending on the monomer concentration and the Al/Zr ratio, we carried out a set of experiments on propylene polymerization in toluene (Table 1, experiments 4–9). Figure 1 shows that the catalytic system is deactivated according to an exponential law in all experiments. An increase in the Al/Zr ratio from 50 to 300 at a constant monomer concentration (Table 1, experiments 4–7) is accompanied by an increase in the catalytic activity. The product of the reaction at Al/Zr = 50 was a low-molecular oil-like product was produced at Al/Zr = 50. The molecular weight of polypropylene formed at Al/Zr = 100–300 is rather high and increases with an increase in TIBA concentration.

An increase in the propylene concentration leads not only to an increase in the molecular weight of polypropylene, but also to an increase in the activity (Table 1, experiments 7–9). In analyzing the catalytic activity of the system depending on the monomer and TIBA concentrations, we used the values of the initial rates of propylene polymerization ($w_{\text{p},0}$), because the deactivation rate is different at different TIBA and propylene concentrations. Analysis of results presented in Fig. 2 showed that the initial rate of propylene polymerization

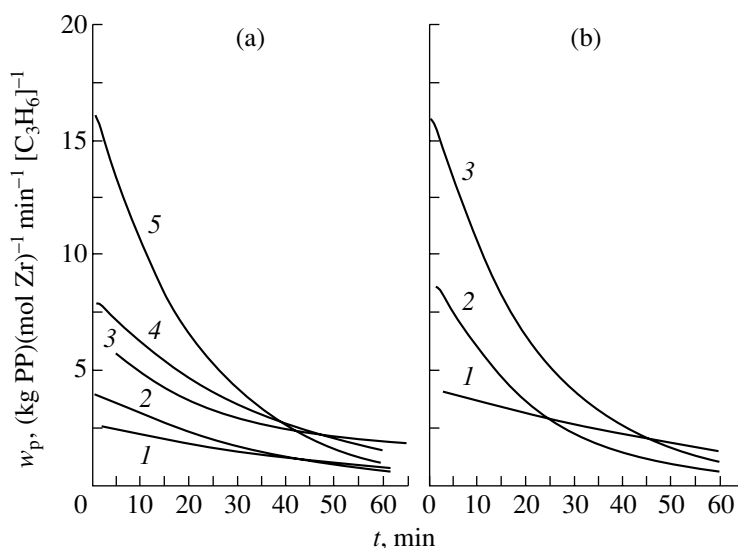


Fig. 1. Changes in the polymerization rate of propylene with time in the presence of the catalytic system (2-PhInd)₂ZrMe₂/TIBA: (a) [C₃H₆] is equal to (1, 3–5) 4 mol/l and (2) 12.3 mol/l; Al/Zr = (1) 50, (2) 120, (3) 100, (4) 200, (5) 300 mol/l; (b) Al/Zr = 300, [C₃H₆] = (1) 1.5, (2) 2.5, (3) 4.0 mol/l.

is characterized by the first order with respect to TIBA (0.99 ± 0.15) and nearly the second order with respect to the monomer (2.39 ± 0.04). These dependences indicate that TIBA and the monomer participate in reactions leading to the formation of active centers.

Earlier, the reaction order higher than unity with respect to the monomer concentration was observed in

olefin polymerization catalyzed by metallocene complexes activated by MAO [27–33]. Assuming that two monomer molecules are coordinated with an active center containing a metal cation and an alkyl group, the authors found that the calculated and experimental data [34, 35] were in good agreement. However, the dependences of the propylene polymerization rate on TIBA and

Table 1. Propylene polymerization at 30°C by catalytic systems (2-PhInd)₂ZrCl₂/MAO (I) and (2-PhInd)₂ZrMe₂/TIBA (II) and the characteristics of polypropylene formed

Experiment	Catalyst	Zr, μmol	Al/Zr	[C ₃ H ₆], mol/l	<i>t</i> , min	w_{sp}^{a}	$w_{\text{p},0}^{\text{b}}$	M_w , g/mol	M_n , g/mol	M_w/M_n	D_{998}/D_{973}
1	I ^c	6.5	1000	12.3	120	156	16	190000 ^e	48000	4.0	0.25
2	I ^c	1.8	4000	12.3	120	281	5	160000 ^e	53000	3.0	0.24
3	II ^c	5.6	120	12.3	120	102	5	230000 ^e	82000	2.8	0.26
4	II ^d	3.5	50	4.0	60	105 ^f	3	Low-molecular product	–	–	–
5	II ^d	3.5	100	4.0	60	128	4	80000 ^g	22000 ^h	–	0.32
6	II ^d	3.5	200	4.0	60	269	8	116000 ^g			0.17
7	II ^d	3.5	300	4.0	60	419	16	220000 ^g	48000 ^h	–	0.18
8	II ^d	3.1	300	2.5	60	204	9	102000 ^g	32000 ^h	–	0.16
9	II ^d	3.1	300	1.5	60	183	4	62000 ^g	19700 ^h	–	0.18

Note: ^a The specific activity of polymerization, (kg PP) (mol Zr)^{–1} h^{–1} [C₃H₆]^{–1}.

^b Initial specific polymerization rate, (kg PP) (mol Zr)^{–1} min^{–1} [C₃H₆]^{–1}.

^c Polymerization in liquid propylene.

^d Polymerization in toluene, 65 ml.

^e GPC data.

^f Calculated from monomer consumption.

^g Data obtained from the measurement of the viscosity of polymer solution.

^h Calculated from NMR spectra.

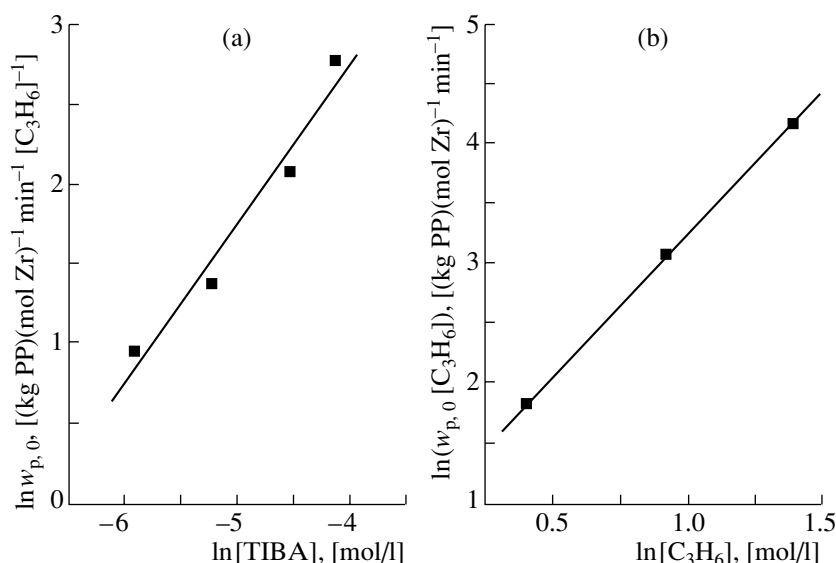
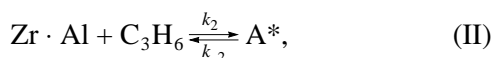
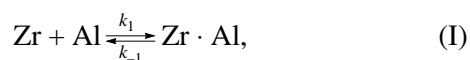


Fig. 2. $w_{p,0}$ and $w_{p,0} [\text{C}_3\text{H}_6]$ as functions of (a) TIBA and (b) propylene concentrations. The plots are given in logarithmic scale. The catalytic system is $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$, 30°C .

the monomer concentrations observed in our experiments for the catalytic system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ can be explained in a different manner.

Because the catalytically active cationic metal-alkyl complexes are formed from dimethylzirconocene and TIBA in the presence of the monomer, it is reasonable to assume that the following series of equilibrium reactions takes place:



where $\text{Zr} = (2\text{-PhInd})_2\text{ZrMe}_2$, $\text{Al} = \text{Al}(\text{iso-Bu})_3$, $\text{Zr} \cdot \text{Al}$ is a neutral bridged heteronuclear complex, C_3H_6 is a propylene molecule, and A^* is the cationic metal-alkyl complex with the coordinated monomer. This complex is formed by a shift of one methyl ligand from zirconium to aluminum under the action of olefin ($\text{Zr}^+\text{R}\cdots\text{AlR}_4$). Assuming that the concentrations of reactants in reactions (I) and (II) are at equilibrium, the following set of equations can be written:

$$\frac{d[\text{Zr}]}{dt} = -k_1[\text{Zr}][\text{Al}] + k_{-1}[\text{Zr} \cdot \text{Al}] = 0, \quad (1)$$

$$\begin{aligned} \frac{d[\text{Zr} \cdot \text{Al}]}{dt} &= k_1[\text{Zr}][\text{Al}] - k_{-1}[\text{Zr} \cdot \text{Al}] \\ &- k_2[\text{Zr} \cdot \text{Al}][\text{C}_3\text{H}_6] + k_{-2}[\text{A}^*] = 0, \end{aligned} \quad (2)$$

$$\frac{d[\text{A}^*]}{dt} = k_2[\text{Zr} \cdot \text{Al}][\text{C}_3\text{H}_6] - k_{-2}[\text{A}^*] = 0. \quad (3)$$

Taking into account the material balance with respect to zirconium

$$[\text{Zr}]_0 = [\text{Zr}] + [\text{Zr} \cdot \text{Al}] + [\text{A}^*], \quad (4)$$

where $[\text{Zr}]_0$ is the total concentration of Zr in all three complexes, the solution to Eqs. (1)–(3) is

$$[\text{A}^*] = \frac{[\text{Zr}]_0[\text{C}_3\text{H}_6][\text{Al}]}{\frac{1}{K_2}\left([\text{Al}] + \frac{1}{K_1}\right) + [\text{C}_3\text{H}_6][\text{Al}]}, \quad (5)$$

where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$.

For the polymerization reaction



assuming that the reaction is of the first order with respect to the monomer and active center concentrations, the rate equation is

$$\frac{d[\text{C}_3\text{H}_6]}{dt} = k_p[\text{A}^*][\text{C}_3\text{H}_6], \quad (6)$$

where k_p is the polymerization rate constant. We assumed that n -fold addition of the monomer according to reaction (III) does not remove A^* complexes from equilibrium reaction (II). This assumption corresponds to a situation when the specific coordination of the monomer activates the complex, but the reversible dissociation of the monomer converts the active center into a “sleeping,” temporarily inactive state independent of the size of alkyl radical at zirconium.

The substitution of (5) into Eq. (6) gives

$$\left. \frac{d[\text{C}_3\text{H}_6]}{dt} \right|_{t \rightarrow 0} = \frac{k_p[\text{Zr}]_0[\text{C}_3\text{H}_6]^2[\text{Al}]}{\frac{1}{K_2}\left([\text{Al}] + \frac{1}{K_1}\right) + [\text{C}_3\text{H}_6][\text{Al}]}, \quad (7)$$

where the polymerization rate linearly depends on the square of monomer concentration, if $\frac{1}{K_2} \left([\text{Al}] + \frac{1}{K_1} \right) \gg [\text{C}_3\text{H}_6][\text{Al}]$.

The values of K_1 , K_2 , and k_p determined using the initial reaction rates (Table 1, experiments 4–9) and the least-squares method were equal to $K_1 = 30.1$ l/mol, $K_2 = 3.75 \times 10^{-2}$ l/mol, and $k_p = 5900$ l mol⁻¹ min⁻¹ for the respective values of $[\text{Al}]$ and $[\text{C}_3\text{H}_6]$. We used the initial rates to exclude the influence of deactivation on the polymerization kinetics. The experimental values of the initial reaction rates are compared with the values calculated using Eq. (7) in Table 2. The standard deviation is lower than 0.19. These results confirm the mechanism of active center formation described by equilibrium reactions (I) and (II). One can see that the value of K_1 is almost three orders of magnitude higher than the value of K_2 . This means that the concentration of cationic complexes is very low and equals 1–5 mol % under experimental conditions (Table 2).

In principle, the proposed mechanism explains why the order of polymerization rate with respect to the monomer concentration is also higher than unity for the metallocene catalytic systems with the participation of MAO in a situation when K_1 is high and the monomer promotes the dissociation of the neutral complex with the formation of cationic complexes and when K_2 is low. A similar situation in catalytic systems activated by MAO can occur in the case of the formation of “sleeping” centers, for example, cationic metal–alkyl complexes stabilized by weak interaction with the methyl groups of MAO. It has been shown in [36] that, under certain conditions, the dissociation equilibrium in the dimethylzirconocene/MAO system substantially shifts toward the formation of coordinatively saturated “sleeping” centers.

It was mentioned above that an increase in the Al/Zr ratio leads to an increase in the molecular weight (M_w) of polypropylene (Fig. 3). This means that TIBA is not the main agent of chain transfer. The IR and NMR

spectroscopy of polymeric samples did not reveal final unsaturated fragments that are products of chain transfer onto the monomer or as the products of β -elimination of (H or CH₃) on zirconium. We excluded TIBA from consideration as an efficient agent of chain transfer and analyzed possible channels of chain transfer and the ratios of the respective rate constants using the expression

$$\frac{1}{\bar{P}_n} = \frac{k_{p,\text{mon}}[A^*][\text{C}_3\text{H}_6] + k_{p,\beta}[A^*]}{k_p[A^*][\text{C}_3\text{H}_6]} \quad (8)$$

$$= \frac{k_{p,\text{mon}}}{k_p} + \frac{k_{p,\beta}}{k_p[\text{C}_3\text{H}_6]},$$

where \bar{P}_n is the average polymerization degree, $[A^*]$ is the concentration of active centers, $[\text{C}_3\text{H}_6]$ is the monomer concentration, $k_{p,\text{mon}}$ is the rate constant of transfer onto the monomer, and $k_{p,\beta}$ is the constant of β -elimination (H– or –CH₃). The reactivity of the metal–carbon bond of the active center is revealed not only in the reaction of chain growth but also in reactions limiting chain growth. Therefore, using published data [23, 37–39], we analyzed analogous relationships for the catalytic system (2-PhInd)₂ZrCl₂/MAO (Fig. 4). The respective values of the slopes of lines representing dependences $(1/\bar{P}_n - 1/[\text{C}_3\text{H}_6])$ and the intercepts on the ordinate axis are summarized in Table 3. Table 3 shows that the results of different studies where MAO was used as a cocatalyst were not convergent under the same conditions. However, if the data of [23] are excluded, the ratio of rate constants $k_{p,\beta}/k_{p,\text{mon}}$ is equal to 13 for the system (2-PhInd)₂ZrMe₂/TIBA and 1–3 for the system (2-PhInd)₂ZrCl₂/MAO. Thus, for the catalytic system (2-PhInd)₂ZrMe₂/TIBA, chain transfer via β -elimination dominates. The values of $k_{p,\text{mon}}/k_p$ are close for both systems.

The catalytic system (2-PhInd)₂ZrMe₂/TIBA leads to the formation of stereoblock polypropylene with a rather high molecular weight in both the liquid mono-

Table 2. Comparison of experimental values of initial specific rates of propylene polymerization in the presence of the catalytic system (2-PhInd)₂ZrMe₂/TIBA with values obtained using Eq. (7) at $K_1 = 30.1$ l/mol, $K_2 = 3.75 \times 10^{-2}$ l/mol, and $k_p = 5900$ l mol⁻¹ min⁻¹

Experiment*	Zr, μmol	Al/Zr, mol/mol	$[\text{C}_3\text{H}_6]$, mol/l	$w_{p,0}$, (kg PP) (mol Zr) ⁻¹ min ⁻¹ $[\text{C}_3\text{H}_6]$ ⁻¹		A^* , mol %
				experiment	calculation	
4	3.5	50	4.0	3	2.8	1.1
5	3.5	100	4.0	4	5.2	2.0
6	3.5	200	4.0	8	9.0	3.5
7	3.5	300	4.0	16	11.9	4.6
8	3.1	300	2.5	9	7.1	2.8
9	3.1	300	1.5	4	4.1	1.6

* The numbers of entries correspond to Table 1.

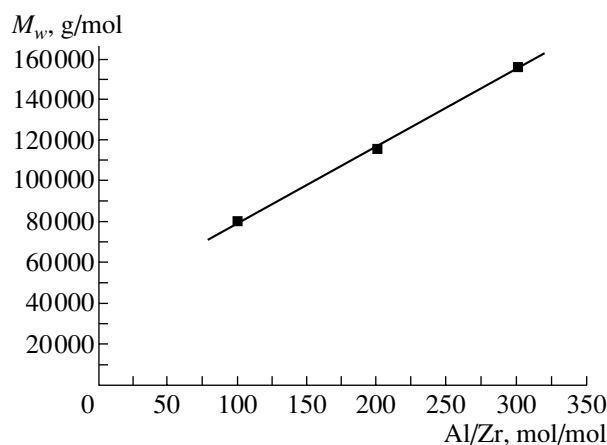


Fig. 3. Molecular weight of polypropylene formed in the presence of catalytic system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ as a function of Al/Zr at constant zirconocene concentration (Table 1, experiments 5–7).

mer and in toluene as a reaction medium. Comparison of the pentad composition of polypropylene formed under different reaction conditions on dichlorozirconium and dichlorohafnium complexes activated by MAO and dimethylzirconocene activated by TIBA is presented in Table 4 and Fig. 5. One can see that a strong change in the Al/Zr ratio from 1000 to 4800 and in the reaction temperature from 30 to 8°C [19] enables variations in the isotactic pentad content for the catalytic system $(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$ in the range 26–31%. Stereoblock polypropylene with virtually identical stereocomposition was obtained in the catalytic system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ at 30°C and Al/Zr = 120 in liquid propylene (Table 4, experiment 3). The system activity and the molecular weight of polypropylene in this experiment are higher than the corresponding values observed for propylene polymerization with a dichloride complex activated by MAO. At high Al/Zr ratios (Table 4, experiments 7 and 9), polypropylene with a stereocomposition close to the composition of polypropylene formed in the catalytic system $(2\text{-PhInd})_2\text{HfCl}_2/\text{MAO}$ [19] was obtained.

An important feature of the catalytic system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ is the possibility of controlling

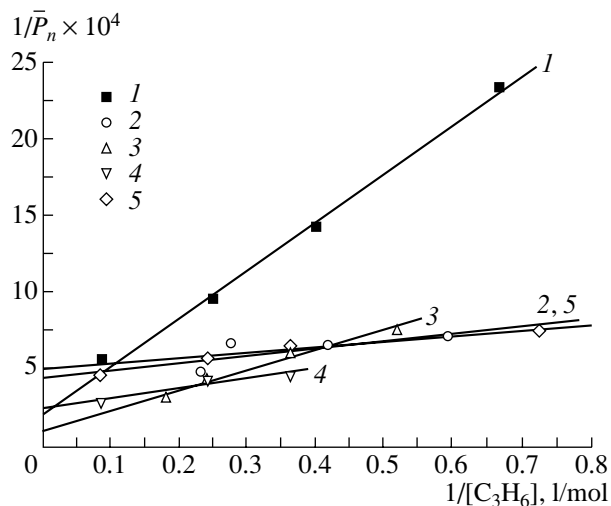


Fig. 4. Reciprocal average polymerization degree as a function of the reciprocal propylene concentration for catalytic systems (1) $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ and (2–5) $(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$ [23, 37–39]. Polymerization conditions are given in Table 3.

the pentad composition by changing the Al/Zr ratio. An increase in the Al/Zr ratio from 100 to 300 mol/mol (Fig. 5, columns 3–5, from left to right) leads to a considerable decrease in the isotactic *mmmm* pentad content. The content of *mmmr* pentads, which are “boundary” with isotactic blocks is practically identical for all samples. However, the content of pentads typical of atactic blocks increases with an increase in the Al/Zr ratio. An increase in the monomer concentration by a factor of 3 does not influence the stereocomposition of polypropylene formed at Al/Zr = 300 (Table 4, experiments 7 and 9). An exponential decrease in the stereoregularity with an increase in the Al/Zr ratio observed in NMR and IR spectra (Fig. 6) and an increase in the content of atactic blocks show that TIBA participates in the formation of stereoblocks. It is difficult to conclude on the mechanism of this participation, but it is possible to make some assumptions.

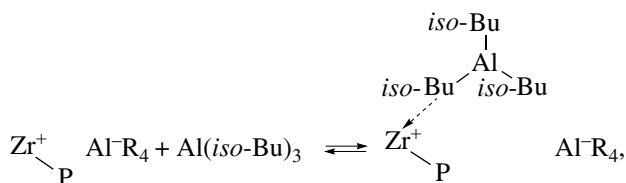
A simultaneous increase in the catalytic activity, an increase in the molecular weight, and a decrease in stereoregularity accompany an increase in the Al/Zr ratio.

Table 3. The comparison of the ratios of the rate constants of chain transfer reaction and chain growth for catalytic systems $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ and $(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$

Catalyst*	T , °C	Al/Zr, mol/mol	$k_{t,\beta}/k_p \times 10^3$	$k_{t,\text{mon}}/k_p \times 10^4$	References
$(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ (1)	30	300	3.10 ± 0.15	2.33 ± 0.60	This work
$(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$ (2)	25	1000	0.36 ± 0.15	4.98 ± 0.78	[37]
$(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$ (3)	20	"	1.27 ± 0.14	1.14 ± 0.45	[23]
$(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$ (4)	20	"	0.65 ± 0.17	2.53 ± 0.43	[38]
$(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$ (5)	20	"	0.45 ± 0.08	4.58 ± 0.35	[40]

* The number of the corresponding curve in Fig. 4 is given in brackets.

A linear increase in the activity is explained by the participation of TIBA in the equilibrium reactions of active center formation. An increase in the molecular weight and a decrease in stereoregularity demonstrate the additional influence of TIBA on the “working” active center. As mentioned above, when Al/Zr = 50, the main product of the reaction is a low-molecular oil-like product. On the basis of the dependence of stereoregularity on the value of Al/Zr (Fig. 6), the high isotacticity of these polymer products is to be expected. We hypothesize that cationic centers formed under the action of TIBA are stabilized in *rac*-form due to the close proximity of bulk counterion and that another equilibrium reaction between cationic complex and TIBA becomes essential with an increase in the Al/Zr ratio:



where P is a growing polymeric chain and R is the alkyl ligand.

In this case, TIBA is weakly bound to a cationic center and is in a state of dynamic equilibrium. Fast exchange processes are possible in the coordinated state between the alkyl group of TIBA and a growing polymeric chain. These processes can reduce the stereoregularity of a growing polymer chain. At the same time, this coordination can stabilize the active center (in

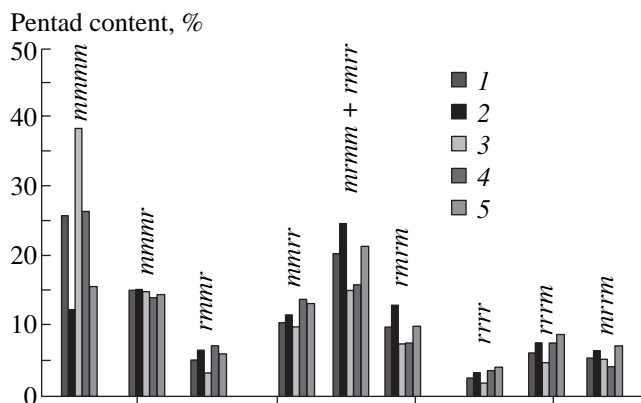


Fig. 5. Pentad composition of polypropylene samples synthesized on catalytic systems (from left to right) (1) (2-PhInd)₂ZrCl₂/MAO [17], (2) (2-PhInd)₂HfCl₂/MAO [19], and (2-PhInd)₂ZrMe₂/TIBA with Al/Zr equal to (3) 100, (4) 120, and (5) 300. NMR data.

the timescale of exchange reaction and olefin addition) with respect to the reactions of β -elimination. It is also possible that the coordination of TIBA molecule may stabilize the *meso*-form.

To check the possibility of these effects, we tried to carry out the statistical analysis of the stereocomposition of polymers formed in catalytic system (2-PhInd)₂ZrMe₂/TIBA at different Al/Zr ratios. The growth of “model” polypropylene molecule was simulated with a computer according to one of the proposed

Table 4. Pentad composition (relative parts) of polypropylene samples synthesized by catalytic systems (2-PhInd)₂ZrCl₂/MAO (**ZrCl**) [40, 19], (2-PhInd)₂HfCl₂/MAO (**HfCl**) [19], and (2-PhInd)₂ZrMe₂/TIBA (**ZrMe**)

Catalyst	<i>mmmm</i>	<i>mmmr</i>	<i>rmmr</i>	<i>mmrr</i>	<i>mrmm</i> + <i>rmrr</i>	<i>rrmm</i>	<i>rrrr</i>	<i>rrrm</i>	<i>mrrm</i>
ZrCl ^a	0.27	0.15	0.07	0.13	0.16	0.10	0.04	0.06	0.04
ZrCl ^b	0.31	0.15	0.06	0.13	0.16	0.08	0.03	0.05	0.04
ZrCl ^c	0.26	0.15	0.05	0.10	0.20	0.10	0.02	0.06	0.05
HfCl ^d	0.12	0.15	0.07	0.12	0.25	0.13	0.03	0.08	0.06
ZrMe (3) ^e	0.27	0.14	0.07	0.14	0.16	0.08	0.04	0.08	0.04
ZrMe (5)	0.49	0.14	0.03	0.10	0.11	0.05	0.01	0.03	0.03
ZrMe (7)	0.18	0.18	0.07	0.15	0.18	0.09	0.04	0.07	0.07
ZrMe (9)	0.21	0.16	0.07	0.17	0.18	0.09	0.03	0.06	0.04

Note: ^a In toluene solution, Al/Zr = 1000, $P_{C_3H_6}$ = 5 atm, 20°C, 60 min.

^b In liquid propylene, Al/Zr = 4800, 30°C, 120 min.

^c In liquid propylene, Al/Zr = 2200, 8°C, 120 min.

^d In liquid propylene, Al/Zr = 2500, 30°C, 120 min.

^e Numbers in brackets correspond to the numbers of experiments (Table 1).

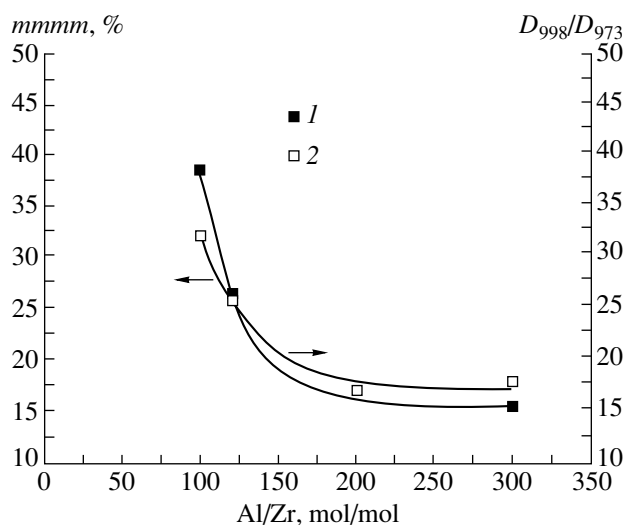


Fig. 6. (1) Pentad composition and (2) macrotacticity index of polypropylene samples synthesized on catalytic system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ as a function of Al/Zr ratio.

models. The length of the simulated macromolecule was chosen to enable statistical analysis (~300000 monomer units).

The mechanism of stereoblock polypropylene formation according to the “oscillating active center” model suggests the presence of two active centers having different stereoselectivity and different activity. These centers can transform into each other with a characteristic time exceeding the time of propylene coordination and insertion. In the investigated catalytic system, the modification of the active center under the action of TIBA is observed so that an increase in the Al/Zr ratio leads to an increase in the molecular weight of polypropylene and an exponential decrease in the content of isotactic pentads.

For the description of the stereoregulating ability of the system and its dependence on the Al/Zr molar ratio we tested model 1. According to this model, the approaching propylene molecule can find the active center either in isospecific state **I** or in aspecific form **A**. We can assume that active center **I** in system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ is the cationic complex $(\text{Zr}^+\cdots\text{Al}^-\text{R}_4)$. This complex is formed by reactions (I) and (II). However, it can transform into nonspecific complex **A**, for example, as a result of TIBA molecule coordination. It was suggested that the enantioselectivity of center **I** determines the formation of $\dots\text{mmmm}\dots$ sequences. To check the isospecific activity of center **I**, we introduced the probability p_m of enantiofacioanal insertion of propylene on this center in the model. The probability of *r*- or *m*-addition (with respect to the last unit) on the nonspecific center was taken as equal to 0.5. We supposed that the equality of *r*- and *m*-addition probabilities can result from the fast inversion of the growing polymeric chain. This inversion averages the content of atactic sequences. Possible chain inversion at the event

of conversion from **A**- to **I**-state was also taken into account. This inversion makes the probabilities of *m*- or *r*-addition equal in the isospecific active center after such an act. The probability of monomer coordination and insertion on center **I** was taken as equal to q and, respectively, equal to $(1 - q)$ on center **A**. Comparison of calculated and experimental data (Table 5) shows the good correlation of the pentad contents. It is possible to see that the values of p_m for the catalytic system $(2\text{-PhInd})_2\text{ZrMe}_2/\text{TIBA}$ are close to unity. The value of parameter q describing the probability of monomer approach to the isospecific center and the isotactic pentad content decrease with an increase in the Al/Zr ratio.

An important element of model 1 is the possibility of chain inversion only on a nonspecific active center, which is, hypothetically, due to a fast exchange reaction with the alkyl group of coordinated TIBA or due to epimerization. Therefore, it was interesting to compare experimental and calculated data on the microstructure of elastomeric polypropylene generated by the $(\text{acac})_2\text{ZrCl}_2/\text{MAO}$ system [41]. To explain virtual stereoblock sequences, the authors of this work suppose that the chain grows on the isospecific center at the same time as chain epimerization. The stereocomposition of polypropylene synthesized in this system at 0°C in methylene chloride (Al/Zr ~ 500) was compared with the stereocomposition calculated using model 1 (line 5). No good coincidence was found. To analyze the composition of stereoblock polypropylene synthesized using the scheme proposed by the authors, we used in our calculation a modified model 2 that includes chain inversion on the isospecific center only. According to this model, the isospecific center provides the addition of a monomer with “proper” orientation with probability p (chain growth) or “makes mistakes” with probability $(1 - p)$. Table 5 shows the good correlation of experimental and calculated spectra in the pentad region.

It is necessary to emphasize that an important assumption in model 1 was the reversible coordination of TIBA by the cationic metal–alkyl complex. Perhaps, this coordination can explain the unexpected stereoregulating behavior of some catalytic systems with TIBA participation. For example, the inversion of stereoselectivity of the metallocene complex $\text{Me}_2\text{Si}(\text{Flu})(\text{N-}t\text{-ret-Bu})\text{ZrCl}_2$ (Flu is fluorenyl) from syndiospecific to isospecific, when the activator is changed from MAO to TIBA/ $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$, was found in [42]. The bisamide complex of titanium with C_{2v} symmetry leads to the formation of isotactic polypropylene with the controlled stereoaction of the active center in the activation of TIBA/ $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ [43]. Probably, the mechanism of stereoblock polypropylene formation according to models 1 and 2, which includes chain inversion as a reaction competing with chain growth on isospecific or, in turn, on isospecific and nonspecific active centers, can be considered as an alternative to the “oscillating” model.

Table 5. The comparison of (e) experimental and (c) calculated (using models 1 and 2) values of the pentad content of stereoblock polypropylene synthesized by different catalytic systems

No.	Catalytic system	$\frac{mmmm_e}{mmmm_c}$	$\frac{mmmr_e}{mmmr_c}$	$\frac{rmmr_e}{rmmr_c}$	$\frac{mmrr_e}{mmrr_c}$	$\frac{(mrrm + rrrr)_e}{(mrrm + rrrr)_c}$	$\frac{rrmm_e}{rrmm_c}$	$\frac{rrrr_e}{rrrr_c}$	$\frac{rrrm_e}{rrrm_c}$	$\frac{mrrm_e}{mrrm_c}$	Er ^a
Model 1											
1	(2-PhInd) ₂ ZrMe ₂ /TIBA ^b $q = 0.79; p_m = 1.0$	$\frac{0.49}{0.49}$	$\frac{0.14}{0.18}$	$\frac{0.03}{0.02}$	$\frac{0.10}{0.08}$	$\frac{0.11}{0.15}$	$\frac{0.05}{0.03}$	$\frac{0.01}{0.01}$	$\frac{0.03}{0.02}$	$\frac{0.03}{0.04}$	0.03
2	(2-PhInd) ₂ ZrMe ₂ /TIBA ^c $q = 0.62; p_m = 1.0$	$\frac{0.27}{0.26}$	$\frac{0.14}{0.20}$	$\frac{0.07}{0.04}$	$\frac{0.14}{0.11}$	$\frac{0.16}{0.21}$	$\frac{0.08}{0.07}$	$\frac{0.04}{0.02}$	$\frac{0.08}{0.05}$	$\frac{0.04}{0.05}$	0.04
3	(2-PhInd) ₂ ZrMe ₂ /TIBA ^b $q = 0.51; p_m = 1.0$	$\frac{0.18}{0.18}$	$\frac{0.18}{0.19}$	$\frac{0.07}{0.05}$	$\frac{0.15}{0.12}$	$\frac{0.18}{0.22}$	$\frac{0.09}{0.09}$	$\frac{0.04}{0.03}$	$\frac{0.06}{0.02}$	$\frac{0.04}{0.06}$	0.02
4	(2-PhInd) ₂ ZrMe ₂ /TIBA ^b $q = 0.60; p_m = 0.95$	$\frac{0.21}{0.21}$	$\frac{0.16}{0.19}$	$\frac{0.07}{0.05}$	$\frac{0.17}{0.12}$	$\frac{0.18}{0.22}$	$\frac{0.09}{0.08}$	$\frac{0.03}{0.02}$	$\frac{0.06}{0.06}$	$\frac{0.04}{0.05}$	0.03
5	(acac) ₂ ZrCl ₂ /MAO [42] ^d $q = 0.64; p_m = 0.99$	$\frac{0.28}{0.27}$	$\frac{0.12}{0.20}$	$\frac{0.00}{0.04}$	$\frac{0.12}{0.11}$	$\frac{0.15}{0.20}$	$\frac{0.08}{0.07}$	$\frac{0.06}{0.01}$	$\frac{0.11}{0.05}$	$\frac{0.09}{0.05}$	0.12
Model 2											
6	(acac) ₂ ZrCl ₂ /MAO [42] ^d $p = 0.76$	$\frac{0.28}{0.25}$	$\frac{0.12}{0.17}$	$\frac{0.00}{0.03}$	$\frac{0.12}{0.17}$	$\frac{0.15}{0.13}$	$\frac{0.08}{0.07}$	$\frac{0.06}{0.03}$	$\frac{0.11}{0.07}$	$\frac{0.09}{0.09}$	0.04

Note: ^a The error was determined using formula $Er = \sqrt{\frac{(J_{ci} - J_{ei})^2}{6}}$, where J_{ci} and J_{ei} are the calculated and experimental values of the intensities of *i*-pentads, respectively. The intensities of the six most intensive pentads were averaged to decrease the contribution of low-intensity peaks.

^b Toluene solution; for conditions, see Tables 1 and 4.

^c Polymerization in liquid propylene, Al/Zr = 1200, 30°C, 120 min.

^d Methylene chloride, Al_{MAO}/Zr = 120, $P_{C_3H_6}$ = 6 atm, 0°C.

ACKNOWLEDGMENTS

Financial support from the Russian Foundation of Basic Research (grant nos. 99-03-32948 and 01-03-97002) is acknowledged.

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