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# Isospecific Bulk Polymerization of Propylene with the Use of *ansa*-Metallocenes as a Mixture of *rac* and *meso* Isomers

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**Abstract**—The effects of various pathways of the formation of catalytic systems based on the *rac*-Me<sub>2</sub>SiInd<sub>2</sub>ZrCl<sub>2</sub> metallocene on the activity and properties of polypropylene prepared by the bulk polymerization of propylene were studied in detail. It was found that the conditions of formation of the catalytic system affect not only its activity and the character of kinetic curves but also the molecular weight of the synthesized polymer. Propylene polymerization was studied with the use of a number of bisindenyl derivatives of zirconium, which were mixtures of *rac* and *meso* forms that differ in the nature of substituents in the Si bridge or the indenyl ligand. The conclusion was drawn that, with the use of metallocenes as a mixture of *rac* and *meso* forms, high-molecular-weight isotactic polypropylene can be prepared with high stereoregularity at a very high rate; thereby, the stage of separation of a pure *rac* isomer can be excluded in the synthesis of the catalyst.

## INTRODUCTION

The discovery of homogeneous catalysts based on bridged sterically hindered *ansa*-metallocenes and polymethylalumoxane (MAO) for the stereospecific polymerization of  $\alpha$ -olefins is one of the most important events in Ziegler–Natta catalysis [1–3]. The use of these highly effective catalysts opened up wide opportunities for producing new materials and extending the range of polyolefins and the areas of application of polyolefins, primarily, polypropylene (PP) [4–6]. Along with high activity, the above catalytic systems provide an opportunity to synthesize polymers with a narrow molecular-weight distribution (MWD) because of the formation of uniform active centers. Either isotactic PP (IPP) or other PP stereoisomers (syndiotactic, hemiisotactic, atactic, and stereoblock isomers) can be obtained depending on the composition, structure, and symmetry of *ansa*-metallocenes.

Presently,  $C_2$ -symmetric *ansa*-metallocenes activated with MAO or boron compounds are the best catalysts for the synthesis of IPP [7]. Among these are Me<sub>2</sub>Si(2-Me-4,5-Bz(e)Ind)<sub>2</sub>ZrCl<sub>2</sub> and Me<sub>2</sub>Si(2-R-4-ArylInd)<sub>2</sub>ZrCl<sub>2</sub>, where R = Me, Et and Aryl = Ph, Naphthyl. In the synthesis of  $C_2$ -symmetric *ansa*-metallocenes, the final complicated stage is the separation of a mixture of *rac* and *meso* isomers. The *rac* isomer is a highly active isospecific catalyst for propylene polymerization, whereas the *meso* isomer is usually inactive. The activity ratio between *rac* and *meso* isomers can vary from 10 to 100 depending on the type of *ansa*-metallocenes [8].

Let us consider published data on the use of catalytic systems based on metallocenes that consisted of

*rac*–*meso* isomer mixtures or pure *meso* isomers in the processes of olefin polymerization.

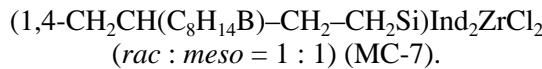
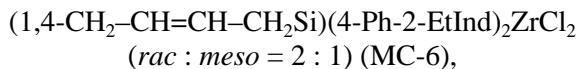
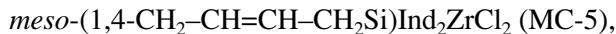
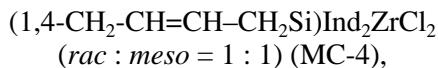
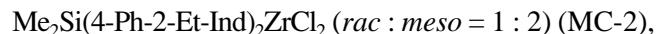
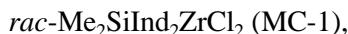
Previously, Kaminsky *et al.* [9] found that the *rac*–*meso* transition can occur in a metallocene solution in toluene under exposure to daylight. This transition resulted in considerable changes in the polymerization behavior of catalytic systems. A study of the photochemical isomerization of metallocenes resulted in the development of new procedures for the synthesis of *rac* isomers [10].

Resconi *et al.* [11] found that the use of a *rac*–*meso* mixture of the *ansa*-metallocenes Me<sub>2</sub>C(3-BuInd)<sub>2</sub>ZrCl<sub>2</sub> and Me<sub>2</sub>C(3-Me<sub>3</sub>SiInd)<sub>2</sub>ZrCl<sub>2</sub> in 2 : 1 and 1 : 1 ratios between *rac* and *meso* isomers, respectively, in the bulk polymerization of propylene resulted in PP with a considerably high molecular weight (MW) and regular regiostructure. The disadvantage of these systems is that high MWs and stereoregularity parameters are characteristic of PP synthesized at a temperature of no higher than 40°C. It is of interest that, in the polymerization of higher  $\alpha$ -olefins such as 1-pentene, 1-hexene, and 1-octene, the *meso* isomers of metallocenes with substituted indenyl ligands Me<sub>2</sub>Si(2-Me-4,5-BzInd)<sub>2</sub>ZrCl<sub>2</sub>, Me<sub>2</sub>Si(2-Me-4-PhInd)<sub>2</sub>ZrCl<sub>2</sub>, and Me<sub>2</sub>Si(2-Me-4,6-i-Pr<sub>2</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> were much more active than the *rac* forms of these compounds [12, 13]. In a number of studies [14–16], it was found that *rac* and *meso* isomers could exhibit different behaviors in the polymerization of olefins with the use of different activators. Some *meso* isomers are highly effective in the copolymerization of ethylene with propylene [17, 18]. Thus, with the use of the metallocene 1,2-CH<sub>2</sub>CH<sub>2</sub>[4-(7-MeInd)]<sub>2</sub>ZrCl<sub>2</sub> with a –CH<sub>2</sub>–CH<sub>2</sub>– bridge through six-membered rings at the

4,4'-positions (in the majority of *ansa*-metallocenes, indenyl ligands are linked with bridges through five-membered rings at the 1,1'-positions), both metallocene species were found to be much more active in the copolymerization of ethylene and propylene than in homopolymerization. In this case, the *meso* form was much more active in both homopolymerization and copolymerization. The activity of the *rac* form in propylene polymerization was equal to 10 kg PP (g Zr)<sup>-1</sup> h<sup>-1</sup> (the concentration of isotactic triads was 77%), whereas the activity in copolymerization was 230 kg EP (g Zr)<sup>-1</sup> h<sup>-1</sup> (EP is an ethylene-propylene copolymer). Under the same conditions (polymerization in liquid propylene at 50°C), the activity of the *meso* form in the formation of atactic PP was as high as 204 kg PP (g Zr)<sup>-1</sup> h<sup>-1</sup> (the concentration of isotactic triads was 28%), whereas the activity in copolymerization was unusually high: 5350 kg EP (g Zr)<sup>-1</sup> h<sup>-1</sup> [18].

Thus, based on this consideration, it is believed that the use of *meso* isomers or their mixtures with other highly effective metallocenes can extend the possibilities of preparing new polymers.

In this work, we studied the bulk polymerization of propylene and the properties of polymers formed with the use of a number of *ansa*-metallocenes with bisindenyl ligands as the mixtures of *rac* and *meso* isomers. Metallocenes containing a known Me<sub>2</sub>Si- or new 1,4-CH<sub>2</sub>-CH=CH-CH<sub>2</sub>Si bridge [19, 20] were studied. Note that the silane bridge containing a double bond is capable of further chemical modification, and we used this opportunity to prepare new metallocene MC-7. The following *ansa*-metallocenes as pure *rac* and *meso* forms were used in this study for comparison:



## EXPERIMENTAL

The following solvents were used in the synthesis of catalysts and in the preparation of metallocene solutions: toluene, tetrahydrofuran (THF), hexane, diethyl ether, pentane, and methylene chloride, which were prepared in accordance with standard procedures [21]. All operations were performed in an atmosphere of dry high-purity argon.

MC-1, MC-2, MC-4, and MC-7 were prepared according to published procedures [19, 22, 23]; MC-3 was obtained from Boulder Co.

The composition and structure of synthesized zirconocenes were supported by elemental analysis and <sup>1</sup>H NMR spectroscopy.

MAO from Witco was used as a 10% solution in toluene.

Propylene of polymerization grade (99.7 vol %) from Moscow Refinery was used in polymerization without additional purification.

Propylene polymerization in a liquid monomer medium was performed in metal units with 0.25- and 0.4-l reactors under conditions of completely filled reactors at pressures higher than the saturation vapor pressure of propylene at a given temperature. The rates of PP formation at different points in time were determined from the amounts of propylene additionally introduced in the course of the process to maintain a constant pressure in the reaction apparatus. To characterize the activity of the test systems, the effective rate constant of polymerization was used:

$$k_{\text{eff}} = w_{\text{pol}}/C_{\text{mon}}C_{\text{Zr}},$$

where *w*<sub>pol</sub> is the rate of propylene polymerization at a given point in time in a unit volume of the reaction mixture, mol l<sup>-1</sup> min<sup>-1</sup>; *C*<sub>mon</sub> is the monomer concentration in a liquid phase, mol/l; and *C*<sub>Zr</sub> is the metallocene concentration in a unit volume of the reaction mixture, mol/l.

The microstructure of PP was determined by IR and <sup>13</sup>C NMR spectroscopy. The parameters of stereoregularity were found from the intensity ratios between absorption bands *D*<sub>998</sub>/*D*<sub>973</sub>, *D*<sub>841</sub>/*D*<sub>1167</sub>, and *D*<sub>841</sub>/*D*<sub>973</sub> according to published procedures [24, 25].

The <sup>13</sup>C NMR spectra of polymer solutions in tetrachlorodideuterioethane were measured at 130°C.

The molecular-weight characteristics of PP samples were studied by gel permeation chromatography on a Waters 150-C high-temperature gel chromatograph. The analysis was performed at 145°C with the use of a linear column ( $\mu$ -styragel HT). The concentration of the polymer solution in *ortho*-dichlorobenzene was 0.04%.

The melting temperature and the degree of crystallinity of PP were determined by differential scanning calorimetry (DSC) on a DuPont Instrument at a heating rate of 20 K/min. The results of the second scanning are presented in this work.

## RESULTS AND DISCUSSION

As distinct from heterogeneous catalysts, homogeneous metallocene catalytic systems are highly sensitive to polymerization conditions (temperature, reactant concentrations, polarity of the medium, procedures of system formation, etc.). Therefore, all of these factors should be carefully studied to optimize the conditions of polymer synthesis.

In this work, we studied the main regularities of the bulk polymerization of propylene. First, we found the most effective ways of forming homogeneous metallocene systems by analyzing various procedures for the activation of MC-1. Second, we examined a number of metallocenes that were a mixture of *rac*–*mesa* isomers (MC-4 and MC-7), which differ in the nature of their bridges, under identical conditions. Third, we tested a number of metallocenes with substituted bisindenyl ligands (MC-2 and MC-6), which were responsible for the preparation of high-molecular-weight IPP.

To study the effects of the procedures used for the formation of catalytic systems based on MC-1 on the activity and the properties of the resulting PP, the polymerization was performed by the following two procedures:

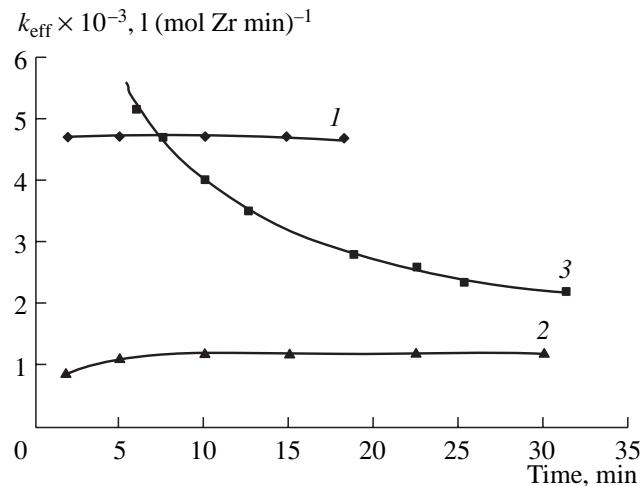
(1) The injection of a metallocene solution in toluene into a reactor filled with liquid propylene, which contained the required amount of MAO (the formation of active species in the presence of the monomer).

(2) The injection of a metallocene dissolved in a 10% MAO ( $\text{Al/Zr} = 280$ ) solution in toluene into a reactor filled with liquid propylene, which contained an additional amount of MAO or  $(i\text{-Bu})_3\text{Al}$  (the formation of active species outside the polymerization zone).

Figure 1 demonstrates the kinetic curves of propylene polymerization with different procedures of formation of catalytic systems. With the use of MAO as a cocatalyst (curves 1, 2), the activity remained unchanged with time; this is likely due to the continuous regeneration of active centers [26].

The maximum activity of a combined cocatalyst including  $(i\text{-Bu})_3\text{Al}$  (curve 3) [27, 28] was observed at the initial moment; thereafter, the value of  $k_{\text{eff}}$  decreased by a factor of  $\sim 2$  in 20 min. This may be due to the bimolecular deactivation of active centers in the course of polymerization, probably because of the partial reduction of metallocenes under the action of  $(i\text{-Bu})_3\text{Al}$ .

Data given in Table 1 suggest that the system prepared in accordance with procedure 2 was three times more active than the system prepared in accordance with procedure 1. Note that, in all cases, PPs with narrow MWs were obtained, which were similar in macrotacticity and melting temperatures. The molecular weight of the polymer obtained in the presence of the MC-1/MAO system activated with MAO or  $(i\text{-Bu})_3\text{Al}$  was lower than that with the use of a toluene solution of MC-1 by a factor of 1.5 (60000 g/mol against 90000 g/mol). It is evident that, in the formation of active centers using the first procedure, a more sterically hindered active center was formed, and this resulted in an increase in the MW of the polymer. The data obtained are indicative of a difference in active centers formed depending on the formation conditions of the catalytic systems, and they can explain the different activities observed in the same system obtained in different studies [29].



**Fig. 1.** The time dependence of the effective rate constant of propylene polymerization in the presence of a catalytic system based on MC-1.  $T = 50^\circ\text{C}$ . Dissolution MC in (2) toluene and (1, 3) MAO. Cocatalyst: (1, 2) MAO, (3)  $(i\text{-Bu})_3\text{Al}$ .

In the study of the polymerization behavior of a number of metallocenes that are mixtures of *rac* and *meso* isomers, we used the most effective procedure for the formation of catalytic systems: the dissolution of metallocenes in MAO and polymerization in the presence of an additional amount of MAO.

Table 2 summarizes data on the bulk polymerization of propylene for the bisindenyl derivatives of zirconium, which were mixtures of *rac* and *meso* forms in a 1 : 1 ratio (MC-4, MC-7). These metallocenes are different in the nature of substituents in the Si bridge. As can be seen in Table 2, with the use of the catalytic system based on MC-4 as a mixture of *rac* and *meso* isomers, the activity observed was lower than that with the use of MC-1, whereas the activity of the pure *rac* form of this compound (calculated) was almost equal to the activity of MC-1. The use of MC-7 with a bulky substituent in the bridge resulted in a certain decrease in the activity of the catalytic system. Data on the polymerization of propylene with the use of the *meso* form of MC-5 are also given in Table 2. As can be seen in Table 2, the activity of the system based on the *meso* isomer was lower than that in the case of the corresponding *rac* isomer of MC-4 by a factor of almost 50.

In all cases, polymers with low MW were obtained (Table 3). It is well known that this is due to low ratios between the rate of growth and the rate of processes responsible for the limitation of a polymer chain for systems based on *ansa*-metallocenes with unsubstituted bisindenyl ligands. This is a consequence of the intense occurrence of  $\beta$ -elimination reactions of hydrogen from a polymer chain to a metal or monomer [3]. With the use of the *meso* isomer MC-5, atactic PP with a very low MW equal to 1700 g/mol was prepared. As can be seen in Table 3, polymers based on a mixture of *rac* and *meso* isomers exhibited rather high stereoregularity.

**Table 1.** Effect of the procedure of formation of catalytic systems based on *rac*-Me<sub>2</sub>SiInd<sub>2</sub>ZrCl<sub>2</sub> on the activity in the bulk polymerization of propylene and on the properties of the synthesized PP

Formation procedure	Al(MAO) Zr	Al( <i>i</i> -Bu) <sub>3</sub> Al Zr	Polymerization time, min	Yield, g	A, kg PP × (mmol Zr) <sup>-1</sup> h <sup>-1</sup>	M, %	M <sub>w</sub> × 10 <sup>-3</sup>	M <sub>w</sub> / M <sub>n</sub>	T <sub>m</sub> , °C
MC-1/toluene + MAO	12600	—	60	20	38	90	90.5	2.0	144
MC-1/MAO* + MAO	12000	—	20	18	130	89	58.4	1.8	145
MC-1/MAO* + ( <i>i</i> -Bu) <sub>3</sub> Al	250	1050	30	38	100	90	60.0	2.1	143

Note: Polymerization temperature, 50°C; [Zr] = 6 × 10<sup>-7</sup> mol/l; A is activity; M is macrotacticity; M<sub>w</sub> is the weight-average molecular weight, g/mol; M<sub>n</sub> is the number-average molecular weight, g/mol; and T<sub>m</sub> is the melting temperature.

\* At the stage of preactivation, Al/Zr = 280.

**Table 2.** Effect of the type of metallocenes on the activity in the bulk polymerization of propylene

Metallocene	<i>rac</i> : <i>meso</i>	[metallocene] × 10 <sup>6</sup> , mol	[metallocene] × 10 <sup>6</sup> , mol/l	Al/Zr	Experiment time, min	Yield, g	A, kg PP × (mmol Zr) <sup>-1</sup> h <sup>-1</sup>	A <sub>1</sub> , kg PP × (mmol Zr ( <i>rac</i> )) <sup>-1</sup> h <sup>-1</sup>
MC-1	1 : 0	0.55	2.2	7400	20	20	122	109
MC-4	1 : 1	1.05	4.2	5200	30	28	54	108
MC-4*	1 : 1	0.7	2.8	5000	40	28	71	140
MC-7	1 : 1	1.2	4.8	4300	30	25	42	84
MC-5	0 : 1	1.6	5.4	3800	120	9	2.8	—

Note: Polymerization temperature, 50°C; at the stage of preactivation, Al/Zr = 280.

\* Polymerization temperature, 70°C.

larity factors (the macrotacticity index was ~85%), which are indicative of a very low contribution of the *meso* isomer to the polymerization of propylene.

Figure 2 demonstrates the time dependence of the effective rate constant of the bulk polymerization of propylene with the use of MC-1, MC-4, and MC-7 activated with MAO. As can be seen in Fig. 2, the activity of the catalytic systems changed only slightly with the time of polymerization in almost all cases.

It is well known that the rate of processes responsible for the limitation of a polymer chain and the fraction of anomalous additions considerably decreased with the use of zirconocenes with indenyl ligands that contain alkyl and aromatic substituents at certain positions; this resulted in a considerable increase in the activity of metallocene-MAO systems, the molecular weight, the degree of regularity, and the melting temperature of PP [6].

To prepare high-molecular-weight IPP, the bulk polymerization of propylene was studied with the use of MC-2 and MC-6, which contained indenyl ligands with ethyl and phenyl substituents at the 2- and 4-positions, respectively, at ratios of 1 : 2 and 2 : 1 between the *rac* and *meso* forms, respectively. Metallocene, which was predissolved in MAO, was injected into a reactor filled with liquid propylene containing an addi-

tional amount of MAO at 10°C; thereafter, a specified temperature (60–70°C) was set.

With the use of MC-2 activated with MAO, we studied in detail the effects of the Al/Zr ratio at the stage of preactivation and of the concentration of zirconium in the reactor on the activity and properties of the resulting PP.

According to data given in Table 4, an increase in the Al/Zr ratio from 200 to 2000 at the stage of preactivation resulted in a considerable increase in the activity and the isotacticity index (fraction insoluble in boiling *n*-heptane). It is well known that the more active *rac* isomer is responsible for the formation of IPP, whereas atactic PP is formed on the *meso* form. Knowing the fraction composition of PP, the activity of the *rac* and *meso* isomers of MC-2 can be calculated. It can be seen in Table 4 that, as the Al/Zr ratio was increased at the stage of preactivation, the activity of the *rac* form of the metallocene (A<sub>1</sub>) increased. Note that under these conditions A<sub>1</sub> increased by a factor of almost 4, whereas the activity of the *meso* form (A<sub>2</sub>) increased by a factor of only 1.5. The A<sub>1</sub>/A<sub>2</sub> ratio changed from 45 to 108. These results may be a consequence of changes in the nature or number of active isospecific centers. The possibility of reactions occurring that result in corresponding changes may be due to the following two reasons:

**Table 3.** Properties of PP prepared in the bulk polymerization of propylene with the use of metallocenes containing unsubstituted indenyl ligands

Metallocene	<i>rac : meso</i>	<i>K</i> , %	<i>M</i> , %	<i>Iso</i>	<i>T<sub>m</sub></i> , °C	<i>M<sub>w</sub></i> × 10 <sup>-3</sup>	$\frac{M_w}{M_n}$
MC-1	1 : 0	71	90	0.75	145	58	1.8
MC-4	1 : 1	73	90	0.81	140	69	2.1
MC-4*	1 : 1	—	—	—	—	38	2.0
MC-7	1 : 1	63	85	0.68	139	63	1.9
MC-5	0 : 1	—	—	—	—	1.7	1.9

Note: Polymerization temperature, 50°C; *K* is crystallinity; *M* is macrotacticity; and *Iso* is isotacticity.

\* Polymerization temperature, 70°C.

(1) The effect of the Al/Zr ratio at the stage of preactivation on equilibrium between the different cationic complexes that may occur in metallocene/MAO catalytic systems. Thus, active species formed by the interaction of catalytic components were identified in spectroscopic studies of a number of metallocene systems [30–34]. In a number of systems based on the bisindenyl derivatives of zirconium, it was found that at ratios of Al/Zr < 30, as well as in Al/Zr ranges of 50–200 and 500–2000, the hypsochromic and bathochromic shifts observed correspond to rapid monoalkylation and slower dialkylation of zirconocene with the formation of associated and dissociated cationic metallocene species. The fact that a new shift increased symbatically with an increase in the polymerization activity suggests that one of the two resulting cationic complexes is inactive [30, 31]. Species formed at high Al/Zr ratios are heterobinuclear cations like  $L_2Zr(\mu\text{-Me})_2AlMe_2^+$  and  $L_2Zr(\mu\text{-Me})_2AlMe_2^+MAOX^-$  [33]. Thus, depending on the Al/Zr ratio at the stage of preactivation, various metal complexes can be formed.

(2) The possibility of isomerization of a *meso* form into a *rac* form through the step of MAO-activated reversible metallocene dissociation at the Zr-cyclopentadienyl bond. As a result, the number of isospecific active centers increased; consequently, the activity and the regularity parameters of the synthesized PP increased.

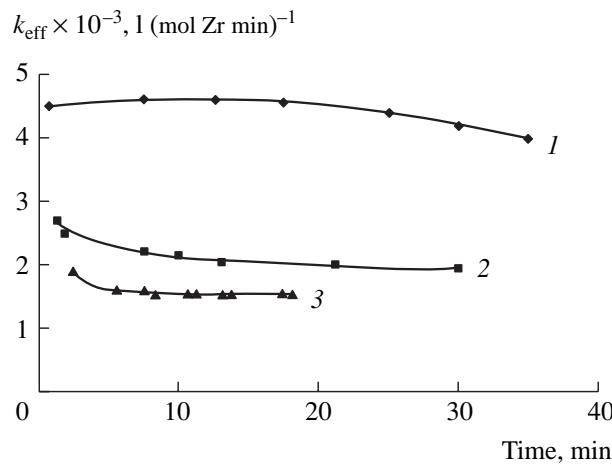
Note that the stereoregularity of a PP fraction that is insoluble in boiling *n*-heptane changed only slightly in the polymers tested. It was noted [35, 36] that the regularity of synthesized polyolefins decreased with metallocene concentration. This may be due to the occurrence of isomerization reactions in the course of polymerization; the rate of these reactions increased with increasing number of active centers. An analysis of the data allowed us to assume that in the test case the concentration of active centers changed only slightly.

The dependence of the activity on catalyst concentration in the reaction zone was also studied in the MC-2/MAO system (Table 5). The concentration of

MAO in the reactor was almost constant and equal to 0.6–0.8 g/l in all of the experiments. The maximum yield of PP was obtained at low zirconocene concentrations.

Figure 3 demonstrates changes in the activity of the MC-2/MAO catalysts with different zirconocene concentrations in the course of the reaction. In all cases, the maximum value of  $k_{\text{eff}}$  was reached 10–15 min after the onset of the process; thereafter, the activity of the system decreased. The highest activity was observed in the system with a higher Al/Zr ratio (1400) at the stage of preactivation and with a low metallocene concentration.

Table 6 summarizes data on the bulk polymerization of propylene with the use of *ansa*-metallocenes with substituted bisindenyl ligands MC-2 and MC-6 activated with MAO. For comparison, results obtained on catalyst MC-3, which was a pure *rac* form, are also given in Table 6. The conditions of formation of the catalytic systems and the conditions of polymerization



**Fig. 2.** The time dependence of the effective rate constant of propylene polymerization on catalysts (1) MC-1, (2) MC-4, and (3) MC-7 activated with MAO. The polymerization temperature was 50°C; the conditions of polymerization are specified in Table 2.

**Table 4.** Effect of the conditions of preactivation of the catalytic system based on  $\text{Me}_2\text{Si}(4\text{-Ph-2-EtInd})_2\text{ZrCl}_2$  (*rac* : *meso* = 1 : 2)/MAO on the activity and properties of PP

Preactivation conditions	$A, \text{kg PP} \times (\text{mmol Zr})^{-1} \text{h}^{-1}$	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$	$M, \%$	$T_m, ^\circ\text{C}$	APP*, wt %	IPP*, wt %	$M(\text{IPP}), \%$	$A_1, \text{kg PP} \times (\text{mmol Zr (rac)})^{-1} \text{h}^{-1}$	$A_2, \text{kg PP} \times (\text{mmol Zr (meso)})^{-1} \text{h}^{-1}$	$\frac{A_1}{A_2}$
MC-2/MAO = 200	117	770	3.5	90	161	3.9	89	98	309	6.9	45
MC-2/MAO = 2000	422	690	2.9	98	163	1.8	97	100	1240	11.5	108

Note:  $\text{Al/Zr} = 20000$ ; [MAO] = 0.6–0.8 g/l.

\* APP is atactic polypropylene, and IPP is isotactic polypropylene.

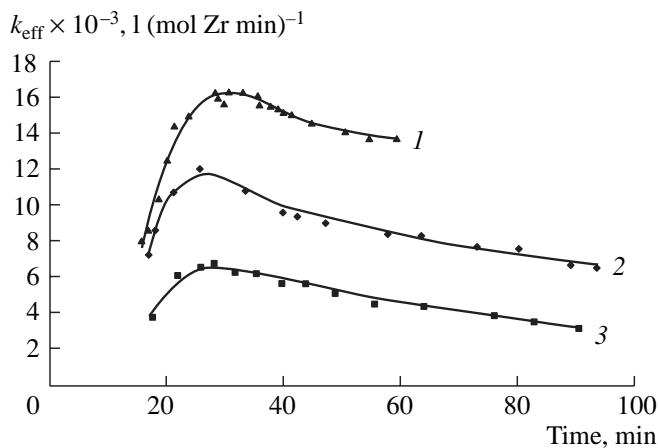
**Table 5.** Effect of the concentration of MC-2 activated with MAO on the activity in the bulk polymerization of propylene

Experiment number	[Metallocene] $\times 10^7$ , mol	$\frac{\text{Al}}{\text{Zr}} \times 10^{-2}$ (preactivation)	$\frac{\text{Al}}{\text{Zr}} \times 10^{-4}$	Experiment time, min	Yield of PP, g	Activity, $\text{kg PP} (\text{mmol Zr})^{-1} \text{h}^{-1}$	
						average over 30 min	average over the experiment time
1	1.7	7.0	2.6	130	43	260	129
2	2.0	7.0	2.3	150	24	130	87
3	3.2	7.0	1.6	145	47	146	75
4	1.7	14.0	3.4	80	67	230	228
5	2.1	14.0	2.7	40	70	215	213
6	2.2	14.0	2.2	190	66	192	148
7	2.6	14.0	2.75	300	27	102	47

Note: Polymerization temperature,  $60^\circ\text{C}$ ; reactor volume, 0.4 l; MAO concentration in the reactor, 0.6–0.8 g/l.**Table 6.** Effect of the type of metallocenes (MC-2, MC-3, and MC-6) on the activity and properties of PP

Catalysts	[Metallocene] $\times 10^7$ , mol/l	$\frac{\text{Al}}{\text{Zr}} \times 10^{-3}$ (preactivation)	$\frac{\text{Al}}{\text{Zr}} \times 10^{-4}$	Experiment time, min	Yield of PP, g	$A, \text{kg PP} \times (\text{mmol Zr})^{-1} \text{h}^{-1}$	$A_1, \text{kg PP} \times (\text{mmol Zr (rac)})^{-1} \text{h}^{-1}$	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$	$M, \%$	$T_m, ^\circ\text{C}$
MC-2	3.0	2	3.2	40	34	427	1270	690	3.7	94	161
MC-2	4.2	1.2–1.4	3.4	80	67	230	700	680	3.6	–	–
MC-2*	3.7	2	1.5	20	35	477	1445	560	–	–	160
MC-6	2.8	1.2–1.4	1.9	30	25	390	590	660	2.5	99	161
MC-3	2.5	1.2–1.4	1.5	40	55	–	485	770	2.2	98	159

Note: Bulk polymerization of propylene;  $T = 60^\circ\text{C}$ .\* Polymerization temperature,  $70^\circ\text{C}$ .



**Fig. 3.** The time dependence of the effective rate constant of propylene polymerization on catalysts MC-2/MAO. Curves 1, 2, and 3 correspond to experiment nos. 4, 1, and 7, respectively, in Table 5.

were identical in all cases. It can be seen that high-molecular-weight IPP with  $T_m = 159-165^\circ\text{C}$  was synthesized with the use of all these metallocenes. This melting temperature is typical of IPP prepared on traditional heterogeneous Ti/Mg catalysts. The activity of the catalytic systems based on metallocenes containing a mixture of *rac* and *meso* forms formed under optimum conditions in relation to total concentration differs only slightly from the activity of the system based on MC-3. The concentration of isotactic *mmmm* pentades was as high as 97% with the use of MC-6/MAO, whereas this concentration was 98% in the case of the MC-3/MAO system [6]. It is interesting that, when the activities of systems based on MC-2 and MC-6 were recalculated based on a pure *rac* form, the resulting values were noticeably higher than data obtained with the use of MC-3 (Table 6).

Thus, high-molecular-weight isotactic PP with high regularity can be prepared at very high rates with the use of metallocenes as a mixture of *rac* and *meso* forms under certain conditions of formation of an active complex. This allowed us to eliminate the stage of isolation of a pure *rac* isomer in the synthesis of catalysts.

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