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Bulk Propylene Polymerization in the Presence of *ansa*-Metallocenes of C_2 and C_1 Symmetries: From a Rigid Thermoplastic to Elastomeric Stereoblock Polypropylene

P. M. Nedorezova[a], E. N. Veksler[a], A. M. Aladyshev[a], V. I. Tsvetkova[a], V. A. Optov[a], G. P. Brusova[b], and D. A. Lemenovskii[b]
[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*
[b] *Moscow State University, Moscow, 117234 Russia*
e-mail: pned@chph.ras.ru

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Abstract—Bulk propylene polymerization in the presence of *ansa*-metallocenes with C_2 and C_1 symmetries has been studied. The catalytic activity, polymerization kinetics, and the molecular weight of polypropylene (PP) depend strongly on catalyst formation conditions. Mixtures of *rac* and *meso* isomers of metallocenes make it possible to rapidly produce a high-molecular-weight isotactic PP with high stereoregularity and mechanical characteristics and thus skip the stage of the isolation of pure *rac* isomer in the catalyst synthesis. The ability of triisobutylaluminum to serve as a cocatalyst is studied for *ansa*-metallocenes of C_1 symmetry. In this case, the molecular weight of PP is higher, indicating that organoaluminum compounds participate in chain termination reactions. An increase in the reaction temperature results in an increase in the stereoregularity and crystallinity of PP. Polypropylene synthesized using *ansa*-metallocenes of C_1 symmetry has good elastomeric properties.

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The area of application of the materials based on α-olefin homopolymers and copolymers has been substantially extended by the discovery of high-efficiency homogeneous systems based on metallocene complexes of Group IV elements [1–4]. Varying the composition, structure, and symmetry of the metallocene, one can purposefully change the stereospecificity of metallocene systems and produce polyolefins with different microstructures. Due to the uniformity of their active sites, these catalysts make it possible to synthesize polymers with a narrow molecular-weight distribution (MWD) and a uniform distribution of stereoerrors and regioerrors in the polymer chain.

Metallocene-based catalytic systems afford high yields of polymers with unique properties. These are high-rigidity isotactic polypropylene (PP), high-transparency syndiotactic PP with a high shock resistance and γ-irradiation stability, stereoblock PP with very good elastomeric characteristics, etc.

In this work, we studied the effects of polymerization and activation conditions on the catalytic activity of *ansa*-metallocenes of C_2 and C_1 symmetries in PP synthesis in a liquid monomer medium and on the molecular weight, microstructure, and heat-transfer and mechanical properties of PP. The following metallocenes of C_2 symmetry were used: *rac*$Me_2SiInd_2ZrCl_2$ (MC-1), $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (*rac* : *meso* = 1 : 2) (MC-2), and *rac*-$Me_2Si(4\text{-}Ph\text{-}2\text{-}Me\text{-}Ind)_2ZrCl_2$ (MC-3). The metallocenes of C_1 symmetry were *rac*-[1-(9-η^5-Flu)-2-(5,6-cyclopenta-2-Me-1-η^5-Ind)C_2H_4]$ZrCl_2$ (MC-4) and *rac*-[1-(9-η^5-Flu)-2-(5,6-cyclopenta-2-Me-1-η^5-Ind)C_2H_4]$HfCl_2$ (MC-5).

EXPERIMENTAL

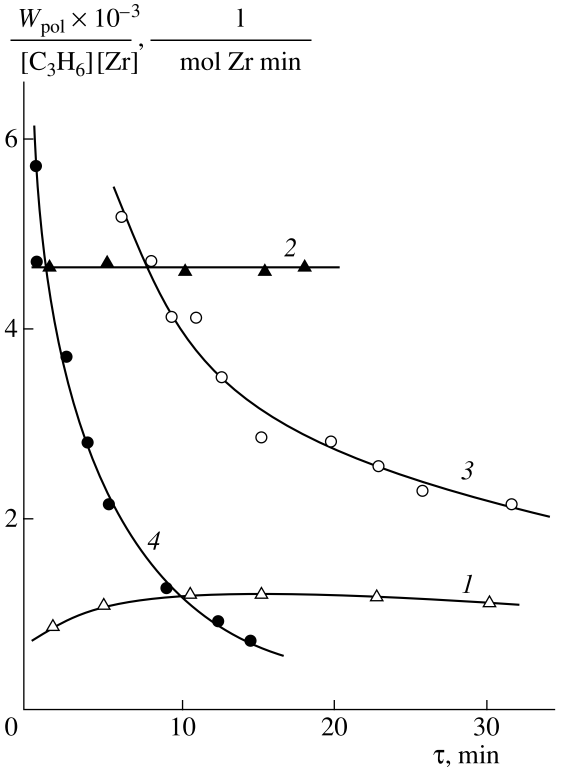
The metallocenes MC-1, MC-2, MC-4, and MC-5 were synthesized according to procedures described in [5–7]. MC-3 was purchased from Boulder Co.

Polymethylaluminoxane (MAO) (Witco) was used as a 10% solution in toluene. Triisobutylaluminum (TIBA) (Aldrich) was used without additional purification.

Propylene (polymerization purity grade) obtained from the Moscow NPZ was used without additional purification.

Propylene polymerization was studied in a system completely filled with liquid monomer. The reactor was preliminarily pumped for 1 h at 60–70°C. For propylene polymerization, MAO or TIBA was introduced in the reactor filled with liquid monomer and a metallocene solution in MAO was then added at the polymerization temperature.

The microstructure of PP and propylene–ethylene copolymers was determined by IR and ^{13}C NMR spectroscopy. Stereoregularity parameters were estimated from the ratios of the absorbances at 998, 841, and



Reduced rate of bulk propylene polymerization versus time for different methods of preparation of the MC-1-based catalytic system: MC-1is dissolved in (*1*) toluene and (*2*, *3*) MAO; the cocatalyst is (*1*, *2*) MAO, (*3*) TIBA, and (*4*) TIBA + $Ph_3CB(C_6F_5)_4$. The polymerization temperature is 50°C.

973 cm^{-1}, D_{998}/D_{973} (*M*) and D_{841}/D_{973}, as described in [8]. The ^{13}C NMR spectra of solutions of copolymers in *o*-dichlorobenzene were recorded on a Brucker DPX-250 instrument at 120°C. The molecular-weight characteristics of PP were determined in *o*-dichlorobenzene on a Waters 150-C gel-permeation chromatograph at 140°C.

Samples for mechanical tests were pressed at 190°C and 150 atm. Their elasticity was characterized by the residual elongation ε_{300} expressed in percent, which was determined using the equation $\varepsilon_{300} = (L_1 - L_0)/L_0 \times 100$, where L_1 is the final length of the sample after the removal of the loading at 300% elongation and L_0 is the initial sample length.

RESULTS AND DISCUSSION

Unlike heterogeneous catalysts, homogeneous metallocene catalytic systems are very sensitive to the polymerization conditions. Hence, it is important to optimize the polymer synthesis conditions.

In this work, we performed the following studies to elucidate the main features of bulk propylene polymerization with the MCs of C_2 and C_1 symmetries: (1) search for the most efficient routes of the formation of the metallocene catalytic systems by examining MC-1 activation pathways; (2) catalytic tests under identical conditions for a series of metallocenes with substituted bisindenyl ligands (MC-2 and MC-3) yielding high-molecular-weight isotactic PP (IPP); (3) study of the effect of the polymerization temperature and of the method of activation for MC-4 and MC-5, metallocenes affording elastomeric PP.

In order to study the effect of the preparation procedure on the activity of the MC-1-based catalytic systems and on the properties of the resulting PP, polymerization was carried out as follows:

(1) Metallocene dissolved in toluene was introduced into the reactor filled with liquid propylene containing an appropriate amount of MAO.

(2) Metallocene dissolved in a 10% solution of MAO in toluene (preactivation stage) was introduced into the reactor filled with liquid propylene containing an additional amount of MAO.

(3) Metallocene dissolved in a 10% solution of MAO in toluene was introduced into the reactor filled with liquid propylene containing TIBA.

(4) Metallocene dissolved in toluene was introduced into the reactor filled with liquid propylene containing TIBA. Thereafter, $Ph_3C\ B(C_6F_5)_4$ was added (B : Zr = 1.2 : 1).

Propylene polymerization kinetics are presented in the figure. When MAO was used as the cocatalyst (curves *1*, *2*), the polymerization rate was nearly constant, likely due to the continuous regeneration of active sites (AS's). When the mixed cocatalyst containing TIBA (curve *3*) or a boron-containing compound (curve *4*) was used, the maximum activity was observed at the beginning of the run and then the polymerization rate noticeably decreased.

Table 1 demonstrates the effect of activation conditions on the activity of the MC-1-based catalytic systems and on the properties of the resulting IPP. The system prepared by the preliminary dissolution of metallocene in a toluene solution of MAO (method 2) is more active than the system prepared by the preliminary dissolution of metallocene in toluene (method 1). In all cases, PPs with a narrow MWD and similar macrotacticities and melting points (T_m) were obtained. The molecular weight of the polymer (M_w) prepared with the use of the MC-1/MAO solution activated with MAO or TIBA (methods 2 and 3) is 1.5 times lower than that of the polymer obtained in the toluene solution of MC-1 (methods 1 and 4). These data indicate that the nature of the AS's depends on the formation conditions of the catalytic system.

To produce high-molecular-weight IPP, bulk propylene polymerization was studied in the presence of MC-2 and MC-3 containing indenyl ligands with ethyl (methyl) and phenyl substituents at the 2- and 4-positions, respectively. These substituents in the indenyl

Table 1. Effect of the method of preparation of catalytic systems based on *rac*-$Me_2SiInd_2ZrCl_2$ on the catalytic activity (*A*) in bulk propylene polymerization and on the properties of the resulting PP

Catalyst preparation method	$\frac{Al(MAO)}{Zr}$	$\frac{Al(TIBA)}{Zr}$	Run duration, min	Yield, g	*A*, kg PP/(mmol Zr h)	*M*, %	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$	T_m, °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* + TIBA	250	1050	30	38	100	90	60.0	2.1	143
MC-1/toluene + TIBA + $Ph_3CB(C_6F_5)_4$	–	650	15	12	48	87	94.3	2.5	143

Note: The polymerization temperature is 50°C; [Zr] = 6×10^{-7} mol/l.
*Al/Zr = 280 at the preactivation stage.

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

MC × 10^7, mol	$\frac{Al}{Zr}$ (preactivation)	$\frac{Al}{Zr}$	Run duration, min	Yield, g	*A**, kg PP/(mmol Zr h)
1.7	700	26000	130	43	130
2.0	700	23000	150	24	87
3.2	700	16000	145	47	75
1.7	1400	34000	80	67	230
2.1	1400	27000	40	70	213
2.2	1400	22000	190	66	148

Note: Polymerization temperature, 60°C; reactor volume, 0.4 l; MAO concentration in the reactor, 0.6–0.8 g/l.
*Average activity during the run.

ligand are known to ensure the formation of high-molecular-weight IPP [9].

The effects of the Al/Zr ratio at the preactivation stage and of the zirconium concentration in the reactor on the catalytic activity and on the properties of the resulting PP were studied for MAO-activated MC-2 (method 2). Table 2 lists activity data as a function of MC-2 concentration for the catalytic system MC–2/MAO prepared at Al/Zr = 700 and 1400 at the preactivation stage. The MAO concentration in the reactor was nearly constant (0.6–0.8 g/l) in all runs. As is clear from Table 2, the highest PP yield is reached at low metallocene concentrations in both series of runs. The highest activity was observed for the system with the largest Al/Zr ratio (1400) at the preactivation stage and with the lowest metallocene concentration.

Table 3 presents data for bulk propylene polymerization in the presence of the MAO-activated MC-2 and MC-3 *ansa*-metallocenes under the same catalyst formation and polymerization conditions. The activity of the system based on MC-2 per total concentration of the *rac* and *meso* isomers differs only slightly from the activity of the MC-3-based system. The proportion of isotactic pentads *mmmm* is 96–97% with MC-2/MAO and 98% with the MC-3/MAO system. Note that the activity of the MC-2-based system converted to its *rac* isomer content substantially exceeds the activity of the MC-3 system.

Table 4 presents the physicochemical characteristics of IPP synthesized with the use of MC-2 and MC-3 and, for comparison, the same properties of the IPP obtained over a commercial Ti/Mg catalyst. Both metallocene catalysts afford a high-molecular-weight IPP with T_m = 160–163°C, which is typical of IPP synthesized over the heterogeneous Ti/Mg catalyst. The uniformity of polymer chains obtained with the use of these metallocenes results in a higher crystallinity and rigidity, and a lower elasticity of the polymer. The IPP synthesized in the presence of MC-2, which contains a larger proportion of amorphous phase owing to the contribution from the *meso* isomer, combines a high elastic modulus and a high elasticity. Note that the IPPs synthesized with MC-3 and MC-2 show a high resistance to oxidative thermal destruction [10]. This is explained by the fact that the amorphous phase of metallocene PP is more homogeneous than that of titanium PP [11].

Hence, the use of mixtures of *rac*- and *meso*-metallocenes under conditions optimal for active complex formation enables one to produce a high-molecular-weight, high-regularity IPP with good mechanical properties at a very high rate. Therefore, it is possible to

Table 3. Bulk propylene polymerization with MAO-activated MC-2 and MC-3

MC	$[MC] \times 10^7$, mol/l	$\frac{Al}{Zr}$	Run duration, min	Yield, g	A, kg PP/(mmol Zr h)	A_1, kg PP/(mmol Zr (*rac*) h)	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$
MC-2*	3.0	32000	40	34	427	1270	690	2.9
MC-2**	4.2	34000	80	67	230	700	680	3.6
MC-3**	2.5	15000	40	55	–	485	770	2.2

Note: The polymerization temperature is 60°C.

*Al/Zr = 2000 at the preactivation stage.

**Al/Zr = 1200–1400 at the preactivation stage.

Table 4. Thermophysical, strain, and strength characteristics of isotactic PP synthesized using the MC-2, MC-3, and Ti/Mg catalysts

Catalytic system	M	$\frac{D_{841}}{D_{973}}$	K, %	T_m, °C	E, MPa	σ_y, MPa	ε_y, %	σ_{br}, MPa	ε_{br}, %
MC-2/MAO	0.95	0.73	55	162	1830	35.6	6.0	39.6	530
MC-3/MAO	0.98	0.87	65	161	1800	38.8	8.1	26.7	130
$Ti/Mg(D_1) + Et_3Al + D_2$	0.96	0.85	48	163	1550	37.3	8.3	34.0	500

Note: Polymerization temperature, 60°C; elongation rate, 50 mm/min. K is the degree of crystallinity (from X-ray diffraction data), E is the elastic modulus, σ_y and σ_{br} are the yield and breaking stresses, and ε_y and ε_{br} are the yield-point elongation and the elongation at break.

*D_1 = dibutyl phthalate; D_2 = silane.

skip the stage of separation of the pure *rac* isomer in catalyst synthesis.

The C_1 symmetric metallocenes are promising for the synthesis of various polymers. Using such metallocenes and varying the nature of the ligands, one can obtain isotactic, hemi-isotactic, and stereoblock PPs containing isotactic blocks separated by regularly spaced errors [12, 13].

A specific feature of the C_1 symmetric metallocenes is their "stereoduality," which is due to the presence of two different active positions accessible to the coordination and incorporation of a monomer [14]. A polymer chain can grow in two ways, specifically, by the migration of the polymer chain to the monomer in the case of two coordination vacancies at the active site and by the migration of the growing chain to a coordination vacancy without incorporation. As the monomer concentration is increased, the probability of the coordination and incorporation of the monomer at a less sterically hindered vacancy increases, resulting in "errors," which are "corrected" by subsequent monomer addition yielding an *mrrm* sequence. An increase in reaction temperature will lead to a relative increase in the rate of chain migration without incorporation and, consequently, in PP regularity. In the PP synthesis in the presence of a C_2 or C_s metallocene, an increase in the monomer concentration and a decrease in the polymerization temperature usually favor an increase in the degree of PP regularity. This effect is likely to be due to the relative decrease in the rates of the processes resulting in stereoerrors and regioerrors in the polymer chain [15–17].

Table 5 presents data illustrating the effect of the polymerization temperature and activation conditions on the catalytic activity of the MAO-activated MC-4- and MC-5-based systems and the properties of the resulting PP. Raising the polymerization temperature from 30 to 70°C increases the activity of the systems and stereoregularity and decreases the molecular weight of PP.

The activity of the MC-5-based catalytic system is lower than that of the MC-4-based system. Although the radii of zirconium and hafnium atoms are similar, the latter has a higher nuclear charge, resulting in metal–carbon bond strengthening. As a consequence, the rates of monomer incorporation and chain termination decrease. For the catalytic systems examined, the variation of the molecular weight of the polymer with polymerization temperature is determined by the difference between the activation energies of chain growth and termination. The activation energy of the polymerization reactions (E_p) was estimated from the activities of the catalytic systems MC-4/MAO and MC-5/MAO at different temperatures, and the difference between the activation energies of chain growth and termination (ΔE_{term}) was determined from the temperature dependence of the degree of polymerization. The following values were obtained: $E_{p,1} = -11.4$ kcal/mol, $E_{p,2} = -16.9$ kcal/mol, $\Delta E_{term,1} = 2$ kcal/mol, $\Delta E_{term,2} = 3.4$ kcal/mol for MC-4/MAO and MC-5/MAO, respec-

Table 5. Effect of propylene polymerization conditions on the activity of MAO-activated MC-4 and MC-5 and on the properties of PP

Run no.	T_p, °C	MC	MC × 10^6, mol	$\frac{\text{Al(MAO)}}{\text{Zr(Hf)}}$, mol/mol	Run duration, min	Yield, g	*A*, kg PP/(mmol Zr (Hf) h)	*M*	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$
1	30	MC-4	1.66	3800	45	26	21	0.25	168	2.5
2	50	MC-4	0.74	4640	60	20	23	0.24	126	2.2
3	70	MC-4	0.63	5060	30	33	104	0.58	85	2.8
4	30	MC-5	2.94	2600	180	13	1.5	0.26	241	2.5
5	50	MC-5	1.73	4087	120	21	6	0.42	135	2.5
6	70	MC-4	1.28	4250	60	35	14	0.45	70	3.1

Table 6. Effect of propylene polymerization conditions and of the nature of activator on the activity of MC-1 activated with the mixed cocatalyst MAO + TIBA and on the properties of PP

Run no.	MC × 10^6, mol	$\frac{\text{Al(MAO)}}{\text{Zr}}$, mol/mol	$\frac{\text{Al(TIBA)}}{\text{Zr}}$, mol/mol	$\frac{\text{Al(TIBA)}}{\text{Al(MAO)}}$, mol/mol	Run duration, min	Yield, g	*A*, kg PP/(mmol Zr h)	*M*	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$
2	0.74	4640	–	–	60	20	23	0.24	126	2.2
7	1.53	300	1050	3.4	60	40	27	0.25	235	3.2
8	1.27	300	750	2.5	60	36	28	0.22	240	2.8
9	2.5	300	220	0.7	40	50	30	0.36	200	3.3

Note: The polymerization temperature is 50°C.

Table 7. Thermophysical, strain, and strength characteristics of PP synthesized on MC-4

Run no.	*K*, %	*E*, MPa	σ_y, MPa	σ_{300}, MPa	σ_{br}, MPa	ε_{br}, %	ε_{300}, %
1	0	3.4	0.9	0.9	>1.5	>1750	19.8
2	4	14.7	1.5	1.9	7.1	1280	47.0
8	7	7.2	–	1.95	8.1	1000	10.8

Note: The elongation rate is 500 mm/min.

tively. The higher values determined for MC-5/MAO are in agreement with the stronger temperature dependence of catalytic activity and molecular weight observed for this system.

As in the case of propylene polymerization in the presence of the C_2 symmetric metallocene MC-1, we studied the effect of partial replacement of MAO with TIBA (Table 6). A decrease in the Al(TIBA)/Zr ratio has virtually no effect on the activity of the catalytic system. Note that the chain regularity at Al(TIBA)/Zr = 750–1050 is close to the chain regularity observed for PP synthesized with MC-4/MAO. Decreasing this ratio to 220 results in a polymer with a higher stereoregularity.

The most interesting fact is an increased molecular weight of PP obtained with TIBA activation. As the Al(TIBA)/Zr ratio increases, the molecular weight of the polymer gradually increases. At Al(TIBA)/Zr = 750–1050, it is nearly twice as high as the molecular weight of the polymer obtained in the presence of MC-4 activated with MAO alone. These data indicate that chain termination slows down in the presence of TIBA. Note that the use of TIBA in propylene polymerization in the presence of C_2 and C_s metallocenes causes no changes in the molecular weight of PP [18].

Our data indicate that TIBA has an effect on the active sites of the catalytic complex, for example, by the formation of a mixed organoaluminum component. It is likely that the new cocatalyst retards the polymerization reaction via the return of the polymer chain without incorporation.

We carried out X-ray diffraction analysis and studied the thermophysical properties and deformation behavior of PP synthesized with the use of MC-4 and MC-5 under various polymerization and activation conditions.

According to X-ray diffraction data, as the reaction temperature is increased, the product changes from a completely amorphous polymer to a polymer with a high degree of crystallinity. Note that the polymer obtained with MC-4/MAO or MC-5/MAO at elevated temperatures crystallizes into the γ-phase of PP apparently because of a significant amount of stereoerrors and regioerrors in the polymer chain [7].

Table 7 lists strain and strength data for the polymers synthesized. The best elastomeric properties are shown by PP samples obtained with MC-4 and MC-5 at a low temperature of 30°C (for run temperatures, see Tables 5 and 6). The PP samples obtained through activation with TIBA are also very good elastomers, whose residual strain after a 300% elongation is only 10.8%.

Hence, one can produce polymers varying from rigid thermoplastics to amorphous elastomers by controlling the structure and symmetry of the metallocene catalyst and the polymerization and activation conditions.

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