A. M. ALADYSHEV*), V. I. TSVETKOVA*),
P. M. NEDOREZOVA*), V. A. OPTOV*),
T. A. LADYGINA*), D. V. SAVINOV*),
M. V. BORZOV**), D. P. KRUT'KO**),
D. A. LEMENOVSKII**)

Syndiotactic polypropylene — synthesis and properties

Summary — Propylene was polymerized with MAO-activated metallocene catalyst $Ph_2C(CpFlu)ZrCl_2$ [$\eta^5,\eta^{5'}$-1,9'-diphenylmethylidene-(cyclopentadienyl)(fluorenyl)]-dichlorozirconium(IV) and properties of the resulting syndiotactic PP (sPP) were measured. The catalytic system selected allowed to achieve high polymerization rates and high values of molecular weight and syndiotacticity of the polymer. Studies on the $\overline{M}_n$ *vs.* [H_2] relationship gave the ratios of the polymer chain propagation and monomer- and/or hydrogen-caused chain transfer rate constants. ^{13}C-NMR spectroscopy data showed each PP to have an almost identical pentad content. As compared with isotactic polypropylene (iPP), sPP is much more elastic and exhibits the higher impact strength.

The development of new metallocene based catalytic systems for stereospecific propylene polymerization has made it possible to produce highly stereoregular polypropylenes of different microstructures [1—4]. The discovery of highly active system $(CH_3)_2C(CpFlu)ZrCl_2$—MAO has opened the route to syndiotactic PP (sPP) [5]. Then several systems have been found for syndiospecific polymerization based on metallocenes possessing C_s-symmetry [6—8].

The upsurge in interest for sPP stems in part from the possibility of both improving the polymerization process and producing polymers with modified mechanical properties [9, 10].

This paper sets out to describe our recent results on the sPP synthesis with $Ph_2C(CpFlu)ZrCl_2$-[$\eta^5,\eta^{5'}$-1,9'-diphenylmethylidene-(cyclopentadienyl)(fluorenyl)]-di-chlorozirconium(IV) as a precatalyst. This metallocene was selected because of its ability to polymerize propylene at high rates and to produce highly syndiotactic and high-molecular-weight sPP [7, 8]. Polymerization kinetics in the bulk is also described at different process conditions and hydrogen contents. The microstructure of chains, drawing behavior and mechanical properties of the resulting sPP were studied and compared with those of isotactic polypropylene (iPP).

EXPERIMENTAL

Each operation was performed in a static atmosphere of dry argon or in a sealed evacuated glass vessel of the Schlenck type. Solvents and initial substances were purified and dried by conventional procedures [11]. The $Ph_2C(CpFlu)ZrCl_2$ metallocene was prepared as described in [8].

Propylene was bulk-polymerized at 50—70°C in a completely filled reactor at a pressure exceeding that of saturated propylene vapor. MAO and zirconocene concentrations in the reactor were 0.5—1.4 g/L and $(0.28—1.34) \cdot 10^{-3}$ g/L [or $(0.5—2.4) \cdot 10^{-6}$ mol/L], respectively. During the polymerization process the pressure in the reactor was maintained by introducing an additional amount of liquid propylene from a graduated cylinder. This was the way to monitor the propylene polymerization. The reactor volume was 0.25 or 0.5 L. The process was conducted either by *in situ* generating the toluene solution of metallocene (MC) directly inside the reactor that had been charged with liquid propylene and MAO (method 1) or by preliminarily dissolving the metallocene in 10% toluene solution of MAO and subsequently injecting the resulting mixture into the reactor with liquid propylene and MAO (method 2) or with R_3Al (R = Et, *i*-Bu) (method 3). In each case the solution was prepared at room temperature. After the reactor had been filled with propylene and the temperature maintained, MAO or R_3Al was added in the required amount. An ampule with the catalyst solution was crashed in several minutes to initiate the polymerization process.

---

*) N. N. Semenov Institute of Chemical Physics, Russian Academy of Science; 4, Kosygin Street, 117977 Moscow, Russia.

**) Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russia

The molecular weight characteristics was obtained by the GPC method at 145°C by using a Waters model 150 C high-temperature gel chromatograph, a μ-styragel HT column, and *o*-dichlorobenzene as solvent.

^{13}C-NMR spectra of polymer solutions in *o*-dichlorobenzene (0.1—0.06 g/L) were recorded on a Bruker XR-400 spectrometer at 130°C.

Polymer melt flow index was measured with a special viscometer at 190°C with a dead-weight load of 2.16 kg and a capillary 2.095 mm in diameter and 8 mm long.

Isotropic sheets, ~0.5 mm thick, were obtained by compression molding at 175°C, cooling rate ~30°C/min.

Drawing tests of sPP samples were made on an Instron 1112 tensile machine, crosshead speed 10 mm/min at room temperature. Hysteresis tests were carried out to establish the ratio of the elastic to plastic deformations accumulated in the material and thus to evaluate its elasticity.

The impact strength data were obtained in accordance with ASTM D 256 (Himont).

RESULTS AND DISCUSSION

Propylene polymerization runs and properties of sPP produced with catalytic systems formed by different methods and under different polymerization conditions are summarized in Tables 1 and 2. The activities of the catalyst systems were characterized by the average rate of the PP formation (kg PP per g zirconium per hour). The catalytic system formed by method 2 is about 2 to 3 times as active as that prepared by method 1.

With the process temperature raised from 50°C to 70°C, the activity of the method 2 catalytic system rose from 144 to 268 kg PP/(g cat·h). The effective activation energy of the process calculated from these data appears to be equal to 10.6 kcal/mol. With the method 1 system, an increase in the temperature from 60°C to 70°C resulted in the activity reduced from 127 to 98 kg PP/(g cat·h).

For the catalytic system formed by method 2, replacement of MAO for (*i*-Bu)$_3$Al or Et$_3$Al was also investigated. Et$_3$Al diminished the catalytic activity significantly; (*i*-Bu)$_3$Al reduced the activity less significantly, to 127 kgPP/(g cat·h) at 50°C, but enhanced it to 191 kg PP/(g cat·h) at 60°C (see Table 2).

The representative propylene polymerization kinetic curves (Fig. 1) show the activities of the systems formed by methods 1 and 2 to increase at the initial stage and then to level up. The systems in which a combined catalyst activator is used [including (*i*-Bu)$_3$Al, method 3] are less stable. Their activities attain a maximum at the initial stage and in half-an-hour they fall to one-half (Fig. 1). (*i*-Bu)$_3$Al allows the MAO concentration to be reduced to 0.2—0.1 of that employed in the MAO-activated systems.

The propylene polymerization carried out with the catalytic systems examined gave high-molecular-weight sPP with a narrow molecular weight distribution. Even if slightly decreasing from 522,000 to 372,000 when the temperature is raised from 50 to 70°C, $\overline{M}_w$ still remains high (Table 1). The decrease of the $\overline{M}_w$ may be due to the chain transfer reaction rates increasing with the increase in temperature.

The molecular weights of the polymers obtained with the catalytic systems prepared by different methods are almost the same. When the combined cocatalyst is used the content of low-$\overline{M}_w$ sPP decreases, $\overline{M}_n$ increases but slightly and the $\overline{M}_w/\overline{M}_n$ ratio falls to 2.

Table 1. BULK POLYMERIZATION OF PROPYLENE WITH MAO-ACTIVATED $\mathrm{Ph_2C(CpFlu)ZrCl_2}$

Run No.	[Zr]·10^6, mol/L	Al/Zr	[H$_2$]·10^2, mol/L	Temp., °C	t_{pol}, min	Yield, g	A[3]	$\overline{M}_w\cdot10^{-3}$	$\overline{M}_w/\overline{M}_n$
1[1]	1.6	10 000	—	60	64	28	127	390	2.9
2[1]	1.4	5 900	1.8	60	90	47	77	240	2.9
3[1]	1.2	6 200	3.6	60	80	45	78	170	3.0
4[1]	1.1	15 000	—	70	116	28	98	—	—
5[2]	2.4	7 300	—	50	18	20	144	522	3.5
6[2]	0.7	10 000	—	60	30	20	210	465	3.2
7[2]	0.5	16 800	3.6	60	65	18	196	190	3.7
8[2]	0.7	17 000	—	70	58	27	268	370	2.3

[1] Method 1. [2] Method 2. [3] A — activity, (kg PP)(g cat)$^{-1}$h^{-1}.

Table 2. THE EFFECT OF $\mathrm{R_3Al}$ SPECIES ON THE $\mathrm{Ph_2C(CpFlu)ZrCl_2}$ CATALYTIC SYSTEM

Run No.	[Zr]·10^6, mol/L	R$_3$Al, mg	Al[3]/Zr	Temp., °C	t_{pol}, min	Yield, g	A[4]	$\overline{M}_w\cdot10^{-3}$	$\overline{M}_w/\overline{M}_n$
1	2.4	—	7 300	50	18	17	144	522	3.5
2	2.5	204[2]	890	50	16	10	127	584	2.7
3	3.7	161[1]	320	50	109	20	26	—	—
4	0.7	—	10 000	60	30	20	210	465	3.2
5	1.5	140[2]	890	60	30	20	191	466	2.0

[1] Et$_3$Al. [2] Bu$_3$Al. [3] Al from MAO. [4] A — activity, (kg PP)(g cat)$^{-1}$h^{-1}. Reactor volume, 0.25 L.

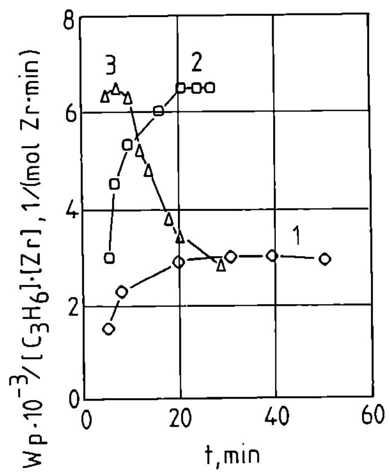

Fig. 1. The catalytic activity of metallocene $Ph_2C(CpFlu)ZrCl_2$ *in relation to the catalytic system generating method: 1 — activated with MAO (method 1); 2 — activated with MAO (method 2); 3 — activated with* i-Bu_3Al *(method 3). Bulk polymerization at* 60^0C

The influence of hydrogen as a polyolefin molecular weight regulator is of interest. The $\overline{M}_w$-values of sPP obtained at different hydrogen concentrations are listed in Table 1. Hydrogen is seen to have influenced the sPP molecular weight over the entire experimental range of hydrogen concentrations and to have reduced $\overline{M}_w$ and $\overline{M}_n$ to nearly one-third. The method used to prepare the catalytic system does not affect the magnitude of $\overline{M}_w$ and $\overline{M}_n$. However, when the catalyst is prepared by method 2, hydrogen has led to a certain increase in polymer polydispersity. In the case of me-thod 1, the value of $\overline{M}_w/\overline{M}_n$ has remained unaffected.

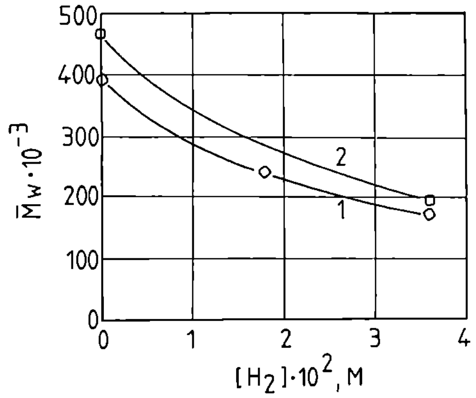

Fig. 2. Average molecular weight ($\overline{M}_w$) *versus* [H_2]*; bulk polymerization at* 60^0C*: 1 — method 1, 2 — method 2*

Studies on the hydrogen concentration effect on M_n allowed us to evaluate the ratios of the rate constants of polymer chain propagation and monomer- and/or hydrogen-effected chain transfer reactions.

In liquid monomer media the monomer-caused polymer chain transfer appears to predominate. Thus,

$$P_n = R_p/\Sigma R_t = k_p[\mathrm{M}]/(k_t^{M}[\mathrm{M}] + k_t^{H_2}[\mathrm{H_2}]) \tag{1}$$

and

$$1/P_n = k_t^{M}/k_p + k_t^{H_2}[\mathrm{H_2}]/\ k_p[\mathrm{M}] \tag{2}$$

where: P_n *is the average polymerization degree,* R_p *and* R_t *are respectively the rates of polymer chain propagation and transfer reactions,* k_p *is the rate constant of the polymer chain propagation reaction, and* k_t^M *and* $k_t^{H_2}$ *are the constants of the monomer- and hydrogen-caused polymer chain transfer, respectively.*

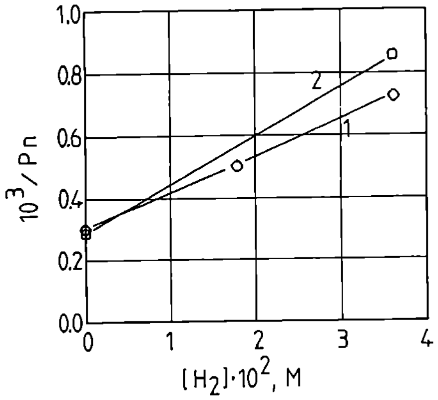

Fig. 3. The reciprocal average polymerization degree ($1/P_n$) *versus* $1/[H_2]$*; bulk polymerization at* 60^0C*: 1 — method 1, 2 — method 2*

The $\overline{M}_w$ and $1/P_n$ *vs.* [H_2] plots (Figs. 2 and 3) gave the following estimates for the k_p/k_t^M, $k_p/k_t^{H_2}$ and $k_t^{H_2}/k_t^M$ ratios

$k_p/k_t^M = 3230$, $k_p/k_t^{H_2} = 8$, $k_t^{H_2}/k_t^M = 408$ (method 1),
$k_p/k_t^M = 3450$, $k_p/k_t^{H_2} = 7.5$, $k_t^{H_2}/k_t^M = 460$ (method 2).

Irrespectively of the method employed to generate the catalytic system each polymer exbibits an almost identical pentad content (Table 3). The polymers are highly syndiotactic with the contents of monomer chains in syndiotactic dyads [r] = 92% and pentads [mmmm] = 83.4%. The numbers of monomer units in syndiotactic

Table 3. PENTAD DISTRIBUTION IN SYNDIOTACTIC POLYPROPYLENE PREPARED WITH $Ph_2C(CpFlu)ZrCl_2$

Run No.	mmmm	mmmr	rmmr	mmrr	mmrm + rmrm	rmrm	mrrm	mrrr	rrrr
1[1)]	0.3	0.3	1.8	3.5	2.2	1.0	0.8	6.7	83.4
2[2)]	0.2	0.2	1.9	3.4	2.0	0.7	0.7	7.0	83.9
3[3)]	0.2	0.3	1.8	3.5	2.3	1.0	0.6	6.9	83.4

[1)] Method 1. [2)] Method 2. [3)] Method 2 with H_2, $3.6\cdot 10^{-2}$ mol/L.

Table 4. MECHANICAL PROPERTIES OF SYNDIOTACTIC POLYPROPYLENE

No.	MFI, g/10 min	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$E \cdot 10^2$, MPa	σ_y, MPa	ε_y, %	σ_b, MPa	ε_b, %	a, kJ/m^2
1$^{1)}$	0.05	390	2.9	6.9	19.4	10.3	16.6	356	49
2$^{1)}$	3.15	240	2.9	7.2	20.4	11.2	17.4	140	6.6
3$^{1)}$	4.62	170	3.0	7.6	21.3	10.3	15.9	123	4.8
4$^{2)}$	0.06	465	3.2	6.7	19.5	11.0	19.4	312	—
5$^{2)}$	6.20	190	3.7	8.1	21.3	9.4	15.3	401	—

$^{1)}$ Method 1. $^{2)}$ Method 2. MFI — melt flow index, E — Young modulus, σ_y — yield stress, ε_y — elongation at yield point, σ_b — stress at break, ε_b — elongation at break, a — impact strength.

and isotactic sequences in sPP are equal to 28—31 and max. 1.7, respectively.

NMR spectroscopy data have shown the sPP obtained in the presence and absence of hydrogen to be highly syndiotactic and to have practically identical pentad contents.

As regards mechanical properties the Young modulus and the strength values were lower than those in isotactic PP (iPP) [10], but the impact strength was significantly higher and, at $\overline{M}_w$ as high as 390,000, the sPP broke unevenly (Table 4).

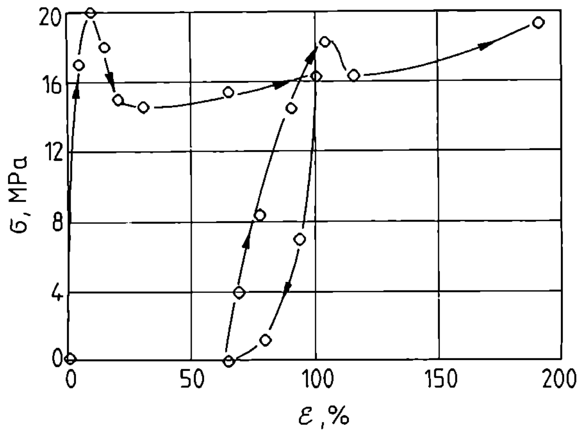

Fig. 4. Stress-strain curve of sPP with the hysteresis test after 100% elongation

Hysteresis tests showed sPPs to be much more elastic than iPP (Fig. 4). After a 100% deformation and removal of load to zero, the residual elongation for sPP was equal to 66% against 95% for iPP.

The different microstructures of sPP and iPP determine differences in both morphology and mechanical behavior [9, 12].

Summing up, the catalytic systems based on $Ph_2C(CpFlu)ZrCl_2$ are seen to give rise to high polymerization rates and high molecular weights and to syndiotacticity of sPP. The sPP molecular weights and rate constant ratios are related to hydrogen concentration; sPP is much more elastic than iPP and exhibits a higher impact strength.

This research was supported by the Grant from the Russian Foundation of Fundamental Research (96-03-34232a).

REFERENCES

1. Ziegler Catalysts (*Eds.* G. Fink, R. Mulhaupt, H. H. Brintzinger), Springer, Berlin 1995.
2. Brintzinger H. H., Fisher D., Mulhaupt R., Rieger B., Waymouth R.: *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 1143.
3. Kaminsky W., Kulper K., Brintzinger H. H., Wild F. W. R.P.: *Angew. Chem. Int. Ed. Engl.* 1985, **24**, 507.
4. Even J. A.: *J. Am. Chem. Soc.* 1984, **106**, 21, 6355.
5. Even J. A., Jones R. L., Razavi A. J.: *J. Am. Chem. Soc.* 1988, **110**, 6255.
6. Rasavi A., Atwood J. L.: *Macromol. Symp.* 1995, 89, 345.
7. Shiomura J., Kohne M., Inoue N., Yokote Y., Akiyama M., Asanuma T., Sugimoto K., Kimura S., Abe M.: Catalyst Design for Tailor-Made Polyolefins, Tokyo 1994.
8. Rasavi A., Atwood J. L.: *J. Organomet. Chem.* 1993, 459, 117.
9. Sakata Y., Unvin A., Ward I. N.: *J. Mat. Sci.* 1995, **30**, 58.
10. Thomann R., Wang C., Kressler J., Jugling S., Mulhaupt R.: *Polymer* 1995, **36**, 20, 3795.
11. Perrin D. D., Armarego W. L. F., Perrin D. R.: Purification of Laboratory Chemicals, Pergamon Press, 1966.
12. Haftka S., Konnecke K.: *J. Macromol. Sci.-Phys.* 1991 **B30**, No. 4, 319.