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Polymerization of propylene with bridged and unbridged indenyl derivatives of zirconium

Summary — The kinetics of propene polymerization in the liquid monomer medium and the properties of the resulting *iso*-PP were studied in relation to the interannular bridge nature, $(\text{CH}_2)_2\text{Ind}_2\text{ZrCl}_2$ (I), $(\text{CH}_3)_2\text{SiInd}_2\text{ZrCl}_2$ (II), $(\text{CH}_3)_2\text{CInd}_2\text{ZrCl}_2$ (III), and asymmetric $(\text{CH}_3)(\text{cyclo-C}_3\text{H}_5)\text{CInd}_2\text{ZrCl}_2$ (IV), in MAO-activated 1,1'-bridged bisindenyl zirconocene dichlorides. Data are also given for the non-bridged $(2\text{-Ph-C}_9\text{H}_6)_2\text{ZrCl}_2$ (V) system used under similar conditions. The systems based on zirconocene III are most active and that based on II is most stable. The replacement of one methyl group in the $(\text{CH}_3)_2\text{C}$ bridge by a cyclopropyl group (compounds III and IV) results in the depressed initial activity and in the greater deactivation of the system during the process of polymerization. The stereoblock polymer was formed with the catalyst system based on metallocene V, used under similar experimental conditions.

Recently, new highly active metallocene-type homogeneous catalysts have been developed for propene polymerization [1–4]. Correspondence has been established between the structure of polypropylene (PP) and that of the catalyst employed as a result of studies on various organometal complexes of transition metals. They have made it possible to prepare *iso*-, *syndio*-, and *atactic* PPs and to generate PP of the stereoblock structure, *i.e.*, built of *iso*-, *syndio*- or *atactic* blocks.

By now, many catalysts systems have been known, based on metallocenes and methylalumoxane (MAO) suitable for preparation of isotactic PP. The systems containing the bridged bisindenyl zirconocene moiety have been most broadly used [5].

At least two ways are known to modify the catalyst systems and consequently the properties of PP: (i) addition of a substituent to either of the indenyl rings [6, 7]; (ii) bridging the atom(s). Both electron and steric effects exercised by the substituent on the zirconium atom can affect considerably the nature and the activity of catalyst centers and, in turn, the ratio of the polymer chain propagation/termination rates [8, 9].

This paper sets out to describe some of our recent results on the influence of the interannular bridge nature, *viz.*, $(\text{CH}_2)_2\text{Ind}_2\text{ZrCl}_2$ (I), $(\text{CH}_3)_2\text{SiInd}_2\text{ZrCl}_2$ (II), $(\text{CH}_3)_2\text{CInd}_2\text{ZrCl}_2$ (III), and asymmetric $(\text{CH}_3)(\text{cyclo-C}_3\text{H}_5)\text{CInd}_2\text{ZrCl}_2$ (IV) in MAO-activated 1,1'-bridged bisindenyl zirconocene dichlorides, on the kinetics of propene polymerization in the liquid monomer medium and on the properties of the resulting PP. Comparative data are also presented for the non-bridged $(2\text{-Ph-C}_9\text{H}_6)_2\text{ZrCl}_2$ (V) system used under similar experimental conditions.

EXPERIMENTAL

All operations were performed in a static atmosphere of dry argon. Solvents were purified and dried by conventional procedures [10]. Merck's ZrCl_4 , (N,N-dimethylamino)tri-*n*-butyltin, indene, and $[\eta^5, \eta^{5'}\text{-1,1'-(1,2-ethanediy)]\text{bis}(\text{indenyl})\text{dichlorozirconium(IV)}$ (I) were used as supplied. ^{13}C - and ^1H -NMR spectra were recorded on a Varian VXR-400 spectrometer.

Preparation of metallocenes

$[\eta^5, \eta^{5'}\text{-1,1'-(1-Methylethylidene)}\text{bis}(\text{indenyl})\text{dichlorozirconium(IV)}$ (III), $[\eta^5, \eta^{5'}\text{-1,1'-(1-cyclopropylethylidene)}\text{bis}(\text{indenyl})\text{dichlorozirconium(IV)}$ (IV), and $[\eta^5, \eta^{5'}\text{-bis}(2\text{-phenylindenyl})\text{dichlorozirconium(IV)}$ (V) were prepared as described previously [11, 12].

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DL-Bisindenyl dimethylsilane $\text{Me}_2\text{Si}(\text{IndH})_2$

A suspension of indenyllithium prepared from freshly distilled indene, 145.0 g (1.25 mol), and 2.55 M *n*-butyllithium in hexane, 355 mL (0.905 mol), in 400 mL ether was added progressively to dimethyldichlorosilane, 58.4 g (0.453 mol), in 400 mL ether at -40°C with stirring. Stirring was continued at -40°C for 2 hours, then the mixture was allowed to warm up to room temperature, stirred and refluxed for 1 hour and left overnight. Then the mixture was quenched with water, the organic layer was separated and the aqueous layer was extracted with ether (3 x 70 mL). The ethereal extracts were combined, washed with water and dried with CaCl_2 , and the solvent was removed at a reduced pressure. The residual viscous red oil was taken up with warm methanol and kept at -5°C for 10 hours. The snow-white crystals precipitated were filtered off, washed with cold (-10°C) methanol and dried in high vacuum to yield $\text{Me}_2\text{Si}(\text{IndH})_2$, 53.0 g (0.184 mol, 40.6%). Concentrating of the mother liquor followed by a similar workup gave an additional amount of a similarly pure product, 38.5 g (0.133 mol, 29.5%); total yield, 91.5 g (0.317 mol, 70.0%).

The compound converted into an equimolar mixture of *DL*- and *meso*-isomers in a CDCl_3 solution at room temperature during 10 hours.

NMR (CDCl_3 , 30°C , 400 MHz) δ ppm ^1H :

a) *DL*-form 7.51, 7.44, 7.28, 7.19 (d, $J = 7.8$ Hz, 2H; d, $J = 7.2$ Hz, 2H; t, $J = 7.5$ Hz, 2H; t, $J = 7.5$ Hz, 2H; aromatic protons); 6.98, 6.66 (d, $J = 5.3$ Hz, 2H; dd, $J = 5.3$ Hz, $J' = 1.8$ Hz, 2H; $-\text{CH}=\text{CH}-$ indenyl); 3.61 (s, 2H, $>\text{CH}-\text{Si}$); -0.31 [s, 6H, $>\text{Si}(\text{CH}_3)_2$];

b) *meso*-form 7.50, 7.47, 7.28, 7.20 (d, $J = 7.8$ Hz, 2H; d, $J = 7.2$ Hz, 2H; t, $J = 7.5$ Hz, 2H; t, $J = 7.5$ Hz, 2H; aromatic protons); 6.94, 6.48 (d, $J = 5.3$ Hz, 2H; dd, $J = 5.3$ Hz, $J' = 1.8$ Hz, 2H; $-\text{CH}=\text{CH}-$ indenyl); 3.61 (s, 2H, $>\text{CH}-\text{Si}$); -0.08, -0.49 [s, 3H, $>\text{Si}(\text{CH}_3)_2$].

$[\eta^5, \eta^5-1,1'-(\text{Dimethylsilylidene})\text{bis}(\text{indenyl})\text{dichlorozirconium(IV)} (\text{Me}_2\text{SiInd}_2)\text{ZrCl}_2$ (II)

(*N,N*-Dimethylamino)tri-*n*-butyltin, 34.15 g (102.2 mmols), was added slowly to a solution of *DL*-bisindenyl dimethylsilane $\text{Me}_2\text{Si}(\text{IndH})_2$, 14.74 g (51.1 mmols), on stirring. The mixture was allowed to warm up to room temperature and stirred for 1 hour. Volatile components were removed in a high vacuum and the residual brown oil was taken up with 50 mL of toluene. The resulting solution was added dropwise, with vigorous stirring, to a suspension of ZrCl_4 , 11.91 g (51.1 mmols), in 100 mL toluene, the reaction mixture was stirred at $70-80^\circ\text{C}$ for another 3 hours and cooled to 0°C . The precipitate was filtered off, dried in high vacuum and recrystallized from CH_2Cl_2 to yield a mixture of diastereomeric *ansa*-complexes, 15.0 g (33.4 mmols, 65.4%). The *DL*-isomer was isolated by fractional crystallization from dimethoxyethane.

NMR (CDCl_3 , 30°C , 400 MHz) δ ppm ^1H :

a) *DL*-isomer 7.62–7.05 (m, 8H; aromatic protons); 6.93, 6.09 (AB, $J = 4.0$ Hz, 4H; $-\text{CH}=\text{CH}-$ indenyl); 1.12 [s, 6H, $>\text{Si}(\text{CH}_3)_2$];

b) *meso*-isomer 7.62–7.05 (m, 8H; aromatic protons); 6.92, 6.11 (AB, $J = 2.8$ Hz, 4H; $-\text{CH}=\text{CH}-$ indenyl); 1.35, 0.96 [s, 3H; s, 3H, $>\text{Si}(\text{CH}_3)_2$].

Polymerization of propene and kinetic studies

Witco's 10% solution of MAO in toluene was used without further workup. Toluene was refluxed with, and distilled from, sodium wire into ampules in an argon atmosphere.

Propene was polymerized in the liquid monomer medium at a pressure exceeding that of the propene saturated vapor pressure and at a constant temperature within the range of $30-70^\circ\text{C}$. The process was conducted by either *in situ* generating the toluenic metallocene solutions inside the reactor charged completely with liquid propene and MAO (method i) or by preliminarily dissolving the metallocene in 10% toluenic MAO and injecting the resulting mixture into the reactor with liquid propene and MAO (method ii). The resulting PP powder was discharged, washed with ethanol and dried *in vacuo* at 60°C .

The microstructure of PP was determined by IR and ^{13}C -NMR spectroscopy. Stereoregularity parameters (macrotacticity) were evaluated from the IR absorption band intensity ratio (D_{998} to D_{973}).

The molecular weight distribution characteristics was studied by gel chromatography by using a Waters model 150 C chromatograph equipped with a Styragel-HT column at 145°C with *o*-dichlorobenzene as eluent; PP solution concentration, 0.04%.

Thermophysical characteristics of the isotactic PP were measured with a DSC-910 microcalorimeter, heating rate $20^\circ\text{C}/\text{min}$. The subsequent heating was preceded by cooling the sample in the calorimeter from 200°C to room temperature at a rate of $100^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Propene polymerizations with complexes **I–IV** as precatalysts are summarized in Table 1 and presented in Figs. 1–3. The activity of the catalyst system was characterized by the average rate of PP formation expressed as kg of PP per mmol zirconium per hour. This value varied from 10 to 235 units (Table 1). Figure 1 presents the PP yield (per gram precatalyst) in relation to polymerization time. Figures 2 and 3 present the kinetic curves of polymerization as the specific polymerization rates plotted against the polymerization time.

The activity of these catalyst systems is seen to vary slightly during the experimental time under the polymerization conditions used. The systems based on zirconocene **III** are most active, whereas that based on **II**

Table 1. PROPENE POLYMERIZATION IN BULK WITH METALLOCENES (I–IV) ACTIVATED WITH MAO

MC	[Zr]·10 ⁷ , mol	Al/Zr	Temp., °C	<i>t</i> _{pol} , min	Yield, g	A ^{***}	$\bar{M}_w \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$	M, %	<i>T</i> _m , °C
1 ^{*)}	13	4 800	30	60	11	10	101	3.0	—	—
1 ^{*)}	6.2	8 900	50	105	55	64	37	1.7	84.5	141
2 ^{*)}	7.2	12 600	50	60	20	38	91	2.0	90	145
3 ^{*)}	6.3	12 200	50	160	25	16	90	3.8	90	134
2 ^{**)}	4.9	8 900	50	20	20	132	58	2.1	90	144
3 ^{**)}	3.4	12 000	50	45	35	137	63	4.5	—	—
4 ^{**)}	4	17 000	50	60	45	110	16	2.2	—	132
4 ^{**)}	2.5	15 000	70	40	30	235	13	3.0	—	—

^{*)} Method i; ^{**) method ii; ^{***}) activity, (kg PP)(mmol Zr)⁻¹·h⁻¹.}

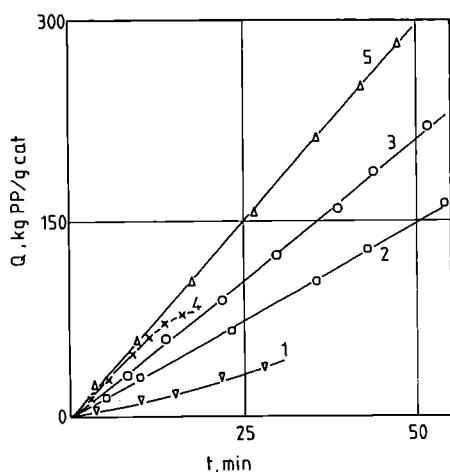


Fig. 1. Yield vs. time for the I–IV systems activated with MAO. Polymerization in bulk at 50°C; 1, 4 — metallocene II; 2 — metallocene I; 3 — metallocene IV; 5 — metallocene III; 1, 2 — method i; 3–5 — method ii

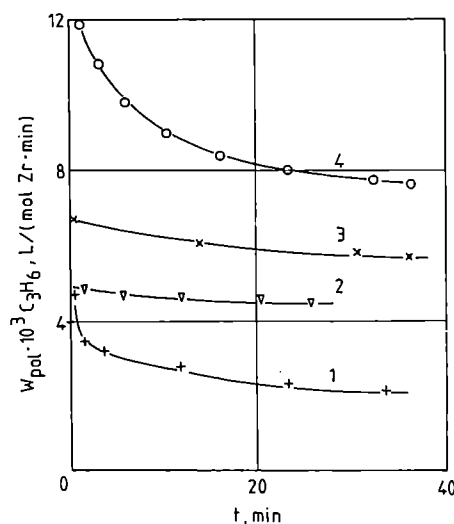


Fig. 3. Polymerization rate vs. time profiles for metallocene II–IV activated with MAO (method ii); 1, 4 — metallocene IV; 2 — metallocene II; 3 — metallocene III. Polymerization in bulk at 50°C (1, 2, 3) and at 70°C (4)

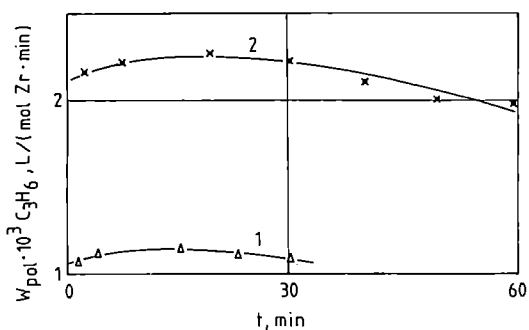


Fig. 2. Polymerization rate vs. time for metallocene I and II activated with MAO (method i), 1 — metallocene I, 2 — metallocene II. Polymerization in bulk at 50°C

is most stable. The replacement of one of the methyl groups in the (CH₃)₂C< bridge by a cyclopropyl group (compounds III and IV) results both in the depressed initial activity and in the greater deactivation of the system during polymerization.

The preliminary dissolution of metallocene in toluenic MAO solution (method ii) leads to a considerable increase in activity.

The systems based on zirconocenes II and III have

led to PPs with highest MWs (Table 1). Remarkably, application of the catalyst systems prepared by method i has led to PPs with significantly higher MWs (90,500 against 58,400 in the case of II and 90,300 against 62,700 in the case of III at the polymerization temperature of 50°C). The catalyst system based on metallocene IV has resulted in a dramatic fall of PP's MW to 16,300 under similar polymerization conditions and even to 13,000 at 70°C.

The stereoregularity characterizing parameters (e.g., mp), follow the descending order II > III > IV. Thus, with IV, the mp of PP is only 132°C. According to the α-agostic insertion mechanism, the α-agostic interaction may be an important factor influencing the stereoselectivity of insertion [13]. By using a chiral catalyst, α-agostic stabilization of the transition metal center is expected to augment the stereoselectivity of insertion. An increase in the electron density at the metal center should render the α-agostic stabilization of the transition state less important. Thus, the stereoselectivity of insertion appears to decrease with the electron density increasing at the metal center in the series of catalysts possessing similar steric environments (metallocene II and III).

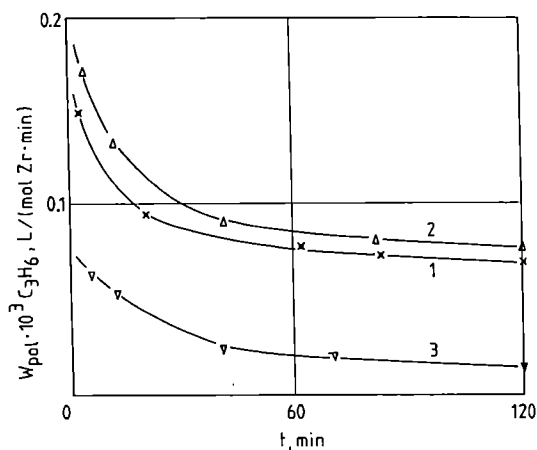


Fig 4. The influence of polymerization conditions on the catalytic activity of metallocene (V) activated with MAO systems. Polymerization in bulk at 30°C (1, 2) and at 8°C (3). Method i — 1, 3; method ii — 2

metallocene V is maximum at the initial moment and decreases slightly as the polymerization proceeds. The kinetic curves are almost independent from the method (i or ii) of catalyst system preparation. With method ii, the system is slightly more active and the mp of PP is higher than that obtained with the method i system; but, in either case, the MWs of PPs are practically identical (Table 2). The yield of solid PP was maximum at 30°C, 6 kg PP/(mmol Zr·h).

Table 3 presents the ^{13}C -NMR spectroscopy data on the pentad content of three elastomeric polypropylenes. The isotactic pentad content achieves approximately 32% and varies only slightly with the temperature of polymerization. Preactivation of the unbridged metallocene has led to a certain increase in the mmmm pentad content. Thus, the stereoblock polymer was formed under similar experimental conditions ^{13}C -NMR spectra of

Table 2. PROPENE POLYMERIZATION IN BULK WITH METALLOCENES (V) ACTIVATED WITH MAO

Catalyst (run No.)	Temp., °C	Al/Zr	[Zr]·10 ⁷ , mol	<i>t</i> _{pol} , min	A ^{*)}	mmmm	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$
5/tol (1)	50	8 800	8	90	9	—	—	—
5/tol (2)	30	4 800	18	120	5.6	30.6	145	3
5/MAO (3)	30	3 000	18	120	6	32.6	139	4
5/tol (4)	8	2 250	35	120	1.6	—	410	4
5/tol (5)	-2	840	90	60	0.6	25.7	340	3.6

^{*)} Activity, (kg PP) (mmol Zr)⁻¹·h⁻¹.

Table 3. PENTAD DISTRIBUTION OF ELASTOMERIC POLYPROPYLENE PREPARED WITH V

Run ^{*)} , No.	mmmm	mmmr	rmmr	mmrr	mmrm + rmrn	rrmm	mrmm	mrrr	rrrr
2	30.6	14.6	6.0	12.6	16.3	8.0	3.0	5.0	4.0
5	25.7	14.9	5.0	10.3	20.2	9.9	5.4	6.2	2.4
3	32.8	14.7	4.2	10.1	17.2	8.4	5.3	5.0	2.2

^{*)} Same as in Table 2.

The MAO-activated non-bridged zirconocene V exists in two atropomeric forms of C₂ and C_s symmetry, which are known to undergo interconversion. The interconversion may occur repeatedly while the chain propagates to yield PP of a stereoblock structure [14–16].

At 50°C, the catalyst system based on metallocene V produced very small quantities of solid PP. However, at lower temperatures, the PP MW rose considerably (Fig. 4). The activity of the catalyst system based on

Table 4. MECHANICAL PROPERTIES OF STEREOBLOCK POLYPROPYLENE

Run ^{*)} No.	<i>E</i> kg/cm ²	$\epsilon_b^{**})$ %	δ_b kg/cm ²	$\epsilon_{1/2}$ %	$\overline{M}_w \cdot 10^{-3}$	Cryst. %	<i>T</i> _m , °C
2	90	68	47	1070	160	4	140
5	122	31	79	1170	340	5	141
3	287	101	68	1015	140	12	150

^{*)} same as in Table 2, ^{**) elastic recovery (%) after 300% strain.}

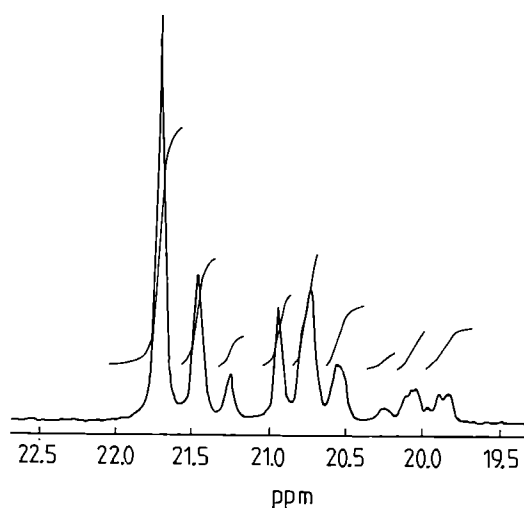


Fig. 5. ^{13}C -NMR spectra of the methyl pentad region of elastomeric polypropylene produced with metallocene (V) in combination with MAO at 30°C (run 3, Table 2)

the method **ii** polypropylene generated at 30°C are shown in Fig. 5.

The mechanical properties of PP are listed in Table 4. The PP with higher MW is endowed with the higher elasticity and higher tensile strength. The method **ii** PP has the highest isotactic pentad content and degree of crystallinity and the highest modulus. Thus, while the MWs are close (145,000 and 139,000), it is the degree of crystallinity that depends mostly on mechanical properties. The elastomeric PP does not yield in mechanical properties to the ethene-propene copolymers (with the content of ethylene of 60 wt.%) prepared with other Ti, V, and Zr compounds [17].

Thus, in the propene polymerization in the liquid monomer medium with MAO-activated bridged and/or non-bridged bisindenylzirconocene dichlorides, the catalyst system activity and the properties of the resulting PPs can be modified by changing the interannular bridge nature or by varying the procedure of catalyst system preparation.

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