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Stereospecific bulk polymerization of propylene over *ansa*-zirconocene catalysts

Summary — Bulk polymerization of propylene was studied over four *ansa*-zirconocene catalysts, *viz.*, $Me_2SiInd_2ZrCl_2$ (**1**), $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (**2**) (rac:meso = 1:2), $Ph_2C(CpFlu)ZrCl_2$ (**3**), and $Me_2C(3\text{-}Me\text{-}CpFlu)ZrCl_2$ (**4**), which were characterized by different symmetries (C_1, C_2, C_s). The structure of the metallocene affected the structure of PP. Upon reactions with methylaluminoxane (MAO) or triisobutylaluminum (TIBA), compounds **1**—**4** produced very active catalytic systems which catalyzed the polymerization to yield various structures of PP. Catalysts **1** and **2** gave isotactic PP, catalyst **3** gave syndiotactic PP and catalyst **4** gave hemiisotactic PP. Hemiiso-PP was similar in structure to amorphous PP and had no melting point. The catalytic activity of the system and molecular weight and stereospecificity of PP were studied in relation to the mode of preparation of the catalyst. Kinetic parameteres were evaluated, *viz.*, time of insertion of the propylene molecule (0.001—0.0001 s) and the time of growth of a single PP macromolecule (3—6 s), and from these data the minimum degree of polymerization was determined. Activation energies were evaluated for the polymerization carried out over each catalyst system. Young's modulus, molecular weight and stereoregularity of the PP prepared were determined.

Key words: propylene, polymerization, *ansa*-zirconocenes, isotactic, syndiotactic and hemiisotactic PP, molecular weight, stereoregularity.

The development of stereospecific homogeneous metallocene (MC) catalysts is a very important step in the Ziegler-Natta catalysis in recent years [1—5]. The metallocene catalysts enable almost each kind of stereoregular polymers to be synthesized. These catalytic systems exhibit high activity. In contrast to heterogeneous complex metal catalysts, owing to the presence of uniform active centers, they allow to produce polymers with narrow *MWD*. Depending on the metallocene composition and structure, they allow to produce isotactic polypropylene (PP) and other stereoisomers like syndiotactic, hemiisotactic and stereoblock PP.

The stereospecificity of a polymer produced over *ansa*-metallocene catalysts is closely related to their symmetry type. The three lowest symmetry point groups are C_1, C_2 and C_s. Complexes with C_1 symmetry allow to perform no symmetry operations by which they can be converted into itself and they produce iso, hemiiso- and stereoblock PP. The C_2 symmetry complexes have only one C_2-axis and they produce isotactic PP. The C_s-symmetry precursor complexes have only a mirror plane and they produce syndiotactic PP. The main idea of stereospecific polymerization over MC catalytic systems is that it should proceed by a mechanism [6] in which the polymer chain and the coordinated monomer exchange their positions at each polymerization step (alternating mechanism).

We studied the bulk polymerization of propylene by isotactic PP (IPP) over C_2-symmetry *ansa*-metallocenes $Me_2SiInd_2ZrCl_2$ (**1**) and $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (rac:meso = 1:2) (**2**) by producing syndiotactic PP (SPP) with *ansa*-metallocene (C_s)-symmetry $Ph_2C(CpFlu)ZrCl_2$ (**3**) and by producing hemiisotactic PP (hemiiso-PP) over C_1-symmetry *ansa*-metallocene $Me_2C(3\text{-}Me\text{-}CpFlu)ZrCl_2$ (**4**).

The literature data, first of all Spaleck's works [2, 5, 7], have shown that, of the known zirconocene systems,

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the systems with indenyl ligands substituted in position 2 and 4 have the maximum catalytic activity and isospecificity. The main chain termination reaction is the β-hydrogen transfer with the monomer. This reaction is very effectively suppressed by substituents in position 2 of the indenyl ring. Aromatic substituents in position 4 give rise to additional electronic effects. The relationship between M_w and monomer concentration examined over various MC isospecific catalysts [7, 8], has shown the ratio of the rate constants for β-H transfer on the metal and other components (MAO) over that for polymer growth to be practically unrelated to catalyst type. In the presence of *ansa*-zirconocenes with α-methyl substituents and at high concentration of propylene, *viz.*, in the liquid monomer medium, the transfer on a monomer is strongly decreased and PP can be produced having higher molecular weights.

The present work sets out to analyze some data on stereospecific bulk polymerization of propylene as a function of the conditions of preactivation of different MC catalysts and polymerization conditions. Selected mechanical properties of the resulting polymers are also discussed.

EXPERIMENTAL

Materials

Polymerization-grade propylene (99.8% by vol. propylene/propane 0.2% by vol) was used without any additional purification. Active admixtures, *viz.*, CO, CO_2, and H_2O, were less than 5 ppm. Polymethylalumoxane (MAO) (Witco's 10% by wt. solution in toluene) was used without further treatment.

Dimethylsilyl-bis(indenyl)zirconium dichloride $Me_2SiInd_2ZrCl_2$ (**1**), diphenylmethylidene-(cyclopentadienyl)(fluorenyl)zirconium dichloride $Ph_2C(CpFlu)\ ZrCl_2$ (**3**) and isopropylidene(3-methyl-cyclopentadienyl)(fluorenyl)zirconium dichloride $Me_2C(3\text{-}Me\text{-}CpFlu)\ ZrCl_2$ (**4**) were prepared as described in [9], [10] and [11], respectively.

Dimethylsilylbis(4-phenyl-2-ethyl-indenyl)zirconium dichloride $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (rac:meso = 1:2) (**2**) was prepared as described in [7] with some modifications.

Bulk polymerization of propylene and characteristics of PP

These were described elsewhere [9]. The process was conducted either by *in situ* generating the toluene solution of MC or by preliminarily dissolving MC in toluenic 10% MAO at varying Al/Zr ratios ([Zr] = (1—4) 10^{-3} mol/l) directly inside the reactor that had been charged with liquid propylene and MAO or with triisobutylaluminum (TIBA) (Zr = 10^{-7}—10^{-5} mol/l).

RESULTS AND DISCUSSION

Synthesis of isotactic PP

The activity, molecular weight and stereoregularity of polymers produced over metallocene catalysts, as contrasted with the heterogeneous Ti/Mg catalysts, are very sensitive to the polymerization conditions: polymerization temperature, monomer concentration, nature of solvent, catalyst concentration, Al/Zr ratio, *etc.* To determine optimum conditions of propylene polymerization over an MC catalyst, it is important to investigate the influence of the ways of formation of catalytic systems in the propylene polymerization and to determine the properties of the PP produced.

Preliminary dissolution of **1** in a toluenic MAO solution has led [9] to a considerable increase in activity and to PP having lower M_w (58400 *vs.* the 90500 at polymerization temperature 50°C). In this work, the catalyst activity and the properties of PP produced in bulk polymerization carried out over **2** activated with MAO, were studied in relation to Al/Zr ratio at the preactivation stage. The Al/Zr ratio was found to affect considerably the activity of the metallocene catalytic system at this stage. Figure 1 present the kinetic curves of polymerization, obtained with the **2**/MAO catalytic system at a polymerization temperature of 60°C. The reaction rate profiles are characterized by a period of activation, *i.e.*, a period of activity increasing before the maximum activity has been reached, and a period of deactivation. At ratios Al/Zr = 200 and Al/Zr = 2000 at the preactivation stage, the activity of the **2**/MAO catalytic system in different runs changed by a factor of three.

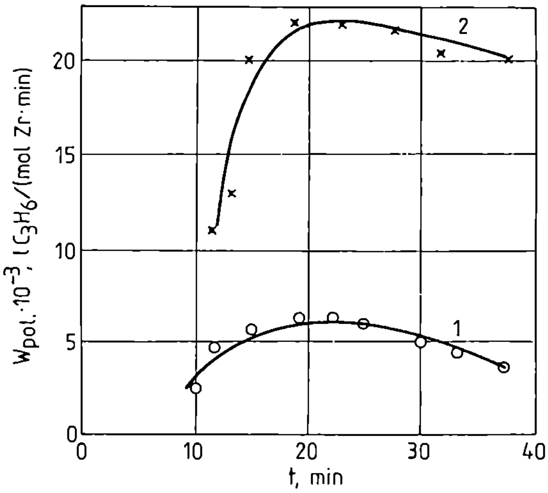

Fig. 1. The catalytic activity of $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (rac:meso = 1:2)/MAO in relation to the catalytic system preparation method: preliminary dissolution of MC in toluenic 10% MAO at (1) Al:Zr = 200, (2) Al:Zr = 2000; bulk polymerization at 60°C, [MAO] = 0.6—0.8 g/l

Table 1. Influence of preactivation methods on the activity of the catalytic systems based on $(CH_3)_2SiX_2ZrCl_2$/MAO and PP characteristics

X ligand	Method of preactivation	$[Zr]\cdot 10^7$ mol/l	Polym. temp., °C	Activity kg PP/ /(mmol Zr·h)	D_{998}/D_{993} %	$M_w \cdot 10^{-3}$	M_w/M_n	T_m, °C
Indenyl	MC/tol	28	50	38	90	90	1.98	144
Indenyl	MC/MAO Al:Zr = 1000	20	50	130	89	58	1.8	145
4-Ph-2-Et-Indenyl	MC/MAO Al:Zr = 200	8	60	117	90	770	3.5	161
4-Ph-2-Et-Indenyl	MC/MAO Al:Zr = 2000	3	60	422	98	690	2.9	163

$[C_3H_6]$ = 10—11 mol/l; concentration of MAO in reactor, 0.6—0.9 g/l.

The activity and property data on PP produced over the **1**/MAO and the **2**/MAO catalytic systems differing in the mode of preactivation, are shown in Table 1. The increase in the activity at varying Al/Zr ratios at the preactivation stage for **2** is seen to be followed by an increase in the isotacticity index of PP. Because **2** represents a mixture of the rac and meso isomers, the increase in the ratio of Al to Zr was supposed to give rise to the activation of the rac-form of this metallocene.

There are some speculations on the nature of the active centers in metallocene catalytic systems such as ions, ion pairs, solution separated ion pairs, and monomer separated ion pairs [12].

Preactivation of *ansa*-metallocene complexes with MAO at varying ratios is likely to shift the equilibrium of all these species. Different catalyst precursors can thus affect the polymerization process. Spectroscopic investigations of various MC/MAO systems allowed to identify the nature of the active species. For the systems built on the basis of bisindenyl zirconocene with the ethylene bridge at Al/Zr ratios lower than 30 and equal to 200 and 2000, bathochromic shifts were observed corresponding to monomethylation of zirconocene and to the formation of associated (dimeric) and dissociated (monomeric) cationic metallocene species [13, 14]. The increasing proportion of the latter was accompanied by the rising catalytic activity. These spectroscopic data correlate with our results on the influence of the ratio of catalytic components at the preactivation stage. The activity rising under increasing Al/Zr ratios may be due to a more complete alkylation of the MC by MAO and to an increase in the concentration of monomeric cationic MC species.

Molecular weight and stereoregularity of MC-isoPP are very sensitive to the polymerization temperature, in contrast to the Ti/Mg isoPP. This fact is explicable in terms of flexibility of the ligands and the rate of β-hydride elimination increasing at elevated temperatures. The data in Table 2 show the polymerization temperature to affect activity and molecular weight of PP prepared over the MAO-activated system on the basis of **2**. As the polymerization temperature was decreased, the molecular weight of PP increased. The maximum molecular weight was equal to $2 \cdot 10^6$ for the PP produced at 30°C. At 80°C, the molecular weight was equal to $4 \cdot 10^5$ only.

Table 2. Effect polymerization temperature on the activity and molecular weight of iso—PP

Bulk polymerization over $Me_2Si(4\text{-}Ph\text{-}2\text{-}Et\text{-}Ind)_2ZrCl_2$ (rac:meso = 1:2)/MAO

Polym. temp. °C	Activity, kg PP/ /(mmol Zr· h)	$M_w \cdot 10^{-3}$	M_w/M_n
30	162	2100	2.2
50	211	1140	2.7
60	422	720	2.9
70	585	570	2.9
80	435	430	3.0

The molecular weight data show that, in the case of the **2**/MAO system producing the higher molecular weight PP, there is a greater difference between the activation energy of chain propagation and that of the chain termination, -8.5 kcal/mol *vs.* the -3.1 kcal/mol for the **1**/MAO. These data are in agreement with the higher molecular weight of PP produced over the **2**/MAO catalytic system.

Synthesis of syndiotactic PP

To synthesize SPP, we used metallocene **3** with the bisdiphenylmethylidene bridge. Razavi was the first to describe the preparation of high molecular weight SPP over this MC [10]. The SPP obtained over this catalyst had M_w five times greater than that of the SPP produced over the parent isopropylidene MC. This increase was related to the difference in hapticity of these molecules in solution and in their cationic forms as active species [15, 16].

As regards the syndiospecific catalyst systems, we investigated the influence of the activation mode on the catalyst activity and the molecular weight characteristics of SPP [17]. Four activation modes were studied: 1 — the process was conducted by generating the toluenic solution of MC directly in the reactor to which liquid propylene and MAO had been charged; 2, 3 — MC was preliminarily dissolved in a toluenic solution of MAO (Al/Zr = 600) and the resulting mixture was injected into the reactor together with liquid propylene and MAO at a temperature of run equal to 60°C or 10°C; 4 — MC was preliminarily dissolved in a toluenic solution of MAO and the resulting mixture was injected into the reactor together with liquid propylene and TIBA.

Table 3. Effect of catalyst formation method on the activity and properties of SPP. Bulk polymerization of propylene over $Ph_2C(CpFlu)ZrCl_2$ at 60°C

Run	Al/Zr (preact.)	$[Zr]\cdot 10^7$ mol/l	Cocatalyst	Al/Zr (MAO)	Al/Zr (R_3Al)	Polym. time, min	Yield, g	Activity, kg PP/ /(mmol Zr·h)	$M_w \cdot 10^{-3}$	M_w/M_n
1	0	16	MAO	10000	—	64	28	71	390	2.9
2	600	7.1	MAO	10000	—	30	30	118	465	3.2
3	600	5.3	MAO	16000	—	85	44	100	504	1.96
4	600	1.5	(i-Bu)3Al	800	2300	30	20	80	466	1.96

1 — process conducted by generating a toluene solution of metallocene (MC) directly in the reactor charged with liquid propylene and MAO;
2—4 preliminary dissolution of MC in toluenic 10% MAO and injecting of the resulting mixture into the reactor with liquid propylene:
2— and MAO at temperature of run;
3— and MAO at temperature of 10°C;
4— and TIBA at temperature of run.

Figure 2 presents the respective kinetic curves. The maximum catalytic activity is seen to have been achieved by method 2. With TIBA, the activity was initially high and later low. The decreasing polymerization rate is satisfactorily described by the reciprocal polymerization rate *vs.* time relationship, suggestive of a bimolecular mechanism of termination of active centers in this system. The stable rate in methods 2, 3 indicates that MAO is necessary for the reactivation of inactive complexes formed by the hydrogen transfer reaction and for preventing the bimolecular process. The possible activation of the MC-system by TIBA results in reduced consumption of MAO, but also in reduced catalytic activity of the systems.

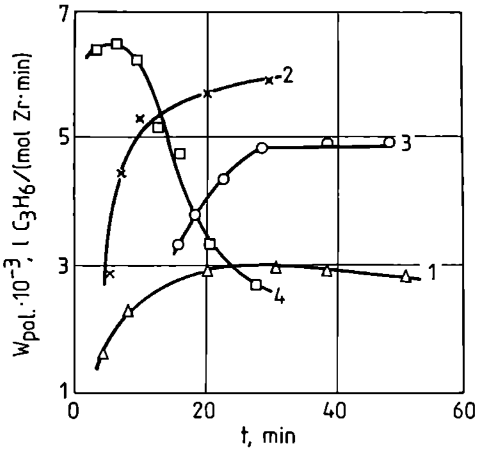

Fig. 2. The catalytic activity of $Ph_2C(CpFlu)ZrCl_2$ in relation to the catalytic system preparation method: 1 — process conducted by generating the toluenic solution of metallocene (MC) directly in the reactor charged with liquid propylene and MAO; 2, 3 — preliminary dissolution of MC in toluenic 10% MAO and injecting the resulting mixture into the reactor with liquid propylene and MAO at temperature of run 60°C (2), at 10°C (3); 4 — preliminary dissolution of MC in toluenic 10% MAO and injecting the resulting mixture into the reactor with liquid propylene and TIBA; bulk polymerization at 60°C

Table 3 shows the molecular weight characteristics of SPP produced by the different catalyst preparation methods. The high molecular weight of PP is seen to have been received in each run. Only at low temperature of polymerization (method 3) and in the presence of TIBA (method 4), the resulting SPP had a narrow *MWD* of about 2. We can conclude that, only under such conditions, a "single-site" can be produced with a constant ratio of the rates of chain growth and termination.

Synthesis of hemiisotactic PP

With the Ph group replaced by a Me group in the carbon bridge of 3, polymers with low M_w were produced, whereas the presence of Me in the Cp-ring resulted in hemiisotactic PP. Figure 3 shows data obtained in the study on the kinetics of bulk polymerization of propylene over of 4/MAO. Zirconocene 4 was preactivated by preliminary dissolution in MAO at Al/Zr = 600. In this case the activity depends on the Al/Zr ratio and

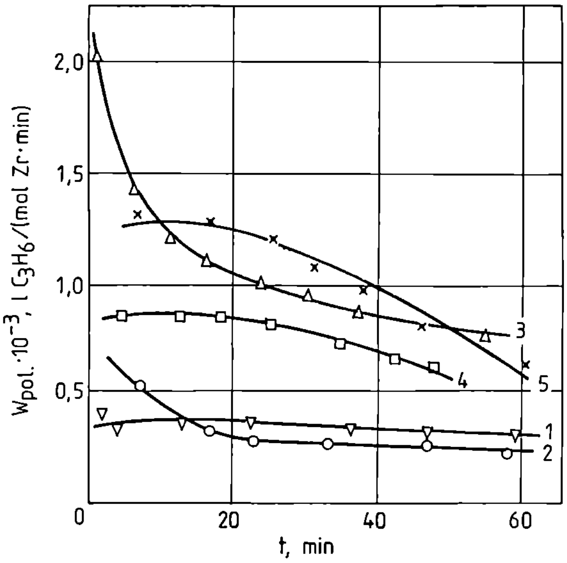

Fig. 3. The catalytic activity of metallocene $Me_2C(3\text{-}MeCpFlu)ZrCl_2$ with MAO in relation to polymerization temperature: 1, 2 — 30°C; 3 — 50°C; 4 — 60°C; 5 — 70°C

Table 4. **Bulk polymerization of propylene over $Me_2C(3\text{-}MeCpFlu)ZrCl_2/MAO$**

Polym. temp., °C	[MC] · 10^6, mol/l	Al/Zr	Polym. time, min	Yield, g	Activity, kg PP/ /(mmol Zr· h)	$M_w \cdot 10^{-3}$	M_w/M_n
30	7.2	1500	75	24	10.5	95	2.4
30	7.6	3050	134	33	8	80	1.9
50	3.8	5500	100	37	23	52	2.2
60	4.1	4700	50	18	21	52.5	2.0
70	2.3	5700	60	17	24	45	1.9

Table 5. **Pentad distribution in polypropylene prepared over $Me_2C(3\text{-}MeCpFlu)ZrCl_2/MAO$**

Polym. temp., °C	mmmm	mmmr	rmmr	mmrr	mmrm + rmmr	rmrm	rrrr	rrrm	mrrm
30	13	11	7	25	0	0	23	14	6
60	17	14	5	23	5	0	16	12	8

polymerization temperature. Table 4 lists the data on the effect of polymerization temperature on activity and molecular weight characteristics of PP. As the Al/Zr ratio was decreased, the **4**/MAO catalytic system activity decreased. A similar phenomenon was observed in [18] when propylene polymerization was studied over this system in a toluene medium at $[C_3H_6]$ = 1.59 mol/l. This inhibiting effect was explained by the blockade of active zirconocene centers by the complex MAO compound.

The microstructure of hemiiso-PP samples was tested by ^{13}C-NMR spectroscopy. According to [19], in the ideal structure of hemiiso-PP, the pentad ratio should obey the following ratio: mmmm : mmmr : rmmr : mmrr : mmrm : rmrm : rrrr : rrrm : mrrm = 3 : 2 : 1 : 4 : 0 : 0 :3 : 2 : 1. According to our data the PP produced at 30°C is most consistent with this distribution (Table 5). Analysis of our data on bulk polymerization and data of [18] shows the high concentration of propylene not to affect the PP microstructure. As the temperature is increased, the proportion in the pentad mmmm, mmmr, (mrmm + rrmr), mrrm increases and the proportion of the pentad rrrr, rmmr, mmrr, rrrm decreases. In all spectra, no signals for the rmrm pentad were detected.

Hemiisotactic PP looks like amorphous and sticky, having no melt temperature.

For each MC-catalytic system studied, energy characteristics were derived from the Arrhenius plot. The effective activation energy for bulk polymerization of propylene, calculated from the maximum activity at different temperatures, was 9.5 kcal/mol for **1**/MAO, 10.1 kcal/mol for **2**/MAO catalytic system and 10.5 and 8.5 kcal/mol for propylene syndiospecific polymerization over the **3**/MAO activated system (method 2) and over the **4**/MAO system, respectively.

If in each system studied each zirconium atom is supposed to form an active complex [20, 21] and with the catalytic systems activity data and molecular weight characteristics of the polymers produced, one may evaluate the minimum polymers chain number per one mol Zr during the polymer chain growth step and the time required to insert one propylene molecule. One zirconium atom produces 600—1000 mol/PP per hour. The insertion time of one propylene unit is only 10^{-3}—10^{-4} s. The time of growth of one polymer molecule in the Zr-cene system is 3—6 s.

Properties of MC-PP

The metallocene catalyst can be used to make new PP materials endowed with enhanced properties or unprecedented property combinations [22, 23]. Some properties of PP produced are shown in Table 6.

Table 6. **Mechanical properties of PP**

Type of PP	mc-iso	Ti/ /Mg-iso	mc- -syndio
Molecular weight, $M_w \cdot 10^{-3}$	560	800	465
Young's modulus, MPa	1900	1550	690
Yield stress, MPa	36.8	37.3	19.4
Strength at break, MPa	39.5	32.4	16.6
Elongation at break, %	490	500	360
Izod notched impact strength, kJ/m^2	9	7	49

Determinations of mechanical properties showed the principal feature of metallocene-catalyzed isotactic PP to be the high Young modulus of up to 1900 MPa. For comparison, Young's modulus of typical commercial PP is 1200—1500 MPa only. The high modulus is the result of high PP homogeneity, narrow *MWD* and high crystallinity, close to 70—80%. The polymers obtained over **2** had a high melt temperature (161—164°C) independent of the molecular weight, evidencing for a high regioselectivity of the **2**/MAO catalytic system.

As compared with isotactic PP, syndio-PP exhibits a lower density depending on tacticity, a lower crystallization rate, a lower degree of crystallinity, and a lower melting point. The small crystal size syndiotactic PP causes a higher clarity of the material. SPP films are transparent to visible light. The transparency degree is 90—95% (evaluated from the intensity of light absorption of SPP 150-μm films in the region 400—800 nm). It is much more elastic and exhibits the higher impact strength [17]. SPP is more resistant to thermooxidative degradation [24] and ultra-violet radiation than is isotactic PP. It can be used in medical appliances which require sterilization procedures.

The hemiisotactic PPs were used as pour-point depressants. Introduction of 50—100 mg of hemiisotactic PP into 1 L of an oil caused the solidification temperature to decrease from +16 to -4°C, which essentially simplifies oil transportation. These results allow to recommend the hemiisotactic PP as a depressant mixture for oils.

Summing up, the synthesis of IPP, SPP and hemiiso-PP over metallocene catalysts opens new vistas for the production of materials on the basis of PP endowed with valuable combination of properties.

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