Combining Ziegler-Natta and Metallocene Catalysis: New Heterophasic Propylene Copolymers from the Novel Multicatalyst Reactor Granule Technology

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ABSTRACT: A new process that combines the excellent morphology control of Ti-based catalysts with the unique features of polyolefins from metallocenes has been devised. First, propylene is polymerized with the Ti-based catalysts, having spherical form; then, activated metallocene catalysts are introduced into the porous PP spheres, through an *in situ* impregnation and drying process, once the Ti has been deactivated. Then, the olefins polymerization, catalyzed by the metallocene, is carried out in gas phase. This step, as well as the morphology of the as-polymerized polymer particles, has been investigated in detail. New heterophasic copolymers (PP/EPR) having free-flowing spherical form have been achieved, and the morphology of the copolymer spheres pointed out that the rubber is well dispersed inside the polymer granule. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66**: 1831–1837, 1997

Key words: replication phenomenon; metallocenes; reactor granule technology; heterophasic copolymers; polyolefins

INTRODUCTION

Since the discovery of the catalysts for olefins polymerization by K. Ziegler and G. Natta, many research efforts have been done to understand and control the basic principles of catalysis and polymerization mechanism.[1] As a consequence, both catalyst activity and catalyst isospecificity have been greatly improved. However, an other aspect of catalyst behavior revealed to be crucial for the successful development of new technologies: the catalyst/polymer replication phenomenon. In our company, detailed studies began in 1968–1970[2] and are still in progress[3–5]; they pointed out that the replication of catalyst morphology by olefin polymerization is allowed when the catalyst has a uniform distribution of active sites and high porosity; in addition, a progressive and controlled fragmentation of the catalytic granule has to be carried out. Hence, it has been possible to synthesize porous polyolefins having free-flowing spherical form by tailoring the catalyst morphology (shape, dimension, and porosity) and by properly design the polymerization process. The pores of the PP particles actually behave as microreactors for further polymerizations catalyzed by the still active Ti or by other suitable chemical species. New processes for the synthesis of new olefinic and nonolefinic polymers and alloys have been developed[6–8] by exploiting this concept, named the Reactor Granule Technology. Recently, new catalysts (i.e., the metallocenes) have been proven useful for olefin polymerization: they allow the synthesis of homo- and copolymers endowed with narrow molecular weight distribution (MWD), narrow distribution of stereoregu-

larity, and narrow chemical composition distribution. Further, they allow control over the stereoregularity in 1-olefins polymerization and the comonomer placement in copolymerization; these molecular features turn into new or improved physical-mechanical properties.[1,9–13] However, these catalysts have to be supported to obtain the morphology control needed for using them with the existing technology, in the existing plants. Thus, the Reactor Granule Technology has been exploited to take advantage of both the excellent morphological control for polymers synthesized with heterogeneous catalysts and the outstanding properties offered by the polyolefins prepared with metallocenes. Indeed, a new process has been devised[14] and named Multicatalyst Reactor Granule Technology. In the first step, propylene is polymerized with a porous, highly isospecific, $MgCl_2$-supported heterogeneous catalyst; then, the activated metallocene is introduced into the PP spheres, after deactivating the still active Ti sites. Finally, olefin copolymerization is carried out the in gas phase, catalyzed by the metallocene. Aiming at a better knowledge around the metallocene-catalyzed step, our attention has been focused on the ethylene/propylene copolymerization step performed in the gas phase with different metallocenes and alumoxanes, at different pressure and hydrogen concentration. Also the morphological features of the as-polymerized spheres have been investigated and discussed.

EXPERIMENTAL

Synthesis of the Heterogeneous Catalyst

The $MgCl_2$-based support is obtained in spherical form by quenching with cold hydrocarbons an emulsion of molten $MgCl_2 \cdot nEtOH$ in paraffinic oil. The catalysts synthesis is described in EP-A 395083. Typically, the spherical adduct $MgCl_2 \cdot nEtOH$ was reacted at 100°C for 2 h with $TiCl_4$ in the presence of diisobutylphthalate (DIBP) (Mg/DIBP = 8 molar). The hot liquid was syphoned off, and the $TiCl_4$ was added to the solid; such a mixture reacted for 1 h at 120°C. Again, the liquid was syphoned off and the solid was washed several times with hexane and dried under nitrogen. The chemical composition was Ti = 2.34 wt %, Mg = 18.8 wt %, DIBP = 6.8 wt %.

Metallocenes

Racemic-ethylene-bis-(4,5,6,7,tetrahydroindenyl)-zirconiumdichloride

(r-EBTHI) was prepared according to the method described in ref. 15. Meso-ethylene-bis-(4,7-dimethylindenyl)zirconiumdichloride (m-EBDMI) was prepared according to the method described in ref. 21.

Aluminoxanes and Aluminumalkyls

Modified methylaluminoxane (MMAO) was purchased from Witco (20 g/100 mL solution in Isopar-C); tetraisobutylaluminoxane (TIBAO) was purchased from Schering (30 g/100 mL in cyclohexane), and Tris-(2,4,4-trimethylpentyl)aluminum (TIOA) was purchased from Witco.

Multicatalyst Reactor Granule Technology

The detailed procedure for such a continuous process has been described elsewhere[14]; in this work the process was divided in two main parts: the first one is the homopolymer synthesis, with the deactivation of Ti active centers; then, portions of the same PP were used for the introduction of the metallocene into the spheres followed by the gas phase olefins polymerization.

Synthesis of Porous Polypropylene and Deactivation

The homopolymerization was carried out in a 4-L stainless steel batch reactor in the following way: the solid catalytic component was precontacted with the cocatalyst mixture (triethylaluminum and dicyclopentydimethoxysilane at Al/Si = 10 molar) at an Al/Ti = 200 molar for some minutes at room temperature. It was injected into the reactor, and the suitable amount of liquid propylene was added at 25°C together with 1944 mL of hydrogen; after that, the temperature was quickly raised to 70°C and the polymerization was performed for 2 h. Then, the monomer was vented out and replaced with 1 L of wet hexane (H_2O/Ti >400 molar) and the mixture was stirred for 30 min at 50°C. The liquid was syphoned off, the polymer was dried under vacuum, and stored under nitrogen. The PP intrinsic viscosity was 1.55 dL/g; the isotactic index was 97 wt %.

Gas Phase Copolymerization with MMAO and TIBAO

Around 50 g of PP were charged in a 4-L stainless steel batch reactor under nitrogen atmosphere. Then, 500 g of dried propane were added and the

temperature was raised to 40°C; in the meantime, the metallocene was reacted, under inert atmosphere, with the alkylaluminoxane solution at 25°C for 10 min. Then, the activated metallocene was injected into the reactor and kept at 40°C for 15 min under stirring. After that, the propane was vented out and replaced with the ethylene/ propylene gaseous mixture, having the proper composition (hydrogen was also added in some runs). The gas phase copolymerization was performed until the desired amount of rubber was produced; the composition of the mixture was kept constant throughout the reaction by properly feeding both monomers.

Gas Phase Copolymerization with TIOA-O

The only variation regards the precontact step: once the propane was added to the reactor containing the porous PP spheres, the suitable amount of water was injected too ($Al/H_2O = 2$ molar). In the meantime, r-EBTHI was reacted with Tris-(2,4,4-trimethylpentyl)aluminum, at room temperature for 10 min. Then, the procedure previously described was followed.

Copolymer Characterization

Xylene solubility (XS) was determined through dissolution of the sample in o-xylene at 135°C and successive recrystallization at 25°C. Intrinsic viscosity of polymers was measured at 135°C in tetrahydronaphtalene. Molecular weight distribution was measured in o-dichlorobenzene at 135°C with a GPC WATERS Model 200. The ethylene content was determined by infrared spectroscopy using a NICOLET 20SXC spectrometer.

Morphological Characterization

Scanning electron microscopy was used to study the morphology of the polymer particles. The samples were mounted on specimen holders and coated with gold. The observations were carried out by using a Philips 515 electron microscope at 25 KV. To study the heterophasic samples in terms of phase distribution, the interference contrast mode in optical microscopy was used. In interference microscopy the illumination is split into two beams. Thus, a region of constant properties shows no contrast because both beams interact with the same material, but a sudden change of thickness or refractive index gives strong contrast; in transmission, the technique gives appar-

ent relief to the images. Thus, the rubber is well distinguished from the PP phase by using interference microscopy.

Transmission electron microscopy was used to study the distribution of the phases in the heterophasic copolymer at a far higher resolution than the one achieved by using optical microscopy. Very thin slices were observed with TEM Philips 301 operating at 80 KV. The slices were obtained after staining with Ruthenium Tetroxide using a cryo-ultramicrotome LEICA ULTRACUT S operating at −30°C and equipped with a diamond knife.

RESULTS AND DISCUSSION

Polymerization Results

Various metallocenes have been proven to efficiently copolymerize ethylene and propylene in a liquid pool[9,16–20]; among others, the r-EBTHI[19,20] and m-EBDMI[21] have been selected for the gas phase copolymerization. In particular, the latter has been selected due to its capability to synthesize polyethylene and ethylene-1-olefins copolymers endowed with very high molecular.[21]

They have been activated with MMAO, TIBAO, and Tris-(2,4,4-trimethylpentyl)aluminum reacted *in situ* with water (TIOA-O). In Table I the results achieved in the gas phase copolymerization of ethylene and propylene with such catalytic systems are reported. It should be observed that the xylene solubility of all the heterophasic copolymers is always very close to their rubber content. This means that the elastomeric component synthesized with metallocenes is fully soluble in xylene, at least for the experimental conditions selected in the present work. As the rubber is always the major component of the material and as the solubles coming from the homopolymer part are very low, it can be said that the molecular features measured on the soluble fraction are representative of those of the whole elastomer, at least in a first approximation. Then, it is worthwhile to note, by comparing runs 1 and 2, that the copolymer molecular weight (MW), catalyst activity, and reactivity toward the comonomer have been greatly affected, upon a change of the metallocene. The different reactivity toward the comonomer has already been discussed on the basis of the different symmetry of the zirconocene,[22] which would induce nonbonding interactions between the incoming bulkier monomer and the

Table I Gas Phase Synthesis of Heterophasic Copolymers (PP/EPR) via Multicatalystss Reactor Granule Technology. (Metallocenes/Alumoxane)

Run	u.m.	1	2	3	4
PP	g	40	49.5	33.4	50.5
M_w/M_n		n.d.	5.8	n.d.	5.8
Metallocene		r-EBTHI	m-EBDMI	r-EBTHI	r-EBTHI
amount	mg	10	1	5	1
alumoxane		MMAO	MMAO	TIBAO	TIOA-O
Al/Zr	molar	200	200	200	1000
Pressure	bar	13	13	13	13
temperature	°C	40	40	40	40
ethylene, feed	wt %	44	28	44	44
time	min	18	64	253	86
activity	g/gZrh	77,000	550,000	15,000	400,000
EPR	wt %	55.2	69.5	67.2	70.8
XS	wt %	56.5	70	67	71
free-flowing		Sticky	Yes	Sticky	Yes
bulk density	g/mL	n.d.	0.4	n.d.	0.38
M_w/M_n		n.d.	4.8	n.d.	4.9
[a]C2, sol.	wt %	61	68.3	68	65
[a]IV, sol.	dL/g	1.2	4.9	2.3	3.4
[a]M_w/M_n, sol.		2.8	2.9	2.7	2.9

[a] Measured on the fraction soluble in xylene at room temperature.

growing chain in the C_{2v} metallocenes. Then, it is not clear if the different activities are due to the structure of the ligands [23,24] or due to the low Al/Zr ratios that might favor the m-EBDMI over the other metallocene, at least for the gas phase polymerization. The increase of the molecular weight

of the rubber, observed on going from the r-EBTHI to m-EBDMI, might be due to enhanced steric crowding around the Zr atom in the meso-complex, which prevents the chain transfer phenomena. As the MW of the rubber increases, the particles became free flowing; further, they have a good

Table II Gas Phase Synthesis of Heterophasic Copolymers (PP/EPR) via Multicatalysts Reactor Granule Technology (Effect of the Pressure)

Run	u.m.	5	4	6
PP	g	50	50.5	49.8
Metallocene		r-EBTHI	r-EBTHI	r-EBTHI
Amount	mg	1	1	1
Alumoxane		TIOA-O	TIOA-O	TIOA-O
Al/Zr	molar	1000	1000	1000
Pressure	bar	9	13	23
Temperature	°C	40	40	40
Ethylene, feed	wt %	44	44	44
Time	min	100	86	28
Activity	g/gZrh	146,000	400,000	1,150,000
EPR	wt %	51	70.8	69.7
XS	wt %	52	71	70
Free-flowing		Yes	Yes	Yes
C2, sol.	wt %	58.4	65	65
IV, sol.	dL/g	2.7	3.4	5.4
M_w/M_n, sol.		3	2.9	3

Table III   Gas Phase Synthesis of Heterophasic Copolymers (PP/EPR) via Multicatalysts Reactor Granule Technology (Effect of Hydrogen)

Run	u.m.	7	8	6
PP	g	50	50.2	50
Metallocene		r-EBTHI	r-EBTHI	r-EBTHI
amoung	mg	1	1	1
alumoxane		TIOA-O	TIOA-O	TIOA-O
Al/Zr	molar	1000	1000	1000
Pressure	bar	23	23	23
temperature	°C	40	40	40
ethylene, feed	wt %	44	44	44
hydrogen, feed	mol %	0.3	0.02	none
time	min.	30	33	28
activity	g/gZrh	757,000	995,000	1,150,000
EPR	wt %	61.8	70	69.7
XS	wt %	62.4	72	70
free-flowing		Sticky	Yes	Yes
C2, sol.	wt %	61	62.8	65
IV, sol.	dL/g	1.73	3.7	5.4
M_w/M_n, sol.		3.6	3.7	3

bulk density. Also, the cocatalyst influenced both the activity and the MW of the rubber, the TIOA-O allows the highest activity and MW when r-EBTHI is used; this would suggest that branched alkyl groups bonded with the Al atom positively affect the ratio K_p/K_{tr}, provided that the higher Al/Zr ratios did not greatly affect the molecular weight of the rubber. Then, it can be observed that the MWD of the soluble polymer is relatively narrow, as it would be expected on the basis of the present knowledge about the homogeneous catalysts behavior.[1] Nevertheless, the MWD of the heterophasic material is still quite broad, close to that of the homopolymer part; thus, a good processability in the melt state could be foreseen for these polymers. In Table II are reported the results obtained in the gas phase ethylene/propylene copolymerization step with r-EBTHI/TIOA-O at different pressures but with the same monomer ratios. Both the catalyst activity and the MW of the rubber increased as the pressure increased from 9 bar up to 23 bar; it can be accounted for by the increase of the total monomer concentration that positively affected polymerization rate and molecular weight. In Table III are reported the data obtained in the gas phase copolymerization step performed with r-EBTHI/TIOA-O at different hydrogen concentrations. Catalyst activity and polymer MW decrease upon addition of hydrogen; a similar behavior has already been described[10] for the ethylene polymerization with metallocenes. Hydrogen acts as a molecular

weight regulator through a chain scission reaction, whereas it is not clear why the catalyst activity is decreased.

MORPHOLOGICAL CHARACTERIZATION

The morphology of the PP used in this work is presented in Figure 1. The porous particle has the same spherical form as the catalysts that generated it. Figure 2 shows the appearance of the particles of the as-polymerized heterophasic copolymer (run 2): they are spherically shaped and free flowing. Then, they have been cut and the section observed with an optical microscope. Figure 3

**Figure 1** Scanning electron microscopy (SEM). The section of a polypropylene porous particle.
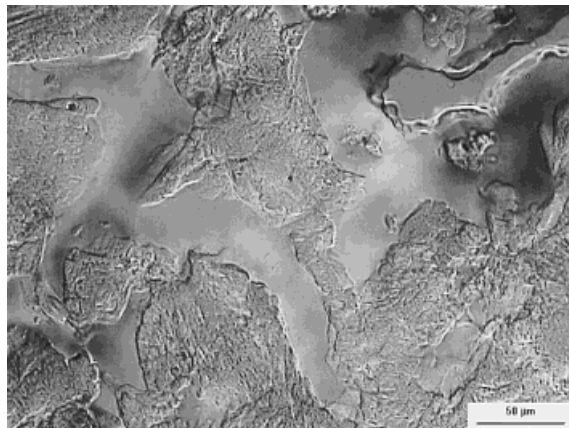
Figure 2 Scanning electron microscopy(SEM). The surface of an as-polymerized copolymer particle.

points out that the elastomeric polymer, synthesized with metallocenes, is well dispersed into the PP granule. Figure 4 (Transmission Electronic Microscopy technique has been used) supports even more of this statement, as it shows that rubbery particles (dark area) smaller than 1 mm are present within the polypropylene globules (white area). This evidence suggest that such alloys could have improved physical-mechanical properties with respect to similar materials obtained through melt mixing.

CONCLUSIONS

The excellent morphology control of Ti-based polyolefins and the unique molecular features of Zr-based polyolefins have been combined in the new proprietary process (Multicatalysts Reactor
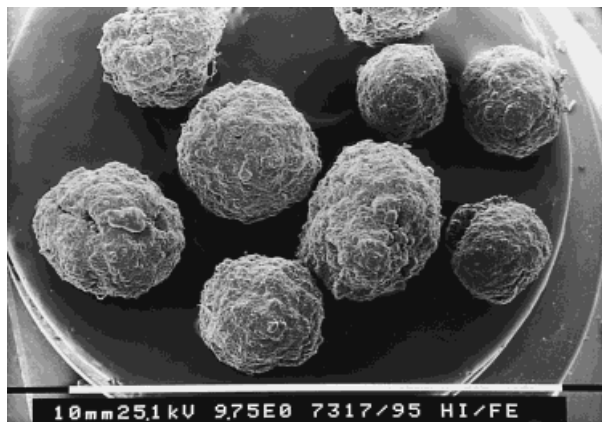
Figure 3 Optical microscopy(OM). The cross-section of an as-polymerized copolymer particle.
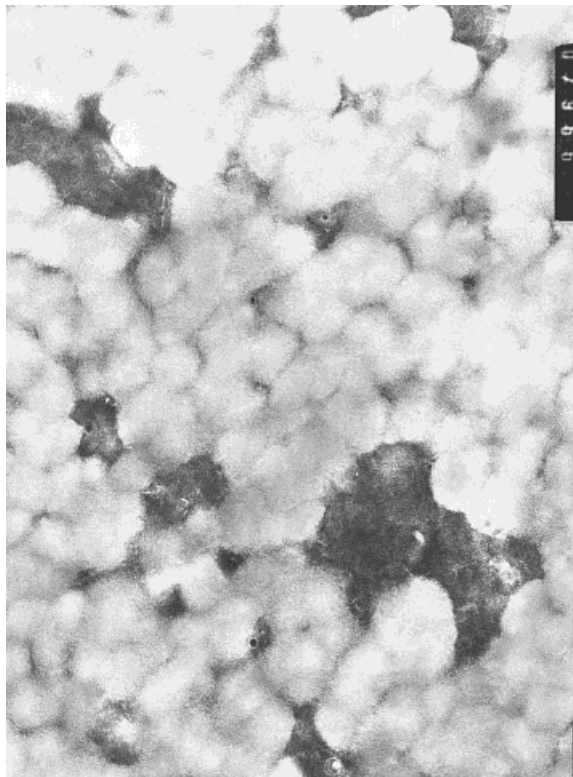
Figure 4 Transmission electron microscopy(TEM). The cross-section of an as-polymerized copolymer particle.

Granule Technology). It allows the gas phase synthesis of heterophasic copolymers in free-flowing spherical form; the semicrystalline polymer is synthesized with the Ti-based isospecific heterogeneous catalyst, whereas the elastomeric polyolefin copolymer is prepared with the metallocene, in the gas phase. Both the metallocene and the alkylaluminoxane affect the polymerization reaction and copolymer molecular structure; catalyst activity and copolymer MW increase with the pressure, whereas they decrease with hydrogen concentration. The characterization of the as-polymerized particles pointed out that a good dispersion of the rubber into the PP granule has been achieved.

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