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Bimodal Poly(propylene) through Binary Metallocene Catalytic Systems as an Alternative to Melt Blending

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Summary: Propylene was polymerized by three homogenous metallocene catalytic systems: rac-Me_2Si $(Ind)_2ZrCl_2$ (CAT-1), rac-$Et(Ind)_2ZrCl_2$ (CAT-2) and rac-Me_2Si(2-Me-benzoind)$_2ZrCl_{22}ZrCl_2$ (CAT-3) at 50 °C. In function of the molecular-average weight results of poly(propylene)s obtained, rac-$Et(Ind)_2ZrCl_2$ (CAT-2) and rac-Me_2Si(2-Me-benzoind)$_2ZrCl_2$ (CAT-3) were combined in different proportions (wt %/wt %) of (CAT-2/CAT-3) for obtaining a new poly(propylene) with a bimodal molecular weight distribution consisting in clearly separated low and high molecular weight polymer fractions with a difference between them of an order of magnitude. The polymers obtained were compared with those coming from melt mixing of two poly(propylene)s with different molecular weights in an extruder. Both methods allow obtaining bimodal poly(propylene)s, but polymer melt blending shows partial miscibility effects and less crystallinity while binary catalytic systems have several advantages such as lower costs and easier to process that can be controlled to tailor properties together with intimate mixing of high and low molecular weight components.

Keywords: blends; catalysts; molecular weight distribution; poly(propylene) (PP)

Introduction

Since the discovery of stereoselective olefin polymerization in 1954,[1] and the development of poly(propylene) (PP) by Natta[2,3] using Ziegler type catalysts, PP has become in one the most commercially important thermoplastic, being the estimation of PP homopolymer for 2013 of 5000 Ktn.[4]

This growth in production is due to, the relatively low polymer cost that, in turn, can be attributed to low monomer cost and efficient polymerization technology. Also, PP has the ability to be processed at low cost and can be modified for a variety of applications.

With the development of metallocene catalytic systems, ansa C_2-symetric metallocene catalysts are one of the research topics that have received a great deal of attention in the last two decades. These catalysts are high- isoselective in propylene polymerization and have high activity, together with a degree of structural regularity (or irregularity) that can be varied over a wide range. These can not be achieved with the commercially used Ziegler-Natta catalysts, since they have several active sites and the PP obtained has a broad tacticity distribution. On the contrary, using homogeneous "single site" metallocene catalysts, the tacticity distribution is much narrower.[5] In addition, the synthesis of different PP steroisomers as a function of the relative distribution of methyl groups: isotactic, sindiotactic and atactic is also possible.

Apart from tacticity, in polypropylene processing it is important to take into acount the molecular weight (M_w) and the molecular weight distribution (MWD) that determine the properties and the applications. For example, in a numerous applications such as extrusion, blow moulding

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as well as packaging, polypropylene with wider or bimodal molecular weight distributions (BMWD's) is required[6]. It is generally known that M_w affects to the mechanical properties, while the MWD is responsible of the plastic rheology.[7–8] Polymers with a unimodal molecular weight distribution and low molecular weights will not have good strength and hardness, but will be easily processable.[9–12] But with high molecular weights the properties will be reverse. So, polymers with bimodal MWD are required in many applications because with both fractions of low and high molecular weight, is possible to get polymers with higher stiffness, strength, impact resistance and processability than the unimodal plastics.

Several methods have been proposed to produce polypropylene with BMWDs and controlled M_w. The first method consists in melt blending, where at least two different molecular weights polypropylenes are blended together before or during processing. The obtained blends usually contain high gel levels and consequently, miscibility problems can arise. The second method involves the use of multistage polymerization, where each reactor is maintained under different polymerization conditions. However, this method is not acceptable because it involves additional process and increases capital cost considerably. The third method consists in using two catalysts or a binary catalytic system in a single reactor with the subsequent cost saving. This last method typically comprises a combination of a heterogeneous Ziegler-Natta catalyst and a homogeneous metallocene catalyst providing a means to control the MWD and polydispersity of the polyolefin. A disadvantage of this particular binary system comes from triethyl-aluminium (TEA) used to activate Ziegler-Natta that has a serious detrimental effect on metallocene active sites.[13,14] Therefore, an economical and attractive route is to use two or more metallocene precursors simultaneously yielding a polypropylene mixture consisting of the polymer fractions produced by the different metallocenes individually.[15–17] In this sense, it is important to decide which catalytic sites with different kinetic responses, such as different propagation and termination rate constants are needed in order to produce a blend of polymeric chains with different predominant molecular weights.

The aim of this work is the production of bimodal polypropylene using three metallocene catalysts: rac-Me_2Si $(Ind)_2ZrCl_2$ (CAT-1), rac-$Et(Ind)_2ZrCl_2$ (CAT-2) and rac-$Me_2Si(2\text{-}Me\text{-}benzoind)_2ZrCl_2$ (CAT-3). Polypropylenes obtained with catalysts mixtures (binay catalytic systems) were compared with those resulting from the melt blending of polymer produced by each metallocene. Besides, the effect that the microstructure and the molecular weight have on the final properties exhibited by the polypropylenes will be discussed.

Experimental Part

Catalyst Preparation and Poly(propylene) Synthesis

Polymerization reactions were performed in a 2 L autoclave reactor filled with 1 L of n-heptane as diluent at 50 °C and keeping the MAO/metallocene ratio in 250.[18] The monomer consumption was followed by a mass-flow indicator in order to keep the reactor pressure at 2.5 bar during the polymerization. Constant polymerization conditions were ensured by sitting the solution at 600 r.p.m. After 30 minutes, polymerization reaction was stopped by depressurization and quenched by addition of acidified (HCl) methanol. Finally, the precipitated polypropylene was filtered and dried in an oven at 70 °C.

To obtain the binary catalytic systems two metallocene catalysts were mixed in a MAO/toluene solution with different compositions (wt %/wt %), i.e. 25/75, 50/50 and 75/25. On the other side, the melt blending was carried out by mixing polypropylenes produced by each metallocene catalyst. Polymer blends were prepared in a mini-extruder Hake minilab where different proportions of each polypropylene (25/75, 50/50 and 75/25 wt/wt) were mixed at 190 °C as processing temperature. The rotation speed of the spindles was 80 r.p.m. and the homogenization time was 4 minutes with the addition of 0.4% of Irganox stabilizing agent.

Characterization Techniques

The weight-average molecular weight of the polypropylenes obtained and molecular weight distribution were measured using a Water 150 C plus gel permeation chromatograph (GPC) equipped with a refractive index detector, using a set of a Polymer Plgel columns and 1, 2, 4-trichlorobenzene as solvent at 145 °C.

The melting temperature was measured using a METTLER-TOLEDO differential calorimeter model DSC822. Three runs (heating, cooling and second heating) were performed by a heating rate of 10 °C/min in the temperature range of −45 to 190 °C. The second heating was taken as a melting point.

The polypropylene isotacticity (%mmmm) was determined using ^{13}C-NMR spectra, which were recorded and measured on a Bruker AC300 spectrometer operating at 75 MHz and 100 °C.

Viscoelastic properties were measured with a Q800 (TA) dynamic mechanical analysis working in a tensile mode. The complex modulus and the loss tangent of each sample were determined at 0.1, 1 and 10 Hz over a temperature range from −140 to 150 °C, at a heating rate of 20 °C/min.

The determination of melt flow index (MFI) was measured using a CEAST plastometer equipment, consisting of a heated hopper, where the material flows though of a nozzle of 2 mm with a load applied of 2.16 Kg at 190 °C.

Results and Discussion

Individual Catalysts

Figure 1 shows the catalytic activity and the molecular weight distribution obtained for the three catalytic systems employed in this work.

The activity response of CAT-1 and CAT-2 seems to be similar, however CAT-3 shows a quite higher catalytic activity at the same conditions. This behaviour is due to the geometry of each catalyst. Dimethylsilylene-bridged bisindenylzirconocenes with substituents in 2- and 4- positions yield to high molecular weight isotactic polypropylene with important activity values.[19]

Table 1 show the results obtained from molecular characterization of the different metallocene iPP samples. The GPC curves show narrow molecular weight distributions, typical of single-site zirconocenes catalysts, with polydispersity index around 2–3. The thermal characterization shows a glass transition bellow 0 °C for all polypropylenes obtained, followed by the main melting endotherm, that appear at higher temperatures when the molecular weight and isotactic content increase. Consequently, higher crystallinity is also obtained for iPP-3.

As deduced from Table 1, iPP-1 and iPP-2 are very similar with low molecular weigh but high MFI indicating a good processability. So, they can be mixed with higher Mw like iPP-3 to get polypropylene containing both fractions in a broader molecular weight distribution which advantages where commented in the introduction section. As CAT-1 and CAT-2 are very similar, binary systems were done with CAT-2/CAT-3 mixed in different proportions.

Bimodal Poly(propylene)

Table 2 summarizes the characterization of polypropylenes obtained by CAT2/CAT3 binary systems and iPP2/iPP3 polypropylene blends prepared at three different proportions 25/75, 50/50 and 75/25.

Isotactic polypropylenes with a bimodal molecular weight distribution were obtained by the two methods (Figure 2a). Polymers obtained in an extruder present a bimodal MWD consisting of low and high molecular weight fractions as a function of the molecular weight of each polypropylene. Is possible to notice in the second melting (Figure 2b), the presence of a

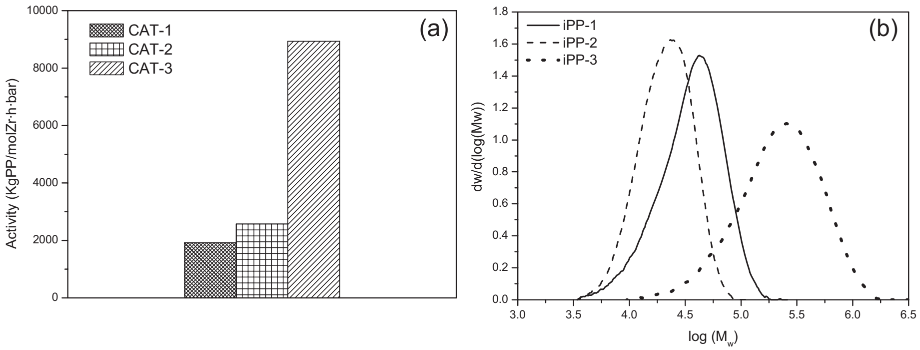

Figure 1.
(a) Catalytic activities and (b) molecular weight distributions of polypropylenes produced at 50 °C using metallocene catalytic systems.

Table 1.
Characterization of polypropylene obtained at 50 °C using metallocene catalytic systems.

	M_w (g/mol)	MWD	mmmm (%)	T_g (°C)	T_m (°C)	X_c (%)	$MFI_{2.16}$ (g/10min)
[iPP-1] rac-$SiMe_2$ $(Ind)_2$ $ZrCl_2$	42586	1.9	86	−10	139	47	500
[iPP-2] rac-$Et(Ind)_2ZrCl_2$	27594	1.7	89	−8	132	49	460
[iPP-3] rac-Me_2 Si(2-Me-benz[e]$Ind)_2$ $ZrCl_2$	256534	2.3	94	−6	146	51	2.5

Table 2.
Characterization of bimodal polypropylenes obtained by polymer blends iPP2/iPP3 and binary catalytic systems CAT-2/CAT-3.

Catalytic Systems	Activity (Kg PP/molZr*h*bar)	M_w (g/mol)	MWD	T_g (°C)	T_m (°C)	X_c (%)
iPP-2/iPP-3 (25/75)	–	150923	4.8	−6	145	50
iPP-2/iPP-3 (50/50)	–	150331	5.0	−4	143	47
iPP-2/iPP-3 (75/25)	–	105794	4.6	−5	143	49
CAT-2/CAT-3 (25/75)	4281	289847	3.0	−9	147	52
CAT-2/CAT-3 (50/50)	2767	264670	4.8	−10	147	53
CAT-2/CAT-3 (75/25)	3622	196206	5.0	−6	145	53

unique signal at a temperature between those of individual polymers, this may be taken as an evidence of partial miscibility, although it is not conclusive since the melting process could be influenced by the organization process during heating among other factors.[20] However, the dependency of the position of these peaks with proportions employed is variable. Careful observation of the endothermic curves, especially for 25/75 and 50/50 proportions reveals a partial miscibility that could be attributed to the melting of formed co-crystals. However, it would be necessary to carry out experiments such as isothermal crystallization to discriminate between the effect of nucleation due to the miscibility or a combined effect of nucleation of iPP-2 or iPP-3 during crystallization.

On the other hand, bimodal polypropylene is obtained by the combination of CAT-2 and CAT-3. In this case, the activity of each catalyst (Table 2) is an important variable for obtaining a polymer with low and high molecular weight fractions with desired properties.

When the binary catalytic systems are added to the reactor, under the same

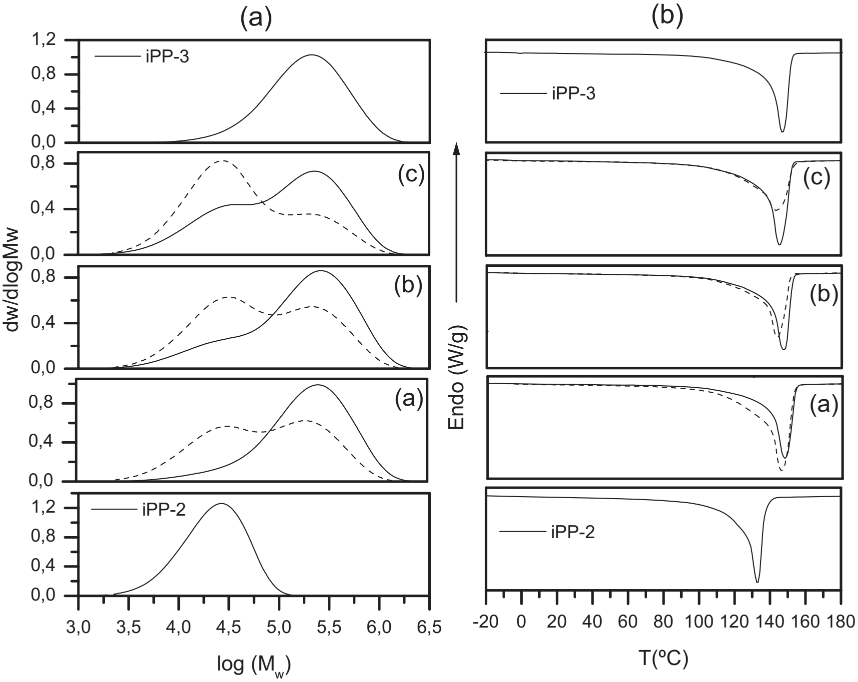

Figure 2.

a) Molecular weight distributions and b) melting thermograms of polypropylenes obtained by binary catalytic systems (—) and polymer blends (—) iPP-2/iPP-3 at three different proportions: (a) 25/75, (b) 50/50 and (c) 75/25.

polymerization conditions, the activity obtained was the expected respect to the individual metallocene catalysts. In the same way, the evolution of low and high molecular weight fractions depends of each catalyst individually and the proportion employed, being higher the contribution of the fraction corresponding to the polypropylene produced by CAT-3 in all proportions since it, presents higher weight-average molecular weight. However, the contribution of the polypropylene from CAT-2 begins to appear when the proportion is above of 50%. In addition, in all cases, one melt temperature peak is obtained.

The relaxation process observed in a conventional isotactic polypropylene shows the presence of three relaxation,[21] labelled as γ, β and α, in order of increasing temperatures.

Figure 3 (a) shows the storage and loss moduli and tanδ at 1 Hz for the polypropylene obtained by individual catalytic systems. It can be seen that storage moduli measured at 23 °C is lower for the iPP-3, which presents higher molecular weight. In comparison, for the same reason, attending to the values summarized in Table 3, higher values are obtained for polypropylene blend at 50/50 proportion.

The temperatures for the different transitions are shown in Table 3. The γ relaxation, attributed to local motions of methyl groups within the amorphous phase, appears as a broad relaxation process in the tanδ plot and it seems to be at slightly lower temperatures at lower molecular weights. The glass transition (β relaxation), for both unimodal polypropylenes, presents the maximum around 15 °C, a slight shift to higher temperatures is observed as molecular weight increases. Finally, the crystalline α transition, related to the defects diffusion within the crystal, is dependent on molecular weight, moving to slightly higher

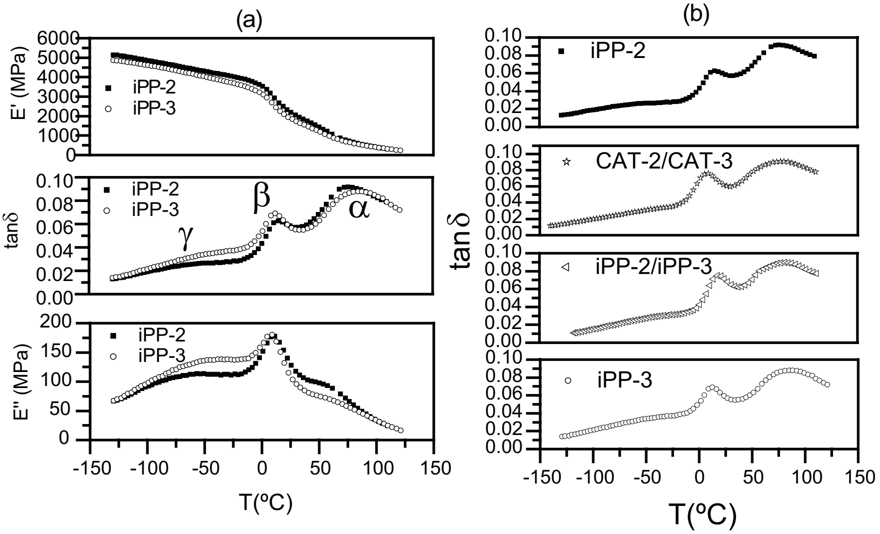

Figure 3.
(a) Temperature dependence of E', E'' and Tan δ of the polypropylenes obtained by individual metallocene catalysts; (b) Comparison of the mechanical properties of the polypropylenes obtained by binary catalytic systems and polymer blends.

temperature for iPP-3 with the higher molecular weight, due to its higher crystallinity that hinders motions within crystalline regions.

According to the apparent activation energies determined from tanδ assuming an Arrhenius behaviour, those relaxations are not very sensitive to the molecular weight in the range studied. Finally, the values presented in Table 3 corresponding to the individual catalysts in comparison with the binary system and the polymer blend studied show a lower crystallinity, so a less amorphous phase, for samples melt in an extruder respect to the binary systems and consequently present a decreasing in the intensity of β relaxation.

Conclusion

Through the preparation of binary catalytic systems, in which each catalyst produces polypropylenes with molecular weights having a difference between them of an order of magnitude, is possible to obtain polypropylenes with modified final properties. On the other hand, the use of an extruder for carrying out this kind of polymer blends results in problems of miscibility. This polypropylene blends present less crystallinity respect to the polypropylene obtained by binary catalytic systems, so higher storage moduli and lower intensity of the β relaxation. Therefore, binary catalytic systems allow obtain-

Table 3.
Temperature of the different relaxations and apparent activation energies calculated from tanδ.

	T_γ (°C)	T_β (°C)	T_α (°C)	É (MPa) 23 °C	ΔH_γ (KJ/mol)	ΔH_β (KJ/mol)	ΔH_α (KJ/mol)
[iPP-2] rac-Et(Ind)$_2$ZrCl$_2$	−57	15	79	2107	147	>400	274
CAT-2/CAT-3 (50/50)	−53	9	77	1648	141	>400	200
iPP-2/iPP-3 (50/50)	−55	7	76	1829	135	>400	215
[iPP-3] rac-Me$_2$ Si(2-Me-benz[e]Ind)$_2$ ZrCl$_2$	−46	13	85	1963	163	>400	261

ing new polypropylenes with tailored properties. Moreover, there are many advantages of using this method to produce a bimodal polypropylene in comparison with melt mixing of polypropylenes with different molecular weights, such as lower investment costs, less process complexity, intimate mixing of high and low molecular weight components (improved product quality) and simplified start-ups and shutdowns (less preparation stages).

[1] K. Ziegler, E. Holkamp, H. Breil, *Angew. Chem.* **1995**, *67*, 541.

[2] H. Sinn, W. Kaminsky, H. J. Vollmer, W. Rüdiger, *Angew. Chem. Int. Ed.* **1980**, *19*, 390.

[3] W. Kaminsky, *Macroml. Chem. Phys.* **1996**, *197*, 3907.

[4] AMI Consulting (Applied Market Information) 2009.

[5] J. T. Xu, L. X. Feng, *Eur. Polym. J.* **1999**, *35*, 1289.

[6] J. R. Severn, J. C. Chadwick, *Tailor made polymers: via immobilization of alpha-olefin polymerization catalysts*, Wiley - VCH Verlag GmbH & Co, KGaA Weinheim **2008**, 352.

[7] H. Mark, *Encyclopedia of Polymer Science and technology*, 3rd ed. Wilwy-Interscience New Jersey, **2033**, Vol.2.

[8] K. Premphel, W. Paecharoechal, *J. Appl. Polym. Sci.* **2002**, *85*, 2412.

[9] K. Soga, M. Terano, Catalyst Design for tailor-made polyolefins. *Elservier* **1994**.

[10] M. Sugimoto, Y. Masubuchi, J. Taimoto, K. Koyama, *Macromolecules* **2001**, *34*, 6056.

[11] F. Rodriguez, *Principle of Polymer Systems, 2nd ed. McGrawHill*, **1983**.

[12] E. Laiho, *Eur. Pat. Appl.* **2004**, *878*, 1449.

[13] C. L. P. Shan, J. B. P. Soares, *Polymer* **2002**, *43*, 7345.

[14] T. O. Ahn, S. C. Hong, W. S. Hugh, Y. C. Lee, D. H. Lee, *Polym. Eng. Sci.* **1999**, *29*, 1257.

[15] A. Tynys, T. Saarinen, M. Bartke, B. Lofgren, *Polymer* **2007**, *48*, 1893.

[16] A. Ahlers, W. Kaminsky, *Makromol. Chem. Rapid. Commun.* **1988**, *9*, 457.

[17] L. Dagnillo, J. B. P. Soares, A. Pendilis, *J. Polym. Sci. Polym. Chem.* **1998**, *36*, 831.

[18] W. Kaminsky, *Metallocene Catalysis. A. Applied Catalysis A: General* **2001**, *47*, 222.

[19] S. Jüngling, S. Koltzenburg, R. Mülhaupt, *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 1.

[20] M. L. Aran, J. J. Sánchez, A. J. Müller, *Polymer* **2001**.

[21] C. Joyrdan, J. Y. Cavaille, J. Perez, *J. Polym. Sci. Part B Polym. Phys.* **1989**, *27*, 2361.