Supporting information for:

Structure-Property Correlations in Polypropylene from Metalloocene Catalysts: Stereodefective, Regioregular Isotactic Polypropylene

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Experimental section

Propylene polymerization with MAO-activated catalysts in liquid propylene.

All propylene polymerizations have been performed in liquid propylene at polymerization temperatures between 30 and 70 °C with MAO-activated metalloccenes. Some of the MAO-activated complexes were also supported on porous polyethylene or polypropylene spheres, as previously described (Covezzi, M.; Fait, A. (Basell Italy) PCT Int. Appl. WO 01/44319, 2001).
The melting temperatures were obtained with a differential scanning calorimeter (DSC) Perkin Elmer DSC-7 performing scans in a flowing N\textsubscript{2} atmosphere and heating rate of 10 °C/min.

The intrinsic viscosities were measured in 1,2,3,4-tetrahydronaphtalene solutions at 135 °C, using standard Ubbelohde viscosimeter. The average molecular weights of i-PP samples were obtained from their intrinsic viscosity values according to $[\eta] = K(\overline{M})^\alpha$, with $K = 1.93 \times 10^{-4}$ and $\alpha = 0.74$ (Moraglio, G.; Gianotti, G.; Bonicelli, U. Eur. Polym. J. 1973, 9, 693).

The microstructures of chains of the i-PP samples were determined by solution $^{13}\text{C}$ NMR analysis. $^{13}\text{C}$ NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode, at 120 °C. The samples were prepared by dissolution of 40 mg of polymer in 0.5 mL of 1,1,2,2-tetrachloroethane-$d_2$ at 120 °C. The peak of $\text{mmmnn}$ pentad (21.8 ppm) was used as internal reference. Each carbon spectrum was acquired with a 90° pulse, 12 seconds of delay between pulses and CPD (waltz 16) to remove $^1\text{H}$-$^{13}\text{C}$ coupling. About 3000 transients were stored in 32K data points using a spectral window of 60 ppm. Statistical modeling of pentad distributions of the samples was satisfactorily done using a model based on enantiomorphic site control, where the probability of insertion of the monomer with the correct enantioface is indicated with $b$.

**Structural Characterization.** The various i-PP samples were isothermally crystallized from the melt at different temperatures. As-prepared samples were melted at 200 °C and kept for 5 min at this temperature in a N\textsubscript{2} atmosphere; they were then rapidly cooled to the crystallization temperature, $T_c$, and kept at this temperature, still in a N\textsubscript{2} atmosphere, for a time $t_c$ long enough to allow complete crystallization at $T_c$. The samples were then rapidly cooled to room temperature and analyzed by X-ray diffraction and DSC. In the various isothermal crystallizations, the crystallization time $t_c$ is different depending on the crystallization temperature. The shortest time is 24 h for the lowest crystallization temperature and increases with increasing the crystallization temperature, up to two weeks for the highest crystallization temperature. As a further check that in any experiment the crystallization time is long enough to complete the crystallization at the temperature $T_c$, and no appreciable crystallization occurs during the cooling to room temperature, we have verified that the melting temperature of each sample increases regularly with increasing $T_c$ and that in the
corresponding DSC melting curve of the crystallized sample, besides the melting peak, no broad endotherms are present at lower temperatures due to the melting of materials possible crystallized during the quenching from $T_c$ to room temperature.

Oriented fibers of the i-PP samples have been obtained by stretching at room temperature and at drawing rate of 10 mm/min compression molded samples. Compression-molded samples have been prepared by heating powder samples at temperatures higher than the melting temperatures under a press at low pressure, and slowly cooling to room temperature.

X-ray diffraction patterns were obtained with Ni filtered CuKα radiation. The powder profiles were obtained with an automatic Philips diffractometer, whereas the fiber diffraction patterns were recorded on a BAS-MS imaging plate (FUJIFILM) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800). The X-ray fiber diffraction patterns have been recorded for stretched fibers soon after the stretching and keeping the fiber under tension, as well as for relaxed fibers, that is, after keeping the fiber under tension for two hours and then removing the tension allowing the complete relaxation of the specimens.

The relative amount of crystals in the $\gamma$ form present in our samples was measured from the X-ray diffraction profiles, by measuring the ratio between the intensities of the $(117)_\gamma$ reflection at $2\theta = 20.1^\circ$, typical of the $\gamma$ form, and the $(130)_\alpha$ reflection at $2\theta = 18.6^\circ$, typical of the $\alpha$ form: $f_\gamma = I(117)_\gamma/[I(130)_\alpha + I(117)_\gamma]$. The intensities of $(117)_\gamma$ and $(130)_\alpha$ reflections were measured from the area of the corresponding diffraction peaks above the diffuse amorphous halo in the X-ray powder diffraction profiles. The amorphous halo has been obtained from the X-ray diffraction profile of an atactic polypropylene, then it was scaled and subtracted to the X-ray diffraction profiles of the melt-crystallized samples.

The index of crystallinity $x_c$ was evaluated from the X-ray powder diffraction profiles by the ratio between the crystalline diffraction area ($A_c$) and the total area of the diffraction profile ($A_t$), $x_c = A_c/A_t$. The crystalline diffraction area has been obtained from the total area of the diffraction profile by subtracting the amorphous halo.
Mechanical Characterization. Mechanical tests have been performed at room temperature on compression-molded films and oriented fibers with a miniature mechanical tester apparatus (Minimat, by Rheometrics Scientific), following the standard test method for tensile properties of thin plastic sheeting ASTM D882-83. Compression-molded films have been prepared by heating powder samples at temperatures higher than the melting temperatures between perfectly flat brass plates under a press at very low pressure, and slowly cooling to room temperature. Special care has been taken to obtain films with uniform thickness (0.3 mm) and minimize surface roughness, according to the recommendation of the standard ASTM D-2292-85.

Mechanical tests have been first performed on the unstretched compression-molded films. Rectangular specimens 10 mm long, 5 mm wide and 0.3 mm thick have been stretched up to the break or up to a given deformation $\varepsilon = [(L_f - L_0)/L_0] \times 100$, where $L_0$ and $L_f$ are the initial and final lengths of the specimen, respectively. Two bench marks were placed on the test specimens and used to measure elongation.

Similar tests have been then performed at room temperature on the strained and then stress-relaxed fibers. Stress-relaxed fiber specimens have been prepared by stretching the compression molded films of initial length $L_0$ up to a strain of 500% (final lengths $L_f = 6L_0$), keeping the fibers under tension for ten minutes at room temperature, then removing the tension, allowing the specimens to relax to the final length $L_r$.

Values of tension set and elastic recovery were measured according to the standard test method ASTM D412-87. The specimens of initial length $L_0$ were stretched up to a length $L_f$, i.e. up to the deformation $\varepsilon = [(L_f - L_0)/L_0] \times 100$, and held at this elongation for ten minutes, then the tension was removed, and the final length of the relaxed specimens $L_r$ was measured after 10 minutes. The tension set was calculated by using the following formula: $t_s(\varepsilon) = [(L_f - L_0)/L_0] \times 100$, whereas the elastic recovery was calculated as $r(\varepsilon) = [(L_f - L_0)/L_r] \times 100$.

Mechanical cycles of stretching and relaxation have been performed at room temperature on the stress-relaxed fibers and the corresponding hystereses have been recorded. In these cycles the stress-relaxed fibers of i-PP samples, having the new initial length $L_r$, have been stretched up to the final
lengths \( L_f = 6L_0 \), i.e. up to the elongation \( \varepsilon = [(L_f - L_0)/L_0] \times 100 \), and then relaxed at controlled rate. After each cycle, the values of the tension set have been measured. The final length of the relaxed specimens \( L_r' \) has been measured ten minutes after the end of the relaxation step and the tension set has been calculated as: \( t_s(\varepsilon) = [(L_r' - L_r)/L_r] \times 100 \).

Values of tension set and elastic recovery have also been measured on unoriented compression-molded films of elastomeric samples after breaking. Specimens of initial length \( L_0 \) have been stretched up to the break, i.e. up to the elongation \( \varepsilon_b = [(L_f - L_0)/L_0] \times 100 \). Ten minutes after breaking the two pieces of the sample have been fit carefully together so that they are in contact over the full area of the break and the final total length \( L_r \) of the specimen has been obtained by measuring the distance between the two bench marks. The tension set \( t_b \) and the elastic recovery \( r_b \) after breaking have been calculated as: \( t_b = [(L_r - L_0)/L_0] \times 100 \) and \( r_b = [(L_f - L_r)/L_r] \times 100 \), respectively.

In the mechanical tests the ratio between the drawing rate and the initial length was fixed equal to 0.1 mm/(mm×min) for the measurement of Young’s modulus and 10 mm/(mm×min) for the measurement of stress-strain curves and the determination of the other mechanical properties (stress and strain at break and tension set).

The values of the mechanical properties are reported in the Table S1. All the reported values are averaged over at least five independent experiments.
Table S1. Young’s modulus ($E$), stress ($\sigma_b$) and strain ($\varepsilon_b$) at break, stress ($\sigma_y$) and strain ($\varepsilon_y$) at the yield point, tension set ($t_b$) and elastic recovery ($r_b$) at break, and crystallinity ($\chi_c$) of unoriented compression molded films of i-PP prepared with catalysts of Charts 1 and 2, evaluated from the stress-strain tests.a

<table>
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<tr>
<th>Samples</th>
<th>Catalyst</th>
<th>mmmm %</th>
<th>rr %</th>
<th>$M_v$</th>
<th>$E$ (MPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\varepsilon_y$ (%)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
<th>$t_b$ (%)d</th>
<th>$r_b$ (%)d</th>
<th>$\chi_c$ (%)</th>
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<tr>
<td>iPP1</td>
<td>1/MAO</td>
<td>97.55</td>
<td>0.49</td>
<td>195700</td>
<td>198±32</td>
<td>17±2</td>
<td>16±2</td>
<td>22±3</td>
<td>310±50</td>
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<tr>
<td>iPP8</td>
<td>9/MAO/PE</td>
<td>87.61</td>
<td>2.54</td>
<td>106000</td>
<td>125±24</td>
<td>21±4</td>
<td>32±8</td>
<td>23±2</td>
<td>250±24</td>
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<td>-</td>
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<tr>
<td>iPP9</td>
<td>7/MAO/PP</td>
<td>82.19</td>
<td>3.70</td>
<td>202400</td>
<td>70±6</td>
<td>17±3</td>
<td>45±7</td>
<td>20±8</td>
<td>356±56</td>
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<td>-</td>
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<td>iPP10</td>
<td>4/MAO</td>
<td>73.91</td>
<td>5.52</td>
<td>505800</td>
<td>90±9</td>
<td>12±3</td>
<td>20±5</td>
<td>14±2</td>
<td>454±50</td>
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<td>-</td>
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<td>iPP11</td>
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<td>72.17</td>
<td>5.92</td>
<td>210900</td>
<td>64±6</td>
<td>12±1</td>
<td>65±1</td>
<td>16±2</td>
<td>1248±96</td>
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<td>-</td>
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<td>27±6</td>
<td>10±2</td>
<td>48±6</td>
<td>22±4</td>
<td>850±140</td>
<td>580±92</td>
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<td>11.01</td>
<td>123400</td>
<td>19±4</td>
<td>9±1</td>
<td>109±46</td>
<td>32±4</td>
<td>1787±214</td>
<td>381±3</td>
<td>292±10</td>
<td>42</td>
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</table>

a) The contents of fully isotactic pentad $mmmm$ and $rr$ defects and the molecular masses ($M_v$) of the samples are also reported.