Electronic Supplementary Information (ESI)

Tailoring properties of polypropylene in the polymerization reactor using polymeric nucleating agents as prepolymer on the Ziegler-Natta catalyst granule.

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Experimental.

Three iPP samples (iPP-0, iPP-PTMAS and iPP-PVCH) have been prepared in the laboratory of Basell Polyolefins (Ferrara, Italy) with Ziegler-Natta (ZN) catalysts composed of $MgCl_2/TiCl_4$/ID + $(C_2H_5)_3Al$/ED (ID = internal donor, ED = external donor), with diisobutylphthalate as the internal donor in combination with dicyclopentyl dimethoxy silane as external donor. The sample iPP-0 is a neat iPP prepared with the mentioned catalyst without nucleating agent, whereas the samples iPP-PTMAS and iPP-PVCH have been prepared with the same catalyst and polymerization condition but using trimethylallylsilane and vinylcyclohexane, respectively, as monomer in the prepolymerization step before the polymerization of propene, producing a skin of isotactic poly(trimethylallylsilane) (PTMAS) or poly(vinylcyclohexane) (PVCH), respectively, on the catalyst particles. The procedures for the preparation of phthalate-based solid catalyst and of the prepolymerized catalyst and for the polymerization of propylene are reported in the following sections.

Preparation of the phthalate-based solid catalyst component from the spherical adduct.

At room temperature and under nitrogen atmosphere, 300 ml of $TiCl_4$ were introduced into a 500 ml round bottom flask, equipped with mechanical stirrer, cooler and thermometer. After cooling to 0°C, while stirring, diisobutylphthalate (DIBP) and 9.0 g of the spherical $MgCl_2$ ethanol adduct (prepared as described in Example 2 of ref. S1) were sequentially added into the flask. The amount of charged DIBP (internal donor) was such to have a Mg/donor molar ratio of 8.

The temperature was raised to 100 °C and maintained for 2 hours. Thereafter, stirring was stopped, the solid product was allowed to settle and the supernatant liquid was siphoned off at 100 °C.

After removing the supernatant, additional fresh $TiCl_4$ was added to reach the initial liquid volume again. The mixture was, then, heated at 120°C and kept at this temperature for 1 hour.

Stirring was stopped again, the solid was allowed to settle and the supernatant liquid was siphoned off. The solid was washed with anhydrous hexane six times in temperature gradient down to 60 °C and one time at room temperature.

The obtained solid was then dried under vacuum and analysed for composition. Data are reported in Table S1.

Table S1. Neat and prepolymerized catalyst compositions

	Mg (wt %)	**Ti (wt %)**	**DIBP wt (%)**	**Solvent (wt %)**	**Prepolymer/catalyst[a] weight ratio**
neat catalyst	18.8	2.1	6.9	6.3	-
TMAS-prepolymer	13.6	1.4	nd [b]	3.8	1.4
VCH-prepolymer	12.7	1.2	nd [b]	2.0	1.5

[a]) prepolymer conversion measured from Mg content and expressed as gram of prepolymerized catalyst per gram of neat catalyst.

[b]) nd = not determined.

Preparation of the prepolymerized catalysts

Into a 1 L reaction vessel, purged with nitrogen and equipped with thermometer and stirrer, 10 g of the phthalate-based solid catalyst component is suspended in 143 mL of i-hexane at 10 °C. Then, 2 g of triethyl aluminum (as solution 10 %wt in i-hexane) is added, to have an Al/Ti molar of 4 (calculated from the titanium on the catalyst).

The suspension is kept at 10 °C for 30 minutes under stirring. After this, 10 g of trimethyl-allyl-silane (TMAS) is added drop wise into the reaction vessel, over a 15 minutes period and the temperature was allowed to rise to 50 °C. The monomer is then polymerized to poly(trimethyl-allyl-silane) (PTMAS)at 50 °C for 4 h, under stirring.

After this time, stirring was stopped and the solid was allowed to settle and the supernatant liquid was siphoned off. Fresh i-hexane was added to the remaining solid and stirring was started again to wash the solid at ambient temperature. Stirring was stopped again, the solid was allowed to settle, and the liquid was siphoned off.

Subsequently, the solid was dried under vacuum at 30 °C and analysed. All these operations were carried out under nitrogen atmosphere using anhydrous solvent in order to avoid the poisoning of prepolymerized catalyst.

Available data on the PTMAS-prepolymerized catalyst, including the conversion in terms of prepolymerized catalyst amount obtained per gram of initial catalyst (calculated from magnesium content of the solid catalyst before and after prepolymerization), are reported in Table S1.

The vinyl-cyclohexane (VCH) prepolymerized catalyst was prepared following exactly the same procedure described above, 10 g of vinyl-cyclohexane were used. Data obtained on VCH-prepolymerized catalyst are reported in Table S1.

General procedure for the polymerization of propylene

A 4–litre steel autoclave equipped with a stirrer, pressure gauge, thermometer, catalyst feeding system, monomer feeding lines and thermostating jacket, was purged with nitrogen flow at 70 °C for one hour. A suspension containing 75 ml of anhydrous hexane, 0.76 g of triethyl aluminum (6.66 mmol), 0.33 mmol of dicyclopentyldimethoxysilane as external donor and 0.006 ÷ 0.010 g of solid catalyst component, previously precontacted for 5 minutes, was charged.

The autoclave was closed and 1150 mL of hydrogen was added. Then, under stirring, 1.2 kg of liquid propylene was fed. The temperature was raised to 70°C in about 10 minutes and the polymerization was carried out at this temperature for 2 hours. At the end of the polymerization, the non-reacted propylene was removed; the polymer was recovered and dried at 70 °C under vacuum for 3 hours. Then the polymer was weighed and characterized. The condition of polymerization and data on the characterization of polymer samples are reported in Table S2.

Table S2. Polymerization of propene with either neat or prepolymerized ZN catalysts (at 70 °C for 2 h), concentration of PTMAS and PVCH nucleating agents on the catalyst particle, melt flow rate (MFR), crystallization temperature form the melt (T_c) and melting temperature of the melt-crystallized samples (T_m) of the so-obtained iPP samples.

sample	**Monomer in prepolymerization**	**MFR[a] (g/10min)**	**[PTMAS] or [PVCH][b] (ppm)**	**[*mmmm*][c] (%)**	**T_c [d] (°C)**	**T_m[d] (°C)**
iPP-0	-	1.4	-	97.5	108	168
iPP-PTMAS	trimethylallylsilane	0.75	14	97.6	117	168
iPP-PVCH	vinylcyclohexane	1.2	34	97.5	124	168

[a]) The melt flow rate was measured at 230 °C subjecting the samples to a weight of 2.16 kg.

[b]) The concentration of PTMAS and PVCH in the iPP samples were estimated indirectly, by analyzing the catalyst particles immediately after polymerization of trimethylallylsilane and vinylcyclohexane.

[c]) The *mmmm* pentad concentration was measured via ^{13}C NMR on the xylene Insoluble fraction.

[d]) The melting temperature (T_m) and the crystallization temperature form the melt (T_c) were measured from DSC heating and cooling curves at scanning rates of 10 °C/min.

Characterization

The stereoregularity of the iPP samples in term of concentration of the fully isotactic pentad *mmmm* were determined by solution ^{13}C NMR analysis.

The melting and crystallization temperatures were obtained with a differential scanning calorimeter Mettler Toledo DSC-1 performing scans in a flowing N_2 atmosphere and heating or cooling rates of 10 °C/min.

Unoriented films of iPP samples used for structural analysis and mechanical tests have been obtained by compression molding of as-prepared samples. All samples have been slowly crystallized from the melt in the conventional α and β forms, or rapidly quenched from the melt at 0 °C. Powders samples have been heated at 200 °C between perfectly flat brass plates under a press at very low pressure, kept at 200 °C for 10 min, and then crystallized by slow cooling at 10 °C/min to room temperature, or by fast quenching in a bath at 0 °C.

The indices of crystallinity (x_c) were 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. The scattering of the amorphous phase has been obtained from the X-ray diffraction profile of an atactic polypropylene, after scaling for a suitable factor. The values of the degree of crystallinity are reported in Table S3.

X-ray powder diffraction profiles have been obtained with Ni filtered CuKα radiation with an automatic diffractometer X'Pert by Panalytical.

Mechanical tests have been performed at room temperature on compression-molded films slowly crystallized in the α or β forms, or rapidly crystallized by quenching at 0 °C in the mesophase or in the α form, with a universal mechanical tester Zwicky by Zwick Roell, following the standard test method for tensile properties of thin plastic sheeting ASTM D882-83. Rectangular specimens 10 mm long, 5 mm wide and 0.3 mm thick have been stretched up to the break. Two benchmarks have been placed on the test specimens and used to measure the deformation $\varepsilon = 100(L_f - L_0)/L_0$, where L_0 and L_f are the initial and final lengths of the film, respectively. 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 others mechanical parameters.

The values of the mechanical parameters evaluated form the stress-strain curves for samples slowly crystallized from the melt by cooling at 10 °C/min in the α or β forms or rapidly crystallized by quenching the melt at 0 °C in the mesophase or in the α form, are reported in the Table S2. The reported values of the mechanical properties are averaged over at least five independent experiments.

Thins films (90-120 μm thick) of the iPP samples have been prepared for AFM experiments and slowly crystallized in α or β forms or quenched at 0 °C in the mesophase or in the α form. Small amounts of the powder samples have been sandwiched between glass cover slips, melted at ≈200 °C and then crystallized by slow cooling to room temperature at 10 °C/min or by fast quenching at 0 °C. Atomic force microscopy images have been obtained operating in tapping mode at room temperature with a Veeco Caliber microscope using standard silicon cantilevers TESP-MT and a resonant frequency and force constant of about 250kHz and 50Nm^{-1}, respectively. Height and phase images have been recorded.

References

S1) M. Sacchetti, G. Govoni, A. Fait, *Magnesium dichloride-alcohol adducts, process for their preparation and catalyst components obtained therefrom*. Patent WO 1998 044009 A1, Montell Technology Company B.V. **1998.**

Table S3. Elastic modulus (*E*), stress (σ_b) and strain (ε_b) at break, stress (σ_y) and strain (ε_y) at the yield point, crystalline form and X-ray crystallinity (x_c) of unoriented compression molded films of samples iPP-0, iPP-PTMAS and iPP-PVCH crystallized by slow cooling from the melt and by fast quenching of the melt at 0 °C.

sample	**Monomer in prepolymerization**	**Condition of crystallization**	**Crystalline form**	x_c **(%)**	*E* **(MPa)**	σ_y **(MPa)**	ε_y **(%)**	σ_b **(MPa)**	ε_b **(%)**
iPP-0	-	Slow cooling	α	65	530 ± 30	-	10 ± 1	37 ± 1	16 ± 2
iPP-0	-	Quenching at 0 °C	Mesophase	40	380 ± 10	18 ± 2	10 ± 1	32 ± 3	810 ± 70
iPP-PTMAS	trimethylallylsilane	Slow cooling	$\alpha + \beta$	66	660 ± 90	36 ± 1	10 ± 1	32 ± 1	580 ± 60
iPP-PTMAS	trimethylallylsilane	Quenching at 0 °C	α	50	550 ± 20	31 ± 3	10 ± 1	36 ± 3	900 ± 100
iPP-PVCH	vinylcyclohexane	Slow cooling	α	65	650 ± 50	-	-	32 ± 1	14 ± 2
iPP-PVCH	vinylcyclohexane	Quenching at 0 °C	α	56	500 ± 50	30 ± 1	14 ± 1	39 ± 5	1100 ± 200