Propylene−Styrene Multiblock Copolymers: Evidence for Monomer Enchainment via Opposite Insertion Regiochemistry by a Single-Site Catalyst

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ABSTRACT: Polymerization of propylene promoted by the post-metallocene catalyst **1** and methylaluminoxane (MAO) produces oligomers containing prevailingly unsaturated chain ends which are diagnostic of a primary (1,2) regiochemistry of insertion. The styrene polymerization in the presence of propylene produces multiblock copolymers containing long isotactic styrene sequences interrupted by short isotactic propylene strings. The microstructure of these copolymers elucidated by ^{13}C NMR analysis shows that the opposite regiochemistry of insertion of the two monomers is retained in the copolymerization, producing tail-to-tail and head-to-head linkages between the homopolymer blocks.

Introduction

Ethylene, propylene, and styrene are important chemical commodities used extensively in the manufacturing of polymers with a large spectrum of applications. The molecular weight, the chemical structure, and the stereochemistry of the repetitive units are important characteristics that strongly influence the polymer physical properties and thus its industrial applicability. No less important are the copolymers that could have different properties depending on the composition and distribution of the monomers in the polymeric chain. Copolymerization of ethylene with propylene was performed in the late 1950s by Natta and co-workers[1] using homogeneous vanadium catalysts, producing materials which are now important thermoplastic elastomers. The development of new catalytic systems based on group 4 *ansa*-metallocenes[2] in the mid-1980s allowed not only a more precise control of the microstructure in the ethylene−propylene[3] copolymers, but also the synthesis of ethylene−styrene copolymers with a large variety of compositions and structures[4] and with properties ranging from amorphous elastomers to crystalline thermoplastics. However, even in the presence of the most active metallocenes toward styrene and propylene homopolymerization, the propylene−styrene copolymerization has been elusive. The explanation of this behavior can be ascribed to the opposite regiochemistry of insertion of these two monomers in the metal−polymeric chain bond: the secondary (2,1) insertion of the styrene unit after a propylene unit which has been inserted with primary (1,2) regiochemistry prevents further chain growth. To overcome this problem, Oliva and co-workers elegantly used small amounts of ethylene in propylene−styrene copolymerization to reactivate the catalytic center after the styrene insertion.[5] More recently, the search of new active catalysts for the synthesis of new polyolefin-based materials has rapidly expanded, providing access to unprecedented polymer architectures.[6] We recently developed a new class of group 4 metal catalyst precursors which incorporate a tetradentate ligand having two phenoxo units linked through a 1,ω-dithiaalkanediyl bridge $S(CH_2)S_n$ (n = 2 and 3).[7] In particular, titanium catalyst having two carbons in the ligand bridge (Figure 1) possesses a C_2-symmetric structure and is very active toward isotactic polymerization of styrene, 4-methyl-1,3-pentadiene,[8] and ethylene−styrene copolymerization.[9]

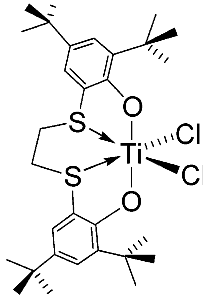

Figure 1. Dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenoxy)}titanium (**1**).

Ethylene homopolymerization results into the production of branched polyethylenes[10] due to the concomitant production, by β-hydride abstraction, of higher α-olefins, which are copolymerized with ethylene. In this article we report on the propene polymerization behavior of this catalyst and the synthesis of *i*PS-*block*-*i*PP-*block*-*i*PS and their complete characterization by ^{13}C NMR.

Results and Discussion

In Figure 2 the ^{13}C NMR spectrum of polypropylene produced in the presence of the above-mentioned catalyst and methylaluminoxane (MAO) is reported.

As can be noted, this polymer has a stereoirregular microstructure; its low molecular weight makes the signals due to the chain-end groups clearly visible[11] (see Chart 1): saturated n-propyl (**1**) and isobutyl (**2**) end

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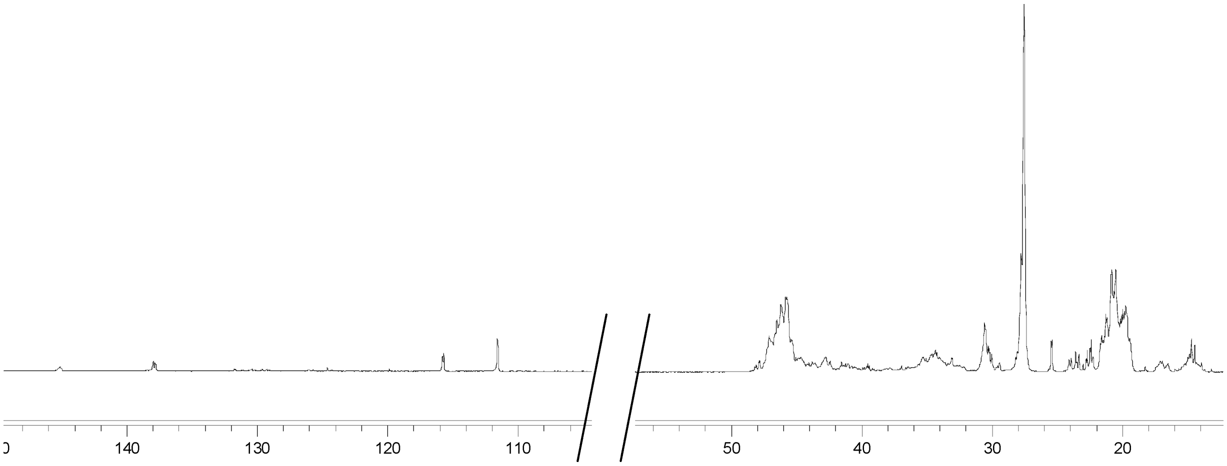
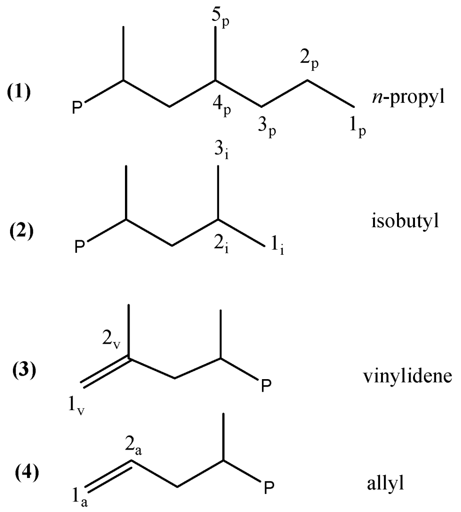


Figure 2. ^{13}C NMR spectrum of polypropylene sample synthesized in run 1.

Chart 1: Polypropylene Chain End Groups Present in the Polypropylene Sample Synthesized in Run 1[a]



Carbon atom	^{13}C NMR chemical shifts (ppm relative to TMS)
1_p	14.7
2_p	20.1
3_p	h
4_p	h
5_p	h
1_i	22.4
2_i	25.5
3_i	23.7
1_v	111.6
2_v	145.1
1_a	115.8
2_a	137.9

[a] h indicates signals not identified or hidden by other signals.

Table 1: Propylene Homopolymerization and Propylene−styrene Copolymerization in the Presence of 1/MAO

entry[a]	M_w ($\times 10^3$)	M_w/M_n	T_m (°C)	yield (g)	propylene content (%)[h]
1[b]	1.3	1.4		14.8	100
2[c]	33	1.9	171/192	4.5	4.2
3[d]	2.1	1.6		0.9	33.4
4[c,e]	27	2.3	166/192	2.9	5.3
5[c,f]	60	2.4	173/197	8.2	1.2
6[c,g]	34	2.4	165/193	6.1	6.6

[a] [Ti] = 2.5 × 10^{-5} mol; Al/Ti = 500; t = 2 h. [b] Propylene pressure 6 bar; T = 25 °C. [c] Propylene pressure 1 bar, styrene 20 mL; T = 25 °C. [d] Propylene pressure 6 bar, styrene 20 mL; T = 25 °C. [e] T = 0 °C. [f] T = 70 °C. [g] T = 25 °C; Al/Ti = 1000. [h] From ^{13}C NMR spectroscopy.

groups are diagnostic of the primary insertion of propylene into the metal−hydride bond or metal−methyl bond, respectively; unsaturated vinylidene (**3**) and allyl (**4**) end groups are produced, respectively, by β-methyl transfer and β-hydride abstraction on the last propylene unit enchained in 1,2 fashion. These facts suggest that both the initiation step and termination step are highly regiospecific.

The signals between 16.5 and 17.1 and 33.0 and 35.2 ppm are relative to the head-to-head and tail-to-tail arrangements of two propylene units which could be ascribed to the partial loss of regioregularity during the chain propagation.[12] A certain number of internal olefins (isobutenyl, 2-butenyl) due to double-bond isomerization or occasional misinsertion is also clearly visible in the olefinic region (124.2−131.8 ppm).[11]

In Table 1 are reported the data concerning propylene homopolymerization (run 1) and propylene−styrene copolymerization (runs 2 and 3). GPC analyses of the polymers show a monomodal molecular weight distribution and polydispersity indices less than 2, as predicted for a single-site catalyst. This fact and the unsuccessful extraction experiments in common organic solvents

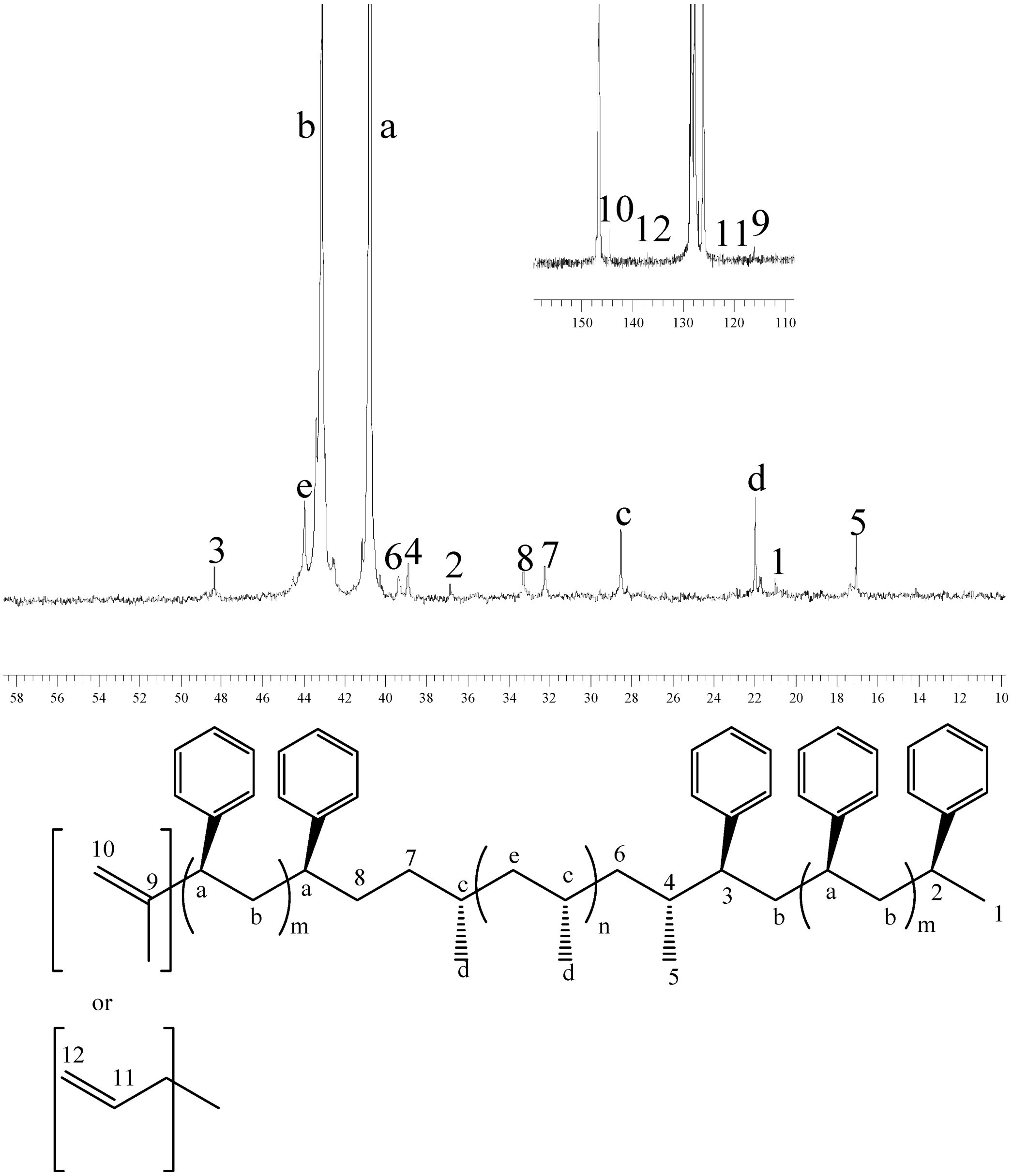


Figure 3. Aliphatic and olefinic carbon region of ^{13}C NMR spectrum of the *i*Ps-*block*-*i*PP-*block*-*i*Ps sample (run 2) with complete resonance assignment (the aromatic carbons are not labeled for the sake of clarity).

(acetone, *n*-hexane, THF) suggest the presence of a true copolymer.

One can observe that increasing propylene in copolymerization feed reduces the yield and molecular weight of the polymers, allowing us to assume that the termination step of polymer growth is dependent on propylene insertion. Further support to this hypothesis is the fact that homopolymerization of styrene performed with the same catalyst system, as previously reported,[7] produces polymers in much higher yield and molecular weights with respect to propylene–styrene copolymerization. This behavior confirms again the preference of this catalyst for vinyl-aromatic monomers vis-à-vis α-olefins, and it is the opposite of the behavior commonly observed for group 4 metallocenes.[4e–g]

The expanded NMR spectrum of the copolymer obtained in run 2 and the relative assignments are reported in Figure 3.

The signals at 20.7 and 36.5 ppm are relative to the carbon atoms deriving from the 2,1 styrene insertion on Ti–H bond,[12] while the signals at 113.7, 144.2 and 115.7, 136.8 ppm are carbons belonging to vinylidene and allyl propylene end groups, respectively, due to the same termination process observed for propylene homopolymerization. No signals relative to styrene or propylene insertion into the Ti–CH_3 bond are detected under these reaction conditions.

One can observe that the resonances of the unsaturated terminal carbons are slightly different from those reported for polypropylene because of the influence of styrene units near the unsaturated propylene end groups. Therefore, by analysis of the end groups and considering that styrene insertion into the titanium–carbon bond is secondary,[7] we can assert that the chain begins by secondary insertion of styrene into the Ti–H bond and terminates by *β*-hydride abstraction or *β*-methyl transfer of a primary propylene unit.

Deeper insight into the details of the copolymer microstructure comes from analysis of the aliphatic region of the spectrum: the narrow signals present at 21.7, 28.2, and 43.9 ppm can be safely attributed to methyls, methines, and methylenes of polypropylene block in isotactic arrangement. These stereoregular propylene sequences can be, in principle, connected to the polystyrene by two different kinds of joints: a propylene unit following a 2,1 styrene unit with the same or opposite regiochemistry.

In addition, methyl (16.7 ppm) and methine (38.6 ppm) resonances are similar to those observed in homopolypropylene with methyl (17.3 ppm) and methine (38.1 ppm) carbons in tail-to-tail arrangement.[11] These signals are thus diagnostic of the presence of secondary styrene units followed by propylene units inserted by primary regiochemistry. Because of this tail-to-tail arrangement, the methine carbon of the styrene unit is shifted quite downfield (48.2 ppm) with respect to the resonance of methines in styrenic chain (41 ppm), similar to the polystyrene methine carbons in tail-to-tail arrangement.[14]

Furthermore, the signals at 31.9 and 32.9 ppm are relative to methylene carbons deriving from secondary styrene insertion after the last propylene unit of a short isotactic block; these resonances are in the same region as that observed by Oliva et al. for the ethylene junctions in propylene−styrene copolymers.[5]

From these observation we conclude that the copolymer microstructure consists of long isotactic polystyrene sequences in 2,1 arrangement, interrupted by short isotactic oligopropylene links made of an average of five units enchained in a 1,2 fashion (Figure 3).

The thermal behavior furthermore indicates a multiblock microstructure. As a matter of fact, the presence of the propylene comonomer in the isotactic polystyrene chains reduces the melting temperature of the copolymers with respect to the isotactic polystyrene. A similar behavior is also observed for isotactic polystyrene containing isolated ethylene units.[9b]

The relative stereochemistry of the two monomers, however, can be not elucidated on the basis of ^{13}C NMR spectroscopic analysis due to the slight chemical shift differences between the two possible situations.[4e]

A rise in the propylene pressure (run 3) in the feed results in the formation of a less stereo- and regioregular copolymer as observed for the propylene homopolymer, suggesting that the styrene monomer assists the stereocontrol during the polymerization.

These results show that this post-metallocene catalyst can produce propylene−styrene copolymers with a molecular architecture that is inaccessible using *ansa*-metallocene catalysts. Further investigation is in progress to gain more information about the factors governing the regio- and stereochemistry for this class of catalysts.

Experimental Section

Materials. Toluene (Carlo Erba Analytical Grade) was refluxed 48 h under nitrogen atmosphere over sodium and benzophenone before using. Toluene and $Al(CH_3)_3$ present in MAO 10% (Witco) solution were removed under reduced pressure. The residual white powder was washed with dry *n*-hexane, dried in vacuo, and stored in a glovebox under nitrogen. Styrene was purchased from Aldrich and distilled under reduced pressure over CaH_2. Propylene was purchased from SON (Società Ossigeno Napoli) and used without further purification. Catalyst precursor **1** was prepared as reported previously.[7a]

Polymerizations. Run 1 (propylene homopolymerization) was performed by introducing sequentially in a 500 mL Büchi autoclave 1.25×10^{-2} mol of MAO in 130 mL of dry toluene, 2.5×10^{-5} mol of catalyst in 20 mL of dry toluene, with Al/Ti = 500 and a propylene pressure of 6 bar.

Runs 2−6 (propylene−styrene copolymerization) were performed by introducing sequentially in a 500 mL Büchi autoclave the desired excess of MAO in 100 mL of dry toluene and 20 mL of dry styrene, 2.5×10^{-5} mol of catalyst in 30 mL of dry toluene, with Al/Ti = 500 and a propylene pressure of 1 and 6 bar, respectively.

The polymerizations were quenched by fast introduction of 30 mL of ethanol/HCl. The polymer was filtered, washed several times with fresh ethanol, and dried under vacuum until constant weight.

Instrumentation. *NMR Spectroscopy.* The NMR spectra were recorded on an AM 400 Bruker spectrometer operating at 100 MHz in Fourier transform mode at 295 K. The samples were prepared dissolving in an NMR tube 25 mg of the polymers with $CDCl_3$. The content of propylene in the copolymers is calculated comparing the integrals relative to the methine carbons.

GPC. The molecular weights were determined by gel permeation chromatography. The polymer samples were analyzed in THF at 40 °C by a Waters Alliance 2695 chromatograph equipped with a Waters 410 differential refractometer as the detector. The chromatographic separation was obtained with four Styragel HR (Waters) columns with pore dimensions of 100, 500, 1000, and 10 000 Å. The flow rate of the eluent was 1 mL/min. The data were processed by Millennium (Waters) software. The number- and weight-average molecular weights of the styrene−propylene copolymers were determined with the direct calibration method. The calibration curve was obtained by using nine narrow polydispersity polystyrene standards (Polymer Laboratories Ltd.).

Thermal Analysis. The calorimetric measurements were carried out on a DuPont 2920 differential scanning calorimeter operating under nitrogen flow and calibrated by measurement of the melting point of indium. The samples were first heated at a rate of 10−300 °C, kept at this temperature for 10 min to allow the complete melting of the crystallites, and then cooled to room temperature. After the first run no further transitions were observed.

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Supporting Information Available: DSC thermogram for the copolymer obtained in run 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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