The exceptional magnetic inequivalence in helical form I of poly-1-pentene

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ABSTRACT

A sample of isotactic poly-1-pentene has been synthesized by using a metallocene catalyst, and two specimens have been prepared displaying the most stable Form I of this polymer, reported to adopt a 3_1 helical conformation. The solid-state ^{13}CNMR study of this helical form shows an exceptional splitting of the resonances, indicative of an important magnetic inequivalence in the unit cell. The maximum separation (amounting to 4.7 ppm) is obtained for carbon 2B: the methylene next to the terminal methyl in the lateral branch. This exceptional splitting is interpreted as originating from either intermolecular (packing) or intramolecular (conformational) differences (or both), leading to well non-equivalent sites for all the carbons. The comparative analysis of the relaxation times in the rotating frame between isotactic poly-1-pentene and isotactic polypropylene indicates that the two polymers display a rather similar relaxation behavior for both the crystalline and amorphous components.

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1. Introduction

A great interest has been devoted to polymers exhibiting helical conformations. One of the motivations for this attention can be found in the fact that the most relevant macromolecule, for obvious reasons, is the double-helix DNA.

Among synthetic polymers, one of the most remarkable cases of helical dispositions are the low members of poly-1-olefins, isotactic polypropylene, iPP, being the most important one, both industrially and academically. It is well known that iPP is able to crystallize (depending on microstructural features and crystallization conditions) under different polymorphs [1–11], but all of them share in common a 3_1 helical conformation. Particular interest has been devoted in recent years to the study of the mesomorphic phase [1,4,5,10,12] and of the new trigonal polymorph obtained in copolymers (or terpolymers) of propylene with high contents of 1-pentene or 1-hexene [7–9,13–16].

Regarding isotactic poly-1-pentene, iPPent, several crystalline forms [17–24] have been reported for this polymer. Modification I is reported to be the more stable and shows also a 3_1 helix chain configuration.

Solid-state NMR experiments are a very useful tool for studying polymer conformations in the condensed phase. Clear differences can be observed not only related to amorphous and crystalline environments, but also between the different polymorphs, which, eventually, may exhibit magnetic inequivalence, not observed in solution [25–32], what may be of valuable help in structure determinations. And, specifically, variations in the helical conformation of the macromolecule are also expected to produce variable chemical shifts [26].

The degree of order can be investigated via linewidth and/or relaxation studies, considering that well ordered crystals present narrow lines and long relaxation times, contrary to the case of non-ordered amorphous-like molecules, characterized by broader less resolved resonances and short relaxation times.

It is essential to be considered, however, that differences in the solid-state spectra are anticipated when there are changes in the local field around a certain nucleus. And those variations can have an intramolecular (conformational) or an intermolecular (packing) origin.

This work is concerned with a solid-state ^{13}C NMR study of the helical form I of isotactic poly-1-pentene. As will be seen, an exceptional magnetic inequivalence is observed.

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1.1. Experimental part

The isotactic poly-1-pentene sample was synthesized by polymerization of 1-pentene (Acros) in a glass reactor, at 25 °C for 110 min. The reaction was started by incorporation of the catalyst, where the precursor metallocene *rac*-dimethylsilylbis(1-indenyl) zirconium dichloride (Strem) was previously activated with co-catalyst methylaluminoxane (MAO-Aldrich, 10 wt % solution in toluene), using a [Al]/[Zr] = 900 relationship. The reaction was ended by adding 5 mL of ethanol (Aroca, 96%). Subsequently, it was precipitated with a mixture of ethanol and HCl (VWR, 37%). The so-precipitated polymer was stirred overnight, filtrated, washed with ethanol and, finally, dried under vacuum at room temperature.

The ^{13}C solution NMR analysis of iPPent was carried out with 1,1,2,2-tetrachloroethane-d_4 as solvent (10% wt./vol.), at 80 °C, using an Inova 400 spectrometer (100 MHz). 8000 scans were recorded with broad band proton decoupling, an acquisition time of 1 s, a relaxation delay of 4 s and a pulse angle of 45°. From the solution spectrum, a value of *mmmm* = 96.3% is deduced for the iPPent sample.

The molecular weights were determined by gel permeation chromatography in a Waters 150 CV-plus system equipped with an optical differential refractometer (model 150C). The following values were obtained: M_n = 27,300, M_w = 60,600, polydispersity index: 2.22.

The molecular weight was also estimated from the measurement of its intrinsic viscosity in toluene, at 30 °C. A value of 0.31 dl/g was obtained, which allowed deducing a M_n for this sample of around 25,000 from the intrinsic viscosity − molecular weight values reported for iPPent [33]. It compares fairly well with the value obtained by GPC.

Two specimens of that iPPent sample have been analyzed: the original powder obtained directly from the reactor, and a compression-molded film, prepared at 100 °C, and slowly cooled down to room temperature (cooling rate around 0.3 °C/min). Both specimens have remained at room temperature for more than one week prior to any analysis.

A commercial iPP sample (from Repsol) has been also analyzed, for comparison purposes. The molecular characteristics [34] of this sample are: 91.8% *mmmm* pentad content; M_w = 350,000; M_w/M_n = 4.0; melt flow index (ASTM method D 1238, at 230 °C) MI = 8.5.

The thermal properties were studied in a Perkin−Elmer DSC-7 calorimeter connected to a cooling system (Intracooler 2P from Perkin Elmer) and calibrated with different standards (indium, zinc and *n*-dodecane).

The conventional X-ray diffractograms have been taken in the reflection mode by using a Bruker diffractometer (D8 Advance) provided with a Göbel mirror and a PSD Vantec detector (from Bruker, Madison, Wisconsin), using Cu Kα (λ = 0.1542 nm) radiation and operating at 40 kV and 40 mA.

Solid-State ^{13}C NMR spectra were acquired, at room temperature, on a Bruker AVANCE 400 spectrometer, operating at 100.615 MHz. The sample, inside 4 mm rotors, was rotated with a magic-angle spinning (MAS) of 5000 Hz. A cross-polarization, CP, time of 1 ms was used. In addition, different spin-locking, SL, times have been included. Typically, 1500 transients were acquired for each experiment, using a recycle delay of 5 s. A secondary standard, adamantane, was employed as reference for the chemical shift [35].

2. Results and discussion

2.1. X-ray diffraction and thermal properties

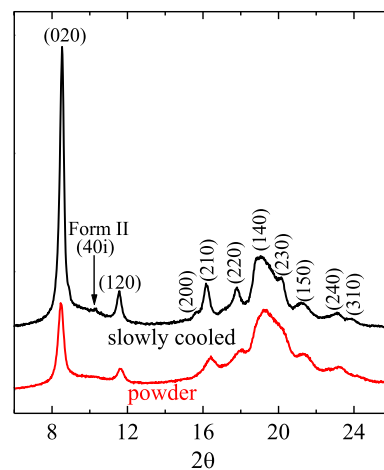Fig. 1 shows the X-ray diffractograms of the two specimens of

Fig. 1. Room-temperature X-ray diffractograms for the two specimens of iPPent.

iPPent. The two profiles are characteristic of Form I, with a very minor amount of Form II (diffraction at around 10.2°). Both diffractograms are rather similar, but a close inspection reveals that the slowly cooled sample seems to involve slightly more perfect crystals.

The first DSC melting run for the powder specimen (after several weeks at room temperature) is shown in Fig. 2. A complex melting endotherm is observed, with two peaks, centered at around 66 and 72 °C, including a total enthalpy of melting of only 41 J/g. Preliminary variable-temperature diffraction experiments have shown that the second peak corresponds to crystal thickening on melting.

No crystallization is observed during the subsequent cooling from the melt, so that the second melting (upper curve in Fig. 2) shows a clear glass transition centered at −37 °C, and a minor melting endotherm, following a small recrystallization exotherm above 30 °C. The neat enthalpy of this second melting is practically zero, thus confirming the absence of crystallization during the cooling process. It is concluded, therefore, that the present sample of iPPent crystallizes rather slowly at any temperature.

From the actual enthalpy in the first heating run, the enthalpy of melting of a 100% crystalline sample can be determined, provided that the crystallinity is known. For that, and taking advantage of the slow crystallization rate, the diffraction profile of a totally amorphous sample, at room temperature, was acquired before the
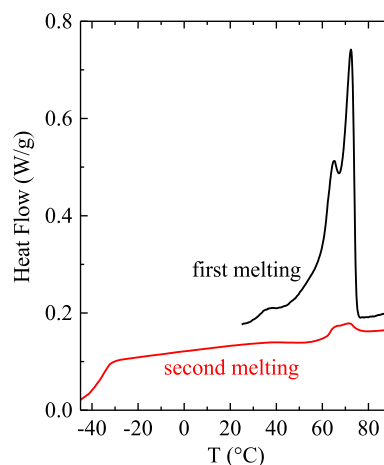

Fig. 2. DSC curves (first and second melting runs, at 10 °C/min) for the iPPent reactor powder. The curves have been vertically shifted for clarity.