MAS NMR Characterization of Syndiotactic Polypropylene: Crystal Structure and Amorphous Phase Conformation

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ABSTRACT: The high-resolution solid-state ^{13}C NMR characterization of highly syndiotactic polypropylene (sPP) was performed. Each carbon atom of the repeating unit shows at different temperatures several resonances, which were fully assigned to conformational sequences in different phases or different states of the same phase. The helix chain conformation was confirmed to be the only one present in the crystal structure. Fine details about the crystalline packing were obtained from the methyl signals and explained by the introduction of statistical disorder in the distribution of the chirality of the chains within the lattice. The average chemical shift of the mobile amorphous phase was determined at high temperature, giving for the first time an accurate measurement of the conformer distribution and supporting a model described by a considerable *trans* content in the amorphous phase. On the other hand, the conformations in the amorphous phase below the glass transition (at 203 K) were singly identified. A further phase interpreted as a rigid amorphous phase, showing different relaxation properties and temperature dependence, could be also detected. The as-polymerized polymer was shown to be rich in this phase, which lies probably at the interfaces, associated with a less regular crystallization.

Introduction

The presence of even minor microstructural defects is known to produce dramatic changes in the phases and properties of the materials. Syndiotactic polypropylene (sPP) of high structural purity is now available, being synthesized by a new family of Ziegler–Natta homogeneous catalysts, and is becoming more attractive for possible applications.[1,2] However, as characterization methods continue to improve, they may reveal unexpected details about the phase structure of the materials. Therefore, we reexamined the solid-state NMR characterization of sPP, which constituted one of the early examples of the application of MAS NMR to polymers.[3]

In the case of sPP, the sensitivity of the methylene ^{13}C chemical shift to the main-chain conformation is quite exceptional. Therefore, this polymer constitutes a good candidate for the following of crystal phase transitions and of the conformation and the mobility of the amorphous phase. Along this line, we recently presented a case in which the macroscopic stretching of the sPP specimen produces an "extended-chain" crystal and, as a consequence, the carbon signals due to the "*gauche*" conformations disappear.[4]

The present work was conceived for exploring by NMR the conformational arrangements accessible to the chain, whether static or averaged, and, consequently, for obtaining the knowledge of the structure of a sPP sample when subjected to a variable thermal and mechanical history.

Experimental Section

Synthesis. Syndiotactic polypropylene was obtained by Ewen's catalyst system, $Me_2C(Cp)(9\text{-}Flu)ZrCl_2[-Al(CH_3)O-]_n$ according to the procedure already reported by one of the authors.[2] The characterization reported in the following will deal with three different specimens obtained by the same synthesis and different thermal treatments.

Viscosity. The inherent viscosity of the samples, measured in tetralin solution at 408 K (0.25 wt %), was 1.20 dL/g.

GPC. Gel permeation chromatography was performed on a Waters 150-C GPC instrument equipped with Progel TSK columns, working at 408 K with *o*-dichlorobenzene as a mobile phase. The polymer shows a weight-average mololecular weight M_w of 164 000, with a dispersion index $M_w/M_n = 2.2$.

DSC. A Perkin-Elmer DSC-7 calibrated with indium and tin standards was used for the calorimetric analysis, in the range 253–453 K at a heating rate of 10 K/min.

X-ray Analysis. X-ray diffraction spectra were recorded on a Philips automatic diffractometer, scanning the range of 2θ from 5° to 35° by steps of 0.05° 2θ. Ni-filtered Cu Kα radiation was used.

NMR. Solution State. Solution state ^{13}C NMR spectra were obtained at room temperature in 1,2-dideuteriotetrachloroethane on a Bruker AM 300 instrument operating at 75.5 MHz. The following pentad distribution was obtained: *rmmr* = 1.3%; *mmrr* = 2.6%; *rmrr* = 1.3%; *rrrr* = 91.2%; *rrrm* = 3.3%; *mrrm* = 0.3%; intensities of the other pentads are zero.

Solid State. MAS ^{13}C NMR analysis was performed using a Bruker CXP 300 spectrometer operating at 75.5 MHz. The samples (50–100 mg) were spun in a range between 203 and 393 K in zirconia rotors at a rate of 4500 Hz. For CPMAS spectra, the best contact time was found at ca. 2 ms; for MAS without cross-polarization, a 90° pulse for carbon of 3.8 μs was used. High-power decoupling (DD) of 15 G was applied, and delay between pulses was 5 s for CPMAS and 2 and 5s for MAS. For each spectrum 500–1000 transients were collected. The resolution was checked on glycine (width at half-height = 26 Hz). Crystalline polyethylene (PE) was used as an external reference at 33.63 ppm from tetramethylsilane (TMS). Chemical shift correction with temperature was applied; PE spectra were run before and after each experiment.

Results and Discussion

The following treatment will deal with a homogeneous series of specimens of sPP obtained by the same synthesis.

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Table I. DSC and X-ray Diffraction Characterization of sPP Samples

sample	crystallinity (%) X-ray	crystallinity (%) DSC[a]	T_m (°C)
A	0.39	0.42	143
B	0.58	0.58	155
C	0.25	0.23	140

[a] The evaluation is given referred to sample B based on the melting enthalpy.[2]

The samples will be identified as follows. *Sample A* was obtained by precipitation with methanol from the polymerization medium (also called "native"). *Sample B* was obtained after purification and annealing of sample A. The polymer was hot washed with toluene, precipitated with methanol, dried under vacuum, melted, and annealed at 140 °C for 12 h. This sample is called the "annealed" sample. *Sample C* was obtained by quickly cooling from the melt and is also called the "quenched" sample. *Sample D* was obtained from sample C by drawing at 0 °C and is also called the "stretched" sample.

The main part of the paper will be devoted to samples A, B, and C, since the solid-state NMR characterization of sample D has already been given in ref 4. However, the latter was useful for comparison.

The calorimetric properties of samples A and B have been recently reported by some of the authors.[2] The crystalline content and phase properties are presented in Table I.

The Crystalline Phase. CPMAS spectra of the annealed sample B recorded at temperatures ranging from 293 to 360 K and at 2 ms[5] of contact time are presented in Figure 1. A MAS spectrum recorded without CP and a long recycle time (100 s) is also reported. This spectrum should represent a relaxed spectrum, and, therefore, the proportions between the signals of different carbons in the different phases are close to quantitative. Five narrow signals are detected: two for methyls, one for methines, and finally two main singals for methylenes, far apart from one another. Their appearance and line width are not much influenced by the temperature. The broad or minor signals appearing in different proportions in the spectra will be discussed in a following paragraph. The chemical shifts (CSs), spin–lattice relaxation times T_1, and the assignments are listed in Table II. In particular, the chemical shifts and the assignments of the main narrow peaks are reported and assigned to the helix crystal phase, as will be explained later.

The rigid nature of this phase appears to be clearly indicated by the nearly complete lack of dependence of the chemical shifts and the relaxation times on the temperature and by the fact that the relaxation times themselves are of the order of some tens of a second for methylenes and methines. In addition, only the nuclei placed in a rigid phase can cross-polarize efficiently under the adopted experimental conditions. Isotactic PP shows for the α- and β-crystalline phases relaxation times of the same magnitude.[6] As regards the methyls, the characteristic mobility of this group about the bond connected to the main chain lowers considerably the relaxation times even for rigid phases.

(a) Chain Conformation. The methylene carbons are exceptionally sensitive to the polymer chain arrangement. Apart from minor chemical shift effects (<0.5 ppm), which may be produced by the crystal packing and will be the subject of the following paragraph, the main features of the spectra can be interpreted as the results of the isolated polymer chain conformation. In the following we do not presume any crystal cell arrangement. The reasoning, although completely consistent with the previously proposed interpretation,[3] originates entirely from the NMR evidence and simple conformational considerations.

It is well established that the effect of the conformation on the chemical shift is mainly due to the rotation about the next neighbor bond.[7] The quantitative evaluation of

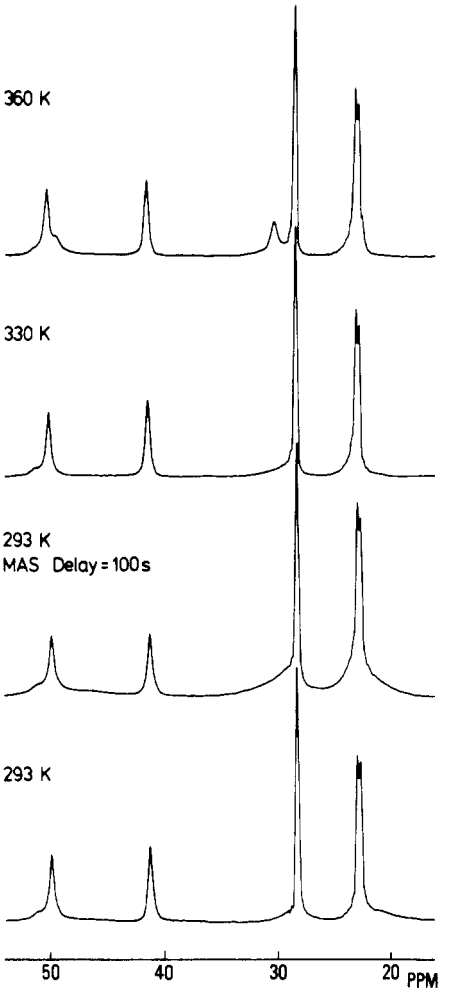

Figure 1. 75.5-MHz ^{13}C CPMAS spectra of sample B at the indicated temperatures. A MAS spectrum without CP and long recycle times is also presented for comparison.

Table II. Chemical Shifts, T_1s, and Assignments of sPP

carbon type	phase	conformation[a]	chemical shifts (ppm) 203 K	298 K	330 K	360 K	375 K	T_1[b] (s)
CH_3	amorphous	$>T_c$ averaged				21.4	21.5	1.1
		$<T_c$ (see text)	18.8	broad	broad			
	stretched	g^*g^*		20.8				
	helix	$g't'$	21.9	21.9	21.9	21.9		0.7
	helix	$g't'$	22.1	22.1	22.1	22.1		0.7
CH	helix	$ggtt$ ($t'g^*$)	27.5	27.4	27.4	27.4	27.4	31
	stretched	$tttt$ (g^*g^*)		28.9				
	amorphous	$>T_c$ averaged			28.8	29.1	29.2	0.2
		$<T_c$ (see text)		broad				
CH_2	helix	$gttg$	40.2	40.2	40.2	40.2	40.2	54
	amorphous	$>T_c$ averaged				48.1	48.1	0.2
		$<T_c$ $gttt$	45.5					
		$tggt$	48.7	broad				
		$tttt$	50.2					
	helix	$tggt$	48.7	49.0	49.1	49.1	49.1	49
	stretched	$tttt$		50.2				

[a] g' or t' indicates the interaction CH_3–CH (see Figure 8); g^* indicates distorted *gauche* conformation (see text). [b] At room temperature, except for the averaged amorphous above T_c, which was measured at 375 K; for each phase the dependence on temperature is small.

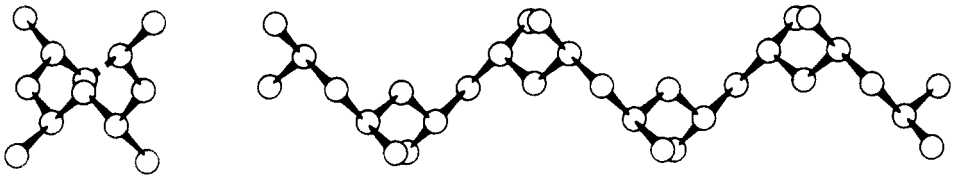

Figure 2. Chain conformation of sPP in the crystalline phase.

the shift may be calculated by an additive contribution of ca. −5 ppm for each *gauche* (*g*) bond. Since the two methylene signals are about 9 ppm apart from one another, the high-field signal must indicate two *gauche* contributions. In terms of conformational sequences the signals are due to *txxt* and *gxxg* sequences, respectively, starting from downfield, where *x* is an unknown conformation next to the observed carbon atom. In addition, the two sequences are equally probable, as is evident from the comparable intensities of the signals, and they must be arranged in a regular succession, according to the "equivalence principle" usually valid in the crystal state.[8] By interleaving the two sequences *txxt* and *gxxg* in an alternate disposition and shifted by two letters (next methylenes lie two bonds apart), a general $(ttgg)_n$ microstructure is produced.

We cannot establish the sign of *g* conformations, which is ineffective on the chemical shift. If we take into account, however, the fact that two *gauche* conformations of opposite sign are prevented by strong steric interactions as in pentane molecules,[9] the only possible succession of bonds shows pairs of *g* conformations of the same sign. This logical procedure permits the construction of a 3-dimensional structure of the polymer chain, which is an s(2/1)2 helix described by the following sequences: $(ttg^+g^+)_n$ or $(ttg^-g^-)_n$; the sign depends on the chirality (Figure 2). The s(2/1)2 helix was first proposed on the basis of energy calculations by Allegra et al. as the most stable arrangement of sPP[10] and was confirmed by X-ray diffraction evidences.[11]

As regards the methine and methyl CSs, they are also related to the chain conformation. For those nuclei, however, the $(ttgg)_n$ sequence is seen from a different point of view, i.e., from in between the *tt* and *gg* groups. Those nuclei experience the chain conformation in a unique way, with the *ttgg* sequence indistinguishable from the *ggtt*; in other words, each methyl or methine is related to any other by symmetry operations. One *gauche* contribution originates from the relation of the methyls to the methine carbons when the chain is arranged in the *trans* conformation, thus affecting the chemical shifts of both atoms (see Figure 8). For methine carbons another *gauche* effect can be produced by the methylenes of the chain when the chain contains *gauche* bonds. These considerations of conformation explain both the absence of splitting due to conformational origin and the values of the chemical shifts; however, the last point will be further clarified by the comparison with the chemical shifts in the amorphous phase.

(b) Packing of the Chains. Thus far we have discussed the single-chain conformation, which agrees with conformational calculations[10] and the period along the crystal axis *c*.[11,12] We now describe the chain packing as indicated by NMR results. The discussion is essentially based on the 1:1 CH_3 splitting clearly presented here for the first time (a clue of CH_3 splitting can be seen in ref 13).

The methyl splitting observed in the annealed sPP (sample B) must be due to two different methyls in the repeating units of the chain. We do not believe that the splitting of the signal could be due to the contribution of the amorphous phase, because the chemical shift of the amorphous phase is different (Table II). The signal splitting does not change the internal ratio (1:1) when temperature and other experimental conditions were changed; the two signals show the same relaxation time. We looked for the explanation of the splitting by considering the symmetry of the crystal cells and the chirality of the chains.

A number of space groups and structures have been taken into account for sPP polymorphs as derived by X-ray and electron diffraction data: the main features of those proposals are given in note 14, along with the literature sources.

The chain arrangement proposed by Corradini on the basis of the early X-ray diffraction studies performed on constitutionally defective sPP samples is presented in Figure 3 (cell I).[11] In this structure the space group $C222_1$ implies helices of the same chirality. Furthermore, the symmetry elements of this space group force the atoms lying on the four corners of the helix (CH and CH_3, as seen from above) to be equivalent. The chains packed in this way cannot produce more than one methyl crystalline signal, the methyl carbons being exposed to the same environment.

An accurate refinement of the crystal cell and morphology performed by electron and X-ray diffraction of sPP is the object of some works by Lovinger, Lotz, and Davis.[15-18] They took into account the chirality of the helix: the same number of helices of opposite handedness must in fact be present in the system. They concluded that a different degree of specificity is present on the two lateral faces of the chain *b*–*c* and *a*–*c*, and this is the origin of different crystal structures. In particular, the structure of the most regular crystal packing, derived from electron diffraction spectra of selected crystallites produced at high temperatures (140 °C on thin layers), is described by Lovinger et al. as a succession of chains of alternate chirality in both dimensions.[17]

The space group of the proposed lattice (called cell III) is *Ibca*, and the parameters of the cell are a = 14.5 Å, b = 11.2 Å, and c = 7.4 Å (Figure 3). The value *b* in cell III is double compared to that in cell I.[14] The doubling of the original unit cell in the *b* dimension is connected to the presence of a peak in the X-ray diffractograms, indexed as 211. Our bulk-crystallized sPP sample seems to be completely comparable, concerning both the microstructure and the material preparation, and it shows the same prominent peak at 2θ = 18.2°, as presented in Figure 4. The diffractogram may be compared for example to that presented in Figure 5c of ref 18.

This regular lattice, however, does not explain the methyl splitting, since the structural repeat unit of the cell corresponds to a single monomer residue. The proposed cell III is to be considered a limiting structure toward the maximum degree of order, and cells containing statistical disorder are also to be examined.

A first hypothesis assumes the existence of a statistical disorder introduced by the location of the chains in the texture: the disposition indicated by cell I (Figure 3) mixed with that indicated by cell III (Figure 3). The disorder

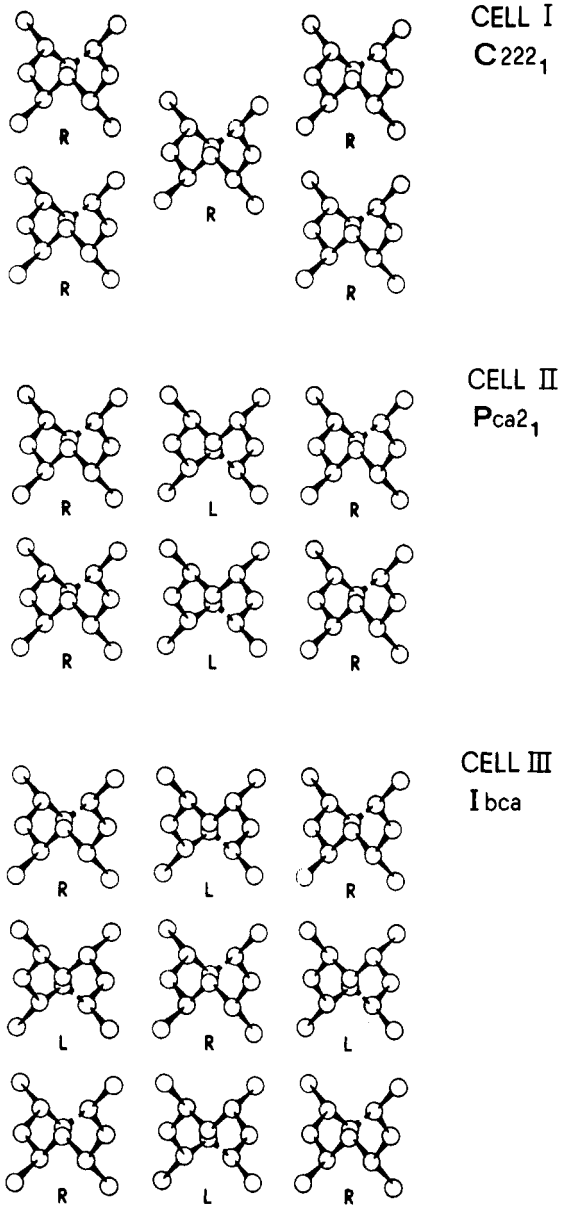

Figure 3. Crystal packing of the chains, as proposed by X-ray and electron diffraction data (see text), taking into account the chirality (*R* or *L*) of the chains.

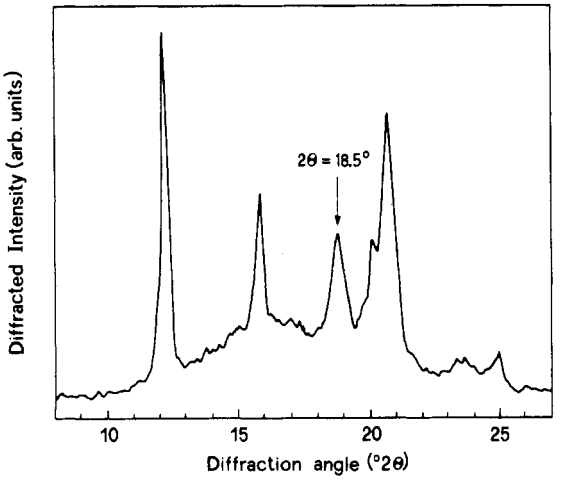

Figure 4. X-ray diffractogram of the annealed sample B. The peak at 18.2° 2θ, indexed as 211,[18] is indicated.

must be placed essentially along the *b* face of the cell. This is supported by the streaks in the diffraction pattern, which increase if the annealing temperature is lower.[17] The disorder along *b* can in principle account for two kinds of interactions and, consequently, to a couple of chemical shift values. The 1:1 ratio between the interactions should lead to the expectation of an extensive amount of this disorder. This conclusion, however, seems implausible for describing the crystal structure of sample B. The structures presenting a lower degree of order[14] are inconsistent with the crystallographic and calorimetric characterization of the sample (Table I, Figure 4). Furthermore, the statistical replacement of chains of opposite chirality should lead to a number of relationships between chains increasing the number of NMR signals. The resonances should be distributed so close to each other as to produce a blurring of CSs and one unresolved Gaussian-shaped signal. This arrangement probably occurs in the crystals of native sPP and in samples of a low crystallinity, as later shown.

Alternatively, we must consider the statistical replacements of chains of opposite chirality within a regular disposition of the chains, such as the one indicated in Figure 3 as cell II and cell III. The molecular modeling demonstrates that the *RR*(*LL*) and *RL*(*LR*) relationships along the *b* axis implies comparable energy requirements. These relationships are *not* irrelevant for the distances between methyls and the nuclei on the other chains and, therefore, on the chemical shifts.[17] This means that two kinds of interactions can be distinguished and can be defined as "diads" m and r (m meaning *RR* or *LL* and r meaning *RL* or *LR*), by analogy with Bovey's terms *m* and *r* introduced for describing the microtacticity of the vinyl polymer chains.[20] These terms have the advantage of defining relationships (relevant for NMR) instead of absolute configurations (their differences being indistinguishable in NMR spectra). Thus, the two NMR methyl signals at 21.9 and 22.1 ppm, or vice versa, were assigned to m and r.

The observation that the signals are slightly unbalanced from a 1:1 ratio is explained by the energetic differences of the m and r interactions. The difference is clear-cut at high temperature, due to the sharpening of the minor underlying amorphous component (complications may arise if more than one CS is associated with a single relationship). If the previous assumptions about the higher energetic stability of the r interaction (alternation of chirality) are correct, the signal at 22.1 ppm (more intense) is produced by the ...$rrrr$... arrangement.

Since the experimental sensitivity is limited to "diads" (pairs of chains), it is not possible to determine the statistical distribution of the relationships,[20] but it is worthwhile to observe that the ...$rrrr$... sequence corresponds to the previously introduced cell III (Figure 3) and ...$mmmm$... to cell II (Figure 3).[14] However, since it is unlikely that two extensive crystalline phases coexist in balanced proportions, the straightforward conclusion is that we have a statistical distribution of "diads", as, for example, in the sequence ...$mrmmrrrm$... (Figure 5). In other terms, our suggestion implies a structure containing statistical disorder in the *b*–*c* laths, i.e., in one dimension. Taking into account the regularity on the *a*–*c* plane, it requires a template effect of the next *b*–*c* sheet, reproducing the same sequence by interchanging m and r, as already proposed.[17]

The statistical distribution may be at random or not, depending on the crystallization and annealing conditions. In the example of Figure 5, cell II or cell III could be recognized within the statistical lattice, giving account for the emergence of corresponding reflections in the diffraction spectra in the presence of a larger extent of

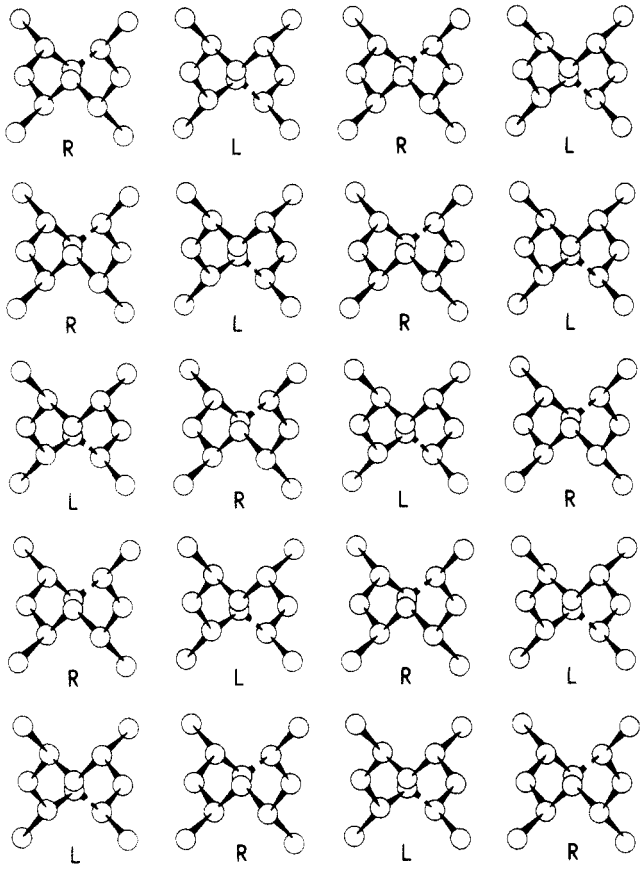

Figure 5. Proposal of the crystal packing of sPP in sample B, showing a statistical disorder of the chain chirality in one dimension (see text).

those regularities. This is also consistent with the suggestions for the existence of an "irregular doubling of the crystal cell" or "localized alternations" appearing in ref 17.

The Amorphous Phase. The samples under consideration contain in any case at least 42% of the amorphous phase; this is the value measured in sample B. In the previously presented CPMAS spectra (Figure 1), the contribution of this phase is underestimated, due to the change in the mobility of this phase with changes in temperature. In particular, at room temperature the frequency of motions is in such a range that broadening occurs on several signals. This may be the reason why the description of this phase was not taken into account in the published studies.[13] At higher temperatures the higher mobility of this phase prevents an efficient cross-polarization experiment.

For a careful characterization of the amorphous phase behavior, a series of MAS ^{13}C experiments without CP and with dipolar decoupling were performed (Figure 6). Under those conditions and repetition times of 5 s the signals due to short relaxing and mobile carbons were enhanced. The relaxation times for the amorphous phase were measured by inversion–recovery and can be compared in Table II with the values measured for the crystalline phase.

Two ranges of temperatures are determined for the amorphous phase signals: one beginning at ca. 330 K and characterized by a single CS value for each carbon atom in the monomer unit, and the second one below 330 K, in which multiple and broad CSs are observed. Over the range of temperatures 203–375 K the complete and reversible transformation is observed in the spectra. A collapse temperature, defined as T_c, is closely related to the glass transition (T_g) of the polymer, although shifted

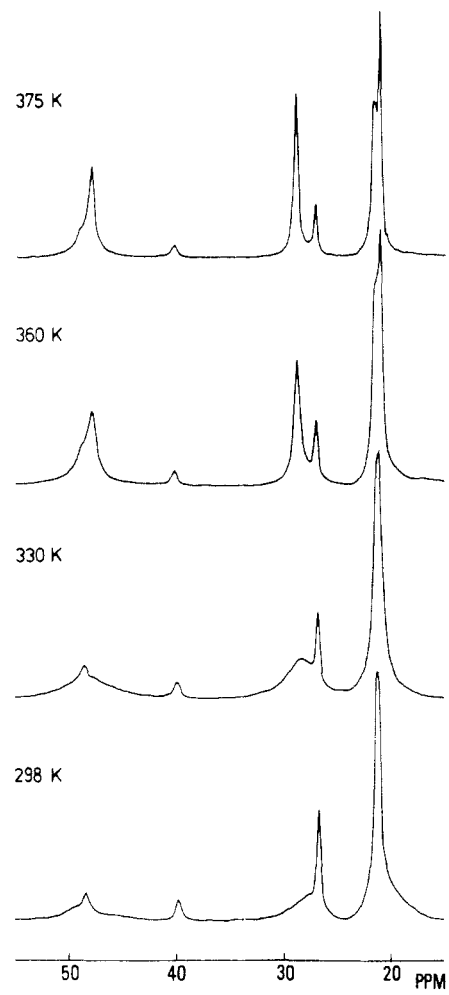

Figure 6. 75.5-MHz ^{13}C MAS spectra of sample B at the indicated temperatures (recorded without CP and 5 s of recycle time).

toward higher temperatures. For isotactic and atactic polypropylene it was observed at a temperature 50–70 K higher than T_g.[20,21]

(a) Chain Conformation above T_g. The observation of the CSs well above T_g produces an average value, thus indicated as CS_{av}. By assuming that the CS is chiefly produced by an intrachain conformational effect, we can determine the average conformation of the polymer chain (Figure 7). As a first approach we can try to calculate the probability of finding a bond in the *gauche* or *trans* conformation.

The CS is due to the conformation of two bonds far apart from one another, and, therefore, the conformation of those bonds is initially treated as being independent according to a Bernoulli model:

$$CS_{av} = p_t^2 CS_{tt} + 2p_t p_g CS_{tg} + p_g^2 CS_{gg} \qquad (1)$$

where p_g is the probability of occurrence of a *gauche* bond, $p_t = 1 - p_g$ is the probability of occurrence of a *trans* bond, and CS_{xy} is the chemical shift determined by the conformations (x and y) effective on the observed atoms.

If the various CSs are all referenced to CS_{tt}, introducing new variables $CS^*_{xy} = CS_{xy} - CS_{tt}$, it follows that $CS^*_{tt} = 0$ and

$$(CS^*_{gg} - 2CS^*_{tg})p_g^2 + 2CS^*_{tg}p_g - CS^*_{av} = 0 \qquad (2)$$

from which p_g can be easily obtained as a function of the CS values. However, under the reasonable assumption that γ *gauche* contributions are additive[7] and independent of each other, then $CS_{gg} - 2CS_{tg} = 0$ and the solution is

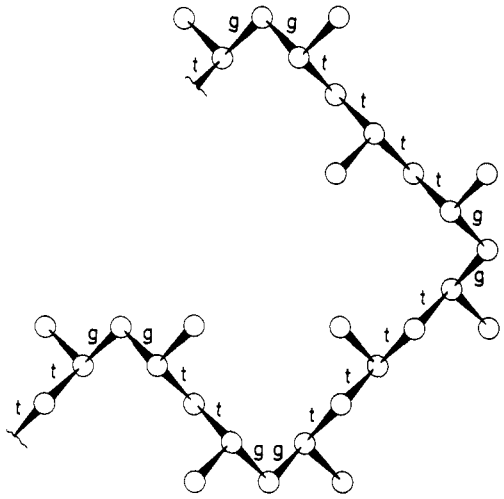

Figure 7. Chain segment of sPP describing the high contenent of *trans* conformation in the amorphous phase, consistent with the ^{13}C NMR chemical shifts (see Table I).

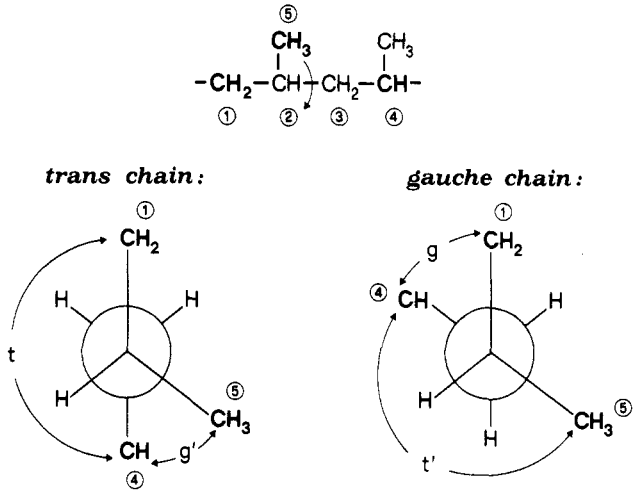

Figure 8. Newman projection for the rotation about the 2,3 bond, affecting the chemical shifts of carbon atoms the 1, 4, and 5. *g'* and *g* represent *gauche* interactions, respectively involving and not involving the methyl carbon.

reduced to

$$p_g = CS^*_{av}/2CS^*_{tg} \quad (\text{or } p_g = CS^*_{av}/CS^*_{gg}) \qquad (3)$$

This result, giving the fraction of *gauche* bonds instantaneously present in the polymer, is valid independent of the distribution of the sequences.

For the methylenes the CSs are known with considerable accuracy. The methylene chemical shift of the *trans* structure can be deduced by the stretched sPP crystalline modification (sample D). This conformation, although slightly distorted from a 180° angle, is a valuable reference sample for obtaining the *tttt* sequence chemical shift, because the CS shows a flat dependence from the angle close to the *trans* conformation.

The NMR characterization of a stretched sPP sample has been recently presented by several of the authors.[4] In that paper the CS of the *tttt* sequence is given as 49.1 ppm; the value adopted in the following will be 50.2 ppm as reported in Table II.

The fraction of *gauche* conformation (p_g) in the amorphous phase above T_c was measured according to eq 3 as $-2.1/-10.0 = 0.21$.

In a complete conformational analysis, however, some selection rules apply, as partly described previously during the conformational description of the crystalline phase. *gg* and *tt* diads centered on methylenes can properly describe the main-chain conformation, and sequences of *gauche* conformations longer than diads are forbidden, because two *gauche* conformations surrounding the methine carbon constitute an inaccessible high-energy arrangement.[22]

On the basis of this model, the frequency of occurrence (P_i) of the sequences *tttttt*, *ttggtt*, *ttttgg*, and *ggttgg* was calculated, and the observed chemical shift values (CS_i) of the central methylenes in the sequence were taken into account (Table II). Consequently, the average CS_{av} of an unperturbed sPP chain as defined in ref 22 (with probability of occurrence of *gg* equal to 0.28 and probability of *gg* following a *tt* arrangement equal to 0.37) should fall at 46.6 ppm. This value is considerably upfield of the measured 48.1 ppm CS for the amorphous phase at 360 K. Therefore, in well-crystallized samples of sPP the amorphous phase is richer in *trans* conformations (and, consequently, the end-to-end distance larger than for the singular case of the unperturbed chain) (Figure 7).

The methyl carbon signal due to the mobile amorphous phase is less easily discriminated in MAS spectra than the methylene signal, even applying a 2-s recycle delay (even shorter than that applied for the spectra of Figure 6); this is due to the short relaxation times of the crystalline methyls (Table II). However, a definite signal, upfield of the main ones, is detected at high temperature (21.5 ppm).

We must recall that the point of observation is shifted in this case, compared to methylenes, one bond along the chain; therefore, a *trans* planar bond on the chain corresponds to methyls placed in a *gauche* interaction, according to the representation as a Newman projection (Figure 8). From the comparison of the methyl CSs it may appear surprising that polypropylene methyl resonances are so crowded in a small region, with little sensitivity to the chain conformations. They show in solution the highest sensitivity to stereosequences ever described.[23] This sensitivity is known to be transmitted through the conformational equilibria adopted by the chain.[9] Actually, methyl signals can cover in principle a 10 ppm range of the spectrum like methylene signals. Nevertheless, we need to consider that the *gggg* chain sequence, which may lead to a chemical shift for the methyl due to a *t't'* conformation arrangement (the conformations involving the methyls will be indicated by a prime), is forbidden; this prevents observation of resonances in the downfield region.

The *tttt* chain sequences are instead accessible conformations that must lead (Figure 8) to *gauche* sequences for the methyl carbons. One should, therefore, expect a signal about 5 ppm upfield from the *trans–gauche* signal determined in the helix crystal. The stretched polypropylene sample shows the methyl CS at 20.8 ppm, which is considerably close to the *g't'* signal (ca. 22 ppm). As a matter of fact, the difference between the two signals may be erroneously taken as a measure of a single *gauche* contribution; the value obtained is too small (1.2 ppm) and implausible. Consequently, we suggest that in the stretched modifications methyls experience distorted *gauche* contributions, called *g**, which produce less severe carbon–carbon interactions.

According to this interpretation and in the hypothesis of independence of the contributions.

$$2g^* - g = -1.2 \text{ ppm}$$

Since $g \cong -5$ ppm, it follows that $g^* \cong -3.1$ ppm, compatible with an angle considerably larger than that of the regular *gauche* conformation.

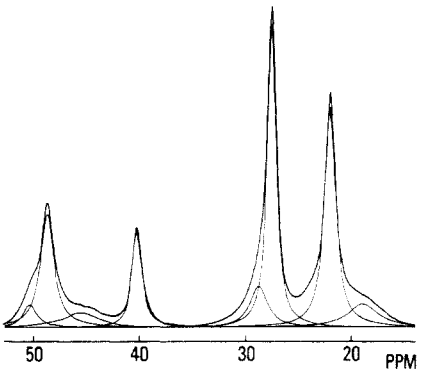

Figure 9. 75.5-MHz ^{13}C CPMAS spectrum at 203 K and simulation by Lorentzian curves, showing the amorphous component below the glass transition.

In a shorter *gauche* sequence the conformation may be nonrelaxed. The signal at 17–18 ppm already observed in some polypropylene samples in the solid state and not interpreted represents the signal due to a pair of unperturbed *gauche* contributions in the amorphous phase.

On the basis of statistical considerations the frequency of occurrence of *tttt* along the chain is equal to the frequency of occurrence of *tt* pairs multiplied by the probability that *tt* follows *tt*. For unperturbed chains the frequency is 0.45, and, similarly, *ttgg* is 0.55, while *gggg* is equal to zero. Due to the low sensitivity of the CS_s, one cannot establish, as was done for the methylenes, how great is the departure from the unperturbed chain model. The CS is, however, close to the *tttt* signal and substantially confirms what we deduced from the methylene spectrum.

Methines can in principle form *gauche* interactions both with methyls and with methylenes (Figure 8). When the former interaction is *trans*, the latter is *gauche*. Therefore, two γ *gauche* interactions, one for each side of the chain, contribute in any case to the observed CS. This can explain the stability of the sPP methine signal, both in solution and in the solid state.[7] Evaluating the effective *gauche* contributions in the stretched sPP ($2g^*$) and in the helix sPP (only one *gauche* is effective in the *ggtt* sequence), one can compare the difference to the experimental result (1.5 ppm):

$$2g^* - (g^* + g) = 1.5 \text{ ppm}$$

Thus

$$g^* - g = 1.5 \text{ ppm}$$

$g = -5$ ppm and $g^* = -3.5$ ppm fit the equation in good agreement with that deduced from the methyls. By analogy to the previous discussion, the signal for the average amorphous methine should fall close to the signal found in the stretched sPP (Table II), and, in fact, is practically coincident.

(b) Chain Conformation below T_g. In Figure 9 is presented the CPMAS spectrum of sPP (sample B) at 203 K. The pattern does not change over the range 203–273 K (not presented).

In this spectrum the crystalline and glass amorphous components coexist and cannot easily separate due to the similar motional behavior in the observed range of temperatures. The deconvolution of the spectrum presented in Figure 9 shows two families of signals (crystalline and amorphous), as indicated in Table II. The most informative part is again the methylene spectrum, in which some amorphous sequences are resolved and others coincide with the same sequences in the crystalline phase (*tggt* and *gttg*). However, the *gttg* sequence is present with a low probability in the amorphous phase (4%), and

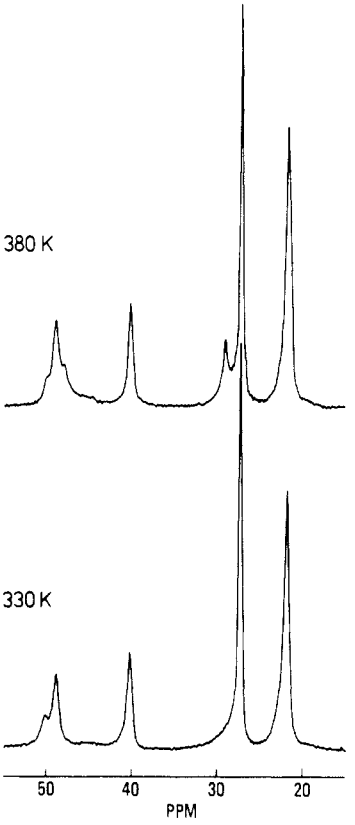

Figure 10. 75.5-MHz ^{13}C CPMAS spectra at the indicated temperatures for the as-polymerized sPP (sample A).

the main part of the signal is due to the crystalline phase. The intensities of *tttt* (50.2 ppm) and *tttg* (45.5 ppm) and the difference of *tggt* (48.7 ppm) and *gttg* (40.2 ppm) quantify the distribution of immobilized sequences in the amorphous phase of a 42% amorphous sPP sample (Table I). The distribution corresponds well to that derived by the above-described statistics.

At the adopted values of contact times the amorphous phase seems, however, not as efficiently detected by CPMAS as the crystalline part.

As-Polymerized Polymer. The "native" polymer A was analyzed by the same techniques which were previously described for the other samples.

MAS spectra recorded without CP at variable temperature (not shown) show a behavior identical to that of sample B (Figure 6), except for the fact that the amount of the amorphous phase is increased (Table I). The conformational structure of the amorphous phase becomes mobile on the NMR time scale at high temperature (360 K), as discussed above for sample B. The different nature of the sample is instead apparent in the CPMAS spectra of Figure 10. In the methylene region two signals assigned to the conformations *tttt* and *tttg* (see Table II) are clearly detected, virtually independently of the temperature. The signals are the same as indicated in the deconvolution of the CPMAS low-temperature spectrum (Figure 9).

These signals belong, therefore, to a rigid phase that is not the conventional crystalline phase and not the conventional amorphous phase. The contribution of the conventional amorphous phase becomes apparent at high temperature, with the resonances at 48.1 ppm for CH_2 and 29.2 ppm for CH indicating chain mobility. The signal at 50.2 ppm cannot be assigned to sPP chains in a crystalline phase with extended conformation, because this phase is not stable at a temperature above 50–60 °C.[22] Actually, the NMR signals of the stretched phase shift with temperature to those of the helix crystal, as observed

by us.[25] The assignment of the 50 ppm signal in the as-polymerized sPP to an all-trans sPP,[13] by analogy to the stretched form, is, therefore, inconsistent with the evidence that the pattern is not changing with temperature. These conclusions do not take into account that the amorphous phase itself can contain a relevant amount of *tttt* sequences, as previously demonstrated.

In addition, the spectra show, even at the highest temperatures, the signal at 45.5 ppm assigned to the *tttg* sequence (Table II); this conformation was previously associated with the amorphous phase.

The persistence at high temperature of *tttt* and *tttg* together in fixed conformations indicates chains fixed in rigid structures endowed with a complex conformational distribution. These structures are at the interfaces of the crystallites and within strained or disordered areas of the crystallites themselves.[25]

High-temperature annealing can reduce the content of this phase but a small part often remains, as one can observe by looking carefully at the baseline between the signals and the small peak at 50.2 ppm in the CPMAS spectra produced by sample B (Figure 3).

The same behavior was observed in the quickly cooled sample C (Table I).

Conclusions

The example studied in the present paper demonstrates with considerable clarity the abundance of information provided in the ^{13}C MAS NMR of a polymer containing a very regular and simple monomeric unit.

In particular, the chemical shift of the amorphous phase in semicrystalline highly syndiotactic polypropylene above the glass transition could be detected for the first time. This constitutes an average value, which, compared to the chemical shifts assigned to specific conformational sequences, provides a precise measurement of the conformational equilibria in the amorphous bulk. The distribution of interconverting conformers is shifted toward a major content of *trans* sequences.

The helix conformation of the crystalline phase could also be determined in agreement with a previous NMR report.[3] In addition, the resolution obtained by this work and the selection of suitable samples was proper for obtaining a description of the crystalline phase in terms of packing of the chains. We do not believe our results to be conclusive, but in our opinion this is a novel contribution to the current debate about the crystal structure of syndiotactic PP.[16,18,26]

An interfacial phase at the edges of a regular crystal structure was identified by the relaxation properties[25] and the variable-temperature behavior. This phase appears to be more relevant in samples showing a low crystallinity and in the as-polymerized polymer.

As for the interpretation of the phenomena, the methodology adopted here was unusual (mainly for the discussion of the crystalline chain conformation) and attempted to fully exploit the NMR results before making comparisons to results obtained by other methods. Since the nature of magnetic resonance yields information quite different from that derived by other solid-state techniques, NMR data can produce complementary models which amplify the prospective of the possible proposals. The greater sensitivity of NMR to the solid-state disorder has been stressed several times. However, the contribution from MAS NMR in the determination of the crystalline structure of polymeric materials appears to be important as well.

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