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Solid State ^{13}C Nuclear Magnetic Resonance Spectrum of Syndiotactic Poly(4-methyl-1-pentene)

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ABSTRACT: The chain conformation and the crystal packing of syndiotactic poly(4-methyl-1-pentene) have been studied by solid state ^{13}C NMR cross polarization/magic angle spinning (CPMAS) spectroscopy. The presence in the CPMAS spectrum of two distinct resonances separated by ≈5 ppm (one γ-gauche effect) for the methyl carbons indicates that the two methyl carbons belonging to the monomeric unit are nonequivalent. This has been explained on the basis of the conformation of the lateral groups proposed in the literature. A single resonance of the backbone methylene carbons, although broad and with various shoulders, is present. The absence of the splitting of ≈10 ppm for this resonance, typical of other syndiotactic polymers having *TTGG* helical conformation, like polypropylene and poly(1-butene), is still fully consistent with the helical *TTGG* conformation of the chains of syndiotactic poly(4-methyl-1-pentene), since the conformational assignment of the lateral groups makes the two methylene carbons in conformational environments *TG.GT* and *GT.GT*, nearly equivalent. The narrow splitting of the resonance of the backbone methine carbons indicates that the helical *TTGG* conformation of the chains, approximately described with a **s**(12/7)2 symmetry, should be better described with a complex nonuniform helix with slightly different values of the backbone torsion angles of different structural units. In this nonuniform helix, backbone methine carbons of different structural units are nonequivalent since they experience different amounts of the γ-gauche shielding effect resulting in the asymmetric splitting of the corresponding resonance. Both resonances of the methyl carbons present narrow splittings, which can be traced back to packing effect. These splittings are easily interpreted on the basis of the model of packing proposed in the literature.

Introduction

The structural characterization of highly syndiotactic poly(4-methyl-1-pentene) (s-P4MP) has been recently reported.[1,2] One crystalline form of s-P4MP with melting and glass transition temperatures of 210 and 50 °C, respectively, has been found so far.[1]

A complex helical conformation of the chains of s-P4MP with a sequence of torsion angles of the kind $(TTGG)_n$, approximately described by a **s**(12/7)2 helical symmetry and an identity period $c = 46.9$ Å, was suggested on the basis of X-ray fiber diffraction data and conformational energy calculations.[1] Chains with complex **s**(12/7)2 helical conformation are packed in a tetragonal unit cell with axes $a = 18.03$ Å and $c = 46.9$ Å, according to the space group $P\bar{4}$.[2]

It is worth noting that the helical $(TTGG)_n$ conformation with **s**(12/7)2 symmetry, found for s-P4MP, corresponds to a succession of torsion angles of the main chain, $\theta_1 = G$ and $\theta_2 = T$, slightly deviated from the exact gauche (60°) and trans (180°) values, which are typical of the **s**(2/1)2 helical conformation found for the chains of other syndiotactic polymers, like poly(1-butene),[3−5] polypropylene,[6] and polystyrene.[7] For syndiotactic polymers, the isodistortion of the torsion angles of the main chain and the formation of a complex helical symmetry have been already observed for form II of poly(1-butene).[3,8]

In this paper the crystalline s-P4MP is examined by solid-state high-resolution ^{13}C NMR spectroscopy using cross polarization/magic angle spinning (CPMAS), to

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test the proposed conformational assignment. Indeed, the observed chemical shifts in CPMAS ^{13}C NMR spectra of solid polymers provide information concerning the conformation of polymers in the crystalline state. A conformationally sensitive γ-gauche shielding effect[9] has been observed in syndiotactic polymers, like polypropylene,[10,11] poly(1-butene),[5] polystyrene,[12,13] and poly(*p*-methylstyrene),[14] which have chains in trans planar or **s**(2/1)2 helical conformations with torsion angles of the main chain in the staggered *T* and *G* values. In addition, analyses of the CPMAS ^{13}C NMR spectra of the various crystalline forms of isotactic poly(1-butene)[15] and, more recently, of isotactic poly(4-methyl-1-pentene) (i-P4MP)[16] have shown that the γ-gauche shielding effect is reduced when the torsion angles of the main chain deviate from the exact gauche and trans values. The analysis of the CPMAS ^{13}C NMR spectra of s-P4MP, which is characterized by chain conformation with torsion angles deviated from the exact gauche and trans values, provides an example of reduction of the γ-gauche shielding effect for syndiotactic polymers.

Experimental Section

Two different samples of s-P4MP were used. The first one was obtained by hydrogenation of syndiotactic 1,2-poly(4-methyl-1,3-pentadiene) as described in ref 17. The second one, supplied by Montell, was obtained by polymerization of 4-methyl-1-pentene in the presence of syndiospecific homogeneous catalyst composed of isopropylidene(cyclopentadienyl)-(9-fluorenyl)zirconium dichloride and methylalumoxane.[18] The inherent viscosities of the samples are 0.62 and 0.29 dL/g, corresponding to molecular weights of 5.0×10^4 and 2.0×10^4, respectively. The samples are highly syndiotactic with fully syndiotactic pentad contents [*rrrr*], evaluated by ^{13}C NMR solution spectra, equal to 95%.

The two available samples of s-P4MP, obtained by the two different synthetic routes, present similar X-ray diffraction patterns and ^{13}C NMR spectra. The present analysis is therefore general and does not depend on the kind of s-P4MP sample used. For this reason only the results for the sample obtained by polymerization of 4-methyl-1-pentene with the metallocene catalyst are reported.

Wide-angle X-ray powder diffraction patterns were obtained with nickel-filtered Cu Kα radiation with an automatic Philips diffractometer.

The ^{13}C NMR solution spectrum was recorded on a AM 250 Brucker spectrometer at 120 °C in deuterated tetrachloroethane. Tetramethylsilane (TMS) was used as an internal reference.

Solid state ^{13}C CPMAS NMR spectra were recorded at room temperature on a Brucker AC-200 spectrometer, equipped with an HP amplifier ^{1}H 200 MHz, 120 W continuous wave, and with a pulse amplifier M3205. The samples (100 mg) were packed into 4 mm zirconia rotors and sealed with Kel-F caps. The spin rate was kept at 8.0 kHz. The 90° pulse was 3.5 μs, the contact time for the cross polarization experiment was 0.8 ms, and the relaxation delay was 4 s. Spectra were obtained with 512 words in the time domain, zero filled, and Fourier transformed with size of 1024 words; 4000 scans were performed for each spectrum. Crystalline polyethylene was used as external reference at 33.6 ppm from tetramethylsilane.

The assignment of the resonances observed in the CPMAS spectrum was made by comparison with the solution spectrum and by CPMAS experiments performed using cross polarization (CP) in combination with polarization inversion (CPPI).[19] This method allows the selective observation of different carbon atoms. The CPPI spectrum was obtained with a contact time for the cross polarization (CP) of 0.8 ms while the length of the pulse used for the polarization inversion (PI) was 30 μs. The setup requirement for these experiments was identical to that used in CPMAS experiments.

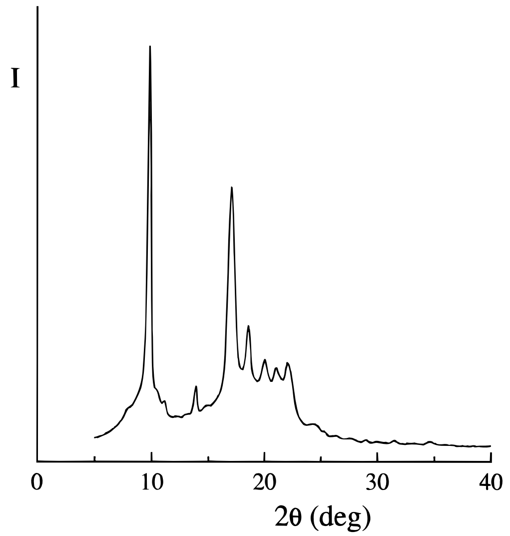


Figure 1. X-ray powder diffraction pattern of s-P4MP.

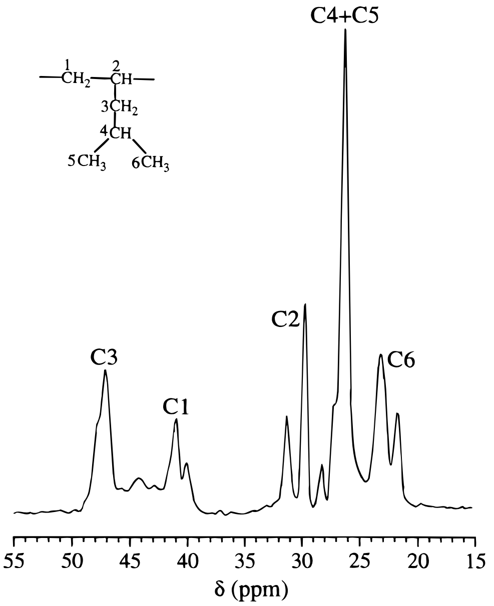


Figure 2. Solid state ^{13}C NMR CPMAS spectrum of s-P4MP.

Results and Discussion

The X-ray powder diffraction pattern of s-P4MP is reported in Figure 1. The crystallinity index evaluated from this X-ray pattern is nearly equal to 50%. The corresponding ^{13}C NMR CPMAS spectrum is shown in Figure 2. The assignment of the observed resonances was made by comparison with the solution spectrum (Table 1) and by CPMAS experiments performed using cross polarization in combination with polarization inversion (CPPI).[19] Indeed, in the CPPI spectrum obtained with a long CP time (1−2 ms) and a short PI time (30−35 μs), ^{13}CH signals disappear, ^{13}CH$_2$ signals become negative with a relative intensity about $^1/_3$, and methyl signals remain positive and are attenuated by about 62%.[19] This allows us to recognize the resonances of methine, methylene, and methyl carbons.

The CPPI spectrum of s-P4MP is reported in Figure 3. It is easily realized that the negative signals correspond to methylene carbons, labeled as C1 and C3. The resonances at $\delta = 29.45$ and 30.96 ppm in the CPMAS spectrum of Figure 2 disappear in the CPPI spectrum of Figure 3; hence they can be attributed to

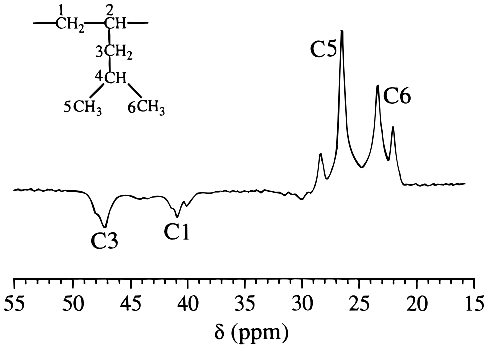


Figure 3. Solid state ^{13}C NMR CPPI spectrum of s-P4MP obtained using cross polarization (CP) in combination with polarization inversion (PI).

Table 1. Chemical Shifts from TMS of the Resonances Observed in the Solid State ^{13}C NMR CPMAS Spectrum of s-P4MP of Figure 2 and in the Solution Spectrum

	δ (ppm)	
	solid crystalline	solution
CH_3 (C6)	21.55, 22.97	
CH_3 (C5)	26.04, 27.93	23.50
$(CH)_{side}$ (C4)	26.04	25.78
$(CH_2)_{side}$ (C3)	46.52	45.84
$(CH)_{backbone}$ (C2)	29.45, 30.96	31.33
$(CH_2)_{backbone}$ (C1)	39.77, 40.69	42.79

methine carbons. The only positive signals present in the spectrum of Figure 3 correspond to the resonances of methyl carbons, labeled as C5 and C6, both split in an asymmetric doublet.

It is worth noting that the intensity of the resonance at 26.04 ppm (Figure 2) is attenuated by about 34% in the CPPI spectrum of Figure 3, while that of the doublet at 22.97 and 21.55 ppm (Figure 2) is attenuated by 68% (Figure 3), as expected for a methyl signal. This indicates that the resonance at 26.04 ppm corresponds to the sum of the resonances of the methine carbons C4 and methyl carbons C5. In the CPPI spectrum of Figure 3 the resonance of the methine carbons C4 is suppressed and only the signal of the methyl C5 is present. A similar overlapping of the resonances of methine carbons C4 and methyl carbons C5 has been also found in the CPMAS spectra of the various forms of isotactic poly(4-methyl-1-pentene).[16]

The chemical shifts of the resonances observed in the spectrum of Figure 2 and the assignment of the resonances are reported in Table 1 along with the chemical shifts of the resonances observed in the solution spectrum.

The two methyl carbons in the monomeric units C5 and C6 are not equivalent and give two resonances separated by roughly 5 ppm. Both resonances of the methyl carbons C5 and C6 are split in asymmetric doublets at 26.04 and 27.93 ppm and at 21.55 and 22.97 ppm, respectively.

The nonequivalence of the C5 and C6 methyl carbons is fully consistent with the proposed conformation of the chains of s-P4MP,[1,2] reported in Figure 4. The conformation of the lateral groups is evidenced in Figure 5. As discussed in the Introduction the chains of s-P4MP are in a complex helical conformation, which is approximately described with the **s**(12/7)2 symmetry and characterized by sequences of torsion angles ... *TTGG* .... According to the crystal structure,[1,2] the values of the torsion angles along the main chain are $\theta_1 = 70.1°$, $\theta_2 = 196.3°$ (with the bond angles τ_1 and τ_2 equal to 113° and 111°, respectively), while the values of the torsion angles that characterize the conformation of the lateral groups are $\theta_3 = 202.5°$, $\theta_4 = -50°$. The definitions of

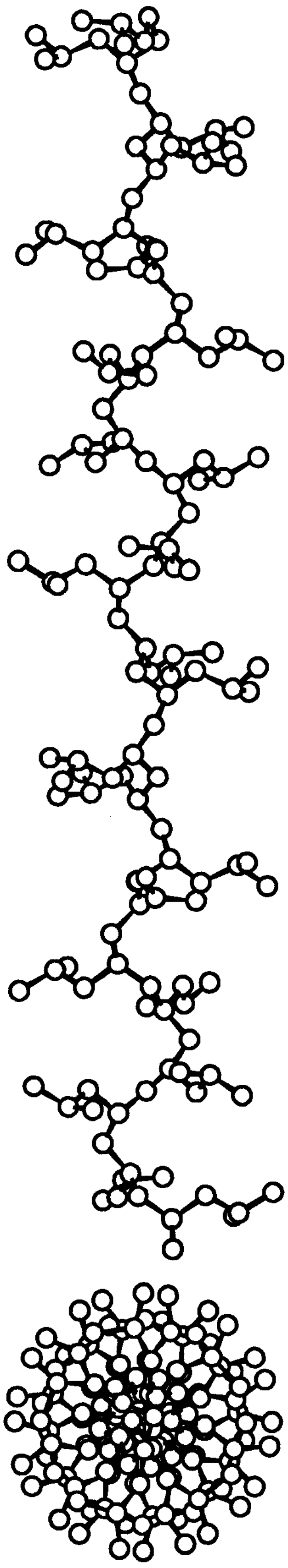


Figure 4. Projections along and perpendicular to the chain axis of the chain of s-P4MP in the **s**(12/7)2 helical conformation.[1]

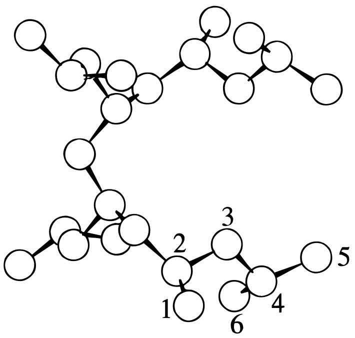


Figure 5. Conformation of the lateral group in the **s**(12/7)2 helical chain of s-P4MP.

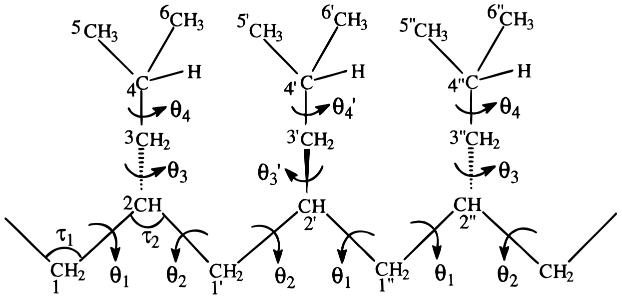


Figure 6. Definition of the torsion angles θ_1, θ_2, θ_3, θ_4 and the bond angles τ_1, τ_2 for a chain of s-P4MP having **s**(M/N)2 line repetition symmetry. The torsion angles that characterize the conformations of the lateral group in the conformational repeating units (θ_3, $\theta_3{}'$) are defined with respect to the same CH_2 group (C1′). Both torsion angles θ_4 and $\theta_4{}'$ are defined with respect to the hydrogen atoms of the $-CH(CH_3)_2$ groups. The binary axes, crossing the CH_2 groups of the main chain, for the **s**(M/N)2 symmetry, impose $\theta_3 = \theta_3{}'$ and $\theta_4 = \theta_4{}'$. The values of the torsion angles are reported in Table 2.

Table 2. Values of the Most Important Torsion Angles (deg) of the Chain of s-P4MP in the s(12/7)2 Helical Conformation[2,a]

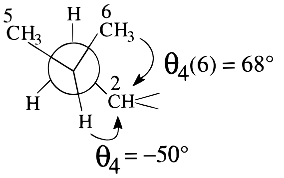
θ_1	70.1
θ_2	196.3
θ_3 (C4−C3−C2−C1′)	202.5 = −157.5
$\theta_3{}'$ (C4′−C3′−C2′−C1′)	202.5 = −157.5
θ_{3A} (C4−C3−C2−C1)	79.0
θ_{3A} (C4″−C3″−C2″−C1″)	79.0
$\theta_{3A}{}'$ (C4′−C3′−C2′−C1″)	79.0
θ_4 (H−C4−C3−C2)	−50.0
$\theta_4{}'$ (H−C4′−C3′−C2′)	−50.0
$\theta_4(6)$ (C6−C4−C3−C2)	68.0
$\theta_4(5)$ (C5−C4−C3−C2)	−168.0

[a] The labels of the carbon atoms refer to Figure 6.

the torsion and bond angles are shown in Figure 6, and the values of the most important torsion angles are reported in Table 2.

From Figure 5 it can be easily realized that the methyl carbons C5 and C6 have the same methine carbon C2 in the γ-position, but C2 is in a gauche arrangement with respect to the methyl C6 and in a trans arrangement to the methyl C5 (see also Scheme 1). The methyl carbon C6 is therefore shielded by one γ-gauche effect; according to the literature,[9] the resonance of C6 is then expected to occur at 5−6 ppm upfield from that of C5, as actually found (Figure 2 and Table 1). The splittings of both resonances of methyl carbons C5 and C6 in asymmetric doublets at 26.04 and 27.93 ppm and at 21.55 and 22.97 ppm, respectively, should be traced back to packing effects,[9] as will be discussed below.

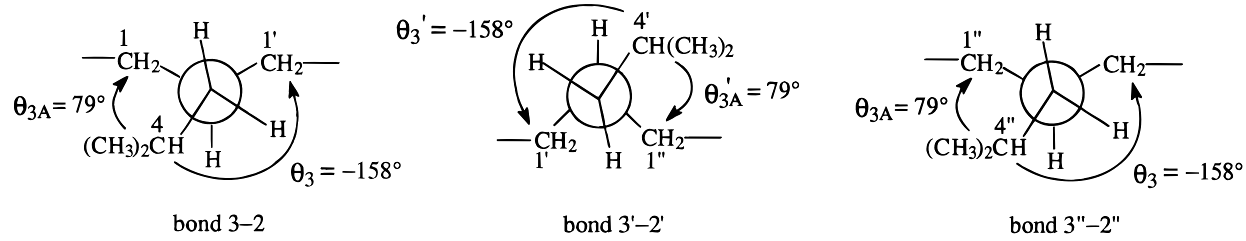
Scheme 1. Conformation of the Side Group in the s(12/7)2 Helical Chains of s-P4MP



It is worth noting that only one resonance of the backbone methylene carbons C1 is present in the spectrum of Figure 2, although it appears broad and with various shoulders (a narrow splitting in at least two components at 39.77 and 40.69 ppm can be observed). We recall that in the CPMAS spectra of other syndiotactic polymers having chains in *TTGG* helical conformation, like polypropylene[10,11] and poly(1-butene),[5] the resonance of the backbone methylene carbons is split into two components separated by ≈10 ppm (two γ-gauche effects), attributed to the two nonequivalent methylene carbons in conformational environments *TG.GT* and *GT.TG* (where the dot indicates the methylene carbon). This splitting is absent in the spectrum of s-P4MP of Figure 2 despite the helical *TTGG* conformation of the chains. This is fully consistent with the proposed conformation of the lateral groups.[1,2] Indeed, the methylene carbons in conformational environments of the kind *GT.TG* (C1′ in Figure 6) are in a gauche arrangement with both the backbone methine carbons in the γ-position, while the methylene carbons in conformational environments of the kind *TG.GT* (C1″ in Figure 6) are in a trans relationship to both the methine carbons in the γ-position. The backbone methylene carbons *GT.TG* should experience two γ-gauche shielding effects that are due to the gauche torsion angles $\theta_1 = 70.1°$ (see Figure 6 and Table 2) slightly distorted from the exact gauche value (60°). Besides the backbone methine carbons, the methylene carbons of the main chain have two methine carbons of the adjacent lateral groups in γ-position (see Figure 6). The presence of binary axes crossing the methylene groups of the main chain for the **s**(12/7)2 symmetry, imposes that the torsion angles θ_3 and $\theta_3{}'$, which define the conformation of the lateral groups of two adjacent monomeric units, must be equal, $\theta_3 = \theta_3{}'$ (θ_3 and $\theta_3{}'$ are defined with respect to the same CH_2 group, C1′ in Figure 6, see also Table 2). Since $\theta_3 = 202.5°$, the backbone methylene carbons of the kind *GT.TG* (C1′ in Figure 6) are in a nearly trans arrangement with respect to both the lateral methine carbons in γ-position (C4 and C4′ in Figure 6, see also Scheme 2). Since $\theta_{3A} = C4''-C3''-C2''-C1'' = \theta_{3A}{}' = C4'-C3'-C2'-C1'' = 79°$, the backbone methylene carbons of the kind *TG.GT* (C1″ in Figure 6) are in a nearly gauche arrangement with respect to both the lateral methine carbons in the γ-position (C4′ and C4″ in Figure 6, see also Scheme 2). Therefore also the methylene carbons *TG.GT* should experience two γ-gauche shielding effects that are due to the torsion angle $\theta_{3A} = 79°$. Both different backbone methylene carbons of s-P4MP in the conformational environments *GT.TG* and *TG.GT* experience two γ-gauche effects, and therefore they should be equivalent. This explains the presence of a single resonance for the methylene carbons in the spectrum of Figure 2.

Owing to the different values of the gauche torsion angle responsible of the γ-gauche effects experienced by the methylene carbons C1′ and C1″ ($\theta_1 = 70.1°$ and $\theta_{3A} = 79°$, respectively), these methylene carbons are not

Scheme 2



exactly equivalent. Indeed, it is well-known that the γ-gauche shielding effect strongly depends on the exact value of the torsion angle and is reduced when the torsion angle deviates from the exact gauche value of 60°.[15,16,20] Experimental evidence for the dependence of the γ-gauche effect on the torsion angle has been reported in the literature[15,16] through the analysis of the ^{13}C NMR CPMAS spectra of the polymorphic forms of isotactic poly(4-methyl-1-pentene)[16] and poly(1-butene);[15] from these analyses it was shown that the γ-gauche shielding parameter, normally -5 ppm when the *gauche* angle is $\approx$60°, decreases to nearly -2.5 ppm when the torsion angle deviates by nearly 20°.[16,15] Therefore the methylene carbons C1′ and C1″, which experience two γ-gauche effects due to $\theta_1 = 70.1°$ and $\theta_{3A} = 79°$, respectively, should give signals at only slightly different values of the chemical shift. This is in agreement with the presence of the narrow splitting (or shoulders) of the broad resonance of the methylene carbon C1, observed in the spectrum of Figure 2.

It is worth noting that in the case of form I of syndiotactic poly(1-butene) the resonance of the backbone methylene carbons is split into the two components separated by $\approx$10 ppm, attributed to *TG.GT* and *GT.TG* methylene carbons[5] (as occurs in syndiotactic polypropylene),[10,11] because of the particular "double gauche" conformation of the lateral ethyl groups found in the crystal structure.[3,4] Indeed, the methyl carbons of the side groups are in gauche arrangement with respect to both adjacent backbone methylene carbons,[3,4] so that the latter are still nonequivalent and their resonance are still separated by $\approx$10 ppm.[5]

It is apparent from Figure 2 that the resonance of the backbone methine carbons C2 is split in an asymmetric doublet at 29.45 and 30.96 ppm. Analogous splitting of $\approx$1.5 ppm for the resonance of the backbone methine carbons was observed in the solid state ^{13}C NMR spectra of forms I and IV of i-P4MP.[16] In ref 16, it was shown that the chemical shift of the resonance of the backbone methine carbons of i-P4MP strongly depends on the torsion angles of the helical chain. Moreover the splitting of the resonance of the backbone methine carbons of form I was attributed to a conformational effect.[16] Indeed, chains of i-P4MP in form I are characterized by a nonuniform $^7/_2$ helix[21] with values of the backbone torsion angles slightly different in the seven monomeric units included in the *c* axis. Backbone methine carbons of different monomeric units are therefore nonequivalent since they experience different amounts of the γ-gauche shielding effect owing to the different values of the gauche torsion angle (variable from $\approx$60° to $\approx$80° with an average value of 72° for the $^7/_2$ helix)[21] of different monomeric units.[16]

The splitting of the C2 methine carbons resonance in the spectrum of s-P4MP could be explained by a similar conformational effect. Indeed, the complex helical **s**(*M*/*N*)2 conformation of the chains of s-P4MP has been described with a ratio *M*/*N* approximated to $^{12}/_7$, by assuming an approximate value of the chain repetition of 46.9 Å occurring exactly after 12 structural units.[1,2] As a matter of fact, as described in ref 2, a repeat distance *c* is meaningful only when its value is small compared with the dimension of the crystal in the *c* direction and a departure of the ratio *M*/*N* from an exact rational value prevents the definition of an exact identity period *c*. Therefore the **s**(12/7) helical symmetry is only an approximate description of the chain conformation of s-P4MP.[1,2] The chains of s-P4MP are probably characterized by a nonuniform complex helix which cannot be described by a simple line repetition symmetry. On the other hand, the broadening and the splitting along the reciprocal coordinate ζ of the reflections in the X-ray fiber diffraction pattern[1,2] of s-P4MP is a clear indication of a nonuniform complex helical conformation.

The splitting of the resonance of the backbone methine carbons C2, observed in the ^{13}C NMR CPMAS spectrum of Figure 2, is accounted for this kind of chain conformation since in a nonuniform helix the backbone gauche torsion angles of different structural units can assume slightly different values, as occurs in form I of i-P4MP.[21] Therefore the methine carbons C2 should be nonequivalent since they should experience different amounts of the γ-gauche shielding effect.[16]

It is worth noting that an experimental relation between the chemical shift of the backbone methine carbon resonance of i-P4MP and the torsion angles (and hence between the γ-gauche shielding effect and the torsion angle) has been given in ref 16. By interpolating the values of the chemical shift of the C2 resonance of s-P4MP on the curve of Figure 13 of ref 16, an average value of $\approx$70° for the backbone torsion angle θ_1 is obtained, in accordance with the value found in the crystal structure of s-P4MP.[1,2] This confirms the feasibility of the relation found in ref 16 and indicates that s-P4MP provides a further example, besides isotactic poly(1-butene)[15] and isotactic poly(4-methyl-1-pentene),[16] of the strong dependence of the γ-gauche shielding effect on the exact value of the torsion angle.

Packing Effect. As observed above, the resonances of the methyl carbons C5 and C6 in the spectra of Figures 2 and 3 show narrow splittings (1$-$2 ppm) that should be traced back to packing effects.

The model of packing of the chains of s-P4MP is shown in Figures 7 and 8 in the *ab* and *ac* projections, respectively. Chains in helical **s**(12/7)2 conformation are packed in the tetragonal unit cell according to the space group $P\bar{4}$.[2] The values of the closest intermolecular distances, which define the crystallographic environments of the methyl carbons C6 and C5 of different monomeric units and of adjacent chains, are reported in Table 3. It is apparent from Figure 8 and Table 3 that the methyl carbons C6 of adjacent chains are not all equivalent. For instance, the methyl carbons C6 and

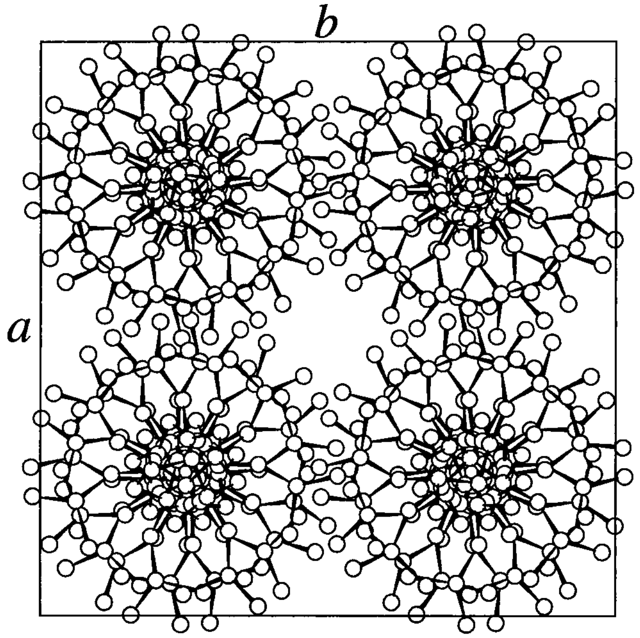


Figure 7. $a-b$ projection of the model of packing of **s**(12/7)2 helical chains of s-P4MP in the tetragonal unit cell with axes $a = 18.03$ Å and $c = 46.9$ Å and space group $P\bar{4}$.[2]

C6$^{\mathrm{I}}$ in Figure 8 are nonequivalent since they have different contact distances with neighboring atoms. All contact distances of methyl C6$^{\mathrm{I}}$ are greater than 4.5 Å (according to the crystal structure),[2] whereas methyl C6 has one critical distance with methyl C6$^{\mathrm{X}}$ at 3.46 Å. The analysis of the packing model of Figure 8 reveals that there are more than two nonequivalent methyl C6; indeed, although methyl C6 and C6$^{\mathrm{VII}}$ are equivalent, and, C6$^{\mathrm{I}}$ is equivalent to C6$^{\mathrm{V}}$, methyl C6$^{\mathrm{VI}}$, which is equivalent to methyl C6$^{\mathrm{VIII}}$, is different from either methyl carbons C6 and C6$^{\mathrm{I}}$. This can explain the asymmetric splitting of the resonance of the methyl carbon C6 in the spectrum of Figure 2.

It is easily realized, from Table 3, that also the methyl carbons C5 of different monomeric unit, and of adjacent chains, are not all equivalent. For instance methyl carbons C5$^{\mathrm{I}}$ and C5$^{\mathrm{II}}$ are nonequivalent since they have different contact distances with neighboring atoms. Methyl carbon C5$^{\mathrm{I}}$ has two critical contact distances with the methylene carbon C1$^{\mathrm{IV}}$ at 3.42 Å and with the methine carbon C4$^{\mathrm{II}}$ at 3.60 Å, while all contact distances of the methyl carbon C5$^{\mathrm{II}}$ are greater than 4.1 Å[2] (Table 3). Also in this case there are more than two nonequivalent methyl carbons C5; indeed, methyl carbon C5$^{\mathrm{II}}$ is equivalent to C5$^{\mathrm{III}}$ and methyl C5$^{\mathrm{I}}$ is equivalent to C5$^{\mathrm{V}}$, but methyl carbon C5$^{\mathrm{IV}}$ is different from either methyl carbons C5$^{\mathrm{I}}$ and C5$^{\mathrm{II}}$. This can explain the asymmetric splitting of the resonance of the methyl carbon C5 in the spectrum of Figure 2.

Conclusions

Crystalline s-P4MP has been studied through solid state ^{13}C NMR CPMAS spectroscopy. The assignment of the resonances in the ^{13}C NMR CPMAS spectrum was made by comparison with the solution spectrum and by CPMAS experiments performed using cross polarization in combination with polarization inversion (CPPI).[19]

The presence of two distinct resonances separated by ≈5 ppm (one γ-gauche effect) for the methyl carbons indicates that the two methyl carbons belonging to the monomeric unit are nonequivalent. This has been explained on the basis of the conformation of the lateral groups of s-P4MP proposed in the literature.[1,2]

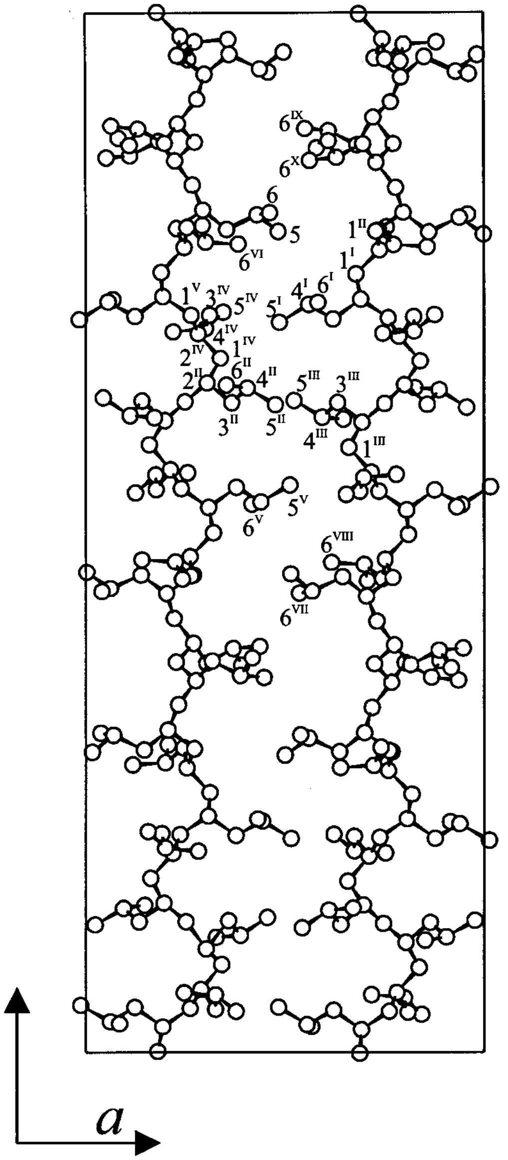


Figure 8. $a-c$ projection of the model of packing of s-P4MP.

A single resonance of the backbone methylene carbons, although broad and with various shoulders, is present in the ^{13}C NMR CPMAS spectrum. The absence of the splitting of ≈10 ppm for this resonance, typical of other syndiotactic polymer having *TTGG* helical conformation, like polypropylene[10,11] and poly(1-butene),[5] is still fully consistent with the helical *TTGG* conformation of the chains of s-P4MP,[1] since both methylene carbons in conformational environment *GT.TG* and *TG.GT* experience two γ-gauche shielding effects due to the backbone and lateral methine atoms, respectively. The amount of the γ-gauche shielding effects experienced by the two methylene carbons is different owing to the different values of the gauche torsion angle (70° vs 79°). This explains the shoulders or the narrow splitting observed for the backbone methylene resonance.

The narrow splitting of the resonance of the backbone methine carbons has been attributed to a conformational effect. It indicates that the helical *TTGG* conformation of the chain of s-P4MP, which was approxi-

Table 3. Closest Intermolecular Distances (Å) in the Model of Packing of s-P4MP of Figures 7 and 8[a]

contact distances of C6	contact distances of C6$^{\mathrm{I}}$
C6–C6$^{\mathrm{X}}$ = 3.46	C6$^{\mathrm{I}}$–C6$^{\mathrm{VI}}$ = 4.51
C6–C6$^{\mathrm{IX}}$ = 4.37	C6$^{\mathrm{I}}$–C5$^{\mathrm{II}}$ = 5.03
C6–C4$^{\mathrm{I}}$ = 4.57	C6$^{\mathrm{I}}$–C4$^{\mathrm{II}}$ = 5.05
C6–C1$^{\mathrm{II}}$ = 4.89	C6$^{\mathrm{I}}$–C6 = 5.14
C6–C1$^{\mathrm{I}}$ = 4.93	C6$^{\mathrm{I}}$–C4$^{\mathrm{IV}}$ = 5.50
C6–C5$^{\mathrm{I}}$ = 5.00	C6$^{\mathrm{I}}$–C6$^{\mathrm{II}}$ = 5.69
C6–C6$^{\mathrm{I}}$ = 5.14	
contact distances of C5$^{\mathrm{I}}$	**contact distances of C5$^{\mathrm{II}}$**
C5$^{\mathrm{I}}$–C1$^{\mathrm{IV}}$ = 3.42	C5$^{\mathrm{II}}$–C5$^{\mathrm{I}}$ = 4.14
C5$^{\mathrm{I}}$–C4$^{\mathrm{II}}$ = 3.60	C5$^{\mathrm{II}}$–C1$^{\mathrm{III}}$ = 4.34
C5$^{\mathrm{I}}$–C1$^{\mathrm{V}}$ = 4.06	C5$^{\mathrm{II}}$–C3$^{\mathrm{III}}$ = 4.49
C5$^{\mathrm{I}}$–C2$^{\mathrm{IV}}$ = 4.09	C5$^{\mathrm{II}}$–C5$^{\mathrm{V}}$ = 4.90
C5$^{\mathrm{I}}$–C5$^{\mathrm{II}}$ = 4.14	C5$^{\mathrm{II}}$–C6$^{\mathrm{I}}$ = 5.03
C5$^{\mathrm{I}}$–C3$^{\mathrm{IV}}$ = 4.25	C5$^{\mathrm{II}}$–C5$^{\mathrm{III}}$ = 5.14
C5$^{\mathrm{I}}$–C3$^{\mathrm{II}}$ = 4.25	C5$^{\mathrm{II}}$–C4$^{\mathrm{III}}$ = 5.17
C5$^{\mathrm{I}}$–C2$^{\mathrm{II}}$ = 4.32	
C5$^{\mathrm{I}}$–C6$^{\mathrm{II}}$ = 4.54	
C5$^{\mathrm{I}}$–C6$^{\mathrm{VI}}$ = 4.55	
C5$^{\mathrm{I}}$–C5$^{\mathrm{III}}$ = 4.90	
C5$^{\mathrm{I}}$–C6 = 5.00	
C5$^{\mathrm{I}}$–C5 = 5.10	

[a] The labels of the carbon atoms refer to Figure 8.

mately described with a **s**(12/7)2 symmetry,[1,2] should be better described with a complex nonuniform helix with slightly different values of the backbone torsion angles of different structural units. In this nonuniform helix the backbone methine carbons of different structural units should be nonequivalent since they should experience different amounts of the γ-gauche shielding effect, resulting in the asymmetric splitting of the corresponding resonance.

Both resonances of the methyl carbons present narrow splittings that can be traced back to packing effect. These splittings are easily interpreted on the basis of the model of packing proposed in the literature[2] and, hence, provide a confirmation of the proposed crystal structure.[1,2]

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