Solid-State ^{13}C Nuclear Magnetic Resonance Spectra of Four Crystalline Forms of Isotactic Poly(4-methyl-1-pentene)

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ABSTRACT: Four crystalline forms of isotactic poly(4-methyl-1-pentene) (i-P4MP) (forms I, II, II, and IV) have been studied through solid-state ^{13}C NMR CP-MAS spectroscopy. The assignment of the resonances observed in the ^{13}C NMR CP-MAS spectra was made by dipolar dephasing experiments. The presence in all spectra of two distinct resonances, separated by ≈3 ppm, of the methyl carbons indicates that the two methyls belonging to the monomeric unit are nonequivalent. This has been explained on the basis of the γ-*gauche* shielding interaction and of the conformations of polymer chains and lateral groups. The resonances observed in the spectrum of form III are markedly deshielded compared to those of other forms, whereas the resonances of form I are deshielded compared to those of form IV. This deshielding has been consistently interpreted on the hypothesis that the amount of the γ-*gauche* shielding effect depends on the value of the torsion angles of the main chain. Indeed, the torsion angles of the main chain for the 7/2 helical conformation of form I deviate, on average, by 12−15° from the exact staggered values of 60° and 180° (the average values of the torsion angles are $\theta_1 = 72°$ and $\theta_2 = 195°$); they deviate by 22−26° for the 4/1 helical conformation of form III ($\theta_1 = 82°$ and $\theta_2 = 206°$). The γ-*gauche* shielding parameter, normally −5 ppm when the *gauche* angle is nearly 60°, decreases to a value between −2 and −2.5 ppm when the torsion angle deviates by nearly 20° from 60°. In the form IV, the upfield shift of the resonances, compared to forms I and III indicates that the carbon atoms experience a full γ-*gauche* shielding interaction and, hence, the main chain torsion angles θ_1 and θ_2 are near 60 and 180°, respectively, typical of a helical 3/1 conformation. This analysis allows us to suggest that the form IV of i-P4MP is characterized by chains in 3/1 helical conformation. The resonances of the methyl carbons of the four forms of i-P4MP show narrow splittings (1−2 ppm) which should be traced back to packing effects. This has provided a chance of testing the packing model of form I and form III proposed in the literature. In the spectrum of form I, the resonance of backbone methine carbons is also split in a doublet. This splitting is due to conformational effects, rather than packing effects and confirms that, according to the refinement of the crystal structure of form I, the chains assume a helical conformation slightly distorted from the uniform 7/2 helix. The succession of torsion angles along the main chain is ...TGT′G′T″G″..., instead of $(TG)_n$. Therefore, backbone methine carbons of different monomeric units are conformationally nonequivalent because they experience different amounts of γ-*gauche* shielding effects owing to different values of the *gauche* torsion angle θ_1 of different monomeric units.

Introduction

Isotactic poly(4-methyl-1-pentene) (i-P4MP) presents a complex polymorphic behavior. Five different crystalline forms have been described so far.[1−6]

The different modifications can be obtained from crystallization in semidilute solutions depending on the solvent and the thermal history of the solutions.[5,6]

Form I is the ordinary crystalline form which occurs in melt crystallized samples and in extruded fibers; it can be also obtained from crystallization in solutions of high-boiling solvents, like normal alkanes with number of carbon atoms greater than 9, a branched dodecane and branched decane.[6] Form I is characterized by chains in 7/2 helical conformation packed in a tetragonal unit cell with axes $a = 18.66$ Å and $c = 13.80$ Å[1−4] according to the space group $P\bar{4}$.[2,3] Slight deviations from the uniform 7/2 helix have been suggested by a refinement of the crystal structure of form I;[4] according to this refinement, chains in a slightly distorted conformation are packed in the space group $P\bar{4}b2$.[4]

Form II was prepared for the first time by isothermal crystallization at 20 °C from dilute xylene solutions[7−9] and, recently, by crystallization from tetramethyltin solution[6] or as a minor component in a mixed structure crystallized in carbon disulfide solutions.[6]

For the form II, Takayanagi et al.[9] proposed, from X-ray diffraction spectra on single crystal mats, a tetragonal unit cell with axes $a = 19.16$ Å and $c = 7.12$ Å with chains in 4/1 helical conformation.

In lower linear (five to seven carbon atoms) and branched (six to nine carbon atoms) alkanes, as well as in carbon tetrachloride and cycloalkanes containing 6−10 carbon atoms, form III, is recovered.[5,6] This form was already obtained from dilute solutions in xylene (by isothermal crystallization at 65 °C)[7−9] and in decalin.[10−11] Charlet et al.[5] have proposed, from electron diffraction of single crystals of form III, a tetragonal unit cell with axes $a = 19.38$ Å and $c = 6.98$ Å with chains in 4/1 helical conformation, according to the unit cell previously proposed by Takayanagi et al.[8,9] The complete crystal structure of form III has been recently determined and refined;[12,13] chains in 4/1 helical conformation are packed in a tetragonal unit cell with axes $a = 19.46$ Å and $c = 7.02$ Å according to the space group $I4_1$.[12,13] Form III transforms into form I after annealing at ≈100 °C and under stretching.[5]

Form IV was obtained, in both unoriented and uniaxially oriented state, by annealing modification I above 200 °C under pressure (4500 atmospheres).[14] The same crystalline modification has been obtained also from cyclopentane solutions.[15] Stretching of an unoriented

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sample in form IV leads to a fiber in form I;[15] however, a partially oriented sample in form IV was obtained by swelling a fiber of form I in saturated cyclopentane vapor at 50 °C.[15] Charlet and Delmas[15] have proposed for form IV a hexagonal unit cell with axes $a = 22.17$ Å and $c = 6.69$ Å. Form IV transforms into form I by annealing at 130 °C.

Form V has been obtained from concentrated cyclohexane gels[16] and by crystallization from cyclohexane and carbon tetrachloride solutions.[6] Form V transforms into form I by annealing at ≈90 °C.

It is worth noting that only for form I and form III has a complete crystal structure been reported.[2−4,12,13] Only unit cell parameters have been proposed for the tetragonal form II[9] and for the hexagonal form IV.[15]

In this paper the four crystalline forms of i-P4MP are examined by solid state ^{13}C NMR spectroscopy using cross-polarization/magic-angle spinning (CP-MAS), in order to obtain new structural information on the various crystalline forms. Indeed, the observed chemical shifts in ^{13}C NMR CP-MAS spectra of solid polymers provide information concerning the conformation of polymers in the crystalline state. Conformationally sensitive *γ-gauche* shielding effect[17] has been observed in various isotactic polymers, like polypropylene,[18,19] poly(1-butene),[20] and poly(3-methyl-1-butene).[21] The solid state ^{13}C NMR spectra of these polymers have been convincingly interpreted in terms of *γ-gauche* interactions with the same *γ-gauche* shielding parameter of ≈−5 ppm used in the prediction of the solution ^{13}C NMR spectra.[22]

In addition, the analysis of the solid state ^{13}C NMR spectra of the three different crystalline forms of isotactic poly(1-butene) (forms I, II, and III),[20] which adopt $(TG)_n$ helical conformations with 3/1, 11/3, and 4/1 helical symmetry, respectively, has shown that the *γ-gauche* shielding parameter depends on the value of the torsion angle of the *gauche* bond of the chain backbone. Indeed, the standard value of −5 ppm for the *γ-gauche* shielding effect is observed when the *gauche* torsion angle is near 60°, as occurs in the 3/1 helical conformation of the chains in form I, whereas it is reduced when the torsion angle is increased to 77°, as occurs in the 11/3 helical conformation of the chains in form II, and it is reduced to about half its standard value when the torsion angle is further increased to 82°, as occurs in the 4/1 helical conformation of the chains in form III.[20]

The analysis of the ^{13}C NMR CP-MAS spectra of the different modifications of i-P4MP, presented in this paper, can allow us to find further experimental relations between the *γ-gauche* shielding parameter and the torsion angle, since the different forms of i-P4MP are characterized by helical $(TG)_n$ conformations with 7/2 (form I) and 4/1 (form III) symmetry. From this relation and from the value of the *γ-gauche* shielding parameter observed in the spectrum of form IV, a conformation of the chain in this modification will be suggested.

Experimental Part

i-P4MP was prepared with Ziegler−Natta type catalysts.

The most stereoregular fraction of the polymer (≈85% extracted in boiling *n*-heptane) presents an inherent viscosity, measured in decalin at 135 °C, of 1.35 dL/g corresponding to a molecular weight of 5×10^4.

Form I of i-P4MP was prepared by crystallization from the melt of the as-polymerized sample or by annealing of form III, in an N_2 atmosphere, at 155 °C for 1 h.

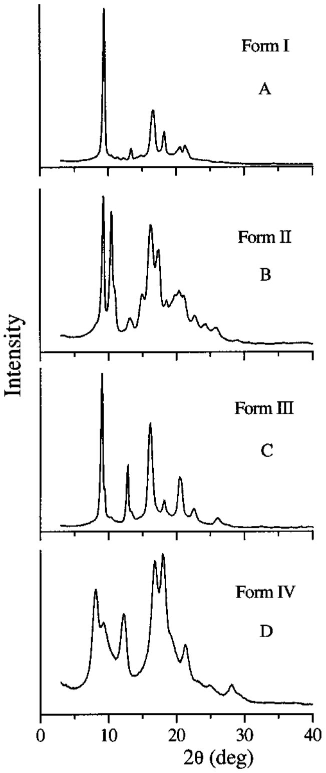


Figure 1. X-ray powder diffraction profiles of four crystalline forms of i-P4MP: (A) form I; (B) form II; (C) form III; (D) form IV.

The others crystalline forms of i-P4MP were prepared by crystallization from solutions following the method described in ref 6. The solutions (polymer volume fraction $\phi = 0.05$) were prepared in sealed glass tubes. Dissolution was achieved by heating the sealed tube at the temperature T_{max} for 20 h. The solution was then cooled rapidly or slowly to room temperature, and the polymer was recovered by evaporation of the solvent at room temperature.

Form II was obtained by crystallization in a tetramethyltin solution heated at $T_{max} = 165$ °C and rapidly cooled to room temperature. Form III was crystallized from a heptane solution heated at $T_{max} = 135$ °C, by rapid cooling to room temperature. A sample of i-P4MP in form IV was prepared by crystallization in cyclopentane solution heated at $T_{max} = 85$ °C and slowly cooled to room temperature.

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

Solid-state ^{13}C CP-MAS NMR spectra were obtained with a Bruker AC-200 spectrometer, equipped with an HP amplifier, ^{1}H 200 MHz, 120 W cw and with a pulse amplifier M3205. The spin rate of the sample was 8 kHz. The $\pi/2$ pulse width was 3.2 μs, the contact time for the cross-polarization experiment was 5 ms, and the relaxation delay was 6 s. ^{13}C spectra were obtained with 1K in the time domain, zero filled and Fourier transformed with a size of 2K. Crystalline poly(ethylene) was used as external reference at 33.6 ppm from tetramethylsilane.[23]

Dipolar dephasing experiments were performed introducing a variable delay, spanning from 1 up to 100 μs, between the development of ^{13}C magnetization with the mix pulse and data aquisition with full proton decoupling.[24] Intensities of the resonances were reported as a function of the variable delay.

Results and Discussion

X-ray Powder Diffraction Patterns and ^{13}C NMR CPMAS Spectra of the Four Forms of i-P4MP. The X-ray powder diffraction profiles of the four crystalline modifications of i-P4MP (forms I, II, III and IV) are reported in Figure 1. The Bragg distances of the

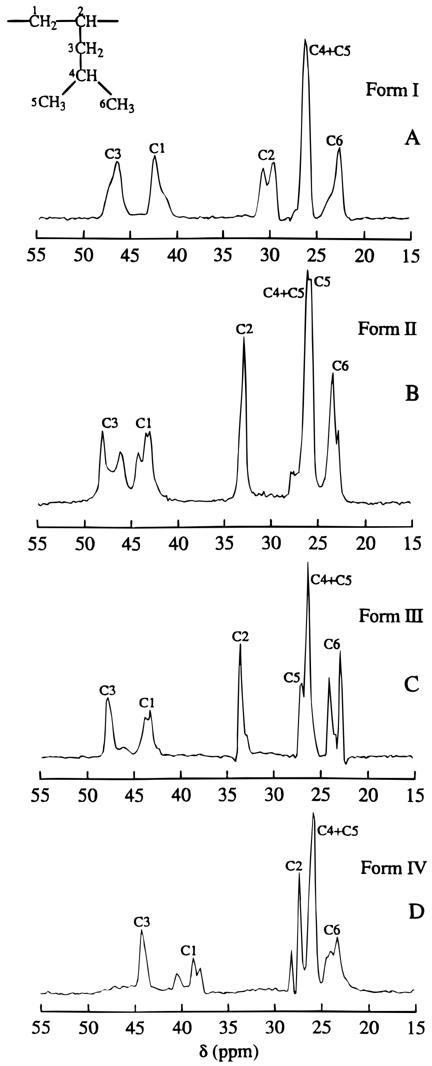


Figure 2. Solid-state ^{13}C NMR CP-MAS spectra of four crystalline forms of i-P4MP: (A) form I; (B) form II; (C) form III; (D) form IV.

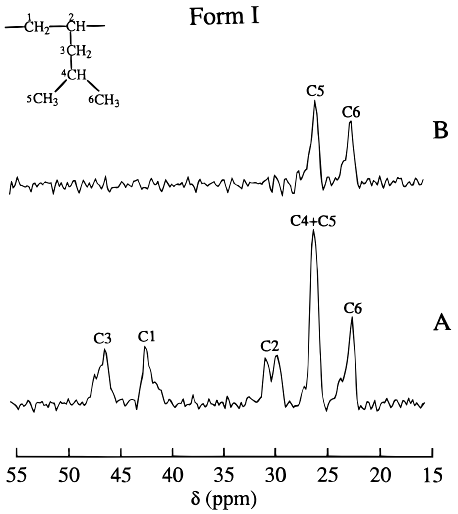


Figure 3. ^{13}C NMR CP-MAS spectra of form I in dipolar dephasing experiments with delay time of 1 μs (A) and 100 μs (B).

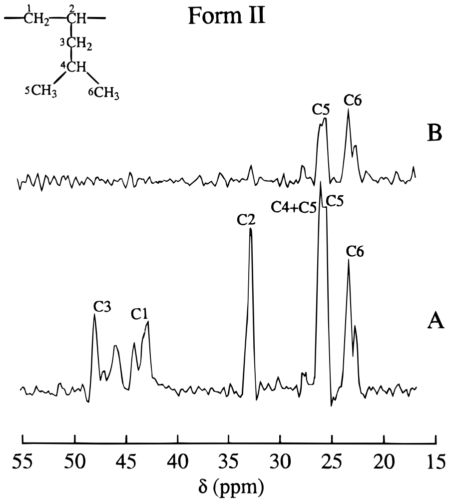


Figure 4. ^{13}C NMR CP-MAS spectra of form II in dipolar dephasing experiments with delay time of 1 μs (A) and 100 μs (B).

reflections observed in the X-ray patterns of the four forms of Figure 1 are in agreement with those reported in the literature[6,12] and with those calculated from the published unit cells;[2−4,6,12,13,15] this indicates that pure crystalline forms I, II, III, and IV have been obtained.

The ^{13}C NMR CP-MAS spectra of forms I, II, III, and IV of i-P4MP are reported in Figure 2. The assignment of the observed resonances was made by comparison with the solution spectrum[25] and by dipolar dephasing experiments.[24]

Indeed, in dipolar dephasing experiments a brief delay without proton decoupling is inserted between the development of ^{13}C magnetization with the mix pulse and data acquisition with full proton decoupling.[24] This procedure allows to eliminate entirely the resonances of methylene and methine carbons, whereas the methyl carbons resonances, which decay slowly, are not entirely eliminated.

The ^{13}C NMR CP-MAS spectra of forms I, II, III, and IV of i-P4MP in dipolar dephasing experiments with short and long delay time are reported in Figures 3−6, respectively. It is apparent that, for all forms, the spectra obtained for long delay time (100 μs) present only the resonances of the methyl carbons which are, therefore, easily recognized. The relative intensities of the observed resonances in dipolar dephasing experiments are reported as a function of the delay time in Figures 7−10 for forms I, II, III, and IV, respectively. It is apparent from the plots of Figures 7−10, that the resonances at $\delta = 44-48$ ppm and at $\delta = 39-43$ ppm are already eliminated for short delay time (20−25 μs), then, with the increase of the dephasing time (40 μs), the resonances at $\delta = 27-33$ ppm are also eliminated, whereas those at $\delta = 22-24$ ppm and at $\delta = 26-27$ ppm are not entirely eliminated, at least for a delay time of 100 μs. The slow decay observed for the resonances at $\delta = 22-24$ ppm (generally split in doublets) and at $\delta = 26-27$ ppm shows that they arise from methyl carbons. Instead, the rapid decay of the resonances at $\delta = 44-48$ ppm and $\delta = 39-43$ ppm indicates that they can be assigned to methylene carbons.

The assignment of the resonances observed in the spectra of Figure 2 is reported in Table 1.

It is worth noting that, for forms I, II, III and IV the resonances at $\delta = 26.36$, 26.24, 26.29, and 26.06 ppm in the spectra of Parts A−D of Figure 2, respectively, correspond to the resonance of the methyl carbon C5 plus the resonance of the methine carbon of the side group C4; the latter is eliminated in the dephasing experiment with long delay time (100 μs) and only the resonance of the methyl carbon C5 is left (Figures 3B, 4B, 5B and 6B). In the plots of Figures 7−10, the

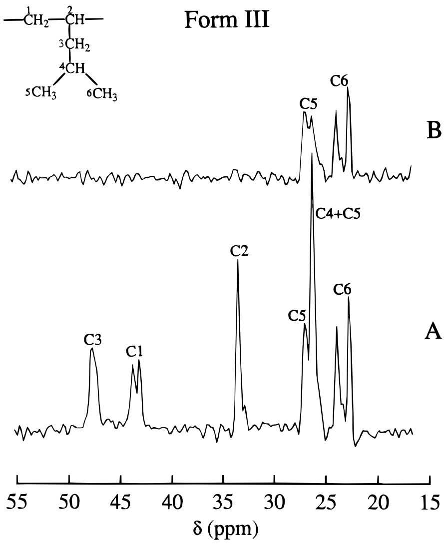


Figure 5. ^{13}C NMR CP-MAS spectra of form III in dipolar dephasing experiments with delay time of 1 μs (A) and 100 μs (B).

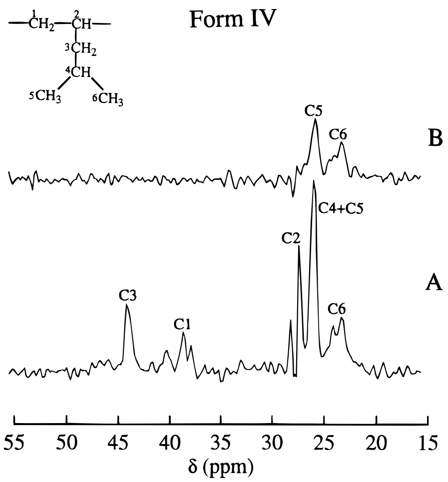


Figure 6. ^{13}C NMR CP-MAS spectra of form IV in dipolar dephasing experiments with delay time of 1 μs (A) and 100 μs (B).

resonances at $\delta = 26.36$, 26.24, 26.29, and 26.06 ppm of forms I, II, III, and IV, respectively, decay rapidly up to 40 μs, owing to the decay of the resonances of the methine carbons C4; then they remain constant and correspond to the resonance of the methyl carbons C5.

For form III, by eliminating the resonance of the methine carbon C4 at $\delta = 26.29$ ppm, besides the visible resonance at $\delta = 27.06$ ppm of the methyl carbon C5 (Figure 5A), a resonance at $\delta = 26.29$ appears (Figure 5B). This indicates that the resonance of the methyl carbons C5 is split into a doublet at $\delta = 27.06$ and 26.29 ppm and the component at 26.29 ppm is concealed, in the spectrum of Figure 2C, by the resonance of the methine C4. Similar splitting of the resonance of the methyl carbons C5 at $\delta = 26.24$ and 25.71 ppm is observed for form II (Figure 4B).

Moreover, it is apparent from Figure 2 that for all forms of i-P4MP, the upfield resonances of the methyl carbons C6 are also split in various components. For form I a shoulder at downfield of the resonance at $\delta = 22.66$ ppm is apparent (Figures 2A and 3), whereas well resolved doublets at $\delta = 22.73$ and 23.44 ppm for the form II (Figures 2B and 4), and at $\delta = 22.76$ and 23.97 ppm for the form III (Figures 2C and 5) are observed.

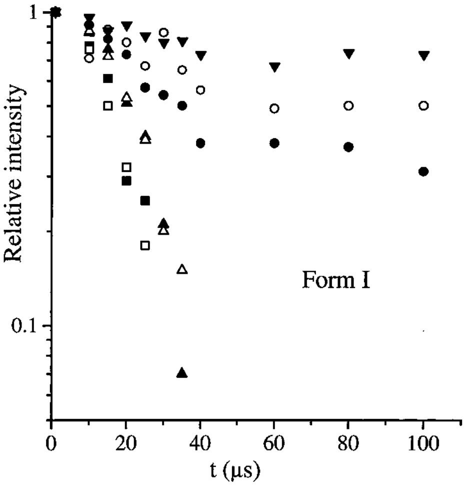


Figure 7. Relative intensities of the resonances observed in the ^{13}C NMR CP-MAS spectra of form I in dipolar dephasing experiments, reported as a function of the dephasing delay time: (□) resonance of C1 at 42.52 ppm; (▲) resonance of C2 at 30.85 ppm; (△) resonance of C2 at 29.63 ppm; (■) resonance of C3 at 46.41 ppm; (●) resonance of C4 + C5 at 26.36 ppm; (○) resonance of C6 at 23.86 ppm; (▼) resonance of C6 at 22.66 ppm. The components at 41.41 and 47.24 ppm of the resonances of C1 and C3, respectively, were not considered owing to their low intensities.

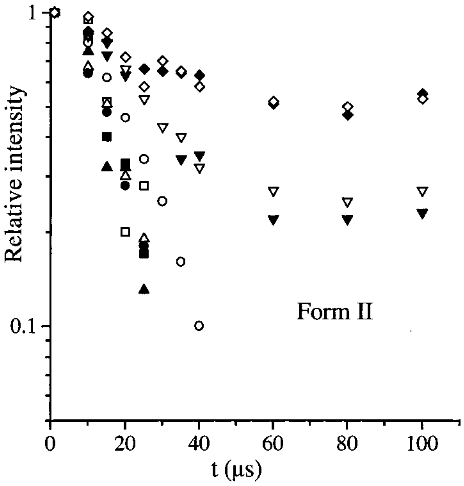


Figure 8. Relative intensities of the resonances observed in the ^{13}C NMR CP-MAS spectra of form II in dipolar dephasing experiments, reported as a function of the dephasing delay time: (▲) resonance of C1 at 44.19 ppm; (△) resonance of C1 at 43.37 ppm; (●) resonance of C1 at 42.96 ppm; (○) resonance of C2 at 32.85 ppm; (■) resonance of C3 at 47.97 ppm; (□) resonance of C3 at 45.94 ppm; (▼) resonance of C4 + C5 at 26.24 ppm; (▽) resonance of C5 at 25.71 ppm; (◆) resonance of C6 at 23.44 ppm; (◇) resonance of C6 at 22.73 ppm.

For the form IV the resonance of the methyl carbon C6 is separated in three component at $\delta = 23.39$, 24.16 and 24.60 ppm (Figures 2D and 6).

For all forms the resonances of the backbone methylene carbons C1 are split in various components (Figure 2 and Table 1), whereas splittings of the resonances of the methylene carbons C3 appear for forms I and II (Figures 2A and B)

For the form I also the resonance of the backbone methine carbon C2 is split in a doublet at $\delta = 29.63$ and 30.85 ppm (Figure 2A).

Conformation of the Side Groups. The presence in the ^{13}C NMR CPMAS spectra of the four forms of i-P4MP of two distinct resonances of the methyl carbons C5 and C6 indicates that the two methyl carbons

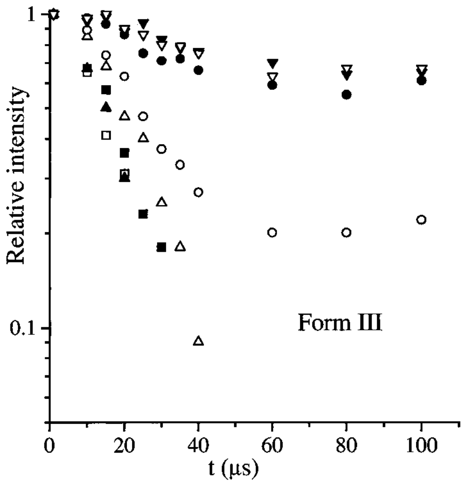


Figure 9. Relative intensities of the resonances observed in the ^{13}C NMR CP-MAS spectra of form III in dipolar dephasing experiments, reported as a function of the dephasing delay time. (□) resonance of C1 at 43.76 ppm; (▲) resonance of C1 at 43.16 ppm; (△) resonance of C2 at 33.50 ppm; (■) resonance of C3 at 47.77 ppm; (○) resonance of C4 + C5 at 26.29 ppm; (●) resonance of C5 at 27.06 ppm; (▼) resonance of C6 at 23.97 ppm; (▽) resonance of C6 at 22.76 ppm.

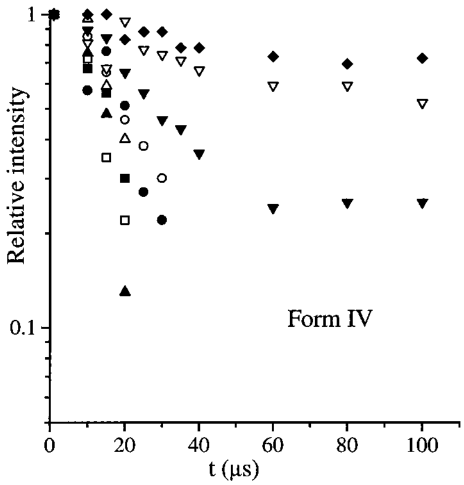


Figure 10. Relative intensities of the resonances observed in the ^{13}C NMR CP-MAS spectra of form IV in dipolar dephasing experiments, reported as a function of the dephasing delay time: (□) resonance of C1 at 40.39 ppm; (▲) resonance of C1 at 38.68 ppm; (△) resonance of C1 at 37.96 ppm; (●) resonance of C2 at 28.26 ppm; (○) resonance of C2 at 27.41 ppm (■) resonance of C3 at 44.08 ppm; (▼) resonance of C4 + C5 at 26.06 ppm; (▽) resonance of C6 at 24.16 ppm; (◆) resonance of C6 at 23.39 ppm. The component at 24.60 ppm of the resonance of C6 was not considered owing to its low intensity.

belonging to the monomeric unit are not equivalent. This could be explained on the basis of the proposed conformations for the polymer chains. Projections of chains of i-P4MP in the helical 7/2 and 4/1 conformations of the forms I and III, respectively, are shown in Figure 11. The definitions of the torsion angles θ_1, θ_2, θ_3, and θ_4, which characterize the conformation of the chain of i-P4MP, and of the bond angles τ_1 and τ_2 are reported in Figure 12. The most important values of the torsion angles of the chains of i-P4MP in the forms I and III are reported in Table 2;[4,12,13] the bond lengths C−C are 1.54 Å, the bond angles are $\tau_1 = 114°$ and $\tau_2 = 109.5°$, for form I,[4] and $\tau_1 = 113°$ and $\tau_2 = 111°$, for form III.[12,13]

Table 1. Chemical Shifts (ppm) of the Resonances Observed in the ^{13}C NMR CP-MAS Spectra of Forms I, II, III and IV of i-P4MP of Figure 2

	form I	form II	form III	form IV
$(CH_2)_{backbone}$, C1	42.52 41.41	44.19 43.37 42.96	43.76 43.16	40.39 38.68 37.96
$(CH)_{backbone}$, C2	30.85 29.63	32.85	33.50	28.26 27.41
$(CH_2)_{side}$, C3	47.24 46.41	47.97 45.94	47.77	44.08
$(CH)_{side}$, C4	26.36	26.24	26.29	26.06
$(CH_3)_{trans}$, C5	26.36	26.24 25.71	27.06 26.29	26.06
$(CH_3)_{gauche}$, C6	23.86 22.66	23.44 22.73	23.97 22.76	24.60 24.16 23.39

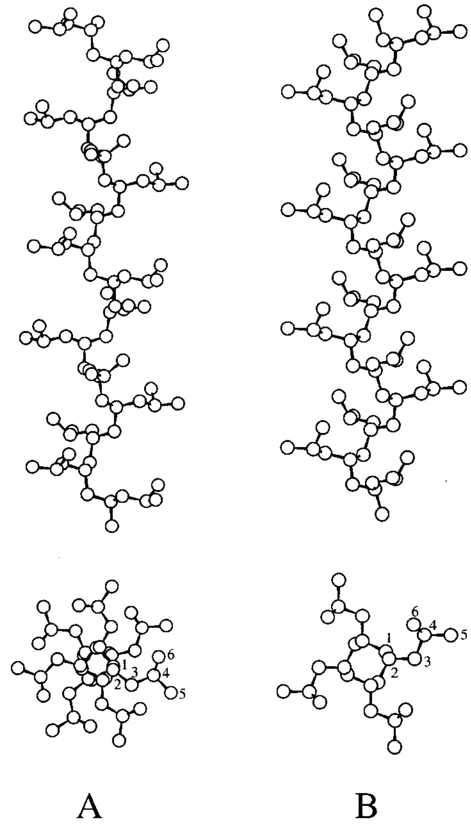


Figure 11. Projections of chains of i-P4MP in the helical 7/2 conformation of form I[3,4] (A) and in the helical 4/1 conformation of form III[12] (B).

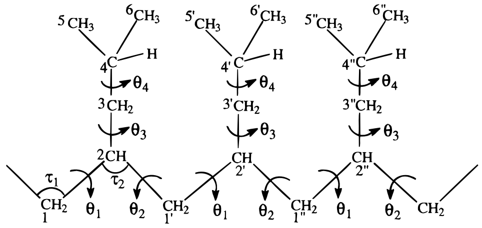


Figure 12. Definition of the bond angles τ_1 and τ_2 and of the torsion angles θ_1, θ_2, θ_3, and θ_4 which characterize the conformation of the chain of i-P4MP in the **s**(*M*/*N*) helical symmetry. The torsion angle θ_4 is defined with respect of the hydrogen atom of the $CH(CH_3)_2$ group (θ_4 = H−C4−C3−C2)

From Figure 11 it can be easily realized that the methyl carbons C5 and C6 have the same methine carbon C2 in the γ-position, but, for both 7/2 and 4/1 helical conformations, 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 for form III).

Table 2. Values of the Torsion Angles (deg) Which Characterize the Conformation of the Chains in the Crystal Structures of Form I[4] and Form III[12,13] of i-P4MP, Where the Labels of the Carbon Atoms Correspond to Those Shown in Figure 12

Form I

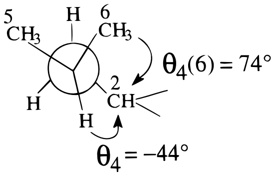
monomeric unit	θ_1	θ_2	θ_3	$\theta_4(5)$	$\theta_4(6)$	θ_{3A}
1	77.5	−162.6	84.5	−153.0	86.7	−155.1
2	68.6	−157.9	103.2	−158.3	81.8	−137.6
3	64.2	−161.9	89.4	−172.8	90.5	−149.4
4	81.4	−168.2	95.8	−140.8	99.4	−143.5
5	64.7	−169.0	107.2	−150.1	90.0	−131.8
6	78.2	−171.9	88.7	−147.0	88.3	−151.7
7	71.8	−164.2	81.6	−158.7	81.0	−159.5

θ_3 = C4−C3−C2−C1
θ_{3A} = C4−C3−C2−C1′
$\theta_4(5)$ = C5−C4−C3−C2
$\theta_4(6)$ = C6−C4−C3−C2

Form III

θ_1	82	θ_{3A} = C4−C3−C2−C1′	−163
θ_2	−154	C3′−C2′−C1′−C2 = ∼(θ_1 + 120°)	−154
θ_3 = C4−C3−C2−C1	73	C3−C2−C1′−C2′ = ∼(θ_2 − 120°)	82
θ_4 = H−C4−C3−C2	−44		
$\theta_4(5)$ = C5−C4−C3−C2	−162		
$\theta_4(6)$ = C6−C4−C3−C2	74		

Scheme 1. Conformation of the Side Group in the 4/1 Helical Chains of Form III



The methyl carbon C6 is therefore shielded by one γ-*gauche* effect; according to the literature;[17] the resonance of C6 is then expected to occur at 4−5 ppm upfield from that of C5, as actually found for form I as well as for form III (parts A and C of Figure 2 and Table 1).

Whatever the chain conformation of forms II and IV may be, the conformation of the side groups in the forms II and IV is probably of the kind shown in Scheme 1, in agreement with the presence of the two resonances for the methyl carbons C5 and C6 observed in the spectra of parts B and D of Figure 2.

Dependence of the γ-*Gauche* Shielding Parameter on the Torsion Angle. From the data of Table 1 we observe that the resonances of the methine carbons of the side groups (C4) and of the methyl carbons C5 and C6 of the four crystalline forms of i-P4MP are nearly at the same values of the chemical shift, whereas the resonances of the methylene carbons of the side groups (C3), of the backbone methylene carbons (C1) and of the backbone methine carbon (C2) are shifted downfield passing from form IV to form I and then to form III.

In other words for the resonances of carbons C4, C5, and C6, whose chemical shifts do not depend on the torsion angles of the main chain and, hence, on the chain conformation, we observe a chemical shift nearly constant for the four forms of i-P4MP. Indeed, for these resonances the chemical shift depends on the torsion angles that characterize the conformation of the lateral groups, θ_3 (for C4) and θ_4 (for C5 and C6), which, as shown in Table 2, are very similar for the forms I and III and are probably the same also for forms II and IV.

Instead, the chemical shifts of the resonances of carbons C1, C2, and C3 depend on torsion angles of the main chain θ_1 and θ_2 and, hence, on the kind of helical chain conformation, despite the fact that all forms have $(TG)_n$ conformation.

With reference to Figure 12, for a chain of i-P4MP in helical $(TG)_n$ conformation, the methylene carbon C1 experiences two γ-*gauche* interactions with both backbone and side chain methine carbons, whose arrangements with respect to C1 depend on torsion angles θ_1 and θ_3 respectively. The methine carbon C2 experiences three γ-*gauche* interactions with the backbone methylene carbon, with the methylene carbon of the adjacent side group and with the methyl carbon C6, whose arrangements with respect to C2 depend on the torsion angles θ_1, θ_2 ($\approx\theta_2 - 120°$), and θ_4, respectively. The methylene C3 of the side group experiences one γ-*gauche* interaction with the backbone methine carbon, whose arrangement depends on θ_2 ($\approx\theta_2 - 120°$).

As shown in Table 2, the torsion angles of the main chain deviate, on average, by 12−15° from the exact staggered values of 60 and 180° in the form I (average values of the torsion angles are $\theta_1 = 72°$ and $\theta_2 = 195°$;[3,4] they deviate by 22−26° in form III ($\theta_1 = 82°$ and $\theta_2 = 206°$).[12,13]

The downfield shifts of the resonances of the carbons C1, C2, and C3 passing from form IV to form I and then to form III, indicate a reduction of the γ-*gauche* shielding effect experienced by those atoms when the torsion angle θ_1 deviates from the value of 60°. The more the deviation of θ_1 from 60°, the more the reduction of the γ-*gauche* shielding parameter. In form III, for which there is the greater deviation, the resonance of the methine carbon C2 is shifted by ≈5.5 ppm compared to form IV, whereas the resonances of the methylene carbons C1 and that of the methylene carbons of the side group C3 are shifted by ≈4 ppm and ≈3.5 ppm, respectively, compared to form IV (Table 1). Since two of the three γ-*gauche* interactions experienced by the methine carbons C2 depend on the torsion angles θ_1 and θ_2 ($\approx\theta_2 - 120°$), the reduction of the shielding effect in form III is greater for the methine carbon C2 than for carbons C1 and C3.

In form IV, the upfield shift of the resonances of the carbons C1, C2, and C3 compared to forms I and III indicates that these atoms experience a full γ-*gauche* shielding interaction, and hence, the main chain torsion angles θ_1 and θ_2 are near to the values of 60 and 180°, respectively, typical of a helical 3/1 conformation. This analysis allows us to suggest that form IV of i-P4MP is characterized by chains in 3/1 helical conformation.

The values of the chemical shifts of the resonances observed in the spectra of the four forms of i-P4MP (Figure 2 and Table 1) are reported in Figure 13 as a function of the torsion angle θ_1 (for form IV we assume $\theta_1 = 60°$). It is apparent the reduction of the γ-*gauche* shielding effect as the torsion angle increases of nearly 22°. The chemical shift of the resonance of methine carbons C4 (shown as an example in Figure 13) is instead nearly constant with θ_1. The deshielding of nearly 5 ppm of the methine carbon C2 in form III, compared to form IV, indicates that both the γ-*gauche* shielding interactions experienced by C2 with the backbone methylene carbon and with the methylene carbon of the adjacent side group are reduced by ca. half, resulting in deshielding by nearly a full standard γ-*gauche* value. Similar conclusions were obtained by the analysis of the ^{13}C NMR CPMAS spectra of the three crystalline forms of isotactic poly(1-butene) reported in the literature.[20]

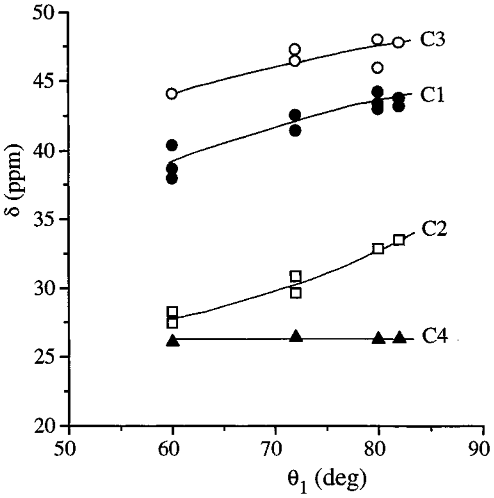


Figure 13. Chemical shifts of the resonances of carbon atoms C1, C2, C3, and C4 observed in the spectra of the four forms of i-P4MP (Figure 2 and Table 1) as a function of the torsion angle θ_1 (for form IV it has been assumed $\theta_1 = 60°$).

It is apparent from Table 1 that the chemical shifts of the resonances of the carbon C1, C2, and C3, observed in the spectrum of the form II (Figure 2B), are similar to those of form III. This indicates that a value of θ_1 similar to that of the chains in form III, can be assumed for the chains in form II, according to the 4/1 helical chain conformation suggested for form II (9). An approximate value of the torsion angle θ_1 can be tentatively obtained by interpolating the values of the chemical shifts of the resonances of the carbons C1, C2, and C3 of form II on the curves of Figure 13. A value of $\theta_1 \approx 80°$, compatible with a 4/1 helical conformation,[9] is obtained.

It is worth noting that the reduction of the *γ-gauche* shielding parameter with increasing the value of the torsion angle explains the fact that the difference of chemical shifts of the resonances of methyl carbons C5 and C6 (separated by one *γ-gauche* effect) is ≈3 ppm (see Table 1 and the previous section), lower than the standard *γ-gauche* shielding value (5 ppm), since the values of the torsion angle θ_4 for forms I and III deviate from 60° (Table 2).

Narrow Splitting in the Backbone Methine Resonance of Form I: Conformational Effect. In the ^{13}C NMR CPMAS spectra of form I shown in Figure 2A, the resonance of the backbone methine carbons C2 is split in a doublet at $\delta = 30.85$ and 29.63 ppm.

Although the two components of the doublet are separated by only 1 ppm, this splitting could be due to a conformational effect, rather than packing effects. Indeed, according to the refinement of the crystal structure of form I (4), the chains of i-P4MP in the form I assume a helical conformation slightly distorted from the uniform 7/2 helix with a succession of torsion angles ...TGT′G′T″G″..., instead of $(TG)_n$. In other words the torsion angles of the main chain θ_1 and θ_2 in the seven monomeric units are slightly different.

The values of torsion angles θ_1 and θ_2 in the seven monomeric units, according to the crystal structure,[4] are reported in Table 2. As discussed above, the average values of torsion angles are $\theta_1 = 72°$ and $\theta_2 = 195°$, but it is apparent that for some bonds $\theta_1 \approx 60°$ whereas for other bonds $\theta_1 \approx 80°$. Since the *γ-gauche* shielding parameter depends on the exact value of the torsion angle θ_1 (Figure 13), backbone methine carbons C2 of different monomeric units are conformationally nonequivalent because they can experience different amounts of *γ-gauche* shielding effects. This conformational effect can explain also the observed splittings of the resonances of the methylene carbons C1 and C3 of form I (Figure 2A and Table 1), since also the chemical shifts of these resonances depend on the value of the torsion angle θ_1.

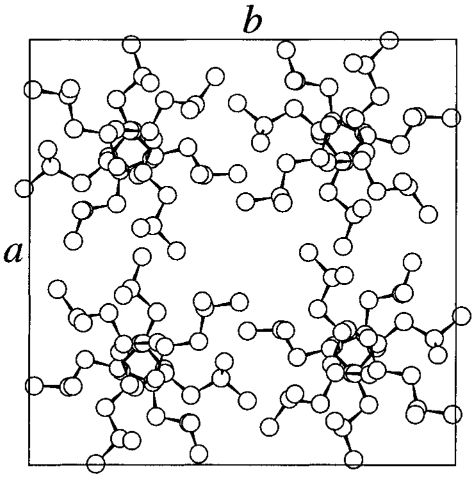


Figure 14. Model of packing, in the *ab* projection, of the nonuniform 7/2 helical chains of form I of i-P4MP in the space group $P\bar{4}b2$.[4] Only up chains are shown.

Narrow Splittings in the Methyl Carbon Resonances: Packing Effects. As observed above, the resonances of the methyl carbons of the four forms of i-P4MP in the ^{13}C NMR CPMAS spectra of Figure 2 show narrow splittings (1−2 ppm) which should be traced back to packing effects. This provides a chance of testing the packing model of forms I and III proposed in the literature.[4,12,13]

Form I. In the spectrum of form I (Figure 2A) the resonance of the methyl carbon C6 is split in an asymmetric not well resolved doublet at $\delta = 22.66$ and 23.86 ppm.

The model of packing of the chains in form I is shown in Figures 14 and 15. Chains in helical conformation slightly distorted from the uniform 7/2 helix originally proposed[2,3] are packed in the tetragonal unit cell according to the space group $P\bar{4}b2$.[4] Statistical disorder in the positioning of anticlined chains in each site of the lattice is present. In Figures 14 and 15 only up chains are shown. The values of the closest intermolecular distances, which define the chemical environments of the methyl carbons C6 of different monomeric units and of adjacent chains, are reported in Table 3. It is apparent from Figures 14 and 15 and Table 3 that the methyl carbons C6 of a same chain, which are conformationally equivalent, or of adjacent chains are nonequivalent. For instance, the methyls C6 and $C6^{II}$ in Figure 15 are nonequivalent since they have different contact distances with neighboring atoms. All contact distances of the methyl C6 are greater than 4 Å (according to ref 4), whereas methyl $C6^{II}$ has one critical contact distance with the methyl C5 at 3.8 Å. The analysis of the packing model of Figures 14 and 15 reveals that there are more than two nonequivalent methyls C6. For instance the methyl $C6^{VI}$ is different from either methyls C6 and $C6^{II}$ since their chemical environments are different etc. (Table 3). This can explain the asymmetric splitting of the resonance of the methyl carbon C6 in the spectrum of form I of Figure 2A. The statistical disorder in the positioning of up and down helices produces the presence of methyl carbons

C6 in statistical positions modifying further on the chemical environments of the nuclei.

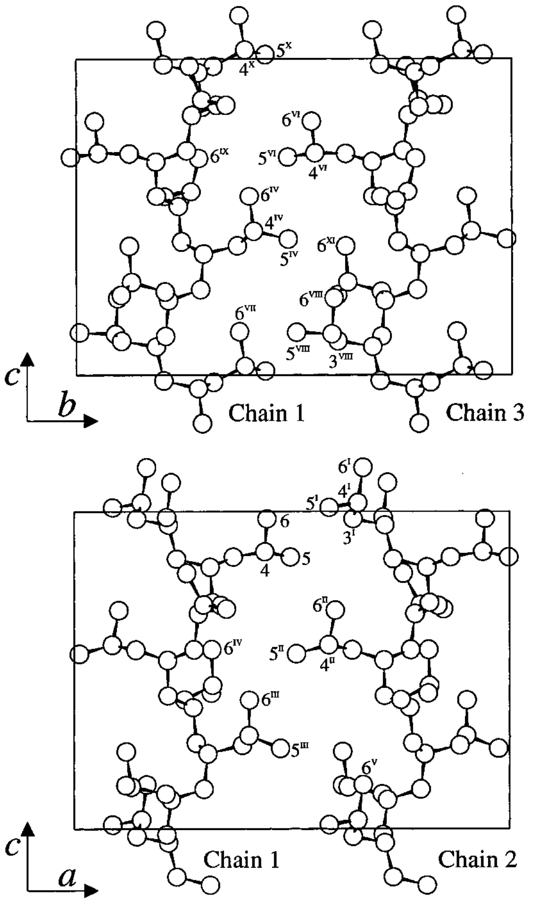


Figure 15. Model of packing, in the *ac* and *bc* projections, of the nonuniform 7/2 helical chains of form I of i-P4MP in the space group $P\bar{4}b2$.[4] Only up chains are shown. Chains 1, 2, and 3 are the chains with chain axis in the positions ($x/a = y/b = 0.25$), ($x/a = 0.75$, $y/b = 0.25$), and ($x/a = 0.25$, $y/b = 0.75$), respectively.

Table 3. Closest Intermolecular Distances in the Model of Packing of Form I of i-P4MP in Figures 14 and 15, Where the Labels of the Carbon Atoms Refer to Figure 15

contact distances of C6	contact distances of C6$^{\mathrm{II}}$
$\mathrm{C6-C3^{I}} = 4.00$	$\mathrm{C6^{II}-C5} = 3.80$
$\mathrm{C6-C5^{I}} = 4.56$	$\mathrm{C6^{II}-C4} = 4.10$
$\mathrm{C6-C6^{II}} = 5.00$	$\mathrm{C6^{II}-C6} = 5.00$
$\mathrm{C6-C6^{I}} = 5.33$	
$\mathrm{C6-C5^{II}} = 5.97$	
contact distances of C6$^{\mathrm{III}}$	**contact distances of C6$^{\mathrm{IV}}$**
$\mathrm{C6^{III}-C5^{II}} = 3.89$	$\mathrm{C6^{IV}-C5^{VI}} = 3.93$
$\mathrm{C6^{III}-C4^{II}} = 4.70$	$\mathrm{C6^{IV}-C4^{VI}} = 4.03$
	$\mathrm{C6^{IV}-C5^{II}} = 4.45$
	$\mathrm{C6^{IV}-C6^{VI}} = 4.46$
contact distances of C6$^{\mathrm{V}}$	**contact distances of C6$^{\mathrm{VI}}$**
$\mathrm{C6^{V}-C5^{III}} = 3.92$	$\mathrm{C6^{VI}-C6^{IV}} = 4.46$
	$\mathrm{C6^{VI}-C4^{X}} = 4.52$
	$\mathrm{C6^{VI}-C5^{X}} = 4.53$
contact distances of C6$^{\mathrm{VII}}$	**contact distances of C6$^{\mathrm{VIII}}$**
$\mathrm{C6^{VII}-C5^{VIII}} = 4.73$	$\mathrm{C6^{VIII}-C5^{IV}} = 3.50$
$\mathrm{C6^{VII}-C3^{VIII}} = 4.87$	$\mathrm{C6^{VIII}-C4^{IV}} = 4.66$
contact distances of C6$^{\mathrm{IX}}$	**contact distances of C6$^{\mathrm{XI}}$**
$\mathrm{C6^{IX}-C5^{VI}} = 3.96$	$\mathrm{C6^{XI}-C5^{IV}} = 4.78$
$\mathrm{C6^{IX}-C4^{VI}} = 5.38$	

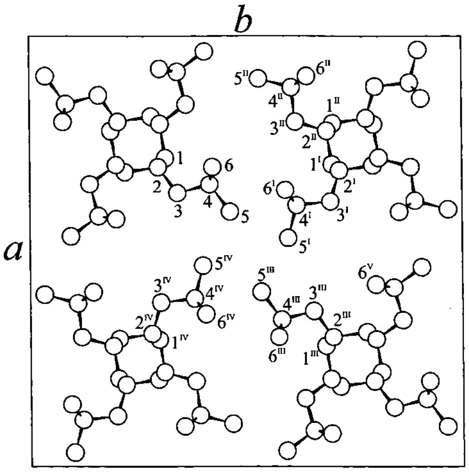


Figure 16. Model of packing of the 4/1 helical chains of form III of i-P4MP in the space group $I4_1$.[12,13]

Narrow splittings of either methyl C6 and methine C2 resonances are, therefore, accounted for by the model of crystal structure proposed for form I.[4]

Form III. In the ^{13}C NMR CPMAS spectrum of form III of Figures 2C and 5 the resonances of the methyl carbons C5 and C6 are split in doublets at $\delta = 27.06$ and 26.29 ppm and at $\delta = 23.97$ and 22.76 ppm, respectively. Also these splittings are due to packing effects.

It is worth noting that the two components of the resonance of the methyl C6 (at $\delta = 23.97$ and 22.76 ppm) are well resolved. This is relevant because all splittings of ≈1 ppm reported in the literature so far,[19,21,26] which have been attributed to packing effects, have always produced nonresolved doublet.

The model of packing of the chains in the form III recently proposed[12,13] is shown in Figure 16. Chains in 4/1 helical conformation are packed in the tetragonal unit cell according to space group $I4_1$.[12,13] In the limit ordered crystals every chain is surrounded by four enantiomorphous and isoclined chains. The enantiomorphous chains are independent, i.e., not related by any element of symmetry of the space group. The asymmetric unit is composed by the two monomeric units of the two enantiomorphous, independent chains (atoms 1−6 and 1^{I}−6^{I} in Figure 16). The chains included in the unit cell are assumed isoclined although some degree of disorder in the positioning of up and down helices can be present.[13]

The ^{13}C NMR CPMAS spectrum of form III (Figure 2C) presents at least seven well resolved resonances according with the presence of two independent chains in the unit cell. It is apparent, from Figure 16, that the conformationally equivalent methyl carbons of the two independent chains, C6 and C6$^{\mathrm{I}}$ or C5 and C5$^{\mathrm{I}}$, present different chemical environments since the contact distances with the neighboring atoms are different. The values of the intermolecular distances which define the chemical environments of the atoms C6, C6$^{\mathrm{I}}$, C5, C5$^{\mathrm{I}}$, C4, C4$^{\mathrm{I}}$, C3, and C3$^{\mathrm{I}}$ are reported in Table 4.

It is easily realized, from Table 4, that the methyl carbons C6 and C6$^{\mathrm{I}}$ are not equivalent since all contact distances of the methyl C6 are greater than 4.1 Å, whereas the methyl carbon C6$^{\mathrm{I}}$ present a critical contact distance at 3.8 Å with the methyl carbon C5. The model of packing for the form III proposed in the literature[12,13] indicates that two nonequivalent kinds of methyls C6 are included in the unit cell, according with the two

Table 4. Closest Intermolecular Distances in the Model of Packing of Form III of i-P4MP in Figure 16, Where the Labels of the Carbon Atoms Refer to Figure 16

contact distances of C6	contact distances of C6$^{\mathrm{I}}$
C6−C3$^{\mathrm{II}}$ = 4.14	C6$^{\mathrm{I}}$−C5 = 3.80
C6−C4$^{\mathrm{II}}$ = 4.89	C6$^{\mathrm{I}}$−C4 = 4.27
C6−C5$^{\mathrm{II}}$ = 4.30	C6$^{\mathrm{I}}$−C6 = 4.97
C6−C6$^{\mathrm{I}}$ = 4.93	
C6−C4$^{\mathrm{I}}$ = 4.79	
contact distances of C5	**contact distances of C5$^{\mathrm{I}}$**
C5−C6$^{\mathrm{I}}$ = 3.80	C5$^{\mathrm{I}}$−C5$^{\mathrm{IV}}$ = 4.39
C5−C5$^{\mathrm{III}}$ = 3.90	C5$^{\mathrm{I}}$−C6$^{\mathrm{V}}$ = 4.30
C5−C5$^{\mathrm{IV}}$ = 4.30	C5$^{\mathrm{I}}$−C5$^{\mathrm{III}}$ = 4.23
C5−C4$^{\mathrm{I}}$ = 4.80	C5$^{\mathrm{I}}$−C4$^{\mathrm{III}}$ = 4.88
C5−C5$^{\mathrm{I}}$ = 4.73	C5$^{\mathrm{I}}$−C5 = 4.73
	C5$^{\mathrm{I}}$−C3$^{\mathrm{III}}$ = 4.65
	C5$^{\mathrm{I}}$−C6$^{\mathrm{III}}$ = 4.86
contact distances of C4	**contact distances of C4$^{\mathrm{I}}$**
C4−C6$^{\mathrm{I}}$ = 4.27	C4$^{\mathrm{I}}$−C5 = 4.78
C4−C5$^{\mathrm{IV}}$ = 4.88	C4$^{\mathrm{I}}$−C6 = 4.79
	C4$^{\mathrm{I}}$−C6$^{\mathrm{V}}$ = 4.89
contact distances of C3	**contact distances of C3$^{\mathrm{I}}$**
C3−C5$^{\mathrm{IV}}$ = 4.65	C3$^{\mathrm{I}}$−C6$^{\mathrm{V}}$ = 4.14

distinct resonances for the methyl C6 at $\delta = 23.97$ and 22.76 ppm observed in the spectrum of Figure 2C.

From Table 4 we can observe that also the methyl carbons C5 and C5$^{\mathrm{I}}$ have different chemical environments. Indeed, the minima contact distances of the methyl C5 are at 3.8 Å with the methyl C6$^{\mathrm{I}}$ and at 3.9 Å with the methyl C5$^{\mathrm{III}}$, whereas all contact distances of the methyl C5$^{\mathrm{I}}$ are greater than 4.2 Å. Therefore, in the proposed structure of form III there are two nonequivalent kinds of methyl C5 (C5 and C5$^{\mathrm{I}}$), according to the splitting of the resonance of the methyl carbon C5 in a not-resolved doublet at $\delta = 27.06$ and 26.29 ppm observed in the spectrum of Figure 5B.

The difference of chemical environments of the methine and methylene carbons of the side groups of the two independent chains, C3−C3$^{\mathrm{I}}$ and C4−C4$^{\mathrm{I}}$, are less relevant (the contact distances are always greater than 4.1 Å) so that in the spectrum of Figure 2C visible splittings of the resonances of these nuclei are not observed.

In conclusion, the analysis of the narrow splittings of the resonances of the methyl carbons in the ^{13}C NMR CPMAS spectrum of form III of Figures 2C and 5B confirms the model for the crystal structure of form III proposed in the literature.[12,13]

It is worth noting that narrow splittings of the resonances are observed also in the spectra of forms II and IV. Since the complete crystal structures of forms II and IV have not been resolved so far, the interpretation of these splittings is difficult. However, the observation of splittings of the resonances of methyl carbons C6 of both forms (parts B and D of Figure 2), which are probably due to packing effects, can be helpful in the definition of the crystal lattice symmetries of forms II and IV.

Conclusions

Four crystalline forms of i-P4MP have been studied through solid state ^{13}C NMR CP-MAS spectroscopy. Form I of i-P4MP was prepared by crystallization from the melt, whereas forms II, III, and IV were prepared by crystallization from solution depending on the solvent and the solution temperature. The four crystalline forms have been identified by X-ray diffraction.

All forms of i-P4MP give well-resolved ^{13}C NMR CP-MAS spectra. The assignment of the resonances observed in the ^{13}C NMR CP-MAS spectra was made by comparison with the solution spectrum and by dipolar dephasing experiments.[24] The presence in all spectra of two distinct resonances of the methyl carbons, labeled as C5 and C6, indicates that the two methyls belonging to the monomeric unit are nonequivalent. This has been explained on the basis of the conformations of the polymer chains and of the lateral groups. Indeed, the methyl carbons C5 and C6 have the same methine carbon C2 in the γ-position, but for both 7/2 and 4/1 helical conformations of forms I and III, respectively, C2 is in *gauche* arrangement with respect to the methyl C6 and in *trans* arrangement to the methyl C5. This conformation of the lateral group is expected to occur also for forms II and IV, whatever the chain conformation of forms II and IV may be. The methyl carbon C6 is therefore shielded by one γ-*gauche* effect and its resonance occurs at ≈3 ppm upfield from that of C5 in the spectra of all forms.

The resonances observed in the spectrum of form III are markedly deshielded compared to those of other forms, whereas the resonances of form I are deshielded compared to those of form IV. This deshielding can be consistently interpreted on the hypothesis that the amount of the γ-*gauche* shielding effect depends on the value of the torsion angles of the main chain. Indeed, the torsion angles of the main chain for the 7/2 helical conformation of form I deviate on average by 12−15° from the exact staggered values of 60 and 180° (average values of the torsion angles are $\theta_1 = 72°$ and $\theta_2 = 195°$); they deviate by 22−26° for the 4/1 helical conformation of form III ($\theta_1 = 82°$ and $\theta_2 = 206°$). The γ-*gauche* shielding parameter, normally −5 ppm when the *gauche* angle is nearly 60°, decreases to a value between −2 and −2.5 ppm when the torsion angle deviates by nearly 20° from 60°.

In the form IV, the upfield shift of the resonances, compared to forms I and III indicates that the nuclei experience a full γ-*gauche* shielding interaction and, hence, the main chain torsion angles θ_1 and θ_2 are near 60 and 180°, respectively, values typical of a helical 3/1 conformation. This analysis allows us to suggest that form IV of i-P4MP is characterized by chains in 3/1 helical conformation.

The resonances of the methyl carbons of the four forms of i-P4MP in the ^{13}C NMR CPMAS spectra show narrow splittings (1−2 ppm) which should be traced back to packing effects. This has provided a chance of testing the packing model of form I (tetragonal unit cell and space group $P\bar{4}b2$) and form III (tetragonal unit cell and space group $I4_1$) proposed in the literature.[4,12,13]

In the spectrum of form I also the resonance of the backbone methine carbon is split in a doublet. This splitting is due to a conformational effect, rather than packing effects and confirms that, according to the refinement of the crystal structure of form I,[4] the chains assume a helical conformation slightly distorted from the uniform 7/2 helix. The succession of torsion angles along the main chain is ...TGT′G′T″G″..., instead of $(\mathrm{TG})_n$. Therefore, backbone methine carbons of different monomeric units are conformationally nonequivalent because they experience different amounts of γ-*gauche* shielding effects owing to different values of the *gauche* torsion angle θ_1 of different monomeric units.

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