computer simulation of the fragmentation patterns.

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Magic Angle Spinning Carbon-13 NMR Spectroscopy of Three Crystalline Forms of Isotactic Poly(1-butene)

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ABSTRACT: The same influences which determine the dependence of carbon-13 chemical shifts on chain microstructure in solution spectra appear to be operative also in the solid state. We have investigated the magic angle spinning (MAS) ^{13}C spectra of three forms of isotactic poly(1-butene). Each crystalline form is identified by X-ray diffraction. The percent crystallinity for each sample is determined from density measurements and from the comparison of the melting endotherm with the heat of fusion obtained by differential scanning calorimetry (DSC). Like most isotactic polymers, poly(1-butene) adopts a 3_1 ...(gt)(gt)(gt)... helical conformation, termed form I, at room temperature. This has main-chain dihedral angles of 60° for gauche and 180° for trans conformations. But at ca. 90 °C and above, it prefers an 11_3 helix with g and t angles of 77° and 163°, respectively, called form II. When prepared in film form by solvent (chloroform) evaporation, it yields form III, a 4_1 helix with g and t angles of 83° and 159°. Form I gives a well-resolved MAS spectrum. The resonances of form II are much broader and somewhat deshielded compared to those of form I. The spectrum of form III is well resolved, with all resonances markedly deshielded compared to those of form I. (There is also a splitting of the methyl resonance, attributed to crystal packing effects.) This deshielding can be consistently interpreted on the hypothesis that the γ-gauche shielding parameter, normally ca. −5 ppm when the gauche angle is ca. 60°, is angle dependent, decreasing to ca. −2.5 ppm at 81–83° and to an intermediate value at 77°.

Introduction

The same influences which determine the dependence of carbon-13 chemical shifts on chain microstructure in the solution NMR spectra of macromolecules appear to be operative also in the solid state. Thus, the solid-state magic angle spinning (MAS) carbon-13 spectra of crystalline isotactic[1–4] and syndiotactic[4] polypropylenes may be convincingly interpreted in terms of γ-gauche interactions with the same γ-gauche shielding parameter of ca. −5 ppm used in the prediction of the solution carbon-13 spectrum of atactic polypropylene.[5] In addition, the differences in chemical shift observed between crystalline and amorphous carbons in polyethylene,[6] poly(oxymethylene),[7] and poly(oxyethylene)[8] can also be explained on the basis of γ-gauche interactions.[9] This difference in chemical shift is the result of different conformations adopted by crystalline and amorphous chains.

Like most isotactic vinyl polymers, isotactic poly(1-butene) adopts a 3_1 ...(gt)(gt)(gt)... helical crystalline conformation at room temperature.[10] The chains have dihedral angles of 60° for gauche and 180° for trans conformations and are packed in a trigonal unit cell (form I). But at ca. 90 °C and above this polymer is known to prefer a tetragonal form, called form II, in which the chain conformation is an 11_3 helix with alternating "gauche" and "trans" angles of 77° and 163°, respectively.[11–13] At room temperature form II spontaneously transforms into form I within a few days. In films, this transformation proceeds from the surface inward[14] and is in general associated with pressure and mechanical stress. We have found that in bulk it is markedly accelerated by magic angle spinning (cf. seq.). There is also a third polymorph, form III,[15–18]

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which may be crystallized from a variety of solvents, by evaporation of chloroform solutions, or by freeze-drying of benzene solutions. This form is orthorhombic and has a 4_1-helical conformation with "gauche" and "trans" angles of 83° and 159°. It is stable at room temperature but can be transformed to form II at 94–96 °C.[17]

We have investigated the MAS carbon-13 NMR spectra of these polymorphs and of the amorphous polymer. We find, in agreement with Harris et al.,[19] that form I gives a well-resolved spectrum whereas the resonances of form II are much broadened under all conditions of preparation and observing temperature. We report here also the spectrum of form III, not studied by Harris et al. It is well resolved and exhibits several features of interest.

Experimental Section

The poly(1-butene) employed in this work was obtained from Aldrich Chemical Co. It has an intrinsic viscosity, measured in heptane at 35 °C, of 2.41 dL·g^{-1}, corresponding to $\bar{M}_w = 7.65 \times 10^5$ according to Stivala et al.[20] The 50.3-MHz carbon-13 spectrum, observed in 1,2,4-trichlorobenzene solution (10% (w/v)) at 20 °C, indicated by relative peak intensities in the side-chain methylene spectrum (ca. 27 ppm[21]) that this material is at least 95% isotactic measured as triads. Both solution- and solid-state studies were carried out on a Varian XL-200 spectrometer, corresponding to a carbon-13 frequency of 50.3 MHz. The solid-state spectra were obtained under conditions of MAS, high-power dipolar decoupling (DD) at ca. 11 G ($\gamma B_2/2\pi$ = 45 kHz), and ^{1}H–^{13}C cross-polarization (CP). The temperature of the MAS sample was determined by placing a thermocouple in the variable-temperature gas stream ~0.5 cm from the sample.

A study of CP times was carried out on a form I crystalline sample and a melt-quenched amorphous sample. It was found that even at the extremely long CP time of 10 ms, magnetization from the amorphous carbon nuclei was not observed. For the crystalline sample the optimum CP time was found to be 500 μs. Therefore, a CP time of 500 μs was employed in recording the solid-state spectra of the three crystalline polymorphs of poly(1-butene). For the observation of the amorphous sample, CP was not employed and the interval between sampling pulses was 0.5 s.

Form I was obtained from a 10-mil-thick film melt-quenched from ca. 175 °C into dry ice and then annealed at room temperature for 10 days; under these conditions the transformation to form I is complete, as verified through X-ray diffraction by the replacement of the form II 200 diffractometer peak (2θ = 11.7°) by the 110 peak of form I (2θ = 9.9°). Form II was obtained by annealing a molten sample at 90 °C for 2 h, followed by quenching in liquid nitrogen and observation at −60 °C in the MAS rotor. Form III was prepared as a film by evaporation of a chloroform solution. Density measurements were performed by density gradient and pycnometry methods. The extents of crystallinity were estimated from both density and differential scanning calorimetry (DSC). The amorphous sample was prepared by quenching a molten sample into dry ice.

Results and Discussion

X-ray Identification of Crystalline Forms. Crystallographic identification of the samples described in the Experimental Section was made by using X-ray diffraction. Flat-film photographs obtained in the transmission geometry are shown in Figure 1. The reflections identified in parts a–c of this figure correspond respectively to forms I, II, and III of poly(1-butene), and their interplanar spacings are in agreement with the published unit cells for this polymer.[13]

The specimens obtained by quenching the melt and annealing at room temperature for 10 days (Figure 1a) are almost exclusively of form I. A trace amount of form II is also present in these samples as evidenced by a very weak 200_{II} reflection in Figure 1a; the polymorphic composition of these samples is not changed by further annealing at room temperature for at least 5 months.

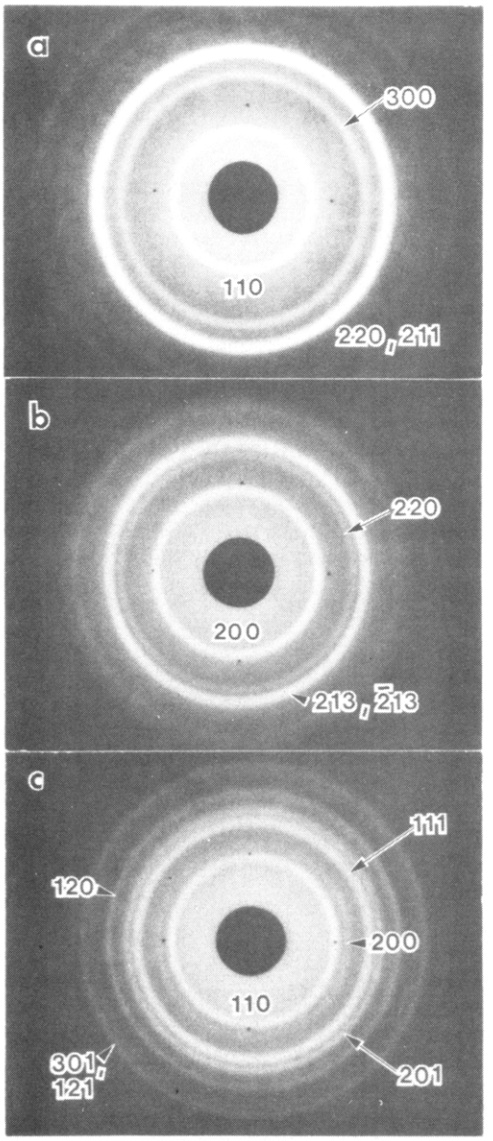


Figure 1. X-ray diffraction patterns of the three crystalline polymorphs of isotactic poly(1-butene): (a) form I; (b) form II; (c) form III.

Polymer pellets as received are also predominantly in form I but contain a significant minority population of form II crystals.

Form II films, produced by annealing the molten specimens for 2 h at 90 °C, show no detectable contamination by crystals of the other two polymorphs (Figure 1b).

The form III samples, prepared by evaporation of a chloroform solution at room temperature, are free from form I admixture (see Figure 1c) and remain unchanged after annealing at that temperature for at least 5 months. The presence of form II crystals in our form III samples cannot be excluded from our photographic X-ray diffraction patterns, because its reflections overlap (within experimental resolution) those of form III [note, e.g., the 200, 220, and {213, $\bar{2}$13} form II reflections vs. the 110, 111, and 201 reflections of form III in Figure 1b,c]. However, high-resolution diffractometric scanning in the range of 2θ = 11–13° shows only a single peak characteristic of form III at 2θ = 12.1°. The diffraction peak at 11.8°, as shown by Geacintov et al.[17] to be characteristic of form II, is not observed. Thus, the form III samples are free of form I and II polymorphs.

Crystalline Contents of Poly(1-butene) Polymorphs. The densities of the three polymorphs and

Table I
Densities,[a] Calorimetric Properties, and Crystalline Fractions of Three Polymorphs of Isotactic Poly(1-butene)

form	ρ, g/cm^3	ρ_c, g/cm^3	X_ρ	T_m,[g] °C	ΔH_{obsd}, cal/g	ΔH_f, cal/g	X_H
I	0.914[b,c]	0.951[d]	0.60	133	19.5	34[h]	0.57
II	0.889[b,c]	0.920[e]	0.46	118	9.5	29[h]	0.33
III	0.797[c]	0.897[f]		100	9.2	28[i]	0.33
amorphous	0.864[c]						

[a] At 25 °C. [b] Density gradient method. [c] Pycnometry, using methanol as nonsolvent. [d] Reference 22, p 388, and ref 13. [e] Reference 26. [f] Reference 23. [g] Temperature corresponding to the peak of the DSC melting endotherm. [h] Reference 24. [i] Reference 16.

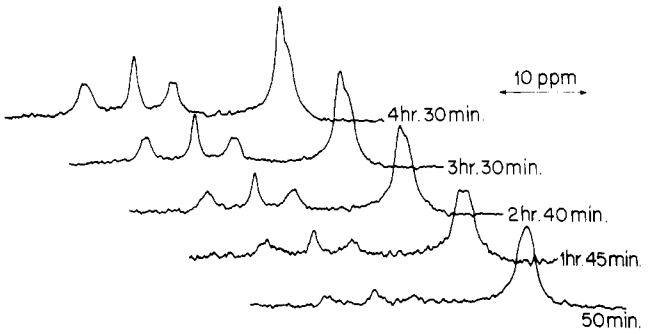


Figure 2. Solid-state MAS/DD/CP carbon-13 NMR spectra of isotactic poly(1-butene) form II converting to form I at room temperature with continuous spinning at 2400 Hz.

amorphous poly(1-butene) employed in this study are listed in column 2 of Table I. From the measured sample densities and the unit cell densities, ρ_c (column 3, Table I), we can obtain an estimate of the crystallinity, X_ρ, of our samples from[22]

$$X_\rho = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \quad (1)$$

where ρ is our sample density and ρ_a is the density of the amorphous phase. The fraction crystallinity, from eq 1, for the samples of form I and form II is given in column 4, Table I. The low density of the form III sample arises from the high porosity of the film, which has been observed previously.[23] As a result we are unable to determine its degree of crystallinity by measurement of its density.

In columns 5 and 6 of Table I we present the melting temperatures and melting endotherms measured by DSC for our isotactic poly(1-butene) samples. Division of the observed melting endotherms, ΔH_{obsd}, by the heat of fusion for the pure crystalline polymorphs,[16,24] ΔH_f, leads to a calorimetric estimate of the crystalline fraction, X_H, as[25]

$$X_H = \Delta H_{obsd}/\Delta H_f \quad (2)$$

There is good agreement between the density and calorimetric estimates of form I crystallinity, while the X_H for form II is significantly lower than the X_ρ value for this polymorph. Due to the high porosity of the form III film we are limited to the calorimetric estimate of its crystalline fraction.

Solid-State Carbon-13 MAS/DD/CP Spectra. The MAS/DD/CP spectrum of form II shows only a methyl resonance at 25 °C. Only at observation temperatures of −30 to −60 °C is a broad featureless band observed for the methine and methylene carbons. In Figure 2 we show the spectra of the form II sample at room temperature and follow its conversion to form I. As indicated above, this transformation is normally quite slow[14] even at the optimum transformation temperature of 25 °C. However, under our conditions of magic angle spinning at 2400 Hz the mechanical stress obviously accelerates this transformation, the conversion of form II to form I being complete after only about 5 h. This may be compared with the results of Harris et al.,[19] who reported that complete transformation without continuous MAS required at least 2 days.

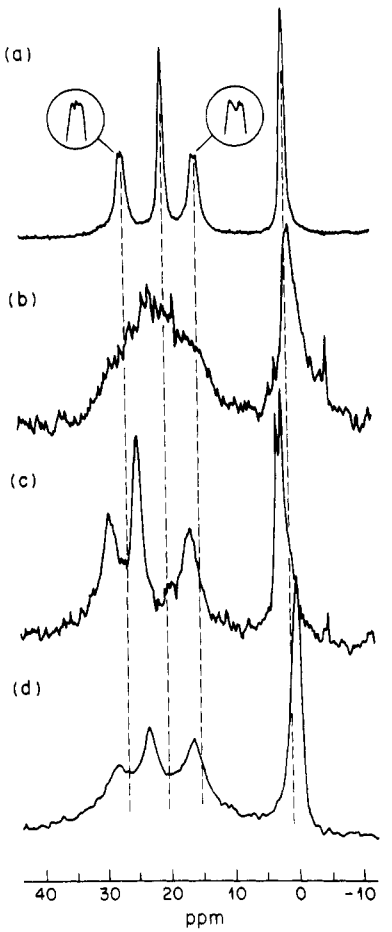


Figure 3. Solid-state MAS/DD/CP 50.3-MHz carbon-13 spectra of poly(1-butene): (a) form I at 20 °C; (b) form II at −60 °C; (c) form III at −10 °C; (d) amorphous at 43 °C. The vertical dashed lines represent the peak positions of form I. The chemical shift scale is referenced to the amorphous methyl resonance as 0.00 ppm.

Table II
Solid-State Carbon-13 Chemical Shifts[a] of Poly(1-butene)

	carbon			
	side-chain			
state	CH_3	CH_2	α-CH	β-CH_2
form I	1.55	15.46	20.68	27.19
form II	0.75	(ca. 17)	(ca. 22)	(ca. 28)
form III	3.05	16.96	25.21	29.78
	2.25			
amorphous	0.00	16.40	23.46	28.32

[a] Referred to the CH_3 resonance of the amorphous form as zero.

The MAS spectra for the three crystalline polymorphs and the amorphous polymer are shown in Figure 3. The chemical shifts (ppm) are referenced to the CH_3 resonance of the latter and are summarized in Table II. To facilitate

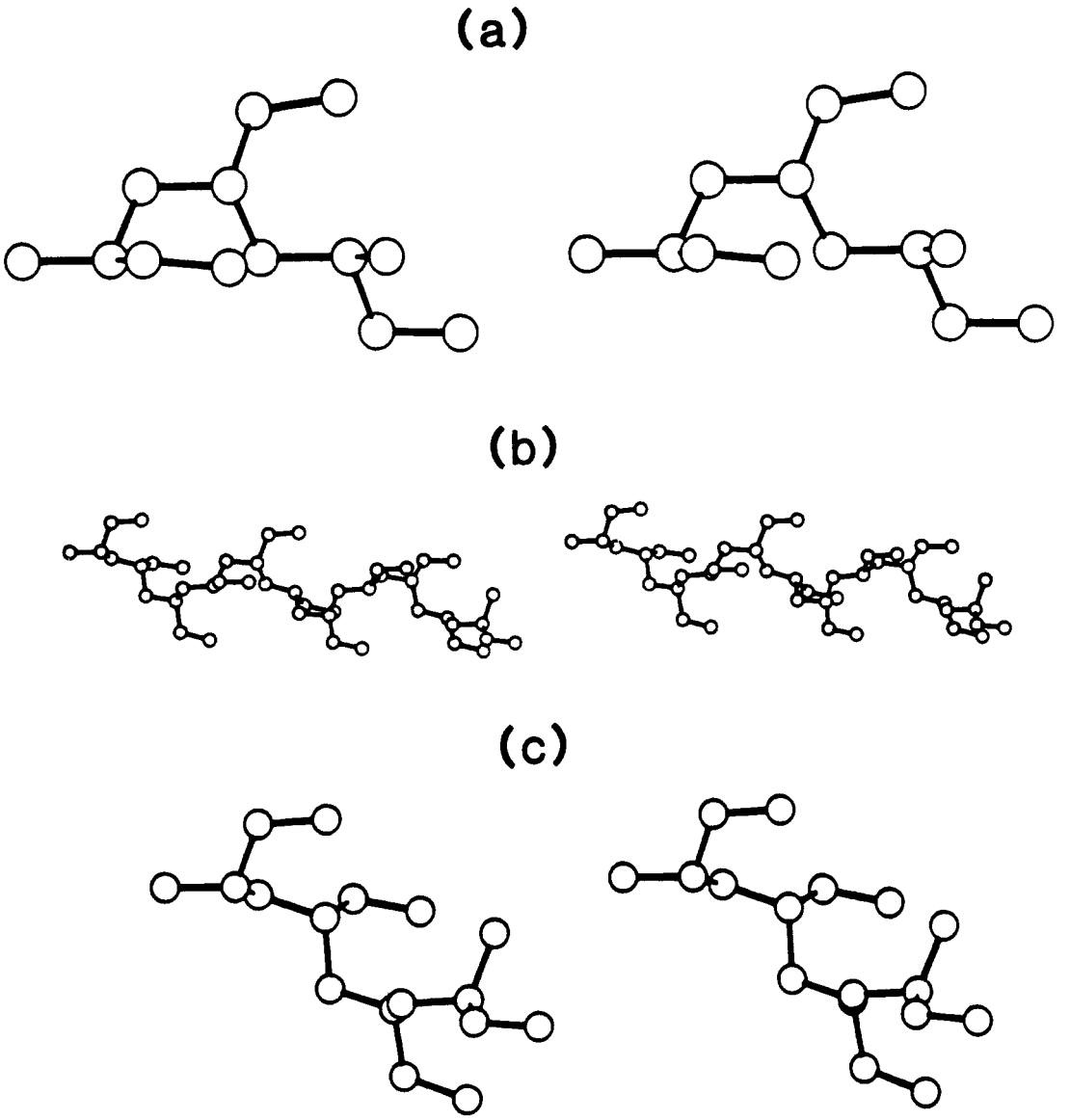


Figure 4. Stereoscopic drawings of the three crystalline polymorphs of isotactic poly(1-butene): (a) form I, 3_1 helix, (b) form II, 11_3 helix; (c) form III, 4_1 helix.

comparison, vertical dashed lines represent the chemical shifts of form I. It will be observed that the spectrum of form I (a) shows narrow equal splitting of the methylene resonances of both the main chain and side chains and that the methyl resonance of form III (c) shows a similar but larger splitting. These effects are tentatively attributed to chain packing, as are the similar observations for isotactic polypropylene,[2-4] although it is not evident, in the case of form I, why only the methylene carbons should be affected.

Our principal concern is with the marked chemical shift dependence on helical form despite the fact that all three helices have a ...(gt)(gt)(gt)... conformation. We believe this reflects primarily the variations in gauche angles. In figure 4a–c are shown a pair of stereoscopic drawings for each of the three helices. Careful viewing of these helices will illustrate the change in the backbone conformation on going from the 3_1 to the 11_3 to the 4_1 helix.

In Figure 5 are shown Newman projections of the three helices. Here, we are to imagine that we are looking first (left) along the C_β–C_α bond in the direction of the gauche bond and then (right) in the opposite direction, i.e., toward the trans bond. In form I the dihedral angles have their standard values (vide supra); in particular, the C_α–C_β angle is 60° in g as is the C_α–CH_2(side chain) angle in t. These interactions may be expected to correspond to the "standard" γ-gauche shielding parameter of ca. −5.3 ppm.[5] In form II g, the C_α–C_β dihedral angle is 77°, while in t the C_α–CH_2(side chain) angle is 77°. The main-chain carbon resonances of form II are too poorly resolved to enable definite conclusions to be drawn, but it appears (Table II) that the α-CH is somewhat deshielded compared to its position in the form I spectrum. In form III g, the C_α–C_β angle is opened out to 83° and in t the C_α–CH_2(side chain) angle has increased to 81°. Here, the shielding of α-CH has been strikingly reduced, by 4.5 ppm compared to form I. The main-chain and side-chain CH_2 carbons have been affected by about half this value.

These observations find a ready explanation in terms of Figure 5, if one assumes that the γ-gauche shielding parameter is not constant but is dependent on dihedral angle and is reduced to about half its standard value when this angle is increased to 82 ± 1°. In a ...(gt)(gt)(gt)... helix, each α-CH experiences gauche interactions with both β-CH_2 and CH_2(side chain). In form III, both of these interactions are reduced by ca. half, resulting in deshielding by nearly a full standard γ-gauche value. The spectrum of the amorphous polymer indicates that in this state, in addition to nonrepeating t and g conformations, all three helical conformations participate significantly, probably

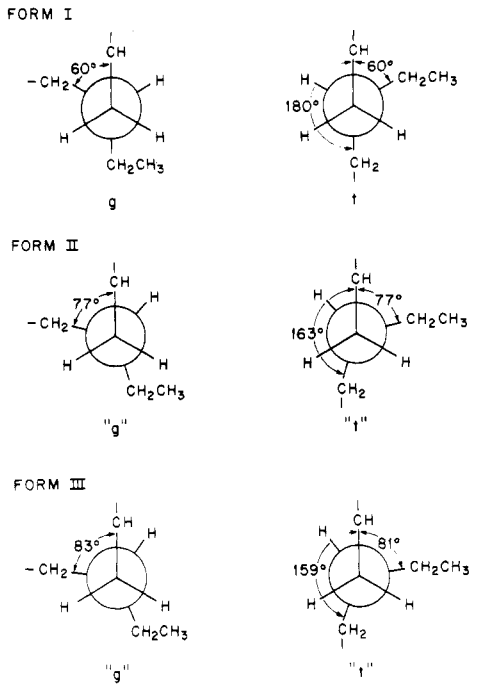
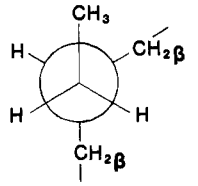


Figure 5. Newman projections of poly(1-butene) crystalline conformations.

because the rotational potential well is nearly flat over the angular range 60–80°.[13] The differences in chain packing between the crystalline polymorphs and the amorphous region may also contribute to the differences observed in the carbon-13 chemical shifts. A comparison of the solid-state amorphous spectrum and the spectrum recorded for a molten sample shows the chemical shift separation between the four carbon resonances to be the same.

The X-ray structures of all three helical forms show the side chain to have the following conformation:



This side-chain conformation, in which the methyl carbon is trans to one neighboring backbone methylene carbon and gauche to the other, can be clearly seen in the side views of the three helices in Figure 4.

The alternative conformation about the C_α–CH_2(side chain) bond, in which the methyl carbon is gauche to both neighboring methylene groups, may occur to a small extent in the amorphous phase. This conformation would be expected to move the amorphous methyl carbons upfield relative to the crystalline polymorphs as is observed (see Table II). In addition, the chemical shifts of the methyl carbons are probably sensitive to the different modes of packing in the three crystalline polymorphs and the amorphous phase. This has been observed in the α and β polymorphs of isotactic polypropylene.[2-4]

From this study of isotactic poly(1-butene) it appears that the conformations of crystalline polymer chains can be fruitfully studied by solid-state MAS carbon-13 NMR. Differences in the observed chemical shifts between the polymorphs are primarily determined by the conformationally sensitive γ-gauche interactions.

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