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Notes

^{13}C Solid-State NMR of Solution-Prepared Polymorphs of Poly(α-isobutyl L-aspartate)

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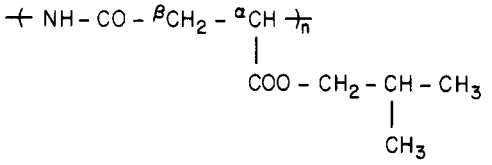
Two solid forms of poly(α-isobutyl L-aspartate) (PAIBLA, **1**), have recently been prepared.[1] The X-ray diffraction patterns and morphological characteristics (orientability) of these solid phases point to two distinctly different solid-state structures. While PAIBLA may be regarded as a derivative of nylon 3, it may also be thought of as a polypeptide into the main chain of which a methylene unit has been added. The X-ray diffraction diagrams of the two forms of PAIBLA can be interpreted in terms of helical structures held together by systems of hydrogen bonds similar to those found in α-helical polypeptides. Model studies[1a] have allowed the selection of some possibilities for the conformational state of the monomer unit in either of the two solid forms.



1

Studies of polypeptides have been reported using ^{13}C NMR in the solid state,[2] and it has been found that, as in solution,[3] the ^{13}C chemical shifts are sensitive to chain conformation. We have performed such experiments on PAIBLA, employing magic-angle spinning with ^1H–^{13}C cross-polarization and dipolar decoupling (abbreviated MAS-CP-DD).[4] It was our hope that such measurements might be informative concerning both chain conformation and dynamics in the two seemingly different crystalline forms. PAIBLA is also distinguished from polypeptides in having a substantial amorphous fraction, and it appeared that ^{13}C NMR might be useful in characterizing this phase.

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Experimental Section

Sample. The polymer used in this study was obtained by a slight modification of the preparative procedure reported previously:[1a] isobutyl alcohol was added instead of sodium isobutoxide. The degree of polymerization is approximately 800. Depending on the manner in which a chloroform solution of the polymer is treated, two solid forms may be obtained:[1a]

Form A. When ethanol is added to a chloroform solution of the polymer,[1a] a powder precipitates. Even though single crystals of this form have been grown, no fibers have yet been obtained from this material.

Form B. A film of this form is prepared by drying a chloroform solution of the polymer. The orientability of form B distinguishes this solid phase from form A.

Calorimetric Measurements. An amount of 3.22 mg of form A was heated, at a rate of 10 deg/min, on a Perkin-Elmer DSC-4.

NMR Measurements. All measurements were carried out at 50.31 MHz on a Varian XL-200 instrument. The probe and Al_2O_3 rotor were manufactured by Doty Scientific, Inc. Pulses at 90° of 5.3-μs duration were employed with an interval between pulses of 3 s. The scalar proton decoupling (SD) was carried out at a B_2 field strength ($\gamma B_2/2\pi$) of 4400 Hz or ca. 1 G. The high-power proton decoupling (DD) field was 45 kHz or ca. 11 G. All spectra were observed at 24 °C; spin–lattice relaxation times were measured at 21° by using the cross polarization method of Torchia.[5]

Results and Discussion

The MAS-CP-DD carbon-13 spectra of the two forms are shown in Figure 1. The assignment of resonances was made by comparison to solution spectra.[6] At this field, amide and ester carbonyl resonances are not resolved in the solid state. (At ca. 100° a partial resolution is observed, resulting in a high-field shoulder on the carbonyl resonance; this may be the ester carbonyl.) The carbon-13 spectrum of form A shows a markedly greater signal-to-noise ratio than that of form B. This is evident from a comparison of spectra a and b in Figure 1. Since the same amount of sample (50 mg) was used for both experiments, this observation suggests a higher degree of crystallinity for form A, but a quantitative measurement was not carried out.

The most significant observation is that the main-chain carbon chemical shifts are identical for both forms (Table I) within experimental error (±0.5 ppm). The sensitivity of carbon-13 chemical shifts to changes in conformation has been thoroughly established both in solution and in the solid state (see, for example, ref 2 and 3). Polypeptides in the solid state show different chemical shifts for the β-sheet and α-helical forms.[2,7–9] Particularly relevant to

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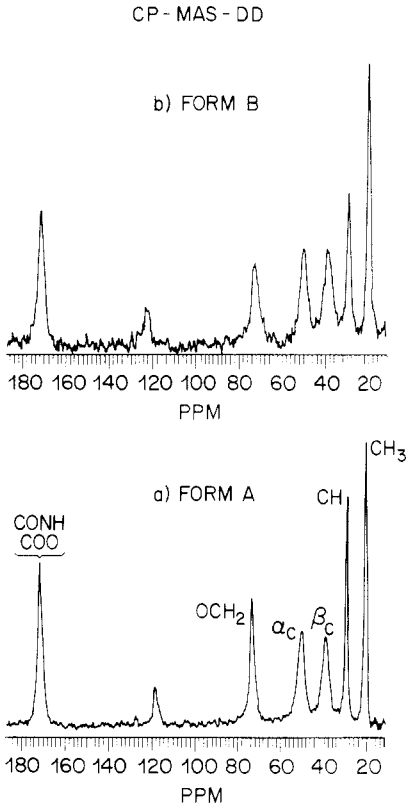


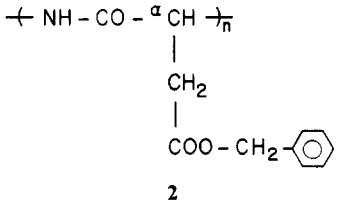
Figure 1. 50.3-MHz CP-MAS-DD ^{13}C spectra of two solid forms of PAIBLA: (a) form A, spinning rate = 2.5 kHz, contact time = 4 ms, and number of transients = 1843; (b) form B, spinning rate = 2.4 kHz, contact time = 2 ms, and number of transients = 2264. A 20-Hz exponential filter has been applied to both spectra. The peak at about 120 ppm corresponds to a spinning side band of the carbonyl resonance. The difference in signal-to-noise ratios should be noted.

Table I
^{13}C Chemical Shifts to Two Solid Forms of PAIBLA (in ppm)[a]

	form A	form B
CO	171.7	171.3
$^{\alpha}CH$	50.3	49.7
$^{\beta}CH_2$	39.4	38.7
OCH_2	73.4	72.5
CH	29.4	29.1
CH_3	20.7	20.1

[a] Relative to poly(oxymethylene) (89.1 ppm).

our discussion is the case of poly(β-benzyl-L-aspartate) (PBLA, **2**). PBLA can crystallize in several forms, including left- and right-handed α-helics.[10] In this polymer, the conformational changes associated with the different helical senses are clearly manifested in the ^{13}C spectra; shifts to higher field, of 2.5 and 3.8 ppm, respectively, are observed for the C_α and peptide carbons in going from a right- to a left-handed α-helical conformation.



2

A possible explanation for the similarity in the ^{13}C spectra of the two forms of PAIBLA is that the amorphous material could be well below its T_g and therefore could contribute to the spectrum of both forms under cross-polarization conditions. Thus, appearance of large amorphous signals would tend to mask any chemical shift difference the carbons may exhibit in the two crystalline forms. However, two observations suggest this is not the case: (i) the absence of a glass transition in the range 60–200 °C, as measured by DSC, and (ii) the detection of backbone carbon signals under conditions of magic angle spinning with *scalar* decoupling (MAS-SD), as shown in Figure 2 (vide infra). The latter observation indicates that the amorphous phase is relatively mobile at room temperature.[10] The CP-MAS-DD ^{13}C spectra of forms A and B of PAIBLA therefore point to very similar conformations of the main chain in both crystal habits.

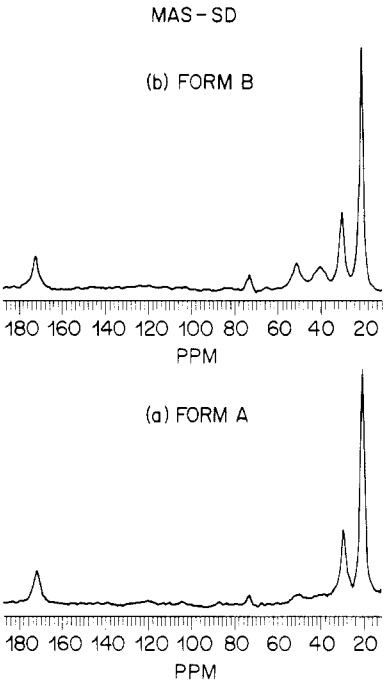


Figure 2. 50.3-MHz MAS-SD ^{13}C spectra of forms A and B of PAIBLA: (a) form A, spinning rate = 3.3 kHz, number of transients = 25 000, (b) form B, spinning rate = 3.1 kHz, number of transients = 17 700. A 50-Hz exponential filter has been applied to both spectra.

For the side-chain carbons, we observe (Table I) very little variation in chemical shift between forms A and B *except* for the methylene carbon, CH_2. This carbon exhibits a low-field shift of 1.1 ppm for form B compared to form A. Since this methylene carbon has as its only γ-neighbor an ester carbonyl, an interpretation of this low-field change in terms of three-bond effects[12] seems difficult because of the strong tendency of ester bonds to remain in the trans conformation. However, the detection of this change in chemical shift indicates that there are some differences in the way the side chain is arranged in each solid form.

As mentioned above, PAIBLA is characterized by the presence of a substantial amorphous phase. At room temperature, the mobility of the amorphous material is relatively high, since signals corresponding to main-chain carbons are observed under magic-angle spinning with scalar (low power) decoupling, MAS-SD, as shown in Figure 2. In this experiment, the relatively small power delivered to the ^1H–^{13}C spin system is enough to collapse the splittings due to proton–carbon J coupling ($J \leq 200$ Hz) but does not affect the direct carbon–proton dipolar interaction (ca. 10 kHz). As a result, only those portions of the polymer enjoying relatively high conformational freedom are observed.[11] Figure 2 displays the MAS-SD spectra of forms A and B. It can readily be seen that the

Table II
CP T_1 of the Polymorphs of PAIBLA[a] (in s)

	form A	form B
CO	27 (1)	17 (0.5)
$^{\alpha}CH$	20	8.5
$^{\beta}CH_2$	28	5
OCH_2	0.4	0.3
CH	0.5	0.5
CH_3	0.5	0.5

[a] We report in parentheses the estimates for the fast components of the decay.

peak intensities of the main-chain carbons differ significantly in the two spectra, those of form B being the stronger. This is consistent with the conclusion that form B has a higher content of amorphous material than form A. It seems therefore that PAIBLA, even though stereoregular and semicrystalline, enjoys considerable freedom in the amorphous regions.

In an attempt at characterizing the dynamics of the polymer in the two crystalline environments, T_1's were measured at 21 °C for both forms (Table II), using the CPT1 method of Torchia.[5] The decay of the magnetization of the backbone carbons is biexponential, showing short and long time components during the CPT1 experiments. Rough estimates of 1 s and ca. 0.5 s are obtained for the fast time constants in forms A and B, respectively. These values are extracted from the curves corresponding to the carbonyl signals in both forms. The assignment of these short time constants to interfacial or amorphous regions, as has been possible in other cases,[10] is complicated by the overlap of peptide and ester carbonyl resonances. The longer time constants may correspond to main-chain carbons located in the crystalline regions of the material. The T_1's for form A are longer than those for form B. We may conclude from these data that backbone motions are somewhat more restricted in form A than in form B. The side chain, on the other hand, displays essentially the same motional behavior in both phases.

Summarizing our results, we conclude the following: (i) The conformation of the monomer unit, as attested by ^{13}C NMR and infrared spectroscopy,[1a] does not differ significantly in the two crystalline forms. (ii) Some changes in the motional behavior of the main chain do occur in going from one form to the other. These may arise from differences in the morphologies of the two solid forms. (iii) A considerable portion of the polymer is in the amorphous phase and experiences a relatively high degree of mobility at room temperature.

Registry No. PAIBLA (homopolymer), 35239-25-9; PAIBLA (SRU), 37768-91-5.

References and Notes

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	PAIBLA	
	hexagonal (A)	tetragonal (B)
amide A	3292	3298
amide B	3091	3087
CO lateral group	1751	1755
amide I	1660	1661
amide II	1548	1543
amide V	671	668

Another form of PAIBLA, different from the ones we are discussing in this communication, was reported by: (b) Yuki, H.; Okamoto, Y.; Taketani, Y.; Tsubota, T.; Marubayashi, Y. *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 2237–2251.

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Stereochemical Investigation of the Initiation Step of Propene Polymerization with Differently Activated $TiCl_4/MgCl_2$-Supported Catalysts

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In the field of Ziegler–Natta catalysis for α-olefins polymerization, the discovery of $MgCl_2$ as the ideal support for the fixation of $TiCl_4$ marked an exceptional improvement in the industrial polymerization process, and several methods for the preparation of highly active and stereospecific $TiCl_4/MgCl_2$-based catalysts are reported in scientific[1] and patent literature.[2] For the preparation of all these catalytic systems, a fundamental stage is the activation of the support $MgCl_2$. In fact, the reaction between anhydrous $MgCl_2$ powder and $TiCl_4$ results in hardly any fixation of titanium. This is probably due to the small surface area of $MgCl_2$ and its high crystallinity. Various procedures are used to decrease $MgCl_2$ crystalline order and to enhance its surface area and number of sites suitable to titanium fixation. The most common among them is a prolonged milling of $MgCl_2$ in the presence or the absence of $TiCl_4$ and/or an electron donor. Many studies have been performed to correlate the structural changes in $MgCl_2$ caused by the activation procedures with the activity and stereospecificity of the corresponding catalytic systems.[1] In the present work, we approach this problem from a different viewpoint, i.e., by the study of the effect of the kind of procedure by which $MgCl_2$ is activated on the steric structure of atactic and isotactic sites of the corresponding catalytic systems. The method we use to obtain structural information on the active sites is the investigation, by ^{13}C NMR, of the initiation step in propene polymerization in the presence of the selectively ^{13}C-enriched cocatalyst $Al(^{13}CH_2CH_3)_3$. In this case, the initiation step is the insertion of propene into the reactive titanium–ethyl bond resulting after the exchange between the titanium halide and triethylaluminum. In our previous publications,[3–5] we have shown that the stereochemical structure of the ethyl chain end groups, resulting after the initiation, is extremely sensitive to any change of the constitution of the active sites. Therefore, the extent of the first step stereoregularity is a characteristic of each catalytic system and consequently supplies noticeable information on the characteristic steric features of the active sites of the various catalytic systems.

Figure 1 shows the ^{13}C NMR spectra of the isotactic (heptane insoluble) fractions of polypropene samples obtained respectively in the presence of the conventional δ-$TiCl_3$-based catalyst and of a $TiCl_4$ supported on $MgCl_2$ catalyst, using selectively enriched $Al(^{13}CH_2CH_3)_3$ as co-

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