# Solid State CP/MAS $^{13}$C Nuclear Magnetic Resonance Spectra of Poly(4-hydroxybenzoate)s

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*Received April 9, 1996; Revised Manuscript Received July 24, 1996*⊗

ABSTRACT: The high-resolution solid state $^{13}$C NMR spectra of the different crystal modifications of poly(4-hydroxybenzoate)s and their copolymers have been obtained by means of high-power proton decoupling, cross-polarization, and magic angle spinning. The resolution was sufficient in order to resolve the resonance lines of all seven differently bonded carbon atoms in the PHBA repeat unit. From the chemical shift splitting of the ortho ring carbon atoms it is deduced that, in crystalline PHBA, the torsional angle between the ester plane and the phenylene ring plane deviates from 90°. The deviation increases in the order modification II > modification III > modification I. The variable-contact-time measurements indicate that the chain packing in crystal modification I is denser than in the crystal modification II.

## Introduction

The homopolyester of 4-hydroxybenzoic acid (PHBA) and its copolyesters are of continuing commercial and academic interest. From the application point of view, they are of interest because of their high moduli and high temperature resistance. The academic interest arises from their thermotropic liquid crystalline character.

At room temperature, two different orthorhombic crystal modifications of PHBA have been found, by using X-ray diffraction:[1−3] modification I ($a = 0.752$, $b = 0.570$, $c = 1.249$ nm) and modification II ($a = 0.377$, $b = 1.106$, $c = 1.289$ nm). Above 330 °C these modifications reversibly transform to a pseudohexagonal structure (modification III). The high symmetry and regularity of the molecular structure cause an exceptionally high degree of crystallinity which entails an extremely low solubility in all common solvents. For better understanding of the properties of the materials it is very important to obtain more information on the solid state structures.

Recently, cross-polarization magic angle spinning high-power proton decoupling nuclear magnetic resonance (CP/MAS/DD) has become a powerful tool for characterization of polymers in the solid state.[4−9] It was demonstrated that this experimental method is sensitive to local molecular conformations and short range order, giving a complementary view to that provided by diffraction techniques.[10,11] As in solution, the NMR chemical shifts of the NMR lines measured in the solid state represent the "isotropic" values and reflect the local molecular environment of the nuclei observed. Thus the values of the shift are sensitive to the conformations in the solid state. In addition, the line widths in the $^{13}$C CP/MAS/DD NMR spectra depend on the local short-range order of the nuclei observed. Through interpretation of these complex spectra, particularly in conjunction with X-ray diffraction data, it is possible to obtain detailed information on the crystalline structure of both natural and synthetic polymers. It was shown[12,13] that a spectrum of five peaks can be observed from the seven carbon atoms in PHBA. From this it follows that not all the NMR lines could be resolved. The different lines were assigned to the different carbon atoms. In addition, the molecular motion at high temperature was investigated.[14] However, no investigation of the different crystal modifications was performed.

In the present work, the solid state structures of the PHBA modifications I−III are investigated by means of CP/MAS NMR. The pure crystal modification I was obtained in PHBA whiskers, needlelike crystals. A sample containing 80% modification II was prepared by means of the conventional polymerization procedure. As it is impossible to obtain PHBA in the pure modification III at room temperature, the copolyester of poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN) and PHBA (20/80), in which the PHBA exists in the modification III,[29] was investigated in addition to the homopolymer PHBA.

## Experimental Section

**Sample Preparation.** The synthesis of the whiskers (PHBA I) and slablike crystals (PHBA I + II) is described by Kricheldorf and Schwarz.[3] The copolyester of PEN-*co*-PHBA (20:80) has been synthesized by transesterification of PEN with *p*-acetoxybenzoic acid.[15]

**Fourier Transform $^{13}$C Nuclear Magnetic Resonance.** The $^{13}$C solid-state NMR measurements were performed at room temperature on a Bruker MSL 300 FT NMR spectrometer operating at 75.14 MHz and equipped with a cross-polarization accessory and double bearing rotor. By using adamantine as a reference, the radio frequency amplifiers were adjusted to satisfy the Hartmann−Hahn condition[16] at 110 kHz. The high-power proton decoupling field was of the same strength as the spin-lock field. The spectra were obtained by the cross-polarization, magic angle spinning, high-power proton dipolar decoupling (CP/MAS/DD) technique. The proton 90° pulse length was 4.4 $\mu$s. The "magic angle" was set by maximizing the intensity of the carbonyl resonance of glycine. The sample spinning frequency was 4.5 kHz. The cross-polarization contact time was 1.5 ms, and the recycle time of the pulse was 5 s. The spectra were accumulated 1000 times. The spin sidebands, which commonly occur in the spectra of rigid glassy polymers, were suppressed by using the pulse sequences TOSS.[17] The signal of adamantine was used as an external reference for the chemical shifts.

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

S0024-9297(96)00537-2 CCC: $12.00

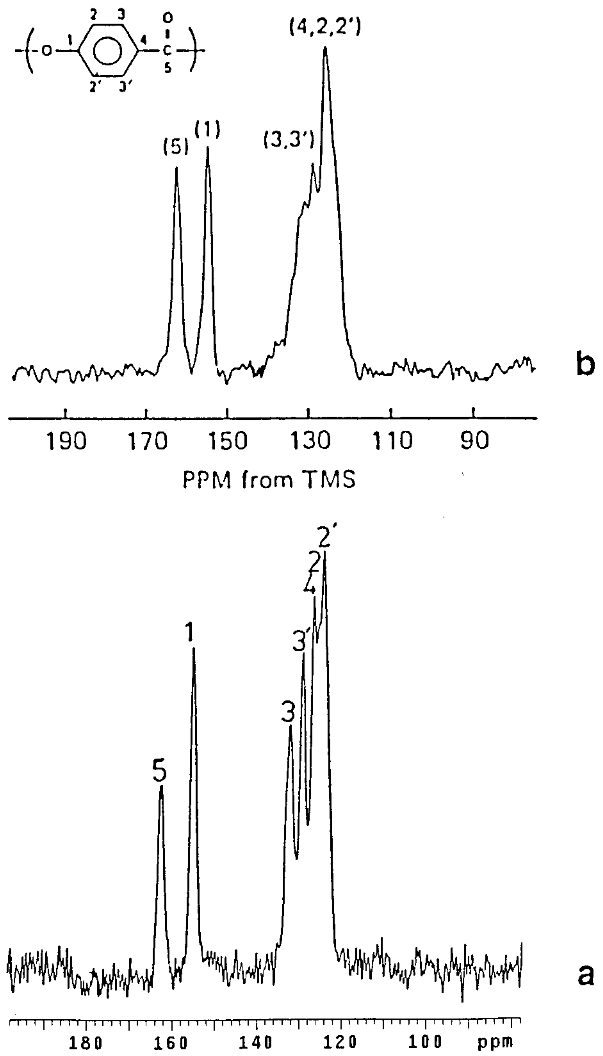

**Figure 1.** (a) Solid state $^{13}$C CP/MAS/DD NMR spectrum of PHBA whisker (PHBA I). (b) Spectrum of PHBA obtained by Fyfe et al.[11]

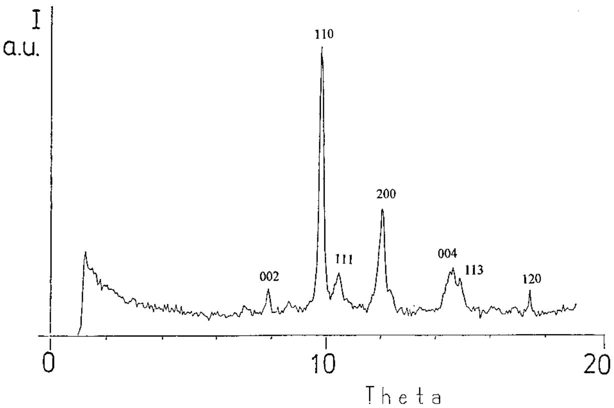

**Figure 2.** WAXS of PHBA whisker (PHBA I). The reflections of modification I were labeled.

## Results and Discussion

**Spectrum of Whisker Crystals (PHBA I).** The solid state CP/MAS spectrum of the PHBA whiskers is shown in Figure 1a. The whiskers are crystallized in the pure crystals modification I. This is evidenced by the WAXS spectrum shown in Figure 2 in which the crystal peaks arising from modification II cover an area of less than 5%. As one can see, the resonance lines of all seven carbon atoms in the spectrum are separated.

**Table 1. Chemical Shifts of the Different $^{13}$C Atoms of PHBA in the Solid State and of the Tetramer in Solution in ppm Downfield from $Me_4Si$**[a]

| | chemical shifts | | |
|---|---|---|---|
| carbon | tetramer[11] | PHBA (sample of Fyfe) | PHBA (our whisker sample) |
| 5 | 162.9 | 162.4 | 162.77 |
| 1 | 154.7 | 155.0 | 155.45 |
| 3 | 131.0 | 131.6 | 132.48 |
| 3′ | 131.0 | 128.2 | 129.43 |
| 4 | 126.0 | 125.4 | 126.91 |
| 2 | 121.8 | 125.4 | 125.76 |
| 2′ | 121.8 | 125.4 | 124.66 |

[a] See structure in Figure 1 for numbering of the carbon atoms.

For comparison, the pioneering spectrum obtained by Fyfe et al.[12] is shown in Figure 1b. In this spectrum some superposition of the lines occurs. Only five lines can be observed. The better resolution of our spectrum seems to be due to the fact that the PHBA investigated by Fyfe et al. must have contained a mixture of modifications I and II while our sample was crystallized in the pure modification I. The assumption that the poor resolution is due to the presence of different crystal modifications is supported by our results on the slablike crystals containing modifications I and II shown in Figure 4 (see next section). We also have to point out that we used a higher magnetic field (7.046 T) than Fyfe et al. (1.409 T), which also might have contributed to improve the resolution.

The assignment of the lines to the different carbon atoms was performed in such a way that the best agreement with the assignment given by Fyfe et al. and with that given for the tetramer in solution is achieved. Table 1 represents the values of the chemical shift and the assignment of the lines for the different carbon atoms of the tetramer in solution[12] (second column), for the spectra of Fyfe et al.[12] (third column), and for our spectrum of PHBA I (fourth column). While the lines of the carbon atoms 4, 2, and 2′ are not resolved in the spectrum of Fyfe et al., a clear separation is obtained in our data.

In order to obtain information on the conformation of the chains in the PHBA crystals, it is interesting to compare the values of the chemical shift obtained for the crystal with those obtained for the solution of the tetramer. In the solution, the phenylene ring carbon atoms (3, 3′) in the ortho position with respect to the carboxyl group are equivalent since the phenylene ring can rotate freely about the 1,4 axis. The same is true for the carbon atoms in the meta position (2, 2′). In the solid state, however, the phenylene ring motion is frozen. This causes a steric nonequivalency of the resonance lines of the carbon atoms 3 and 3′ as well as of the carbon atoms 2 and 2′. As a consequence, the single resonance line of the carbon atoms in the ortho position, which appears at 131.0 ppm in the solution, is separated into a doublet at 132.48 and 129.43 ppm in the solid state. In the same way the single resonance line of the aromatic carbon atoms in the meta position, which lies at 121.8 ppm in the solution, is separated into a doublet at 125.76 and 124.66 ppm in the solid state. Such a splitting indicates that the motion of aromatic rings is restricted to small-amplitude torsional oscillations about an axis which is not axially symmetric.[18] There exist many examples for this effect in other polymer molecules.[19−25]

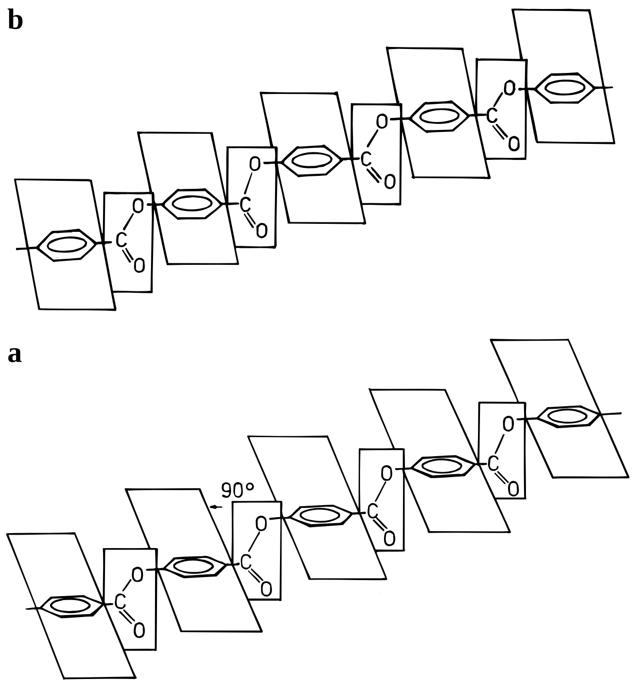

**Figure 3.** Representation of different conformations of PHBA: (a) the phenylene rings including an angle of 90° with the plane of the ester linkage; (b) the phenylene rings including an angle different from 90° with the plane of the ester linkage.

From the chemical shift splitting in solid PHBA I we can conclude that the molecules in PHBA I assume a conformation in which the ester linkage and the phenylene ring plane form a torsional angle which slightly deviates from 90°, as depicted in Figure 3b. This deviation results in a nonequivalency of the carbon atoms which is the reason for the splitting. In the case of a torsional angle of 90° (see Figure 3a) no splitting of these NMR lines is expected. A deviation from 90° has been also found by means of X-ray scattering.[26–28]

Comparing the value of the chemical shift splitting, we find that the splitting of the aromatic carbon atoms in the ortho position (2 and 2′) is smaller than the splitting of aromatic carbon atoms in the meta position (3 and 3′). This is due to the fact that the distance from the carboxyl group to the carbon atoms 2 and 2′ is longer than that to the carbon atoms 3 and 3′.

**Spectrum of Slablike Crystals (PHBA I + II).** The solid state CP/MAS/DD NMR spectrum of slablike PHBA crystals is shown in Figure 4a. From the results of Kricheldorf and Schwarz[3] it is concluded that the slablike PHBA consists of about of 20% modification I and 80% modification II. Therefore, in order to obtain the spectrum of the pure modification II, the difference of the spectrum of slablike PHBA and the spectrum of the PHBA whisker of Figure la, multiplied by 0.2, was calculated. The result is shown in Figure 4b. The value of the chemical shift of the resonance lines of the two spectra are listed in the first two columns of Table 2. As one can recognize, the correction performed results in small changes in the position of the resonance lines.

It seems most important to us to compare the chemical shift splitting value of carbon atoms 3 and 3′ in the spectra of the different modifications: This splitting can be considered to be a measure of the torsional angle between the ester plane and the phenylene plane indicated in Figure 3. The values of the chemical shift splitting are listed in Table 3. As one can see, the chemical shift splitting of the PHBA whisker (PHBA I) is smaller than that of PHBA in modification II. From this we conclude that the deviation of the torsional angle between the ester plane and the phenylene ring plane from 90° is smaller in modification I than in modification II.

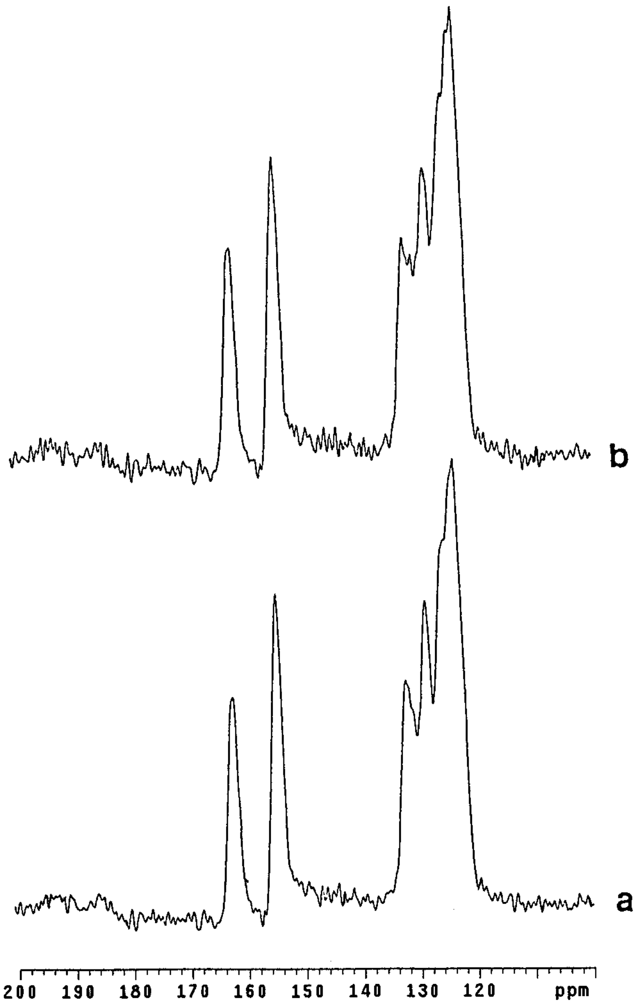

**Figure 4.** (a) Solid state $^{13}C$ CP/MAS/DD NMR spectrum of slablike PHBA crystals (PHBA I + II). (b) Differential spectrum of of slablike PHBA and PHBA whisker multiplied by 0.2.

**Table 2. Values of the Chemical Shifts of the Different $^{13}C$ Atoms of PHBA and Its Copolymers in Different Crystal Modifications in ppm Downfield from $Me_4Si$[a]**

| | chemical shifts | | |
|---|---|---|---|
| carbon | PHBA I + II (slablike PHBA) | PHBA II (from PHBA-co-PEN) | PHBA III (from PHBA-*co*-PEN) |
| 5 | 162.44 | 161.90 | 162.82 |
| 1 | 154.69 | 154.32 | 154.59 |
| 3 | 132.21 | 132.02 | 133.27 |
| 3′ | 128.72 | 128.42 | 129.92 |
| 4 | 125.87 | 125.41 | 126.37 |
| 2 | 124.34 | 124.27 | 122.85 |
| 2′ | 123.71 | 123.34 | 122.85 |

[a] See structure in Figure 1 for numbering of the carbon atoms.

The splitting of the lines of carbon atoms 2 and 2′ is not evaluated because it is much smaller than that of 3 and 3′ and, therefore, cannot be determined with enough accuracy.

**Spectrum of PEN-*co*-PHBA (20:80).** The two different orthorhombic crystal modifications (I and II) at

**Table 3. $^{13}$C Chemical Shift Splittings of the Atomic Carbon Atoms of PHBA in Different Crystal Modifications Measured in ppm[a]**

| carbon | PHBA I (whisker PHBA) | PHBA I + I (slablike PHBA) | PHBA II (differential spectrum) | PHBA III (from PHBA-*co*-PEN) |
|---|---|---|---|---|
| 3-3′ | 2.98 | 3.43 | 3.60 | 3.35 |
| 2-2′ | 1.07 | 0.63 | 1.14 | 0 |

[a] See structure in Figure 1 for numbering of the carbon atoms.

room temperature reversibly change to a pseudohexagonal chain packing[1,2] above 330 °C. This structure is called the high-temperature modification or modification III. Unfortunately, in our instrument it was not possible to reach temperatures above 300 °C for the CP/MAS/DD experiment. However, it has been previously shown[29] that PHBA crystallizes in modification III even at room temperature if it is incorporated into a copolyester of poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN) having a PHBA content larger than 70 mol %. We therefore investigated the copolyester PEN-*co*-PHBA (20:80). To do this, the average sequence length of PHBA in the copolymer sample should be obtained. Unfortunately, like the PHBA homopolymer, PEN-*co*-PHBA (20:80) cannot be dissolved in any solvent. Our recent work about $^{13}$C NMR sequence distribution analysis of series PEN-*co*-PHBA samples shows that PHBA has a greater than random chance of being bonded to another PHBA in PEN-*co*-PHBA.[30,31]

Figure 5a shows the solid state CP/MAS/DD spectrum of this copolyester. In order to eliminate the influence of the PEN component, we subtracted the spectrum of PEN which is shown in Figure 5b. The scale of the spectrum of PEN is adjusted in such a way that the intensity of the resonance line of the methylene carbon atoms at 63.11 ppm is the same in PEN and in the copolyester PEN/PHBA. Figure 5c shows the difference of the two spectra. The values of the chemical shift and of the chemical shift splitting are listed in Tables 2 and 3, respectively.

The results show that the chemical shift splitting of carbon atoms 3 and 3′ is larger than in the case of modification I and smaller than in the case of modification II. From this we conclude that the torsional angle between the ester plane and the phenylene ring plane is intermediate between that of PHBA I and PHBA II.

**Variable-Contact-Time Spectra of Whisker PHBA (Modification I) and Slablike PHBA (Modifications I + II).** Differences in relaxation times are often used to distinguish between differently bonded carbon atoms. In the cross-polarization experiment the carbon atoms are polarized by the proton reservoir at different rates, depending on the strength of the static $^{13}$C$-$$^{1}$H dipolar interaction. This interaction is influenced by the number and the proximity of protons surrounding the carbon atom and by averaging of the interaction resulting from any molecular motion. Thus, cross-polarization spectra measured at different contact times between the carbon atoms and the proton spin reservoir can be used to assign the resonance lines[18] and to get information about the molecular motion and chain packing in the heterogeneous system.[9]

Some CP/MAS/DD $^{13}$C NMR spectra of PHBA whiskers (modification I) and slablike PHBA (modifications I + II) measured at different spin-lock cross-polarization times (in $\mu$s) are given in Figure 6. The general features of the spectra support the assignment of the lines given in Table 1. For example, one can assume that the quaternary carbon atoms, 1 and 4, polarize less quickly than the protonated aromatic carbon atoms. This clearly demonstrates that carbon atom 4 resonates at 126.63 ppm. In a previous work on the CP/MAS/DD $^{13}$C NMR spectrum of PHBA,[12] the carbon atom 4 line was not observed separately and it was incorrectly assigned to the upfield line of the carbon atoms 2 and 2′.

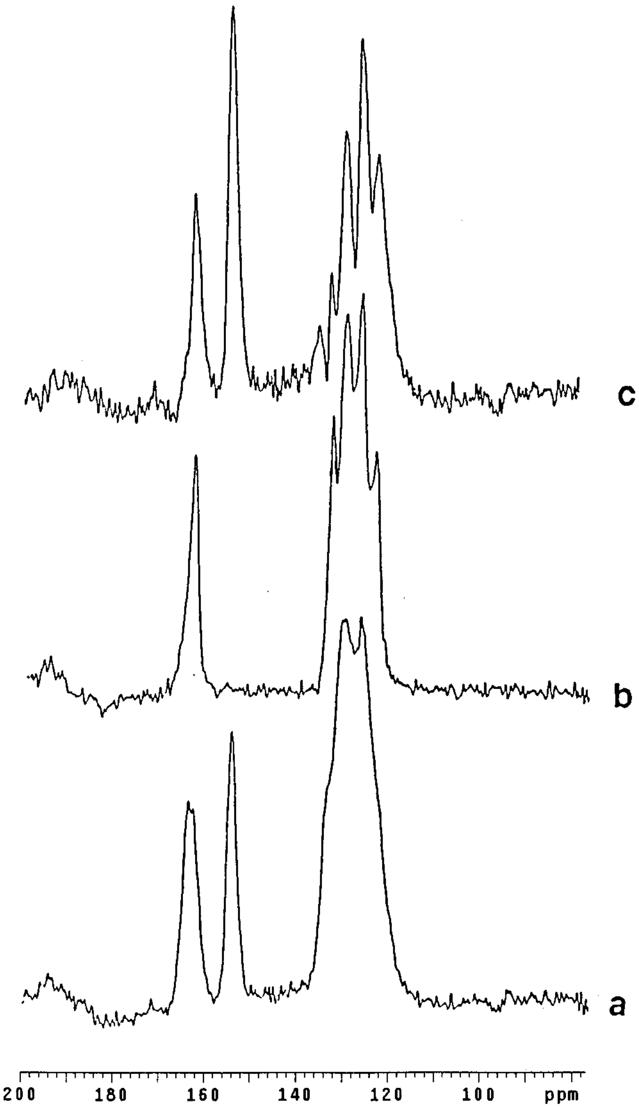

**Figure 5.** $^{13}$C CP/MAS/DD NMR spectra of (a) the copolyester of PEN and 20 mol % PHBA and of (b) PEN and (c) the differential spectrum of PEN/PHBA (20/80) and PEN.

By comparing the variable-contact-time spectra of the whisker PHBA (modification I) and slablike PHBA (modifications I + II), we find that the lines of carbon atoms 1 and 5, at 155.45 and 162.77 ppm, respectively, develop more quickly in the whisker crystals than in the slablike crystals. For example, after a contact time of 0.05 ms these lines are clearly visible in the spectrum of the whisker PHBA while they do not appear at all in the other spectrum. The more rapid polarization in the whisker PHBA is explained by the fact that the chain packing in whisker crystals is denser than the chain packing in modification II.

**Acknowledgment.** We are very indebted to professor H. Spiess and Mr. N. Egger from the Max-Planck Institute fur polymerforschung, Mainz, and to Dr. G. Schwarz in our institute for helpful discussion. In

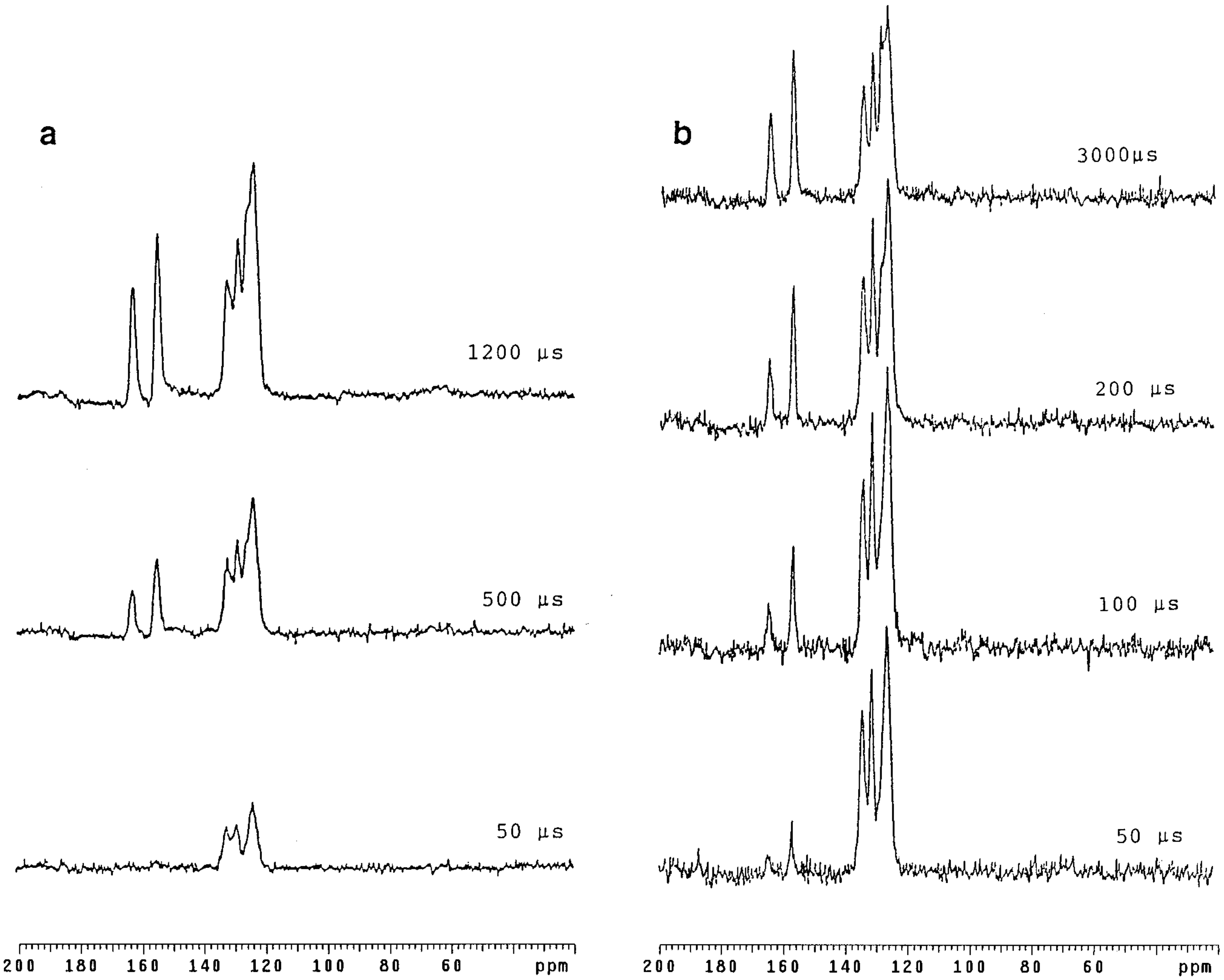

**Figure 6.** $^{13}C$ CP/MAS/DD NMR spectra of PHBA as a function of cross-polarization contact time (in $\mu$s): (a) slablike PHBA crystals (PHBA I + II); (b) PHBA whisker crystals (PHBA I). All spectra obtained from 8k FT of 1000 FID accumulation at a 5 s experiment repetition time.

addition, Dr. G. Schwarz kindly provided the PHBA samples. M.G. thanks the Alexander von Humboldt Foundation for supporting this work by a fellowship.

## References and Notes

(1) Blackwell, J.; Lieser, G.; Gutierrez, G. A. *Macromolecules* **1983**, *16*, 1418.
(2) Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1661.
(3) Kricheldorf, H. R.; Schwarz, G. *Polymer* **1990**, *31*, 481.
(4) Pines, A.; Gibby, M. G.; Waugh, L. S. *J. Chem. Phys.* **1973**, *59*, 569.
(5) Andrews, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1972**, *8*, 1.
(6) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(7) Jelinski, L. W. *Chemtech.* **1986**, *16*, 186.
(8) Fyfe, C. A. *Solid NMR for Chemists*; C.F.C. Press: Guelph, 1984.
(9) Yu, T.; Guo, M. *Prog. Polym. Sci.* **1990**, *15*, 825.
(10) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.
(11) Bovey, F. A. *Chain Structures and Conformation of Macromolecules*; Academic: New York, 1982.
(12) Fyfe, C. A.; Lyerla, J. R.; Volksen, W.; Yannoni, C. S. *Macromolecules* **1979**, *12*, 757.
(13) Muhlebach, A.; Economy, J.; Lyerla, J. R.; Yannoni, C. S.; Facey, G.; Fyfe, C. A.; Geis, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (1), 40.
(14) Lyerla, J. R.; Economy, J.; Maresch, G. G.; Muhlebach, A.; Yannoni, C. S.; Facey, G.; Fyfe, C. A. In *Liquid-crystalline Polymers*; Weiss, R. A., Ober, C. K., Eds.; ACS Symposium Series 435; Washington, DC, 1990; p 359.
(15) Chen, D.; Zachmann, H. G. *Polymer* **1991**, *32*, 1612.
(16) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *12*, 2404.
(17) Dixon, W. T. *J. Chem. Phys.* **1982**, *77*, 1800.
(18) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.
(19) Garroway, A. N.; Ritchey, W. M.; Moniz, W. B. *Macromolecules* **1985**, *15*, 1051.
(20) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300.
(21) Lippmaa, E. T.; Alla, M. A.; Pehk, J. J.; Engelhardt, G. *J. Am. Chem. Soc.* **1978**, *100*, 1929.
(22) English, A. D. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 805.
(23) Hays, A. D. *J. Chem. Soc., Perkin Trans.* **1983**, *2*, 1049.
(24) Uryu, T.; Kato, T. *Macromolecules* **1988**, *21*, 378.
(25) Uryu, T.; Kato, T. *Chem. Lett.* **1987**, 211.
(26) Yoon, D. O.; Masciocchi, N.; Depero, L. E.; Parrish, W. *Macromolecules* **1990**, *23*, 1793.
(27) Coulter, P. T.; Hanna, S.; Windel, A. H. *Solid Cryst.* **1989**, *5* (5), 1603.
(28) Coulter, P. T.; Windel, A. H. *Macromolecules* **1989**, *22*, 1129.
(29) Buchner, S.; Chen, D.; Gehrke, R.; Zachmann, H. G. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 357.
(30) Guo, M.; Zachmann, H. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (1), 825.
(31) Guo, M.; Zachmann, H. G. *Polymer*, submitted for publication.

MA960537Q