compounds. The N→O group appearing in reaction 2 does not belong to any of these groups. However, part of the broad band observed at 1000 cm^{-1} may well be assigned to this group. Thus the ESCA data as well as the infrared spectra support the structural changes described in reaction 2. The P=O formation has also been reported in thermal rearrangement of poly[bis(methoxy)phosphazene].[3]

Conclusions

The ESCA data and the infrared spectra of poly[bis(trifluoroethoxy)phosphazene] exposed to pyrolysis, UV light, and electron beams reveal the structural changes taking place in the polymer backbone due to the crosslinkage and the oxygen shift to the nitrogen upon the side group elimination. These studies support the mass spectroscopic data of the gaseous products formed in the elimination of the side groups. The increasing energy input increases the relative yield of CF_3H to CF_3CH_3. The latter and CO_2 are the major products in low-temperature pyrolysis and UV light exposures. The ESCA data may support the photooxidation mechanism proposed.

References and Notes

(1) For a review, see H. R. Allcock, *Angew. Chem., Int. Ed. Engl.*, **16**, 147 (1977).
(2) J. P. O'Brien, W. T. Ferrar, and H. R. Allcock, *Macromolecules* **12**, 108 (1979); H.R. Allcock, J. P. O'Brien, W. Ferrar, and K. Kosydar, "Final Report to N.A.S.A. (Langley)", Grant NBG 1141, July 1977.
(3) V. D. Mochel and T. C. Cheng, *Macromolecules*, **11**, 176 (1978).
(4) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965); H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966); see also ref 2.
(5) The elementary analyses were carried out by Childers Microanalytical Laboratories, Milford, N.J. 08848.
(6) H. Hiraoka, *IBM J. Res. Dev.*, **21**, 121 (1977).
(7) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.
(8) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, R. F. Heden, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969; see also D. T. Clark, *Adv. Polym. Sci.*, **23**, 125 (1977).
(9) B. Ranby and J. F. Rabek, "Photodegradation, Photo-Oxidation and Photo-Stabilization of Polymers", Wiley, New York, 1975, pp 45–48.
(10) K. Nakanishi, "Infrared Absorption Spectroscopy", Nankodo, Tokyo, 1960.
(11) H. Hiraoka and W. Lee, *Macromolecules*, **11**, 622 (1978).

High-Resolution Carbon-13 Nuclear Magnetic Resonance Studies of Polymers in the Solid State. Aromatic Polyesters

C. A. Fyfe,‡ J. R. Lyerla,* W. Volksen, and C. S. Yannoni*

IBM Research Laboratory, San Jose, California 95193. *Received December 18, 1978*

ABSTRACT: High-resolution ^{13}C NMR spectra have been obtained for the insoluble, highly crystalline homopolymer of *p*-hydroxybenzoic acid, two methoxy derivatives of this polymer, and two copolymers with biphenylene terephthalate by use of proton dipolar decoupling, magic-angle spinning, and ^{13}C-{^{1}H} cross-polarization techniques. Resolution is sufficient that the majority of carbons in the homopolymer repeat units appear as individual resonance lines. The widths of resonance lines (≤15 Hz) are 3–6 times more narrow than those obtained for glassy polymers—a result which is attributed to both the rigidity of these aromatic polyesters and the homogeneous local environment associated with crystal habit.

The design of polymers which possess a specific set of material properties requires understanding of structure–property relationships for macromolecules. Basic to the elucidation of these insights is the necessity of having characterization techniques which permit detailed analysis of polymer structure. In this regard, one of the more useful techniques in delineating the composition, conformation, and microstructure of chain molecules has been high-resolution NMR spectroscopy. The high resolving power of proton and carbon-13 NMR usually results in each of the nonequivalent proton or carbon nuclei of a repeat unit being individually identifiable in the respective spectrum, thereby providing either multiple sites for compositional analysis or specific main chain and side chain sites for assessment of the motional features of a polymer.

Unfortunately, in the past high-resolution NMR spectra have been obtainable only for polymer melts or polymers in solution. In the solid state, nonaveraged nuclear dipole–dipole interactions give rise to spectral broadening which results in only a single broad (tens of kilohertz) resonance line. This line width makes it impossible to utilize high-resolution NMR as a characterization technique for the many polymer systems which are essentially insoluble unless subjected to extensive degradation. However, in a recent set of papers, Schaefer et al.[1-3] have demonstrated that it is possible to obtain "high-resolution" carbon-13 NMR spectra for solid glassy polymers by combining line-narrowing techniques for solids (i.e., proton dipolar decoupling,[4] DD, to eliminate ^{13}C-^{1}H dipolar broadening and magic-angle spinning,[5] MAS, to eliminate chemical shift anisotropy broadening)[2] with a matched spin-lock cross-polarization (CP) experiment to enhance sensitivity.[4-6] For these experiments, the analytical sample consisted of compression-molded solid polymer plugs machined in the form of cylindrical rotors which were spun about an axle support by impingement of a driving gas (N_2) on the rotor. The approximate 100-Hz resolution achieved enabled many of the magnetically nonequivalent carbons both in the side and main chains of the polymer repeat units to be resolved as individual resonance lines. This degree of spectral resolution, of course, adds new potential for the use of ^{13}C NMR as a characterization technique for insoluble polymer systems.

In the work reported here, we have explored, in a preliminary manner, the use of ^{13}C NMR to characterize the highly insoluble polyesters based on *p*-hydrobenzoic

‡ On leave from Guelph–Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

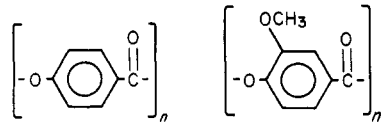
0024-9297/79/2212-0757$01.00/0

Table I
^{13}C Chemical Shifts[a] of *p*-Oxybenzoyl Tetramer and Polymer

tetramer		polymer	
carbon[b]	shift[c]	carbon	shift[e]
5	162.9	5	162.4
1	154.7	1	155.0
3,3′	131.0	3 } [d]	131.6 }
4	126.0	3′ }	128.2 }
2,2′	121.8	4,2,2′	125.4[f]

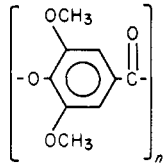
[a] In ppm downfield from Me_4Si. [b] See structure in Figure 1 for numbering. [c] Shifts were determined relative to internal Me_2SO-d_6 (solvent) and converted to Me_4Si scale. The spectrum was obtained at 90 °C to enhance solubility. Digital resolution was 1.25 Hz (0.06 ppm). [d] Resonance lines from low to high field, not assignments. [e] Shifts were determined relative to external CH_3OH and converted to Me_4Si scale. Digital resolution was 11.98 Hz (0.79 ppm). [f] Value is for the maximum of the asymmetric resonance line; the C-2 and C-2′ carbons absorb at a lower value of chemical shift.

acid. Interest in this class of materials derives from their structure which is analogous to the aromatic polyamides used in high-temperature applications and as high-strength, high-modulus fibers.[7] The materials selected for investigation were the homopolymer[8] of *p*-hydroxybenzoic acid (I), two methoxy derivatives (II and III) of this

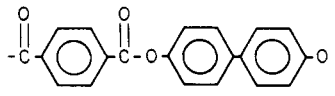


I

II



III



IV

polymer, and two copolymers of *p*-hydroxybenzoic acid with biphenylene terephthalate (IV), BPT.

Results

The carbon-13 spectrum of a 43-mg polycrystalline sample of the *p*-oxybenzoyl polymer (I) ($M_n \sim 10000$) obtained at 27 °C under the conditions of DD, MAS, and CP is shown in Figure 1. The integrated intensities of the resolved resonance lines correspond to a ratio of 1:1:5 (from low to high field) consistent with seven carbons in the repeat unit.[9] The chemical shifts of the two more downfield resonances and of the three partially resolved lines at higher field are compared in Table I to the chemical shifts, obtained in a Me_2SO-d_6 solution, of the central units of the tetramer prepared from *p*-acetoxybenzoic acid. Clearly, the two downfield single intensity lines (Figure 1a) can be assigned to the carboxyl and ring carbon bonded to oxygen. The assignment of the remaining carbons to specific resonances in the 125–135-ppm region can only be made on a tentative basis owing to overlap. In Figure 1b is the ^{13}C spectrum of I at −80 °C using the same DD, MAS, and CP parameters as in Figure 1a. The spectrum, which is the first low-temperature high-resolution ^{13}C spectrum of a crystalline polymer, is equivalent to 1a except that the resonance lines in the region of overlap are somewhat better defined. The three partially resolved lines are in an approximate intensity ratio of 1:1:3 with the line of threefold intensity being asymmetric on the high-field side. This pattern of intensities clearly indicates that at least one pair of ortho ring carbons is inequivalent. Such a result would be expected in the solid state if the aromatic rings are restricted to small-amplitude torsional oscillations about a nonaxially symmetric direction.[1] On the basis of this argument and the chemical shift assignments in the tetramer, the resonances at 131.6 and 128.2 ppm are assigned to the 3,3′ carbons (see Figure 1 for numbering scheme). The remaining carbons are assigned to the line of threefold intensity.

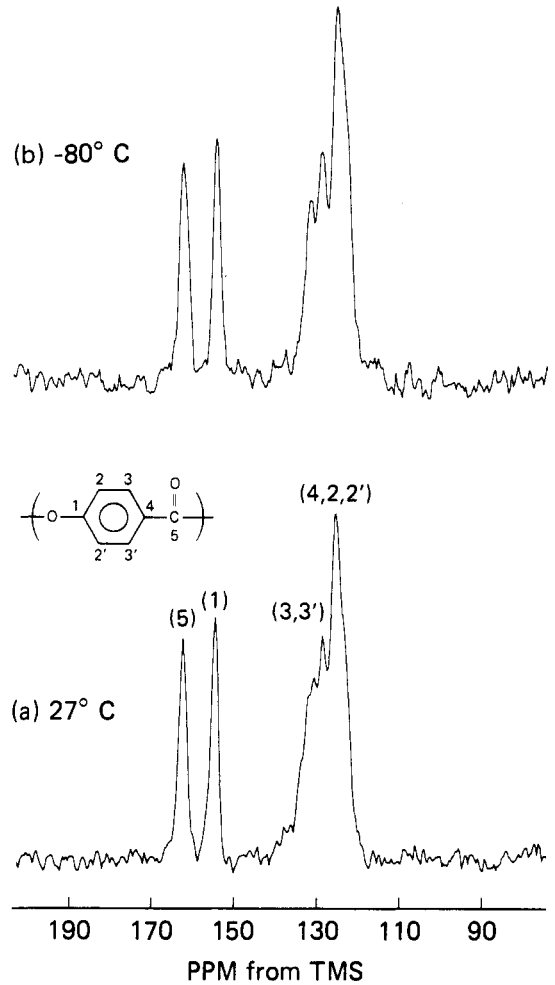


Figure 1. (a) Magic-angle CP ^{13}C NMR spectrum of I at 27 °C. Spectrum obtained from 2K FT of 2500 FID accumulations with a CP contact time of 1.5 ms and experiment repetition time of 3.5 s. (b) Spectrum of I at −80 °C with the same conditions as (a) but with 1300 accumulations.

In the cross-polarization experiment, the buildup of magnetization for a particular carbon is governed by the cross-relaxation time in the rotating frame which in turn is related to the strengths of the static dipolar interactions between carbons and protons.[1,4] Provided the carbons in a polymer repeat unit are subject to similar motion,[10] carbons with directly bonded protons would be expected to cross-polarize more rapidly than carbons without direct interactions owing to the shorter interaction distance and therefore larger local dipolar field. Thus, as Schaefer et al.[3] have suggested, cross-polarization spectra as a function of the contact time between carbon and proton spin reservoirs can be exploited as a tool for the assignment of resonance lines and as a possible resolution-enhancing technique in regions of spectral overlap. Spectra of the *p*-oxybenzoyl polymer (I) as a function of the spin-lock cross-polarization time are given in Figure 2. The general features of the spectra lend credence to the resonance

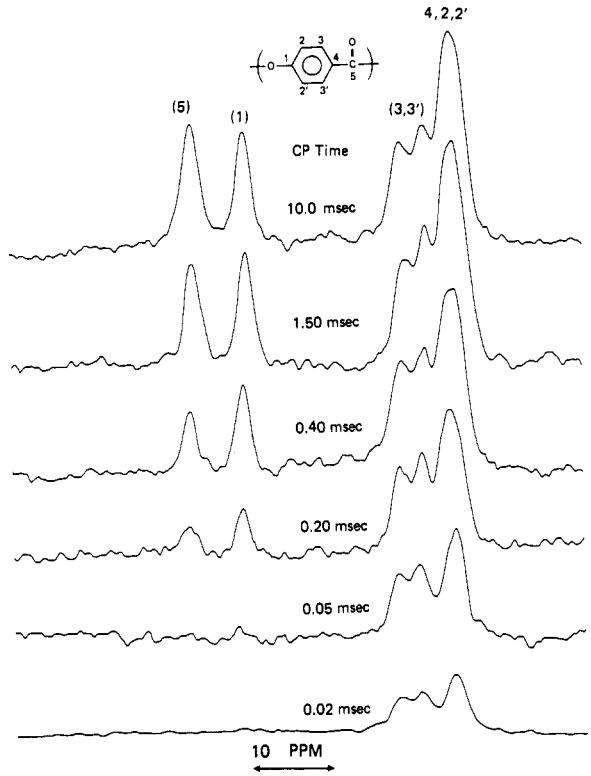


Figure 2. Magic-angle CP ^{13}C NMR spectrum of I at 27 °C as a function of CP contact time (in ms). All spectra obtained from 2K FT of 1000 FID accumulations at a 3.5 s experiment repetition time.

assignments (Figure 1) for the polymer in the following ways: (1) in the spectra obtained at short contact times, 0.02 and 0.05 ms, only the resonances assigned to ortho ring carbons are present—consistent with a larger static dipolar interaction for proton-bearing carbons; (2) at longer contact times, the region between the lines of the 2,2′ and 3,3′ carbons begins to develop intensity and at ca. the same rate as the line assigned to C-1. The development of line asymmetry in the 120–135-ppm region is clearly due to C-4 and demonstrates that this carbon resonates at 125.4 ppm, downfield of carbons 2 and 2′; and (3) the resonance assigned to the carboxyl carbon polarizes at the slowest rate, as expected if the relative cross-relaxation rates follow a simple scheme of C–H intramolecular interaction distance.

The magic-angle CP spectra obtained from 25 mg powder samples of polymers II and III are shown in Figure 3a,b, respectively. The perturbations in the electron shieldings of I caused by the methoxy substituents result in extremely well-resolved solid-state spectra. By applying chemical shift substituent parameters for a methoxy group introduced onto an aromatic ring[11] to the chemical shifts of I, it is possible to tentatively assign the resonance lines in Figure 3 to specific carbons of the repeat units of II and III. Chemical shift data and line assignments are summarized in Table II. The observed line intensities indicate that at this value of cross-polarization time, the spectra are essentially quantitative. The apparent nonequivalency of the methoxy carbons and 3,3′ ring carbons in III again indicates restricted reorientation of the aromatic ring in the solid. Because the monomethoxy polymer would be expected to have a repeat unit composed entirely of nonequivalent carbons, it is not possible to make any qualitative conclusions regarding motion without the benefit of relaxation studies.[12]

Clearly, the spectral resolution demonstrated in Figures 1 and 3 is sufficient to allow ^{13}C NMR to be used for

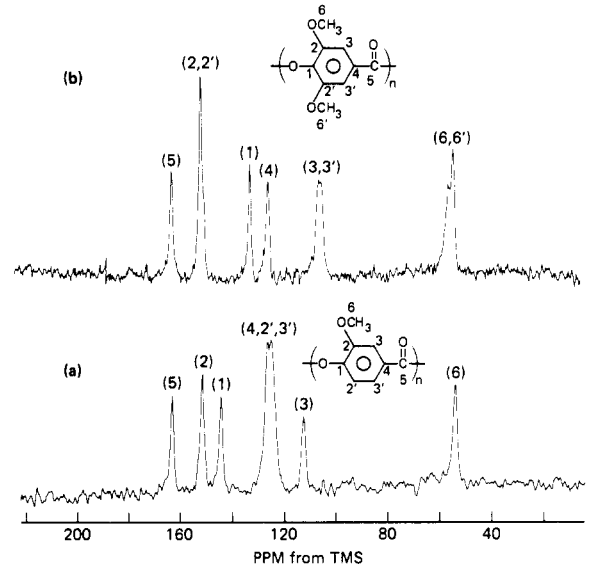


Figure 3. (a) Magic-angle CP ^{13}C NMR spectrum of II at 27 °C. Spectrum obtained from 2K FT of 21 900 FID accumulations with a CP contact time of 2.5 ms and experiment repetition time of 3.0 s. (b) Magic-angle CP ^{13}C NMR spectrum of III at 27 °C. Spectrum obtained from 4K FT of 19 000 FID accumulations with other conditions as in (a).

Table II
^{13}C Chemical Shifts[a] and Resonance Assignments of Polymers II and III

II		III	
carbon[b,c]	chemical shift	carbon[b,c]	chemical shift
5	162.8	5	163.6
2	151.1	2,2′	152.1
1	144.1	1	133.4
4	126.5	4	126.4
3′,2′	125.0	3	107.0
3	112.5	3′	106.3
6	54.0	6	56.9
		6′	55.0

[a] In ppm downfield from Me_4Si. [b] See Figure 3 for numbering scheme. [c] The assignments were made by taking the chemical shift perturbations caused by an OCH_3 substituent on the ring carbons of benzene (+30.2 at point of substitution, −15.5 ortho, 0.0 meta, and −8.9 para with a (−) denoting upfield shift) and applying these to the carbon shifts of I to assign the resonances in II. The effects of the OCH_3 observed between I and II were then used as a refinement of the substituent parameters to assign the resonances of III.

structure identification of the aromatic polyesters in the solid state. The line widths at half-maximum of $\lesssim$15 Hz[13] for many of the carbons in the spectra are 3–6 times narrower than the 50–100-Hz line widths reported for glassy systems.[1] Since the magnitude of the proton decoupling field is ca. the same as that used by Schaefer et al.,[1] it is unlikely that the narrowing results from better dipolar decoupling—indeed, the $\gamma_H H_{1H}$ field is only comparable to the proton line width and thus could be a source of residual broadening. More efficient removal of broadening from chemical shift anisotropy with our spinning apparatus does not account for the narrowing since spectra we have obtained (using the same apparatus) on PMMA, polycarbonate, and poly(phenylene oxide) have line widths of 40–100 Hz, values which are similar to those reported in ref 1. Since the "mechanics" of the experiment do not appear to account for the narrower line widths obtained for the aromatic polyesters, explanation must be sought in the rigid, highly crystalline nature of these polymers.

The proposed structure[8] of I is a double helix with the two chains having a reversed head-to-tail order. Such a structure would result in a highly rigid polymer chain. The NMR data support a rigid structure in several ways: (1) the nonequivalent ^{13}C chemical shifts of the 3,3′ carbons indicate the limited torsional oscillations of the aromatic ring; (2) the fact that the line widths of the spectrum of I at −190 and −80 °C are the same as those at 27 °C suggests that temperature reduction does not produce any dispersion in chemical shift due to nonaveraging conformations nor any significant change in lattice motions since the marginal decoupling field (6.5 G) still removes proton broadening effects at the low temperature—both these conclusions support a highly rigid polymer chain at ambient temperature; (3) the proton spectrum of I which is characterized by a line width of ca. 6 G and a T_1 value of 3–4 s at 25 °C is also unchanged at −80 °C; (4) it was not possible to obtain a spectrum of I with DD, MAS, and $\pi/2$ repetitive pulses on the carbon spin system using up to 20 s recycle times (i.e., a conventional FT experiment) even with 8000 FID accumulations. Since this experiment depends on ^{13}C spin–lattice relaxation for carbon polarization, the result suggests the carbons have long T_1 values which implies limited spectral density in the 15-MHz region. On the other hand, for glassy polymers such as PMMA, T_1 values at ambient temperature are in the 1–10-s range[3] for all carbons, and spectra can be readily obtained by $\pi/2$ pulse methods as well as cross-polarization techniques. While this only points out the disparity in the density of motions in the megahertz region for the *p*-hydroxybenzoic acid polymers vs. glassy systems, it provides indirect proof of the rigidity of I. (Note, the evidence for rigidity does not support or dismiss a double-helix structure for I. Studies are currently in progress on the shifts of model esters of known geometry in the solid state to try to use the chemical shift difference between 3,3′ carbons of I to determine the angle the aromatic ring makes with the plane of the carboxyl group.)

One consequence of the chain rigidity of I–III may be a substantial reduction of motions in the 10^4–10^5-Hz region, as well as in the megahertz region, relative to that for glasses. Motions in the 10^4–10^5 frequency region do not result in complete motional averaging but instead yield a dipolar broadening which is not removable by realistically achievable proton-decoupling fields nor with currently achievable magic angle spinning speeds.[1] Thus, a reduction of these motions in the aromatic polyesters may, in part, account for the narrower resonance lines relative to glassy systems.

If a greater homogeneity of the local environments experienced by each repeat unit can be associated with crystal habit, then the high degree of crystallinity of these aromatic polyesters may result in substantial reduction of line broadening from dispersions of isotropic chemical shifts. Such dispersions are associated with the steric (in vinyl polymers) and conformational isomerism common in the glassy state.[1] If reduced shift dispersion is indeed the primary source of the line narrowing in polymers I–III relative to glasses, it would support the proposal[1] that it may not be possible to narrow lines in glassy polymers below 40–50 Hz.

In further support of the conclusion that the line widths in crystalline polymers may be expected to be narrower than those in glassy systems, recently we[14] and others[15] have obtained DD–MAS spectra of polyethylene (PE) in which resonance lines arising from the crystalline and noncrystalline regions are distinctly resolved.[16] The spectra of the ca. 60% crystalline PE in Figure 4 obtained with

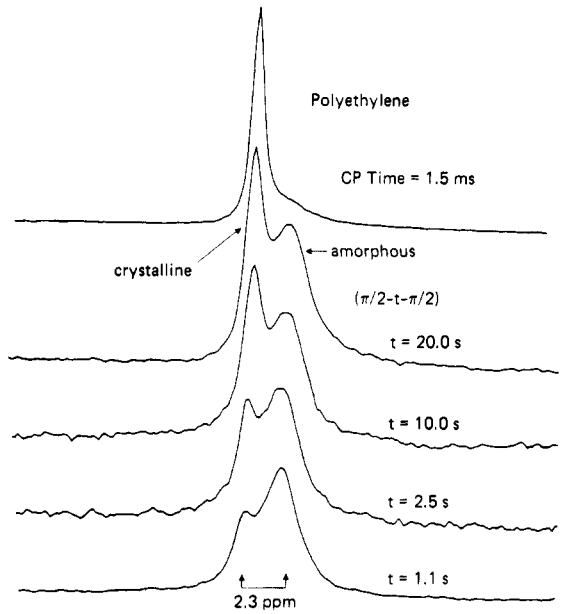


Figure 4. Magic-angle CP and $\pi/2$ ^{13}C NMR spectra of semicrystalline polyethylene at 27 °C. The spectra obtained with a $\pi/2$–t–$\pi/2$ pulse sequence used the indicated values of t. The number of FID accumulations varied from 2000–4500, but the spectra are displayed on a normalized scale. The spectrum obtained from the CP experiment used a CP contact time of 1.5 ms and an experiment recycle time of 2 s. The spectrum is the result of 400 FID accumulations.

$\pi/2$ pulses[17] (rather than cross-polarization) show the line width of the crystalline resonance is 10 Hz, while that of the noncrystalline resonance is ca. 40–50 Hz. The chemical shift between the resonance maxima is ~2.3 ppm and presumably arises from constraint to trans bond conformations in the crystalline region as opposed to trans/gauche bond conformations in the amorphous regions. At this time, it is not known whether shift dispersion or incomplete motional narrowing or both account for the width of the line in the noncrystalline region. (However, see ref 15.)

The CP–MAS spectra obtained from 70-mg samples of the two *p*-hydroxybenzoic acid/biphenylene terephthalate copolymers are given in Figure 5. The monomer reactant ratios for the compounds were 2/1 and 1/2 molar ratios, respectively. Although the spectra show considerable overlap from the many aromatic resonances, the lines corresponding to the carboxyl carbons and the aromatic carbons bonded to oxygen are resolved. The resonance of the carbon bonded to oxygen in the HBA units differs in chemical shift from that of the corresponding carbons in the BPT units. For the 2/1 copolymer, the two resonance lines would be of equal intensity, since the BPT unit has two equivalent carbons of this type, while in the 1/2 copolymer the ratio of the resonance lines would be 1/4. Clearly, these are the approximate ratios observed for these two resonance lines in Figure 5. This result demonstrates that under the appropriate cross-polarization conditions the spectra can be used for quantitative compositional analysis on the copolyesters. The degree of resolution is not sufficient in these spectra to allow sequence data to be obtained.

In summary, the results presented here demonstrate that ^{13}C NMR spectroscopy can be useful as a characterization technique for insoluble aromatic polyesters when spectra are obtained using line-narrowing and cross-polarization techniques. Under appropriate cross-polarization conditions, quantitative spectra can be obtained which makes possible compositional analysis for copolyesters. Currently

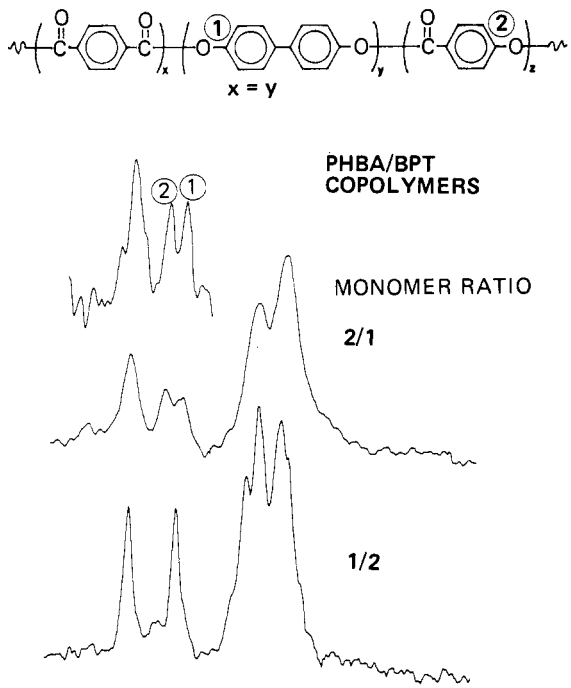


Figure 5. Magic-angle CP spectra for 2/1 and 1/2 HBA/BPT copolymers at 27 °C. Spectra were obtained with CP times of 3 ms and recycle times of 2.5 s. The spectra are the result of 8000 accumulations. The inset spectrum for the 2/1 copolymer is one obtained with better setting of the magic-angle spinning condition.

we are investigating by ^{13}C NMR the structure and motional features of the *p*-hydroxybenzoic acid polyesters as a function of temperature.

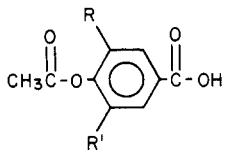
Experimental Section

A. NMR Spectra. Spectra were obtained on a Nicolet TT-14 NMR spectrometer having operating frequencies of 15.087 and 60.0 MHz for ^{13}C and ^{1}H, respectively. The spectrometer was modified for cross-polarization and high-power (dipolar) decoupling by adding external gating circuitry and radiofrequency amplifiers and by rerouting some of the timing logic. A probe was built to withstand the high-voltage and heating effects of the large radiofrequency fields used in the experiment. Samples of the polyesters were prepared by loading the powdered polymers into Kel-F rotors (volume ca. 70 μL). The filled rotors were placed in the stator assembly, which fits in a tube with an inside diameter of 10.2 mm, and spun using He as the driving gas.[18] Spectra were obtained using a Hartmann-Hahn single-contact cross-polarization experiment with matching condition $(\gamma_C/2\pi)H_{1C} = (\gamma_H/2\pi)H_{1H} \sim 28$ KHz and sample spinning rates between 3 and 5 KHz. The amplitudes of two radiofrequency fields were adjusted with a precision of 1 dB for matching, and the magic angle was fixed within ±1°. Proton decoupling was provided by the spin-locking field. The low-temperature spectrum of I was obtained by precooling the He gas by flow through a heat exchanger immersed in liquid nitrogen in much the same fashion as samples are normally cooled in NMR experiments. Temperature was measured with a thermocouple placed in the exit gas flow.

The ^{13}C spectrum of the tetramer prepared from *p*-acetoxybenzoic acid was obtained at 90 °C on a Varian CFT-20 NMR spectrometer (20 MHz ^{13}C operating frequency) from a saturated solution of the tetramer in Me_2SO-d_6.

Proton spectra were measured at 23 MHz on a home-built NMR spectrometer.

B. Preparation of Polymers. The starting materials for all three homopolymers were the respective *p*-acetoxy derivatives



I, R = R′ = H
II, R = H; R′ = OCH_3
III, R = R′ = OCH_3

prepared by acetic anhydride acetylation of the respective *p*-hydroxy acids. Acetylation was followed by recrystallization from acetone/water in the case of I and toluene for II and III. Polymerizations were carried out under a nitrogen atmosphere in diphenyl sulfone as a solvent with rapid mechanical stirring. The precipitated polymers were then extracted with boiling acetone and dried in vacuo at 120 °C. The polymers were characterized by IR spectroscopy through the disappearance of acetoxy and acid absorptions. Wide-angle X-ray analysis was utilized to obtain a relative degree of crystallinity—in all cases ≳80%. The tetramer was prepared according to the synthetic procedure of Fischer and Freudenberg.[19]

The copolyester samples were obtained in experimental quantities from a commercial source.

Acknowledgment. We thank B. L. Dawson for assisting in the preparation of the polymers and R. D. Kendrick for modifications to the spectrometer electronics.

References and Notes

(1) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).
(2) J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976).
(3) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **8**, 291 (1975).
(4) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
(5) E. R. Andrew, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two*, **4**, 173 (1976).
(6) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).
(7) P. W. Morgan, *Macromolecules*, **10**, 1381 (1977), and references therein.
(8) J. Economy, R. S. Storm, V. I. Matkovich, S. G. Cottis, and B. E. Nowak, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2207 (1976).
(9) No signals from terminal units are apparent in the spectra.
(10) Clearly, for a rapidly rotating side group such as a methyl, a carbon could have substantially reduced C–H dipolar interactions relative to a main chain methine or methylene and hence have a slower cross-relaxation time despite having three direct C–H interactions.
(11) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 197.
(12) Currently, we are engaged in a study of the molecular motion in these polymers.
(13) 15 Hz after removal of 5 Hz digital broadening; digital resolution employed was only 11.8 Hz; thus, the line widths approach this value.
(14) J. R. Lyerla, Jr., and C. S. Yannoni, unpublished results.
(15) W. L. Earl and D. L. VanderHart, *Macromolecules*, following paper. These authors give a full account of the results on polyethylene.
(16) The Hartmann–Hahn condition was matched at ca. 55 kHz in CP experiments and $\gamma_H H_{1H}$ was ca. 70 kHz in $\pi/2$ experiments. The sample was a solid machined rotor.
(17) The growth of the crystalline peak as a function of t (Figure 4) indicates the much longer spin–lattice relaxation time for carbons in the crystalline regions. Of course, this result is consistent with the limited mobility in the crystalline regions relative to noncrystalline regions, see ref 15.
(18) C. A. Fyfe, H. Mossbrugger, and C. S. Yannoni *J. Magn. Reson.*, in press.
(19) E. Fischer and K. Freudenberg, *Justus Liebigs Ann. Chem.*, **372** (1910).