Macromolecules 1992, 25, 576-581

Solid-State ^{13}C NMR Study of the Molecular Dynamics in Amorphous and Crystalline Poly(β-hydroxyalkanoates)

Frederick G. Morin and Robert H. Marchessault*

Department of Chemistry, McGill University, 3420 University Street, Montreal, Quebec, Canada H3A 2A7

Received December 19, 1990; Revised Manuscript Received August 22, 1991

ABSTRACT: Carbon-13 (^{13}C) solid-state NMR has been used to investigate a high molecular weight, biodegradable poly(β-hydroxyalkanoate) produced by *Pseudomonas oleovorans* from sodium octanoate as substrate. This polymer contains 85% *n*-pentyl side chains and is a thermal elastomer of approximately 25–33% crystallinity. ^{13}C spectra of the polymer in the amorphous regions are easily obtained without cross polarization and magic angle spinning (CP/MAS) due to the rapid and nearly isotropic motion that the chains undergo at room temperature in this phase. Variable-temperature NMR spectra reveal that there is also significantly different dynamics for the side chains and backbone. The backbone carbons experience severe line broadening at temperatures close to room temperature because the molecular motion occurs at a frequency which results in a reduced efficiency for the proton decoupling, while the side-chain motion is relatively fast at all temperatures studied. Application of CP/MAS allows the observation of the crystalline phase where the chemical shifts are different from those in the amorphous domains. ^{13}C spin–lattice relaxation times (T_1) have also been measured for the amorphous regions of the polymer. The temperature dependence of the T_1s of the side-chain and backbone carbons also clearly reveals that these two moieties undergo very different dynamics, the former being on the fast-motion side of the T_1 minimum, while the latter are on the slow-motion side.

Introduction

Poly(β-hydroxyalkanoates) (PHA) are high molecular weight isotactic polymers produced by bacteria intracellularly as a carbon and energy reserve material.[1] Studies of these biodegradable polymers have concentrated on the homopolymer poly(β-hydroxybutyrate) (PHB) and butyrate/valerate copolymers (PHB/V) which are highly crystalline and possess glass transition temperatures in the range +10 to −10 °C, decreasing with percent valerate content.[2-4]

The microstructure of bacterial and synthetic PHB/V has been shown by NMR and degradative techniques to be Bernouillean.[5] Accordingly, one might expect a linear relation between % HV and the glass transition temperature (T_g), which is a direct function of the "hole" content of the amorphous phase. Figure 1 is a plot of T_g vs % HV for PHB/V.[4]

While PHB is produced by a wide variety of organisms using substrates as different as H_2 and sucrose,[1] it is now understood that the common feature of biopolyesters is the β-propionate backbone, with the substitution at the asymmetric β-carbon depending mainly on the substrate. In recent times the ubiquity of copolyesters in nature rather than the homopolyester PHB has come to be understood. Rohwedder[6] was the first to explore the unusual range of such copolyesters which are formed in estuarean sediments. His careful analytical mass spectrometry showed that PHAs with side chains ranging from R = CH_3 to $C_{10}H_{21}$ were present (Figure 2). Witholt et al.[7] and then Lenz[8] explored the PHA reserve material produced by *Pseudomonas oleovorans* whose composition was found to be remarkably dependent on the substrate. In a classic study Lenz et al.[8] showed that the principal monomeric component had the same number of carbon atoms as the alkanoate substrate and minor comonomer components had ±2 carbon atoms. The latter comonomer units are derived from the well-known β-oxidation process operating on the substrate prior to incorporation in the chain. During biosynthesis, the carboxylate, along with the α and β carbons, is incorporated into the backbone of the polymer, with the remaining carbons forming the pendant side chain. Thus, when the fermentation is carried out with sodium octanoate as the carbon source, 85% of the monomer units in the resultant polymer have *n*-pentyl (C_5) side chains (Figure 2). These PHAs with longer side chains have quite different mechanical properties than PHB or PHB/V, being thermal elastomers with lower glass transition temperatures ranging from −25 to −40 °C and decreasing with the average length of the side chain.[8] They are also of

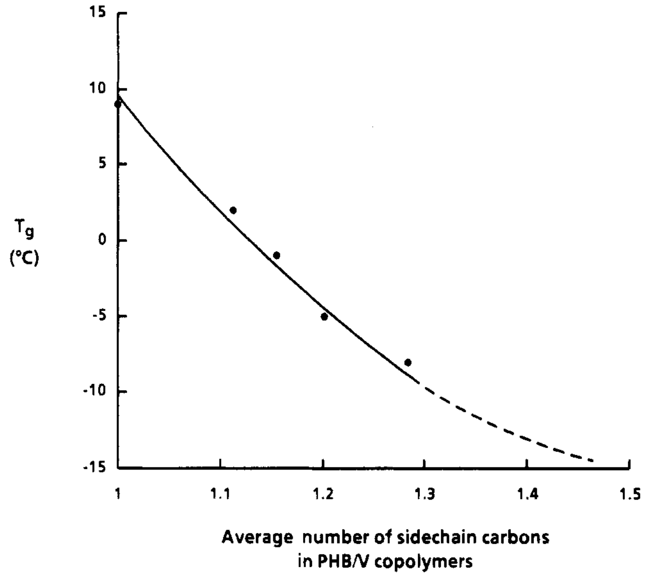
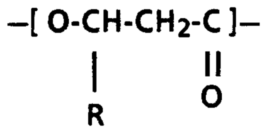


Figure 1. Glass transition temperatures measured by differential scanning calorimetry for PHB/V samples plotted as a function of the average number of carbons in the side chain. The broken part of the curve is extrapolated from the known values of longer side-chain PHAs.[8]



$$-[\,O\text{-}\underset{\displaystyle R}{\underset{|}{C}}H\text{-}CH_2\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\,]-$$

Figure 2. Structure of the poly(β-hydroxyalkanoate) polymers. The alkyl side chain R can vary from CH_3 to C_9H_{19}.[8]

much lower crystallinity[9] than PHB/V copolyesters, i.e., about 25% vs 60–70%.

^{13}C NMR has proven invaluable in the study of polymers in the solid state where the techniques of cross polarization and magic angle spinning (CP/MAS) allow the observation of the rigid crystalline regions.[10] However, it is not necessary to use CP/MAS in order to observe the amorphous component of polymers at room temperature if the T_g is low enough that rapid and nearly isotropic motion averages the chemical shift anisotropy and dipolar couplings.[11] We report our solid-state ^{13}C NMR studies of the biopolyester which contains 85% of poly(β-hydroxyoctanoate) (PHO) including the observation of the ^{13}C spectra of both the crystalline and amorphous domains of PHO as well as the measurement of ^{13}C spin–lattice relaxation times (T_1) of the protonated carbons in the amorphous region. These relaxation times have been simulated using the Hall–Weber–Helfand[12] (HWH) model for segmental motion including libration, and the results are also reported herein.

Experimental Section

The sample of poly(β-hydroxyalkanoate) was produced from *P. oleovorans* grown using sodium octanoate as the carbon source and was composed of 85% octanoate units.[8] The remaining monomer units were roughly equally distributed between valerate, caproate, and decanoate units. It had a T_g of -36 °C, a T_m of 61 °C, and a weight-average molecular weight of approximately 160 000. It was provided by Prof. R. W. Lenz of the University of Massachusetts from samples prepared as part of a project supported by the Office of Naval Research, Molecular Biology Program.

The ^{13}C NMR spectra without CP/MAS were obtained at 75.4 MHz on a Varian XL-300 spectrometer using a normal Bloch decay pulse sequence (45° pulses and recycle times of 0.5–1 s). Low-power proton decoupling, relative to solid-state NMR, was used (γB_1 = 3 kHz). The samples were prepared by placing small pieces of the polymer into a 5-mm NMR tube, melting them overnight in an oven at 80 °C, and allowing them to cool at room temperature for 1 week. No lock solvent was employed, and no shimming of the magnetic field was attempted. Spinning at 10 Hz had no effect on the ^{13}C line widths.

^{13}C spin–lattice relaxation times were measured on the same instrument using the standard 180°–τ–90° inversion–recovery technique with block averaging of the τ values to minimize the effects of temperature and field instabilities. Recycle times were 5–10T_1, and the data were fit to a three-parameter relaxation equation. The NOE values were measured with recycle times $>7T_1$ of the methyl group and $30T_1$ of the remaining protonated carbons.

^{13}C CP/MAS spectra were obtained on a Bruker CXP-200 spectrometer at 50.3 MHz using a Doty Scientific probe. Spinning speeds were typically 2 kHz, the contact time for cross polarization was 1 ms, and a ^1H decoupler field strength of 65 kHz was employed. To facilitate the magic angle spinning, the sample was cut into small pieces and mixed with some fine-mesh silica gel to stabilize the rotor.

All calculations were carried out on a Digital Equipment Corp. VAX 750 computer. The correlation times were calculated using the MOLDYN program.[13] The ^{13}C relaxation parameters were simulated using the HWH model, modified to include libration effects, with the observed T_1 of NOE for both the CH and CH_2 groups of the backbone at a given temperature as input. A Simplex routine was used to vary the correlation times until the sum of the squares of the differences between the observed and calculated relaxation parameters was a minimum.

Results and Discussion

^{13}C NMR Spectra of the Amorphous Domains of Poly(β-hydroxyoctanoate). ^{13}C NMR spectra, without CP/MAS, of the amorphous component of solid PHO are given in Figure 3. Only the aliphatic region is shown, and the backbone and side-chain carbons are labeled bb and sd, respectively. The major peaks are due to the monomer units with a C_5 side chain, and the minor peaks are due to the C_3 and C_1 side chains that result from β-oxidation reactions that take place during the biosynthesis. At any temperature where the resonances are narrow enough to allow an accurate measurement of the chemical shifts, they are identical to the $CDCl_3$ solution shifts.[8] The ability to observe a ^{13}C spectrum of a solid polymer using a solution-state NMR spectrometer and standard solution NMR techniques was demonstrated before the advent of Fourier transform methods.[11] Spectra of solid elastomers such as polybutadiene and polyisoprene at temperatures well above T_g are easily obtained because the motion of the molecules is so rapid and nearly isotropic that the "line-broadening" effects of the chemical shift anisotropy and ^{13}C–^1H dipolar coupling are effectively averaged out by the motion; hence, MAS is not required to obtain an isotropic spectrum. The spectra of PHO in Figure 3 confirm that there is also a large amorphous component of this polymer that is very mobile at room temperature, which is ~50–60 °C above T_g. (This sample consists of approximately 66% noncrystalline material.[9])

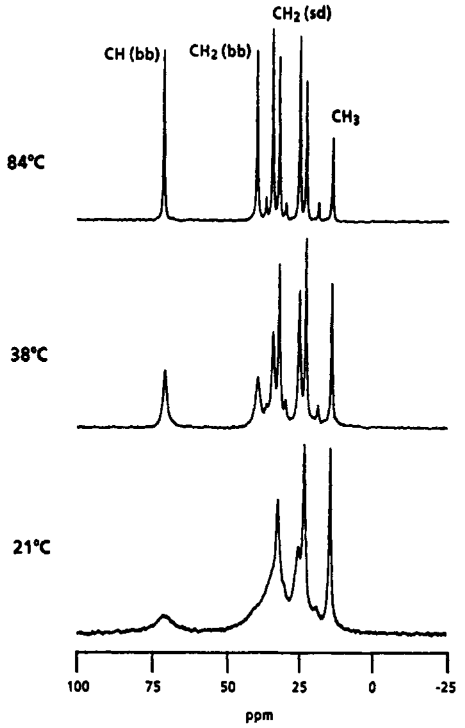


Figure 3. ^{13}C NMR spectra of the amorphous component of solid PHO as a function of temperature. Spectra were obtained with 45° pulses and without MAS. Only the aliphatic region is shown, and the backbone and side-chain carbons are labeled bb and sd, respectively. The differential dynamics of the backbone and side chains are evident in the differential line widths.

Another striking feature of the variable-temperature spectra of the amorphous component of PHO (Figure 3) is the very different line widths for the resonances of the backbone versus the side-chain carbons of the polymer at ambient temperatures. The latter are rather sharp while the former only become so at higher temperatures. This differential in line widths (i.e., T_2 values) is the result of the slower molecular motions of the backbone compared to the inherent mobility of the side chains in the disordered regions of the polymer at room temperature. More will be said about the origin of this T_2 effect in the discussion of the MAS spectra. With increasing distance from the site of attachment, the lines monotonically narrow as the

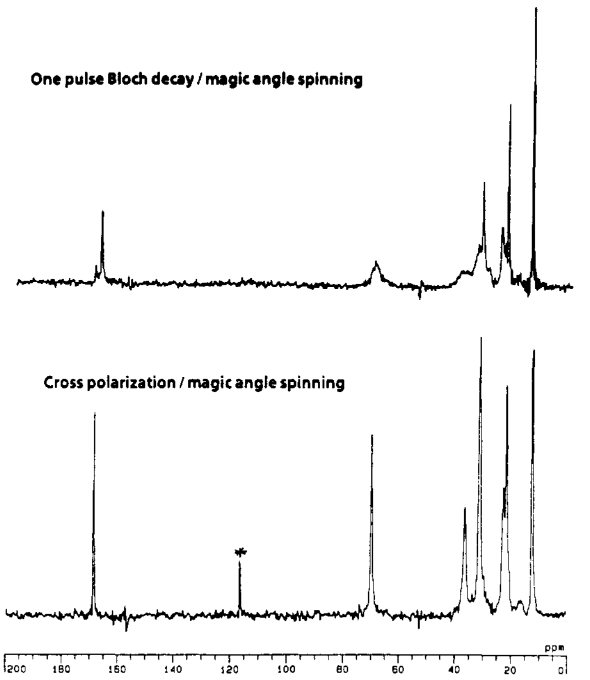


Figure 4. Room-temperature ^{13}C magic angle spinning spectra of solid PHO. The chemical shift range shown includes the carbonyl group. (Top) Obtained with 45° pulses. The magic angle spinning has reduced the line widths somewhat, but the resonances due to the backbone carbons are still considerably broader than those of the side-chain carbons. (Bottom) Same but with cross polarization (contact time = 1 ms). A spinning sideband of the carbonyl group is marked with an asterisk.

Table I
Chemical Shifts of the Amorphous and Crystalline Components of PHO[a]

	component[b]		$CDCl_3$ solution[c]
	crystalline	amorphous	
C=O	171.5	169.4	169.4
CH(bb)	72.3	71.1	70.8
CH_2(bb)	38.8	38.5	39.1
CH_2(1)	33.7[d]	33.7	33.7
CH_2(2)	25.1[e]	25.3[e]	24.7
CH_2(3)	33.7[d]	32.3	31.5
CH_2(4)	24.2[e]	23.2[e]	22.5
CH_3	14.6	14.5	14.0

[a] bb = backbone. Numbering for the side chain increases from the point of attachment of the side chain to the backbone. [b] Relative to TMS, measured from the methyl oarbon of an external sample of hexamethylbenzene at 17.4 ppm. [c] Relative to internal TMS. From ref 8. [d] Overlap. [e] Uncertain assignments.

number of degrees of freedom increase, the CH_3 resonance being the narrowest.

The ^{13}C spectra of the amorphous domains of this polymer, now under conditions of MAS, are also quite revealing (Figure 4). The top trace in Figure 4 shows the spectrum obtained with 45° pulses, high-power proton decoupling, and MAS. The chemical shifts of the resonances in these two spectra are given in Table I. Although the line widths in the top spectrum of Figure 4 are reduced from the spectra without MAS (cf. Figure 3), the protonated backbone carbons and the α-CH_2 carbon of the side chain are still noticeably broadened. The mechanism causing this line broadening for carbons with directly bonded protons has been outlined previously[14] and is a direct result of the molecular dynamics of the polymer chains. When slow motion is occurring as in crystalline material, the ^{13}C–^{1}H dipolar couplings which broaden the ^{13}C peaks are removed simply by irradiating the ^{1}H spins while observing the ^{13}C signal. Fast (and isotropic) motion itself, as in solution, will also remove these couplings. If, however, the motion in the solid is of an intermediate frequency, it reduces the effectiveness of the proton decoupler radio-frequency field in removing the ^{13}C–^{1}H dipolar couplings and a broadened resonance results. This effect is schematically shown in Figure 5. The broadening is greatest when the frequency of the motion is near the frequency of the radio-frequency field, here ~65 kHz. (In terms of correlation times, $\tau \sim 10^{-6}$ s.) In the disordered phase of the solid the motion of the backbone falls within the intermediate range while the motion of the side chain is fast enough that this broadening mechanism is not observed. This temperature-dependent line-broadening effect has also been noted in the ^{13}C spectra of other polymers such as polypropylene[15] as well as crystalline compounds such as hexamethylbenzene.[14] This broadening effect outlined above is not relevant for the C=O group because it has no directly attached protons. The possibility that these larger line widths of the backbone carbons are the result of a distribution in chemical shifts due to a number of different conformations of the backbone chain can be ruled out, as this would also result in a distribution of chemical shifts for the carbonyl as well, which is not observed.

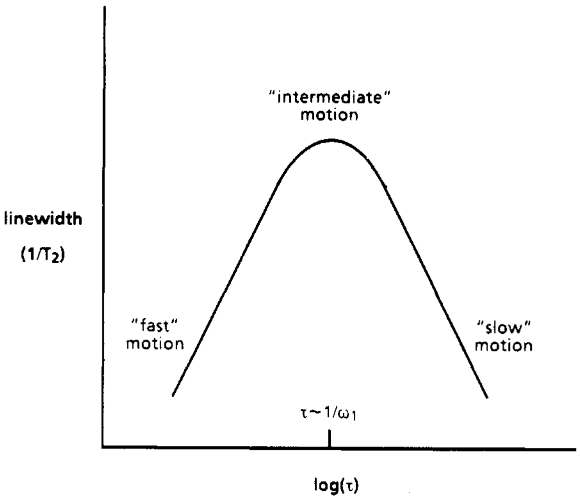


Figure 5. Behavior of the ^{13}C line width, under conditions of ^{1}H decoupling, when the frequency of the motion of the ^{13}C–^{1}H internuclear vectors is on the order of the strength of the decoupling field (expressed in frequency units). ω_1 is often ~50–70 kHz in solid-state NMR experiments.

^{13}C NMR Spectra of the Crystalline Domains of Poly(β-hydroxyoctanoate). The bottom trace of Figure 4 shows the CP/MAS spectrum of the rigid crystalline domains of this polymer. The rigid structure of the polymer backbone in the ordered regions is indicated by several observations. First, none of the peaks in this spectrum has the same chemical shift as found in the spectra of the amorphous domains. For example, the carbonyl carbon has a chemical shift of 171.5 ppm in the crystalline fraction and 169.5 ppm in the amorphous fraction (both peaks are observable in the top trace of Figure 4, the one-pulse Bloch decay spectrum). Undoubtedly, the conformational freedom of the polymer chains in the amorphous phase is greatly reduced in the crystalline phase, and it is probable that the side chains have adopted an all-trans conformation similar to that discovered for other comb polymers with lengthy (C_{15}–C_{18}) side chains such as poly(γ-n-octadecyl L-glutamate)[16] and derivatives of dehydroalanine.[17] This extended planar zigzag structure of the side chains has been shown by X-ray diffraction to be the most likely crystalline organization.[9] Unfortunately, the effects on the chemical shifts of the side-chain carbons

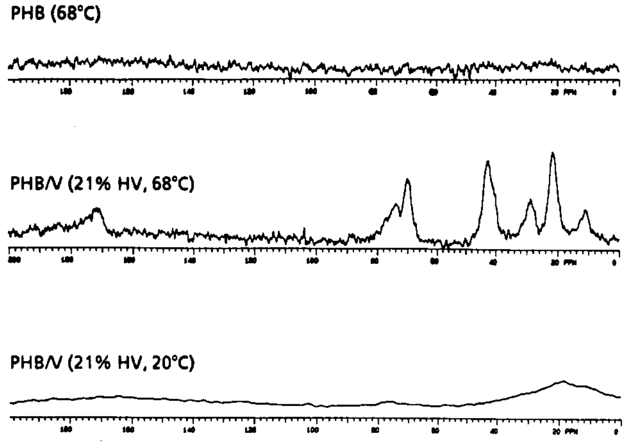


Figure 6. (Bottom) ^{13}C NMR spectrum of the amorphous component of solid PHB/V (21 mol % HV) at 20 °C. (Middle) Same but at 68 °C. (Top) ^{13}C NMR spectrum of the amorphous component of solid PHB at 68 °C. Spectra were obtained with 45° pulses, recycle delays of 0.5 s, and without MAS. Under these conditions, only the PHB/V at high temperature shows a spectrum.

due to changes in the rotameric populations will be somewhat obscured by the effects on the chemical shifts of the various intermolecular interactions that are present in the solid. Low-temperature studies are presently being performed to verify whether there is still conformational mobility in the side chains in the crystalline phase at room temperature which may be frozen out at lower temperatures.

A second indication of the immobility of the backbone in the crystalline phase is the presence of a spinning sideband (marked with an asterisk) associated with the carbonyl resonance. The chemical shift tensor of the carbonyl group produces a spinning sideband during MAS, revealing that it is immobile in the crystalline phase. In contrast, no spinning sidebands are observed in the spectrum of the mobile amorphous phase, demonstrating that the motion of the backbone is fast enough to average the chemical shift tensor to zero. The static and well-ordered nature of the backbone in the crystalline regions is also evident in the narrowness of the resonances for all the CH and CH_2 carbons.

Comparison to ^{13}C NMR Spectra of PHB and PHB/V. Equivalent nonspinning spectra were obtained for the amorphous component of the PHB/V copolymer, but higher temperatures were needed to observe sharp ^{13}C lines, as the T_g for this sample is about 30 °C higher (Figure 6). The signal to noise ratios in these spectra were significantly less, presumably due to the smaller amorphous fraction of PHB/V relative to the elastomeric PHO. Also, an unidentified extra resonance appears in the CH–O region (75 ppm) which does not correspond to the chemical shifts of either the HB or HV unit.

No spectra could be obtained for solid PHB. The homopolymer has a T_g of 10 °C, and so the amorphous component is still somewhat "glassy" at room temperature and the motion is not sufficiently rapid (or isotropic) to allow the observation of a spectrum in a "solution NMR-like" experiment. The noncrystalline regions of PHB do not experience the dynamic disorder of the copolymers, but rather the disorder is static in nature. This reflects the differences in mechanical properties among the thermoplastic PHB and PHB/V and the thermal elastomeric PHO.

High-resolution spectra of PHB granules in aqueous solutions of whole cells have recently been obtained by Barnard and Sanders,[18] revealing the high mobility of the polymer in the native state. The temperature-dependent spectrum[18] of PHB granules is very similar to that of the thermal elastomer PHO shown in Figure 3. The estimated[18] T_g of PHB within never-dried granules is between −20 and −70 °C while the T_g for solid PHO is −36 °C, and therefore the similarity of the variable-temperature spectra of the two polymers is not surprising. Thus, the polymer scientist who is interested in practical applications of thermal elastomeric PHAs has the choice of utilizing native PHB granules to exploit their properties in the never-dried state or of utilizing the longer side-chain PHAs which have the advantage of being more easily handled as a solid.

Table II
Relaxation Times (in ms) and NOEs (in Parentheses) for the Backbone Carbons of PHO

temp, °C	CH	CH_2
20.6	835 (1.40)	overlap
27.1	702 (1.40)	overlap
32.7	568 (1.65)	308 (1.53)
38.3	431 (1.47)	229 (1.52)
46.1	365 (1.48)	185 (1.51)
49.7	329 (1.47)	178 (1.45)
54.1	291 (1.46)	156 (1.47)
61.0	249 (1.48)	143 (1.53)
70.0	215 (1.52)	124 (1.53)
84.9	196 (1.60)	120 (1.62)

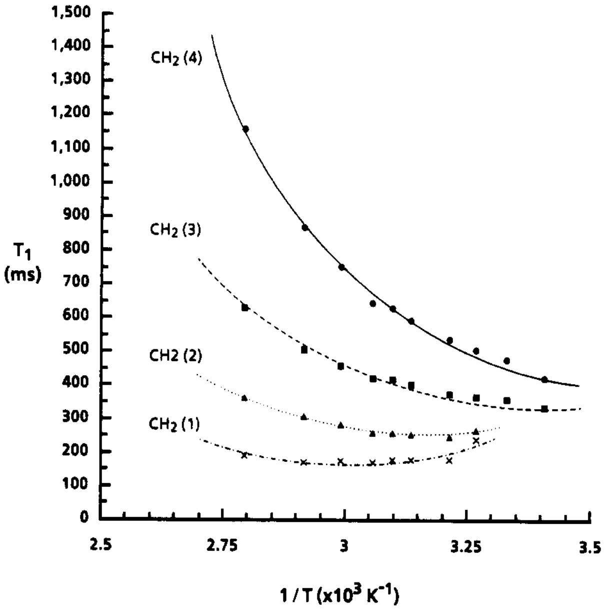


Figure 7. ^{13}C spin–lattice relaxation times (T_1, in ms) of the methylene carbons of the side chain of PHO as a function of temperature. The carbons are numbered according to increasing distance from the backbone.

^{13}C Spin–Lattice Relaxation in the Amorphous Domains of Poly(β-hydroxyoctanoate). ^{13}C spin–lattice relaxation times (T_1) have been measured as a function of temperature for the resonances of the amorphous component shown in Figure 3 and are tabulated in Table II. Plots of the observed T_1 values for the side-chain carbons are given in Figure 7 and for the backbone carbons in Figure 8. The relaxation times clearly demonstrate the differential dynamics of the backbone relative to the side chain for this chiral biopolyester. The T_1 values of the latter increase with increasing temperature and therefore fall within the "fast-motion regime"; i.e., $\omega^2\tau^2 \leq 1$ where ω is the Larmor frequency of 75 MHz. The correlation time for the motion, τ, can be considered to be somewhat less than $\sim 10^{-9}$ s for the side-chain carbons, with the exception of the α-CH_2 group whose motion is slower than this. At a given temperature, T_1 increases

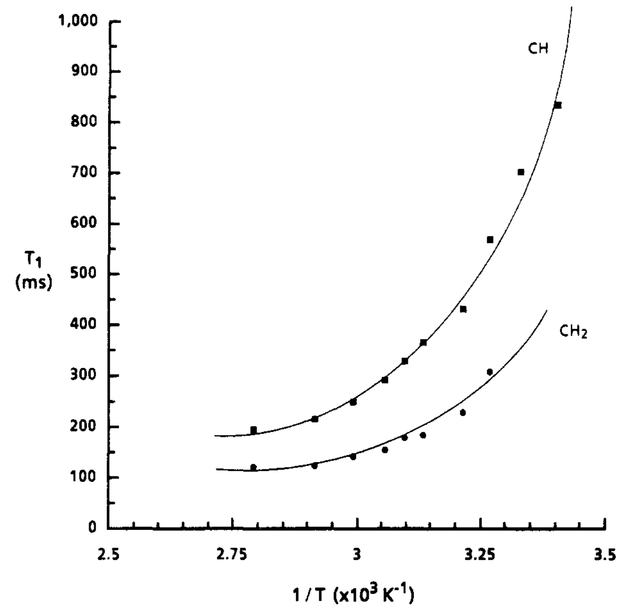


Figure 8. ^{13}C spin–lattice relaxation times (T_1, in ms) of the protonated backbone carbons of PHO as a function of temperature.

monotonically with distance from the site of attachment, a trend that is reminiscent of the solution behavior of *n*-alkyl chains which have at one end a heavy atom or functional group capable of hydrogen bonding, e.g., *n*-decanol.[19] The hydroxyl group in this example restricts the motion of the chain end while allowing greater motional freedom further along the length of the chain. The polymer backbone serves the same purpose in the PHO case.

This motional mobility of the side chain in the amorphous state probably has a major influence on the crystallization of PHO, during which the side chain needs to adopt a completely extended planar zigzag conformation.[9] It has been calculated that two conformations resulting from a 60° rotation around the first "exo-helix" carbon–carbon bond extending from the helical backbone differ by only ~1 kcal/mol.[9] This has the effect of allowing two conformers to be present in nearly equal amounts and thereby hinders development of the crystallization.

In direct contrast to these observations for the side-chain carbons, the T_1 values for the backbone in the amorphous phase decrease with increasing temperature. This demonstrates that these carbons experience motions which are within the "slow-motion regime", i.e., significantly slower than the motions of the side-chain carbons. The PHO molecule thus represents a case where the backbone acts as a slow-moving molecular fiber with relatively fast-moving but bulky hydrocarbon side chains acting as a diluent. Studies are underway in this laboratory on the ^{13}C relaxation behavior of the crystalline domains of this polymer as well as the synthetic analogues prepared from the corresponding lactones. ^2H NMR on specifically labeled bacterial and synthetic PHAs are also underway. It may also be possible to find conditions whereby bacteria will incorporate monomer units with still longer side chains which might alter the roles of the backbone and side chains if the latter can be made long enough to begin to resemble a polyethylene chain.

In order to obtain a more accurate estimate for the correlation times of the polymer backbone in the solid state, the T_1 data have been analyzed using a modification to the model of Hall, Weber, and Helfand (HWH).[12] The HWH model has previously been used to analyze the motions of PHB in tetrachloroethane[20] as well as chloroform[21] solutions. It includes two correlation times: τ_0, the correlation time for single conformational transitions such as gauche–trans rotations about single bonds, and τ_1, the correlation time for cooperative or correlated transitions of several bonds. The single-bond transitions result in a swinging motion of the entire end of the polymer chain, a rather unfavorable process, while the cooperative transitions usually involve "crankshaftlike" counterrotations of neighboring bonds which keep the motion localized. These latter motions are expected to be important in the segmental motion of polymers.

The HWH model alone failed to adequately reproduce the relaxation data, especially the NOE values. Other recent studies of elastomers in the solid[22] and solution[23] state have demonstrated the necessity of including the effects of bond libration to account for the ^{13}C relaxation rates. The HWH model was therefore modified to include these librational effects.[23] The T_1 values determined at 38 °C for the CH and CH_2 backbone carbons in the amorphous regions of solid PHO are 431 and 229 ms, respectively. The ratio $T_{1,CH}/T_{1,CH_2}$ is 1.88, close to the theoretical value of 2 expected if the CH and CH_2 groups are dynamically equivalent, and it was assumed that these two carbons effectively move in concert as a unit. The amount of experimental data being rather limited, it was necessary to assume values for some of the parameters in the model and hold them constant while fitting the remaining parameters. It was assumed that the librational motion has a correlation time of 0.5×10^{-11} s and sweeps out a cone with a half-angle of 20°. It was also found that the correlation time for the single-bond rotations, τ_0, had no effect on the calculated times and was therefore held at 1×10^{-6} s, slow enough that it would not effectively contribute to T_1 relaxation. The calculated correlation times for cooperative segmental motions, τ_1, ranged from 1.5×10^{-9} to 9×10^{-9} s over the observed temperature range, with an apparent activation energy of 30 kJ/mol, a value that is approximately 10 kJ/mol higher than found for PHB in solution.[20] The higher activation energy in the amorphous solid relative to solution can be explained by the increased chain interactions in the solid, in essence an increase in the viscosity of the surroundings which necessitates more energy in order to surmount the barrier for the segmental motion.

Acknowledgment. Financial support of the Xerox Corp. is acknowledged. All ^{13}C CP/MAS NMR spectra were obtained at the Xerox Research Centre of Canada. Stimulating discussions and moral support from Dr. G. Hamer and Dr. T. Bluhm of the Xerox Research Centre of Canada were invaluable in the execution of this study. Prof. Photis Dais, University of Crete, kindly provided advice concerning modeling.

References and Notes

(1) Dawes, E. A. *Microbial Energetics*; Blackie: Glasgow, U.K., 1986.

(2) Holmes, P. A.; Wright, L. F.; Collins, S. H. Eur. Pat. Appl. 0 052 459, 1981. Eur. Pat. Appl. 0 069 497, 1983.

(3) Bluhm, T. L.; Hamer G. K.; Marchessault, R. H.; Fyfe, C. A.; Veregin, R. P. *Macromolecules* **1986**, *19*, 2871.

(4) Mitomo, H.; Barham, P. J.; Keller, A. *Polym. Commun.* **1988**, *29*, 112.

(5) Kamiya, N.; Yamamoto, Y.; Inoue, Y.; Chujo, R.; Doi, Y. *Macromolcules* **1989**, *22*, 1676. Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Impallomeni, G.; Montaudo, G. *Macromolecules* **1989**, *22*, 2107.

(6) Wallen, L. L.; Rohwedder, W. K. *Environ. Sci. Technol.* **1974**, *8*, 576.

(7) Witholt, B.; Lageveen, R. G.; Huisman, G. W.; Preusting, H.; Nijenhuis, A.; Kingsma, J.; Tijsterman, A.; Eggnik, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 592.

(8) Gross, R. A.; DeMello, C.; Lenz, R. W.; Brandl, H.; Fuller, R. C. *Macromolecules* **1989**, *22*, 1106.

(9) Marchessault, R. H.; Monasterios, C. J.; Morin, F. G.; Sundararajan, P. R. *Int. J. Biol. Macromol.* **1990**, *12*, 158.

(10) Fyfe, C. A. *Solid State NMR for Chemists*; CFC Press: Guelph, ON, Canada, 1983.

(11) Duch, M. W.; Grant, D. M. *Macromolecules* **1970**, *3*, 165. Schaefer, J. *Macromolecules* **1972**, *5*, 427.

(12) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651. Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275. Weber, T. A.; Helfand, E. *J. Phys. Chem.* **1983**, *87*, 2881.

(13) Craik, D. J.; Kumar, A.; Levy, G. C. *J. Chem. Inf. Comput. Sci.* **1983**, *1*, 30.

(14) Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1981**, *74*, 2721.

(15) Lyerla, J. R.; Yannoni, C. S. *IBM J. Res. Dev.* **1983**, *27*, 302.

(16) Yamanobe, T.; Tsukahara, M.; Komoto, T.; Watanabe, J.; Ando, I.; Uematsu, I.; Deguchi, K.; Fujito, T.; Imanari, M. *Macromolecules* **1988**, *21*, 48.

(17) Mathias, L. J. *Polym. Commun.* **1988**, *29*, 352.

(18) Barnard, G. N.; Sanders, J. K. M. *J. Biol. Chem.* **1989**, *264*, 3286.

(19) Doddrell, D.; Allerhand, A. *J. Am. Chem. Soc.* **1971**, *93*, 1558.

(20) Dais, P.; Nedea, M. E.; Morin, F. G.; Marchessault, R. H. *Macromolecules* **1989**, *22*, 4208.

(21) Dais, P.; Nedea, M. E.; Marchessault, R. H. *Polymer*, in press.

(22) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 122. Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2045.

(23) Dais, P.; Nedea, M. E.; Morin, F. G.; Marchessault, R. H. *Macromolecules* **1990**, *23*, 3387.

Registry No. PHO (homopolymer), 120659-38-3; PHO (SRU), 86175-71-5; NaO, 1984-06-1.