

Segmental Dynamics in Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)s above the Glass Transition Temperature: ¹³C Nuclear Magnetic Relaxation in the Amorphous Phase

A. Spyros[†] and R. H. Marchessault*

Department of Chemistry and Pulp and Paper Research Centre, McGill University, 3420 University Street, Montreal, Quebec H3A 2A7, Canada, and Sektion Kernresonanzspektroskopie, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany

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ABSTRACT: Variable-temperature ¹³C NMR spin–lattice relaxation times, T_1 , and nuclear Overhauser enhancements (NOE) at two magnetic fields have been recorded for the amorphous phase of semicrystalline poly(4-hydroxybutyrate), P4HB, and two random copolymers: poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) with 18% (P3/4HB-18) and 69% (P3/4HB-69) 4hb units. The T_1 and NOE data were successfully interpreted by the DLM model in terms of conformational transitions and librational motions of the backbone C–H vectors. The mobility of both the 3hb and 4hb units was found to increase with increasing 4hb content of the copolymer. In both copolymers, the segmental motion of the 4hb unit was found to be 2–4 times faster than that of the 3hb unit, thus reflecting the local character of the segmental motions that affect ¹³C relaxation in bulk polymers. In addition, the segmental dynamics followed the Williams–Landel–Ferry equation, indicating that they are involved in the glass transition phenomena. Literature P3HB dynamic modeling data adhere to the Williams–Landel–Ferry data presented here, indicating that P3HB in bacterial inclusions has a T_g similar to that of the extracted material.

Introduction

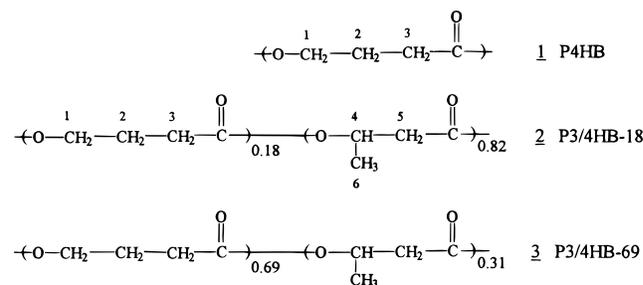
Poly(hydroxyalkanoate)s, PHAs, are a family of bacterially synthesized thermoplastics whose inherent biodegradability has made them notorious.¹ Their chemical composition can be controlled by the fermentation conditions.^{2,3} This has led to the biosynthesis of an ever increasing number of PHA polymers, and by last count 87 different repeating units had been reported.⁴ Recently synthesized materials include poly(4-hydroxybutyrate),¹ poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate),⁵ poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate),⁶ and poly(3-hydroxybutyrate-*co*-3-hydroxypropionate).³ This variety in the chemical composition derives from the search for a PHA that will be biodegradable while possessing the properties desired for a commercial polymer. The commercially available poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), P3HB/HV, under the trade name Biopol is rather brittle due to the high degree of crystallinity regardless of chemical composition.¹

On the other hand, random copolymers of 3-hydroxybutyrate and 4-hydroxybutyrate are less crystalline than P3HB/HV copolymers. This is due to the fact that contrary to the 3hb, the 4hb unit cannot cocrystallize in the P3HB crystalline lattice. This has been shown by X-ray diffraction studies,⁷ molecular mechanics calculations,⁸ and solid state NMR.⁹ The decrease in crystallinity as the percentage of 4hb units in P3/4HB copolymers increases is accompanied by a decrease in T_g , which leads to increased elastomeric behavior at room temperature.¹⁰ The elastomeric nature of these systems allows the study of the local dynamics of the amorphous phase by high-resolution (scalar decoupling) ¹³C NMR relaxation techniques.

¹³C NMR relaxation is a powerful tool for the elucidation of the rates and mechanisms of backbone motion

and side chain internal rotations of polymers in solution.^{11,12} It has been shown that this technique is also well suited for the study of amorphous polymers^{12,13} and the amorphous part of semicrystalline polymers^{12,14} at temperatures well above the glass transition temperature. This has been attributed to the “liquid-like” behavior, from an NMR point of view, of the amorphous polymer chains at $T > T_g$. Motion in this phase is rapid and nearly isotropic, and this results in averaging of the dipolar and chemical shift anisotropy interactions responsible for the broad NMR spectral lines observed in solids. Thus the measurement of the ¹³C relaxation parameters, the spin–lattice relaxation time, T_1 , and the nuclear Overhauser enhancement, NOE, of the protonated carbon atoms of amorphous polymer chains is feasible by conventional scalar decoupling techniques.¹² These measurements, when performed as a function of temperature and magnetic field strength, can be used to describe the local chain motions of amorphous polymers, with the aid of theoretical dynamic models proposed to study NMR relaxation.¹⁴

In the present contribution, we present the measurement of the variable-temperature ¹³C relaxation parameters of semicrystalline poly(4-hydroxybutyrate) (P4HB, **1**) and two copolymers of 3-hydroxybutyrate and 4-hydroxybutyrate (P3/4HB-18, **2**, and P3/4HB-69, **3**) with 18% and 69% 4hb content, at two magnetic field



* Author to whom correspondence should be addressed at McGill University.

[†] Universität Ulm.

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strengths. The physical properties of the polymers are presented in Table 1. ¹³C NMR experiments¹⁵ showed

Table 1. Physical Properties^a of Poly(4-hydroxybutyrate), P4HB, and Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)s, P3/4HB-18 and P3/4HB-69

	T_g (°C)	T_m (°C)	crystallinity (%) ^b	tensile strength (mPa) ^b	elongation to break (%) ^b
P4HB	-48	54	25 ± 5	104	1000
P3/4HB-69	-36	50	^c	~17	~591
P3/4HB-18	-4	165	30 ± 5	~26	~444

^a Glass transition temperature, T_g , melting point temperature, T_m , and crystallinity as measured by DSC.^{9,23} ^b Mechanical data are from ref 10 and serve as a reference only, since they were measured at 23 °C for copolymers with 64% and 16% 4hb units, respectively. ^c Not determined. Literature data¹⁰ suggest a value in the range 15–18%.

that the two P3/4HB copolymers have a random distribution of repeating units, as observed for all bacterially synthesized PHA copolymers.^{3,5,6} We will show that the T_1 and NOE data can be accounted for by theoretical dynamic models and provide a quantitative picture of the local motions of 4hb units in P4HB and the balance of segmental dynamics between 3hb and 4hb units in the P3/4HB copolymers. ^{13}C T_1 and NOE measurements for P4HB and P3/4HB-18 showed qualitatively that the two types of monomer units in P3/4HB-18 do not share the same local dynamics.⁹

Experimental Section

A sample of homopolymer P4HB was kindly provided by Prof. A. Steinbuechel, Westf. Wilhelms-Universität Münster. Two copolymer samples (P3/4HB-69 and P3/4HB-18) were provided by Profs. Y. Doi of Riken, Tokyo, and G. Braunegg of the Technische Universität Graz. Samples for NMR relaxation measurements were prepared by placing finely ground pieces (~300 mg) of the polymer in 5 mm tubes, heating above the melting point until a homogenous melt phase was produced, and holding them at room temperature for several days prior to conducting any experimental work.^{9,16}

^{13}C relaxation measurements as a function of temperature were performed on Varian Unity 500 and Varian XL-300 instruments operating at 125.7 and 75.4 MHz, respectively, for the carbon nucleus. ^{13}C T_1 relaxation times were measured by the standard inversion–recovery technique, with delays between acquisitions equal to 5 times the longer T_1 measured, using a three-parameter nonlinear fit procedure. A total of 512–1024 acquisitions were accumulated depending on the signal/noise ratio, for a set of 10–12 “arrayed” τ values of the delay time between the 180° and 90° pulses. NOEs were measured by gated decoupling, with delays between acquisitions equal to 10 times the longer T_1 . Each reported NOE value is the average of at least two different experiments.

The temperature was controlled to within ±1 °C by standard instrument hardware and calibrated using ethylene glycol prior to each experiment. No lock solvent was employed, but measurements with and without sample spinning did not show any measurable difference in the ^{13}C line widths due to field inhomogeneity.

Fitting Procedure. Numerical calculations were performed by using the MOLDYN program,¹⁷ modified to include the various dynamic models used in the present study. The parameters of a given model were optimized until the sum of the squares of deviations of the difference between theoretical and experimental relaxation data reached a minimum. Details of the program and the calculation procedure can be found elsewhere.^{17–19} For reasons explained in Results and Discussion, the Dejean–Laupretre–Monnerie,²⁰ DLM, model was used throughout this study for the analysis of the ^{13}C relaxation data.

The dynamics of the 4hb unit in the three polymer systems were explored by fitting the experimental relaxation data of carbon C-3 in P4HB and the two P3/4HB copolymers. For the 3hb unit in the two copolymers, the carbon atom C-5 was used

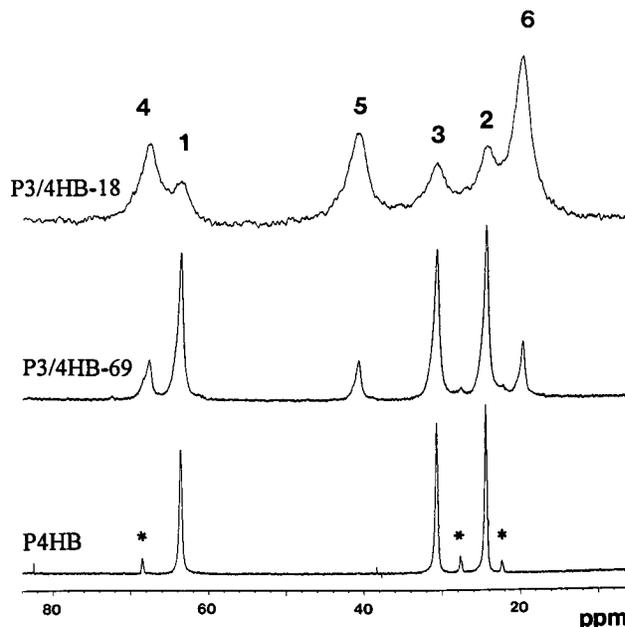


Figure 1. Scalar decoupled ^{13}C NMR spectra of P4HB, P3/4HB-18, and P3/4HB-69 at a temperature of 65 °C and a magnetic field strength of 125.7 MHz. For numbering, see text. Peaks marked with an asterisk (*) are due to traces of thermal degradation products.⁹

for modeling. C-3 and C-5 possess exactly the same position on the backbone chain, e.g., they are both beside the carbonyl group, so the comparability of the simulation is ensured.⁹ The value of the libration angle, θ , for each carbon atom was fitted at the T_1 minimum and held constant throughout the whole temperature range studied. The ratio $z = \tau_0/\tau_1$ and the librational correlation time, τ_2 , were held constant at values of 50 and 5 ps, respectively, for all three polymer systems. It was found that a good fit was always possible as long as $z \geq 50$ and $\tau_2 \leq 5$ ps. The insensitivity of the librational correlation time, τ_2 , during the fitting procedure and the high values of the ratio $z = \tau_0/\tau_1$ for bulk amorphous polymers are well documented in the literature.^{14,21,22} In effect, only the DLM correlation time, τ_1 , was optimized at each temperature by using four independently measured relaxation data. The correlation times τ_1 obtained in this way for each repeat unit were used to predict the T_1 and NOE relaxation data of carbon atoms C-1 in P4HB, C-4 in P3/4HB-18, and C-1 and C-4 in P3/4HB-69. The value of the libration angle, θ , for C-1 and C-4 in each case was optimized at the T_1 minimum and held constant over the whole temperature range studied.

Results and Discussion

Figure 1 depicts the aliphatic part of the ^{13}C scalar decoupled NMR spectra of P4HB, P3/4HB-18, and P3/4HB-69 at a temperature of 65 °C and a magnetic field strength of 125.7 MHz. These spectra were recorded by gated decoupling, so differences in peak intensity reflect the different chemical composition of the three polymer systems. In the P3/4HB-18 spectrum, which has rather low resolution in terms of peak chemical shift separation, 4hb peaks appear as shoulders on the side of the more intense 3hb peaks. The best resolved 4hb unit ^{13}C peak of P3/4HB-18 is C-3, so the C-3 relaxation data were used to analyze the local dynamics of the 4hb monomer unit in this copolymer. In the P3/4HB-69 copolymer, 3HB is the minor component, so 3hb peaks are shorter but narrow enough to produce accurate ^{13}C relaxation parameters. Variable-temperature ^{13}C spectra will be presented elsewhere,²³ along with a detailed analysis of the temperature dependence of the ^1H and ^{13}C line widths of these polymers.

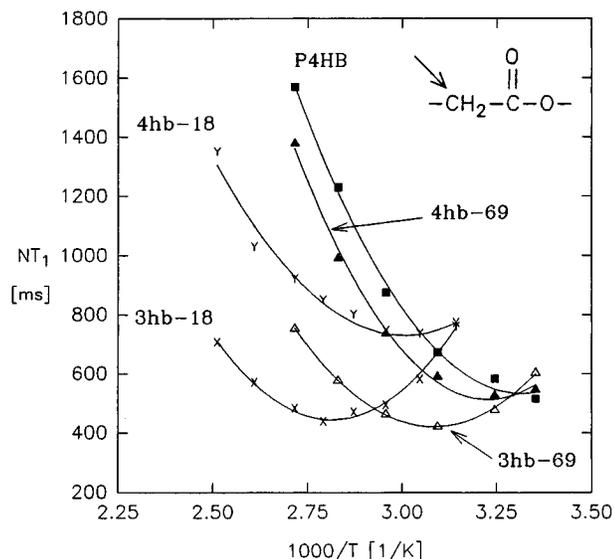


Figure 2. Experimental spin-lattice relaxation times, NT_1 , of the methylene carbon next to the carbonyl (C-3 in P4HB, C-3 and C-5 in P3/4HB-18 and P3/4HB-69, $N = 2$ in all cases) as a function of temperature at a magnetic field strength of 125.7 MHz. Curves were drawn as an aid to the eye.

Table 2. ^{13}C Spin-Lattice Relaxation Times (T_1 , ms) and NOE Values^a of the Protonated Carbon Atoms of Poly(4-hydroxybutyrate), P4HB, in Bulk as a Function of Temperature and at Two Magnetic Field Strengths (B_0 , MHz)

$T(^{\circ}\text{C})/B_0$	T_1 (NOE)					
	C-1		C-2		C-3	
	75.4	125.7	75.4	125.7	75.4	125.7
25	156 (1.75)	226 (1.51)	158 (1.76)	248 (1.50)	169 (1.78)	258 (1.51)
35	190 (1.88)	256 (1.73)	201 (1.95)	273 (1.77)	206 (1.89)	292 (1.75)
50	244 (2.13)	296 (1.99)	273 (2.20)	322 (2.12)	279 (2.13)	337 (2.02)
65	303 (2.33)	384 (2.29)	348 (2.49)	423 (2.49)	354 (2.39)	438 (2.34)
80	410 (2.40)	527 (2.38)	490 (2.56)	614 (2.61)	484 (2.48)	615 (2.48)
95	540 (2.48)	648 (2.48)	661 (2.56)	794 (2.67)	658 (2.50)	785 (2.55)

^a Values in parentheses.

Spin-Lattice Relaxation, NT_1 , and Nuclear Overhauser Effect Data. The T_1 and NOE relaxation data of the protonated backbone carbon atoms of P4HB and the two P3/4HB copolymers in bulk, as a function of temperature and magnetic field strength, are summarized in Tables 2–4, respectively. Figure 2 presents the experimental spin-lattice relaxation times, T_1 , of the methylene carbon right next to the carbonyl (C-3 in P4HB, C-3 and C-5 in P3/4HB-18 and P3/4HB-69) as a function of temperature at a magnetic field strength of 125.7 MHz. The different dynamics of each repeating unit, depending on its local environment, are well illustrated, since we are comparing exactly the same position on the polymer backbone in different repeat units. No discontinuity in the T_1 values is observed as the respective melting point temperatures (Table 1) of the polymers are crossed, in agreement with reports on other semicrystalline polymers.^{13,14,16,22}

Two types of differences are evident in Figure 2: (a) differences in the position of the T_1 minimum vs temperature and (b) differences in the height of the T_1 minimum. The position of the T_1 minimum vs temper-

Table 3. ^{13}C Spin-Lattice Relaxation Times (T_1 , ms) and NOE Values^a of the Protonated Carbon Atoms of Random Poly(3-hydroxybutyrate-co-4-hydroxybutyrate), P3/4HB-18, Containing 18% 4hb Units, in Bulk as a Function of Temperature and at Two Magnetic Field Strengths (B_0 , MHz)

$T(^{\circ}\text{C})/B_0$	T_1 (NOE)					
	4hb unit ^b C-3		3hb unit			
	75.4	125.7	C-4		C-5	
	75.4	125.7	75.4	125.7	75.4	125.7
45			293 (1.57)	703 (1.42)	180 (1.57)	386 (1.50)
55			256 (1.56)	504 (1.42)	149 (1.58)	290 (1.55)
65	236 (2.02)	348 (1.99)	231 (1.65)	456 (1.51)	137 (1.65)	247 (1.57)
75	251 (2.08)	423 (2.02)	241 (1.69)	384 (1.54)	148 (1.75)	235 (1.62)
85	319 (2.19)	483 (2.07)	252 (1.94)	385 (1.63)	153 (1.96)	237 (1.74)
95	388 (2.26)	475 (2.25)	275 (2.02)	398 (1.81)	178 (2.07)	241 (1.90)
110	473 (2.32)	514 (2.26)	349 (2.20)	458 (2.02)	229 (2.30)	285 (2.15)
125	708 (2.65)	666 (2.31)	463 (2.43)	545 (2.24)	314 (2.56)	353 (2.25)

^a Values in parentheses. ^b ^{13}C peaks for C-3 were too broad to allow the accurate measurement of T_1 and NOE at the two lowest temperatures.

ature reflects differences in the rate of the local segmental motion in different monomer units. The lower the temperature at which the T_1 minimum is observed for a monomer unit, the higher its rate of backbone segmental motion. The T_1^{min} values extracted from Figure 2 are <25, 35, 50, ~60, and 85 °C for P4HB, 4hb-69, 3hb-69, 4hb-18, and 3hb-18, respectively (a notation such as 3hb-69 stands for the 3hb repeat unit in the P3/4HB-69 copolymer). This suggests that the mobility of each type of repeat unit at constant temperature decreases in the above order, with the 4hb unit in P4HB experiencing the faster local dynamics. The differences in the position of the T_1^{min} for the two types of repeat units in both P3/4HB copolymers suggest that the 4hb unit is always experiencing faster dynamics than the respective 3hb unit of the same copolymer. This is attributed to the different chemical structure of the two types of units, e.g., the 4hb unit is linear, while 3hb has a methyl side chain.^{9,14}

The differences in the height of the T_1 minimum are more difficult to interpret. In the theory describing the derivation of the DLM model, Dejean de la Batie et al. suggested²⁰ that the height of the T_1 minimum is directly related to the amplitude of a fast librational motion, which is superimposed on the backbone cooperative motion. Such an interpretation would mean that in P3/4HB-18, the librational amplitude of the 4hb unit is much larger than that in P4HB. For the 3hb unit, the difference of the T_1^{min} values in P3/4HB-18 and P3/4HB-69 is smaller, suggesting a smaller change in the librational amplitude as the composition of the copolymer changes. This point will be considered further after the analysis of the complete relaxation data set with theoretical dynamic models for ^{13}C relaxation of polymers in bulk.

The variation of the NOE values of the protonated backbone carbon atoms of P4HB, P3/4HB-18, and P3/4HB-69 with temperature (Tables 2–4) is as expected for semicrystalline polymers at temperatures well above T_g .^{13,14,16} The general trend is an increase in NOE with

Table 4. ^{13}C Spin–Lattice Relaxation Times (T_1 , ms) and NOE Values^a of the Protonated Carbon Atoms of Random Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate), P3/4HB-69, Containing 69% 4hb Units, in Bulk as a Function of Temperature and at Two Magnetic Field Strengths (B_0 , MHz)

$T(^{\circ}\text{C})/B_0$	T_1 (NOE)									
	4hb unit						3hb unit			
	C-1		C-2		C-3		C-4		C-5	
	75.4	125.7	75.4	125.7	75.4	125.7	75.4	125.7	75.4	125.7
25	153 (1.77)	264 (1.73)	148 (1.82)	243 (1.75)	163 (1.77)	274 (1.75)	283 (1.46)	519 (1.45)	145 (1.45)	302 (1.51)
35	157 (1.87)	248 (1.79)	164 (1.97)	239 (1.84)	171 (1.89)	264 (1.78)	227 (1.58)	390 (1.48)	124 (1.57)	239 (1.49)
50	201 (2.13)	269 (1.93)	223 (2.27)	280 (2.08)	224 (2.15)	296 (1.99)	218 (1.75)	343 (1.56)	119 (1.76)	211 (1.57)
65	272 (2.28)	326 (2.13)	322 (2.42)	359 (2.36)	317 (2.32)	369 (2.22)	265 (2.02)	349 (1.82)	156 (2.10)	232 (1.86)
80	366 (2.39)	430 (2.28)	453 (2.58)	495 (2.52)	430 (2.46)	496 (2.37)	351 (2.22)	428 (2.02)	205 (2.38)	279 (2.15)
95	501 (2.46)	579 (2.40)	637 (2.64)	693 (2.63)	594 (2.55)	690 (2.49)	466 (2.37)	560 (2.27)	277 (2.61)	377 (2.45)

^a Values in parentheses.

increasing temperature and decreasing magnetic field strength, as expected from theory.^{11,14} At the low-temperature limit, there is evidence for a leveling off of the NOE values of the 3hb unit in P3/4HB-18 (atoms C-4 and C-5 in Table 3). This phenomenon is well known in the case of semicrystalline polymers^{13,14,22} and has been attributed to the presence of crystallites that affect segmental motion in the amorphous region as the temperature is lowered closer to T_g . It is interesting to note that carbon atoms in different repeat units in both P3/4HB copolymers have quite different NOE values at the same temperature and magnetic field strength. This is in agreement with the differences observed in the T_1 vs $1/T$ behavior of the copolymers (Figure 2) and reflects the differences in the local segmental dynamics of each type of repeat unit.

It is also interesting to examine the ratio of the T_1 values of different protonated backbone carbons of the same repeat unit in the three polymer systems as a function of temperature and magnetic field. According to theory,^{11,14} all the protonated backbone carbon atoms of the same repeat unit share the same motional dynamics and thus should have the same T_1 value, when the number of directly bonded protons is taken into account. This has been shown not to be true in several ^{13}C NMR relaxation studies of amorphous polymers in bulk^{20–22} and also in solution.^{14,18,24} The T_1 ratios for some backbone carbon atoms of the polymers of this study are given in Table 5. The ratio $R_1(\text{C-3/C-1})$ in P4HB should be equal to 1, since both C-3 and C-1 are methylene carbons. Instead, $R_1(\text{C-3/C-1})$ ranges with temperature and magnetic field from 1.08 to 1.22, with a mean value of 1.16 ± 0.3 . In P3/4HB-69 the same ratio increases gradually with increasing temperature from 1.04 to 1.19 in both fields. This suggests that C-3 and C-1 carbons in P4HB and P3/4HB-69 do not experience exactly the same local dynamics. The same behavior is observed in Table 5 for the C-4/C-5 T_1 ratio in both P3/4HB copolymers. In this case, since C-4 is a methine and C-5 a methylene carbon, the ratio should be equal to 2. Significant deviations from this value are noted, with R_1 gradually decreasing with increasing temperature from a value of almost 2 to around 1.5. Similar behavior of the ratio R_1 with temperature has been reported for another polymer of the alkanolate family, poly(3-hydroxyoctanoate).²² The deviations in the various R_1 ratios suggest that ^{13}C spin–lattice relaxation time, T_1 , meas-

Table 5. ^{13}C Spin–Lattice Relaxation Time Ratios (R_1) of Selected Pairs of Protonated Backbone Carbon Atoms of Poly(4-hydroxybutyrate) and Two Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) Random Copolymers with 18% and 69% 4hb Content in Bulk as a Function of Temperature and at Two Different Magnetic Fields (B_0 , MHz)

$T(^{\circ}\text{C})/B_0$	P4HB		P3/4HB-69				P3/4HB-18	
	$R_1(\text{C-3/C-1})$		$R_1(\text{C-3/C-1})$		$R_1(\text{C-4/C-5})$		$R_1(\text{C-4/C-5})$	
	75.4	125.7	75.4	125.7	75.4	125.7	75.4	125.7
25	1.08	1.14	1.06	1.04	1.95	1.72		
35	1.08	1.14	1.09	1.06	1.83	1.63		
45							1.63	1.82
50	1.14	1.14	1.11	1.10	1.83	1.63		
55							1.72	1.74
65	1.17	1.14	1.16	1.13	1.70	1.50	1.69	1.85
75							1.63	1.63
80	1.18	1.17	1.17	1.15	1.71	1.53		
85							1.65	1.62
95	1.22	1.21	1.19	1.19	1.68	1.49	1.54	1.65
110							1.53	1.61
125							1.47	1.54

urements in the P3/4HB copolymers not only are able to differentiate between the different motional characteristics of each type of repeat unit but also reveal some fine differences in the details of the dynamics of different carbon atoms of the same repeat unit.

Dynamic Modeling of P4HB and P3/4HB in the Amorphous Phase. Models used to fit experimental relaxation data of amorphous polymers in the bulk were originally derived for the study of polymer dynamics in solution. These include models based on a distribution of correlation times (i.e., $\log \chi^2$, Cole–Cole distributions),¹¹ the Jones–Stockmayer (JS) model,²⁵ and the Hall–Weber–Helfand (HWH) model.^{26,27} The above models are referred to as unimodal models because they attribute relaxation to a single motional mode, that of the backbone segmental motion. Dejean de la Batie, Laupretre, and Monnerie showed that none of the above models could fit successfully the ^{13}C relaxation data of a series of amorphous polymers above T_g .^{20,28,29} These authors proposed a modification of the original HWH correlation function, which includes an additional fast librational motion of the backbone C–H vectors. The amplitude, θ , of this libration can be different for different C–H vectors on the backbone, e.g., for CH and CH_2 backbone groups as in the case of the 3hb unit in P3/4HB copolymers. This model is referred to as the Dejean–Laupretre–Monnerie (DLM) model and can

Table 6. Simulation Parameters^a of the DLM Model Used To Describe the Backbone Segmental Motion of Poly(4-hydroxybutyrate), P4HB, and Two Random Poly(3-hydroxybutyrate-4-hydroxybutyrate) Copolymers, P3/4HB-18 and P3/4HB-69, Containing 18% and 69% 4hb Units, Respectively, in Bulk

T (°C)	τ_1 (10^{-9} s)				
	P4HB	P3/4HB-18		P3/4HB-69	
		3hb unit	4hb unit	3hb unit	4hb unit
25	0.94			4.01	1.01
35	0.46			1.73	0.61
45		4.63			
50	0.16			0.87	0.26
55		2.47			
65	0.081	1.15	0.44	0.44	0.11
75		0.97			
80	0.038			0.20	0.053
85		0.68		0.20	
95	0.022	0.47	0.13	0.10	0.027
110		0.23		0.090	
125		0.12		0.046	
θ (deg)	C-3 39 C-1 36	C-4 30 C-5 36	C-3 44	C-4 25 C-5 33	C-3 39 C-1 37
E_a (kJ/mol)	47	45	42	46	47
corr coeff	0.999	0.993	0.997	0.998	0.999

^a The values of $z = \tau_0/\tau_1 = 50$ and $\tau_2 = 5$ ps were used in the fitting procedure in all cases.

reproduce experimentally observed deviations of the relaxation time ratio, R_1 , by assigning different values of θ to different carbon atoms. Subsequently, this model was successfully applied to several bulk polymers^{22,28,29} and also to the study of polymer dynamics in solution.^{18,19,24} Through these systematic studies, it has been established that unimodal dynamic models, such as the JS and HWH models, do not reproduce in a satisfactory manner the experimental relaxation data of amorphous polymers.^{14,22,28,29}

From the previous analysis of the R_1 ratios presented in Table 5, it is clear that unimodal models are not capable of reproducing all the experimental ^{13}C relaxation data of P4HB and P3/4HB copolymers. As an additional test, we tried to reproduce the experimental values of the spin-lattice relaxation time, T_1 , at the minimum of the T_1 vs $1/T$ curve for various carbons of the three polymer systems by using unimodal models, such as the HWH and JS models. These attempts were unsuccessful, as the predicted T_1 value was always much smaller than the experimental one at both magnetic fields. Therefore, the DLM model has been used for the modeling of the backbone dynamics throughout this study. This model has four adjustable parameters: τ_1 , the correlation time for cooperative backbone motion; τ_0 , the correlation time for isolated conformational transitions; τ_2 , the correlation time for the librational motion of the individual C-H vectors; and θ , the librational angle. Usually the ratio $z = \tau_0/\tau_1$ is used for the simplification of the fitting procedure, in effect giving τ_0 the same activation energy as τ_1 . Details of the model can be found in the original papers of Dejean, Laupretre, and Monnerie^{20,28,29} and elsewhere.^{14,24}

The results of the fitting procedure (as described in the Experimental Section) for the three polymers of this study by using the DLM model are presented in Table 6. Figure 3 is representative of the good quality of fitting obtained for ^{13}C relaxation data of the three polymer systems by the DLM model. The DLM correlation times, τ_1 , for backbone cooperative motion of Table 6 are presented in Figure 4 in an Arrhenius format, in order to facilitate the comparison. Figure 4

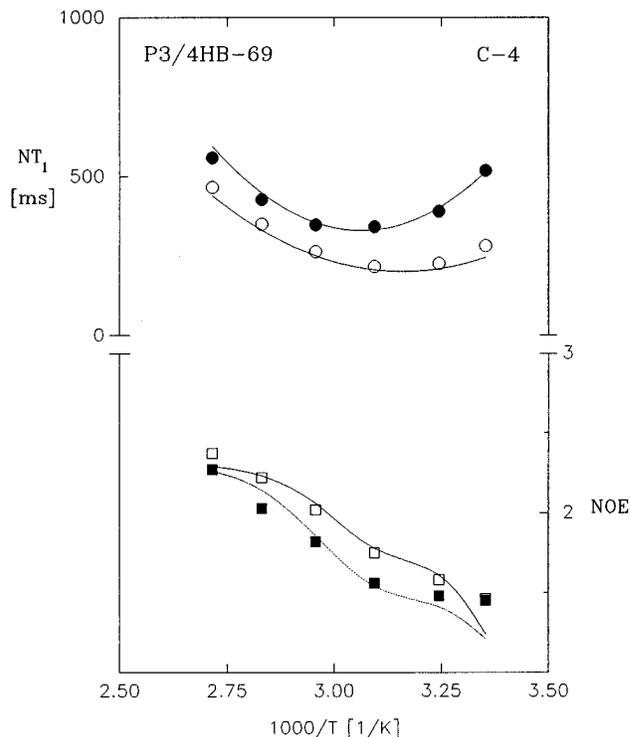


Figure 3. Experimental spin-lattice relaxation times, NT_1 , and NOE values for the C-4 methine backbone carbon of the 3hb unit in P3/4HB-69 as a function of temperature and magnetic field. Solid and dashed lines represent the best fit values calculated by using the DLM model with the simulation parameters of Table 6.

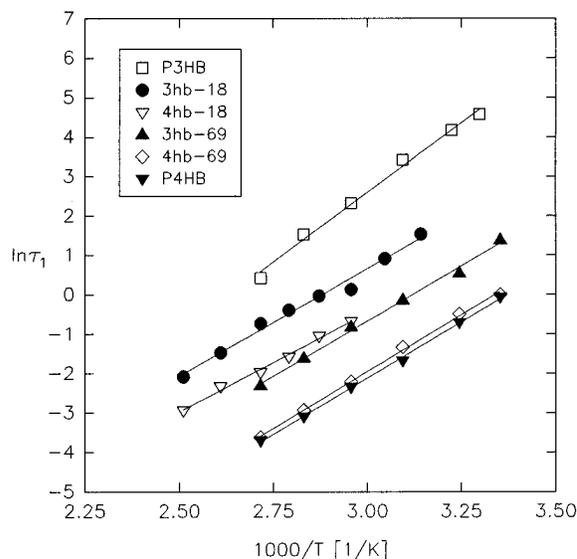


Figure 4. Arrhenius plot of the correlation time for backbone cooperative segmental motion, τ_1 , of P4HB, P3/4HB-18, P3/4HB-69 (3hb and 4hb monomer units), and P3HB in bulk as described by the DLM model. Data for P3HB are from ref 30.

also includes the DLM correlation times reported by Sanders et al.³⁰ for native P3HB inclusions. These authors have shown that P3HB is in its amorphous state in such inclusions, so their work serves as a useful reference point with regard to amorphous P3HB dynamics. Several important conclusions regarding the rate of local segmental motion in P4HB and the two P3/4HB copolymers can be drawn by examining the simulation data of Table 6 and Figure 4.

(1) In the two copolymers P3/4HB-18 and P3/4HB-69, the rate of segmental motion of the two types of

repeat units is significantly different. Over the whole temperature range studied, the motion of the 4hb unit in both copolymers is approximately 2–4 times faster than the motion of the 3hb unit of the same copolymer. This observation demonstrates the highly local character of the dynamics observed by the ^{13}C NMR relaxation technique. Since in P3/4HB-18 ca. one in five repeat units is a 4hb unit and in P3/4HB-69 one unit in three is a 3hb unit, the conformational transitions responsible for ^{13}C relaxation should not involve more than one to two backbone monomer units. This is in agreement with Brownian dynamics simulations³¹ and analytical and numerical approaches based on the dynamic rotational isomeric state (DRIS) formalism.³²

(2) When the motional dynamics of the 4hb repeat unit as a function of the composition of the polymer backbone are examined, the effect of the presence of the 3hb of unit is clear, and vice versa. The mobility of the 4hb unit decreases in the order P4HB > P3/4HB-69 > P3/4HB-18 > P3HB, while that of the 3hb unit increases in the same order. The increasing percent of flexible 4hb units increases the mobility of the neighboring 3hb units, while at the same time 4hb units are retarded with respect to 4hb mobility in P4HB. The increasing mobility of both types of repeat unit with increasing 4hb content is consistent with the increasing elastomeric behavior reported for P3/4HB copolymers with high 4hb content.^{1,10}

(3) The values of the libration angle, θ , reported in Table 6 for the various backbone carbon atoms are consistent with the steric hindrance at each carbon site. Methylene carbons are found to have larger θ angle values than methine ones, in agreement with earlier findings for several amorphous polymers,^{14,20,28,29} where this difference was attributed to a restriction of the librational motion caused by the presence of the substituent on the methine carbon site. It is interesting to note that the amplitude, θ , of the librational angle for C-3 is equal to 39° in both P4HB and P3/4HB-69 but increases to 44° in P3/4HB-18. This increase is in agreement with the significantly raised T_1 minimum exhibited by C-3 in P3/4HB-18, as compared to P4HB and P3/4HB-69 in Figure 2. It supports the assumption made by Dejean de la Batie et al.²⁰ in the derivation of the DLM model that the height of the T_1 minimum is directly related to the amplitude of the librational motion of the C–H backbone vectors. It also shows that in a copolymer like P3/4HB-18, where the presence of 82% stiff 3hb units has decreased the mobility of the 4hb backbone units significantly, the importance of librations in causing relaxation increases.

(4) The activation energies for cooperative backbone motion derived from the DLM model analysis and presented in Table 6 are typical of amorphous polymers at temperatures above T_g .^{14,22} They are much greater than typical activation energies reported for polymers in solution,^{11,14} due to the increased "apparent" viscosity exerted by the amorphous polymer matrix on the moving backbone segment. For example, the activation energies for the backbone motion of P3HB in chloroform³³ and tetrachloroethane¹⁸ solutions were reported to be 17 and 19.5 kJ/mol, respectively. The activation energies reported for P4HB and the 3hb and 4hb units in the P3/4HB copolymers in Table 6 are similar and in the range 42–47 kJ/mol. Interestingly, the activation energy for the 3hb unit motion in the copolymers is ~ 10 kJ/mol lower than that reported for amorphous P3HB.³⁰

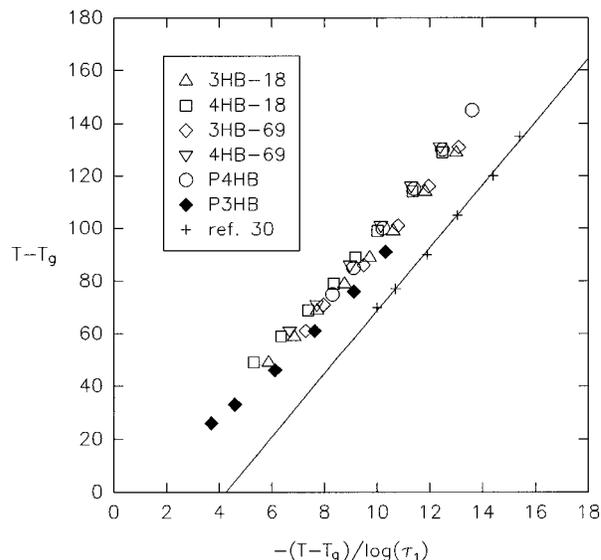


Figure 5. Williams–Landel–Ferry plot of the DLM correlation time, τ_1 , for the backbone cooperative segmental motion of P4HB, P3/4HB-18, P3/4HB-69 (3hb and 4hb monomer units), and P3HB in bulk. The + symbols represent the P3HB DLM data from ref 30, using $T_g = -50^\circ\text{C}$, while the (◆) symbols represent the same data but with $T_g = 4^\circ\text{C}$.

Williams–Landel–Ferry Behavior of the DLM τ_1 Correlation Times. It has been shown^{21,22,34} for several amorphous and semicrystalline polymers that the correlation times obtained by ^{13}C relaxation data obey the Williams–Landel–Ferry (WLF)³⁵ empirical equation, when the glass transition temperature is taken as the reference temperature:

$$\log \frac{\tau(T)}{\tau(T_g)} = - \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

Equation 1 gives the ratio of the correlation time, τ , at a temperature, T , to that at the glass transition temperature, T_g , and is useful in showing that the dynamics observed by ^{13}C NMR are involved in the glass transition phenomena. The parameters C_1 and C_2 vary from polymer to polymer covering the range 11–17 for C_1 and 40–70 for C_2 in the case of amorphous polymers,³⁴ although for semicrystalline polymers lower C_2 values have been reported.^{22,34} The WLF plot of the DLM correlation times, τ_1 , for P4HB and the 3hb and 4hb units in the two P3/4HB copolymers (from Table 5) is presented in Figure 5. It can be seen in Figure 5 that the data points for all three polymer systems fall on the same master line. This proves that the segmental backbone motions probed by ^{13}C NMR relaxation measurements are involved in the glass transition phenomena and that the decrease in T_g on going from P4HB to P3/4HB-69 and P3/4HB-18 is in agreement with the slowing down of segmental motion as modeled by the DLM model.

It is interesting to compare our WLF results with those of Sanders,³⁰ who studied amorphous P3HB in native inclusions. Sanders also used the DLM model in his study and assumed a T_g of -50°C for P3HB.³⁰ This assumption was challenged,³⁶ and subsequently it was shown that there is no significant difference in mobility between native, freeze-dried, and artificial P3HB granules.³⁷ Our data are consistent with the above conclusion regarding amorphous P3HB mobility in native inclusions. Figure 5 illustrates the WLF plot

Table 7. Williams–Landel–Ferry Coefficients of Various Poly(hydroxyalkanoate)s Determined by ^{13}C NMR Relaxation Studies

polymer	C_1	C_2	T_g (°C)
poly(4-hydroxybutyrate)	13.2	35.3	-50
P3/4HB-18 3hb unit	11.1	17.4	-4
4hb unit	11.2	12.3	
P3/4HB-69 3hb unit	11.8	24.6	-36
4hb unit	12.3	23.3	
poly(3-hydroxybutyrate) ^a	12	51	-50 ^a
	12	10	4
poly(3-hydroxyoctanoate) ^b	10.8	26.3	-36

^a For $T_g = -50$ °C results are from ref 30. ^b From ref 22.

of the P3HB DLM τ_1 data, assuming a T_g of -50 °C (+, solid line), and 4 °C (\blacktriangle). This latter value of T_g has been frequently reported for P3HB extracted chemically from native inclusions.¹ It is evident from Figure 5 that when $T_g = 4$ °C is used, the data of ref 30 fall on the same master curve with those of the present study. This observation suggests that P3HB in never-dried granules does not have an unusually low T_g .³⁰ Also, the fact that the dynamics of P3HB in inclusions scale with T_g in the same manner as those of semicrystalline P4HB and P3/4HB copolymers proves that P3HB in inclusions is not in a highly mobile state but rather exhibits the usual dynamic characteristics expected from a semicrystalline polymer above T_g .

The values of the WLF parameters obtained from Figure 5 are reported in Table 7, along with the WLF data reported for semicrystalline PHO.²² These compare well with those reported for other semicrystalline polymers by Dekmezian et al.³⁴ Especially characteristic is the low value of the C_1 parameter, which seems to be common for most semicrystalline polymers studied so far by the ^{13}C NMR relaxation technique.^{22,34} It is worth pointing out that, as seen in Table 7, when the correct value of T_g is used, the WLF parameters of P3HB in native inclusions³⁰ are similar to those of semicrystalline P4HB and P3/4HB copolymers.

Conclusions

This study demonstrates the ability of the ^{13}C NMR relaxation technique to elucidate the local segmental dynamics of amorphous polymers in bulk. The analysis of the variable-temperature/multifield relaxation data by the DLM model led to a quantitative picture of the backbone motion in P4HB and P3/4HB copolymers. It was found that the rate of segmental motion of the 4hb unit decreased with increasing percent of 3hb unit on the polymer backbone. The analysis of the relaxation data of the P3/4HB copolymers also showed that the two different types of backbone units of a P3/4HB copolymer have quite different motional characteristics. The 4hb unit was found to have 2–4 times faster segmental motion than the 3hb unit in both copolymers, in terms of the simulation parameter τ_1 for cooperative segmental motion of the DLM model. In addition, the librational angle, θ , of the various carbon atoms of the polymers studied was found to have values in agreement with expectations from the steric hindrance at each carbon site. Only the DLM model was able to reproduce at the same time the relaxation data of different carbon atoms of the polymer backbone. This indicates the importance of librational motions in the relaxation behavior of amorphous polymers in bulk. The increased value of θ observed for the 4hb unit in P3/4HB-18 was attributed to an increased contribution of librational motions to

^{13}C relaxation. The Arrhenius activation energies derived from the analysis of the temperature dependence of the τ_1 correlation times for cooperative motion were in the range found for most amorphous polymers at temperatures well above T_g .

It was also shown in this study that the local dynamics in bulk of P4HB and P3/4HB copolymers follow the WLF equation and scale in the same manner with the respective glass to rubber transition temperatures. Thus it was concluded that the motions responsible for ^{13}C relaxation in the amorphous phase are involved in the glass transition phenomena. Literature data for amorphous P3HB in inclusions compared very well with the present WLF data, when it was assumed that P3HB in inclusions had the same T_g with that of extracted P3HB polymer. This agrees with earlier results, suggesting that P3HB is not abnormally mobile in inclusions but rather behaves as a regular semicrystalline polymer above T_g .

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