

^{13}C and ^1H Amorphous Linewidths in Semicrystalline Poly(4-hydroxybutyrate) and Poly(3-co-4-hydroxybutyrate) above T_g by High Resolution and Solid-State NMR Experiments

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SYNOPSIS

The high-resolution ^{13}C and ^1H nuclear magnetic resonance (NMR) linewidths of semicrystalline poly(4-hydroxybutyrate), P4HB, and poly(3-hydroxybutyrate-co-4-hydroxybutyrate), (P3/4HB-18, 18% 4HB units) in the amorphous phase and in the melt are studied as a function of temperature and magnetic field strength. Measurements of the ^{13}C spin-spin relaxation times under the same experimental conditions show that the natural linewidth is a minor contributor to the line-broadening observed in the ^{13}C spectra of the solid polymers. A variety of coherent averaging solid-state NMR methods are used to examine possible contributions from various line-broadening mechanisms. It is shown that magnetic susceptibility and chemical shift dispersion are the major factors for the broadening of the proton and carbon resonances of P4HB in the amorphous phase and the melt, respectively. Incomplete motional narrowing due to a slow motional mode restricted in amplitude by the presence of crystallites and/or chain constraints was found to be the major line-broadening factor for P3/4HB-18 in the amorphous phase. Correlations between crystalline morphology, physical and mechanical properties, and polymer chain dynamics are discussed, along with the way these factors affect the NMR linewidth data presented. © 1996 John Wiley & Sons, Inc.

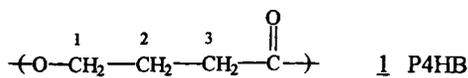
Keywords: Spin-spin relaxation • C-13 linewidth • poly(hydroxyalkanoate)s • solid state NMR • semicrystalline polymers

INTRODUCTION

Recently a new family of bacterially synthesized polymers and copolymers with a high degree of biodegradability¹ has been introduced. This family consists of poly(4-hydroxybutyrate), P4HB 1, and random copolymers of the poly(3-hydroxybutyrate-co-4-hydroxybutyrate) type, 2. The chemical composition of these polyhydroxyalkanoates, PHAs, can be controlled by the nature of the substrate used for fermentation.² In this way random copolymers of 3HB and 4HB content have been synthesized, and this family of mixed linkage copolyesters has different physical properties^{1,2} compared to a

copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate P3HB/HV, which is available commercially under the trade name BIOPOLTM. It has been shown that the rate of enzymatic degradation of P3HB increases with decreasing crystallinity,⁴ and that low 4HB-content P3/4HB copolymers biodegrade faster than P3HB.⁵ It is possible that crystalline morphology and the dynamics in the amorphous phase influence properties such as biodegradability, since they affect the ease by which enzymes can access the polymer chains.³ We have applied ^{13}C NMR spectroscopy to study the amorphous phase dynamics of PHAs and their effect on the physical properties of this family of polymers. The present contribution concentrates on the ^1H and ^{13}C linewidths in the amorphous phase and the melt, and their dependence on temperature and magnetic field strength.

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Scheme 1.

It is established that amorphous polymers give rise to narrow ^{13}C nuclear magnetic resonance (NMR) spectra at temperatures well above T_g , by using standard high-resolution techniques^{6,7} such as scalar decoupling (SD). This has led to an increasing number of applications of high-resolution ^{13}C NMR spectroscopy to describe the amorphous phase of polymers.^{8,9} Areas covered include local dynamics in the amorphous phase,¹⁰ filler-polymer interactions,⁸ and the study of cross-linked systems.⁸ One of the most intriguing aspects of the ^{13}C NMR spectra of amorphous polymers is their dependence on temperature. At temperatures about 100°C above T_g , amorphous polymers show peaks with linewidths in the range 5–30 Hz.^{8,11} However, as the temperature is lowered toward T_g , peaks become broader, and collapse at a temperature range around $1.2\text{--}1.3 T_g$ (in K).¹² Early attempts to assign this phenomenon to a polymer transition do not appear valid, as pointed out by Komoroski.⁸ A large number of factors can influence the amorphous linewidths, their dependence on temperature, and consequently the temperature below which a high-resolution spectrum is not obtained.⁸ These factors include the chemical shift separation of the lines of the specific polymer, the value of the static magnetic field H_0 and of the decoupling field H_1 , the presence of crystallites in semicrystalline polymers or fillers in filled polymers, and the effect of motion of the polymer backbone with frequencies ranging from near static to almost 10^{10} Hz.

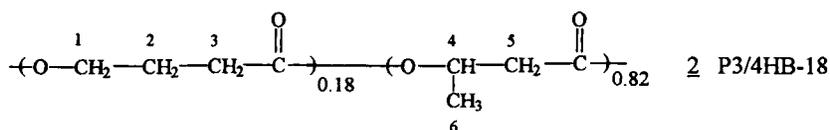
Due to the complicated nature of this problem, a number of different NMR techniques have been used with the purpose of understanding the factors leading to line broadening in amorphous and semicrystalline polymers. Usually a combination of high-resolution and solid-state ^{13}C and ^1H NMR techniques are employed,^{8,9,13,14} as a function of resonance frequency and temperature. The effect of cross-polarization (CP), magic angle spinning (MAS), and high-power proton dipolar decoupling (DD) on the

proton and carbon linewidths can be used to distinguish between proposed chain dynamic models.^{13–15} Polyethylene, PE, is a well-studied case,^{13,16} which demonstrates the importance of sample preparation procedures in studies of this type.^{11,16} Incomplete motional narrowing was proposed as the cause of line broadening in polyethylene.¹⁶ In addition, the amorphous linewidths in semicrystalline PE samples did not depend on the level of crystallinity, but were dependent on the crystalline morphology and superstructure.^{11,16} Komoroski confirmed earlier results¹⁷ and showed that the natural linewidth is the dominant contributor to the polyisobutylene ^{13}C linewidths by using DD/MAS NMR spectroscopy.¹³ English concluded¹⁵ that a rapid motional component spatially inhibited by chain constraints was responsible for the ^{13}C and ^1H linewidths of bulk *cis*-polybutadiene, studied by a variety of coherent averaging techniques in the solid state. Interestingly a totally different mechanism, bulk magnetic susceptibility, was found to operate for *trans*-polybutadiene.¹³

The present study reports the results of a variable temperature high-resolution (scalar-decoupled) ^1H and ^{13}C NMR study of linewidths in semicrystalline poly(4-hydroxybutyrate), (P4HB), and random poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate), (P3/4HB-18, i.e. 18% 4HB units). The physical properties of these two polymers are reported in Table I. The contribution of the natural linewidth has been assessed by measurements of the spin-spin relaxation time T_2 of the protonated carbon atoms in the amorphous phase and in the melt. Solid-state ^{13}C NMR spectra at selected temperatures have been used to study the effect of dipolar decoupling and magic-angle spinning on the amorphous linewidths. The contribution of various mechanisms to the line-broadening in the amorphous phase and the melt for the present polymer systems will be discussed on the basis of the aforementioned experimental data.

EXPERIMENTAL

Samples for the high-resolution spectra were prepared by placing finely ground pieces (~ 300 mg)



Scheme 2.

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

	T_g (°C)	T_m (°C)	Crystallinity ^b (%)	Tensile Strength (mPa) ^c	Elongation to Break (%) ^c
P4HB	-49	54	25 ± 5	104	1000
P3/4HB-18	-4	165	30 ± 5	26 ^d	444 ^d

^a T_g , glass-transition temperature; T_m , melting point temperature, measured by DSC.¹⁸

^b Crystallinity values were measured by DSC.^{18,27}

^c Data from ref. 36 for solvent cast, unstretched films.

^d For a copolymer containing 16% 4HB units.

of the polymer in 5 mm tubes, heating above the melting point until a homogenous melt phase (i.e., no visual bubbles) was produced, and holding them at room temperature for several days prior to conducting any experimental work.^{11,18}

The high-resolution scalar decoupled ¹³C spectra used to measure the linewidths as a function of temperature were recorded on Varian Unity 500 and Varian XL-300 instruments operating for the carbon nucleus at 125.7 and 75.4 MHz, respectively. These spectra were acquired without magic-angle spinning (MAS) and with a scalar-decoupling field of $\gamma H_1 \approx 2\text{--}4$ KHz (depending on field strength), thus only the amorphous material contributes to the high-resolution spectrum.¹³ ¹³C T_2 relaxation times were measured by the standard Carr-Purcell-Meiboom-Gill sequence,^{19,20} with delays between acquisitions equal to 3–4 times the longest T_1 , and without MAS. Proton decoupling was switched off during the echo formation as suggested by Ernst.²¹ A total of 512–2048 acquisitions were accumulated depending on the signal/noise ratio, for a set of 10–12 “arrayed” $\tau = 2nt$ values of the duration of the 180° pulse train, where a delay time between 180° pulses of $t = 1$ ms was used. Test experiments with $t = 0.5$ ms gave indistinguishable results within experimental error. The T_2 values were determined by using a three-parameter nonlinear procedure implemented as standard Varian instrument software, and they are estimated to be accurate within 20–30%, although repeated experiments showed reproducibility was better (i.e., in the range 5–10%). The temperature was controlled to within $\pm 1^\circ\text{C}$ by standard instrument hardware, and calibrated using ethylene glycol prior to each experiment. No lock solvent was employed. Shimming of the ¹³C spectra of P4HB was attainable by using their ¹H spectrum, but the large ¹H linewidths did not allow this procedure for P3/4HB-18. Nevertheless, spinning at 20 Hz did not reduce the ¹³C linewidths, thus inhomogeneity of the magnetic field is a negligible factor for the

scalar-decoupled high-resolution spectra of the present study.

Solid-state NMR experiments were conducted on a Chemagnetics CMX-300 instrument operating at 75.4 MHz for the ¹³C nucleus, with a pulse delay of 3 s between acquisitions (the ¹H T_1 was ~ 0.6 s for the two polymers at the respective temperatures). MAS spectra were accumulated with a spinning rate of 3.5 KHz, and for the dipolar decoupled spectra high power proton decoupling of $\gamma H_1 \approx 60$ KHz was used. Samples for solid-state NMR spectra, unless otherwise stated, were in the form of powder. The linewidth data from the solid-state NMR experiments, reported in Tables II and IV, are for the amorphous peaks of the two polymers. As reported elsewhere,^{18,22} most of the carbon atoms of P4HB and P3/4HB-18 give rise to separate peaks for amorphous and crystalline regions in the solid state.

A Nikon Optiphot-Pol optical microscope was used to examine the morphology of the polymer samples under cross-polarized light. The resolution attainable by this instrument was approximately 2.5 μm . The samples used were hot-pressed films prepared by heating above the melting point and quenching at room temperature, in an effort to imitate experimental conditions inside the NMR tube.

The ¹³C peaks of P4HB were sufficiently narrow at all temperatures to allow direct evaluation of the linewidths from the spectra (see Fig. 1). However, peak-overlaps from the two repeat units, especially at the lower temperatures, were observed in the ¹³C spectra of the P3/4HB-18 copolymer at both fields (see Fig. 1 of ref. 18). Thus linewidth determination for all six carbon atoms of the copolymer was not possible. The linewidth of the C-4 methine carbon was determined by deconvolution techniques. The C-5 methylene peak was sufficiently separated from neighboring peaks to allow direct determination of its linewidth. ¹H linewidths reported in Table III were determined by deconvolution of spectra such as those of Figure 5. All of the overlapped ¹³C and

^1H spectra could be fitted by a sum of Lorentzian lines.

LINE-BROADENING MECHANISMS

The mechanisms that are responsible for the line-broadening of the ^{13}C spectra of bulk polymers have been discussed extensively in the literature.^{8,9,13-15,23} Thus only a brief summary of the mechanisms that is necessary for the comprehension of the present work will be presented here.

Line-broadening mechanisms for the ^{13}C spectra of totally amorphous or semicrystalline polymers can be divided in two general classes. The first involves mechanisms that produce a distribution of chemical shifts, whereas the second contains broadening factors related to relaxation processes. Included in the first category are: (i) inhomogeneity of the static magnetic field B_0 , (ii) variations in bulk magnetic susceptibility, (iii) residual chemical shift anisotropy from incomplete motional narrowing, and (iv) a distribution of isotropic chemical shifts due to conformational variations in the bulk. The second class includes: (v) the so-called natural linewidth, determined by the modulation of dipolar interactions by molecular motion, and (vi) residual static dipolar interaction produced by incomplete motional narrowing.

The individual contributions of each mechanism to the observed linewidth can be identified by examining the response of the linewidth to changes in magnetic field strength, decoupling power, MAS, and temperature. For example, line-broadening (in Hz) mechanisms of the first class depend linearly on the magnetic field strength. MAS will remove static and low frequency dipolar interactions (up to the spinning frequency), along with any residual chemical shift anisotropy interactions. DD will eliminate C-H and H-H dipolar interactions up to the decoupling field strength. The natural linewidth, NLW, can be

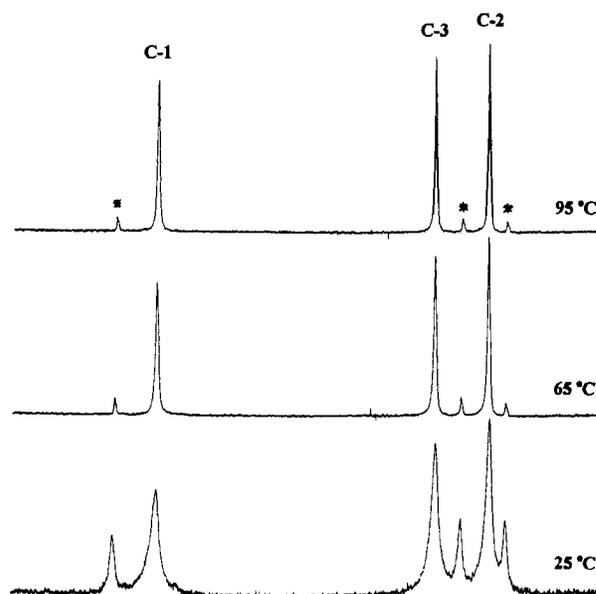


Figure 1. ^{13}C NMR scalar decoupled spectra of P4HB as a function of temperature at a magnetic field strength of 125.4 MHz. A line-broadening of 3 Hz was used. Peaks marked with an asterisk are due to traces of γ -butyrolactone produced during sample preparation.¹⁸

estimated through measurements of the spin-spin relaxation time T_2 of the amorphous phase, using the relationship:

$$\text{NLW} = 1/\pi T_2 \quad (1)$$

It should be mentioned that the values of NLW obtained using (1) are only upper limits to the true natural linewidth, since effects such as diffusion of the macromolecules during the CPMG pulse train also contribute to transverse relaxation.²⁴ Inhomogeneity of the static magnetic field is at most a few Hz with the presently available superconducting magnets, and can be safely ignored for the purpose of this study.⁸

Table II. Linewidths (in Hz) of the amorphous ^{13}C peaks of P4HB by various line-narrowing solid-state NMR methods at room temperature and at a magnetic field strength of 75.4 MHz

	C-1	C-2	C-3	C=O
Scalar-decoupled ^a	109	96	91	172
Magic-angle spinning ^b	39	45	44	39
Natural linewidth (NLW)	19	19	18	—
Dipolar decoupling/magic-angle spinning ^c	59	48	40	35

^a Decoupling field ~ 4 KHz. High-power ^1H decoupling of ~ 60 KHz did not further narrow the ^{13}C peaks.

^b MAS at 3.5 KHz, and zero proton decoupling.

^c MAS at 3.5 KHz, and high-power proton decoupling of $\gamma\text{H}_1 \approx 60$ KHz.

Table III. Linewidths of the ^1H Peaks of P4HB and P3/4HB-18 As a Function of Temperature Obtained from High-Resolution Spectra at a Magnetic Field Strength of 500 MHz

T ($^{\circ}\text{C}$)	P4HB (Hz)			P3/4HB-18 (KHz)	
	H—1	H—2	H—3	T ($^{\circ}\text{C}$)	H^b
25	737	— ^a	—	25	2.4
35	510	—	—	40	2.0
50	367	372	—	60	1.8
65	163	165	136	75	1.7
80	133	137	125	85	1.6
95	120	130	118	95	1.6

^a Overlap between H—2 and H—3 did not allow the evaluation of their linewidths.

^b The ^1H spectrum of this copolymer consisted of a single broad peak (see text).

Magnetic susceptibility in the amorphous phase is governed by either macroscopic or microscopic irregularities present in the sample. Macroscopic inhomogeneities could arise from bubbles, fissures, or other structural irregularities within the sample. This source of contributions to the linewidth necessitates very careful NMR sample preparation.¹¹ Microscopic inhomogeneities in semicrystalline polymers are generated by crystallites and interfacial structures. Due to the different effective diamagnetic susceptibility of the crystallites, equivalent nuclei in the amorphous phase experience slightly different magnetic fields. Daskocilova and Schneider have discussed²⁵ a model for the linewidth of a liquid dispersed in a solid matrix. They showed that this type of broadening can be eliminated by MAS at frequencies greater than the linewidth contribution.

Another significant line-broadening factor is incomplete motional narrowing. This mechanism has been extensively discussed^{7,26} and may involve two different types of motion. In the first case, motion is random and isotropic, but takes place at a relatively slow rate so that all angular space is not sampled or averaged in a time interval equal to T_2 . In the second case, motion is fast but anisotropic, and narrows the amorphous ^{13}C peaks to linewidth values of the order of several hundred Hz. Because the motion is spatially inhibited a residual and effectively static dipolar component exists, which is responsible for the observed LWs. The two types of motion have quite different spectral densities, and so they can be discriminated by performing MAS experiments.¹⁴ If motion in the amorphous phase is relatively slow but isotropic, MAS at currently available frequencies is not fast enough to further narrow the ^{13}C lines. However, MAS will average out dipolar broadening

resulting from static and/or restricted angular amplitude motional components up to the MAS frequency.

RESULTS

Poly(4-hydroxybutyrate)

Figure 1 depicts the scalar decoupled ^{13}C NMR spectra of P4HB as a function of temperature at a magnetic field strength of 125.4 MHz, obtained without MAS. Peaks marked with an asterisk are due to traces of γ -butyrolactone produced during sample preparation.¹⁸ It can be seen in Figure 1 that the backbone methylene carbons C-1, C-2 and C-3 give relatively broad signals at room temperature, which become narrower with increasing temperature above the melting point. Figure 2 depicts the ^{13}C linewidths of the three methylene backbone carbons of amorphous P4HB as a function of temperature at two magnetic fields. These linewidth values were calculated from spectra analogous to those of Figure 1 (e.g., scalar decoupling of ~ 4 KHz and no MAS), and each point represents the average of two different experiments. The natural linewidth values, NLW, for each carbon atom, calculated by eq. (1) from the experimentally measured spin-spin relaxation times T_2 , are also shown in the same figure. The three methylene carbons have similar linewidths LW within the experimental uncertainty of $\pm 10\%$ at each temperature and for a given field. The same is true for the respective natural linewidths, NLW. However the NLWs appear to be field-independent, while the linewidths, LW, display a definite field dependence, which persists also in the melt

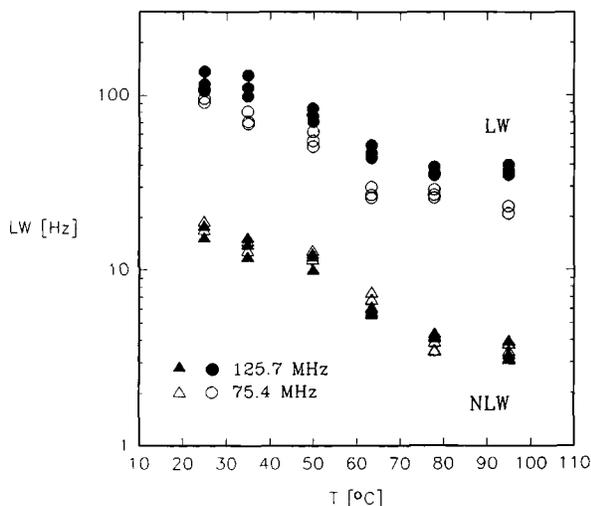


Figure 2. Full linewidths, LW, and natural linewidths, NLW, of the three backbone methylene carbon atoms of P4HB as a function of magnetic field and temperature. Spectral conditions: scalar decoupling of $\gamma H_1 \approx 2\text{--}4$ KHz; no MAS applied.

($T_m = 54^\circ\text{C}$). This suggests that at least one of the field-dependent broadening mechanisms is operating both in the amorphous and in the molten state. Since the NLWs are almost an order of magnitude smaller than the measured linewidths at all temperatures and in both fields, it can be concluded that dipolar relaxation is a minor contributor to the linewidth for P4HB. This is not surprising, as the only elastomer showing ^{13}C lines dominated by the natural linewidth is poly(isobutylene),^{13,17} due to its relatively slow backbone motion with correlation time $\tau_c \sim 10^{-7}$ s. ^{13}C spin-lattice relaxation time measurements in semicrystalline P4HB have shown¹⁸ that throughout the temperature range examined in the present study, the local dynamics of the P4HB backbone are well into the extreme narrowing limit. Analysis of the relaxation data of P4HB by dynamic modeling showed²⁷ that the correlation time for backbone segmental motion decreases from 0.94 ns to 0.022 ns over the temperature range 25–95°C. Thus motion in the amorphous phase is at least two orders of magnitude faster in P4HB than in polyisobutylene.

Another interesting feature in Figure 2 is the behavior of both LWs and NLWs as the melting point is crossed. The NLWs do not show any type of discontinuity as the transition from the amorphous phase to the melt takes place. This is somewhat surprising, since it has been argued²⁸ that in the rubbery state T_2 s are dominated by long-range motions with a negligible contribution from the local dynamics of

the polymer chain. If the former was the case, a pronounced effect on the T_2 s would have been observed at temperatures near the melting point temperature, where any motional restrictions imposed on long range motions by the presence of crystallites should vanish. ^{13}C spin-lattice relaxation times, T_1 , and NOEs, have also been found to be continuous over the melting point for P4HB,¹⁸ and other semicrystalline polymers.^{16,26,29} It is concluded that the natural linewidth of the ^{13}C lines of P4HB, as measured by the CPMG pulse sequence, does not depend strongly on the presence of the crystalline phase.

Contrary to NLWs, the full linewidths of P4HB at both magnetic fields show evidence of reaching a plateau at temperatures above 54°C (Fig. 2). A similar temperature dependence of the ^{13}C linewidths above the melting temperature has been reported recently for poly(β -hydroxyoctanoate) at a single field strength.²⁹ No levelling off above the melting point has been observed for linear and cross-linked polyethylene.¹⁶ This type of temperature dependence suggests that the increase in the linewidth with decreasing temperature below T_m is intimately connected with the presence of a crystalline phase in the bulk. To further illustrate this, we have plotted in Figure 3 the residual linewidths, RLW, of P4HB calculated as

$$\text{RLW} = \text{LW} - \text{NLW} \quad (2)$$

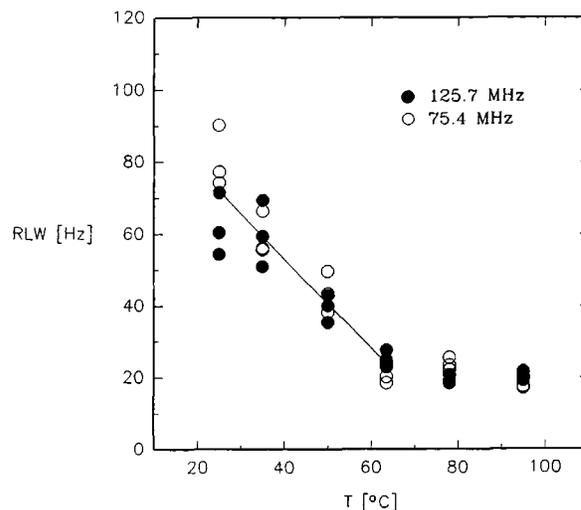


Figure 3. Residual linewidths, RLW, of the three backbone methylene carbon atoms of P4HB as a function of temperature at two magnetic fields. The residual linewidths at 125.4 MHz have been multiplied by 0.6 to show that the data scale linearly with magnetic field strength.

at each temperature, and at both fields. In addition, the residual linewidths at the higher field have been multiplied by $\frac{3}{5}$, the ratio of the two magnetic field strengths, in order to check if any field-independent contribution to the linewidth exists for P4HB. Figure 3 shows that the RLWs are more or less linearly dependent on the magnetic field strength in both the amorphous phase and in the melt, and that no field-independent contribution to the linewidth exists. Thus residual static dipolar interactions due to incomplete motional narrowing can be excluded as a broadening factor in the temperature range examined.

Figure 3 demonstrates the leveling off of the residual LWs above the melting point, where the effect of the crystalline regions has been removed. Despite the absence of crystallites, P4HB RLWs are found to be field dependent in the melt. This observation suggests that chemical shift dispersion and possibly magnetic susceptibility effects contribute to line-broadening in the melt. In an earlier study, Dechter et al.¹⁶ also reported field-dependent ^{13}C linewidths, for polyethylene in the melt. In their study they concluded that magnetic susceptibility was the major contributor to the LW in the melt, with a smaller contribution from dipolar broadening.¹⁶

A mechanism of bulk magnetic susceptibility of the type discussed by Dosekocilova and Schneider²⁵ (see above) seems unlikely in the melt.¹⁶ However, recent studies of PE melts by ^1H spin-spin relaxation have provided evidence that ordered regions with high segmental density persist at temperatures well above the crystalline melting point.³⁰ Koch et al.³¹ and Bachus and Kimmich³² assigned the differences between the ^1H FID of molten PE and the response to a CPMG^{19,20} sequence to local field inhomogeneities within the sample. It was suggested^{31,32} by these authors that the inhomogeneities arise from the presence of microscopic voids²⁴ in the polymer matrix. Thus, despite the absence of crystallites, magnetic susceptibility differences arising from factors such as entanglements, physical cross-links, residual order regions, voids, etc., persist in the melt and could result in a strong field dependence of the ^{13}C residual linewidths, as was observed for P4HB.

In the amorphous phase at temperatures up to T_m , the linewidths in Figure 3 decrease with increasing temperature. To illustrate the mechanisms responsible for line-broadening in this phase, we have conducted solid-state ^{13}C NMR experiments at room temperature and at a resonance frequency of 75.4 MHz to check the effect of dipolar decoupling and magic angle spinning on the amorphous linewidths. The results of these experiments are sum-

marized in Table II, and refer to the *amorphous* peaks of P4HB as observed with solid-state NMR techniques.^{18,22} MAS at 3.5 KHz without any decoupling reduced the amorphous LWs of the methylene carbons from about 100 Hz to a value of ~ 40 Hz. Additional dipolar decoupling of ~ 60 KHz had no narrowing effect on the amorphous LWs. Since the NLW at room temperature is equal to 18–19 Hz, these experiments show that in the amorphous phase a residual LW of about 20 Hz is present, which cannot be further reduced by DD or MAS. The value of 20 Hz is the same with the residual methylene carbon LW observed in the melt at the same magnetic field strength (Fig. 3). This suggests that in both amorphous and molten phases, a ^{13}C chemical shift dispersion of ~ 0.26 ppm due to conformational variations in the backbone is present.

The MAS removable component of the ^{13}C linewidth in the amorphous phase could be attributed to residual chemical shift anisotropy (CSA) due to incomplete motional narrowing, and/or magnetic susceptibility effects. To clarify this, we have performed ^1H MAS experiments at room temperature with variable spinning rate. The ^1H MAS spectra of P4HB from this series of experiments are presented in Figure 4. It can be seen that spinning at a rela-

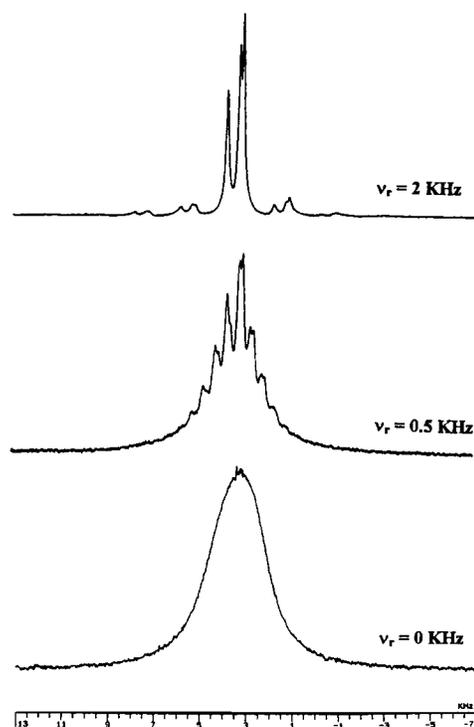


Figure 4. ^1H MAS spectra of P4HB at room temperature as a function of spinning rate ν_r , at a magnetic field of 300 MHz.

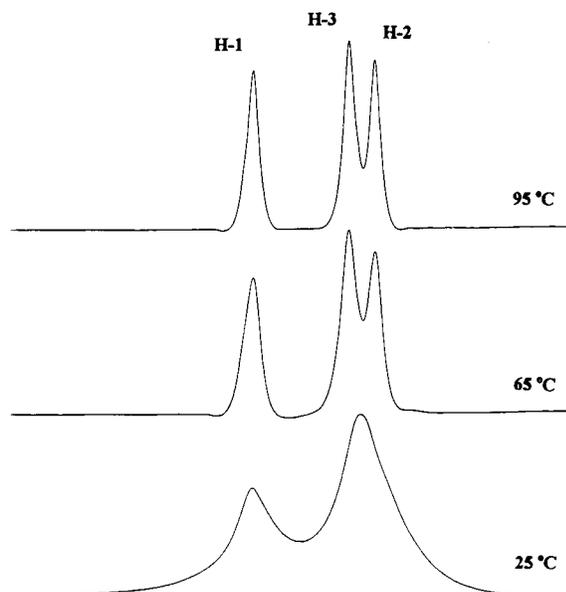


Figure 5. High-resolution ^1H NMR spectra of P4HB as a function of temperature at a magnetic field of 500 MHz.

tively low rate of 500 Hz produces a manifold of sidebands, which get lower in intensity and are removed from the main peaks as the spinning rate increases. This observation, in conjunction with the solid-state ^{13}C NMR results presented above, indicates that most of the broadening at room temperature is inhomogeneous, and can be attributed to magnetic susceptibility effects.¹⁵ From the above experiments the homogeneous linewidth of the ^1H lines at room temperature and at a field of 300 MHz is estimated to be in the range 120–130 Hz.

Figure 5 presents selected high-resolution ^1H NMR spectra of P4HB at a frequency of 500 MHz, as a function of temperature. The proton linewidths as a function of temperature are reported in Table III. It can be seen that linewidths in the amorphous phase are large,³³ but are reduced above the melting point (54°C). The resolution of the spectrum also improves with increasing temperature. The ^1H linewidths at the highest temperature are in the same range as those obtained by MAS, although the latter (Fig. 4) are at a smaller field strength. The abrupt narrowing of the proton lines observed in the melt is similar to what is observed for the carbon spectra (Fig. 3), and could be attributed to averaging of the local field inhomogeneities caused by magnetic susceptibility effects. Thus the presence of the crystallites in the semicrystalline polymer affects in similar ways both the ^1H and the ^{13}C linewidths, as expected.

From the experiments presented so far, it is concluded that differences in bulk magnetic suscepti-

bility due to the presence of crystallites are the major contributor to the line broadening of both ^{13}C and ^1H spectra of P4HB in the amorphous phase. A ^{13}C broadening contribution of 0.26 ppm from isotropic chemical shift dispersion due to conformational variations is present in both the amorphous phase and the melt.

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)

Figure 6a depicts the full linewidths of the methine, C-4, and methylene, C-5 backbone carbons of the

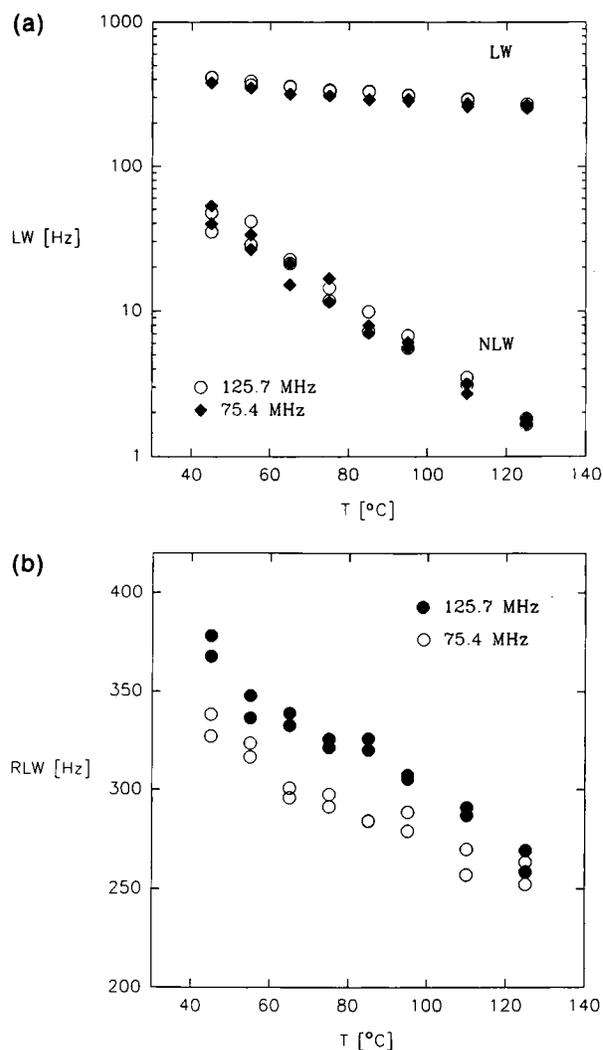


Figure 6. (a) Full linewidths, LW, and natural linewidths, NLW, of the methine (C-4) and methylene (C-5) backbone carbon atoms of P3/4HB-18 as a function of temperature at two magnetic field strengths. (b) Residual linewidths of the C-4 and C-5 backbone carbon atoms of P3/4HB-18 as a function of temperature at two magnetic field strengths. Spectral conditions same as in Fig. 2.

3HB unit of P3/4HB-18, 2, at two field strengths as a function of temperature. The reported LWs are from scalar-decoupled spectra without MAS. Due to the low (18%) 4HB content of the copolymer, it was not possible to obtain accurate LWs for the 4HB carbon atoms from these spectra. Included in Figure 6a are also the natural linewidths (NLW) of the same carbons, as measured by the CPMG pulse sequence.

Both LWs and NLWs decrease with increasing temperature, the effect being more pronounced for the NLWs. Also the full linewidths LW show a small field dependence, thus there is a measurable contribution to line-broadening from field-dependent mechanisms. However, it is clear from Figure 6a that the major contributor to the amorphous linewidth for P3/4HB-18 must be field-independent, so it must arise from either the natural linewidth, or residual dipolar interactions not averaged out by molecular motion. Figure 6a clearly shows (note the logarithmic scale) that the first factor has to be eliminated. The NLWs are in the range 1–50 Hz, and thus contribute little to the broadening observed for the ^{13}C lines in the temperature range 45–125°C. Also to be noted is that the P3/4HB-18 NLWs of Figure 6a are field-independent, and show a steeper decrease with increasing temperature compared to P4HB (Fig. 2).

To get an estimate of the field-dependent contributions to the LW, we calculated the residual LWs for the two backbone carbon atoms of P3/4HB-18 according to eq. (2). These results are plotted in Figure 6b. Dechter et al.¹⁶ showed that the difference in the linewidth with magnetic field strength can be used to separate the contribution of field-dependent and field-independent line-broadening mechanisms. The application of their simple calculation¹⁶ in the data of Figure 6b shows that at 75.4 MHz and over the whole temperature range, the field-dependent contribution to the amorphous ^{13}C linewidth amounts to 15–20%. The rest of the line-broadening should be then attributed to residual dipolar interactions from incomplete motional narrowing, as concluded in the previous paragraph.

To elucidate the nature of motion that is responsible for the residual line-broadening observed for this copolymer, we have performed MAS solid-state ^{13}C NMR experiments at a temperature of 45°C, the results of which are shown in Table IV. As for P4HB, the linewidth data of Table IV refer to the *amorphous* peaks of P3/4HB-18 as observed with solid-state NMR techniques.^{18,22} It can be seen that MAS substantially narrows the ^{13}C lines, and that further narrowing is not achieved by high-power decoupling.

The narrowing is greater than 15–20%, hence it cannot result from averaging out just bulk magnetic susceptibility inhomogeneities sensitive to MAS,²⁵ or residual CSA effects. The above experiments suggest that motion in the amorphous phase is fast but anisotropic, and that line-broadening from incomplete motional narrowing is due to the spatial inhibition of motion by factors such as crystallites or chain constraints.

Despite the narrowing observed by MAS, a residual LW of about 100 Hz remains to be accounted for the 3HB unit backbone carbons, while for the 4HB unit this value is about 40–50 Hz (Table IV). Part of this difference is due to the different natural linewidths of the two types of repeat unit. Application of high-power dipolar decoupling does not further narrow the lines, so any contribution from higher frequency motions (between 4 and 60 KHz) has to be excluded.¹⁶ Since any residual CSA effects should have been eliminated by MAS, it can be concluded that the residual linewidth could be due either to a distribution of isotropic chemical shifts, or anisotropic bulk magnetic susceptibility effects not removed by MAS. Earl and Vanderhart,³⁴ and Dechter et al.¹⁶ have used similar arguments to account for the residual ^{13}C LW observed for polyethylene in the amorphous phase.

^1H MAS experiments performed at various spinning rates agree with the proposed mechanism for line-broadening in P3/4HB-18, and the respective proton spectra are shown in Figure 7. Some resolution is introduced to the spectrum by increasing the spinning rate, in addition to moderate narrowing, but no spinning side bands are produced. This observation elucidates the small contribution of susceptibility inhomogeneities to the ^1H linewidth,¹⁵ similarly to what was observed for the ^{13}C lines. In addition, it was not possible to obtain significant narrowing of the P3/4HB-18 ^1H peaks by raising the temperature. These observations strongly suggest chemical shift dispersion as a major contributor to the ^1H linewidths. ^1H spectra of this polymer in the temperature range 25–95°C consisted of a single broad peak with a small shoulder toward low fields. The variable temperature ^1H linewidths of this peak, obtained by deconvolution, are presented in Table III.

DISCUSSION

Several experimental findings presented in this report deserve further discussion. The strong influence of the crystalline phase on the amorphous carbon

linewidths in semicrystalline polymers,^{9,11,16} has been demonstrated in this study. It was also shown that there are a number of broadening mechanisms by which this influence can be exerted. In the case of P4HB, the semicrystalline polymer is very close to its melting point at room temperature. The melting transition is rather broad for P4HB (15–20°C), as for most linear polymers, and changes in the bulk susceptibility caused by the gradual melting of the crystallites are probably responsible for the decrease in the ¹³C linewidths observed as a function of temperature slightly below T_m . In the melt, chemical shift dispersion accounts for the observed ¹³C linewidths of P4HB, although residual susceptibility effects may not be totally removed as some partial ordering still persists.²⁷

On the contrary, crystallinity affects the amorphous linewidths of P3/4HB-18 via a different line-broadening mechanism. In this case broadening is caused by restrictions imposed by crystallites and/or chain constraints on the angular amplitude of a low-frequency (<3.5 KHz) motional component present in the amorphous phase. This agrees with the small decrease observed in the carbon linewidth with increasing temperature (see Fig. 6a), well below the melting point of P3/4HB-18 ($T_m \sim 165^\circ\text{C}$). When the ¹³C linewidth data of Figure 6b are plotted in an Arrhenius format, an activation energy of ~ 1 Kcal/mol is obtained, and a similar value can be extracted from the ¹H linewidth data of P3/4HB-18 in Table III. This value is clearly too low to be ascribed to a very slow motion such as chain diffusion,¹⁵ or any other type of thermally activated long-range motion. It presumably reflects an increase in the angular amplitude of a slow motional component with increasing temperature.^{15,16} It should be noted that a similar value of 1.5 Kcal/mol has been reported for the temperature dependence of the proton MAS linewidths of *cis*-1,4-polybutadiene.¹⁵

In an attempt to further test our results, we have examined films of the two samples under cross-po-

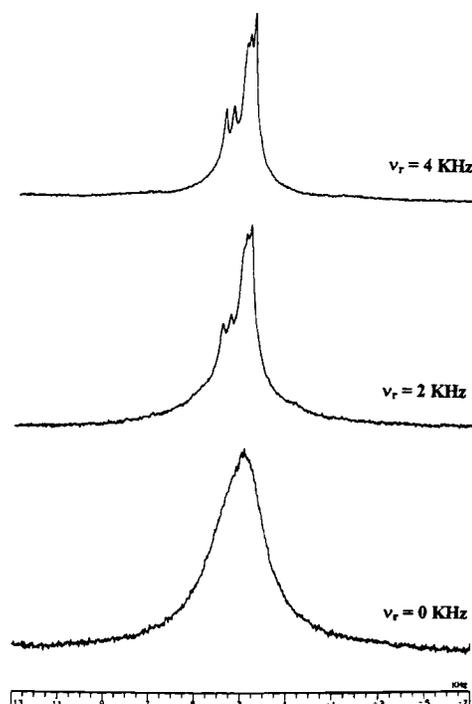


Figure 7. ¹H MAS spectra of P3/4HB-18 at room temperature as a function of spinning rate, ν_r , at a magnetic field of 300 MHz.

larized light. This experiment revealed the existence of large (50–100 μm) birefringent domains for the copolymer P3/4HB-18. Such crystalline structures could be responsible for the restriction in the angular amplitude of low frequency motion in the amorphous phase, and the large linewidths observed for this system.⁹ On the contrary, in P4HB crystalline regions were less distinctive, and of much smaller dimensions than in the copolymer. The smaller crystalline domain dimensions in P4HB are not surprising, as the NMR sample preparation involved quenching from the melt at room temperature. For P4HB this means quenching only $\sim 30^\circ\text{C}$ below the melting point, so large crystalline domains are less

Table IV. Linewidths (in Hz) of the Amorphous ¹³C Peaks of P3/4HB-18 By Various Line-Narrowing Solid-State NMR Methods at a Temperature of 45°C and at a Magnetic Field Strength of 75.4 MHz

	C—1	C—2	C—3	C—4	C—5
Scalar-decoupled ^a	~ 300	303	308	423	380
Magic-angle spinning ^b	54	47	73	120	104
Natural linewidth (NLW)	~ 20	~ 20	~ 20	53	42
Dipolar decoupling/magic-angle spinning ^c	49	37	75	115	107

^a Decoupling field ~ 4 KHz. High-power ¹H decoupling of ~ 60 KHz did not further narrow the ¹³C peaks.

^b MAS at 3.5 KHz, and zero proton decoupling.

^c MAS at 3.5 KHz, and high-power ¹H decoupling of $\gamma H_1 \approx 60$ KHz.

likely to form. In a series of articles, Mandelkern,¹¹ and Komoroski and co-workers¹⁶ showed that for polyethylene the size of the crystalline superstructure played a major role in modulating the ^{13}C linewidth, rather than the overall percentage of crystallinity.³⁵ This is particularly important, since the two polymer systems studied in this contribution have approximately the same level of crystallinity (see Table I),^{18,27} but different crystalline domain structure.

The picture emerging from the combined NMR and optical microscopy data is in agreement with the mechanical properties of the two polymer systems. Doi and co-workers^{1,36} reported a large decrease in the tensile strength and the elongation to break (%) on going from P4HB to a P3/4HB-18 films (Table I). Since both systems have approximately the same crystallinity, the differences in mechanical properties could reflect, apart from their large difference in melting temperature and segmental motion,²⁷ differences in the size and distribution of the crystalline domains, which are expected to affect the elastomeric properties of bulk semicrystalline polymers.

An important aspect of the spin-spin relaxation time T_2 analysis presented here is that it demonstrates the reasons for which T_2 s extracted directly from ^{13}C NMR linewidths cannot be accounted for by dynamic models based on T_1 and NOE data alone.¹⁶ It was shown in the present study that, apart from notable cases such as poly(isobutylene),¹³ natural linewidths are minor contributors to the amorphous high-resolution ^{13}C linewidth. Although this argument has been frequently shown to be true so far,^{8,9,16} it is demonstrated for the first time, to our knowledge, in a variable temperature/variable field study. Another interesting point is the field independence of the spin-spin relaxation times, T_2 , a condition that was shown to hold for all the backbone carbon atoms in the two polymer systems, over the entire temperature range studied.

Finally, one notes a possible correlation of factors such as the glass-transition temperature T_g , and the melting point T_m , with the line-broadening mechanisms operating for different amorphous polymers. For example both polymers studied so far for which bulk magnetic susceptibility dominates, *trans*-polybutadiene¹³ and P4HB, are elastomers with T_g s in the range -50 to -60°C , and T_m around 50°C . On the other hand, for polyethylene^{13,16} and P3/4HB-18, with melting point temperatures well above 100°C , incomplete motional narrowing was found to dominate ^{13}C line-broadening close to room temperature. The extension of NMR studies of this type

to include more polymers is necessary for a better understanding of the underlying physics, and to establish the conditions under which line-narrowing schemes are useful in solid-state NMR applications to polymer science.^{9,16}

CONCLUSIONS

Results presented in this contribution demonstrate the ability of NMR spectroscopy to probe the various motional components present in semicrystalline polymers above T_g . ^1H and ^{13}C DD/MAS coherent averaging experiments complement the conclusions drawn from a variable field and variable temperature high resolution ^{13}C and ^1H NMR analysis of linewidths. It was shown that the crystalline phase plays a crucial role in modulating the ^{13}C linewidths of the amorphous regions of P4HB and P3/4HB-18. Furthermore, this influence can be realized by different line-broadening mechanisms for different polymers, depending among other things on their physical properties and the temperature range at which the experiments are conducted.

The main ^{13}C and ^1H line-broadening mechanism operating for P4HB in the amorphous phase was found to be magnetic bulk susceptibility, causing LWs to decrease accompanying the gradual melting of crystallites as the melting temperature is approached. For P3/4HB-18, residual dipolar interactions due to a relatively slow and restricted in amplitude slow motional component of the anisotropic motion of the polymer backbone were the major contributor to the ^{13}C linewidth. In the melt, chemical shift dispersion is the major contributor to the amorphous linewidth in P4HB, although magnetic susceptibility effects caused by regions displaying residual order cannot be excluded. ^{13}C spin-spin relaxation was found to play a minor role as a line-broadening factor for both polymers.

The picture emerging from the NMR experiments regarding the crystalline morphology of the two polymers at temperatures close to room temperature is consistent with their mechanical properties. Some correlations between the physical properties of polymers and NMR line-broadening mechanisms are emerging, but further work is clearly needed toward this direction.

Assistance from Dr. F. Morin in obtaining the solid-state NMR spectra, is appreciated. We are grateful to Dr. D. VanderHart, National Institute of Standards and Technology, and Prof. Photis Dais, University of Crete, for helpful discussions, and some insightful suggestions. This

study was supported by Xerox and the Natural Sciences and Engineering Research Council of Canada.

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Received November 6, 1995

Revised February 12, 1996

Accepted February 22, 1996