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Observation of Longitudinal Acoustic Mode in Poly(β-hydroxybutyrate)

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ABSTRACT: A Raman active longitudinal acoustic mode (LAM) in the 15 cm^{-1} region has been observed in a biodegradable thermoplastic, poly(β-hydroxybutyrate) (PHB). The inverse relationship between the long period measured by small-angle X-ray scattering and the band frequency was observed. In addition, the intensity of this vibration was found to be extremely intense as is characteristic of longitudinal acoustic modes. This observation is especially intriguing since the chemical structure of PHB is significantly different from those of all known polymers exhibiting LAM bands.

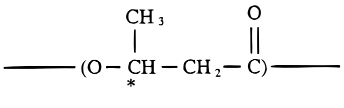
Introduction

Since it was first observed in 1949,[1] longitudinal acoustic modes (LAM) for a number of semicrystalline polymers have been well-established. For polyethylene and *n*-alkanes, in particular, the frequency ν_m of this Raman mode has been found experimentally to be well-described by the relation

$$\nu_m = (m/2cL)(E/\rho)^{1/2} \tag{1}$$

where m is the integer order of the mode, c is the speed of light, L is the length of the vibrating chain or chain segment, E is the elastic modulus of the chain, and ρ is the single chain density.[1−3] Only modes of odd m are Raman active. The chain length versus frequency dependence given by this relation provides an unique morphological tool by which it may be possible to gain insight into the crystalline chain segment length distribution associated with crystalline lamella.[4] LAM has also been observed in poly(tetrafluoroethylene),[5] isotactic polypropylene,[6,7] poly(oxymethylene),[7] and poly(ethylene oxide)[8,9] as well as in some linear aliphatic polyesters.[10−12]

We report here the observation of LAM in a thermoplastic biodegradable polyester, poly(β-hydroxybutyrate) (PHB).



$$-\!\!-\!\!-(O-\underset{*}{\overset{\overset{\textstyle CH_3}{|}}{CH}}-CH_2-\overset{\overset{\textstyle O}{\|}}{C})-\!\!-\!\!-$$

First isolated in 1925, PHB is an optically active polymer produced by a bacterial fermentation process.[13] The polymer is produced as an energy reserve material by a variety of bacteria.[14] It is presently made commercially by Imperial Chemical Industries (ICI) under the trade name Biopol. As previously reported, PHB, due to its exceptional purity and chemical regularity, is a model material for fundamental studies of polymer crystallization and nucleation.[15] Morphological aspects can be complex, however. Studies have suggested the presence of a strain induced β-form of PHB in which the chains are in a highly extended state.[16,17] It has also been reported that, spread at the air−water interface, PHB changes with increasing surface pressure from an expanded monolayer form to a crystalline monolayer and subsequently to a crystalline bilayer in the helical form.[18] Others suggest that the chains crystallize in the β-form at the air−water interface.[19] The observation of LAM in PHB reported in this study provides an additional morphological tool by which these aspects of polymer structure may be further characterized.

The identification of a LAM in PHB is also intriguing from a spectroscopic point of view. In order to develop LAM as a more widely used method for characterizing polymer morphology, numerous attempts have been made to observe LAM-like vibrations in other non-polyethylene-like polymers. In studies along these lines, simple linear aliphatic chains were modified by the placement of well-spaced ester groups along the polymer backbone. A LAM-like vibration was observed.[10−12] Attempts, however, with structures deviating significantly from that of polyethylene have not resulted in much success. Polymers such as well-defined model polypeptides are notable failures.[20−22] Successful observation of LAM has mainly been confined to polymers possessing fairly simple chain conformations and chemical units. PHB differs, in its chemistry and in its equilibrium conformation, significantly from other polymers in which LAM has previously been observed. Thus, in addition to its use as a morphological tool, LAM in PHB provides an opportunity to study the origin of LAM in a structurally more complicated polymer than those in which LAM has been reported by earlier workers. As such, it should assist in the isolation of the factors that dominate the appearance or nonappearance of LAM in specific polymer chains, leading to a better understanding of LAM in non-polyethylene-like structures.

Experimental Section

Poly(β-hydroxybutyrate) of M_n = 133 000 and propylene carbonate were obtained from Aldrich Co. Single crystals of poly(β-hydroxybutyrate) or PHB were grown over a range of crystallization temperatures from dilute (0.04 % (w/v)) propylene carbonate solution by using the self-seeding technique.[23] Samples were first dissolved at 155 °C and quenched to 45 °C, where they were kept for 24 h. Crystal seeds were then obtained by heating the solution slowly (~20 °C/h) until the

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solution cleared. With the seeded solution, highly crystalline samples were grown at specific crystallization temperatures for ~48 h. The solutions were then filtered, forming oriented single crystal mats. The mats were subsequently rinsed with hot propylene carbonate to remove any residual noncrystallized material. This was followed by a final rinsing with methanol to ensure the removal of all propylene carbonate.

Raman spectra were obtained with a Jobin-Yvon U-1000 laser-Raman spectrometer, excited using the 5145 Å line of a Spectra Physics 165-08 Ar ion laser. Bandpass was maintained at 2 cm^{-1} at 5000 Å. Laser power at the sample was maintained at 75 mW. Due to residual fluorescence in some samples, higher laser power may alter the as-prepared samples. The scattered intensity at each frequency was collected for 13–17 s to accumulate sufficient counts to provide an acceptable signal to noise ratio. The scattered intensity collected at the peak for a given LAM spectra was roughly 1000 counts/s. Rayleigh scattering near the excitation frequency was removed using the fitting routine in the data analysis package Lab Calc provided by Galactic Industries Corp. The spectra were also corrected for temperature and frequency effects.[4,24]

Small-angle X-ray scattering of the single crystal mats was obtained with a Rigaku Denki instrument with a camera distance of 230 mm and pinhole collimation. The crystal mats were oriented in the plane of the X-ray beam. Long spacings were measured from the X-ray patterns without further correction.

Results and Discussion

Indicating sample uniformity, second order reflections in X-ray corresponding to lamella long spacings were detected for all single crystal mats. A typical small-angle X-ray scattering (SAXS) pattern is shown in Figure 1. X-ray studies of PHB indicate that PHB packs in an orthorhombic unit cell in a left-handed 2_1 helix with a fiber repeat of 5.96 Å.[17] Previous small- and wide-angle X-ray studies on PHB single crystals indicate the presence of little or no chain tilt; the chains are essentially perpendicular to the lamellar surface, thus making any correction for chain inclination unnecessary.[15] The long spacings measured are listed in Table 1.

The low-frequency Raman spectrum of PHB single crystals crystallized at temperatures ranging from 25 to 87 °C is shown in Figure 2. The as-obtained spectra show a low-frequency band present near 15 cm^{-1} for all samples. The band moves to lower frequencies as the crystallization temperature is increased. This corresponds with longer lamella fold lengths, as indicated by the small-angle X-ray measurements. When the Raman data are corrected by subtraction of the Rayleigh background and then for the effect of temperature, the band near 15 cm^{-1} has a half-width that is about 5 cm^{-1} or less. The frequency and for the most part the half-width of the band both decrease with increasing crystallization temperature, as summarized in Table 1. A second band is apparent near 9 cm^{-1} in some samples. Given the relative intensity of the two low-frequency Raman bands and the fact that only one lamella fold length distribution is indicated by the small-angle X-ray measurements, it is unlikely that the second band is caused by a second distinct lamella fold length distribution. However, due to substantial overlap with the Rayleigh line, it was not possible to isolate this low-frequency band during subtraction of the background.

The strongest evidence that the band near 15 cm^{-1} is due to the LAM associated with the crystalline lamellae is the linear dependence of the band frequency on the reciprocal lamellar thickness, as given by eq 1. A plot of the peak frequency of the band near 15 cm^{-1} from the temperature and frequency corrected spectrum against the inverse long spacing measured by SAXS is shown in Figure 3. In this plot, the data are fitted by least squares to a straight line which essentially intercepts the origin. Failure of such a line to pass through the origin has been interpreted in other LAM studies as indicating the following: (1) presence of an amorphous or loosely folded layer of material at the lamellar surface thus affecting the measured X-ray long spacing[3,11] or (2) anharmonic effects resulting from the significant chain-end amplitude associated with the LAM-1 vibration.[25] LAM originates from the ordered chain segments in the crystalline core and may be perturbed by the presence of the amorphous layer. That

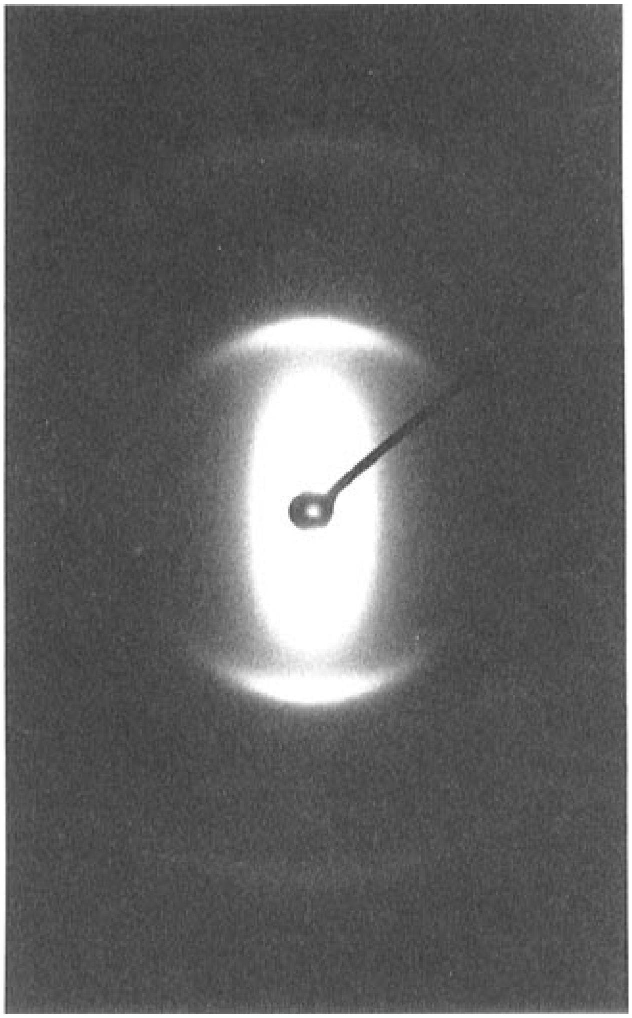

Figure 1. Small-angle X-ray pattern observed for PHB single crystal mat with the X-ray beam incident in the plane of the mat.

Table 1. LAM Frequencies and SAXS Long Spacings of PHB Single Crystal Mats

T_c[a] (°C)	ν_{obt}[b] (cm^{-1})	ν_{base}[c] (cm^{-1})	ν_{corr}[d] (cm^{-1})	$\Delta\nu_{1/2}$[e] (cm^{-1})	L[f] (Å)
25	17.0	18.8	19.5	5.3	41.9
45	16.8	17.8	18.4	5.5	43.4
60	14.6	16.2	16.6	4.5	49.4
70	14.1	14.6	14.9	3.5	53.1
75	12.9	13.8	14.1	3.7	59.2
87	10.7	11.3	11.9	3.6	62.3

[a] Crystallization temperature. [b] As-obtained LAM peak position without corrections. [c] LAM peak position following base-line subtraction. [d] LAM peak position following base-line subtraction and corrections for temperature and frequency effects. [e] Measured half-width of ν_{corr}. [f] Long spacing as measured by small-angle X-ray scattering.

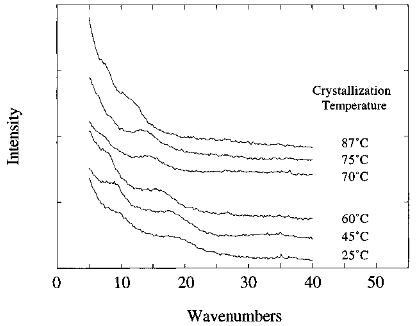

Figure 2. As-obtained low-frequency Raman spectra of PHB single crystal mats crystallized at temperatures ranging from 25 to 87 °C.

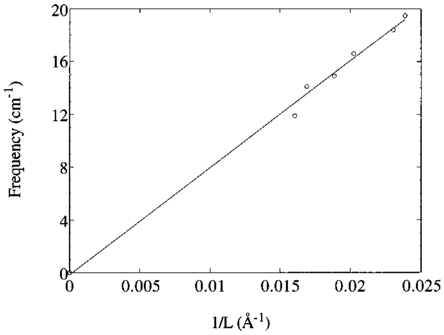

Figure 3. Plot of temperature and frequency corrected Raman frequency centered around 15 cm^{-1} versus L^{-1} for PHB single crystals. L is the measured small-angle X-ray long spacing.

the line does essentially pass through zero for PHB may indicate that the long spacings measured by X-ray correspond closely with the thickness of the crystalline lamella core. This is consistent with earlier observations by Barham et al. in which they suggested that given the thickness and observed values of crystallinity for PHB single crystals, the fold structure cannot consist of much looseness.[15] The range of lamellar thicknesses indicated in Table 1 allow only 6–11 repeat units/fold stem in PHB single crystals.

Additionally, the intensity of the vibration centered around 15 cm^{-1} is high as is characteristic of LAM bands. The peak height of the low-frequency vibration found in the PHB samples is roughly twice that for the CH_2 bending motion in the 1400 cm^{-1} region. The ν vs $1/L$ dependence and the relative intensity of the low-frequency mode found in these samples together provide strong evidence that the observed mode is LAM. In earlier studies dealing with polyethylene-like chains, the strong intensity is due to the large change in polarizability associated with the long-chain motion of this mode and the Boltzman factor associated with low-lying vibrations.[2,26,27] The polarizability change of the PHB chains for this low-frequency mode has yet to be determined and, in fact, may be quite small. Therefore, the strong intensity observed may simply be due to the frequency/temperature effect.[27]

Using the relation given by eq 1, the single chain elastic modulus within a crystalline lamella for PHB was calculated from the slope of the line fitted to the plot of ν vs $1/L$ in Figure 3. Given the crystal density of PHB to be 1.25 g/cm^3,[17] the single chain elastic modulus was calculated to be 29.6 GPa, a value consistent with that expected for a helix. For example, for isotactic polypropylene the measured value and value calculated by using torsional force constants from a valence force field are 41 and 33 GPa, respectively.[6,28]

LAM in the simplest case for all-trans *n*-alkanes is a symmetric accordion-like longitudinal vibration.[1,2,29] Success in finding LAM in polymers with non-polyethylene-like structures has been very scarce. This can be understood from the fact that force as well as mass perturbations along the chain may lead to coupling of transverse and longitudinal motions. This effect has been shown for a series of linear aliphatic polyesters, mentioned previously, in which well-spaced ester groups act as unbalanced mass units which lead to the presence of several LAM-like modes, each with differing amounts of transverse and longitudinal character.[12] This may provide an explanation for the presence of the second unassigned low-frequency band centered around 9 cm^{-1} found for PHB. With increased structural complexity, these effects may become more significant, leading eventually to the total disruption of any longitudinal acoustic mode. The effect of "perturbing" influences within chains, such as methyl side-group placement on *n*-alkanes,[30] double bond placement in *trans*-alkenes[31] and hydrogen bonds,[32] has been studied and shown to affect this mode to varying degrees in both intensity and frequency.

Interestingly, however, PHB, even with a large number of such perturbing groups comprising a mix of both closely spaced methyl units and ester groups as well as possibly an intermolecular effect between ester groups, clearly exhibits LAM. Furthermore, in contrast to the series of linear aliphatic polyesters mentioned previously, PHB, which forms a 2_1 helix in the crystalline state, is conformationally more complex.[17] The ester groups for the linear aliphatic polyesters were sufficiently well-spaced such that in the crystalline state the chains essentially formed a planar zigzag.[12] Previous normal coordinate analysis of crystalline poly(ethylene oxide) has shown that, as opposed to all-trans polyethylene chains, LAM in helical chains has a significant interchain effect due to the large radial component present in the atomic displacement of LAM for such polymers.[9] Compared with polymers such as isotactic polypropylene, poly(oxymethylene), poly(ethylene oxide), and poly(tetrafluoroethylene) in which LAM has also been observed, PHB is clearly the most unlike polyethylene. Nevertheless, the LAM observed in PHB follows a $\nu \propto 1/L$ dependence quite closely, as evidenced by the straight line fit to the Raman and X-ray data in Figure 3.

In summary, a longitudinal acoustic mode is observed in a bacterially produced and biodegradable polymer, poly(β-hydroxybutyrate) (PHB). Studies are currently underway to further identify the exact nature of this vibration.

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