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Measurement of the Crystallinity of Poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) Copolymers by Inverse Gas Chromatography[†]

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ABSTRACT: Inverse gas chromatography (IGC) studies on semicrystalline polymers provide information supplemental to X-ray and differential scanning calorimetry (DSC) experiments. In this work, studies were made of a series of random copolymers of β-hydroxybutyrate (HB) and β-hydroxyvalerate (HV) ranging from 0–27% in HV content. While X-ray data indicated that the degree of crystallinity remained at about 60% throughout this composition range, DSC and density data indicated a substantial reduction. The IGC experiments confirmed the X-ray results, as did studies by Fourier transform infrared spectroscopy. It is concluded that, for polymers which exhibit isodimorphism (unit cocrystallization), the assumptions involved in calculating the degree of crystallinity for the copolymers from the density or heat of fusion of the pure homopolymers, poly(β-hydroxybutyrate) and poly(β-hydroxyvalerate), are incorrect. Cocrystallization of this type apparently introduces defects in the crystal lattice which reduce the heat of fusion without changing the degree of crystallinity.

Introduction

The prediction of the properties of semicrystalline polymers depends on a thorough understanding of their crystalline structure. The crystalline structures of poly(β-hydroxybutyrate) (PHB) and its β-hydroxyvalerate copolymers (P(HB–HV)) are of particular interest, not only for their market potential as biodegradable thermoplastics[1] but also for their range of properties due to cocrystallization.[2–5] For example, the melting temperature of random isotactic P(HB-*co*-HV) varies from 85 to 180 °C depending on the copolymer composition, yet the degree of crystallinity at room temperature is maintained over the entire range of compositions.[3] Maintenance of a high degree of crystallinity for increasing counit concentration is contrary to the classic Flory treatment of random copolymers[6] in which complete exclusion of the "other" comonomer prohibits crystallization at intermediate compositions. Flory was one of the first to recognize that a class of copolymers would not fit this picture of complete exclusion if the size difference and enthalpic interaction between monomer units were small enough to allow cocrystallization.[2,6]

For P(HB-*co*-HV), different measurement techniques have resulted in different values for the degree of crystallinity. Quantitative results are of particular importance since they set limits on the extent of inclusion of the noncrystallizable counits. The results of X-ray analysis[3,4] show that crystallinity remains nearly constant at above 60% for P(HB-*co*-HV) samples over the entire range of compositions. However, other studies report that crystallinity drops significantly for sample compositions from 0 to 47 mol % HV. On the basis of extrapolation of density data, Mitomo et al.[5] reported that the crystallinity decreases nearly linearly from 81% for the homopolymer PHB to 39% at a composition of 28% HV. Results of calorimetry studies[1] suggest a similar decline in crystallinity, which implies a minimal degree of cocrystallization.

The major uncertainty of these methods is that some knowledge of the values of a given property (e.g., density or heat of fusion) of the 100% crystalline polymer must be assumed. Furthermore, it is assumed that this property varies linearly with both the degree of crystallinity and the copolymer composition. These assumptions surely must be invalid for systems such as P(HB-*co*-HV) where different monomers cocrystallize. For example, when chlorine molecules are included in the crystalline phase of polyethylene, the density does not exhibit simple linear behavior with varying copolymer composition.[7]

Inverse gas chromatography (IGC) is a very useful technique for measuring the degree of crystallinity of polymer samples since it does not depend on assumptions about the properties of the 100% crystalline polymer. In IGC, a column is packed with the sample of interest and the retention behavior of suitable "probe" molecules as a function of temperature is measured. Guillet and Stein[8] were the first to show the advantages of applying IGC to measure the crystallinity of a polymer system. This method was subsequently extended to study the crystallinity of copolymers.[9]

In this study, the IGC approach is used to analyze a random copolyester in which cocrystallization is present. The main goal is to determine the degree of crystallinity of P(HB-*co*-HV) at varying HV compositions.

Experimental Section

P(HB-*co*-HV) bacterial copolymers were produced from industrial-scale batch cultures of *Alcaligenes eutrophus* (Imperial Chemical Industries, U.K.). As noted previously,[1,3,4] bacterial P(HB-*co*-HV) is isotactic, exhibits a high molecular weight, and has a random distribution of comonomers. The viscosity molecular weights of the polymers are given in Table I. The polymers were solubilized by first melting in an evacuated oven, quenching rapidly in liquid nitrogen, and then adding these amorphous samples to either chloroform or 1,1,2,2-tetrachloroethane at room temperature. A thin coating of polymer was deposited onto a Chromosorb G AW-DMCS (acid-washed, dimethyldichlorosilane-treated diatomaceous silicates) chromatographic support by slow evaporation with stirring. After vacuum drying at 60 °C for ca. 24 h (which consequently annealed the samples), the packing material was cooled to room temperature and sieved. The column packing was stored under vacuum for up to several weeks to ensure that full crystallization had occurred and to prevent retention of moisture.

All IGC experiments were performed on a Carle AGC-211 GC equipped with a flame ionization detector (FID). Modifications

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Table I
Molecular Weights and Identification of Polymers

% HV	M_v[21] ($\times 10^3$)	lot no.
0	293	BX IRD
7	164	BX P7/66
21	228	BX PV1
27	526	BX PV13

and additions which were made to completely automate injections and data analysis are described elsewhere.[10,11] This included interfacing the FID electrometer, the automatic injector, and the temperature ramp controller to an IBM-compatible Best MKII computer. The FID signal was averaged at 1000 Hz over 20 ms to increase the signal-to-noise ratio and recorded every 0.6 s. The computer-linked injector was a modified Carle 10-μL microvolume valve (Model 2015) and valve actuator used in conjunction with a custom-made stream splitter. The probe sample size was maintained at approximately 0.01 μL of liquid, in the range of "infinite dilution". To validate the assumption of infinite dilution, measurements were made at various injection sizes to ensure that retention volumes and peak symmetry were independent of peak area. The flow-rate dependence of retention volumes was determined using octane and decane on several P(HB-*co*-HV) columns. There was a small dependence at near-ambient temperatures, but above 55 °C it was proven negligible. A complicating factor in this analysis is the thermal sensitivity of the P(HB-*co*-HV) copolymers.[3] A heating rate of 0.5 °C/min was sufficient to achieve equilibrium conditions without degrading the polymer. The PHB homopolymer degraded near its melting point under the slow heating conditions required for IGC and temperature-dependent FTIR. Loading corrections were made following the method of Courval and Gray[12] and Gray[13] to account for surface effects.

DSC data were obtained on a Perkin-Elmer DSC-2C at scan rates of 20 °C/min. FTIR spectra of the copolyesters were recorded using a Nicolet DX single-beam spectrometer interfaced with a Nicolet 20DX data processor. Polymer samples were coated from solution onto KBr plates, annealed at 60 °C for 24 h, and maintained in vacuo until used. A hot stage with 0.5 °C/min temperature ramping was used. The spectrometer was flushed with N_2 during measurement. All spectra were ratioed to the background to correct mainly for moisture in the air. Baseline correction was employed. At a resolution of 2 cm^{-1}, there is a 3% error in peak area as determined with the instrument software. X-ray crystallinity measurements were made on a Philips powder diffractometer Model PW 1710 equipped with a graphite monochromator and pulse-height analyzer. Nickel-filtered Cu Kα radiation (λ = 0.154 nm) was used. Crystallinity was determined from diffracted intensity data by comparing the relative area under the crystalline peaks with that from amorphous scatter, as described by Ruland.[14]

Crystallinity Measurements by IGC. Specific retention volumes, V_g, from the IGC experiment were adjusted to standard conditions using[15]

$$V_g = 273.2\left[\frac{(t_r - t_m)F^0 j(P_a - P_w)}{TwP_a}\right] \qquad (1)$$

where t_r and t_m are the retention times of the probe and the methane marker, j is the James–Martin correction factor for the pressure drop across the column, P_a is the atmospheric pressure, w is the weight of polymer, F^0 is the volume flow rate of the carrier gas measured at the column exit, and P_w is the vapor pressure of water at room temperature T.

For crystallinity studies, the retention behavior of a probe in the polymer is measured over a range of temperatures. Above the melting point, the entire sample is amorphous, and the retention volume in the fully amorphous phase is V_g'. If a fraction C of the polymer is crystalline at lower temperatures, then the amount of the amorphous polymer available to the probe is reduced by a factor of $1 - C$. The observed retention volume V_g at temperature T is then[8,9]

$$V_g = (1 - C)V_g' \qquad (2)$$

where V_g' is extrapolated over the full temperature range. The percent crystallinity is given by

$$\%\ \text{cryst} = [1 - (V_g/V_g')] \times 100 \qquad (3)$$

For temperatures near the melting point, a linear extrapolation can be used, but for more accurate measurements over wider ranges of temperature, it is necessary to account for the curvature of the retention diagrams. The slope of a retention diagram, $\partial \ln V_g/\partial(1/T)$, is not constant but varies with temperature, due to the variation in the latent heat of vaporization of the probe with temperature. In this work, curvilinearity corrections were made following the method of Braun and Guillet.[15]

The weight-fraction activity coefficient of the probe was calculated in the standard way based on the work of Everett[16] and Patterson et al.[17] The required virial coefficients were determined using the McGlashan and Potter[18] complilation, while vapor pressures were calculated using the Antoine equation.[19] Knowledge of the activity coefficient enables the calculation of other thermodynamic quantitites.

Column Packing. It has been suggested that adsorption of the probe onto the support surface will vary depending on the choice of support and the percent loading of the polymer. For example, Card et al.[20] noted that probes were absorbed strongly by the chromatographic packing, even for relatively high loadings, due to incomplete coverage of the support. In order to investigate this possibility, electron micrographs were made of several supports which had been coated by P(HB-*co*-HV) copolymer (Figure 1).

It is clear that for silanized glass beads, Chromosorb G AW-DMCS (diatomaceous silicates) and Chromosorb T (treated Teflon beads), the polymer coating is not uniform and does not completely cover the support. The Chromosorb G sample shown had a 9% coating of polymer, within or even slightly above the recommended proportion of the stationary phase. In fact, for Chromosorb G and Chromosorb T, it is difficult to discern the difference between the polymer coating and the support. Similar micrographs and conclusions have been published for various stationary phases on Chromosorb P and W,[21,22] among other supports. Although uniform and full coverage of the support material is not achieved, it is not certain how to correct for adsorption by the support. Card et al.[20] subtracted the retention volumes obtained using uncoated support directly from the values obtained using a polymer-coated support. Analysis of the micrographs reveals that this correction is not fully appropriate, since it is not clear to what extent the polymer covers the adsorptive sites on the support. It is more suitable to assume that the effect of adsorption by uncoated packing will be accounted for by correcting for different percent loadings. Varying the extent of loading will also vary the number of available adsorptive sites. Thus, the effect of incomplete loading on the column packing is better corrected for by extrapolating results to infinite loading.[12,13] It is worth noting that the nonuniformity of the coating on the support does not invalidate the assumptions behind the estimate of crystallinity, provided the polymer is dispersed in sufficiently thin layers to achieve equilibrium with the moving probe molecule.

Results and Discussion

Retention diagrams of decane on P(HB-*co*-HV) copolymers of 7, 21, and 27 mol % HV are shown in Figures 2–4, respectively. All of the plots show a cusp or local maximum at the respective polymer melting temperatures at values similar to the melting temperatures determined by calorimetry (see Table II). Also apparent are two melting points for each of the three copolymers studied. Two melting peaks are detected by DSC for the polymers on chromatographic packing and for solution-cast films; the peaks are not as well resolved for DSC scans on the polymer powders used as received.[23] Apparently, solution coating (and subsequent annealing) increases the development of two crystalline morphologies. In the case of copolymers, the degree of copolymer inclusion in the crystalline phase would be expected to change the slope of the retention

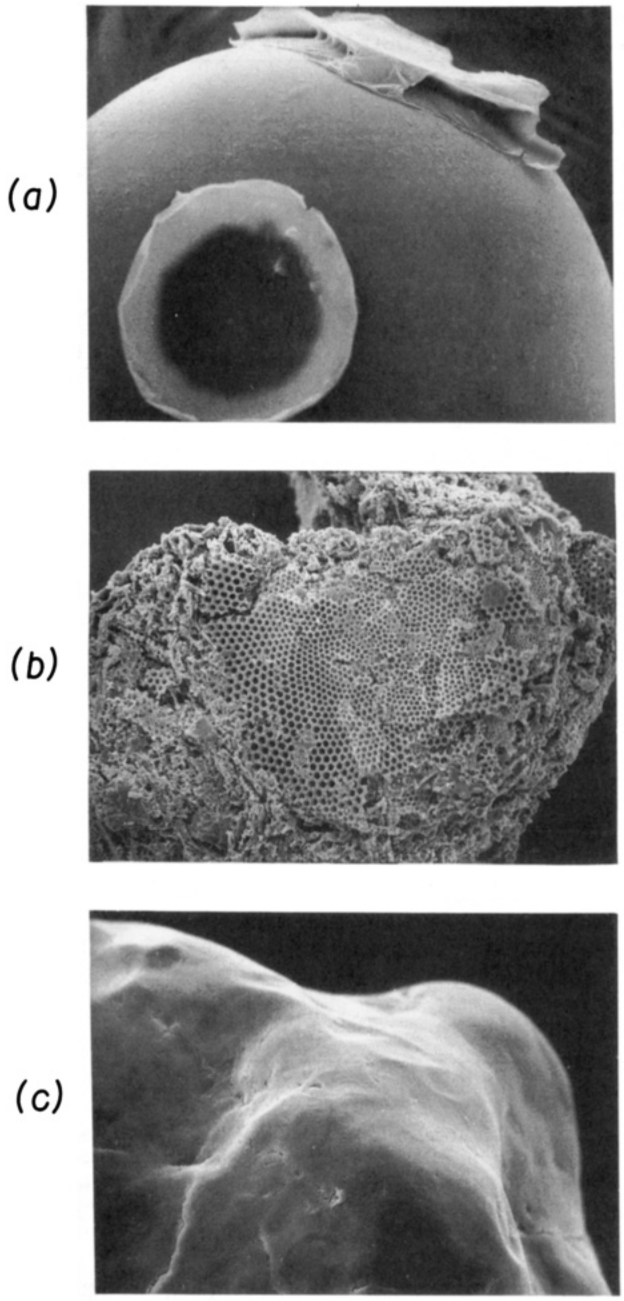

Figure 1. Scanning electron micrographs of polymer-coated IGC packings: (a) glass beads, (b) Chromosorb G (diatomaceous silicates), and (c) Chromosorb T (Teflon 6 particles).

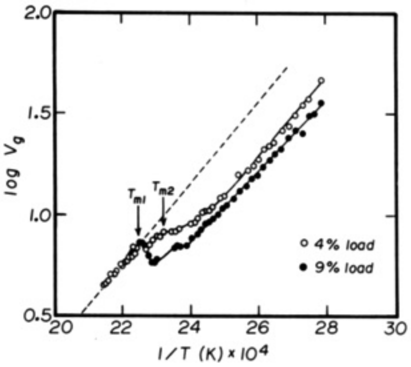

Figure 2. Retention diagram for *n*-decane on bacterial P(HB-*co*-7% HV) solution-coated onto Chromosorb G. Two melting points are detected at T_{m1} = 158 °C and T_{m2} = 149 °C.

diagram near the melting temperature and thus affect the measurement of crystallinity. The slopes of the retention

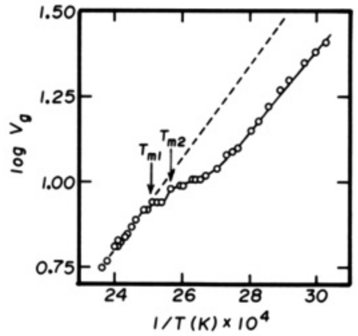

Figure 3. Retention diagram for *n*-octane on bacterial P(HB-*co*-21% HV) solution-coated onto Chromosorb G. Two melting points are detected at T_{m1} = 125 °C and T_{m2} = 109 °C.

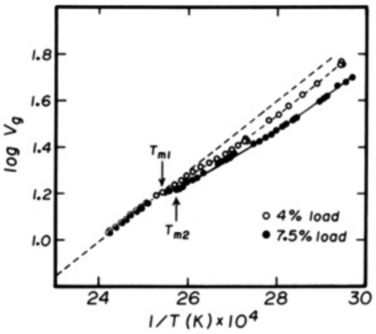

Figure 4. Retention diagram for *n*-decane on bacterial P(HB-*co*-27% HV) solution-coated onto Chromosorb G. Two melting points were detected at T_{m1} = 115 °C and T_{m2} = 98 °C. (- - -) Linear extrapolation of the amorphous retention data.

diagrams for different copolymers are nearly the same for the temperature regions below the melting points. Braun and Guillet[9] measured crystallinity for different copolymers and showed that the measured crystallinity is not affected by the extent of exclusion of the counit.

For each of the samples, the shape of the retention diagram depends on the degree of loading. As predicted by Courval and Gray,[12] higher loading or a lower surface-to-volume ratio results in a more pronounced discontinuity at the melting temperature. In order to correct for the surface effect, the retention volume of the bulk, V_g^b, was determined separately from that of the surface, V_g^s. The observed retention volume is then

$$\begin{aligned} V_g &= (1-C)V_g^{\,b} + V_g^{\,s} \\ &= (1-C)V_g^{\,b} + V_0^{\,s}A(s/w) \end{aligned} \qquad (4)$$

where s is the weight of packing, w is the weight of polymer, V_0^s is the retention volume at 0 °C/m^2 of the phase surface, and A is the area of the stationary phase per gram of support. The bulk retention volume was found by extrapolating the change in V_g versus s/w to s/w = 0, or infinite coating thickness. Linear extrapolation to s/w = 0 was assumed adequate,[13] since the behavior of retention volume is generally linear at low values of s/w.

The crystallinities determined by IGC for P(HB-*co*-HV), after correction for the surface adsorption and curvilinearity, are reported in Table II. The crystallinities for the three copolymer samples are approximately 60% despite a wide range of copolymer compositions. In contrast, crystallinities measured by DSC over the same compositions decrease significantly. For measurement by calorimetry, the degree of crystallinity is determined from the ratio $\Delta H_m/\Delta H_m^\circ$, where ΔH_m is the observed enthalpy and ΔH_m° is the reference heat of fusion. (Here, ΔH_m° = 3427 cal/mol of crystalline repeat unit according to Bloembergen et al.[24]) Lipatov and Nesterov[25] have sug-

Table II
Melting Temperatures and Crystallinity of P(HB-*co*-HV) Measured by DSC, IGC, and X-ray

	melting temp, °C						
	DSC		IGC		deg of crystallinity (25 °C)		
polymer	T_{m1}	T_{m2}	T_{m1}	T_{m2}	$\Delta H_m/\Delta H^\circ_m$	X-ray diffn	IGC
PHB							
neat	179	165			0.59	0.64	
P(HB-*co*-HV)							
7% HV							
neat	155				0.53	0.64	
4% load	154	150	159	150	0.49		
9% load	154	149	156	147	0.51		
infinite load[a]							0.68
21% HV							
neat	121	111			0.32	0.62	
4% load	123	109			0.35		
9% load	121	106	125	109	0.31		
infinite load[a]							0.65
27% HV							
neat		98			0.28	0.63	
4% load	114	98	117	100	0.23		
7.5% load	112	94	113	96	0.24		
infinite load[a]							0.60

[a] Extrapolation.

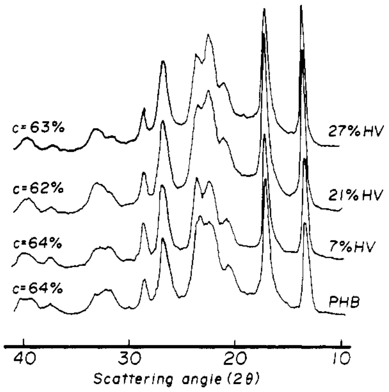

Figure 5. X-ray powder diffraction traces of solution-cast, annealed films of PHB and P(HB-*co*-HV) with increasing HV content. All of the copolymer samples crystallize in the PHB-type lattice. Crystallinity is determined according to Ruland's method in which the scatter due to crystalline order is compared to the total scatter (from crystalline and amorphous).

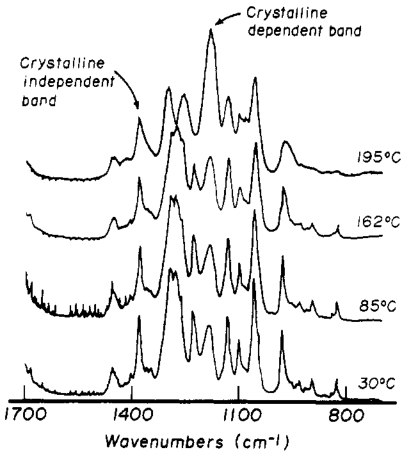

Figure 6. FTIR spectra for a P(HB-*co*-7% HV) solution-cast film as a function of temperature. Crystallinity changes are detected by comparing absorption at 1185 cm^{-1} (a crystalline-dependent band) and at 1382 cm^{-1} (a crystalline-independent band).

gested that the effect of column loadings on retention volumes is not a surface effect but is due to modifications in the polymer morphology; i.e., polymer coatings of different thicknesses have different crystallinities. However, DSC results for the polymer-coated packing show that the heats of fusion do not vary with the degree of loading. Thus, any variations in morphology with the degree of loading are not detectable by calorimetry.

It is clear that DSC and IGC are describing different aspects of the morphology of P(HB-*co*-HV). To examine this difference, crystallinities were determined by X-ray powder diffraction on annealed solution-cast P(HB-*co*-HV). Powder diffraction traces are shown in Figure 5. Maxima are those expected for the pure PHB phase.[3] Furthermore, there are no significant differences in the spectra with respect to mol % HV. Accordingly, the calculated crystallinities are unvarying with the percent of hydroxyvalerate in the copolymer and are in the 57–65% range (±5%) (see Table II). Inverse gas chromatography results confirm the X-ray measurements of solution-cast P(HB-*co*-HV), as well as previously published X-ray measurements for samples used as received,[3] over the 0–27% HV composition range. The failure of DSC to adequately describe the crystallinity of this copolymer system arises from uncertainty about the crystalline morphology and its effect on ΔH_m. That is, the decrease in the heat of fusion with increasing HV content is not describing a decrease in crystallinity but showing that there are decreases in crystallite size and/or crystal perfection.

To further characterize the dynamics of the polymer melt, FTIR spectra were recorded over a wide range of temperatures for P(HB-*co*-HV). Bloembergen et al.[26] showed that several FTIR bands are sensitive to the degree of crystallinity. As shown in Figure 6, crystallinity was determined by the ratio of the absorption at 1185 cm^{-1} (a crystalline-dependent band) to that of the 1382-cm^{-1} band (a crystalline-insensitive band). Crystallinity as measured by FTIR is not considered to be an absolute value, so results were calibrated with X-ray measurements. The melting curves for the three copolymer samples determined from FTIR are very similar to those from IGC (see Figure 7). Thus, the two distinctly different approaches show a significant correspondence.

The IGC melting curves shown in Figure 7 give insight into differences between copolymer samples. As the 7% HV sample is heated, the crystallinity remains relatively high until near the melting temperature T_m and then drops sharply. This drop begins at approximately (T_m − 30) °C.

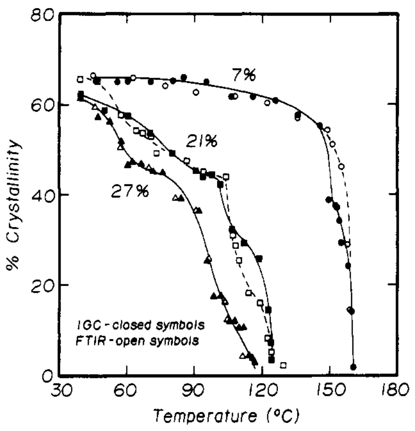

Figure 7. Melting curves of bacterial P(HB-*co*-HV) determined by IGC and FTIR: (●,○) 7% HV, (■,□) 21% HV, and (▲,△) 27% HV. Both techniques show that melting of the 21 and 27% HV copolymers begins just above room temperature.

In contrast, crystallinity for the 21 and 27% HV samples decreases over a much wider range during heating, despite starting at a high level of crystallinity. Melting is spread over the range ($T_m - 60$) °C. One reasonable interpretation for the greater spread in melting behavior is that crystallites are smaller and less perfect with increasing copolymer composition. It is noteworthy that these melting curves qualitatively follow the behavior of Young's modulus as a function of temperature, which was measured previously by several groups.[5,27] This correlation has implications for potential end uses, especially considering that melting is detected at temperatures just above room temperature for the 21 and 27% HV samples.

Conclusions

The determination of crystallinity by IGC has been successfully applied to copolymers of P(HB-*co*-HV). Previous measurements of the crystallinity of these polymers by density[5] and calorimetry[1,27] techniques have shown a decrease in the crystallinity with increasing copolymer composition. The results of IGC are quite similar to those of X-ray diffraction analysis, which shows that the degree of crystallinity does not decrease with copolymerization and is approximately 60% for 0–27% HV. These observations, coupled with the knowledge that P(HB-*co*-HV) is a random copolymer, are in keeping with the observations that the counits of P(HB-*co*-HV) cocrystallize. Calorimetry and density measurements are inappropriate for P(HB-*co*-HV) since it is invalid to make a priori assumptions about the density and heat of fusion of the crystalline phase for copolymers which cocrystallize.

The melting curves determined by both IGC and FTIR exhibit a broader melting region which begins at lower temperature with increasing HV composition. A likely explanation is that, at lower HV compositions, samples crystallize more readily into highly ordered crystallites with a relatively large crystal size. Increasing the percent of hydroxyvalerate decreases the crystallite size, thus reducing the melting point and free energy of melting. It is also likely that inclusion of this "other" counit in the poly(hydroxybutyrate) crystalline phase systematically affects the heat of fusion due to defect formation.

The observation of high crystallinity over the composition range supports a significant degree of cocrystallization for P(HB-*co*-HV). However, the difference in the melting curves between samples of different compositions implies that comonomers are not interchangeable; i.e., some partitioning of HV must be present between crystalline and amorphous phases. Determining the degree of HV inclusion remains a challenge and will further elucidate the structure/property relationship for these copolymers.

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References and Notes

(1) Holmes, P. A. In *Developments in Crystalline Polymers*; Basset, D. C., Ed.; Elsevier: New York, 1988; Vol. 2.
(2) Allegra, G.; Bassi, I. W. *Adv. Polym. Sci.* **1969**, *6*, 549.
(3) Bluhm, T. L.; Hamer, G. K.; Marchessault, R. H.; Fyfe, C. A.; Veregin, R. P. *Macromolecules* **1986**, *19*, 2871.
(4) Kamiya, N.; Yamamoto, Y.; Inoue, Y.; Chujo, R.; Doi, Y.; *Macromolecules* **1989**, *22*, 1676.
(5) Mitomo, H.; Barham, P. J.; Keller, A. *Polym. Commun.* **1988**, *29*, 112.
(6) Flory, P. J. *J. Chem. Phys.* **1949**, *22*, 223; *Trans. Faraday Soc.* **1955**, *51*, 848.
(7) Roe, R. J.; Gieniewski, C. *Macromolecules* **1973**, *6*, 212.
(8) Guillet, J. E.; Stein, A. N. *Macromolecules* **1970**, *3*, 102.
(9) Braun, J.-M.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1119.
(10) Romansky, M. M.Sc. Thesis, University of Toronto, 1989.
(11) Guillet, J. E.; Romansky, M.; Price, G.; van der Mark, R. In *Inverse Gas Chromatography*; Douglas, R., Lloyd, T., Ward, C., Schreiber, H. P., Eds.; ACS Symposium Series 391; American Chemical Society: Washington, DC, 1989; pp 20–32.
(12) Courval, G.; Gray, D. G. *Macromolecules* **1975**, *8*, 326.
(13) Gray, D. G. *Prog. Polym. Sci.* **1977**, *5*, 1.
(14) Ruland, W. *Acta Crystallogr.* **1961**, *14*, 1180.
(15) Braun, J.-M.; Guillet, J. E. *Macromolecules* **1977**, *10*, 101.
(16) Everett, D. H. *Trans. Faraday Soc.* **1965**, 1637.
(17) Patterson, D.; Tewari, Y. B.; Schreiber, H.; Guillet, J. E. *Macromolecules* 1971, *4*, 356.
(18) McGlashan, M. L.; Potter, D. J. B. *Proc. R. Soc. London, Ser. A* **1962**, 478.
(19) Dreisbach, D. R. *Adv. Chem. Ser.* **1959**, *22*, 4, 33, 86.
(20) Card, T. W.; Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1985**, *18*, 1030.
(21) DeMets, M.; Lagasse, A. *Chromatographia* **1969**, *2*, 401.
(22) Barcelo, D.; Galceran, M. T.; Eek, L. *J. Chromatogr.* **1981**, *217*, 109.
(23) Bloembergen, S. Ph.D. Dissertation, University of Waterloo, 1987.
(24) Bloembergen, S.; Holden, D. A.; Marchessault, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 594.
(25) Lipatov, Yu. S.; Nesterov, A. E. *Macromolecules* **1975**, *8*, 889.
(26) Bloembergen, S.; Holden, D. A.; Hamer, G. K.; Bluhm, T. L.; Marchessault, R. H. *Macromolecules* **1986**, *19*, 2865.
(27) Owen, A. J. *J. Colloid Polym. Sci.* **1985**, *263*, 799.

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