Variation in melting point with molecular weight for hydroxybutyrate/ hydroxyvalerate copolymers

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Melting points are measured and equilibrium melting points calculated for hydroxybutyrate/hydroxyvalerate copolymers (PHB/HV) of varying molecular weight, containing 4 and 18% of hydroxyvalerate units. For low-HV copolymer, there is a significant reduction in melting point with molecular weight: values of equilibrium melting point in the range 176–188°C can be obtained from samples with molecular weight between 56 000 and 220 000. For the higher-HV copolymer, complex melting behaviour is observed, which suggests molecular-weight-dependent variations in the degree of exclusion of HV from the crystal lattice.

(Keywords: hydroxybutyrate/hydroxyvalerate copolymers; melting point; molecular weight)

INTRODUCTION

Polyhydroxybutyrate (PHB) is a bacterially produced thermoplastic polyester with considerable potential for use in situations where biodegradability or biocompatibility are required. Owing to better mechanical properties, copolymers of hydroxybutyrate with hydroxyvalerate (PHB/HV) are often preferred for practical use and a range of such materials are now available from ICI under the trade name 'Biopol'[1].

Knowledge of crystal melting points is obviously necessary for anyone wishing to use these polymers. In addition, estimates of the equilibrium melting temperature T_m° (the theoretical melting point of a perfect infinite crystal) are essential for any theoretical modelling of crystallization processes. The preceding paper[2] presented measurements obtained from a series of PHB samples which showed a surprisingly strong dependence of the melting point (T_m) on molecular weight (M_w). In addition to a consistent increase in T_m with M_w for isothermally crystallized samples originating from the same fermentation batch and subjected to various degrees of thermal degradation, there were often large differences in behaviour between different batches of PHB with very similar molecular weights. A further surprising observation was that the slope of the melting point vs. crystallization temperature curve was significantly higher for samples with molecular weights above about 300 000. All these factors make the determination of a meaningful value for the equilibrium melting temperature extremely difficult, and the results could be interpreted to give values anywhere between 179 and 198°C, polymers with low molecular weights having T_m° at the lower end of the range and those of high molecular weight at the upper end.

In this paper similar experiments are described for a pair of PHB/HV copolymers, in order to determine whether the melting points of the copolymers are also strongly influenced by their molecular weights. Interpretation of the melting points of PHB/HV copolymers is complicated by the possibility of exclusion of HV units from the crystals. There is much evidence to suggest that the proportion of HV units incorporated into crystals is a strong function of crystallization temperature (T_c), with more HV excluded as T_c is raised[3–5]. Because of this, the usual methods for determination of an equilibrium melting temperature are inappropriate for copolymers containing more than a few per cent of HV, since melting points obtained from the same copolymer crystallized at different temperatures do not relate to equivalent crystal compositions. Differences in melting behaviour with molecular weight may thus be complicated by variations in the ease of comonomer exclusion for chains of different length.

EXPERIMENTAL

Two copolymers were provided by ICI BioProducts and Fine Chemicals for these studies: a copolymer containing 4.1% HV (batch P039) with $M_w = 747 000$ and a copolymer containing 18.0% HV (batch PSM16) with $M_w = 967 000$. These will be referred to as PHB/4%HV and PHB/18%HV respectively. Each copolymer was deliberately degraded by holding at 190°C for varying times prior to crystallization to provide a series of samples of different molecular weights. The various samples were then crystallized isothermally in a Linkam hot stage at temperatures in the range 70 to 120°C, allowing several days for crystallization at the higher temperatures. The molecular weights were measured after crystallization by gel permeation chromatography, using calibration data for the homopolymer. Each sample was melted in a Perkin–Elmer DSC7 differential scanning calorimeter by heating at 20°C min^{-1}. The positions of any melting

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Table 1 Molecular weights of copolymer samples

Sample	Degradation time (min)	Molecular weight after crystallization
PHB/4%HV	0	220 000
	2	164 000
	5	100 000
	10	56 000
PHB/18%HV	0	463 000
	1	320 000
	2	200 000
	5	120 000
	10	86 000

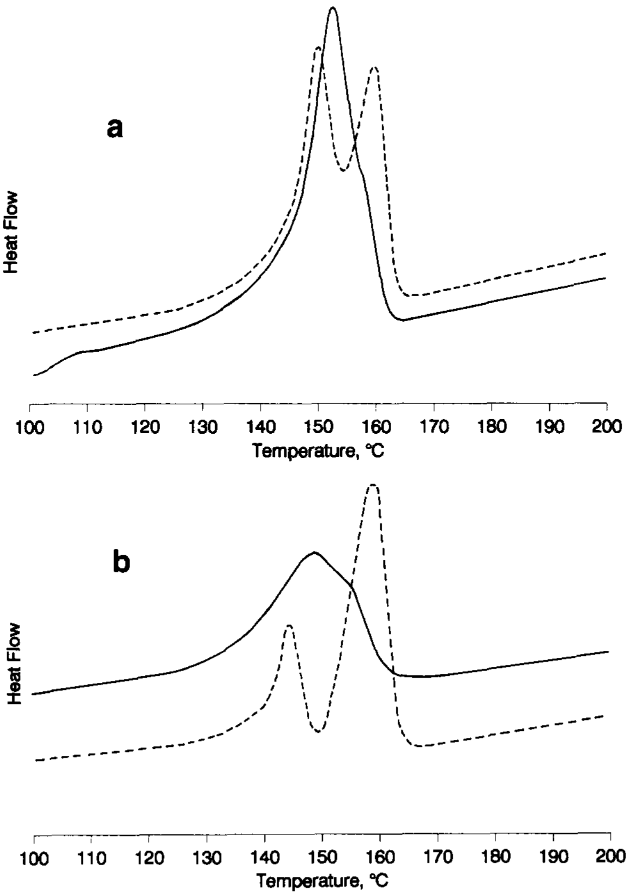

Figure 1 D.s.c. melting endotherms from: (a) PHB/4%HV of molecular weight 56 000 (broken curve) and 220 000 (full curve) and (b) PHB/18%HV of molecular weight 86 000 (broken curve) and 463 000 (full curve)

endotherms were noted, corrected for heating-rate effects and calibrated using indium. Small-angle X-ray diffraction (SAXD) patterns were obtained from a few representative samples using a Rigaku Denki low-angle camera with a specimen-to-film distance of 288 mm and used to calculate the long periods of the crystals, *L*, which give an estimate of crystal thickness.

RESULTS

The molecular weights of the different samples after crystallization are listed in *Table 1*. Molecular weights did not vary greatly for samples crystallized at different temperatures, implying that no further degradation occurred during crystallization.

PHB/HV copolymers often exhibit complex multiple melting peaks[3] but the samples used here both gave reasonably sharp single endotherms for crystallization above 90°C. For crystallization below this temperature, annealing during heating in the d.s.c. gave rise to double melting peaks, as described previously[2]. This was most pronounced in the lower-molecular-weight samples: some typical melting endotherms are shown in *Figure 1*. In each of the examples illustrated, the higher-molecular-weight sample displays a high-temperature shoulder, while for the lower-molecular-weight polymer there are two distinct melting peaks. It is usual to take the lower-temperature peak as the 'true' melting point since this represents the behaviour of the original, unannealed, crystals most closely. In situations where a large proportion of the material undergoes annealing, such as the low-molecular-weight PHB/18%HV shown in *Figure 1b*, this practice may lead to significant underestimation of the melting point, since recording of the endotherm corresponding to melting of crystals grown at T_c is interrupted by exothermic reorganization mechanisms.

Melting points are plotted as a function of crystallization temperature for PHB/4%HV in *Figure 2* and for PHB/18%HV in *Figure 3*. Curves have been drawn through the points corresponding to the lowest and highest molecular weights in each case for guidance. The ringed points illustrate the samples that were used for SAXD: the crystal thickness values obtained are shown alongside each point and each value is subject to an error of approximately ±0.3 nm. For both copolymers noticeable differences are seen between samples of varying molecular weight. For the low-HV copolymer the

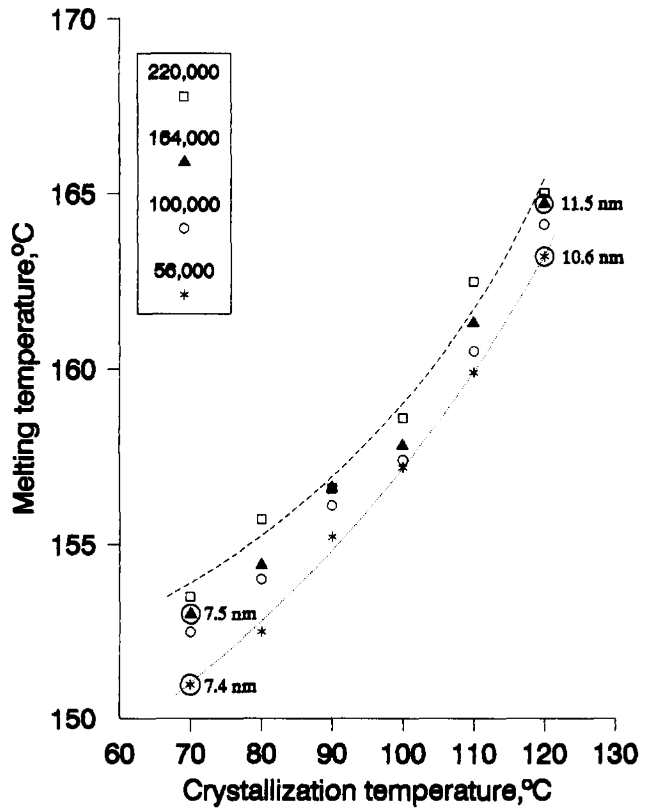

Figure 2 Melting temperature as a function of crystallization temperature for PHB/4%HV of the molecular weights shown. The dotted and broken curves show the curves obtained from the samples of lowest and highest molecular weight respectively. Long spacings measured from SAXS are shown where available and refer to the ringed points

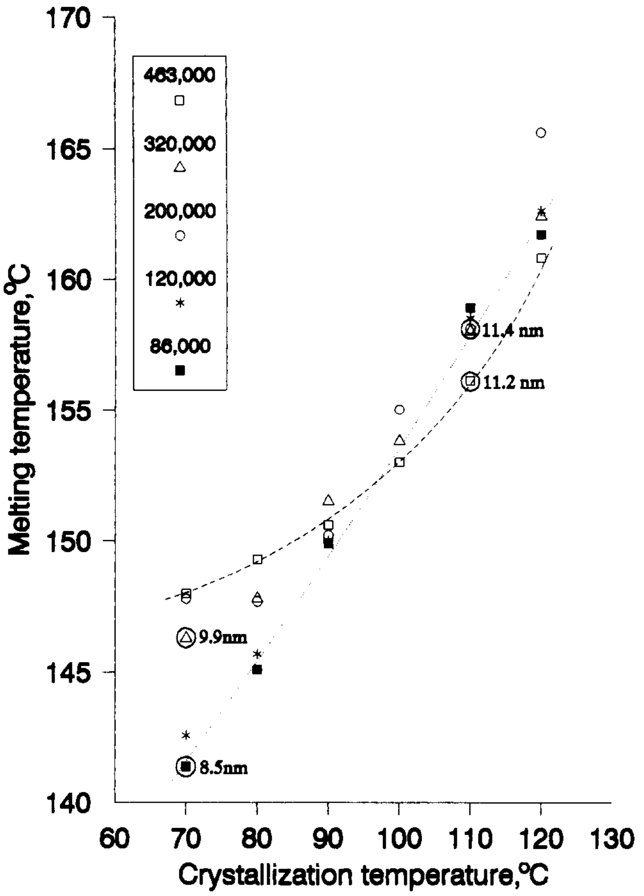

Figure 3 Melting temperature as a function of crystallization temperature for PHB/18%HV of the molecular weights shown. The dotted and broken curves show the curves obtained from the samples of lowest and highest molecular weight respectively. Long spacings measured from SAXS are shown where available and refer to the ringed points

Table 2 T°_m values obtained from PHB/4%HV

Molecular weight	T°_m from all points (°C)	T°_m from highest three points (°C)
220000	177.4	186.5
164000	176.8	188.3
100000	175.5	186.2
56000	176.2	181.6

behaviour is similar to that observed for PHB: there is a small, fairly constant, reduction in melting temperature with molecular weight, which persists over the entire range of crystallization temperature. It is possible to obtain approximate values of equilibrium melting temperature from these data using the Hoffman–Weeks method[6] of extrapolating the T_m vs. T_c curve to the point where $T_m = T_c$. The approximations inherent in this method, discussed in the previous paper[2], are particularly exacerbated in this case (as with PHB) by the high supercoolings at which crystallization is carried out. A very long extrapolation is necessary, which limits the accuracy of the method: the slight curvature apparent in the plots makes this extrapolation particularly difficult. *Table 2* lists values of T°_m for each sample, which have been obtained from least-squares fits either to all the data, or to the three points obtained at the highest crystallization temperatures: *Figure 4* shows examples of the fits obtained for the samples with highest and lowest molecular weights. These results give a range of possible values within which T°_m is likely to lie. The values obtained are, as expected, slightly less than the equivalent figures for PHB.

For the PHB/18%HV copolymer the situation is rather more complicated, as shown in *Figure 3*. For the higher-molecular-weight fractions, very pronounced curvature is seen in the T_m vs. T_c plots (see for example the broken curve in *Figure 3*). Such curvature is too extreme to be accounted for by the approximations in the Hoffman–Weeks analysis. The curves obtained from the lower-molecular-weight fractions are more linear, but the increase in T_m with T_c is much higher than would be expected: in fact, the melting point of the lowest-molecular-weight fraction ($M_w = 86000$, dotted curve on *Figure 3*) exceeds that of the highest molecular weight ($M_w = 463000$; broken curve on *Figure 3*) for crystallization above 100°C. Possible explanations for this peculiar behaviour are discussed below. It is difficult to extract any meaningful estimate of T°_m from these results — as a very rough guide a least-squares fit to all the data gives $T^\circ_m = 184.4$°C, but this is likely to be unrealistically high.

The values of L included in *Figures 2* and *3* show an increase in L with T_c for a given polymer, as would be expected. Long periods measured from crystals grown at similar temperatures are significantly higher in PHB/18%HV than in PHB/4%HV despite lower melting temperatures in the higher-HV copolymer. Variations in L with molecular weight depend very much on the particular copolymer and crystallization conditions employed. These results are discussed below.

DISCUSSION

Polymer crystal melting points can be described theoretically by applying the Gibbs–Thompson equation[7], to give:

$$T_m = T^\circ_m(1 - 2\sigma_e/\Delta H l) \quad (1)$$

where σ_e is the surface free energy of the crystal, ΔH is the heat of fusion and l is the crystal thickness. Crystal thicknesses are related to the supercooling at which the crystal was grown. For homopolymers this relationship is most often modelled using the secondary nucleation theory of Hoffman *et al.*[8] as:

$$l = 2\sigma_e T^\circ_m/(\Delta H \Delta T) + \delta l \quad (2)$$

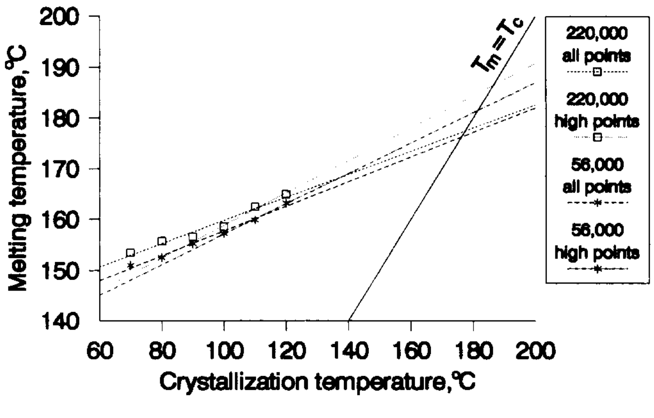

Figure 4 Extrapolation of melting-point data to give values for the equilibrium melting point in PHB/4%HV of the molecular weights shown

where ΔT is the supercooling ($\Delta T = T_m^\circ - T_c$) and δl is a small term usually taken to be roughly constant. This equation cannot be applied strictly to PHB/HV copolymers but provides a useful guide as to the likely qualitative effect of changes in any particular parameter. From equation (1) we see that actual melting points T_m may be affected by changes in T_m°, σ_e, ΔH or l.

T_m° and l are related via (2): a higher value of T_m° implies a lower crystal thickness, which would tend to reduce the melting point. This effect is only likely to be significant at the lowest supercoolings where the change in ΔT is most significant compared with the change in T_m°: in this case for high-HV crystals grown at high temperatures. It is important to note that measured values of long spacing L may not be exactly equivalent to the crystal thickness l discussed above. L includes the thickness of any amorphous layer associated with the crystal surfaces, which may vary with both the copolymer and the crystallization conditions used.

Crystals grown from lower-molecular-weight material will contain a higher proportion of chain ends in both the surface layer and the crystalline interior. The resultant heat of fusion will be reduced, but the effect on the surface free energy is hard to predict. Increased proportions of HV units in the chains will also introduce defects into the crystals and hence reduce ΔH; for the higher-HV copolymer the amount of HV incorporation will be affected by the crystallization temperature, with greater rejection of HV from the crystal occurring at higher T_c. Extra HV units in the surface layer are likely to increase the surface free energy, since bulky side groups increase the work of folding. Thus higher HV levels and lower molecular weights will both tend to lower crystal melting points via reductions in ΔH due to incorporation of HV units or chain ends respectively. Both effects will be greater at low crystallization temperatures. At a given crystallization temperature T_m will also be reduced by the presence of extra HV units in the surface layer, via an increase in σ_e. Such a change could occur due to a higher overall level of HV in the copolymer or a greater degree of HV exclusion from the crystal.

In addition to the complex interplay of variables described above, there is also the possibility that measured melting points may differ from true crystal melting points due to annealing during heating in the d.s.c., as mentioned in the 'Results' section. For PHB it was suggested that melting points greater than 175°C should be ignored since the rate of thickening at such high temperatures is very rapid. For the copolymers all the measured values lie below 170°C and overestimation due to thickening during heating is not considered to present serious problems, particularly since the results obtained are not strongly influenced by heating rate. However, it is possible that the melting points of the crystals most prone to thickening, i.e. those of low molecular weight grown at low crystallization temperatures, have been significantly underestimated due to the superposition of melting endotherms and reorganization exotherms in the d.s.c., as discussed previously.

For PHB/4%HV the variation in melting point with molecular weight is very similar to that seen in PHB, with all values shifted down a few degrees: we obtain $176 \leqslant T_m^\circ \leqslant 188$°C for PHB/4%HV, compared with $179 \leqslant T_m^\circ \leqslant 198$°C for PHB over a similar range of molecular weight. The results are consistent with the Flory analysis[9], which predicts a depression in T_m° due to the presence of the HV units of about 5°C. The general decrease in melting point with decreasing molecular weight is best explained through the reduction in heat of fusion due to the presence of chain ends. For a copolymer with such a low HV level, it is unlikely that differences in the degree of exclusion of HV units from the lattice with temperature have a substantial effect on the results. However, the increase in long spacing with molecular weight measured only at the highest crystallization temperature is probably indicative of a thicker disordered layer between those crystals which could be associated with increased HV exclusion; slight differences in the crystal peak/amorphous halo ratio in the SAXD patterns are consistent with a higher amorphous content in the lower-molecular-weight samples. The greatest source of inaccuracy in this estimation of T_m° is likely to be the intrinsic error in the Hoffman–Weeks analysis due to the large temperature range involved here, as discussed in the previous paper.

The results obtained from the 18% HV copolymer also show an increase in melting temperature with molecular weight at the lower crystallization temperatures, in this case accompanied by an increase in long spacing. The very large variation in molecular weight observed is most probably due to underestimation of the melting point of the lower-molecular-weight samples due to very pronounced annealing during heating, as illustrated in *Figure 1a*. Again, SAXD intensities suggest slightly more amorphous material in the lower-molecular-weight crystals, so the measured long spacings reflect a genuine increase in underlying crystal thickness. Equivalent heats of fusion may be obtained from thinner crystals if a more perfect lattice is achieved via HV rejection. The change in behaviour at the higher crystallization temperatures is unexpected: here there is no systematic variation in melting point with molecular weight, but a trend towards higher melting points from samples of lower molecular weight. In this region, differences in ΔT between samples of different molecular weights will be most pronounced and could lead to higher crystal thicknesses in the lower-molecular-weight material. This is not confirmed by the SAXD measurements: the long spacings obtained from crystals grown at 110°C are virtually identical, and any differences in the underlying crystal thickness are more likely to act in the opposite direction. The melting-point variations can be rationalized if the number of HV units incorporated into the crystals is varying very strongly with molecular weight at these high temperatures. In this case the higher melting points obtained from low-molecular-weight material crystallized at high temperature would imply that exclusion of HV is considerably increased where the polymer chains are shorter, giving rise to more perfect crystals with higher heats of fusion and hence higher melting points. This is plausible given the greater mobility of such chains, and supported by the generally higher level of amorphous material in the lower-molecular-weight samples, but remains largely speculative at present. These results clearly illustrate the difficulties involved in the definition and measurement of an equilibrium melting temperature, or indeed a melting temperature, for such copolymers.

CONCLUSIONS

The melting behaviour of PHB/HV copolymers is influenced by their molecular weight in various ways. For low-HV copolymers, where the results are straightforward, there is an increase in T_m with M_w of similar magnitude to that observed in PHB: typically we observe a change in melting point of about 2°C between samples of molecular weight 56000 and 220000 for a copolymer containing 4% HV. Determination of the equilibrium melting point using the Hoffman–Weeks analysis for the 4% HV copolymer gives values in the range 176–188°C.

For the copolymer containing 18% HV a complex dependence of melting behaviour on molecular weight is observed where the measured value of melting point may go up or down with molecular weight depending on the crystallization temperature. The results are best explained in terms of molecular-weight-dependent variations in the amount of HV that is incorporated into the crystal lattice and offer a salutary warning to anybody attempting to use copolymer melting-point measurements for theoretical analysis.

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