Crystallization and melting behaviour of PHB and PHB/HV copolymer

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The crystallization and melting behaviour of bacterially produced poly(3-hydroxybutyrate) homopolymer and poly(3-hydroxybutyrate/3-hydroxyvalerate) copolymer were investigated by means of optical microscopy, wide-angle X-ray scattering and calorimetric measurements. The spherulitic growth rate and X-ray diffraction patterns were measured at various temperatures, in order to understand the temperature dependence of crystallization kinetics and the changes in the degree of crystallinity which take place on heating. Structural reorganization during heating was investigated further by means of differential thermal analysis measurements at various heating rates.

(Keywords: PHB; PHB/HV copolymers; X-ray diffraction; physical properties; crystallization; melting)

INTRODUCTION

Poly(3-hydroxybutyrate/3-hydroxyvalerate) (PHB/HV) copolymers are produced commercially by a bacterial fermentation process using renewable feedstocks such as glucose (BIOPOL, ICI Biological Products)[1]. These materials are biodegradable, semicrystalline thermoplastics, whose physical properties depend on the amount of HV incorporated into the PHB molecular chains[2–4]. The physical behaviour of these copolymers, however, depends not only on the HV content but also on the crystallization conditions during processing, and there is still much to be learnt about the way these materials respond to thermal treatment. This work was, therefore, aimed chiefly at characterizing the structural reorganization which takes place on heating PHB and PHB/HV copolymer.

EXPERIMENTAL

Materials and methods

PHB/HV samples were provided by ICI Biological Products Division (Billingham, UK). They were in the form of films of PHB homopolymer and a PHB/HV copolymer with 17% HV, together with a sample of PHB powder. The films had been cast from solution using methylene chloride as solvent.

Three experimental techniques were used.

1. Optical microscopy using a polarizing microscope equipped with a Mettler hot-stage. For these measurements, samples (between a glass slide and a cover slip) were first heated above their melting region (190–200°C) for a time of the order of 1 min, then cooled rapidly in the hot-stage to the required crystallization temperature. When a suitable spherulite had been located under crossed polars, its radius was then measured as a function of time. From this, the spherulite growth rate was obtained.

2. Wide-angle X-ray scattering. A monochromatic CuKα radiation source was used in conjunction with a Philips diffractometer (model PW1050). Samples were heated to a particular temperature (in a heating unit, model HTK10, Anton Paar), and held at that temperature for 1 h prior to the X-ray measurement. The sample was then further heated to the next temperature and the procedure repeated. Scattering patterns were also obtained during a cooling sequence after complete melting; the sample was again held at each temperature for 1 h. The scattering pattern of a molten sample was used to estimate the form of the amorphous background for each of the partially crystalline samples. The degree of crystallinity was determined from the respective areas of crystalline peak intensity to amorphous scattering area.

3. Differential thermal analysis (d.t.a.). These experiments were carried out using standard Mettler equipment. Samples were weighed and sealed in aluminium pans, then melting endotherms were obtained at various heating rates. Additional measurements of the heat of crystallization were obtained using differential scanning calorimetry (d.s.c.).

RESULTS AND DISCUSSION

Optical microscopy

The crystallization rate of polymers is controlled by the rate of nucleation and the crystal growth rate. The latter can be followed by measuring the growth rate of spherulites at a given crystallization temperature. *Figure 1a* displays a linear relationship between spherulite radius and time, showing that the isothermal growth rate is constant and independent of spherulite size. The growth rate at different temperatures is shown in *Figure 1b* for PHB and PHB/HV. The rate of PHB spherulite growth was much higher at each temperature than that of the

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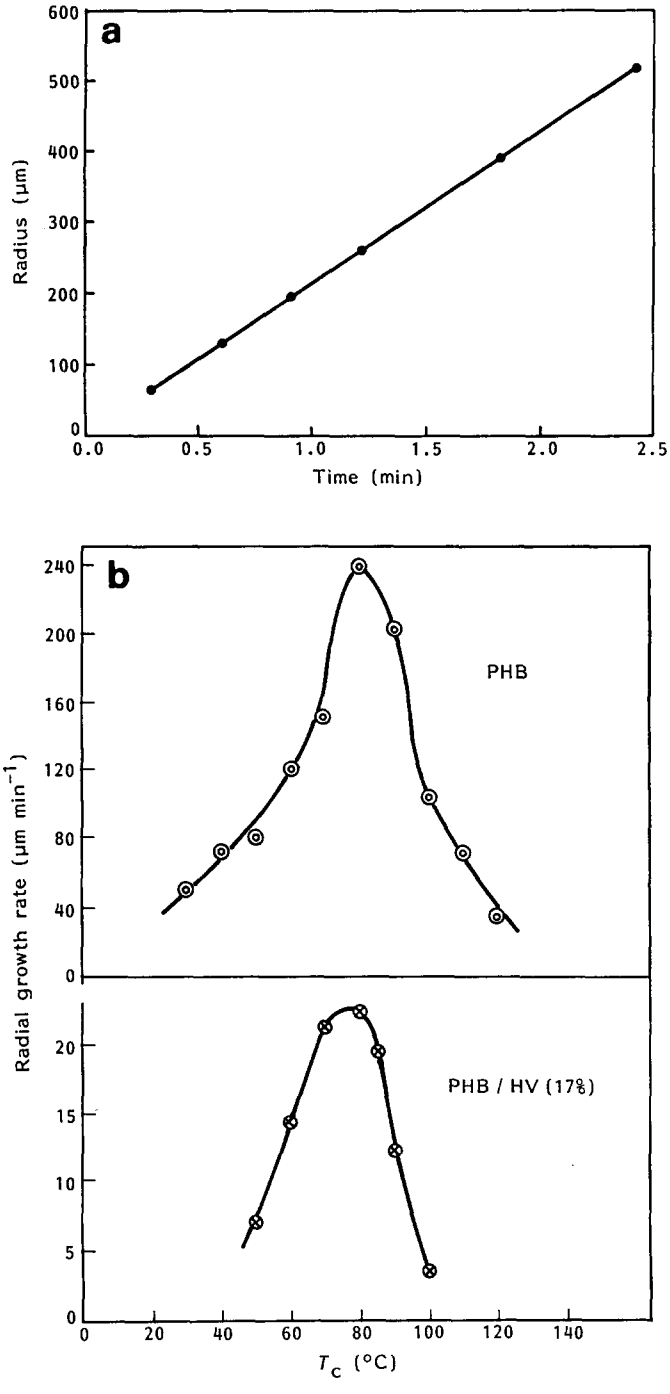

Figure 1 (a) Radius of PHB spherulites plotted as a function of time at a crystallization temperature (T_c) of 80°C. (b) Radial growth rate of PHB and PHB/HV spherulites *versus* T_c

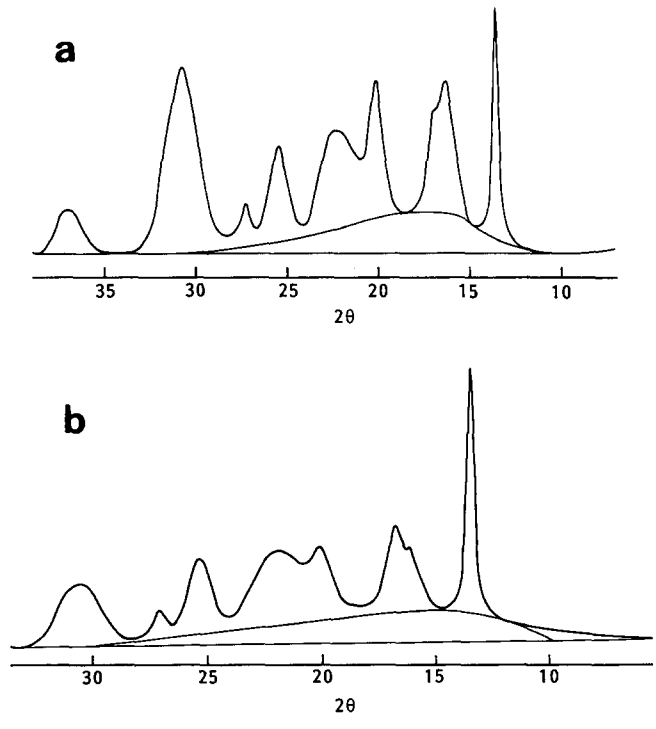

Figure 2 Wide-angle X-ray scattering pattern for (a) PHB film and (b) PHB/HV (17%) film at 27°C. Diffractometer intensity plotted against scattering angle 2θ

copolymer (of the order of 10 times greater). The maximum growth rate of the homopolymer spherulites ($\sim 250\ \mu m\ min^{-1}$) occurred at $\sim 80°C$, whereas the maximum for the copolymer ($\sim 22\ \mu m\ min^{-1}$) lay at a slightly lower temperature. (The results for PHB/HV were obtained by Bauer. They are a correction of results plotted incorrectly in a previous paper[3].) An optically isotropic melt was obtained at temperatures between 170°C and 178°C for PHB and 145°C and 150°C for PHB/HV.

X-ray diffraction

Diffractograms of PHB and PHB/HV film samples are shown in *Figures 2a* and *b*, respectively. Both diffraction patterns correspond to the crystal structure of the PHB homopolymer; this is known from previous work[2,3]. Compared to PHB, the copolymer PHB/HV showed a larger proportion of diffuse scattering and greater half-widths of the peaks, with slight shifts to smaller Bragg angles. This is in accordance with the reduced ability of crystallization for the copolymer and an increase of the unit cell dimensions in the presence of HV monomer units.

Heating of the PHB film caused the following changes in the diffraction pattern: At temperatures up to 120°C a decrease in intensity of the diffraction peaks and an increase in their widths were observed. This suggests a change in the original morphology of the sample. Above 120°C there was a decrease in half-width of the diffraction maxima and a consequent improvement in the resolution of the peaks. This suggests that the crystallite size increases, accompanying improved ordering of the crystalline domains. The degree of crystallinity of the sample was almost constant below 120°C ($\sim 80\%$) but decreased above this temperature, being $\sim 70\%$ at 170°C. At this temperature the X-ray diffraction pattern showed maximum resolution of peaks (*Figure 3a*). The reflections could be indexed in accordance with the orthorhombic unit cell for PHB ($a = 0.576$, $b = 1.320$, $c = 0.596$ nm)[5]. Above 170°C the polymer melted, displaying only the amorphous halo characteristic of the melt.

Table 1 shows the half-width broadening of the (0 2 0) reflection and the corresponding crystallite dimension, together with the degree of crystallinity at different temperatures during the heating sequence. For the PHB sample in powder form, the diffraction pattern at room temperature points to a larger crystallite size and probably better crystalline ordering. With an increase in temperature, the size of the crystalline domains stayed almost constant up to 120°C, whereas above this

Table 1 Broadening ($\Delta 2\theta$) of diffraction maxima (020), crystallite size (L) and degree of crystallinity (X_c) by heating samples

Temperature (°C)	PHB powder			PHB film			PHB/HV film		
	$\Delta 2\theta$ (mm)	L (Å)	X_c (%)	$\Delta 2\theta$ (mm)	L (Å)	X_c (%)	$\Delta 2\theta$ (mm)	L (Å)	X_c (%)
27	0.5	530	79	1.5	280	81	2.4	204	63
60							1.8	248	58
80	0.5	530	74	2.8	180	80	1.5	279	38
100							1.0	358	29
120	0.5	530	70	2.5	200	77			14
150				1.5	280	78			
160	0.0	≅1000	65	1.2	320	73			
170				0.5	530	69			

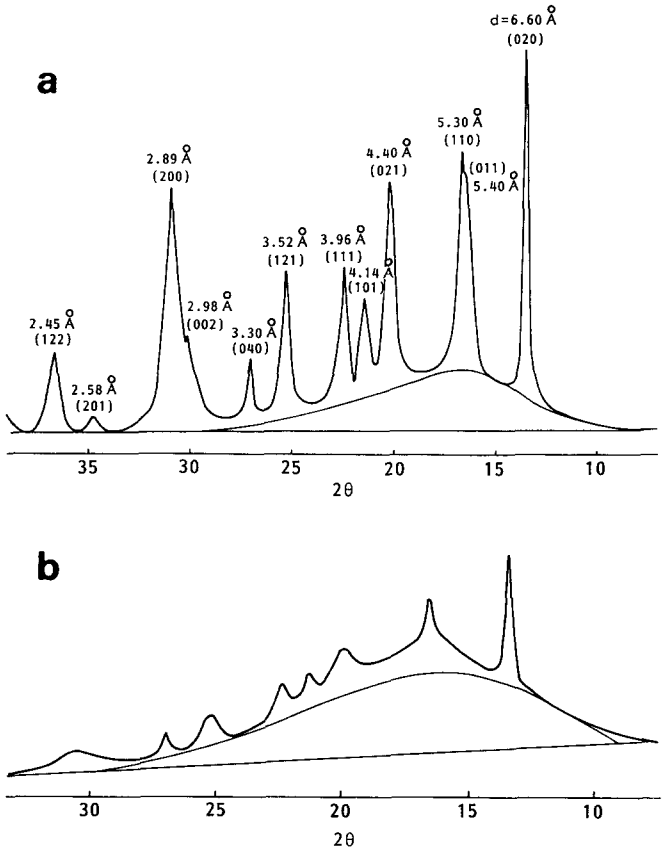

Figure 3 X-ray diffraction pattern for (a) PHB film at 170°C and (b) PHB/HV film at 100°C

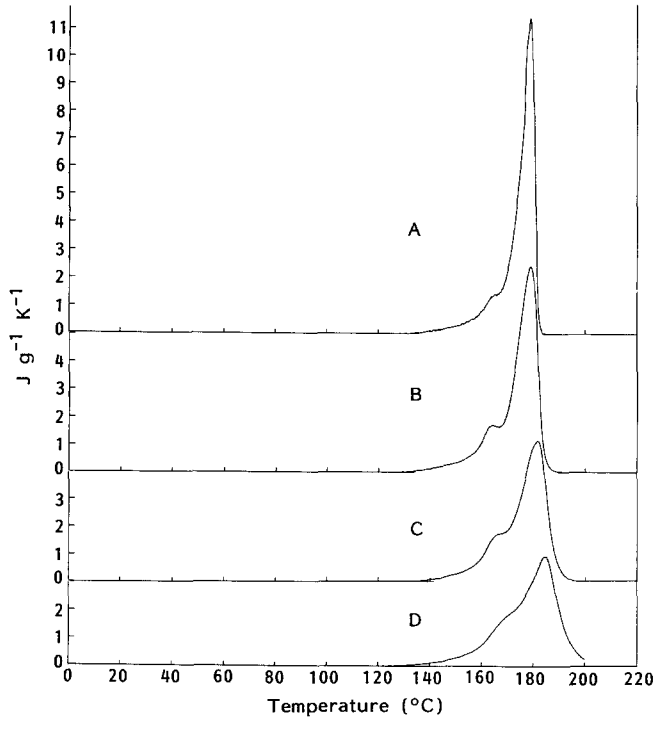

Figure 4 D.t.a. heating curves for PHB film at heating rates of: (A) 2; (B) 5; (C) 10; (D) 20 K min^{-1}

temperature enlargement of crystalline domains and lowering of crystallinity were observed. In the process of cooling the PHB samples from the melt, the first diffraction peaks were already observed at 160°C.

Heating of the PHB/HV copolymer sample from room temperature up to the melting temperature caused a gradual decrease in the half-width of the diffraction peaks and significant lowering of the degree of crystallinity (*Table 1*). At 100°C the degree of crystallinity was about half the original value (at room temperature). The amorphous halo dominated the pattern and the relatively sharp diffraction maxima were of low intensity (*Figure 3b*). The diffraction pattern at 130°C showed only the amorphous halo. During the subsequent cooling procedure, the first diffraction maxima appeared at 80°C.

Calorimetric measurements

D.t.a. heating curves for film samples displayed melting peaks at ~165 and 178°C for PHB and 142 and 153°C for PHB/HV (*Figures 4* and *5*). The ratio of intensity of the lower to higher temperature melting peak varied with heating rate. Generally, such changes could be due to reorganization of crystals during heating. At the highest heating rate applied (20 K min^{-1}), where reorganization has less time to occur, the d.t.a. peaks can be assigned to the original crystallites of the isothermally crystallized sample. During slow heating, reorganization of crystals occurred by the melting of unstable crystals and recrystallization to more stable crystals with a higher melting temperature. The increased intensity of the upper peak at lower heating rates was then predominantly due to reorganized crystals.

In general, the thermal stability of polymer crystals can be attributed to lamellar thickness and/or crystal perfection. These two causes cannot be separated easily: either X-ray reflections of several diffraction orders, such

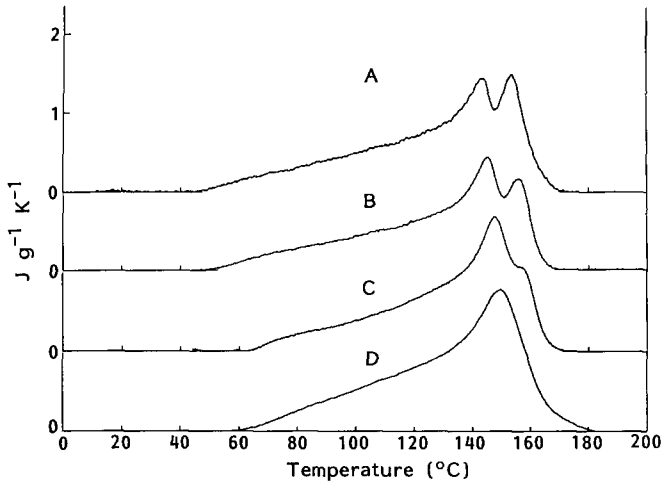

Figure 5 D.t.a. heating curves for PHB/HV film at heating rates of: (A) 2; (B) 5; (C) 10; (D) 20 K min^{-1}

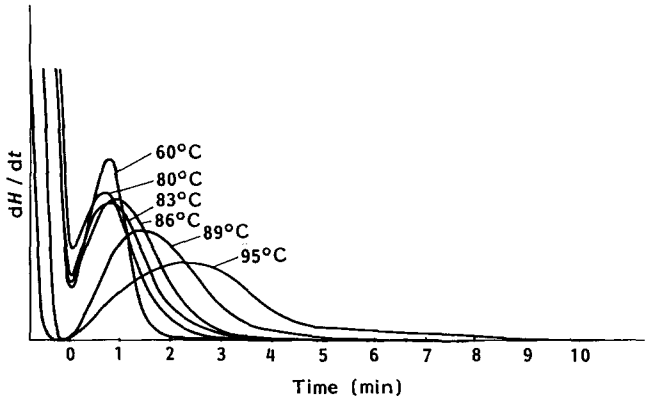

Figure 6 Isothermal d.s.c. response for PHB at various crystallization temperatures

as (020), (040), (060), are required to perform a Hosemann analysis of the broadening[5] or very good resolution electron micrographs of the lamellae are needed.

For PHB, the upper melting peak was strongly dominant at all heating rates used, suggesting that the original sample comprised mostly stable crystals, but with some unstable crystals also being present. During slow heating, the less stable crystals became more stable, since the lower peak became less pronounced.

For PHB/HV, at the highest heating rate used only the lower of the two melting peaks was seen. We attribute this to the presence of only unstable crystals in the original film. During slow heating, an upper melting region appeared due to partial reorganization to more stable crystals.

There are two explanations for this behaviour. The copolymer crystals in the original film could be of the less stable variety because they contain many HV units as defects in the PHB lattice. In that case, the heat of melting, and hence the melting temperature, would be relatively low due to reduced cohesion of the molecules in the crystals. On reorganization, HV units could diffuse out of the crystals, increasing the internal cohesion of the crystals and raising the melting enthalpy and melting temperature. On the other hand, the unstable crystals could be relatively thin, if the HV units, excluded from the crystals, restrict the thickness of the PHB crystal lattice. In that case, the melting enthalpy and temperature are lowered as a result of the large surface energy contribution to the specific enthalpy.

One feature of this copolymer is that the melting range is very wide, extending from ~50 to 170°C, which agrees with the observation by X-ray diffraction that the crystallinity decreases with increasing temperature. A further observation was that the melting peaks were shifted slightly to higher temperatures with increasing heating rate. Since thermal lag in the apparatus had been corrected for using calibration substances with well-defined melting points, we attribute this additional effect to superheating of the crystals.

Kinetics of isothermal crystallization

The kinetics of isothermal crystallization was studied further in the temperature range from 60 to 95°C using d.s.c. equipment. *Figure 6* displays the isothermal d.s.c. response of the crystallizing PHB at several temperatures. The crystallinity as a function of time is shown in *Figure 7*, using the results of *Figure 6*. As can be seen from these diagrams, the crystallization rate decreased with increasing temperature in the range used here. By using the data from *Figure 7* we calculated the coefficients z and n in the Avrami equation:

$$x(t)/x(\infty) = 1 - \exp(-zt^n)$$

The parameter n determined at various crystallization temperatures varied between 2.15 and 2.47, which approximately corresponds to two-dimensional growth of crystals[6].

CONCLUSIONS

Subtle changes occur on heating PHB and PHB/HV. Both d.t.a. and X-ray measurements indicate some melting and structural reorganization at temperatures well below the main melting region. These structural changes were not observed distinctly in the polarizing microscope (only a gradual decrease of birefringence was observed on heating), so that it is to be assumed that the changes occur on a scale not resolved in the light

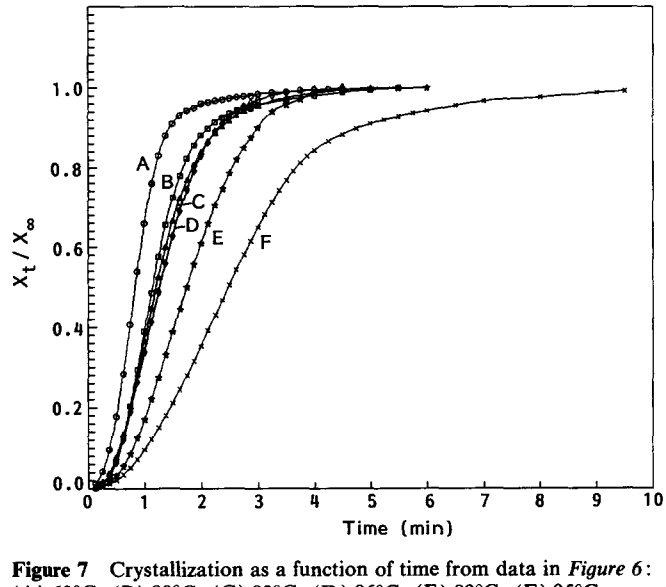

Figure 7 Crystallization as a function of time from data in *Figure 6*: (A) 60°C; (B) 80°C; (C) 83°C; (D) 86°C; (E) 89°C; (F) 95°C

microscope. Although in some cases two or even three d.t.a. melting regions were recorded, distinct spherulite types were not observed.

From X-ray measurements, the effective size of PHB/HV crystals increased with increasing temperature, whereas the degree of crystallinity decreased (*Table 1*). This apparent paradox can be understood by inferring that on heating the sample the unstable crystals melt, which increases the amorphous scattering. The stable, unmelted crystals, having a larger effective size, produce sharper X-ray reflections. Furthermore, some of the melt recrystallizes to the more stable crystal form. A separate crystallographic modification, distinguishing for example the more stable form, was not identified. Further work is now being carried out on the properties of other PHB/HV copolymers together with blends of these copolymers with other thermoplastic and rubbery polymers.

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REFERENCES

1 Holmes, P. A. 'Developments in Crystalline Polymers-2' (Ed. D. C. Bassett), Elsevier, Amsterdam, 1988
2 Bloembergen, S., Holden, D. A., Hamer, G. K., Bluhm, T. L. and Marchessault, R. H. *Macromolecules* 1989, **22**, 1663
3 Bauer, H. and Owen, A. J. *Colloid Polym. Sci.* 1988, **266**, 241
4 Barker, P. A., Mason, F. and Barham, P. J. *J. Mater. Sci.* 1990, **25**, 1952
5 Hosemann, R. *Berichte Bunsen-Gesellschaft* 1970, **74**, 755
6 Sperling, L. H. 'Introduction to Physical Polymer Science', John Wiley & Sons Inc, New York, 1985