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Effect of crystallization temperature on the cocrystallization of hydroxybutyrate/hydroxyvalerate copolymers

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Measurements on the effect of crystallization temperature on the crystallinity, long period and unit cell dimensions of P(HB/HV) copolymers with 0–27% HV crystallized isothermally at 23, 52 and 81°C are presented. The crystal composition has been estimated from the unit cell expansion and the relationship between crystallinity and density. The amount of cocrystallization of HV in the PHB crystal structure is found to decrease as the crystallization temperature is increased: the amount of HV in the crystals formed at 81°C is reduced to 2/3 of the value for crystallization at room temperature. The results are consistent with cocrystallization being an effect of the kinetics of crystallization which becomes less significant as equilibrium crystallization conditions are approached. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyhydroxybutyrate; co-crystallization; isodomorphism)

INTRODUCTION

Background

P(HB/HV) copolymers are a range of biodegradable bacterial thermoplastics produced and marketed by ZENECA Bio Products under the tradename Biopol. The crystal growth, nucleation and morphology of PHB are in many ways typical for polymers[1,2], however the HB/HV copolymers have been found to have high crystallinities at all compositions[3,4], which, since the copolymers are random, implies that the two comonomers must cocrystallize. Wide angle X-ray scattering (WAXS) has been used to infer that copolymers with less than 30% HV crystallize with the PHB structure while samples with more than 49% HV have the PHV structure[4]. The existence of two crystal structures which allowed mutual cocrystallization was termed isodimorphism, in analogy to the equilibrium effects of isomorphism and dimorphism. A phase diagram with a sharply defined transition from the PHB to PHV structure at some composition (*ca.* 35% HV) was implied, however, other work[5,6] suggests that both structures are present at intermediate compositions.

The extent of cocrystallization has been measured by solid state n.m.r.[5,7,8], density[9,10], and lattice strain[8,9].

Solid state n.m.r. experiments have the potential to measure the HV content of the mobile and immobile phases, however the results published to date are inconclusive. The n.m.r. results published by Kamiya *et al.*[7] are shown in *Table 1*. The lack of HV in the crystals of the 18% HV sample is surprising given that such a sample shows a strained crystal lattice and reduced heat of fusion. Sanders *et al.*[5] have presented n.m.r. results showing lower degrees of cocrystallization, however the data were collected at temperatures where some of the samples would have partially melted, and so the results may not be typical of the structure at lower temperatures.

The lattice strain caused when the bulkier HV units crystallize into the PHB structure can be used to estimate the crystal composition (we use the term strain rather than expansion to indicate an increase in lattice dimension to avoid confusion with thermal expansion). This requires an estimate of the volume of the HV unit in the PHB crystal, for which the volume of an HV unit in the PHV structure may be used. We have published results using this method[9] on samples crystallized in a similar manner to industrial processing: holding at 55°C until the spherulites were fully grown and then storing at room temperature until crystallization was complete (which takes several weeks for high HV copolymers). The crystals were found to contain a lower fraction of HV than the sample overall: typically the HV content of the crystal was 2/3 that of the whole sample. A similar analysis by Bonthrone[8] on as supplied powders suggested that the HV composition of the crystals was the same as the sample.

Some of us have published a method for estimating the partition of HV between the crystal and amorphous phases based on sample densities[10], which was used to some success in our previous paper[9]. Furthermore we have used the same argument to show that on a strict two-phase model the densities of samples crystallized at 23 and 81°C imply that the latter have either a lower crystallinity or less HV in the crystalline phase.

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Table 1 Properties of P(HB/HV) crystal from n.m.r. and d.s.c. analysis by Kamiya *et al.*[7]

HV content						
Sample v_s (mol%)	Crystal v_c (mol%)	Amorphous v_a (mol%)	% Crystal χ (mol%)	Enthalpy of fusion ΔH (kJ mol^{-1})	Corrected enthalpy $\Delta H/\chi$ (kJ mol^{-1})	Melting point T_m (°C)
0	–	–	72.3	11.2	15.5	175
18.3	0	47.8	59.4	6.2	10.4	121
31.6	10.2	64.4	60.2	3.2	6.0	81
40.7	14.2	48.6	[a]	[a]	[a]	54

[a] This sample showed crystals in the PHV structure as well as PHB

Table 2 The ICI (Zeneca) batch codes, HV content and molecular weight of samples used

Batch code	Compositon (%HV)[a]	Molecular weight[b]
PHB 300[c]	0	283 000
PV14	7	439 000
PV5	21	116 000

[a] HV content was measured by ICI using ^{1}H n.m.r.

[b] Weight average molecular weight as quoted by ICI (except PHB300 which was measured at Bristol); measured by gel permeation chromatography, polydispersities were all *ca.* 2.5. NB Degradation during melting may change the molecular weight by about 25%

[c] The original ICI code for this material is not known

In this paper we present the results of our investigations on the crystallization of random HB/HV copolymers crystallized under controlled thermodynamic conditions. In particular we investigate the effect of crystallization temperature, albeit over a limited range. The primary method of investigation is X-ray diffraction: we show how the lattice dimensions, lamellar thickness and crystallinity vary with sample composition and crystallization temperature. The samples studied all contain less than 30% HV, the crystal structures are similar to that of PHB homopolymer. This paper is in fact an extension of the work started in ref. 9 increasing the range of crystallization temperatures. Melting of similar samples is discussed in work soon to be published[11].

EXPERIMENTAL

Samples

A range of samples were supplied by ICI Biological Products Business (now ZENECA Bio Products); *Table 2* shows some of the properties of the batches used. Sequence analysis has shown that these samples have a random distribution of HV units[4,12]. These were cleaned by dissolving in chloroform, filtering, and precipitating into alcohol. For all work voidless films were required; these were best prepared by dissolving the sample in chloroform and allowing the solvent to evaporate slowly before final drying in a vacuum oven until constant mass was reached. We are confident that this preparation leaves no voids since such samples had a consistent amorphous density which agreed with the published value[10,13].

For our purposes it is essential that the thermodynamics of crystallization are well defined, therefore the samples were crystallized by remelting them at 190°C and crytallizing them in a silicone oil bath held at constant temperature until they reached constant density (which can take several weeks). (It is not necessary to measure the density at high temperature in silicone oil: after a few days crystallizing, when the spherulites have finished growing, having the samples at room temperature for the few minutes that it takes to measure density does not cause a significant increase in density.)

Ruland–Vonk measurement of crystallinity

The wide angle X-ray scatter was measured using a Rigaku vertical goniometer in symmetric reflection geometry, with collimation and sample size optimized for high intensity rather than angular resolution. Semicrystalline samples were run in step scan mode from 7 to 150° (2θ) whereas amorphous samples were run between 7 and 40° at a scan rate of $16^{\circ}\,\mathrm{min}^{-1}$. The intensity profiles were corrected for absorption and transparency as described by Milberg[14]. The crystallinity was determined by the Ruland–Vonk method[15,16] since this corrects for the effect of diffuse scatter from crystal defects. A version of Vonk's program which had been modified to run on IBM compatible PCs was used.

Long period measurement

The scattered X-ray intensities were read off the exposed films from a Rigaku Denki camera using a Joyce–Loebel optical densitometer at ×10 magnification. The long period was estimated from the peak position by application of Bragg's law.

Lattice strain measurement

X-ray diffraction from the samples was measured using a horizontal Philips goniometer with stepper motor drive. The irradiated volume was kept small in order to minimize peak position aberrations.

Two methods of measuring the peak centroid were used: direct integration was preferred as more objective, however the (1 1 0) and (0 1 1) peaks overlap and so the peaks had to be resolved by curve fitting. In order to measure the centroid by integration it is necessary to remove the amorphous contribution to the scatter around the peak: this was achieved by subtracting a background based on the amorphous scatter which was scaled to fit the 2θ ranges which showed no Bragg scatter.

RESULTS

Crystallinity

Two factors which hindered these measurements are worth reporting: sample orientation and crystallization of material after quenching from the nominal crystallization temperature. The first of these is a result of the low nucleation density for PHB and HB/HV copolymers:

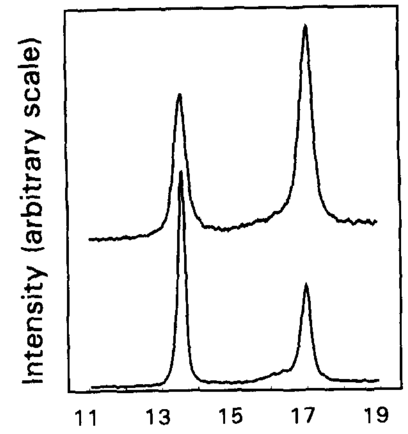

Figure 1 WAXS of PHB showing the effect on the diffraction profile of sample orientation caused by the spherulite size being similar to the sample thickness. The top curve comes from a thick sample crystallized at a low temperature to give small spherulites, the curve below comes from a thin sample crystallized at a high temperature to give large spherulites. NB samples as strongly oriented as the example shown here were not used for crystallinity determination

Table 3 The crystallinities measured by the Ruland–Vonk WAXS method, density and from the heat of fusion

Batch code	Composition (%HV)	Method	Crystallization temperature 23°C	52°C	81°C
PHB300	0	WAXS	62%	74%	78%
		d.s.c.	60%	69%	73%
		Density	62%	n/d	77%
PV14	7	WAXS	n/d	n/d	77%
PV5	21	WAXS	67%	72%	68%

n/d, not determined

when crystallizing at high temperatures the spherulites grown can have diameters of the order of millimetres, i.e. of similar dimensions to the sample thickness. A particularly strong example of this effect is shown in *Figure 1*: this form of orientation may be the cause of the varied relative intensities of (0 2 0) and (1 1 0) reflections which can be found in the literature on PHB. The under representation of the (1 1 0) reflection causes an underestimate of crystallinity. The other phenomenon which affected the measurement, crystallization on quenching, gives rise to melting endotherms below the nominal T_c which can be seen by d.s.c.[7]. The fact that after crystallization at low supercoolings there remains some material which can only crystallize at higher supercoolings is evidence that cocrystallization is disfavoured at high crystallization temperatures.

Both of the factors described above were more pronounced for high HV crystallized at high temperatures; samples strongly affected by these errors have been discarded.

In *Table 3* we show the results of Ruland–Vonk crystallinity measurements, with comparisons to other measures of crystallinity for the same samples. From these we conclude:

(1) The Ruland–Vonk measurement of crystallinity for PHB agrees well with crystallinities measured by density and heat of fusion. For the copolymers the inclusion of HV into the crystal affects the density and heat of fusion and so we cannot make similar comparisons.

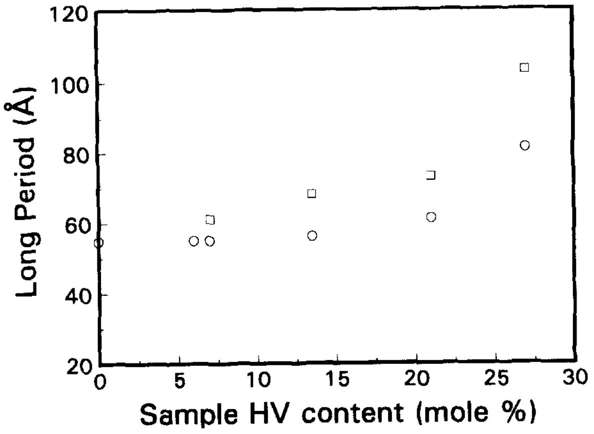

Figure 2 The long periods of various samples crystallized at 23°C (circles) and 52°C (squares). The experimental error is estimated at ±5%

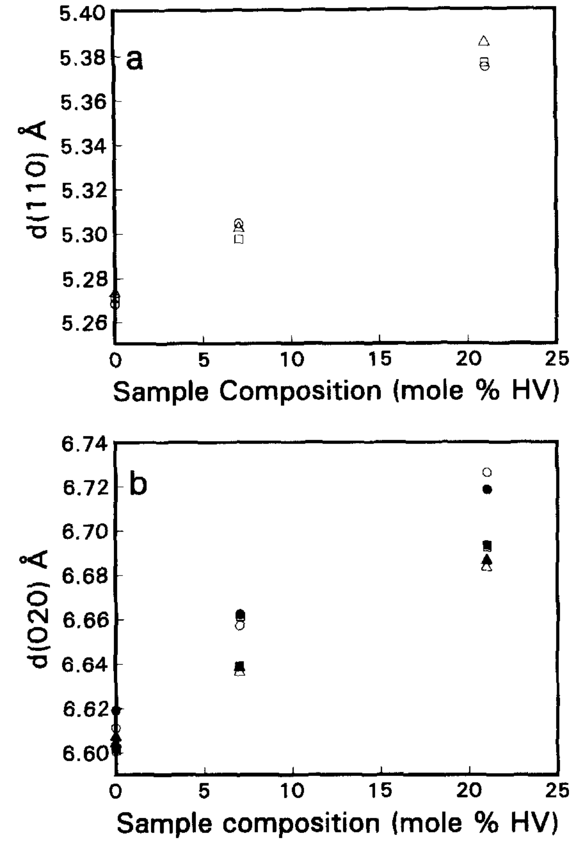

Figure 3 (a) The (1 1 0) and (b) the (0 2 0) unit cell dimensions as a function of sample HV content for after crystallization at 23°C (circles), 52°C (squares) and 81°C (triangles). In (b) the open symbols represent peak positions measured by integration and the filled symbols measurements by curve fitting

(2) For crystallization at room temperature the HV content of the sample does not significantly affect the final crystallinity (the slightly higher value for the 21% HV sample is not significant: if it is real it is quite likely to be a molecular weight effect). This confirms the previous results on samples cast from chloroform solution[3,4] with data from samples crystallized under thermodynamically controlled conditions.

(3) There is no strong evidence that crystallizing HB/HV copolymers at higher temperatures gives lower crystallinitities, contrary to our initial expectations[10].

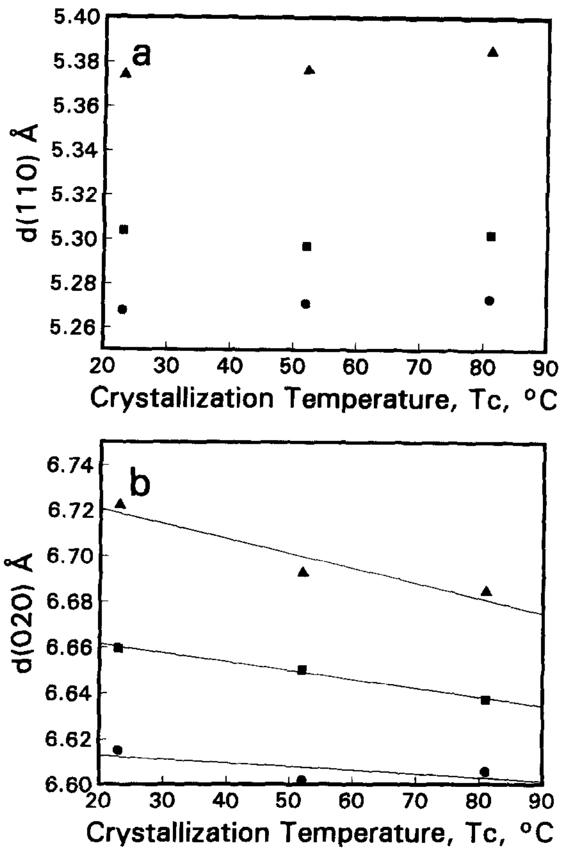

Figure 4 The same data as *Figure 3* but plotted as a function of crystallization temperature for PHB (0% HV) (circles), PV14 (7% HV) (squares) and PV5 (22% HV) (triangles). The (0 2 0) measurements are the averages of the results from integration and curve fitting

The only signs in this direction are the crystallization on quenching described above, and the fact that PHB shows a significant increase in crystallinity over the range of T_cs investigated which the higher HV samples do not. However, given the difficulties with this method for high HV samples crystallized at high temperatures, as discussed above, we do not dare draw any conclusions from this alone.

Long period measurements

The long periods of all samples measured are shown in *Figure 2*. The results are in good agreement with data from de Koning[18] who analysed the whole scattering curve and found that PHB crystallized at 60°C had a long period of 69 ± 3 Å which, modelled as two phases, consisted of 41 Å of crystal and 28 Å of amorphous material.

The increase in L with %HV agrees with Orts *et al.*[19] (who show data for samples with up to 22% HV crystallized at temperatures between 60 and 115°C). However the nonlinearity, i.e. the up turn in the graph at high HV, is present only in their $T_c = 80°C$ sample. At lower temperatures our data suggests that the upturn would be insignificant over the HV range which they studied, while their data suggests that this effect reaches a maximum at $T_c \sim 80°C$, being less significant at higher temperatures.

Lattice parameter measurements

The (1 1 0) and (0 2 0) lattice plane spacings are shown in *Figure 3* as a function of sample HV content for various crystallization temperatures*. Each point shown is the average of two or three independent measurements on different samples from the same batch crystallized under identical conditions; the typical reproducibility of these results was in the range of ±0.005 Å. A similar level of agreement was found between the measurements of the (0 2 0) peak position by direct integration and curve fitting. The (0 1 1) reflection proved to be rather difficult to fit since it is broad and tends to merge into the amorphous halo, this affects the baseline for fitting the (1 1 0) peak, the measured position of which is therefore less certain. However the fit was reproducible enough for us to discern trends in the position of that peak. The trend for the lattice to be increasingly strained as the sample HV increases shown in *Figure 3* agrees well with previous observations[4,8,9,21], and corresponds to increasing amounts of HV in the crystals.

In *Figure 4* we show the variation of the (0 2 0) and (1 1 0) plane spacings for similar samples crystallized at different temperatures. As the crystallization temperature is increased there is a significant decrease in the lattice strain in the (0 2 0) plane spacing for the copolymers. A common cause of variation in unit cell dimensions with crystallization conditions is the change in crystal thickness decreasing the effect of the fold surfaces. However since, at these supercoolings, the change in lamellar thickness with crystallization temperature is small, and does not vary greatly with HV content, and since the PHB interplane distance varies less than that of the copolymer we conclude that the greater decrease in strain for the copolymers is due to less cocrystallization of HV at lower supercoolings. The (1 1 0) lattice parameter showed no clear trend, this may be because it was more susceptible to errors caused by the curve fitting procedure used, or may be a result of the peculiar crystallography of chain folding in PHB (which is predominantly in the [1 1 0] directions[22,23]).

DISCUSSION

Effect of crystallization temperature on HV cocrystallization

The results presented above can be analysed in two independent ways to give estimates of the amount of HV in the crystalline phase: firstly the lattice strain can be assumed to be proportional to the amount of HV in the crystals; secondly the sample density, degree of crystallinity and unit cell size can be related to the partitioning of HV between amorphous and crystalline regions on a two phase model.

Since we have some doubts about the accuracy of the (1 1 0) parameter measurement perhaps the safest approach is to concentrate on the variation in the (0 2 0) lattice spacing (*Figure 4b*). Consider the strain in the **b** direction, i.e. difference between *d*(0 2 0) for PHB and for the copolymers: for samples crystallized at 81°C this is approximately 2/3 that observed when the samples are crystallized at 23°C. We therefore judge that if, for example, a copolymer crystal formed at room temperature contains as much HV as the bulk sample, the same copolymer crystallized at 81°C will have only 2/3 as much HV in the crystals. However we cannot fix the

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*The values differ from those presented by some of us in ref. 20, the early results were incorrect due to misinterpretation of the (0 1 1) reflection and a systematic error in our measurements. Correction of these mistakes has not affected the conclusions of our previous paper

Table 4 The crystal HV content (v_c) estimated from the sample density and degree of crystallinity, χ. The crystallinity value used is (A) that obtained from Ruland–Vonk measurements, (B) the values obtained from density measurements of PHB crystallized at the same temperature and (C) as B but varying with HV content in the same way as A. (Where crystallinity values for PV14 were not determined an estimate was made based on the values for PHB and PV5). The final column (lattice) shows the crystal HV content estimated from the unit cell strain

		A		B		C		Lattice
Batch	%HV	χ (%)	v_c (mol%)	χ (%)	v_c (mol%)	χ (%)	v_c (mol%)	v_c
$T_c = 23°C$								
PV14	7	62	9	62	9	62	9	9
PV5	21	62	19	62	19	62	19	26
$T_c = 52°C$								
PV14	7	74	6	69	8.5	69	8.5	8
PV5	21	73	13	69	14	68	14.5	23
$T_c = 81°C$								
PV14	7	77	3.5	73	5	68	7	7
PV5	21	68	14	73	12	63	16	(24)

absolute composition at any one temperature from this parameter alone, so it is interesting to include our estimates of the other lattice dimensions.

On purely steric grounds we can argue that the volume change in the average unit cell is a linear combination of the volume of the HB and HV units in the crystal [9], from which we derive:

$$v_c = (V - V_B)/(V_V - V_B) \qquad (1)$$

where v_c is the mole fraction of HV in the crystal, V is the unit cell volume of the sample, V_B and V_V are the unit cell volumes of the PHB and PHV unit cells respectively. We have assumed that the $|\mathbf{c}|$ dimension of the copolymer is the same as that of PHB (5.96 Å) to produce the estimates of crystal HV content listed in the final column of *Table 4*. We estimate an accuracy of ±1% HV from consideration of experimental reproducibility, but this does not include errors due to the assumptions of our model. Although the absolute values are too high the trend of less cocrystallization for higher T_c is still present (especially considering that the (1 1 0) spacing for 22% HV, $T_c = 81°C$ sample was not particularly reliable).

Table 4 also shows the HV composition of the crystals obtained from our model of sample density[10]. The greatest uncertainty from this model comes from the necessity of using a value of crystallinity which matches the density-measured value, i.e. is based on crystal packing rather than ordering. We have therefore shown results for three likely trends in crystallinity: (A) that obtained from Ruland–Vonk measurements; (B) that obtained from density measurements on PHB, assumed to be independent of HV content; and (C) that obtained from PHB density but following the same trend observed in the WAXS measured crystallinity. Again the decrease in cocrystallization with increasing crystallization temperature is visible, and of a similar magnitude to the estimates from the (0 2 0) lattice spacing. The third assumption (C), that we should use the crystallinity of PHB measured by density but adjusted to follow the trend observed by the Ruland–Vonk measurements, shows a smaller variation in the crystal HV content than the other treatments. There is, however a reduction in the amount of cocrystallization at high crystallization temperatures since the total amount of crystalline material is less than in assumptions A and B and less than one would expect by comparison with the trend of increasing crystallinity with increasing crystallization temperature.

The observed, high, degree of cocrystallization of copolymers at all compositions is indeed unusual, for most AB copolymers the inclusion of B units into a crystal of A incurs a free energy penalty which is much greater than $K_B T_c$ (3–5 kJ mol^{-1} for T_c in the range 100–300°C). Therefore the exclusion model has been taken as typical of copolymer crystallization behaviour, e.g. Flory's analysis of copolymer melting[24]. In practice even those copolymers which give zero crystallinity at compositions with high B will crystallize if the B content is low enough. The crystals which do form in such copolymers are often observed to have some B monomers in them. For example, chlorinated polyethylene crystals are estimated to have *ca.* 1/4 the Cl content of the sample as a whole (based on measurement of small angle scattering of X-rays or neutrons and density and confirmed by measurements of lattice expansion[25,26]). The question is then whether the cocrystallization which takes place is caused by the kinetics of crystallization 'trapping' energetically unfavourable defects in the crystal, or is the energy penalty for crystallization sometimes low enough to allow some equilibrium concentration of comonomer B in the crystal. This problem has been addressed by the kinetic theories of Helfand and Lauritzen[27] and Goldbeck-Wood[28], and the equilibrium approach of Marchessault and Allegra[29].

The supercoolings used in this study are not particularly low, and the range covered is not large: taking the equilibrium melting point of PHB as our reference we have covered the range of $T_m{}^{\circ} - T_c$ from 110–170°C. All these samples have therefore been crystallized far from equilibrium, and should not be considered as possessing equilibrium properties. It is, however, possible to use this data to show how different the equilibrium crystals would be from those observed. From the extrapolation of melting temperature as a function of crystallization temperature we have been able to estimate that the highest temperature at which HB/HV crystals can grow is *ca.* 170–195°C irrespective of HV content[17,20]. In this limit crystals would grow infinitely slowly, and so equilibrium would dominate kinetic effects. If we extrapolate the trends shown in *Figure 4* we find that there would be no significant difference in the (0 2 0) lattice spacing for different HV contents crystallized at *ca.* 190°C. While we have to be cautious about an extrapolation over such a long range based on so few data, we can say that our present results are consistent with the supposition that HV would be excluded from crystals growth at equilibrium: i.e. the cocrystallization of HV is a kinetic effect.

Finally we must caution that the models used above to calculate the amount of HV in the crystals assume a homogenous crystal phase, it is possible that there may exist crystals with a range of compositions[11]. The measurements given above (and those based on other techniques) will give an average of this range, biased by the sensitivity of that technique to the difference between perfect and defective crystals.

Long periods

The tend for the higher HV samples to have larger long periods may be partly due to changes in the amount of amorphous material between the crystals. However it also agrees with the prediction of kinetic growth theories that copolymers should form thicker crystals than homopolymers if energetically unfavourable cocrystallization takes place[28,30]. The observed crystal thickness is given by

$$l = l_{\min} + \delta l \qquad (2)$$

where $l_{\min}$ is the minimum stable thickness for which the free energy released by crystallization, ΔG_v, is just enough to balance the free energy used at the chain folded surfaces, $2\sigma_e$.

$$l_{\min} = 2.\sigma_e/\Delta G_v \qquad (3)$$

and δl is a small, approximately constant, length which various kinetic growth theories seek to predict. At any temperature, T, the free energy of crystallization can be approximated by

$$\Delta G_v = \Delta H_v(T_m - T)/T_m \qquad (4)$$

If cocrystallization reduces the stability of the crystals then a longer crystal stem is necessary to overcome the energy required by the surfaces. That is to say that the inclusion of defects reduces ΔH and T_m and so the minimum stable crystal thickness is increased. The consequence of this argument is that it is the observed enthalpy and melting point (corrected for surface effects) which govern the crystal thickness, not the equilibrium values normally used. Even if the equilibrium free energy of a crystal in a copolymer system is enough to overcome the surface energy, a real crystal with more defects may not be stable at that thickness, and it is the real crystal which has to exist.

These arguments may explain the upturn in plots of long period *versus* composition and its variation with crystallization temperature: the high HV copolymer crystals grown at lower temperatures contain more defects, are therefore more unstable and so a thicker crystal is necessary to balance the surface energy. However at higher temperatures there is more exclusion of HV from the crystals so that the increase of long period with temperature for the copolymer is less marked than for the homopolymer. A full analysis of the observed long periods to find the thermodynamic parameters governing the crystallization would be prohibitively complicated: equation (4) is only approximate at the high supercoolings used to crystallize PHB/HV[31], the fold surface free energy may be affected by HV content and the exclusion of HV from the crystal cores, and a rigorous treatment to find the thickness of the amorphous material between the crystalline lamellae would be required.

Isodimorphism vs kinetic cocrystallization

In comparing our results with the ideas of isodimorphism, we first note that all of our crystallizations have been carried out at high supercoolings, well away from solidus of phase diagrams predicted by Allegra[29]. Under these conditions the equilibrium concentration of HV in the crystals follows the form exp $(-\epsilon/KT)$ where ϵ is the free energy penalty for including an HV unit in the PHB structure. We find no evidence for the increase in HV cocrystallization with increasing temperature which this predicts. Also, as we have previously noted[20], since the sample HV content, partitioning of HV between crystal and amorphous phase, and crystallinity are interrelated[10], any theory which predicts an equilibrium composition of the crystalline and amorphous phases is, in effect, predicting that the crystallinity is also at an equilibrium value. For polymers this is generally not the case.

It is easier to relate our findings to a kinetic explanation of cocrystallization where the concentration of defects decreases as the crystallization temperature increases since more rearrangement of the chain can take place during crystallization giving opportunity for more stable conditions to be found. In this case the high crystallinity of HB/HV copolymers is due in part to a moderately low defect energy for cocrystallization (we have estimated the enthalpic part to 24 kJ mol^{-1} [9]) but also due to the high undercoolings at which PHB systems can be crystallized. This explanation based on kinetic cocrystallization agrees with the conclusions of a paper by Marchessault reporting on phase separation in blends of copolymers with different HV content[32].

CONCLUSIONS

In a previous paper[10] we argued that a clear trend in sample density shows that increasing the crystallization temperature for HB/HV copolymers leads to less crystallization of HV (either by means of a reduction in crystallinity or by the crystals having less HV in them). Our present analysis shows that while there may be a reduction in crystallinity for the copolymers compared to the homopolymer, with crystallization of the latter at high temperatures excluding some material which can only crystallize on cooling, there is evidence of increasing rejection of HV from the crystal at lower supercoolings. Our best estimate, based on the (0 2 0) unit cell spacing, is that crystallization at 81°C gives crystals with 2/3 the HV:HB ratio obtained by crystallizing at 23°C. We also estimate (from the unit cell volume and relationship between density and crystallinity) that room temperature crystallization gives equal partitioning of HV between the crystal and amorphous parts. Contrary to models based on 'isodimorphism', our results suggest the amount of cocrystallization decreases as equilibrium crystallization conditions are approached.

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