

# Phase separation in a blend of poly(hydroxybutyrate) with poly(hydroxybutyrate-co-hydroxyvalerate)

S. J. Organ\* and P. J. Barham

*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK  
(Received 1 December 1991; revised 1 May 1992)*

Blends containing poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with 18.4% hydroxyvalerate units in various proportions have been studied using differential scanning calorimetry (d.s.c.) and optical and electron microscopy. D.s.c. measurements of melting points and peak areas from crystallized samples show that two-phase crystallization occurs for blend compositions containing 60–70% or more of copolymer, depending on crystallization temperature. The precise composition of the crystal phases obtained is thought to be governed primarily by kinetic factors. Phase separation in the melt was also investigated using d.s.c. by comparing the crystallization behaviour of nucleated and non-nucleated melts subjected to various thermal treatments. A region of liquid–liquid phase separation was identified, indicating partial miscibility between the two blend components. Morphological evidence confirmed the existence of different crystalline phases for the blends of highest copolymer content.

(Keywords: poly(hydroxybutyrate); poly(hydroxybutyrate-co-hydroxyvalerate); blend; phase separation)

## INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB/HV) are thermoplastic polyesters produced by bacterial fermentation<sup>1</sup>. The PHB homopolymer displays rather poor mechanical properties, which are improved by copolymerization: PHB/HV copolymers are now commercially available from ICI under the tradename 'Biopol'<sup>2</sup>. These materials are attractive candidates for many applications owing to their biodegradable and biocompatible properties; however, they are difficult to process and have low durability. Blending provides a potential method for improving these undesirable characteristics.

Previous studies in this area have concentrated mainly on assessing the miscibility of PHB or PHB/HV with other polymers. It has been reported that PHB is miscible in the melt with poly(ethylene oxide)<sup>3</sup>, poly(vinyl acetate)<sup>4</sup> and poly(vinyl fluoride)<sup>5</sup>. In addition, PHB/HV has been shown to be melt miscible with poly(vinyl chloride)<sup>6</sup>, an acrylonitrile–butadiene–styrene copolymer<sup>6</sup>, polystyrene<sup>7</sup> and polycaprolactone<sup>7</sup>. PHB/HV and acrylonitrile–styrene copolymer were partially miscible<sup>7</sup>. Incompatible pairs investigated are PHB with ethylene propylene rubber<sup>4</sup> and PHB/HV with poly(D-lactide) and poly(tetramethylene glycol)<sup>6</sup>. Measurements of the tensile properties and impact behaviour of PHB/rubber blends showed only moderate improvement over the PHB values<sup>8</sup>.

All the above studies concentrate on the interaction of PHB or PHB/HV with other dissimilar polymers. On crystallization, the PHB or PHB/HV component tends to separate out from the surrounding matrix, which may

be either crystalline or amorphous. A rather different situation arises if PHB is itself blended with PHB/HV, since in this case co-crystallization is possible between the two components<sup>9,10</sup>. Such systems could be of considerable practical importance since it is often convenient to mix PHB/HV copolymers of differing HV contents to achieve a particular overall HV level. Blending of PHB with its own copolymers retains the advantages of biodegradability and biocompatibility while offering potential improvement in mechanical properties and/or crystallization kinetics by careful selection of blend composition and crystallization conditions. Previous studies by Marchessault *et al.* on a blend of PHB with a copolymer containing 8% HV found the two to be compatible under the crystallization conditions employed<sup>11</sup>, but the phase behaviour of more dissimilar pairs was not investigated. In this paper we report results obtained from blends containing a PHB homopolymer and a copolymer with 18.4% HV, mixed in various proportions. Phase separation was found to occur in blend combinations containing a high level of copolymer.

Previous investigations of phase separation in polymer blends have utilized a variety of experimental techniques, including measurements of glass transition or melting temperatures, light scattering, rheological and morphological studies. However, many of the experimental methods developed for other systems are not easily transferable to blends of PHB with PHB/HV. In some cases this is because of the similarity in physical properties of the two components: for instance, the glass transition temperature ( $T_g$ ) of PHB/18.4% HV is only about 10°C lower than that of PHB<sup>12</sup>, so that  $T_g$  differences between two closely related components of a phase-separated blend cannot easily be resolved. Other methods, such as rheological measurements in the molten

\*To whom correspondence should be addressed

state, are precluded by the low melt stability of PHB and PHB/HV<sup>13,14</sup>. In addition, for this system, both components of the blend can crystallize, over similar ranges of temperature and time, to produce comparable spherulitic morphologies: thus morphological differences between different blend components can be difficult to identify. In this study we have utilized mainly differential scanning calorimetry (d.s.c.) to identify mixing or phase separation, making use of the differences in melting temperature and heat capacity of the various blend components. Electron and optical microscopy provide some morphological verification for the phase diagram thus obtained.

## EXPERIMENTAL

A range of samples containing PHB (batch G08) and from 0 to 100% of PHB/18.4% HV (batch P029) in 10% intervals were provided by ICI in the form of extruded pellets. The molecular weights were measured by gel permeation chromatography as  $M_w = 417\,000$ ,  $M_w/M_n = 2.8$  for the PHB and  $M_w = 582\,000$ ,  $M_w/M_n = 3.23$  for the PHB/18.4% HV. Analysis of similar copolymers produced by the same fermentation procedure has shown the distribution of HV units along the chain to be essentially random (e.g. refs 15 and 16). Throughout the text the blends will be referred to by the amount of copolymer in them, i.e. a 10% blend contains 90% PHB and 10% PHB/HV, etc.

### Differential scanning calorimetry

All d.s.c. measurements were obtained using a Perkin-Elmer DSC7 differential scanning calorimeter. Sample masses were typically 3–5 mg. Two different experiments were performed, in order to investigate different areas of the phase diagram. These were as follows.

**Isothermal crystallizations.** Small samples of each blend, sealed in aluminium pans, were melted at 200°C for 1–2 min and then quenched into liquid nitrogen. After quenching, they were immediately placed into the DSC7, preset to a crystallization temperature  $T_c$ , and held for a set time  $t_c$ . Samples were then heated in the DSC7, and the positions and areas of all melting endotherms were measured. Quenching the samples into liquid nitrogen ensures that they are in a glassy state: on subsequent heating from the glass, rapid nucleation occurs, so that crystallization times can be kept to a minimum. Preliminary experiments were performed to determine the time required to ensure complete crystallization, to check for any effects caused by prolonged crystallization times and to observe the effect of heating rate on the results obtained. From these results, suitable combinations of  $T_c$ ,  $t_c$  and heating rate were chosen. For the higher crystallization temperatures, the quenching stage was omitted; samples were cooled directly to  $T_c$  from the melt and held for much longer times to ensure complete crystallization. Crystallization temperatures used were 40, 50, 60, 70 and 90°C. Crystallization times were typically 10 min for quenched samples and 24 h for unquenched samples. Blends containing 30, 40 and 50% of copolymer were also crystallized at 140°C for several days. A heating rate of 20°C min<sup>-1</sup> was generally found to be suitable.

**Effect of nucleant on crystallization.** The crystallization behaviour at high temperatures of blends containing 30% and between 50 and 90% of copolymer was compared, with and without the addition of 2% ammonium chloride. The NH<sub>4</sub>Cl, which acts as a nucleant<sup>17</sup>, was dispersed in a solution of the blend and the mixture subsequently dried. Samples were typically melted at 200°C, then cooled quickly to either 120 or 100°C and allowed to crystallize. In some cases an additional step was included whereby samples were held, after melting, at an annealing temperature  $T_a$  ( $200^\circ\text{C} > T_a > 120^\circ\text{C}$ ) for 5–10 min prior to crystallization. Nucleated samples were completely crystallized for 1 h at  $T_c$ . Longer crystallization times were necessary for the samples without nucleant, which were therefore left for 24 h at 100°C or 72 h at 120°C. After crystallization, the samples were melted in the DSC7 at 20°C min<sup>-1</sup>.

### Microscopy

Crystalline samples were examined for evidence of phase separation using optical and transmission electron microscopy (TEM). For optical microscopy, thin films of blend pressed between coverslips were crystallized in a Linkam hot stage and viewed between crossed polars in a Zeiss Ultraphot polarizing optical microscope. Spherulite growth rates were measured and samples examined for morphological inhomogeneity. For TEM studies, samples crystallized under various conditions were etched using methylamine; surface replicas were then made and examined using a Phillips 301 transmission electron microscope.

## RESULTS

### Differential scanning calorimetry

**Isothermal crystallizations.** PHB held isothermally after quenching into the glassy state was found to be fully crystallized within 2 min, PHB/HV copolymer (and thus, by implication, all blend combinations) within 10 min. All subsequent experiments were therefore performed with  $t_c = 10$  min. Further annealing at  $T_c$  had no discernible effect on the subsequent melting behaviour, and in this temperature range very similar results were obtained from unquenched samples crystallized for much longer times.

When interpreting melting points obtained from polymer blends using d.s.c., it is very important to distinguish between multiple peaks arising from phase-separated structures and multiple peaks that often arise as a result of annealing during heating in d.s.c. These may be differentiated by their response to variations in heating rate. *Figure 1* shows examples of d.s.c. melting endotherms obtained at various heating rates from 30% (*Figure 1a*) and 90% (*Figure 1b*) blends after crystallization at 60°C. Results obtained using the highest heating rate of 40°C min<sup>-1</sup> should be treated with caution owing to the low thermal conductivity of polymer samples: nevertheless, double peaks can still be resolved sufficiently that the qualitative form of the results provides a useful comparison. In *Figure 1* double peaks are observed in all cases except the 30% blend heated at 5°C min<sup>-1</sup>, but the variation in the relative areas of the two peaks with heating rate is quite different for the two blends. The 30% blend shows behaviour typical of a homopolymer: as the heating rate is decreased, the

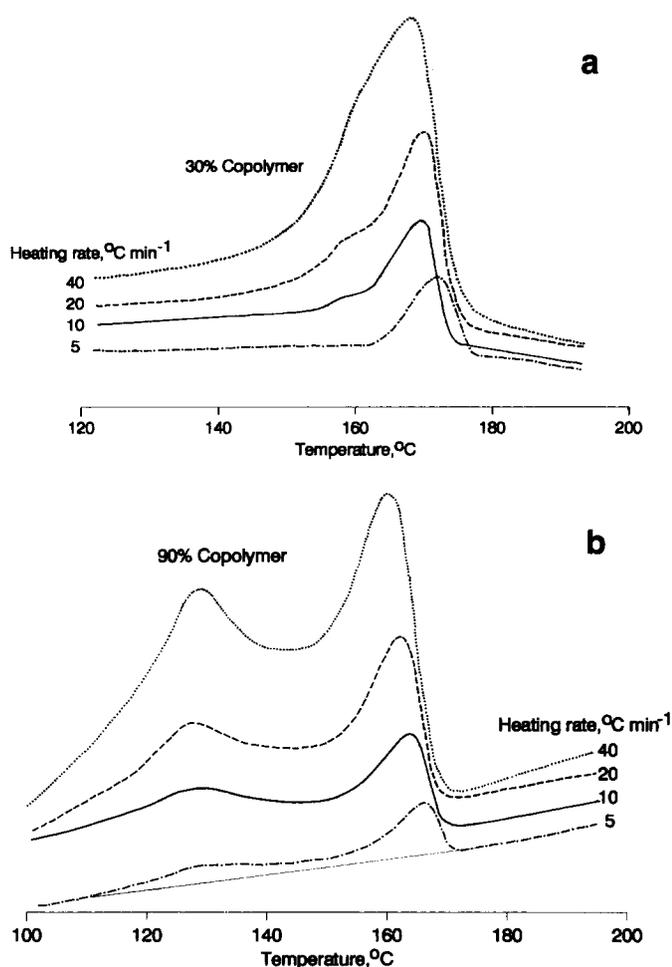


Figure 1 D.s.c. melting endotherms obtained at the heating rates shown from (a) 30% and (b) 90% blends after crystallization at 60°C

proportion of material contributing to the first peak also decreases. At the lowest rate only the higher-temperature peak is observed. This suggests that the original structure of the sample is represented by the lower-temperature peak, but that this structure transforms during heating to one with a higher melting point. Slower heating rates allow time for more material to transform. The 'true' melting point of the material crystallized at 60°C is therefore given by the lower-temperature peak. In contrast, for the 90% blend, two well resolved peaks are seen at all heating rates. The position of the higher peak shifts somewhat as the heating rate is changed, but the proportion of material in each peak remains more or less constant. This rather different behaviour implies that each of the peaks corresponds to a separate phase of the original structure, with some annealing process occurring within the material giving rise to the higher-temperature peak. We suggest that the 30% blend (Figure 1a) demonstrates the behaviour of a single mixed crystalline phase, with the melting behaviour of that mixed phase given by the lower-temperature peak, and that the 90% blend (Figure 1b) shows behaviour characteristic of a two-phase system, where each of the melting peaks corresponds to a separate crystalline phase in the material.

Having established the effect of heating rate on the results, we may consider the melting behaviour of the isothermally crystallized samples. A heating rate of 20°C min<sup>-1</sup> was used for all subsequent measurements. Figure 2 shows examples of the melting endotherms obtained

from PHB, 50% blend, 80% blend and PHB/HV, all crystallized at 60°C. The measured melting points (calibrated using indium) of these and the other blend combinations are plotted in Figure 3. The lower-temperature peaks ( $T_{m1}$ ) lie on a straight line up to 60% copolymer: in Figure 3 this line has been extended to include the value obtained from pure copolymer, and the curve obtained is taken to represent the melting point of mixed crystals. The position of the higher-temperature peaks ( $T_{m2}$ ) remains fairly constant over the whole range. The value of  $T_{m1}$  drops sharply on passing from a 60% to a 70% blend and subsequently remains fairly constant as the copolymer content is reduced further. This constant value is close to the higher-temperature peak obtained from pure copolymer (see Figure 2) and is consistent with the appearance of a phase-separated structure for blends containing >60% copolymer, where one phase corresponds approximately to pure copolymer. Figure 4 shows the corresponding peak areas (equivalent to heats of fusion, plotted in arbitrary units) for crystallization at 60°C: the full line shows the total area expected, calculated simply from relevant proportions of the peak areas obtained from pure PHB and pure

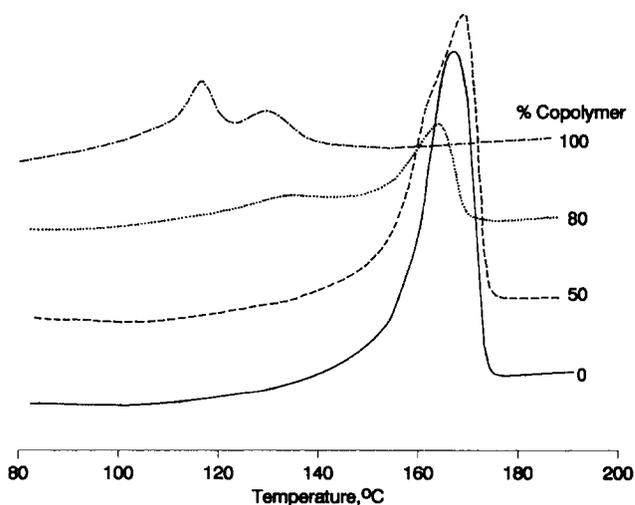


Figure 2 Melting endotherms obtained from samples with the copolymer content shown, all crystallized at 60°C

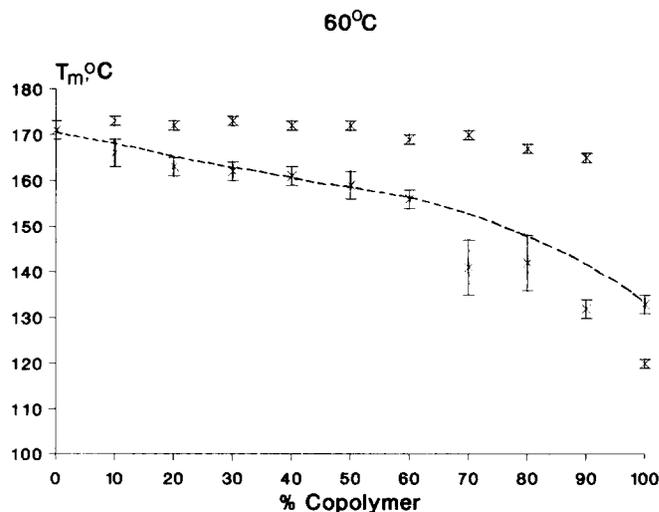


Figure 3 Melting points obtained from samples crystallized at 60°C. The broken curve shows the melting points believed to correspond to a mixed phase

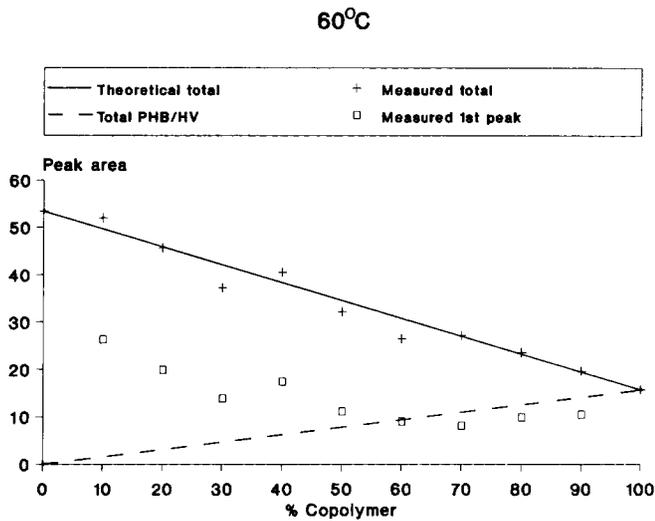


Figure 4 Areas of melting peaks (in arbitrary units) obtained from d.s.c. on blends crystallized at 60°C

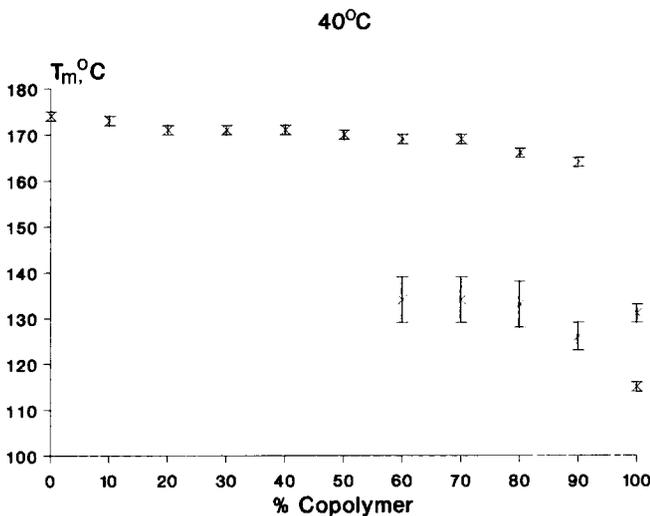


Figure 5 Melting points obtained from samples crystallized at 40°C

copolymer; the broken line shows the contribution expected from the copolymer component alone. The total measured areas correlate well with the expected values. For blends with 50% or less copolymer, the area of the lower-temperature peak is much higher than that available from the copolymer component alone. Thus, this peak clearly does not arise from a copolymer-rich phase in a separated sample and merely represents the fraction of the mixed blend that has not been transformed during heating in d.s.c. For blends containing 60% or more copolymer, the area of the first peak drops below that expected from the copolymer component. These results are thus consistent with the previous suggestion that phase separation occurs at around 60–70% copolymer content. Figures 5 and 6 show equivalent results from samples crystallized at 40°C. In this case only one melting temperature is obtained for 0–50% blends. The measured value is unlikely to represent the melting temperature of the original material since crystals grown at lower  $T_c$  values are more prone to annealing during heating. A distinct change in behaviour occurs once the copolymer content exceeds 50%: for all subsequent blends a lower-temperature peak is also

observed, which gives a  $T_m$  value very close to that obtained from the pure copolymer. The area of the lower-temperature peak is consistently lower than that expected from the copolymer component of the blend, as shown in Figure 6. Once again the results suggest phase separation, in this case commencing at the 60% blend, with one phase corresponding approximately to pure copolymer. Similar results obtained from samples crystallized at 50, 70 and 90°C indicate phase separation for blends containing  $\geq 60\%$ ,  $\geq 70\%$  and  $\geq 70\%$  copolymer respectively.

The 30, 40 and 50% blends crystallized at 140°C for several days and then cooled to room temperature all gave sharp high-temperature melting peaks, accompanied by a lower pair of peaks that lay entirely below the original crystallization temperature, as illustrated in Figure 7 for the 50% blend. Such behaviour is consistent with selective crystallization of a PHB-rich phase from the melt at  $T_c$ , leaving an HV-rich molten phase, which will subsequently crystallize on cooling.

*Effect of nucleant on crystallization.* The phase behaviour of the blends at higher temperatures was investigated by comparing the results of crystallization with and without the addition of ammonium chloride nucleant. On cooling from the melt and crystallizing, there are four possible situations that might arise for a

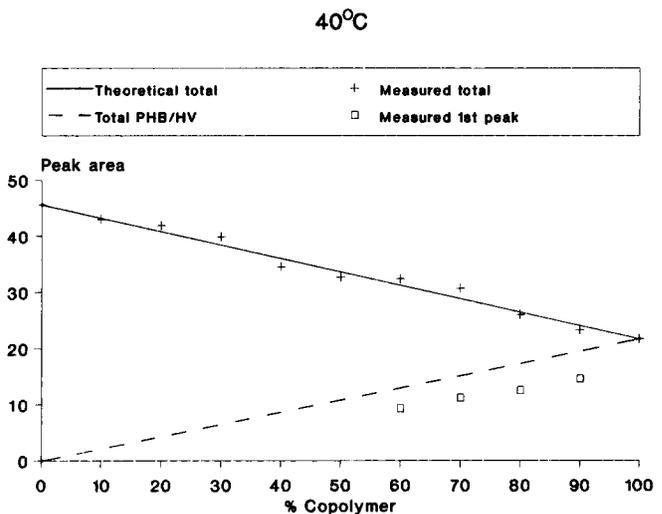


Figure 6 Areas of melting peaks (in arbitrary units) obtained from d.s.c. on blends crystallized at 40°C

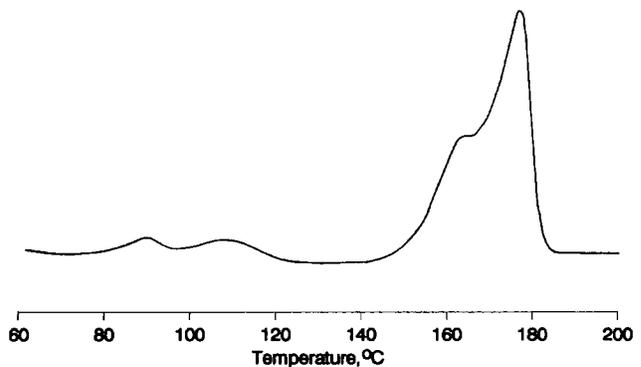
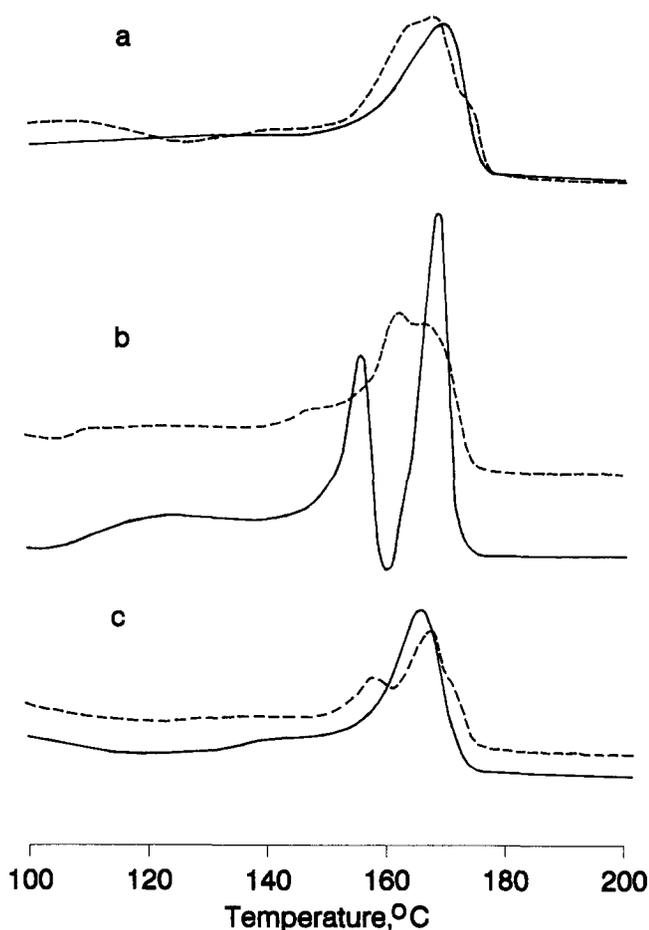


Figure 7 Melting endotherms obtained from a 50% blend crystallized at 140°C for several days, then cooled to room temperature



**Figure 8** D.s.c. melting peaks obtained from a 70% copolymer blend melted at 200°C, then (a) crystallized at 120°C, (b) crystallized at 100°C, or (c) annealed at 180°C then crystallized at 120°C, with (broken curves) and without (full curves) the addition of 2%  $\text{NH}_4\text{Cl}$

two-phase system that can crystallize completely. These are:

- (i) Mixed melt giving rise to mixed crystalline phase.
- (ii) Mixed melt followed by crystallization into two phases of differing composition (two-phase crystallization).
- (iii) Phase-separated melt followed by two-phase crystallization.
- (iv) Phase-separated melt producing mixed crystalline phase – unlikely to occur in practice.

In addition, there may be conditions where only part of the blend may crystallize, as illustrated previously in *Figure 7*. Examples of the various types of behaviour observed in this system are described below.

*Figures 8a* and *8b* show the results obtained from a 70% blend melted at 200°C and then crystallized at 120°C (*Figure 8a*) and 100°C (*Figure 8b*), with and without the addition of  $\text{NH}_4\text{Cl}$ . Homogeneous crystallization at these temperatures is very slow and non-nucleated samples have plenty of time to phase separate during crystallization if it is thermodynamically desirable to do so. The subsequent melting behaviour is thus representative of the crystal blend composition favoured at  $T_c$ . By providing heterogeneous nuclei, the crystallization rate is very greatly increased, and the possibility of changes of composition during crystallization is thus much reduced. The phase composition obtained from nucleated samples is therefore likely to reflect the previous melt composition more closely. In *Figure 8a* the results obtained are very similar for the nucleated and

non-nucleated samples; in both cases the melting behaviour suggests a mixed phase. This corresponds to case (i) above (mixed melt → mixed crystals). For the 100°C crystallization shown in *Figure 8b* the behaviour is rather different. The nucleated sample once again gives rise to a predominantly mixed phase, confirming that the two components are mixed in the melt at 200°C. However, the non-nucleated sample produces a separated system – the mixed melt has separated during crystallization to give a two-phase crystalline structure (case (ii) above). The d.s.c. traces shown in *Figure 8c* also refer to the 70% blend crystallized at 120°C, but in this case the melt has been subjected to an additional annealing stage at 180°C prior to crystallization. The crystals grown from the nucleated sample display multiple melting peaks, implying a tendency to phase separate in the melt at 180°C. In contrast, predominantly mixed crystals are grown from the corresponding non-nucleated sample. This behaviour appears to correspond to case (iv) above, where mixed crystals grow from a phase-separated melt. However, since crystallization of the non-nucleated sample is likely to be very slow at 120°C, a more plausible explanation is that the phase-separated melt remixes after cooling to 120°C, and thus produces mixed crystals (as expected from the result in *Figure 8a*). We may therefore conclude that a region of liquid–liquid phase separation exists for the 70% blend at temperatures between 140 and 180°C. Two crystal phases are obtained for crystallization at 100°C and below, while the two blend components will co-crystallize at 120°C.

*Figure 9* shows the results obtained from the 80% blend for crystallization at 100°C. One sample (*Figure 9a*) was cooled directly from 200°C, while the other (*Figure 9b*) was annealed at 180°C prior to crystallization. The behaviour seen in *Figure 9a* is very similar to that in *Figure 8b*, and once again indicates two-phase crystallization from a mixed melt. When the additional annealing step is included, we see a change in behaviour of the nucleated sample. In this case a phase-separated structure occurs in both samples, indicating that at 180°C the melt separates into two phases: *Figure 9b* illustrates case (iii) above where a separated melt gives rise to two crystalline phases. Thus we may conclude that the boundary for liquid–liquid phase separation of the 80% blend occurs between 180 and 200°C. Similar experiments using different blends and thermal treatments were consistent with the proposed boundaries. A further example of incomplete crystallization was obtained from the 90% blend crystallized at 120°C.

The information obtained from the different d.s.c. experiments is combined in the diagram shown in *Figure 10*. The dashed curve shows the approximate position of the boundary for liquid–liquid phase separation; the dotted curve shows where the crystals obtained *in practice* change from being predominantly mixed to phase-separated.

#### Microscopy

Polarizing optical microscopy revealed that all blend combinations crystallized in the form of banded spherulites. Spherulite growth rates were measured at 70 and 90°C, and these are shown in *Figure 11*. Where a phase-separated structure is thought to occur, we might expect to record different values of growth rate in the

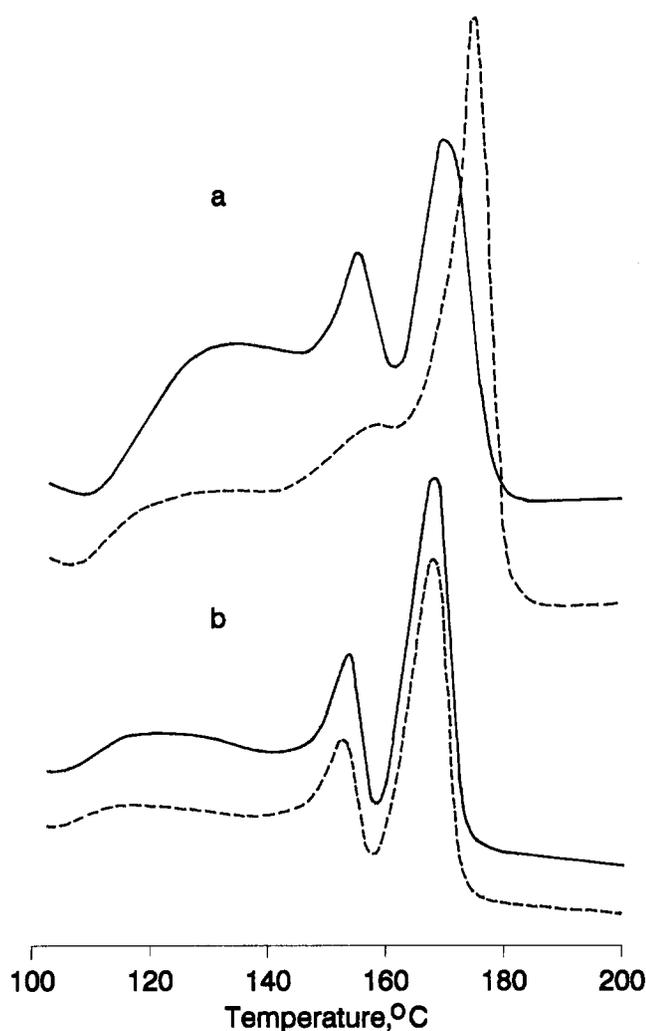


Figure 9 D.s.c. melting peaks obtained from a 90% copolymer blend crystallized at 100°C, (a) after melting at 200°C, or (b) after melting at 200°C then annealing at 180°C for 10 min, with (broken curves) and without (full curves) the addition of 2% NH<sub>4</sub>Cl

same sample, or to see morphological variations across the sample. Two distinct growth rates were observed in only one case – for the 90% blend crystallized at 90°C. The higher rate occurred during the early stages of crystallization and the lower rate in the later stages. Unusual spherulite morphologies were also seen under these crystallization conditions, and some examples are shown in Figure 12. In some cases the spherulites grew unusually shaped outgrowths as shown in Figure 12a, while other crystallizations produced spherulites containing areas with markedly different band spacings and regularity, as shown in Figure 12b. Initial observations of the morphologies obtained using other conditions believed to produce phase separation have as yet not produced conclusive results. Any differences are likely to be harder to spot in the 70 and 80% blends owing to the smaller proportions of copolymer-rich phase likely to be present there.

Electron microscopy of etched samples provides additional evidence for phase separation in both 80 and 90% blends. Figure 13 shows a selection of micrographs exhibiting typical morphologies obtained from mixed and segregated samples; all samples were crystallized at 60°C. Figure 13a comes from PHB and Figure 13b from PHB/18.4% HV. Both show regular lamellar structures,

but the copolymer sample is punctuated by parallel bands of holes, believed to arise from preferential etching of copolymer-rich material segregated during crystallization. Figure 13c shows part of a spherulite grown from a 50% blend, where a very regular morphology is obtained. Figures 13d and 13e both come from an 80% blend; the sample in Figure 13a has been annealed by slow heating to 100°C after crystallization. Two phases are present in Figure 13d, as evidenced by the differences in band spacing. The 'holey' morphology in the smaller spherulite is assumed to correspond to the copolymer-rich phase,

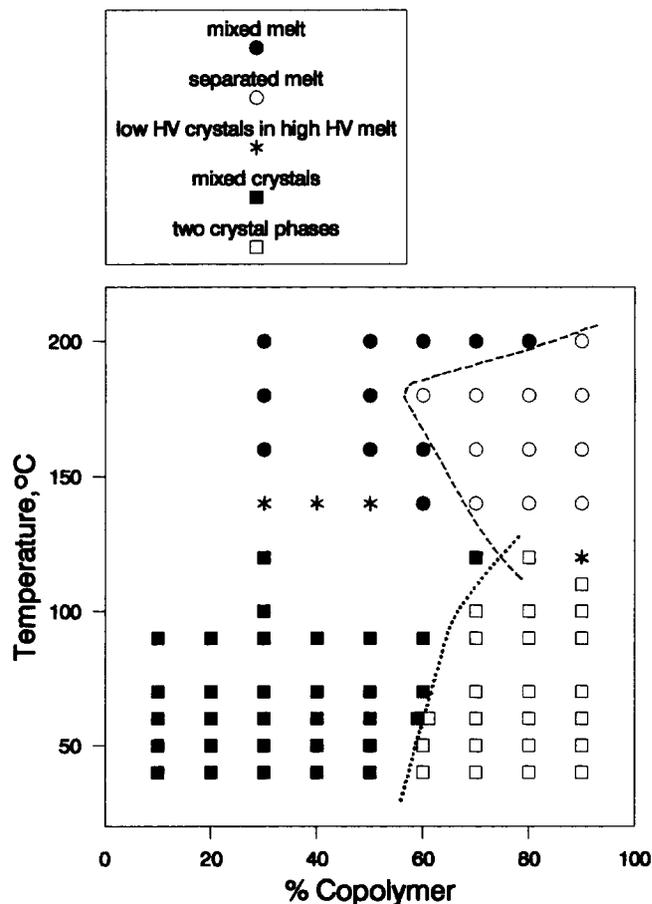


Figure 10 Summary of d.s.c. results. The dashed curve shows the approximate position of the boundary for liquid-liquid phase separation. The dotted curve shows the boundary between single- and two-phase crystallization

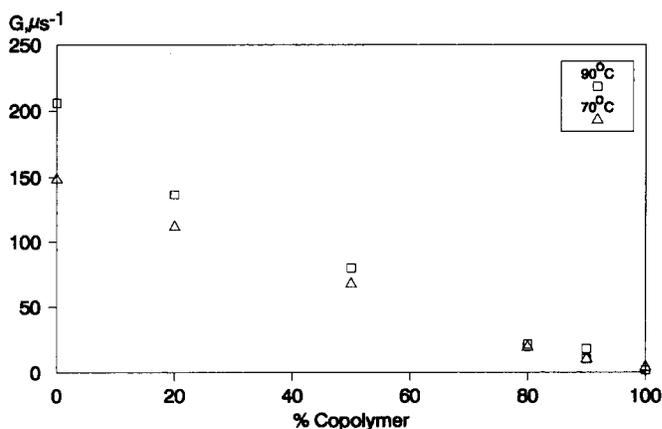


Figure 11 Spherulite growth rates measured from selected blends at 70 and 90°C



**Figure 12** Unusual morphologies observed in a 90% copolymer blend crystallized at 90°C, viewed between crossed polars

by analogy with *Figure 13b*. The segregated structure is very greatly accentuated by annealing, as shown in *Figure 13e*, where part of the structure has been etched more deeply than the rest. Large-scale variations in morphology were also observed in the 90% blend. In general, coherent replicas were difficult to obtain from samples believed to contain two crystal phases as the carbon film tended to disintegrate after removal from the surface. This is probably due to variations in etching effectiveness between regions of differing HV content, and provides further, though rather indirect, evidence for phase separation.

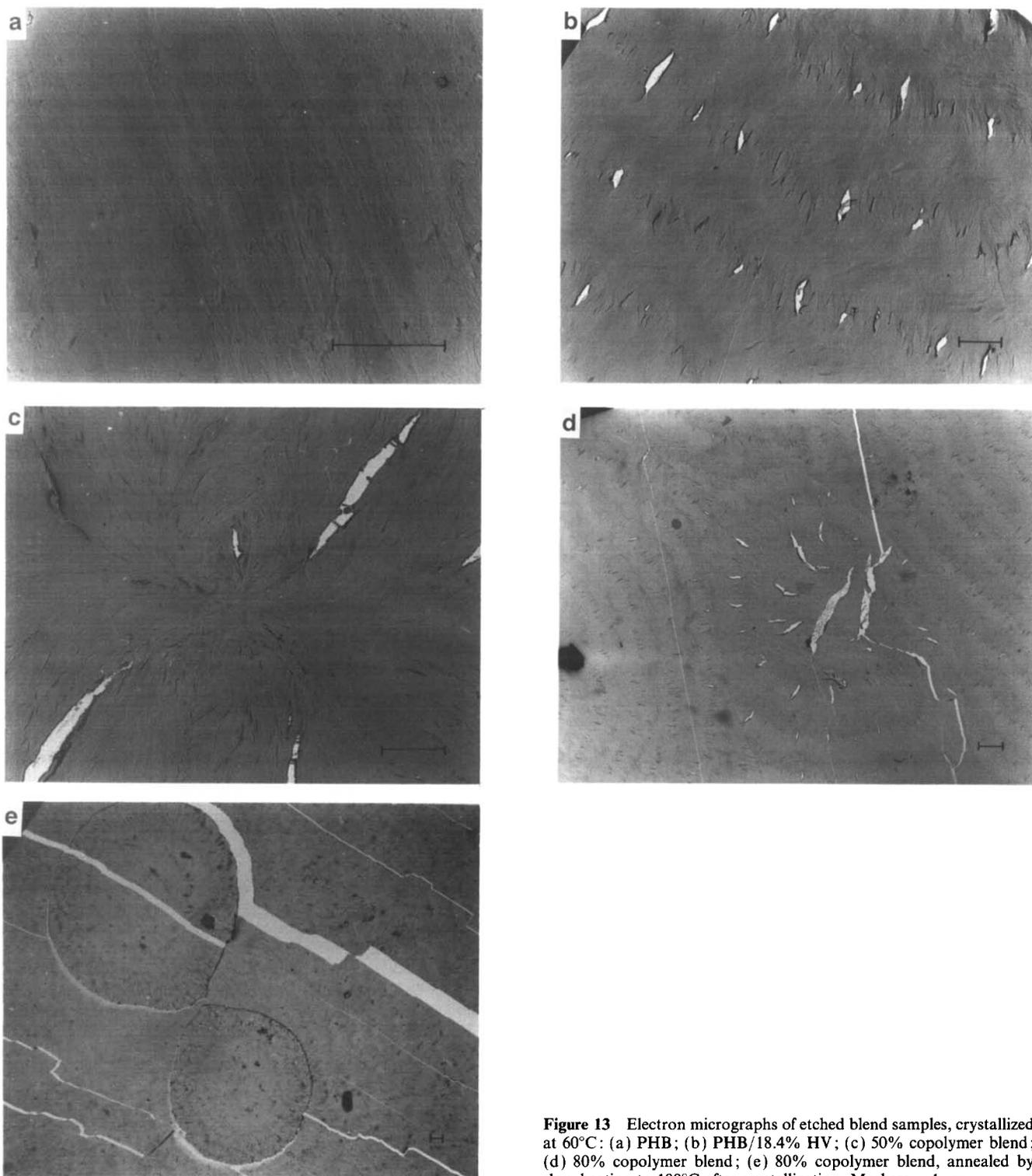
## DISCUSSION

Differential scanning calorimetry and optical and electron microscopy all suggest that blends comprising PHB and PHB/18.4% HV will be mixed over most of the range, but will separate into a two-phase system at higher copolymer concentrations. It is important to distinguish between the two different regions of behaviour included in *Figure 10*. At the higher temperatures both polymers are molten and the diagram demonstrates a region of liquid–liquid phase separation. The boundary obtained is an approximation to equilibrium, within the limitations of the timescale of the experiments. The blends were originally mixed under conditions of high shear (during extrusion), but, since consistent results were

obtained from nucleated samples obtained from solution, this is not thought to have a strong influence on the behaviour observed. The lower-temperature portion of *Figure 10* shows the types of crystal actually produced during crystallization under different conditions of temperature and blend composition. The results obtained are governed largely by kinetic factors, since crystallization prevents the establishment of true thermodynamic equilibrium. The diagram provides a practical guide to what will be obtained when these blends are used. In general, the results are characteristic of a system containing two components that display partial miscibility in the liquid state and partial solid solubility in the solid state. A further region of total miscibility is expected to exist for blends with very high (at least >90%) levels of copolymer. The results are consistent with previous studies by Marchessault *et al.* on a blend of PHB with 8% HV copolymer, where no evidence of phase separation was found<sup>11</sup>. Further experiments using blends containing higher HV content are in preparation, which should both test the generality of the liquid–liquid phase separation behaviour identified here and extend the diagram to include higher proportions of HV. It is unfortunate that the very low melt stability of these polymers prevents extension of the results to higher temperatures.

The behaviour observed in these blends is qualitatively very similar to that which occurs in mixtures of branched with linear polyethylene<sup>18,19</sup>. The apparent generality of the occurrence of liquid–liquid phase separation in blends of homopolymers with their copolymers, where the region of liquid–liquid phase separation is asymmetrically placed towards the copolymer side of the phase diagram, has led us to propose a simple model to explain such behaviour<sup>20,21</sup>. In this model it is argued that there is an additional asymmetric free-energy term not considered by the usual representations of phase behaviour in polymer blends.

The significance of the melting-point values obtained from the isothermal experiments (examples of which are shown in *Figures 3* and *5*) merits some consideration. The values obtained from the mixed phase (shown by the broken curve in *Figure 3*) might be expected to correspond to those obtained from equivalent copolymers crystallized at the same temperature. Accurate comparison between the two is difficult – as well as a strong dependence of  $T_m$  on  $T_c$  (ref. 22), PHB and PHB/HV melting points are particularly sensitive to variations in molecular weight<sup>23,24</sup>, and well characterized melting-point data for the copolymers are scarce. However, the general form of the results is certainly that which would be expected from the equivalent copolymers. The higher-temperature melting peak obtained from these samples comes from annealed material. The position of this peak is very close to that obtained from pure PHB over the range of compositions, suggesting that it is predominantly the PHB component that undergoes annealing. The origin of the double melting peak obtained from pure copolymer (shown in *Figure 2*) is not understood, although complex melting behaviours are very common in PHB/HV copolymers (see e.g. ref. 22). In the phase-separated samples the peaks obtained from copolymer-rich material are always close to the higher of the pure copolymer peaks: there is no discrete peak at lower values, although the peaks are broad enough to encompass the entire range of pure copolymer melting



**Figure 13** Electron micrographs of etched blend samples, crystallized at 60°C: (a) PHB; (b) PHB/18.4% HV; (c) 50% copolymer blend; (d) 80% copolymer blend; (e) 80% copolymer blend, annealed by slow heating to 100°C after crystallization. Markers = 1 μm

behaviour. It appears that the material giving rise to the lower-temperature peaks is more strongly affected by the presence of PHB in the mixture: at present we can offer no explanation for this. In an equilibrium situation it should be possible to relate the melting points of the phases in a separated system to the positions of the boundaries on the phase diagram. This is not possible in the present case – the measured melting points of the high-HV phase are consistently higher than suggested by *Figure 10*, giving a further indication of the non-equilibrium nature of the results. *Figures 4* and *6* show a good correlation between the total peak area obtained

by calculation and from experiment, for both mixed and phase-separated blends. This agreement is perhaps surprising in the case of mixed blends since the heat capacity of co-crystallized materials would be expected to be lower than the total available from the individual components<sup>9</sup>. This anomaly is unlikely to arise simply from experimental error, since the measured values are scattered on either side of the calculated curve. Since much of the area measurement comes from material that has annealed during heating in d.s.c., we assume that the extra perfection attained during the annealing process accounts for the high areas obtained.

The morphological evidence obtained is generally in agreement with the phase behaviour deduced from the d.s.c. results. Where phase separation is clearly observed, the separation is on a large scale, as illustrated in *Figures 12 and 13*. In regions where two crystal phases are expected to be present, but are not observed, this may simply be a consequence of the small proportion of one of the phases present, or may be due to separation on a finer scale that is not easily visible. Small-scale phase separation could account for the difficulty encountered in preparing replicas from many samples believed to be phase separated.

## CONCLUSIONS

From our calorimetric and morphological studies on a system comprising blends of PHB with PHB/18.4% HV we have identified a region of liquid-liquid phase separation in blends containing 60% or more of copolymer. Two-phase crystallization occurs over a similar range of composition, with the precise characteristics of the phases determined largely by kinetic factors. The behaviour is characteristic of a system displaying partial miscibility and shows similarity with results obtained from blends of linear with branched polyethylene.

## ACKNOWLEDGEMENTS

We are indebted to Andy Webb of ICI for providing the blend samples and to Mary Hill for useful discussions during the course of the work. Financial support was provided by SERC and ICI.

## REFERENCES

- 1 Lemoigne, M. *Ann. Inst. Pasteur* 1925, **39**, 144
- 2 Holmes, P. A. in 'Developments in Crystalline Polymers - 2' (Ed. D. C. Bassett), Elsevier, London, 1987, p. 1
- 3 Avella, M. and Martuscelli, E. *Polymer* 1988, **29**, 1731
- 4 Greco, P. and Martuscelli, E. *Polymer* 1989, **30**, 1475
- 5 Marand, H. and Collins, M. *Polym. Prepr.* 1990, **31**, 552
- 6 Dave, P. B., Ashar, N. J., Gross, R. A. and McCarthy, S. P. *Polym. Prepr.* 1990, **31**, 442
- 7 Dave, P., Gross, R. A., Brucato, C., Wong, S. and McCarthy, S. P. *Polym. Mater. Sci. Eng.* 1990, **62**, 231
- 8 Abbate, M., Martuscelli, E., Ragosta, G. and Scarinzi, G. *J. Mater. Sci.* 1991, **26**, 1119
- 9 Barker, P. A., Mason, F. and Barham, P. J. *J. Mater. Sci.* 1990, **25**, 1952
- 10 Sanchez Cuesta, M., Martinez-Salazar, J., Barker, P. A. and Barham, P. J. *J. Mater. Sci.* 1992, **27**, 5335
- 11 Marchessault, R. H., Bluhm, T. L., Deslandes, Y., Hamer, G. K., Orts, W. J., Sundararajan, P. R. and Taylor, M. G. *Makromol. Chem., Macromol. Symp.* 1988, 235
- 12 Mitomo, H., Barham, P. J. and Keller, A. *Polym. Commun.* 1988, **29**, 112
- 13 Grassie, N., Murray, E. J. and Holmes, P. A. *Polym. Degrad. Stab.* 1984, **6**, 47
- 14 Grassie, N., Murray, E. J. and Holmes, P. A. *Polym. Degrad. Stab.* 1984, **6**, 95
- 15 Ballistreri, A., Montaudo, G., Garozzo, D., Giuffrida, M. and Montaudo, M. S. *Macromolecules* 1991, **24**, 1231
- 16 Doi, Y., Kunioka, M., Nakamura, Y. and Soga, K. *Macromolecules* 1986, **19**, 2860
- 17 Organ, S. J. and Barham, P. J. *J. Mater. Sci.* 1992, **27**, 3239
- 18 Hill, M. J., Barham, P. J., Keller, A. and Rosney, C. C. A. *Polymer* 1991, **32**, 1384
- 19 Barham, P. J., Hill, M. J., Keller, A. and Rosney, C. C. A. in 'Integration of Fundamental Polymer Science and Technology 3' (Eds P. J. Lemstra and L. Kleintjens), Elsevier, Amsterdam, 1989, p. 291
- 20 Barham, P. J., Hill, M. J. and Goldbeck-Wood, G. *Proc. Am. Chem. Soc. PMSE Prepr.* 1992, **67**, 197
- 21 Barham, P. J., Hill, M. J., Goldbeck-Wood, G. and Van Ruiten, J. *Polymer* submitted
- 22 Organ, S. J. and Barham, P. J. *J. Mater. Sci.* 1991, **26**, 1368
- 23 Organ, S. J. and Barham, P. J. *Polymer* in press
- 24 Organ, S. J. *Polymer* in press