The use of thermal analysis in the study of liquid–liquid phase separation in ble.ids of some crystallizable homopolymers with their branched copolymers

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Abstract

It is difficult to determine the degree of mixing or demixing in blends in which the two components have closely similar physical properties, such as homopolymer–lightly branched copolymer blends. Direct methods of observation of liquid–liquid phase separation are not possible, but in the course of our studies of blends of linear with branched polyethylenes we have developed several indirect techniques. We examine samples after rapid quenching from the melt in order to determine whether the melts were mixed or demixed prior to quenching. One of the most useful techniques is DSC; however, there are limitations to its applicability and it is usually necessary to use a second technique. This paper describes the techniques in detail and pays particular attention to the strengths and weaknesses of DSC in determining phase separation.

INTRODUCTION

In this paper, we present a review of our research in the determination of liquid–liquid phase separation (LLPS) in crystallizable homopolymer/co-polymer blends. As far as we know, no other workers apply the techniques that we use to examine LLPS in such blends. We shall not discuss blends of non-crystallizable polymers, where other techniques, such as measurements of the structure of the glass transition in quenched blends can reveal information concerning the state of mixing of the melts prior to quenching (see, for example, refs. 1–3 and, especially, a review in ref. 4); nor will we review the extensive literature dealing with segregation or cocrystallization on crystallization (for example, refs. 5–8); nor the recent work on block copolymers by Bates and coworkers [9, 10]. Here we discuss only the use of DSC to study LLPS in crystallizable homopolymer/co-polymer blends.

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Recently, we have pioneered techniques to determine the phase behaviour, particularly LLPS, in blend of crystalline homopolymers with their branched co-polymers [11–26]. We have found differential scanning calorimetry (DSC) to be an invaluable tool. It is not possible to detect LLPS in these homopolymer/co-polymer blend melts by the usual direct methods. The two components have closely similar physical properties so that if there is any LLPS, the contrast between the phases is too small to detect. For instance, cloud points cannot be observed optically because of the similarity of the refractive indices of the two components. However, we have been able to devise indirect methods to deduce the state of the melt. We have argued that the state of the solid, after fast quenching, must reflect the state of the melt before quenching. Large-scale diffusion, e.g. on a scale of microns, cannot take place during a rapid quench.

DSC can give a rapid indication of the state of a melt prior to quenching; simply by noting whether there are one or two melting endotherms present we can usually deduce whether the melt was homogeneous or biphasic. However, the thermograms are open to misinterpretation, especially when used alone. It has been our usual practice to follow up an initial DSC study with transmission electron microscopy (TEM) of surface replicas of quenched blends. The TEM is used to confirm the initial DSC data and can give more detailed information.

Initially our interest was with blends of linear polythylene (LPE) with branched polyethylene (BPE) [11–18, 22, 23], but more recently we have extended our investigations to other systems [19–21, 24–26], in particular to blends on the bacterial polyester, poly(hydroxybutyrate) (PHB) with copolymers of hydroxybutyrate and hydroxyvalerate (PHB/HV) [19, 20, 24–26]. Hydroxyvalerate may be regarded as a branched analogue of hydroxybutyrate. For the work on PHB/HV blends, DSC was often used, alone, in more complex and subtle experiments. We have come to believe that there is LLPS in melts of these blends under some conditions of composition and temperature. Reference 12 describes several other techniques which we have used, on occasion, in combination with DSC.

The purpose of the current paper is to describe our DSC techniques, and how they assist our studies of the phase behaviour of homopolymer–copolymer blends; we shall highlight the advantages, disadvantages and potential pitfalls of the technique. We begin by describing our work on LPE/BPE blends, initially outlining our main conclusions, to put the work in context. We then show, in detail, how DSC was used in combination with TEM to obtain these results. With this background we discuss the merits and demerits of DSC, indicating the strengths and weaknesses of the technique in this type of work. Finally, we show how more complex DSC experiments have been used to investigate LLPS in PHB/HV blends where our TEM technique cannot be used satisfactorily.

LLPS IN BLENDS OF LPE WITH LIGHTLY BRANCHED BPE

We have shown that LLPS frequently occurs when an LPE is blended with a BPE. We have looked at 35 blend systems at the time of writing, mostly binary but some ternary [18, 22]. The LPEs we have used have molar masses from 2500 to 2×10^6 Dalton [11–15]; one deuterated linear polyethylene (DPE) [13] was included. The BPEs include octene co-polymers (2–8 mol% octene) [16], butene copolymers (1–3 mol% butene) [22], and a range of commercial low-density polyethylenes (LDPEs) and linear low-density polyethylenes (LLDPEs) [13, 22] (details of all the polymers we have used are given in Table 1). We have also blended pairs of

TABLE 1

Characteristics of the polymers investigated in our published work (manufacturer given for commercially available materials)

Polymer	Manufacturer		M_w	M_w/M_n	Ref.
Linear polyethylenes					
Sclair 2907	Du Pont		10^5	3	11–15
Rigidex 50	B.P.		7×10^4	7	13, 15
F(1) fraction	Fractionated in Bristol		1.5×10^4	1.4	13, 15
Hizex 245			2×10^6	Now known	13, 15
F(2) fraction	Polymer Labs		2500	1.1	13, 15
DSM LPE	DSM		5×10^4	2.9	16
Deuterated LPE	MSD		2×10^5	2.2	13, 15
Branched polyethylenes		Branch content			
PN 220	B.P.	2.6 per 100	2×10^5	8	11–15
Specially made octene copolymers		Mol% octene			
O(2)	DSM	2.1	51×10^3	2.2	16, 18, 22
O(3)	DSM	3.0	130×10^3	2.0	16
O(5)	DSM	5.2	37×10^3	1.9	16, 22
O(8)	DSM	8.0	43×10^3	2.0	16, 18, 22
O(12)	DSM	11.8	46×10^3	2.0	16
LLDPEs used in our work					
Sclair 8105	Du Pont	1.2 per 100 "short"	10^5		13
B'(2)	Exxon	2 mol% butene	4.17×10^5	4.2	22
B'(3)	Exxon	3 mol% butene	2.2×10^5	4.8	22
O'(3)	DSM	3 mol% octene	3.1×10^5	3.1	22
PHB and PHB/HV					
PHB	Zeneca		4.17×10^5	2.8	19
PHB/HV	Zeneca	18.4% HV	5.82×10^5	3.2	19

more and less branched materials [18, 22]. We have found LLPS in all but one of these systems. LLPS was not found when the LPE was of very low molar mass (fraction F(2) see Table 1 for details); this was not unexpected because LLPS is found to decrease with decreasing molar mass of the LPE [13].

In general our systems show both upper and lower critical temperature (UCT and LCT respectively) behaviour; the LLPS region always appears as a closed loop, asymmetrically placed at high BPE content. Figure 1 shows a generalised phase diagram. Often, although there are clear indications of LCT behaviour, the low temperature part of the loop cannot be fully investigated due to the onset of crystallization; this is the case shown in the figure. However, when crystallization is slow and/or the loop is above the highest temperature for crystallization, the whole loop can be revealed [18, 22]. There are various systematic variations in loop size with molar mass [13] and branch content [16], but these are not the concern of this paper. Our concern here is to describe and discuss the role of DSC in determining the phase behaviour.

THE ROLE OF DSC IN THE DETERMINATION OF LLPS IN LPE/BPE BLENDS

Simple DSC test for mixed and separated melts

Our simple diagnostic DSC test, which is qualitative rather than quantitative, is based on the examination of DSC endotherms obtained on remelting quenched blends, using a Perkin-Elmer DSC-7. Figure 2 shows a range of DSC traces obtained on reheating blends of different compositions quenched from the same temperature. Note that, for our purposes, only the number and relative positions of the melting endotherms are important. The actual heat absorbed and the absolute temperatures are less important. The percentage figure indicates the LPE content of the blend, e.g. a 40% blend contains 40% LPE and 60% BPE. The polymers were blended by dissolving LPE and BPE together in xylene and then quenching into acetone (a non-solvent) at freezing point. Blends were filtered, harvested and dried. Samples of 2–3 mg were then taken for DSC studies. These DSC samples were placed on a Kofler hot bench at some nominated temperature (163°C in the case of Fig. 2) for 20 min before being quenched by flicking into acetone at its freezing point. Samples were held in the melt for 20 min to ensure that equilibrium was reached [12, 14]. The samples were sealed in DSC pans. We did not crystallize blends under nitrogen; however, in extensive separate tests we were not able to detect
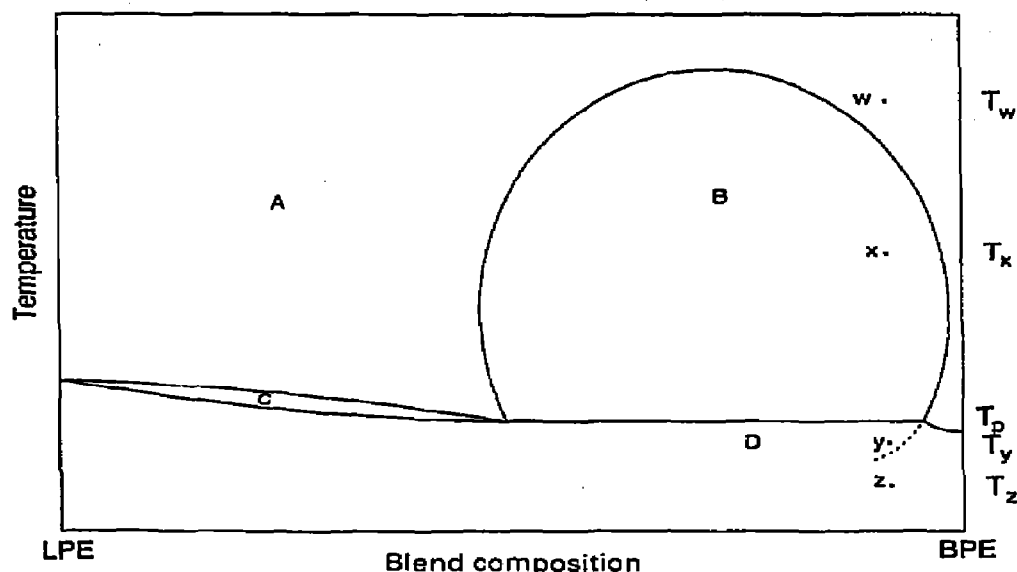
Fig. 1. A schematic phase diagram illustrating the type of phase separation found in most LPE/BPE blends. The region A is of a mixed melt; B is a biphasic melt; C represents a region where crystals of one composition are growing in a melt of a different composition; D represents a non-equilibrium region. The meanings of the various marked temperatures, T_w, T_x, etc., are explained in the text.

any oxidation or degradation affecting the phase behaviour until the samples had been held at over 200°C for well over an hour.

There are a number of points to note from Fig. 2.

(i) Both the homopolymers show single-peaked DSC melting curves, indicating a single population of melting crystals.

(ii) The 80% and 50% blends also show single melting peaks when quenched from 163°C. This again indicates single populations of melting crystals. The enthalpies of melting can be measured from the areas under these single peaks. The areas under the 80% and 50% blend melting peaks are sufficiently large that these peaks cannot be due to the melting of the LPE in the blend alone; some BPE must also be incorporated into the crystals. Further, note that the melting points of the quenched LPE, 80% blend and 50% blend are progressively lower, a further indication of co-crystallization. We consider that a single melting peak of this type indicates that there is one type of co-crystal present, formed on quenching a mixed melt. TEM studies show that in such samples all crystals have approximately equal thickness, i.e. TEM confirms that only one crystal type is present. A micrograph of a surface replica of a sample which gave a single DSC peak is seen in Fig. 3(a).

(iii) In contrast, where the LPE content is lower (35% and below in Fig. 2), two crystal melting peaks are found. However hard the samples are quenched, the DSC trace on reheating shows two peaks and the ratio of
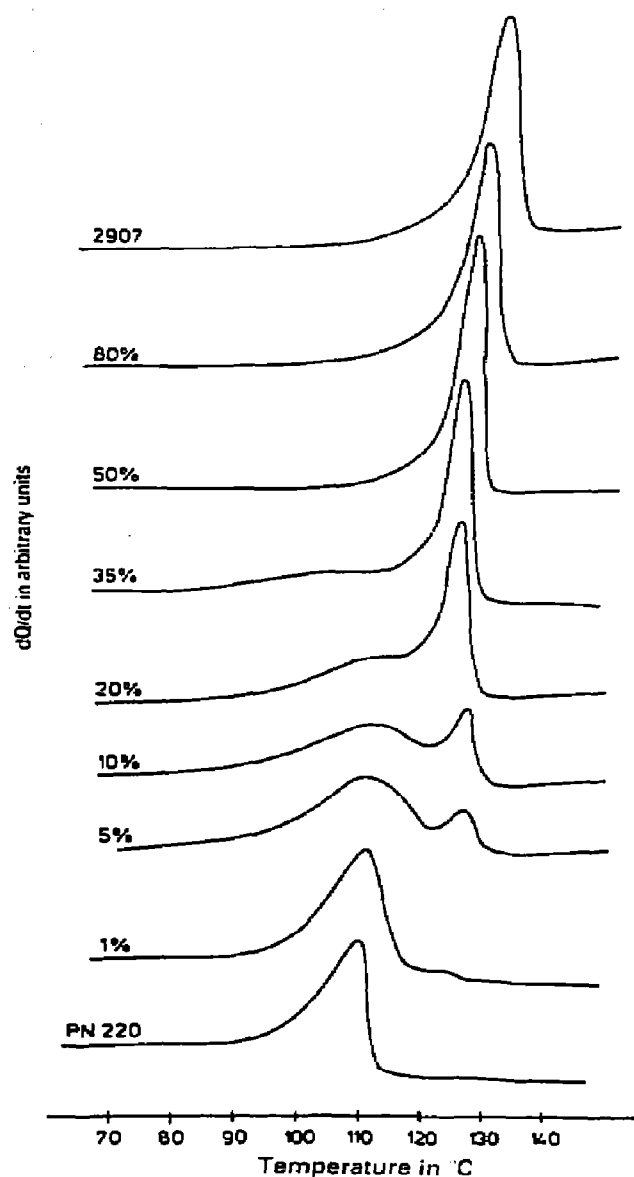
Fig. 2. A series of DSC curves, recorded at a heating rate of 10°C min⁻¹, from blends of different compositions of Sclair 2907 (LPE) with PN220 (BPE) all quenched from 163°C. All traces are plotted with the endotherm direction upwards. The DSC was flushed with nitrogen.

these does not vary with heating rate. Also note that although the relative peak heights vary, the high melting and low melting temperatures are the same for all blend compositions. It was this that suggested LLPS to us in the first place [11]. These results are consistent with two crystal types, one melting at a temperature rather lower than the melting point of the (single population) 50% co-crystals, and the other melting at a temperature very near to the melting point of the pure BPE. This indicates one phase with just less than 50% LPE and one phase of nearly pure BPE.
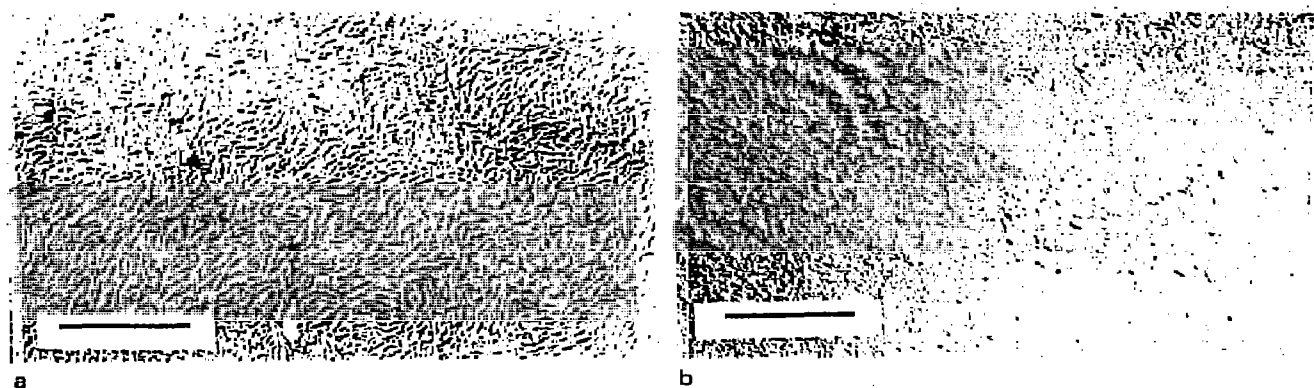
Fig. 3. Transmission electron micrographs of surface replicas of quenched blends of Sclair 2907 (LPE) and PN220 (BPE). (a) A 35% blend quenched from 190°C illustrating a morphology typical of a mixed system: all lamellae are of the same type. (b) A 10% blend quenched from a lower temperature. 140°C. illustrating a typical morphology arising from a segregated melt. Note the two groups of thicker (LPE rich) crystals at the top left and bottom right of the picture: these thicker crystals form banded spherulites. The BPE-rich matrix is composed of very much thinner crystals, only just visible at this magnification: they are not arranged in banded spherulites. The scale bars represent 1 micrometre.

We are aware that two melting peaks can be obtained where there is partial melting and recrystallization, or annealing, of the sample on heating. However we do not believe that this is the case here for several reasons. From thermal analysis we note that the relative peak sizes are not heating rate dependent, and that the transition from one to two peaks is precisely composition dependent [23], but relatively insensitive to quench rate, for any given quench temperature. (It does, however, vary with pre-quench temperature, see below.) We feel that this abrupt change in behaviour taking place (in this case) between 50% and 45% composition must have a serious physical origin; remelting effects would not be so composition dependent.

The thermal data have been supported by extensive transmission electron microscopy (TEM) [11–16]. We have found consistency between DSC and TEM studies. When the TEM of rapidly quenched samples of LPE/BPE blends shows only one distinct crystal population, we see only a single melting peak in the DSC. Conversely, when we see two distinct crystal populations by TEM, we also find two distinct melting peaks in the DSC. Furthermore, in those blends where two distinct crystal populations can be seen, we can measure the sizes of these distinct regions. If the size of the phase morphology (readily seen in the TEM) exceeds the distance over which molecules could diffuse during the crystallization, then we may further deduce that the two crystal populations originated from two distinct regions in the melt, i.e. we may deduce that there was LLPS in the melt. We show in Fig. 3 two examples of surface replicas from our very extensive collection. Figure 3(a) shows a single, uniform, morphology indicating the

melt was mixed. Figure 3(b) shows two distinct crystal populations with crystals of different thicknesses. The separation between groups of thicker crystals like those seen in Fig. 3(b) is, typically, on a scale of microns, a distance greater by two orders of magnitude than the molecules could diffuse in the time available before crystallizing during a fast quench [15]. Thus we may deduce that this sample was quenched from a biphasic melt. These two examples are of blends of different composition. However, for any blend composition where a two-phase melt is found at lower temperatures (for instance at T_x in Fig. 1), a single-phase melt is found at higher temperatures (such as T_w in Fig. 1). These results indicate the UCT nature of the phase separation; numerous examples are given in Ref. 14.

In our work, we have taken the observation of a single peak on remelting a quenched blend to indicate a mixed melt at the quench temperature, and a double peak to indicate a segregated melt. We have used DSC to map out the extent of phase separation in broad terms. Work on a new blend system always begins with the preparation of 75%, 50% and 25% blends, which are then quenched from 140°C and examined by DSC. The results give a good idea of the extent of any LLPS loop. For instance, if the 50% blend shows one peak and the 25% blend two almost equal peaks, the LLPS loop can be assumed to extend to nearly 50% LPE composition at 140°C. However, if the 50% blend shows one peak and the 25% blend has only a small low-melting shoulder, the LLPS loop is likely to extend only as far as about 30% composition at 140°C. From these initial results, it is usually clear which other blends should be made in order to determine the composition of the highest LPE content of the LLPS loop and the highest point (in temperature) of the loop.

We have shown that DSC results are very reproducible, and that our blends are surprisingly homogeneous [13]. However, although DSC is rapid, reproducible and clear, it has some limitations and a second technique (usually TEM) has to be used to plot the phase diagram in detail.

LIMITATIONS OF DSC FOR PLOTTING LLPS LOOPS

Determination of the UCT

When a blend is quenched through a relatively small temperature drop, the results obtained from DSC agree with those from TEM of surface replicas. However, although DSC can indicate that the LLPS region is of a UCT type, it is does not reveal the actual upper critical temperature accurately. An example of this appears in our original work on blends of Sclair 2907 with PN 220. In ref. 11, we show DSC traces obtained on
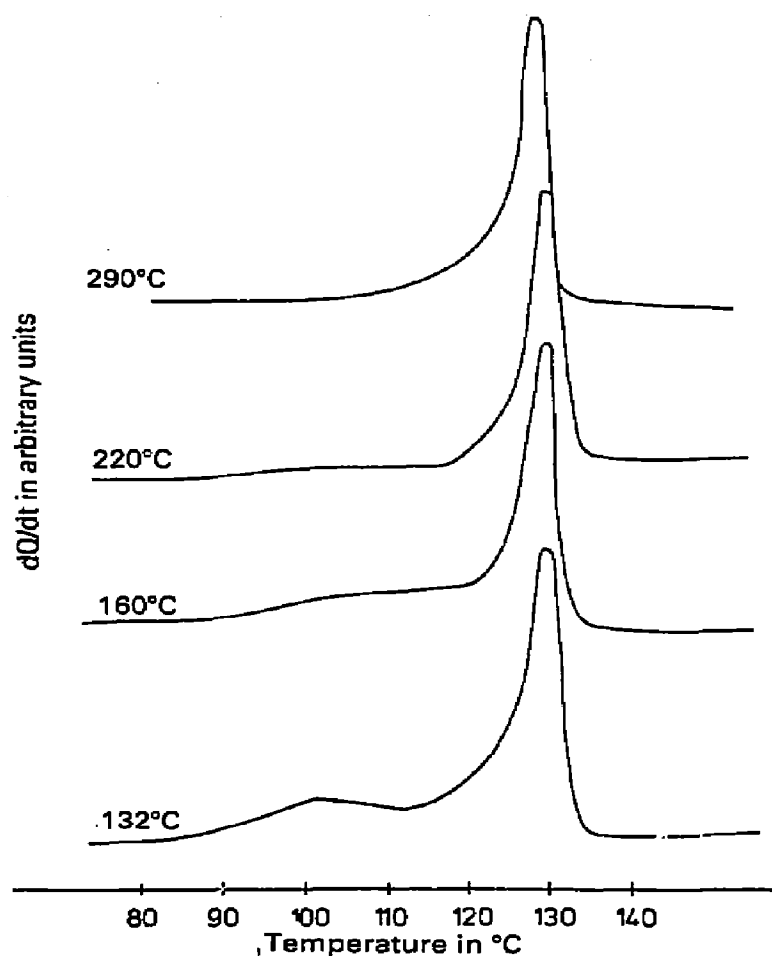
Fig. 4. A series of DSC curves obtained at a heating rate of 10°C min $^{-1}$ from quenched 35% blends of Sclair 2907 (LPE) with PN220 (BPE). The melt temperatures before quenching are indicated in the figure. All traces are plotted with the endotherm direction upwards.

quenching 35% blend samples from 132, 160, 220 and 290°C. The results, reproduced here as Fig. 4, indicate that there is segregation at all temperatures up to 220°C, with a phase boundary somewhere between 220 and 290°C. The separation is less pronounced as the temperature from which the sample was quenched rises up to 220°C, indicating a reduction in the width of the region of LLPS. All this taken together, suggests UCT behaviour. (It also confirms that the segregation does not take place during the quenching of an initially mixed melt, a suggestion made by some colleagues in the initial stages of this work. If the segregation took place on quenching it would be greater, not less, for the sample quenched through the larger temperature drop.)

However, when we compare the DSC results with TEM we find that the phase boundary is at a lower temperature than DSC would indicate. We

can deduce from surface replicas that a 35% blend of Sclair 2907 with PN 220 is segregated (showing two crystal types on quenching) at 150°C, but mixed at 170°C (Fig. 3(a) shows the single morphology obtained on quenching from 190°C). TEM indicates a phase boundary at about 160°C. The morphology of the blend quenched from 220°C is similar to that seen in Fig. 3(a), but DSC gives a double melting peak, as seen in Fig. 4, at 220°C. The reason for this difference lies in the speed of the quench. The actual surface, examined by the TEM technique, is the most rapidly quenched part of the sample. Normal DSC samples have a thickness of some tenths of a millimetre. The thermal conductivity of polyethylene is very poor, and even this thickness is sufficient that the interior of the sample is cooled slowly enough for some segregation to take place as the sample passes through temperatures within the LLPS loop. It is possible to obtain single DSC peaks when quenching from above the LLPS region, through increasingly large temperature drops, by using extremely small, thin samples [14]. However, the maximum segregated temperature for any blend composition cannot be determined satisfactorily by this method; TEM of surface replicas gives a more reliable indication.

Segregation by crystallization

Anomalous DSC results, due to segregation on crystallization, can also be obtained from thick samples. We have compared the outside surfaces with the interiors of 1 and 2 mm thick samples of 75% blends of Rigidex 50 blended with PN 220 quenched from 150°C. DSC endotherms of thin quenched samples show one melting peak. Samples cut from the outside surfaces of thick samples give traces like those of thin samples (with a single endotherm). However, samples cut from the centre of thick pieces of blend quenched from 150°C give DSC melting traces with additional low melting peaks. TEM of surface replicas showed one crystal population, as expected. In contrast, replicas taken after cutting into the interior of the samples showed segregation on a very small scale. We believe this to be due to segregation on crystallization, the most branched material being rejected at the crystallizing surfaces. This is made possible by the much reduced quench rate in the interior of the poorly conducting sample. DSC cannot distinguish between the segregation on a scale of micrometres, which we see by TEM of surface replicas of samples quenched from the LLPS region, and the very small-scale separation which is found on slowly quenching samples mixed in the melt; we believe that this latter type of segregation is a consequence of crystallization. TEM can show the scale of the separation of two crystal types, but DSC can only indicate that there are two crystal types. In this DSC is inferior to our TEM method.

ADVANTAGES OF DSC IN STUDIES OF PHASE BEHAVIOUR

Obtaining a general idea as to the width of the LLPS loop

It is very much faster and simpler to obtain a DSC heating endotherm of a quenched sample than to prepare a replica. Hence, as indicated above, we use DSC to gain a first impression of the range of segregation in a new system, later filling in details with TEM, our choice of samples being guided by the initial DSC results.

Use of DSC in estimating times to mix or demix

We have found that it is possible to estimate the diffusion rates of LPE through the BPE matrix using DSC and TEM in combination [15]. This has been done by studying the low temperature, low LPE part of the phase diagram. It is possible to crystallize blends with low LPE content from the metastable, super-cooled state, at temperatures below the temperature at which, on very slow cooling, the LPE-rich part of all segregated blends would crystallize (T_l, in Fig. 1). This is because the crystallization rate of the LPE-rich portion of these blends can be slow, particularly when the LPE blend content is low [12, 14, 15]. We have found that low LPE content blends re-mix at these low temperatures [11–16, 18]. In some cases the crystallization time is so long that the melt can mix completely [18, 22] before crystallization takes place.

Consider a blend melt cooled from the segregated state (at T_x on the phase diagram, Fig. 1) where crystallization is not possible, to T_y where the melt will remain demixed and crystallization is possible. Isothermal crystallization will take place at T_y to give grouped LPE-rich crystals (of the sort shown in Fig. 5(a)). The grouping of these crystals reflects the fact that the LPE-rich polymer was localized in a droplet prior to crystallization. However, if the melt is cooled from the segregated state at T_x to T_z, the melt is found to mix. Isothermal crystallization from a completely mixed melt gives a distinctive morphology in which the LPE-rich crystals are not grouped, but well separated (Fig. 5(b)). In some cases the mixing and crystallization times are close; then a loose morphology is obtained (Fig. 5(c)) because the melt was in the process of mixing during crystallization.

The DSC melting endotherm cannot tell us if a fully isothermally crystallized low LPE content sample contains grouped or separated crystals (as in Fig. 5(a) or Fig. 5(b)). Only TEM can distinguish unambiguously between the two morphologies. However, the remixing process can be followed by DSC. Examples are given in refs. 11, 12 and 15. One example is reproduced here. Figure 6 (data taken from ref. 15) shows DSC traces obtained on remelting 1% blends of the LPE fraction F(1) with PN 220
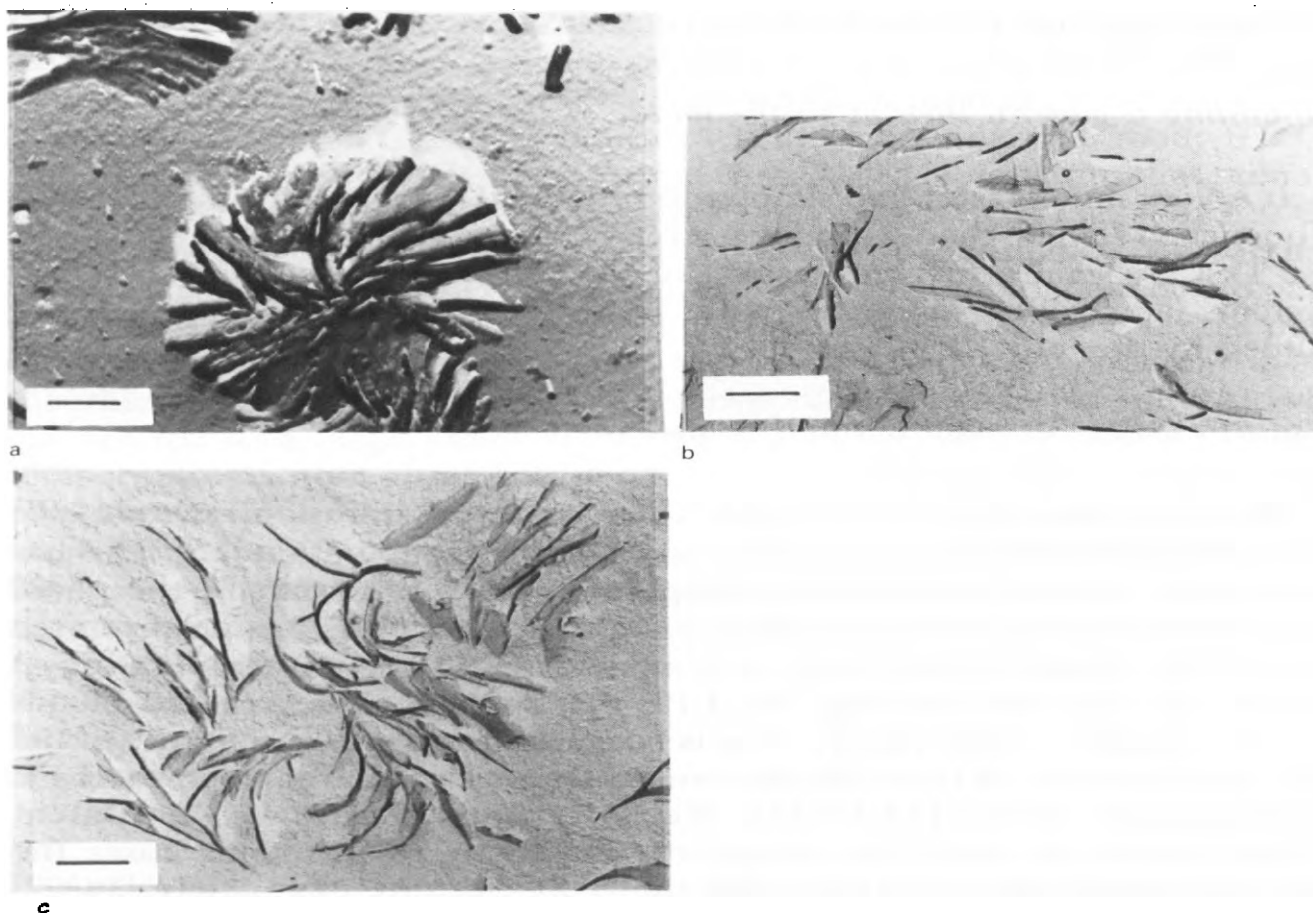
Fig. 5. Transmission electron micrographs of surface replicas of isothermally crystallized 1% blends of Rigidex 50 (LPE) and PN220 (BPE). (a) Crystallized from a segregated melt at 126°C, a temperature equivalent to T_x in Fig. 1, (b) Crystallized from a mixed melt at 122°C, a temperature equivalent to T_y in Fig. 1. (c) Crystallized whilst the melt was mixing at 123°C. The scale bars represent 1 micrometre

after various thermal treatments. By looking at a series of DSC traces such as those shown in Fig. 6, we are able to identify remixing and to determine both the time taken for the melt to remix and the time taken for it to crystallize. In Fig. 6(a), we see DSC traces obtained from a blend first held in the melt at 150°C for 20 min, and then quenched to 122°C, a temperature still within the LLPS loop, i.e. quenching from T_x to T_y in Fig. 1. The samples were held for various times at 122°C (as indicated in the figure) before quenching into acetone at its freezing point. The samples were then melted in the DSC to give the curves shown in Fig. 6(a). The two melting peaks obtained on reheating the blend after storage at 122°C for 0 and 5 min are characteristic of quenching a segregated melt. For samples held at 122°C for 1 h, a sharp, high melting peak appears in addition to the other two. This peak indicates melting of LPE-rich crystals grown isothermally at 122°C. On heating blends stored for longer times at 122°C, the highest
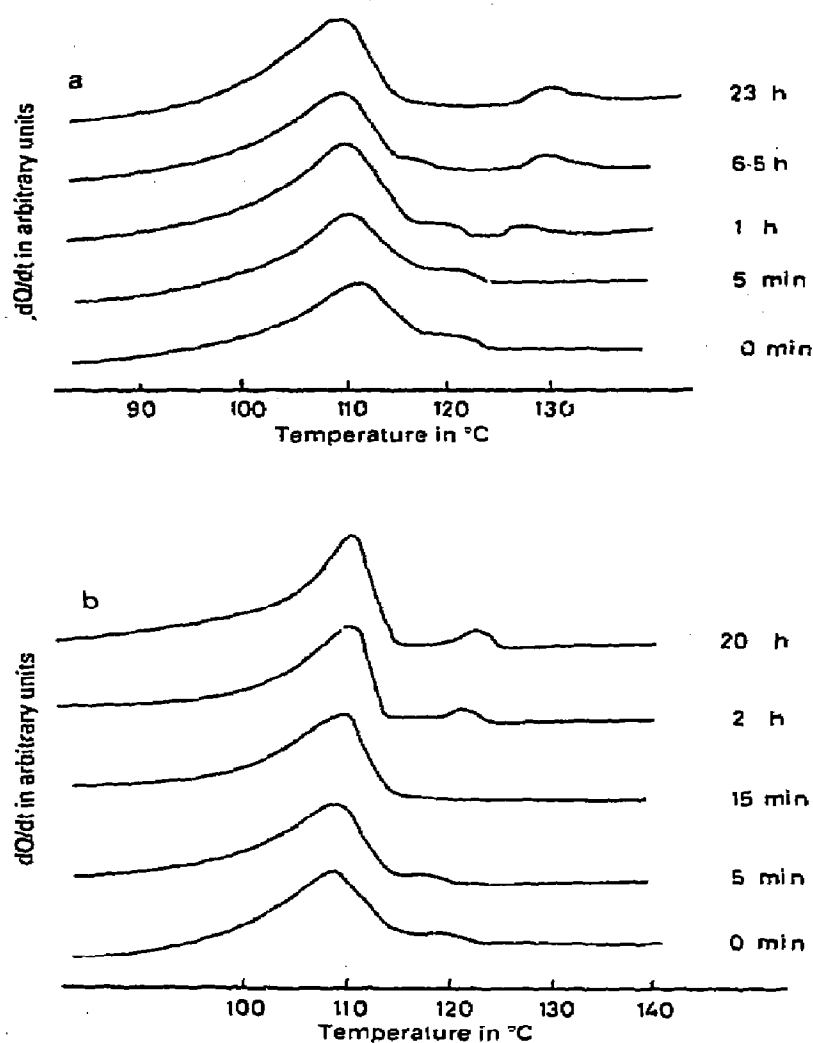
Fig. 6. DSC endotherm traces obtained on heating 1% blends of fraction F(1) (LPE) with PN 220 (BPE) at 10°C min⁻¹. The samples had been held at 150°C for 30 min and then (a) quenched to 122°C or (b) 117°C, and held there for the times indicated, before further quenching into acetone at its freezing point. The DSC was flushed with nitrogen.

melting peaks (isothermally crystallized LPE-rich material) increase in size, at the expense of the peak indicating the melting of quenched LPE-rich polymer. Thus the progress of crystallization can be followed. When we quench the sample from the melt at 150°C to a temperature in the mixed region of the phase diagram, i.e. from T_x to T_z in Fig. 1, in this case $T_z = 117°C$, we see the pattern of behaviour shown in Fig. 6(b). Again samples were held at 117°C for various times (as indicated in the figure) before quenching into acetone at its freezing point. The samples were then melted in the DSC to give the curves shown in Fig. 6(b). In these experiments, remixing takes place and the higher of the melting peaks (due

to quenched material) is seen to decrease in size, and finally vanish, before isothermal crystallization sets in. The remixing time, as well as the crystallization time at the lower temperature, can be assessed in this way.

USE OF DSC IN THE STUDY OF PHASE BEHAVIOUR OF PHB/HV BLENDS

Liquid–liquid phase separation has also been detected in blends of PHB with PHB/HV or of copolymers of differing HV content. The techniques used are similar to those described above, but some modifications are necessary to tailor procedures to the rather different characteristics of these systems. Although it is possible to quench PHB and PHB/HV copolymers into the glassy state, the glass transition temperatures are so similar (always between 0 and 5°C) that it is not possible to use the structure of the glass transition region to determine the phase behaviour. Morphological investigations of the blends can be carried out using methylamine etching [19, 24] followed by replication: however, in this case the crystalline morphologies of the two blend components are very similar, making unambiguous identification of separate phases rather difficult. In addition, variations in etching rate between areas of differing HV content tend to lead to disintegration of replicas made from etched phase-separated samples. For these reasons, most of the results obtained are derived entirely from thermal experiments [19, 20]. Low melt stability restricts the accessible temperature range and the types of experiment which can be performed on these blends.

EXPERIMENTAL METHOD USED IN THE STUDY OF PHB/HV BLENDS

Crystallization rates in unnucleated PHB and PHB/HB are generally slow [25] and it is possible to quench both components into the glassy state without any substantial crystallization occurring. Two different experiments were developed, which permitted investigation of different areas of the phase diagram. These are described below.

Isothermal crystallizations

Small samples of each blend were melted at 200°C either in a Linkam hot-stage or in the DSC for 1–2 min and then crystallized isothermally at temperatures T_c in the range 40–140°C. For the lower crystallization temperatures, an additional quenching stage, from T_c to below T_g, was included between melting and crystallization so that these samples crystallized from the glassy state: this procedure promotes rapid nucleation

so that crystallization times can be kept to a minimum. After crystallization was complete, samples were heated in the DSC at appropriate rates and the positions and areas of all melting endotherms were noted.

Effect of nucleant on crystallization

The crystallization behaviour of the blends at high temperatures was compared, with and without the addition of 2% ammonium chloride. At high T_c, typically 100–140°C, the crystallization rates of unnucleated PHB and PHB/HV are extremely slow and the polymer melts have ample time to reorganize prior to crystallization at T_c, if it is thermodynamically desirable to do so. Addition of NH_4Cl, which acts as a nucleant [26], greatly increases crystallization rates and allows the original structure of the molten blend to be "frozen in" by the process of crystallization. Thus the composition of the melt at the melting temperature T_m can be distinguished from the composition which the melt adopts prior to crystallization at T_c. Additional experiments were carried out whereby samples were held, after melting, at an annealing temperature T_a (200°C > T_a > 120°C) for 5–10 min prior to crystallization, allowing other points in the liquid region of the phase diagram to be investigated. All samples were melted in the DSC after crystallization and the position of all melting endotherms noted.

RESULTS: DSC STUDIES OF PHB/HV BLENDS

All the examples given are taken from a blend system comprising PHB homopolymer (M_w = 417000, M_w/M_n = 2.8) mixed with PHB/HV copolymer containing 18.4% of HV units (M_w = 582000, M_w/M_n = 3.23). The blends will be referred to by the amount of copolymer which they contain, i.e. a 10% blend contains 90% PHB and 10% PHB/HV, etc. The sample masses were the same in all cases (±2%). It should be noted that the notation used for the PHB/HV blends differs from that used for the LPE/BPE blends.

Isothermal crystallizations

When interpreting melting points obtained from these blends using DSC, it is very important to distinguish between multiple peaks arising from phase-separated structures and multiple peaks which often arise as a result of annealing during heating in the DSC. These may be differentiated by their response to variations in heating rate. Figure 7 shows examples of DSC melting endotherms obtained at various heating rates from 30% (Fig. 7(a)) and 90% (Fig. 7(b)) blends after crystallization at 60°C. In Fig. 7,
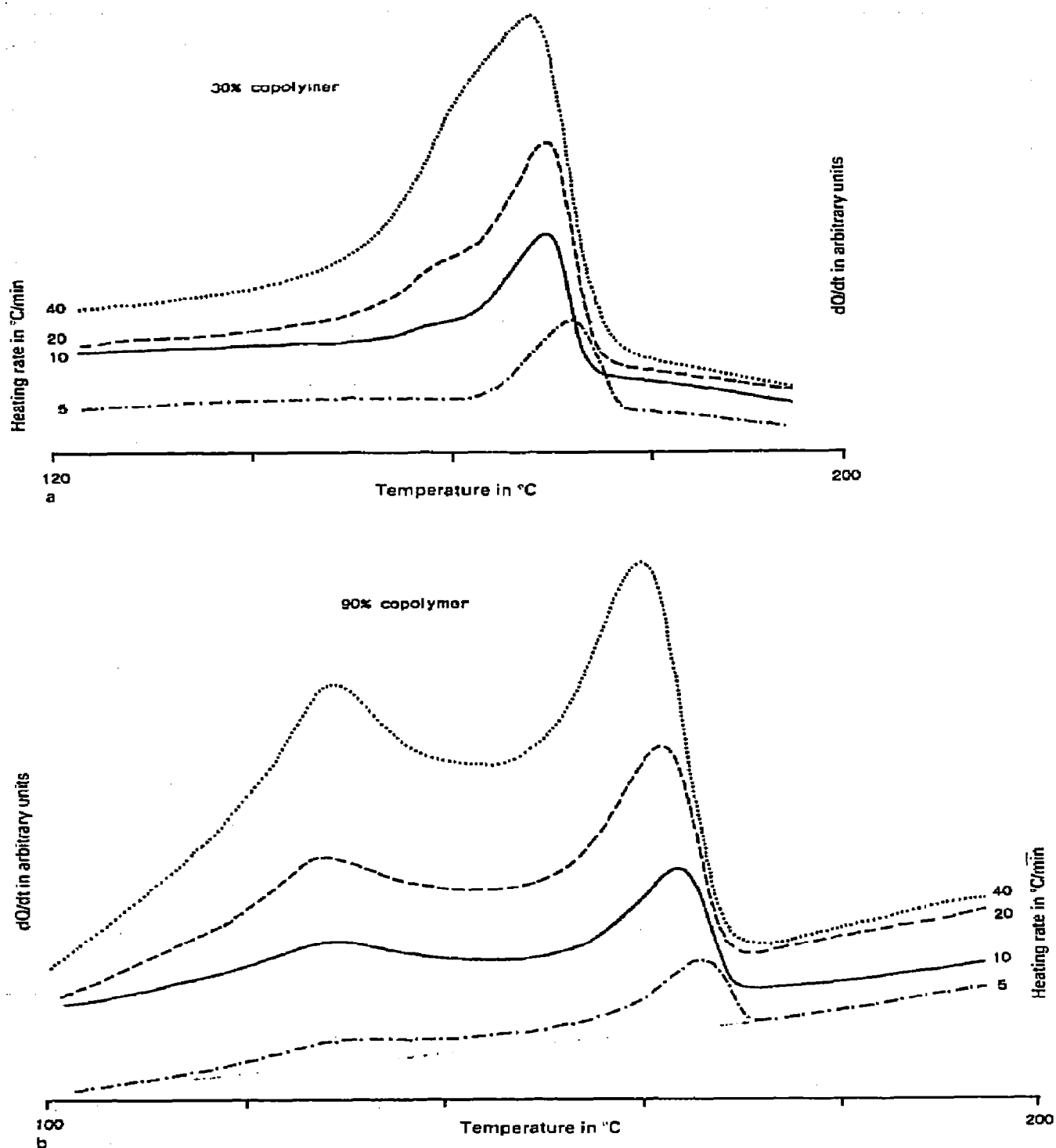
Fig. 7. DSC melting endotherms obtained at the heating rates shown on the figure after crystallization at 60°C. All traces are plotted with the endotherm direction upwards. (a) Blend of 70% PHB with 30% of a PHB/HB copolymer containing 18.4% HV. (b) A blend of 10% PHB with 90% of the same PHB/HV copolymer.

double peaks are observed in all cases except the 30% blend heated at 5°C min^{-1}, 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 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 best approximated 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. Thus the 30% blend (Fig. 7(a)) demonstrates the behaviour of a single mixed-crystalline phase, with the melting behaviour of that mixed phase given by the lower temperature peak. The 90% blend (Fig. 7(b)) 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, the melting behaviour of the isothermally crystallized samples was analysed using a heating rate of 20°C min^{-1}. In all figures, the temperature range is chosen to include all the observed peaks—no evidence for reorganization during heating was observed at lower temperatures. Figure 8 shows examples of the melting endotherms obtained from PHB, 50% blend, 80% blend and PHB/HV, all crystallized at 60°C. The pure copolymer itself gives a double melting peak, but in phase-separated blends the melting point of the copolymer-rich phase is always close to the upper of the two. The 80% blend shows two distinct peaks (not strongly affected by heating rate), indicating a two-phase structure. In the 50% blend, the original material represented by the lower temperature shoulder undergoes annealing during heating in the DSC to give a second peak with a melting point similar to that of PHB. The position of the first peak lies on a smooth curve between the melting points of PHB and pure copolymer, and represents the melting of a mixed blend. The measured areas of the peaks are consistent with this interpretation. At lower crystallization temperatures, the peak arising from the original melting of the single phase in mixed blends is never seen, due to the greater tendency to annealing in such crystals. Figure 9 shows the measured melting points obtained from blends crystallized at 40°C. In this case, only one melting temperature is obtained for 0%–50% blends and
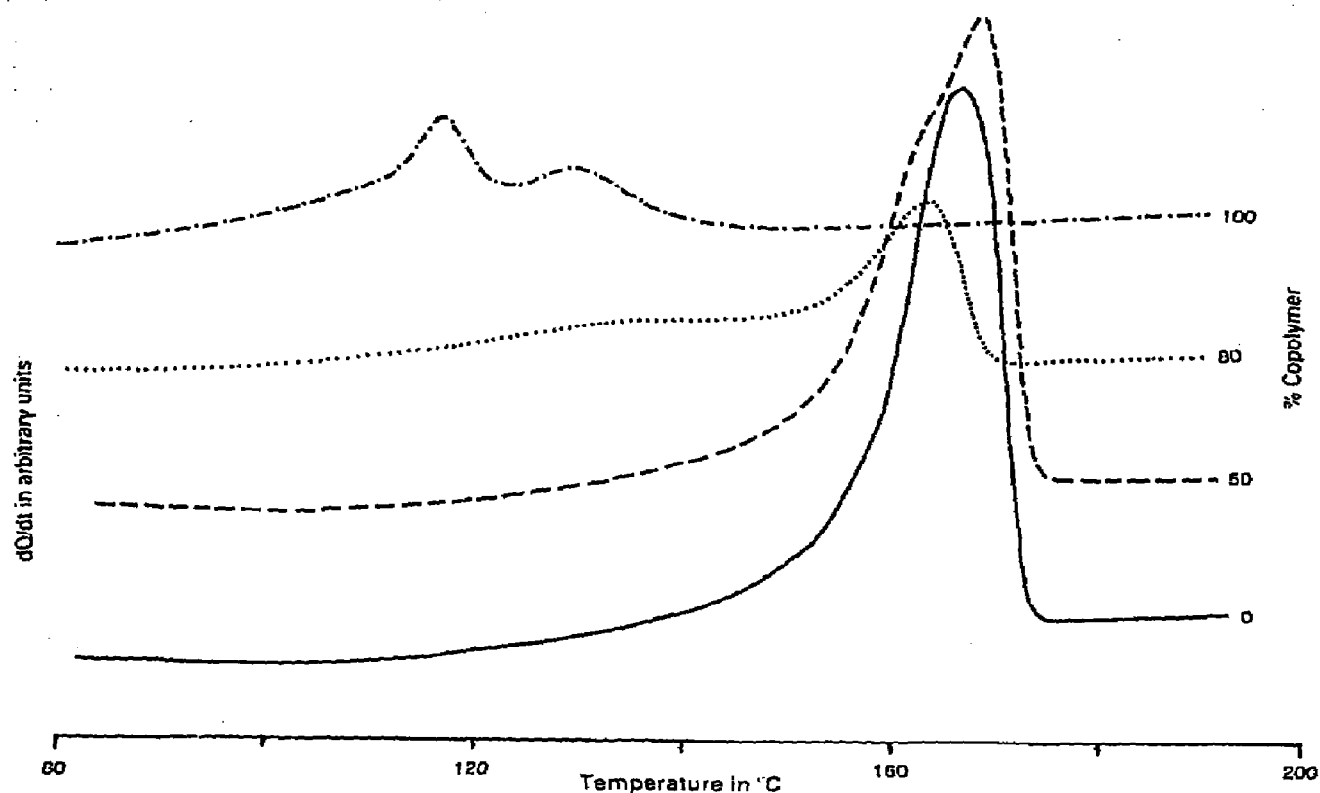
Fig. 8. Melting endotherms obtained from samples with the PHB/HV copolymer contents shown, all crystallized at 60°C. All traces are plotted with the endotherm direction upwards.
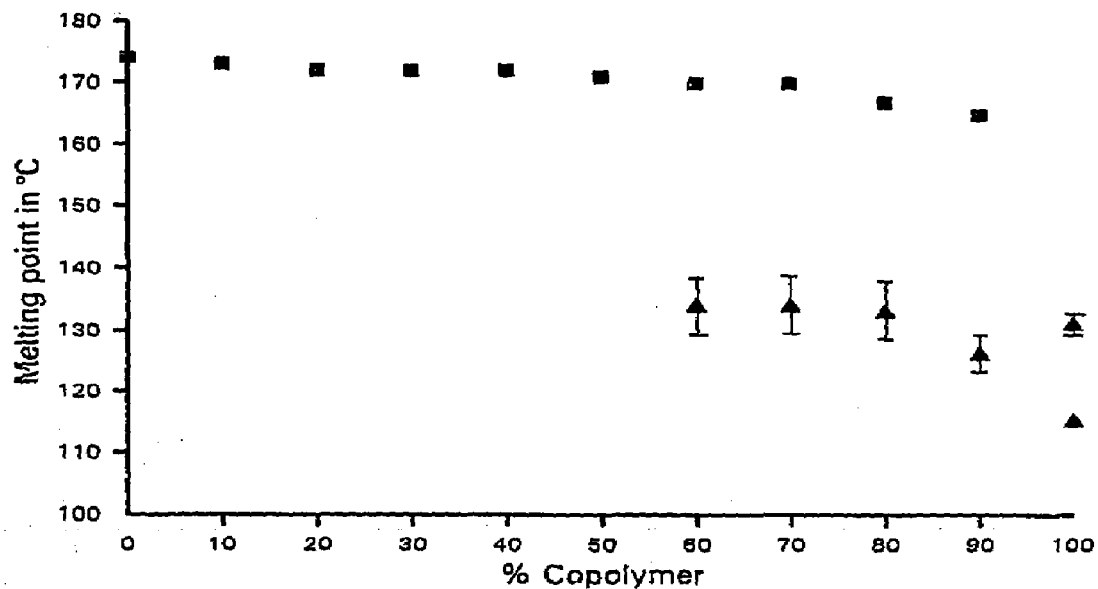

Fig. 9. Melting points obtained from samples of PHB–PHB/HV blends crystallized at 40°C:
▲. ••• ■. •••.

this corresponds to annealed material. A distinct change in behaviour occurs once the copolymer content exceeds 50%: for all subsequent blends a distinct lower temperature peak is also observed, which gives a T_m value very close to that obtained from the pure copolymer. The results indicate phase separation, in this case commencing at the 60% blend, with one phase corresponding, approximately, to pure copolymer.

A rather different crystallization behaviour was sometimes observed at the highest crystallization temperatures: 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 which lay entirely below the original crystallization temperature. 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

These experiments allowed the phase behaviour of the blends in the molten state to be determined 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 which might arise for a two-phase system which can crystallize completely: mixed melt giving rise to mixed crystalline phase; mixed melt followed by crystallization in two phases of differing composition (two-phase crystallization); phase-separated melt followed by two-phase crystallization; and phase-separated melt producing mixed crystalline phase. In addition, there may be conditions where only part of the blend may crystallize, as discussed previously. Examples of all the possible types of behaviour were observed in this system and one illustrative example is given below.

Figure 10(a) and (b) shows the results obtained from a 70% blend melted at 200°C and then crystallized at 120°C (Fig. 10(a)) and 100°C (Fig. 10(b)), with and without the addition of NH_4Cl. Homogeneous crystallization at these temperatues is very slow and thus the melting behaviour obtained from the non-nucleated samples is representative of the crystal blend composition favoured at T_c. By providing heterogeneous nuclei, the crystallization rate is very greatly increased and the phase composition obtained from nucleated samples is therefore likely to reflect the previous melt composition more closely. In Fig. 10(a), the results obtained are very similar for the nucleated and non-nucleated samples; in both cases the melting behaviour suggests a mixed phase, i.e. we have a mixed melt producing mixed crystals. The fact that the nucleated sample apparently shows closely separated multiple peaks over the temperature range 150–170°C probably indicates a slight tendency to phase separation during the time scale of the crystallization process, but the behaviour is
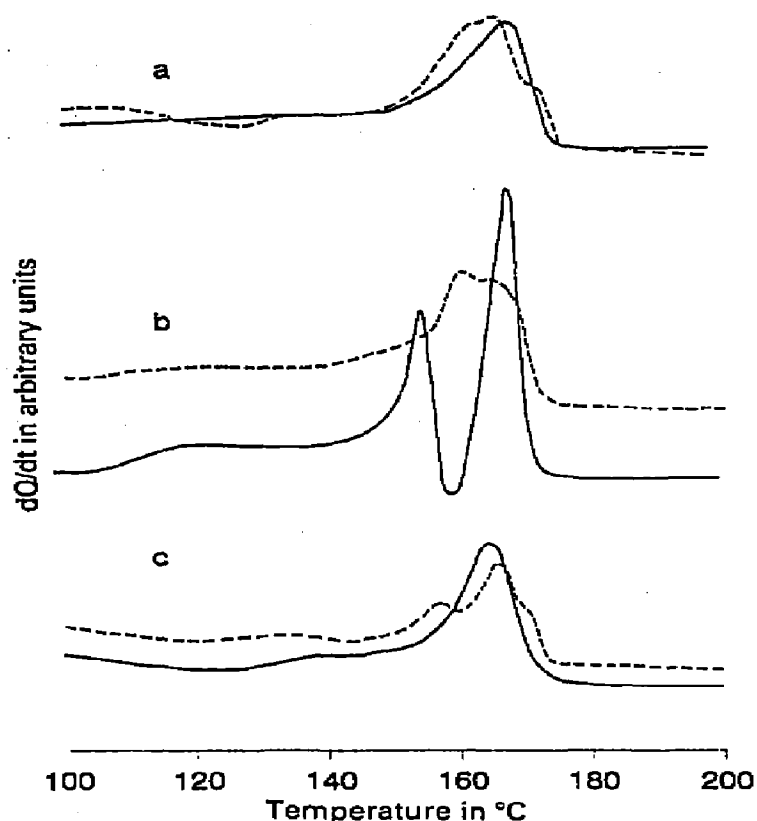
Fig. 10. DSC melting peaks obtained from a blend of 30% PHB with 70% PHB/HV copolymer blend melted at 200°C, then (a) crystallized at 120°C, (b) crystallized at 100°C, or (c) annealed at 180°C then recrystallized at 120°C, with (broken curves) and without (full curves) the addition of 2% NH₄Cl. All traces are plotted with the endotherm direction upwards.

predominantly that of a mixed sample. For the 100°C crystallization shown in Fig. 10(b), the behaviour is rather different. The nucleated sample once again gives rise to a predominantly mixed phase, confirming that the two components were originally mixed in the melt at 200°C. However, the non-nucleated sample produces a separated system—the mixed melt separated during crystallization to give a two-phase crystalline structure. The DSC traces shown in Fig. 10(c) 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 unnucleated sample. This behaviour appears to correspond to the case where mixed crystals grow from a phase-separated melt. However, because crystallization of the unnucleated sample is likely to be very slow at 120°C, a more plausible

explanation is that the phase-separated melt re-mixes after cooling to 120°C, and thus produces mixed crystals (as expected from the result in Fig. 10(a)). 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. Similar experiments allow us to plot the composition in the melt for the whole range of blends.

The information obtained from the different DSC experiments is combined in the diagram shown in Fig. 11. The broken line shows the approximate position of the boundary for liquid–liquid phase separation; the dotted line shows where the crystals obtained *in practice* change from being predominantly mixed to phase separated. These are not equilibrium structures; rather, the crystal composition is determined largely by kinetic factors. Figure 11 illustrates a region of liquid–liquid phase separation asymmetrically placed towards the copolymer side of the diagram, very similar to the behaviour identified in blends of linear with branched polyethylene. Similar studies on other combinations of PHB with PHB/HV or of PHB/HV with a copolymer of different HV content have shown this to be a general phenomenon, where the difference in HV level between the two components exceeds about 12% [20].
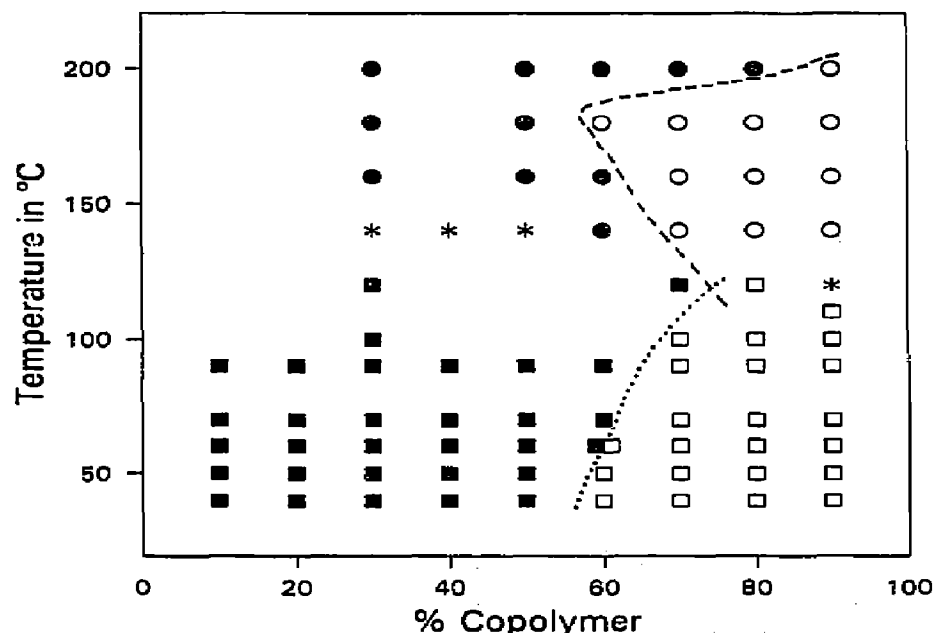

Fig. 11. Summary of DSC results on blends of PHB with a PHB/HV copolymer containing 18.4% HV: ●, mixed melt; ○, separated melt; *, low-HV crystal phase in high-HV melt phase; ■, mixed crystals; and □, two crystal phases. The broken curve shows the approximate position of the boundary for LLPS. The dotted curve shows the boundary between single- and two-phase crystallization.

SUMMARY: THERMAL ANALYSIS TO STUDY BLENDS

In our work on the determination of the extent of LLPS in LPE blends, we have used DSC extensively. We rely on the DSC fingerprints: one peak on remelting quenched mixed blends; two peaks on remelting segregated blends. However, we have found certain ambiguities with the technique, and always use it in association with other experimental methods, particularly TEM (see ref. 12 especially).

We used DSC to give initial indications of LLPS in new blend systems and to map out the likely extent of phase separation. In plotting our ternary phase diagram [18], we mapped the whole system with DSC quenching from a single temperature (involving DSC endotherms from some 70 quenched blend samples). We then checked the phase behaviour at critical points and explored higher temperatures using TEM. If we had not been able to establish the general phase behaviour rapidly by DSC, the whole process would have been prohibitively long.

We have used DSC to assess crystallization times and remixing times. Again this can be done much more rapidly by DSC than with other techniques.

In the case of the PHB/HV blends, we have needed to devise more subtle DSC tests for phase separation, because in this polymer the morphological differences between the phases are more difficult to observe. We have shown that there are two ways in which DSC is particularly useful: in isothermal crystallization studies we are usually able to distinguish between crystallization from mixed and demixed melts; and with the addition of a nucleant to increase the overall rate of crystallization, we can extend the studies further to determine the state of melts at temperatures above the crystallization temperature.

Thus, DSC has been invaluable to us in our work, but we are well aware that DSC results are sometimes open to more than one interpretation, and we have been careful to use other techniques in parallel.

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