Phase segregation in melts of blends of linear and branched polyethylene

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A linear polyethylene (LPE) has been blended with a branched polyethylene (BPE) in a range of concentrations. Using several experimental methods in combination, the full phase diagram for this polymer pair has been mapped out. In particular, the polymers are shown to be conditionally miscible in the melt; the melt segregated region occurs at low LPE content and is of a closed loop shape. It is, however, impossible to reach parts of the region due to crystallization. Considerable co-crystallization takes place whenever any of the blends are crystallized isothermally; crystals commonly include LPE and BPE in the ratio 6:4 and in an extreme case have been found to contain LPE to BPE in the ratio 1:3. Attention is drawn to the wide range of morphologies (and, by implication, properties) which can be obtained from this system.

(Keywords: linear and branched polyethylene; melts; miscibility)

INTRODUCTION

There is at present much interest, both academic and industrial, in the processing and properties of polymer blends. Pairs of immiscible polymers are usually studied. Our interest, however, has been in the phase behaviour of blends of partially miscible, crystallizable polymers. Such systems offer a potential wealth of morphologies and properties depending on the state of phase separation existing prior to, or developing during, crystallization. In two previous publications[1,2] we described how the morphology of a blend of linear and branched polyethylenes depends both on the relative proportions of the two polymers, and on the crystallization conditions. We argued, basing our arguments on the morphological and thermal evidence, that liquid → liquid phase separation occurred in the melt for certain blends. There is a large body of literature concerning the crystallization of blends of linear and branched polyethylenes (for example refs. 3–5). These works have been concerned with phase segregation caused by crystallization (i.e. liquid → solid phase separation). Our primary concern in this study is the effect of liquid → liquid phase separation within the melt prior to crystallization, although we have included liquid → solid phase separation in our studies so as to be able to produce a full phase diagram. We also wish to draw attention to the potential available for morphological (and hence property) control in partially compatible blend systems in general.

The determination of phase separation in a system of a homopolymer and one of its copolymers is no simple matter. The commonly used techniques such as light scattering will be of little use as both polymers have very similar refractive indices so that the refractive index difference between phases of only slightly different relative composition are too small to give significant scattering. Accordingly, we have had to develop new techniques. We have used four methods in this work. The first two, which rely on the assumption that the phase structure is preserved on rapid quenching, involve electron microscopy and thermal analysis of the quenched material. These we have described previously[1,2]. The third technique we have used is to probe the rheological behaviour of the melt and look for changes which can be ascribed to a change in the structure of the melt (and hence by implication are indicative of liquid → liquid phase separation). Some of these results have been checked using a fourth technique, hot stage electron microscopy of melt irradiated thin film samples.

We shall describe each of these methods in some detail and give examples of typical behaviour indicating both liquid → liquid, and liquid → solid phase separation as well as cases where the system exists as a single phase liquid or solid as appropriate. We shall then pull all these results together to compile the full phase diagram for the system.

We should, before moving on to the experimental details, make a few general observations about the nature of the phase diagram for the system we are using. The phase diagram we shall compile is not strictly an equilibrium phase diagram of the type familiar to those working in, for example, metallurgy. There are two distinct parts to the diagram. First, at high temperatures where both components are molten there are regions where the melt is homogeneously mixed and a region where it is separated into two phases, this liquid → liquid phase separation can itself affect subsequent crystallization. Secondly, at lower temperatures where either, or both, components crystallize we again have parts of the phase diagram where mixing (or co-crystallization) occurs and parts where it does not. Any separation or mixing which occurs, is, of course, time dependent and for polymeric systems it can take a long time for mixing or demixing to occur. Thus, on quenching, a homogeneously mixed melt may form a single phase solid where the two components co-crystallize; whilst the same melt, if cooled slowly, may separate into two phases as it crystallizes. In this publication we are using quenching as a technique to probe the liquid state and slow cooling or isothermal crystallization to probe the solid part of the diagram. Accordingly the phase diagram we are

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constructing is as close as we can get to the true or equilibrium phase diagram.

In addition to these general comments about the diagram there are two more specific issues which should be borne in mind when using the phase diagram. First we note that neither of the 'homopolymers' are pure single component systems; one is a linear polyethylene with a broad distribution of molecular weights, and the other a branched polyethylene with a distribution not only of molecular weights but also of branch content. The multi-component nature of the system means that separation (and mixing) is possible not only between the two major components but also within each major component itself. Thus the lines drawn on the phase diagram, shown later in *Figure 9*, are not sharp, as drawn, but somewhat broad and fuzzy. We have seen some separation within the branched component itself on crystallization at low temperatures. Secondly, polymeric systems are rarely, if ever, able to reach equilibrium, for example supercoolings of 20 K are needed to permit crystallization so that the lines on our phase diagram indicating liquid → solid transformations refer to the temperatures at which we observe the onset of crystallization under our particular experimental conditions and are not equilibrium values. The same may be true, to a lesser extent, for the lines indicating liquid → liquid separation.

Despite these reservations about the phase diagram it is nevertheless possible to use it to predict the phase morphologies produced by controlling the melt composition and thermal history. Those readers whose principle interest is in the phase diagram itself and how it may be used to control phase morphology may prefer to skip over all the detail and go directly to the section on the construction of the phase diagram.

EXPERIMENTAL

Materials and blend preparation

The two polymers used were a linear polyethylene (LPE): Sclair 2907 $\bar{M}_w = 98\,000$, $\bar{M}_n = 28\,200$ and a branched polyethylene (BPE): BP PN220 $\bar{M}_w = 208\,100$, $\bar{M}_n = 25\,300$ with long branch content 10, and short 16 branches per 1000 carbon atoms. (Note the short branches are inadvertently omitted in the specification in ref. 1). The blends were prepared by dissolving the two polymers in xylene at 1% (w/v) and precipitating very rapidly by pouring into acetone at −20°C.

Electron microscopy

Bulk samples. Blend samples were prepared by melting at 160°C (or other temperatures when appropriate) and crystallized either by quenching into acetone at its freezing point in d.s.c. pans, or isothermally in an oil bath. Long crystallizations were performed under argon in sealed tubes. Replicas were prepared from these solid samples using the permanganic etching/replication method, following the procedure of Bassett and Hodge described elsewhere[6,7].

Thin film samples. In order to preserve the high temperature melt structure, predicted by some of the rheological data presented below, we specially prepared some samples in the electron microscope. The thin films were first prepared by redissolving small quantities of the blends in xylene on a hot bench and dipping electron microscope grids into the solution. These films were then melted at the required temperature in the electron microscope and irradiated with a dose of approximately 20 Mrads while still at the melt temperature. This irradiation should be sufficient to suppress molecular mobility and hence preserve the melt structure[8]. The films were then allowed to cool, still in the microscope, and the resulting morphologies examined, either at room temperature after they had crystallized, or at 120°C after reheating from room temperature. Only films of standard thickness were used. The thickness was assessed from the reading on the TEM exposure meter when the film was irradiated with a standard beam current density.

TYPICAL RESULTS

TEM: bulk samples

We present in *Figures 1* and *2* electron micrographs of replicas of blends of various compositions crystallized by quenching from 160°C (two of these pictures were published in our earlier papers[1,2]). From these micrographs it can clearly be seen that there are three basic morphologies, shown at low magnification in *Figure 1*. *Figure 2* shows details of a wider selection of blends at higher magnification. The pure LPE and blends of down to 60% LPE content give uniform morphologies of banded spherulites, the pitch of the banding decreasing with decreasing LPE content. The quenched 80% blend, and LPE homopolymer are shown here as examples (*Figures 1a*, *2a* and *2b*). Both the 50% blend and the pure BPE also show uniform morphologies when quenched (*Figures 1b*, *2c* and *2f*); here the lamellae are small and appear randomly arranged. When the quenched blend contains between 40 and 0.2% LPE, however, the morphology is not uniform, but has two clear components (*Figures 1c*, *2d* and *2e*). Both banded and non-banded regions are observed. In summary, the homopolymers and blends of high LPE content show one uniform morphology when quenched, but blends of low LPE content show two distinct morphologies. This, we have previously argued[1,2], is strong evidence that phase separation had occurred in the melt for those samples showing two distinct morphologies. We believe that where there are two morphologies the banded regions are those rich in LPE whilst the non-banded regions are rich in BPE. This technique allows us to explore the liquid → liquid phase separated part of the phase diagram.

If we crystallize samples isothermally, rather than by quenching, we can obtain further information. For example, where there is only one morphology observed we may deduce that we are close to a eutectic. Where two morphologies are observed we have been able to distinguish between crystallization which occurs from two separate phases and that which occurs within a homogeneously mixed phase. A good example of this is illustrated in *Figure 3* (again taken from ref. 1) where we show the morphologies of a blend containing 0.2% LPE crystallized at two temperatures. In both cases the phase containing a large proportion of LPE has crystallized at the crystallization temperature while the remainder has crystallized on subsequent quenching. At the lower crystallization temperature the LPE rich phase has crystallized into individual lamellae, uniformly distributed throughout the sample (*Figure 3a*), while at the (slightly) higher crystallization temperature it has formed more or less spherical aggregates of lamellae (*Figure 3b*).

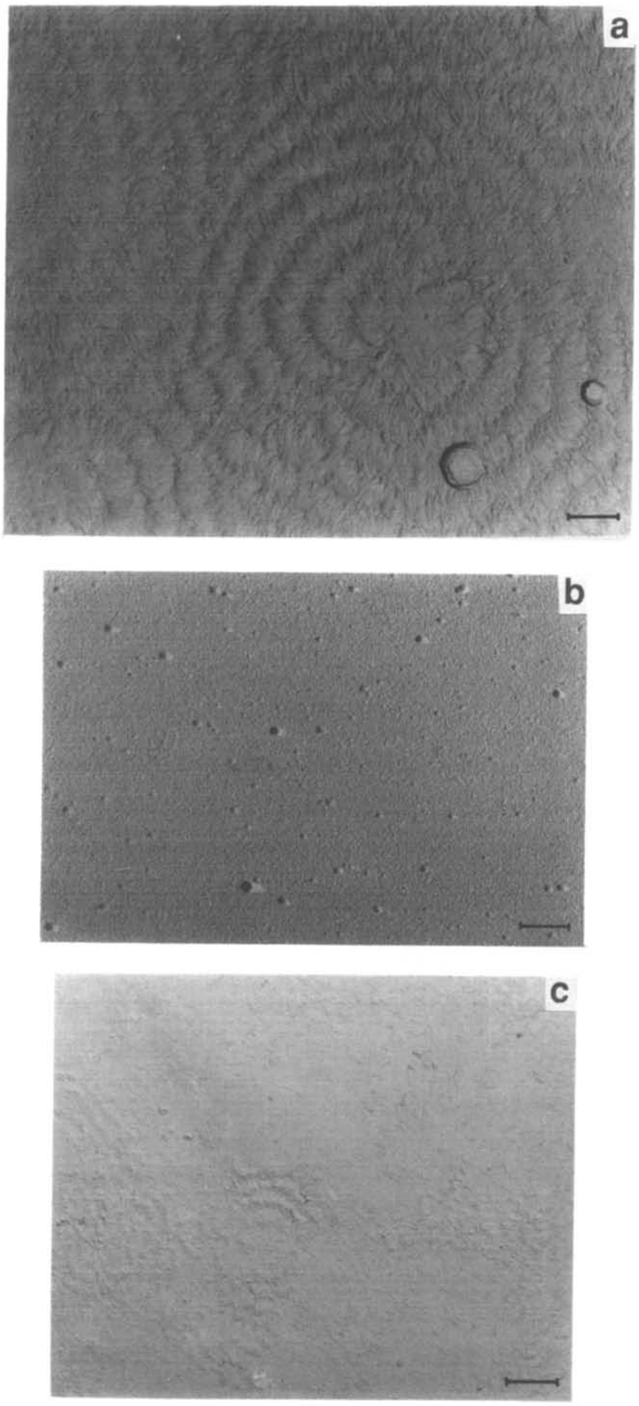

Figure 1 Transmission electron micrographs showing typical examples of the three morphologies commonly found at room temperature after quenching blends from 160°C into freezing acetone. (a) Single morphology of banded spherulites, in this case from an 80% blend. (b) Single morphology without banding, in this case from a 50% blend. (c) Double morphology, having both banded and non-banded regions, in his case obtained from a 5% blend. All specimens prepared for TEM by the permanganic etching and replication technique[6,7]

We suggest this indicates that at the higher temperature the melt was itself separated into two phases, the minority phase consisting of small spheres containing almost all the LPE, and that at the lower temperature the melt was mixed and the LPE uniformly distributed within it. (In references 1 and 2 we showed d.s.c. evidence in confirmation of this hypothesis.) The LPE-rich domains found here, and commonly in these blend samples, are between one and a few micrometres in diameter.

These results allow us to map out substantial parts of the phase diagram. There are, however, several restrictions. First we are entirely restricted to examining the solid material after crystallization and cannot look directly at the melt itself. We shall attempt to overcome this in the subsequent section describing rheological measurements. Secondly, we are restricted to comparatively low melt temperatures because on quenching from higher temperatures the melt will have some time in which it may change its structure (by either mixing, or demixing) prior to the freezing-in of the melt structure by crystallization.

TEM: thin film samples

We have attempted to prevent changes in melt structure during cooling by lightly crosslinking thin films of the polymer in the melt using the electron microscope. We show some examples in *Figure 4*. For example, thin films of 20% LPE blends were melted and then held for 45 min in the electron microscope at both 220 and 170°C. Part of each thin film was irradiated in the melt (where all films appeared featureless), and part left unirradiated. The films were then cooled (at about 30°C min^{-1}) and examined after crystallization.

Figures 4a and *b* show the results obtained from films irradiated and not irradiated when stored at 220°C. *Figure 4a* shows a uniform morphology, indicating crystallization from a mixed melt. *Figure 4b* shows two clearly different morphologies which, we argue, result from a segregation of the melt during cooling. Note that the crystals do not appear as sharp when they grow from an irradiated melt (*Figure 4a* cf. *4b*), a further manifestation of irradiation impeding chain mobility. The films held and irradiated at 170°C show two morphologies, looking as in *Figure 4b*, in both cases (although the crystals are less well defined where the film was irradiated in the melt). Thus it seems that at 170°C the melt is demixed. This experiment indicates that the melt for 20% blends is a single phase at 220°C and is biphasic at 170°C. We conclude that there is a liquid → liquid phase boundary of the UCT type between 170 and 220°C. Using this hot stage TEM technique it is possible to determine the mix/demix boundary to within ± 5°C.

Where two morphologies are seen it can be demonstrated that one is the high melting (LPE-rich) form and the other the low melting, BPE-rich form. Thin films of 1% blends examined at room temperature show two distinct morphologies, banded and non-banded spherulites. In the sample examined, the minority (non-banded) phase appeared, fortuitously, near the centres of the grid squares, surrounded by the majority, (banded) phase. On heating to 112°C we observe the banded material to melt (see *Figure 4c*). The unbanded material remains stable over some 10 to 15°C after the low melting material is no longer crystalline. Homogeneous, one phase morphologies, such as that shown in *Figure 4a*, melt uniformly. It is not possible to find a temperature where some crystals are stable whilst others melt.

These hot stage TEM experiments are in agreement with the findings of other techniques (d.s.c. and rheology, detailed below) in those cases where more than one technique can be used to look at the same part of the phase diagram. In addition hot stage TEM has been used to look at melts of very low LPE content blends which cannot be examined by rheometry.

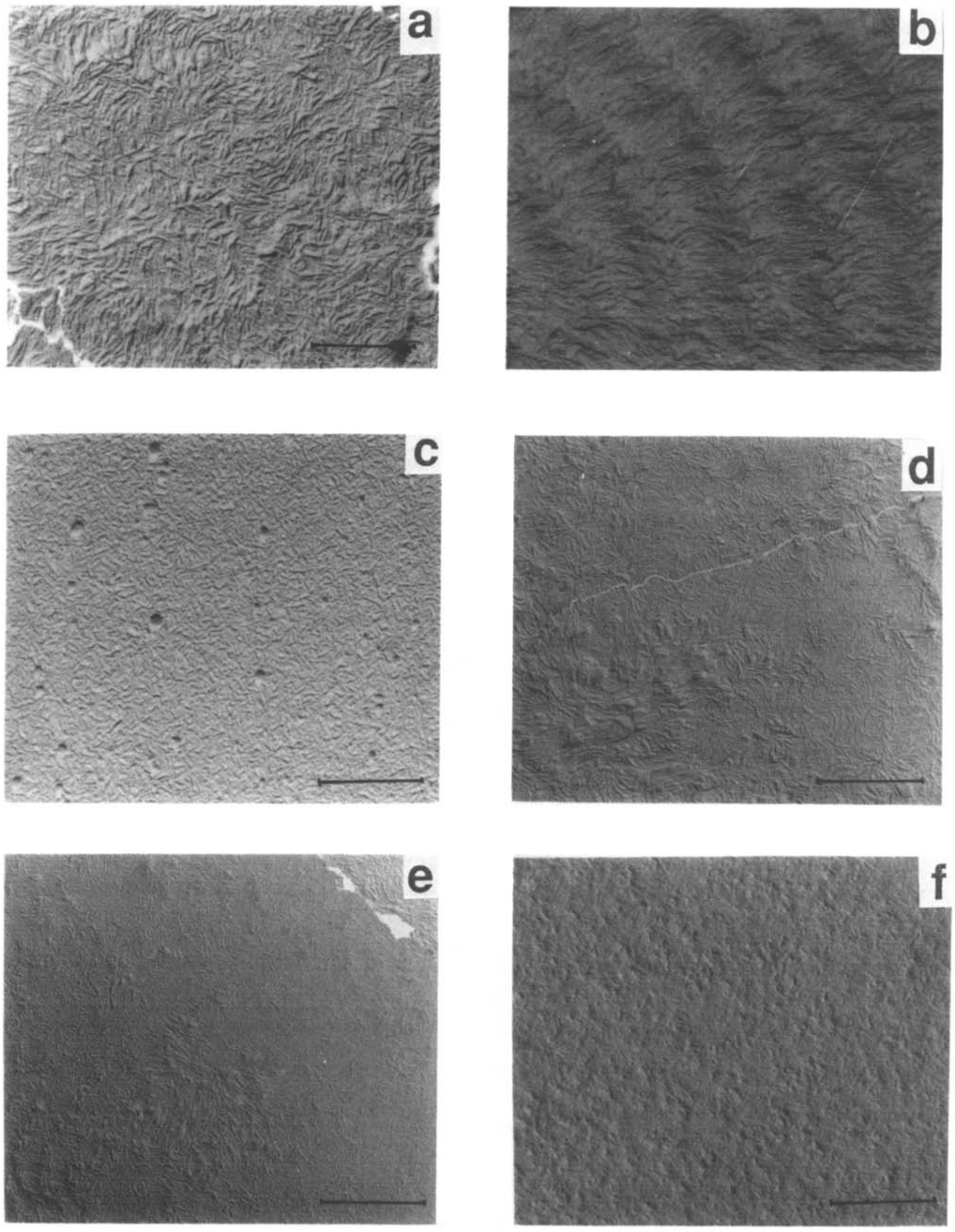

Figure 2 Transmission electron micrographs showing details of quenched blends. (a) LPE, there is a uniform morphology of banded spherulites here, but the banding is so broad that it is not clear at this magnification. (b) 80% blend with uniform morphology of banded spherulites. (c) 50% blend showing a single morphology without banding. (d) 10% blend showing the double morphology. The thicker. LPE rich crystals form banded spherulites in a matrix of non-banded BPE rich material. (e) 1% blend, morphology as for the 10% blend (*Figure 2d*). (f) BPE showing a single morphology without banding. Samples prepared as those in *Figure 1*

Thermal measurements

We contend that each separate crystalline phase observed by electron microscopy should possess its own distinct melting endotherm. Hence by studying the melting behaviour of blends crystallized under various conditions we can also determine parts of the phase diagram. In all our melting experiments we used a Perkin–Elmer DSC-2. The samples all had masses of 2.5–3.0 mg and the heating rate was always 10 K min^{-1}.

We show in *Figure 5* (which appeared in our previous work[1,2]) d.s.c. melting endotherms of the quenched blends corresponding to samples some of whose morphologies are shown in *Figures 1* and *2*. These results were discussed in ref. 1, but they are of such importance that we summarize the argument here. At high LPE content (2907 down to 50%) we see a single melting peak. The peak temperature is not strongly dependent on quenching conditions, and occurs at a lower temperature where the LPE content of the blend is lower. Such single endotherms with melting point decreasing with LPE content indicate that only one crystal type was present in each quenched blend, and hence that the blend melts were fully mixed.

However, very different behaviour is shown by the blends of low LPE content (35% to 1% in *Figure 5*). Here the samples show double peaks on reheating after quenching; the most rigorous quenching was unable to eliminate this peak multiplicity. In each blend the melting

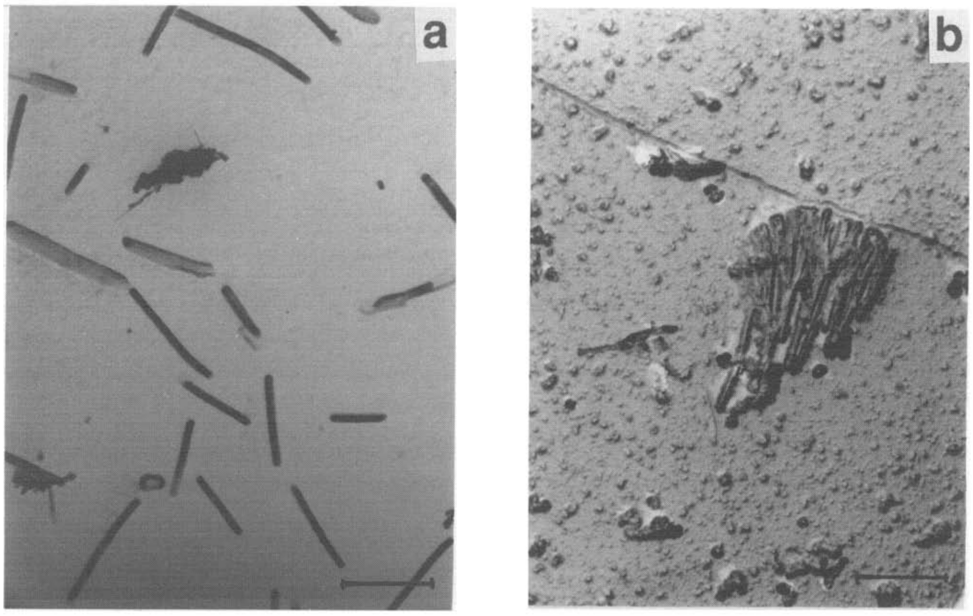

Figure 3 Transmission electron micrographs of replicas of a 0.2% blend of LPE with BPE melted and then held (under argon) for two weeks at (a) 122°C and (b) 128°C before quenching. Samples prepared as those in *Figure 1*

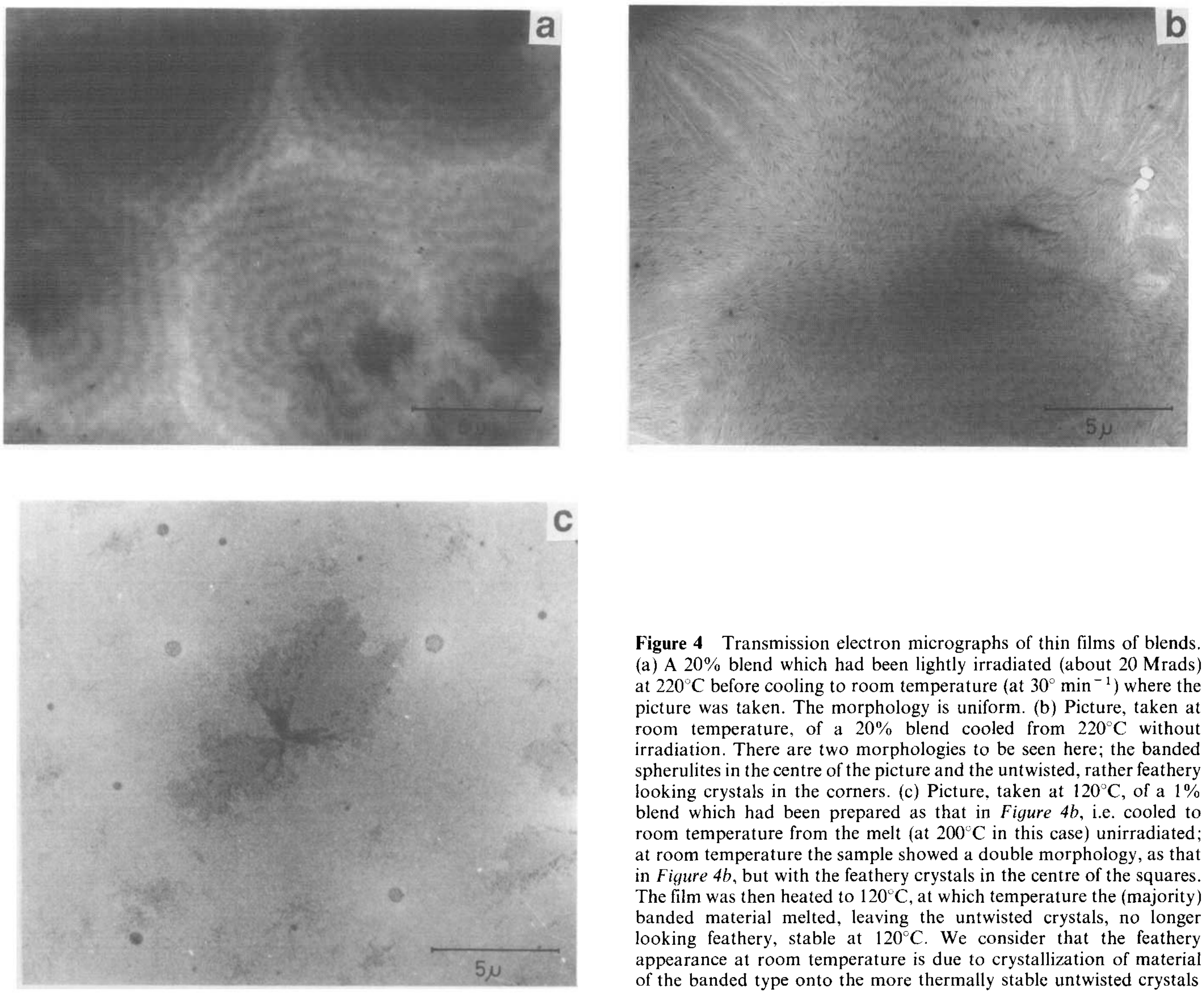

Figure 4 Transmission electron micrographs of thin films of blends. (a) A 20% blend which had been lightly irradiated (about 20 Mrads) at 220°C before cooling to room temperature (at 30° min^{-1}) where the picture was taken. The morphology is uniform. (b) Picture, taken at room temperature, of a 20% blend cooled from 220°C without irradiation. There are two morphologies to be seen here; the banded spherulites in the centre of the picture and the untwisted, rather feathery looking crystals in the corners. (c) Picture, taken at 120°C, of a 1% blend which had been prepared as that in *Figure 4b*, i.e. cooled to room temperature from the melt (at 200°C in this case) unirradiated; at room temperature the sample showed a double morphology, as that in *Figure 4b*, but with the feathery crystals in the centre of the squares. The film was then heated to 120°C, at which temperature the (majority) banded material melted, leaving the untwisted crystals, no longer looking feathery, stable at 120°C. We consider that the feathery appearance at room temperature is due to crystallization of material of the banded type onto the more thermally stable untwisted crystals

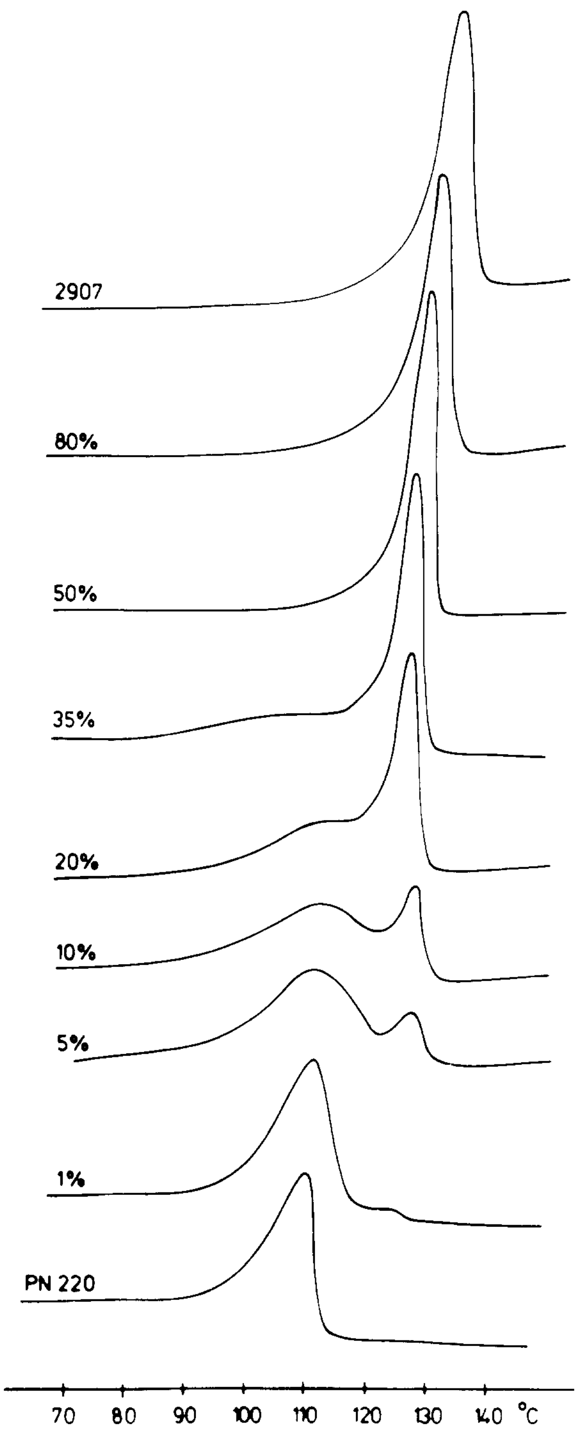

Figure 5 D.s.c. traces obtained by heating blends of LPE with BPE at 10°C min^{-1} after quenching from 160°C into acetone at freezing point. The percentage figure refers to the percentage LPE in the blend. Note that the blends with 50% or more LPE show a single endotherm whose position varies with composition. At lower LPE content there are two endotherms, the relative heights of the peaks vary, but the temperatures do not

peaks are found at the same temperatures, although the relative areas of the peaks vary. The invariance of the positions of the two peaks is quite consistent with the view that there are two distinct crystal populations with different, but invariant, compositions. This, in turn, is indicative of the melt itself, prior to quenching, being of a biphasic nature. There is one further point to note here. It seems to us that this very sudden change in properties irrespective of quenching conditions is unlikely to be due to changes occurring on crystallization but must be due to the blend structure itself. It was this behaviour which originally led us to suspect liquid–liquid phase separation, especially when we found, by subsequent TEM, that there was one morphology in those quenched blends which gave one melting peak whilst two morphologies were found in those quenched blends which gave two melting peaks.

Because d.s.c. experiments yield more quantitative data than electron microscopy we have used this method to map out much of the phase diagram. There are several experiments we can use to look at different parts of the phase diagram. First, to study the liquid → liquid phase separation, we can quench samples with a variety of melt temperatures as explained above. Secondly we may study liquid → solid phase separation by crystallizing isothermally for a long time and then quenching. There are two possibilities here: crystallizing from a one phase melt and crystallizing from a two phase melt. We shall look at these separately. When crystallization at high temperatures (e.g. at 130°C) from a homogeneous melt (i.e. at high LPE content) the solid phase will, in general, have a higher LPE content than the melt. If we permit crystallization to go as far as it can and then quench the system, we detect two melting peaks; the high temperature one from material crystallized isothermally, with a high LPE content and the low temperature one from material crystallized during quenching with a higher BPE content. An example of such a d.s.c. curve is shown in *Figure 6a* for an 80% blend crystallized at 130°C.

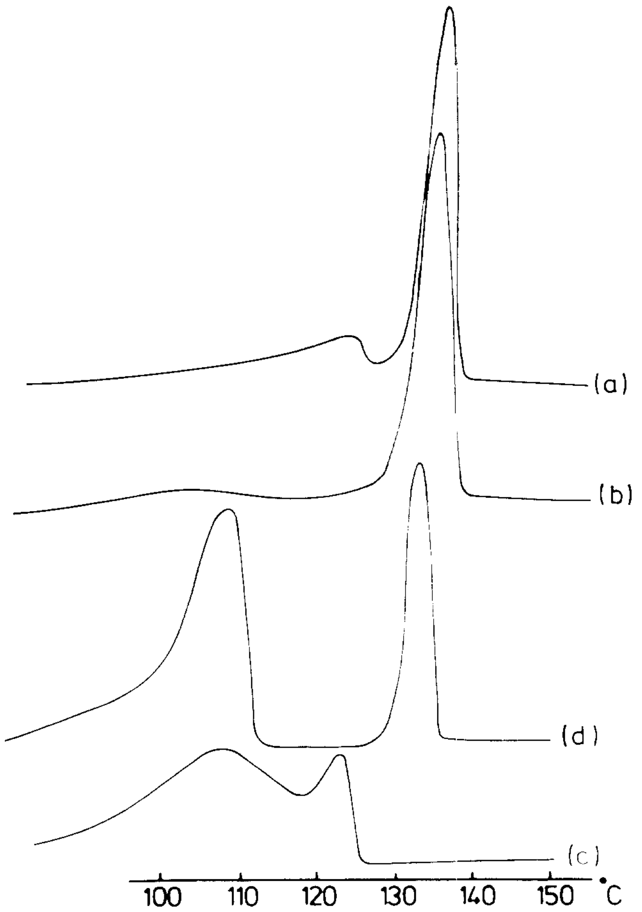

Figure 6 D.s.c. traces obtained from samples heated at 10°C min^{-1} after isothermal crystallization for 2 weeks under argon at the stated temperature prior to quenching. Curve a, 80% blend crystallized at 130°C; curve b, 80% blend crystallized at 128°C; curve c, 10% blend crystallized at 130°C; curve d, 10% blend crystallized at 128°C

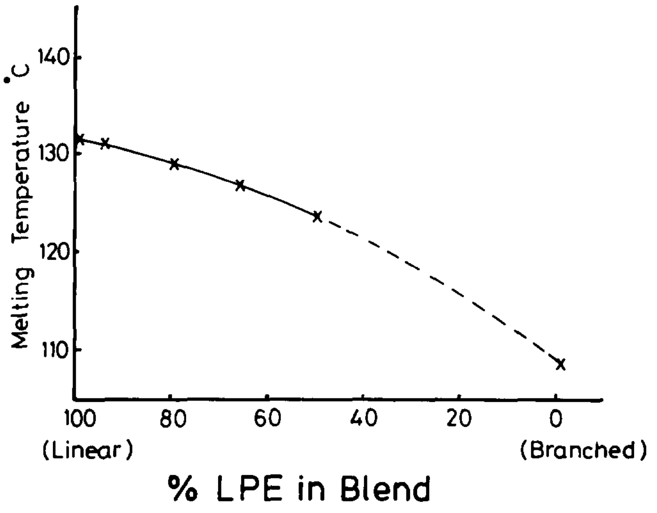

Figure 7 One of the several calibration curves, in this case obtained by plotting the concentrations of quenched blends against the melting points. Only those blends were used for which single peaks were obtained on quenching

Furthermore, from the positions and areas of these peaks we may deduce the composition of both phases. (This is done using calibration curves such as the one shown in *Figure 7* which was derived from data such as that in *Figure 5* obtained by quenching homogeneous melts). Holding the mixed melt at slightly lower temperature, 128°C, for a long period before quenching, results in a greater proportion of material crystallized isothermally (*Figure 6b*). Here the high melting peak is rather broader and the low melting peak much lower in temperature. Most of the blend has crystallized at 128°C, and the material which has not crystallized has a melting point, if anything, lower than that of quenched pure branched polymer. This is indicative of the possibility that there has been some separation within the BPE homopolymer itself according, for example, to branch content.

Now consider the crystallization of blends low in LPE content. *Figure 6c* shows a d.s.c. trace obtained after holding a 10% blend at 130°C for two weeks prior to quenching. The trace appears to be one of a quenched, segregated blend. No crystallization took place at 130°C. After holding at 128°C for two weeks prior to quenching the situation is different (*Figure 6d*). Now there is a sharp high melting peak, indicating crystallization at 128°C, together with a low temperature peak due to quenched (largely branched) polymer. We find that only blends of above 50% LPE concentration can crystallize at 130°C, but all blends down to 0.2% LPE concentration (although not PN220 itself) can crystallize to some degree at 128°C. Further, all blends of less than 50% LPE contents crystallized at 128°C from segregated melts have the same LPE concentration in the high melting peak (just under 60% LPE). This locates an important tie line on the phase diagram as occurring at about 128°C.

Isothermal crystallization at lower temperatures (down to 116°C) followed by quenching leads to very similar results to crystallization at 128°C for blends of 50–5% LPE content. However, for blends of very low linear content the concentration of LPE in the high melting peak falls as the crystallization temperature is lowered. We interpret this as being due to the variation in relative rates of mixing of the melt and of crystallization. A 50% blend crystallizes rapidly at 128°C; our samples cool from the melt at half a degree per minute. Cooling at this rate, the 50% blend will be crystalline well before 122°C is reached, probably at, or just below 128°C, so that the LPE content of the blend at 128°C is reflected in the high melting peak obtained by crystallizing nominally at 122°C but actually at 128°C. A 1% blend, however, crystallizes only very slowly at 128°C (and fairly slowly at 122°C)[1] so that cooling at the same rate to 122°C the melt reaches 122°C and mixes before crystallization takes place[1]. When it does so it is at the concentration characteristic of 122°C. Experiments such as those outlined above enable us to explore further regions of the phase diagram. In all this d.s.c. work we have deduced from the positions and areas of the peaks the relative compositions of the various phases which were present while the sample was crystallizing. By using a combination of these experiments we can map out a substantial part of the phase diagram. However, in all cases where we are trying to determine the composition of a liquid phase, we rely on the assumption that its composition is unchanged during quenching and crystallization, and, further, that the peak melting temperature is characteristic of the composition before the blend was quenched.

Rheological measurements

All rheological measurements were carried out using a Rheometrics RMS 800 mechanical spectrometer with a 2 kg force rebalance transducer and parallel plate geometry, at a frequency of 0.1 rad s^{-1}.

We decided to try to detect phase separation by rheological measurements. Our first approach was to observe how rheological properties changed with blend composition at various fixed temperatures. We expected to see smooth variation of rheological properties with composition when the blend melt was mixed but to observe a change in behaviour when the melt was demixed. We found that the most sensitive parameter was the loss factor, tan δ, of the viscoelastic melts.

We show in *Figure 8* the dependence of the equilibrium value of tan δ on composition at two temperatures: 215°C and 140°C. It is clear that at 215°C tan δ varies continuously with blend composition suggesting that the melt is homogeneously mixed at all compositions.

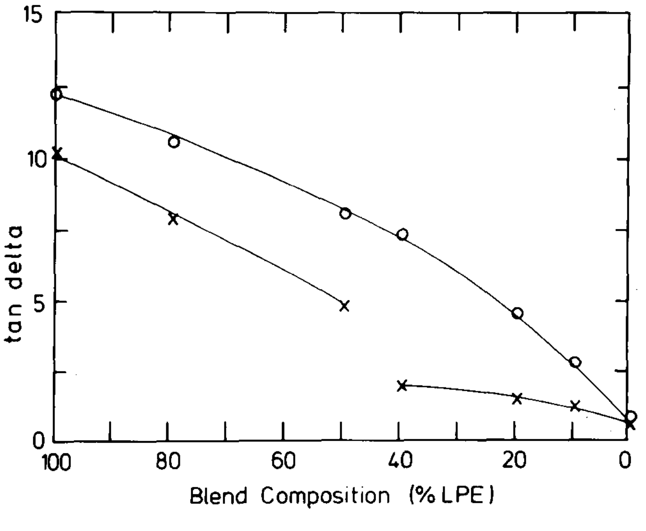

Figure 8 Plots of tan δ against blend concentration for two temperatures; ○, 215°C; +, 140°C. Note that whilst tan δ gradually drops with concentration at 215°C, at 140°C it drops very rapidly at just below 50% LPE content and then decreases very little when the LPE content is further reduced

However, at 140°C a different picture emerges. For blend compositions of 100–50% LPE we see much the same variation in tan δ as the higher temperature; while for compositions of 40% to 0% LPE we see a much lower value of tan δ which is fairly insensitive to composition. We suggest this behaviour indicates that the melts of composition less than 40% LPE are biphasic, and that the branched polymer forms the continuous phase so that its rheological properties are dominant. At concentration of $\sim$50% LPE and above we suggest the melts are homogeneous.

We should note that there is a significant complication not shown on the figures we present. The behaviour we observe is superimposed on any changes which may be caused by the thermal degradation of the polymer. This is particularly pronounced in the pure linear polymer. In this case we observe a continuous decrease in tan δ to values as low as 0.1 during storage at melt temperatures above 200°C. This decrease is irreversible and is accompanied by a decrease in viscosity. However, the branched polymer does not degrade in this way. This difference between the two pure polymers is, we suggest, due to a difference in the amount (and/or effectiveness) of stabilizers which have been added to them. The presence of the stabilizer from the PN220 in the blend materials appears also to stabilize them.

We should note that all the above experiments were conducted at a single frequency (0.1 $\mathrm{rad\,s^{-1}}$). We find that by increasing the frequency the position of the phase boundary is altered. From our preliminary experiments the position of the coexistence curve on the temperature scale is increased by $\sim$5°C when the frequency is raised from 0.1 to 1 $\mathrm{rad\,s^{-1}}$.

CONSTRUCTION OF THE PHASE DIAGRAM

We have used all the data available to us from all the techniques described above to construct the phase diagram for the system LPE (Sclair 2907) and BPE (PN220). This is shown in *Figure 9*. For clarity we have omitted the data points on the full phase diagram. Representative data are given in *Tables 1–4*, and some data points are shown on the partial phase diagrams (drawn on different temperature scales) in *Figures 10a* and *b*. Wherever several techniques have been used to examine the same part of the phase boundary they give excellent agreement.

Region A. Single phase liquid. This part of the phase diagram was explored using all the techniques described.

Region B. Two phase liquid. Here the existence of two liquid phases was deduced from electron microscopy and d.s.c. of quenched melts. The upper part of the phase boundary was explored using rheology (*Figure 8*) and thin film electron microscopy of irradiated melts (*Figure 4*). The lower part of the phase boundary (marked with the dashed line on the lower right of the diagram) at low LPE content was explored using electron microscopy (as in *Figure 3*) and by d.s.c. (ref. 1 figures 7, 8). There is a metastable single phase (mixed) liquid here, which is described in more detail in refs. 1 and 2. We have been able to obtain detailed data except at the very low temperature, very low linear extreme of the diagram. This is because at 114°C and below the PN220 itself begins to show a two phase behaviour, the less branched material crystallizing, whilst the most branched material

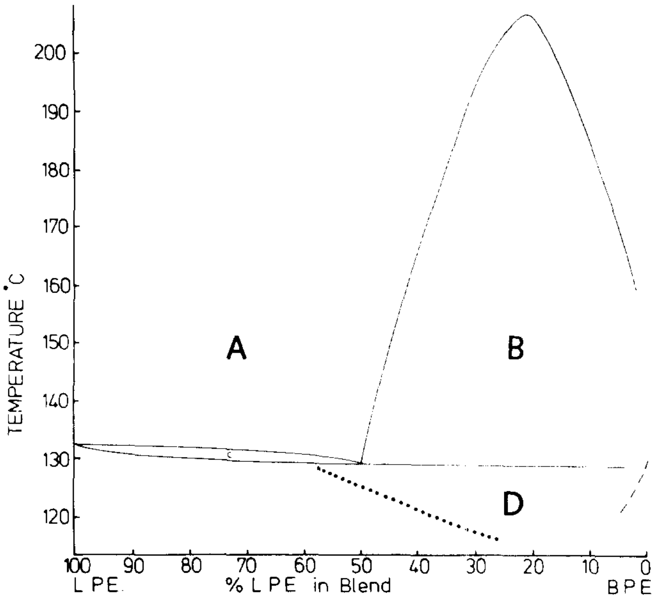

Figure 9 The full phase diagram for LPE (Sclair 2907) with BPE (PN 220). Data points have been omitted for clarity. The four regions are explained in the text. The lines are not, in fact, sharp, as drawn, but intrinsically blurred due to the range of molecular weights in the homopolymers and to experimental errors due to imperfect temperature control during crystallization

Table 1 Representative data for liquid → liquid segregation in the melt. Melt in stable region above 128°C. (Data plotted in *Figure 10a*). Here samples of fixed concentration were used, and the temperatures at which mixing/demixing took place determined

% LPE in blend	Mix/demix temperature (measured to ±5°C)	Experimental method
100 (2907)	Always mixed	Rheometry
	Always mixed	d.s.c.
80	Always mixed	Rheometry
	Always mixed	d.s.c.
60	Always mixed	Rheometry
	Always mixed	d.s.c.
50	134	d.s.c.
40	165	Rheometry
	163	d.s.c.
35	185	d.s.c.
20	205	Rheometry
	208	Hot stage TEM
10	185	Rheometry
	187	Hot stage TEM
5	173	Hot stage TEM
1	160	Hot stage TEM
0 (PN220)	Always mixed	Rheometry
		d.s.c.
		Hot stage TEM

Table 2 Representative data for liquid → liquid segregation in melt. Metastable melt region below 128°C. This is the region where the melt may remix, before it goes on to crystallize. The melt is held at a fixed temperature, and examined for remixing. Details of the method are given in refs 1 and 2. Only blends of very low LPE content crystallize slowly enough for the remixing to be seen

% LPE in blend	Temperature (stability, ±0.5°C)	Mix/demix	Experimental method
1	128	demixed	TEM and d.s.c.
	126	slowly mixing	TEM and d.s.c.
	124	mixed	TEM and d.s.c.
	122	mixed	TEM and d.s.c.

Table 3 Representative data for liquid → solid part of the phase diagram: crystallization at above 128°C, where only blends of high LPE content (greater than 50%) can crystallize. (Data plotted in *Figure 10b*). All these data were obtained by d.s.c. In these experiments the temperatures were held constant (but over long periods variation of up to ±0.5°C could take place). After 'isothermal crystallization', followed by quenching, the % LPE in the two phases was calculated from the d.s.c. traces

Crystallization temperature (stability ±0.5°C)	Blend compositions which crystallized (partially) isothermally	Concentration of LPE rich phase crystallized isothermally	Concentration of LPE poor phase crystallized on subsequent quenching
131.5	homopolymer	100% (but not all crystallized)	
131	95%, 80%	98%	70%
130	95%, 80%, 65%	92%	58%
129	95%, 80%, 65%	85%	55%

Table 4 Representative data for liquid → solid part of the phase diagram: crystallization at below 128°C. Low LPE content melts were able to cool to below 128°C before crystallizing because they crystallize very slowly at 128°C. 1% blends were held at the stated temperature for a week before quenching. The low LPE content polymer cannot crystallize at these temperatures. The %LPE in the LPE poor phase is too low to measure

Temperature (stability ±0.5°C)	Concentration of LPE rich phase (%) (error of measurement +/−5%)
128	57
126	52
124	46
122	40
118	33
116	25

is unable to crystallize until below 100°C. (Although PN220 segregates by crystallization in this way its melt is always mixed, always giving single melting peaks on quenching.)

Region C. Single phase liquid and crystals. This was explored using d.s.c. of isothermally crystallized samples (*Figure 6*).

Region D. Two phase liquid and crystals. This is a non-equilibrium region which can only be studied because crystallization at 128°C is slow. (The observed experimental results (details in *Tables 1–4*) are drawn with a dotted line. It was explored using d.s.c. (*Figure 6*) and TEM (figures 4, 5 of ref. 1).)

We wish to draw attention to a few general features of the phase diagram. There is a principal tie line at 128°C, or just above. The liquid → liquid phase segregated region is of an upper critical temperature nature, as suspected in our previous work[1,2]. However, there is also a melt remixing, prior to crystallization, which takes place on both sides of the phase diagram below 128°C indicating that the segregated area of the melt is indeed a closed loop. Finally, note that there is considerable co-crystallization taking place in the isothermally crystallized samples. The high melting crystals in all the isothermally crystallized samples contain some BPE with the LPE. When crystallizing from segregated melts at 128°C (i.e. on the principle tie line) it can be seen from *Tables 1–4* that we always observe that the high melting crystals contain 41% BPE. When crystallizing isothermally from a single phase melt the proportion of BPE can be greater. We have found a maximum BPE content of 75% (i.e. 25% LPE only) when crystallizing a 1% blend at 116°C.

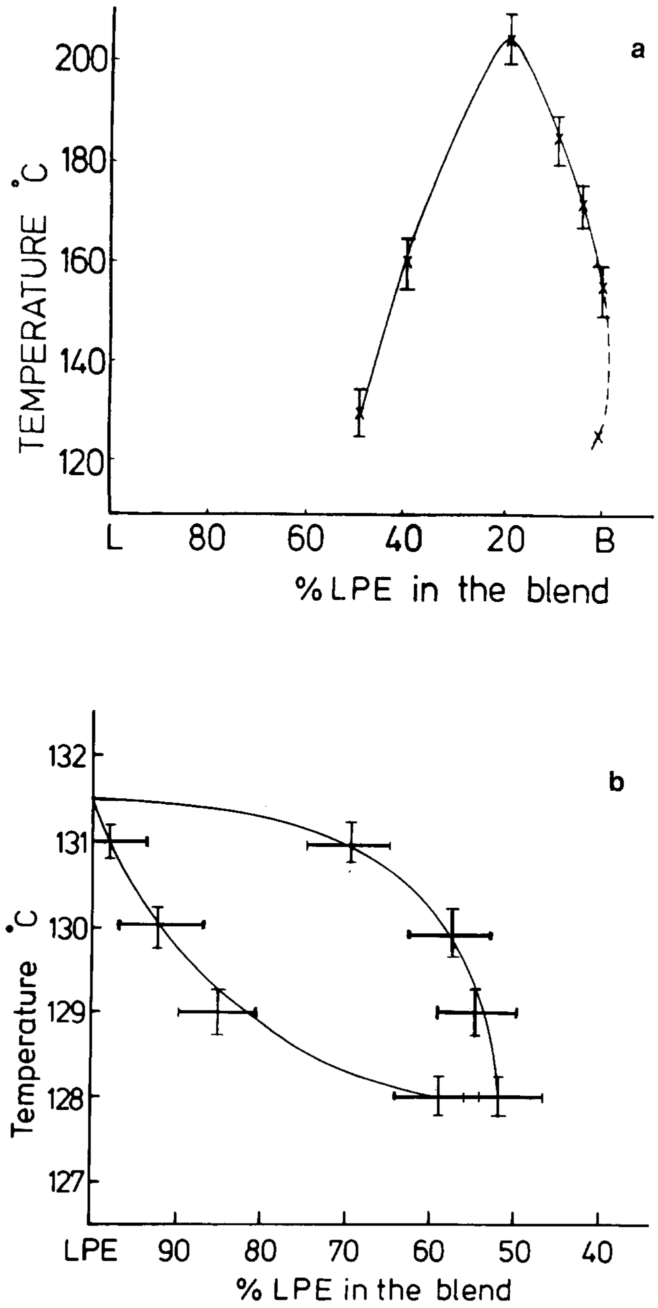

Figure 10 Parts of the phase diagram showing typical experimental errors. (a) The liquid → liquid phase segregated region which is found at high temperatures and low LPE contents; (b) crystallization of high LPE content blends at high temperatures. Note that the temperature scales are quite different in *Figures 10a* and *10b*)

CONCLUSIONS

We have been able, using a variety of complementary techniques, to construct the complete phase diagram for a blend of two particular polyethylenes. Control over blend composition and crystallization conditions allows control over the resulting phase morphology and, in principle at least, over the final mechanical properties.

The behaviour of our chosen PE pair is certainly not unique, because similar segregation effects have been seen in very low density polyethylenes which appear to be blends in themselves[9,10]. Hence the results we have outlined should be of interest to all workers on polyethylene blends.

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