Phase segregation in blends of linear with branched polyethylene: the effect of varying the molecular weight of the linear polymer*

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This paper reports investigations into the phase behaviour of six blend systems containing linear with branched polyethylenes. Five systems used linear polyethylenes of differing molecular weight blended with the same branched polyethylene. The sixth system involved a branched polyethylene of lower branch content and shorter branches. The main experimental methods used were differential scanning calorimetry and transmission electron microscopy. Very good agreement was found between results obtained from both experimental methods. The phase diagrams deduced are of the same general form, all but one showing liquid–liquid phase separation in the melt with both upper and lower critical temperatures. This phase separation is most extensive where the molecular weight of the linear polymer is highest. At the other extreme, for a linear component of molecular weight of 2155, no liquid–liquid phase separation is observed. Of the two branched polyethylenes, that with the higher branch content is more prone to phase separation. These results lead us to conclude that the phase diagram found previously for a similar blend pair is not unique since the various systems studied here all give similar thermal results, morphologies and phase diagrams.

(Keywords: phase separation; polyethylene; blends; phase diagram; differential scanning calorimetry; transmission electron microscopy)

INTRODUCTION

Blends of polyethylenes are extensively used in industry and are, therefore, of great general interest. We have previously studied blends of one particular linear polyethylene/branched polyethylene (LPE/BPE) pair and for that system deduced a 'phase diagram', using several different experimental techniques in combination[1–3]. This 'phase diagram' is not a proper equilibrium phase diagram, but a description of the state in which we find the blends (homogeneous single-phase melt, segregated two-phase melt, crystal and melt, etc.) under specified, practical experimental conditions. The 'phase diagram' we have deduced for the LPE/BPE system we first studied is shown in *Figure 1* of this paper (taken from ref. 3). Its two main features are as follows:

(1) The system shows both upper and lower critical behaviour with an extensive region of liquid–liquid phase separation (LLPS) in the form of a closed loop (partially obscured by crystallization).

(2) Considerable co-crystallization is observed. We believe that such a phase diagram, including both upper and lower critical behaviour, has not been observed previously in any polymer system.

Previous studies of LPE/BPE blends have concentrated on the degree to which co-crystallization occurs[4,5] and have largely ignored the possibility of any demixing in the melt. Indeed, Stein and coworkers assume that the LPE/BPE that they used was mixed in the melt for all blend compositions. On the other hand, in studies where other homopolymer/copolymer systems have been examined, they have usually been found to be immiscible in the melt (see e.g. refs 6 and 7). In addition to the degree of branching, we should expect the molecular weights of the two components to affect their miscibility. In studies using model systems, it is usually found that systems with lower molecular weights show greater miscibility.

Thus it is important to establish the range of LPE/BPE blends that display the novel phase behaviour (previously only recorded in our one LPE/BPE system), by varying both the branch content and the molecular weight of both components. We report on the initial stages of this investigation in this publication. We have blended four further LPEs of differing molecular weights with the BPE that we used in the previous studies; we have also blended one deuterated (linear) PE (DPE) with our original BPE, and our original LPE with one different BPE.

We have used the same methods as previously; TEM and d.s.c. The combined results clearly show that the behaviour we observed previously is not unique; we have obtained closely related 'phase diagrams' from all the systems we have studied. LLPS in the melt has been observed in the DPE/BPE pair and in all the LPE/BPE systems we have looked at except when the LPE was of extremely low molecular weight (molecular weight about 2200). We have observed co-crystallization in all systems.

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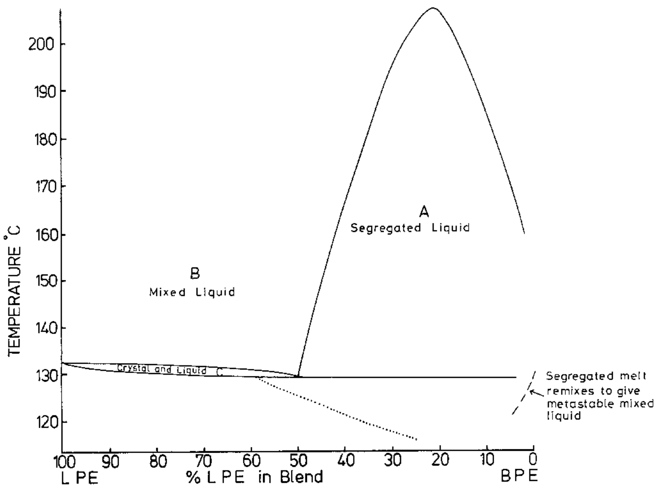

Figure 1 'Phase diagram' obtained for LPE Sclair 2907 blended with BPE PN220 (from ref. 3). Three of the main regions are labelled. In addition, remixing is found for metastable melts to the right of the dashed line. The dotted line indicates the experimentally observed concentrations of LPE-rich crystals crystallized from such metastable mixed melts

EXPERIMENTAL

The various polymers used in this study are listed in *Table 1*, together with their weight-average molecular weights, dispersions and (where relevant) branch contents, as specified in the manufacturers' data.

The experimental methods used in the work reported in this paper have already been described, in some detail, in refs. 1–3. We have mapped out the crystal–liquid coexistence curves (region C of *Figure 1*) using d.s.c., and looked at the melt (regions A and B of *Figure 1*) by examining rapidly quenched samples by TEM and by d.s.c. Although examination of quenched samples is an indirect method, we found, as in our previous studies, that the results obtained were always confirmed when more direct methods were used.

We have looked at co-crystallizatin by a d.s.c. study of isothermally crystallized samples. Further information and confirmation of the phase changes has come from morphological studies using electron micrographs of replicas of these samples.

Notes on blend preparation

Blends were made, as before, by dissolving the two polymers together in xylene to make an approximately 1% solution and then co-precipitating into acetone (a non-solvent) at its freezing point. We have shown[1,2] that this method leads to intimate mixing; single-phase melts can be obtained from material thus blended.

The blends over which most care had to be taken were the 2155/BPE series. These blends had to be made in new glassware, as any traces of LPEs of higher molecular weights led to anomalous indications of segregation, which were, in fact, due to the foreign LPE.

Homogeneity of blending

Tests were carried out to see if the blends were homogeneous. It has been our experience that very high-molecular-weight LPEs are difficult to disperse, often forming gels when crystallized from dilute solution; we feared that Hizex, in particular, would not be uniformly distributed within blends.

Thus 1% and 0.2% blends of Hizex in BPE were made. Small (0.5 g) samples were melted and then crystallized isothermally at various temperatures in the range 126–118°C for a week before quenching. Six 3 mg portions were taken from each of the isothermally crystallized samples and examined by d.s.c. Each sample showed two melting peaks, one of isothermally crystallized LPE-rich material and one of quenched BPE-rich material. Rather to our surprise, in any given isothermal crystallization experiment (e.g. for the 1% blend at 122°C or the 0.2% blend at 118°C), there was less than 10% variation in the ratio of the areas of the two peaks within extreme members of each group of six samples. The ratios of peak areas showed a standard deviation of 5% for blends with low Hizex content – and the standard deviation was lower for samples containing more Hizex and all those containing LPE of lower molecular weight. Thus even with very low Hizex contents, the LPE appears to be uniformly distributed through the sample. All measurements were repeated three times, and further repeated if results showed unexpected variations.

RESULTS

Of the very large number of results obtained, we are able to show only a small selection here. We will give typical examples of results obtained from the various techniques, noting if any pair of blended polymers did not behave in the typical manner.

D.s.c. results

D.s.c. from quenched blends. Figure 2a shows d.s.c. traces of the type usually observed on heating quenched blends (in this case Hizex/PN220 blends) at 10°C min^{-1}. They are similar to those obtained from heating quenched 2907/PN220 blends, as recorded in refs. 1–3 (see for instance Figure 5 in ref. 3). The homopolymers both give single peaks, as does the 75% blend; the 50% to 1% blends always give double peaks, however fast they are quenched, and, although the amount of material contributing to each of the two peaks varies, the positions of the peaks vary only slightly. This we take to be an indication that the blends with LPE content less than 50% are segregated in the melt.

[In *Figure 2a* the low melting peak is at a slightly low temperature for the 50% blend and the high melting peak is at a rather low temperature for the 1% blend. The blends with compositions between 40% and 5% (most

Table 1 Characteristics of polymers used in this study

Polymer	M_w	M_w/M_n	Branches/ 1000 C atoms 'Short'	'Long'
LPEs				
Sclair 2907	10^5	3	–	–
Hizex 240	2×10^6	?	–	–
Rigidex 50	7×10^4	7	–	–
Fraction 15000	1.5×10^4	1.4	–	–
Polym. Lab. 2155	2553	1.1	–	–
DPE				
MSD MD-775	2×10^5	2.2	–	–
BPEs				
BP PN220	2×10^5	8	16	10
Sclair 8105	9×10^4	8.5	16	1

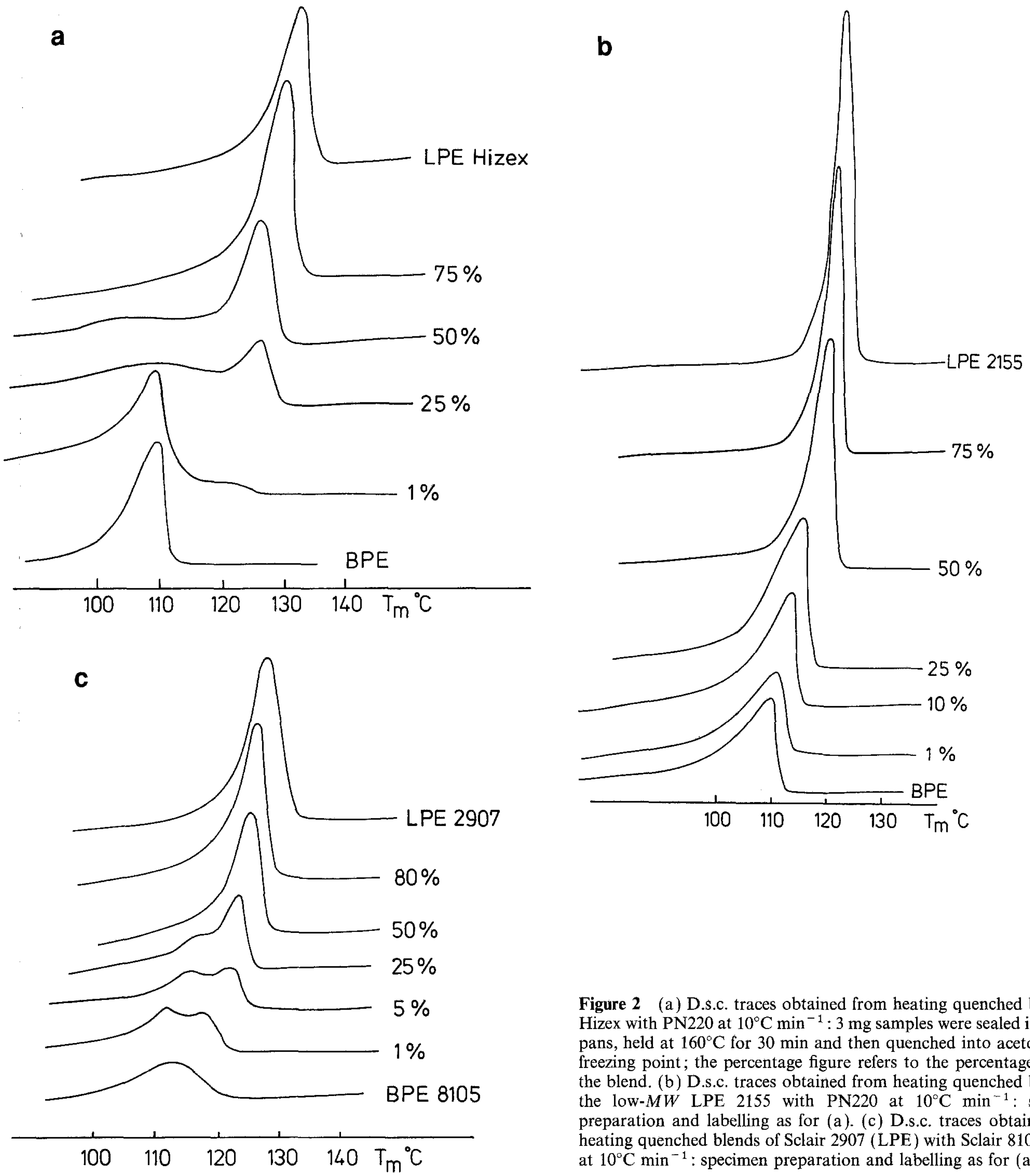

Figure 2 (a) D.s.c. traces obtained from heating quenched blends of Hizex with PN220 at 10°C min^{-1}: 3 mg samples were sealed into d.s.c. pans, held at 160°C for 30 min and then quenched into acetone at its freezing point; the percentage figure refers to the percentage LPE in the blend. (b) D.s.c. traces obtained from heating quenched blends of the low-*MW* LPE 2155 with PN220 at 10°C min^{-1}: specimen preparation and labelling as for (a). (c) D.s.c. traces obtained from heating quenched blends of Sclair 2907 (LPE) with Sclair 8105 (BPE) at 10°C min^{-1}: specimen preparation and labelling as for (a)

not shown here) have both peaks at the same temperatures as those shown for the 25% blend. We believe that the anomalies in the quenched 50% and 1% blends occur for different reasons. The melting point of the lower 50% peak is depressed, we believe, due to depletion of the more linear, and hence higher-melting, molecules of BPE, which are included in the co-crystals whose melting gives rise to the higher melting peak. This effect is only seen when the LLPS occurs over a wide composition range. The anomalous 1% peak is seen in several other blend systems. We suspect that this is an indication that the system is not truly binary and requires a ternary phase diagram for complete description. We return to this point below.]

The melting points of the two peaks enable us to estimate the compositions of the two products of segregation; in this case we found that the high-melting component contained about 56% LPE and the low-melting component was almost pure BPE. Most of the blends studied behave in this way and the values of the LPE concentration in the higher melting of the two peaks can be estimated (see below); the lower-melting material always melts at a temperature very near that of the quenched pure BPE.

We observe that the composition of the phase giving rise to the higher melting peak depends on the molecular weight of the LPE. For higher-molecular-weight LPEs, the temperature of the peak is increased, indicating a

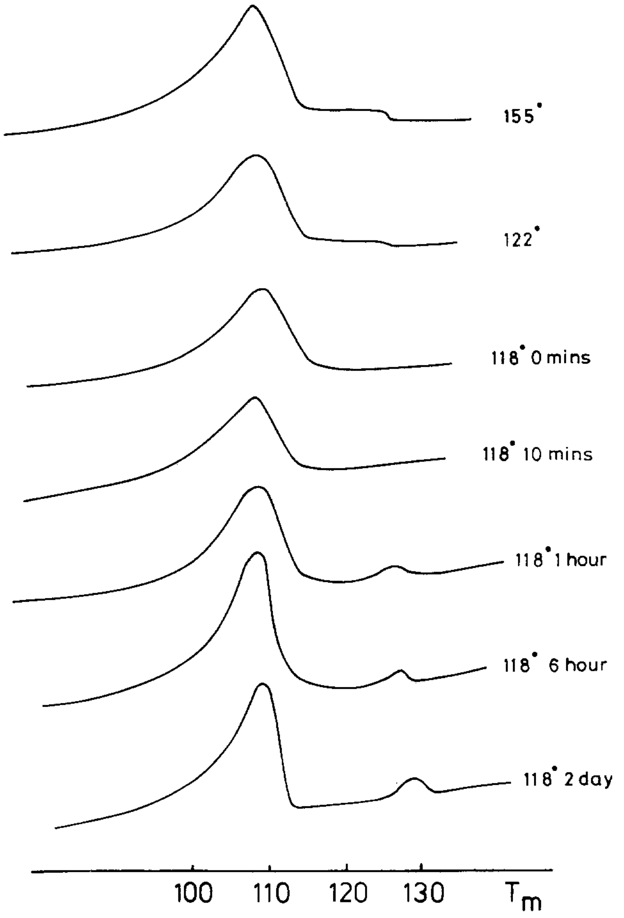

Figure 3 D.s.c. traces obtained from heating 1% blends of Hizex with PN220 at 10°C min^{-1}. All samples were held at 160°C for 30 min and then cooled at 0.5°C min^{-1}; when the temperature reached 155°C, the sample that subsequently gave the top trace was quenched into acetone at its freezing point. Cooling continued; a second sample was quenched from 122°C, and a third from 118°C. The temperature was then maintained at 118°C and further samples quenched after the time intervals indicated

greater proportion of LPE in the phase. Further, for LPEs with high molecular weight, the LLPS region is wide, but as the LPE molecular weight decreases it becomes narrower; in the case of the very lowest-molecular-weight LPE we do not observe LLPS for blends of any composition (see *Figure 2b*).

The d.s.c. results obtained on reheating quenched blends of the linear DPE with branched PN220 and the linear Sclair 2907 with branched Sclair 8105 are slightly different from the others. They again showed single melting peaks for higher LPE contents (in both these cases down to 30%) and two peaks for lower LPE contents, as shown in *Figure 2c*. However, there is a significant difference: the temperature at which the higher melting peak occurs is not constant but decreases with increasing BPE content. These results are considered in the discussion below, where we argue that a ternary phase diagram is required to describe the data.

Calibration curves from d.s.c. of quenched blends. We constructed calibration curves to determine the LPE content of the higher-melting crystals from heat-of-fusion and melting-point data, working from samples where only one melting peak was observed. Further details are described in ref. 3. These curves were used to estimate the LPE content of crystals, produced both by quenching and by isothermal crystallization, in those cases where two melting points were observed.

Clearly, great caution is required when using such calibration curves to deduce the composition of individual phases in the blends, since it is well known that the melting temperature and enthalpy depend not only on the composition but also on the crystallization conditions, annealing history, crystal thickness and morphology. Accordingly we assured ourselves that the calibration curve used in each case was that for the same crystallization conditions as those used to make the particular phase-separated sample.

Remixing at low LPE content and low melt temperature. In refs 1 and 2 it was argued that the liquid–liquid coexistence curve is probably a closed loop – there are clear indications of remixing at low LPE content and low melt temperature. Such indications are again found with the blends used in the present study. *Figure 3* shows d.s.c. traces obtained from 1% Hizex/PN220 blends quenched from various temperatures. A number of samples were held at 160°C for half an hour and then cooled to 155°C. The first sample was quenched from that temperature, and a double melting peak is clearly seen on heating at 10°C min^{-1}, indicating a segregated melt at 155°C. The remaining samples were cooled at 0.5°C min^{-1}. The second sample was quenched when the temperature reached 122°C; the higher melting peak is still present, but reduced in relative size. By the time 118°C is reached, the melt appears to have mixed, and it remains mixed until isothermal crystallization sets in after about half an hour (indicated by the small, high melting peak visible in the 1 and 6 h and 2 day traces). The remixing is particularly clear with this blend because of the relatively slow crystallization of the (Hizex) LPE-rich material.

Isothermal crystallization at high crystallization temperatures. The maximum temperature at which the LPE can crystallize is higher than the maximum temperature at which the BPE can crystallize in all the systems we have examined. As the crystallization temperature is lowered from the highest temperature at which the LPE can crystallize, blends with increasing BPE content are able to crystallize. *Figure 4a* illustrates this, for DPE/PN220 blends that were melted and then held at 125°C for 8 days before quenching. The d.s.c. traces from remelting DPE and 75% blends show peaks at above 130°C; this high-melting material must have crystallized isothermally at 125°C. However, the blends of 50% DPE and below show no material melting above 125°C. From this we deduce that, although the DPE itself and the 75% blend had partially crystallized at 125°C, the 50% to 1% blends had not. [Incidentally, note in *Figure 4a* that the high melting peaks of the 5% and 1% blends are low, and that of the 1% blend appears as a mere shoulder. This suggests a ternary phase system as discussed below.] Note also the lower melting peak in the pure DPE trace, due to material unable to crystallize at 125°C. This is, most probably, low-molecular-weight polymer, segregated here by crystallization. This is a further indication of the heterogeneity of the so-called 'homopolymers' used in this work. On holding the melt at 124°C, the 50% DPE/BPE blend can partly crystallize. In contrast, at 123°C, all blends down to 1% are able to crystallize partially, as the LLPS loop has intersected the

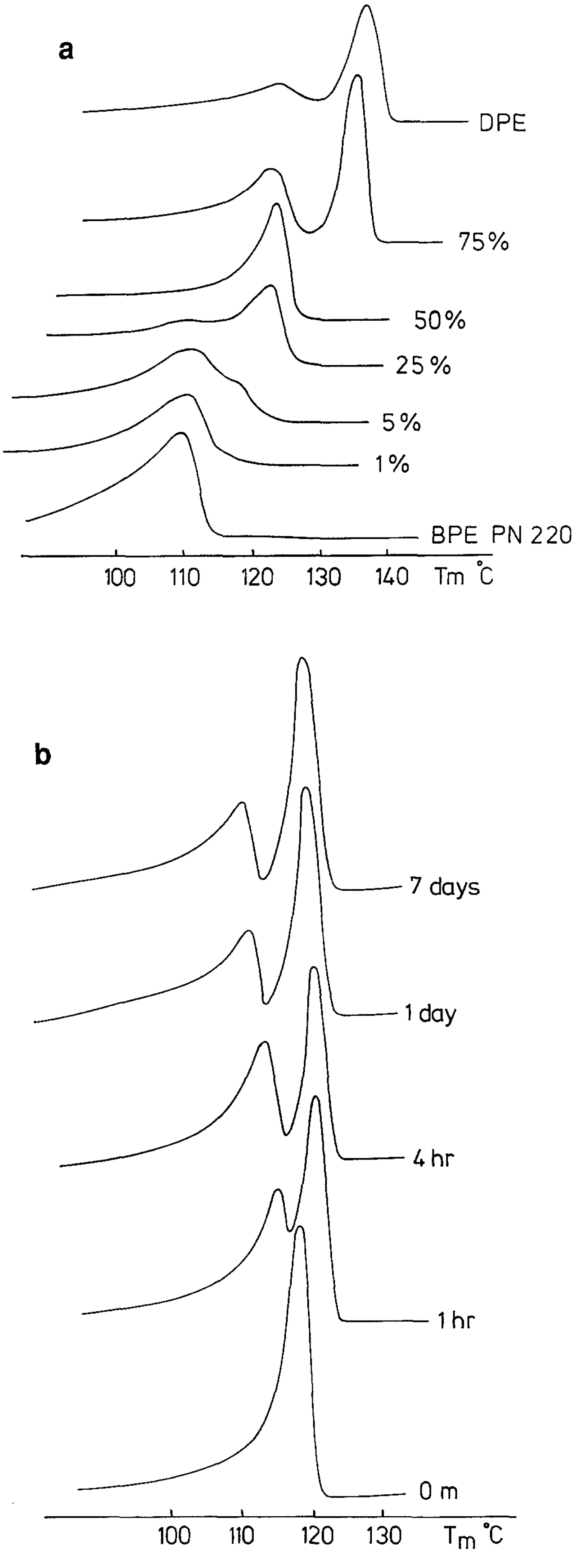

Figure 4 (a) D.s.c. traces obtained from heating blends of DPE with PN220 at 10°C min^{-1}. The blends were held for half an hour at 150°C and then at 125°C for 8 days before quenching. The lower-temperature peak in the top (DPE) trace indicates that some of the DPE was unable to crystallize at 125°C; a clear demonstration of heterogeneity (probably *MW* segregation). (b) D.s.c. traces obtained from heating 50% blends of low-*MW* LPE 2155 with PN220 at 10°C min^{-1}. The blends were held for half an hour at 150°C, then at 116°C for the times indicated, before quenching

liquid–solid coexistence curve; only the BPE itself cannot crystallize at all. (This argument may be clarified with the aid of *Figure 6*. The temperature where the LLPS loop intersects the liquid–solid coexistence curve is T_p. For the DPE/PN220 system, 124°C is above T_p but 123°C is at or below it.)

The development of isothermal crystallization with time is seen in *Figure 4b*; a 50% 2155/PN220 blend is liquid at 116°C at zero time, but has begun to crystallize by 1 h. Crystallization seems to have gone as far as it can by one day; the remaining polymer formed a single-phase melt, which crystallized only on quenching.

Isothermal crystallization at lower crystallization temperatures. Figure 5a shows typical results obtained by remelting blends crystallized near to the temperature at which the LLPS phase boundary meets the liquidus–solidus boundary, the temperature T_p. Here we show Hizex/PN220 blends crystallized at 127°C. All the blends have crystallized to some degree, only the pure BPE being unable to crystallize. Note that Hizex itself is unable to crystallize completely at this temperature (a manifestation of the multicomponent nature of these systems) and that the melting temperatures of both high and low melting peaks are similar irrespective of blend concentration. By measuring the areas below the peaks and using the melting point/heat of fusion calibration curves, it becomes clear that the LPE concentrations in all the high melting peaks are very similar (about 75%) for all blend concentrations.

When crystallization takes place at lower temperatures, there is little difference for the higher LPE content blends (except that the high melting peaks are at lower temperatures, presumably because the annealing took place at a lower temperature – compare *Figures 5a* and *5b*). The 1% blend, however, does show differences. In this blend, the high melting peak is larger in comparison with the low melting peak than it is on crystallization at 127°C, and it has a notably lower melting point than the high melting peaks of the other blends crystallized at 118°C (*Figure 5b*). It was explained in ref. 3 that we take this as an indication of considerable extra co-crystallization, which takes place on crystallization at low temperatures from metastable mixed melts. The LPE-rich material crystallized from 1% Hizex/PN220 blends at 118°C has a concentration of just less than 30% (the concentration on crystallization at 127°C is 72%). This effect is found in all the blend pairs where crystallization at low LPE content and low melt temperature can be studied – it cannot be studied at all with the 2907/8105 blend because the Sclair 8105 itself crystallizes partially at 126°C, only just below the temperature at which the LLPS and liquidus–solidus curves intersect.

Summary of d.s.c. results. The d.s.c. results obtained from the new blends are fundamentally similar to those obtained in our previous work. D.s.c. indicates 'phase diagrams' very like the one obtained for the 2907/PN220 system, with l.l.p.s. always observed except where the LPE is of very low molecular weight. The key parameters that emerge from the d.s.c. are listed in *Table 2* for all LPE/BPE systems; the parameters are T_p, the temperature at which the l.l.p.s. phase boundary meets the liquidus/solidus boundary; T_c, the highest temperature at which the LPE was found to crystallize; and three characteristic concentrations, those found in LPE-rich

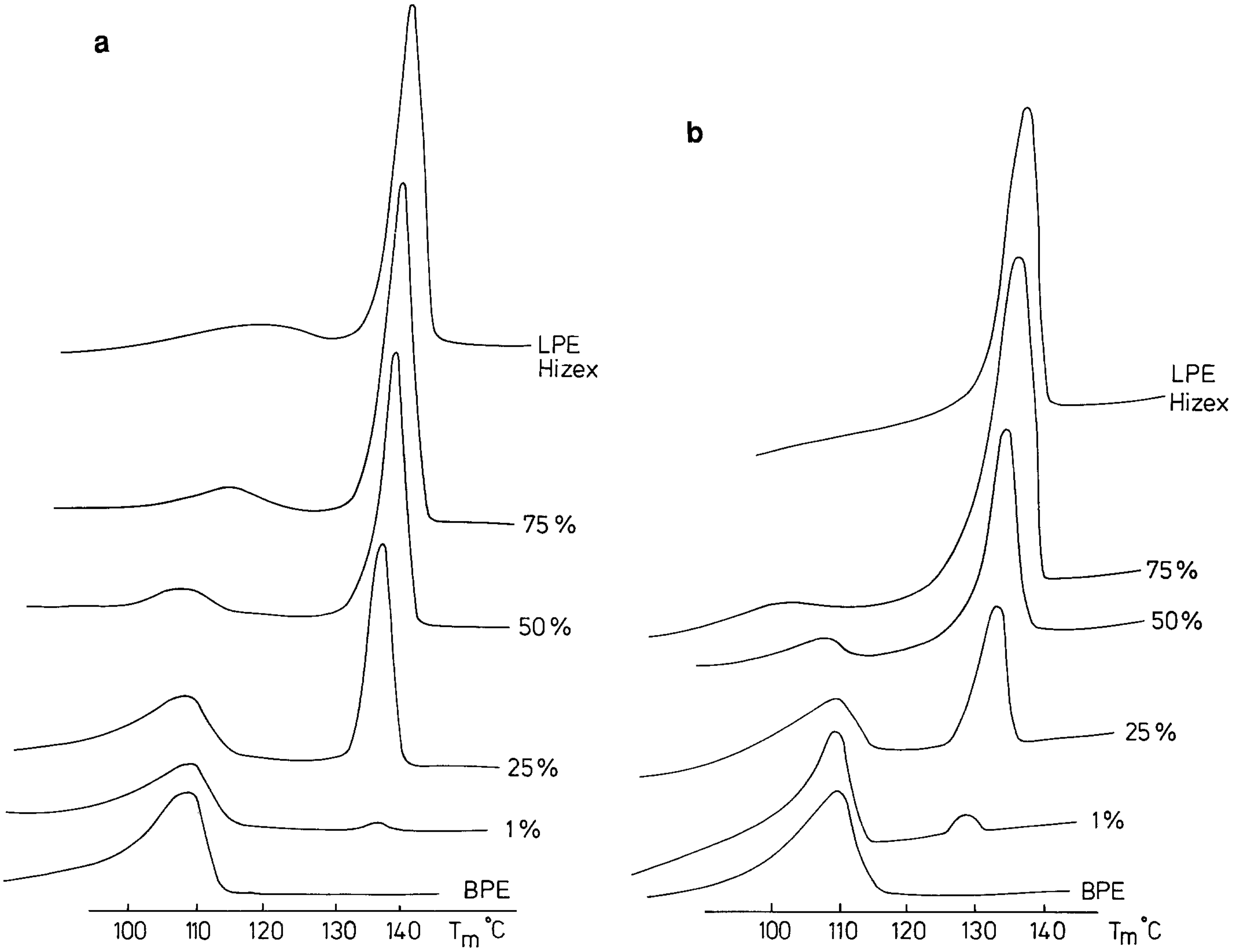

Figure 5 (a) D.s.c. traces obtained from heating blends of Hizex with PN220 at 10°C min^{-1}. The blends were held at 160°C for 30 min and then cooled to 127°C, where they were held for a week before quenching. (b) D.s.c. traces obtained from Hizex/PN220 blends prepared as those shown in (a), but crystallized isothermally at 118°C

Table 2 Reference points on the phase diagram. The points are defined on the sketch in *Figure 6*

	T_c (°C)	T_p (°C)	A (%)	B (%)	C (%) (at 120°C)
LPE blended with PN220					
Hizex	132	127	75	56	38
Sclair 2907	131.5	128	59	52	35
R50	131	127	55	48	21
15000	130	126	70	23	56
2155	124	–	–	–	93 (lower T_c)
DPE	127	123	67	20	45
LPE blended with Sclair 8105					
Sclair 2907	131.5	128	55	38	?

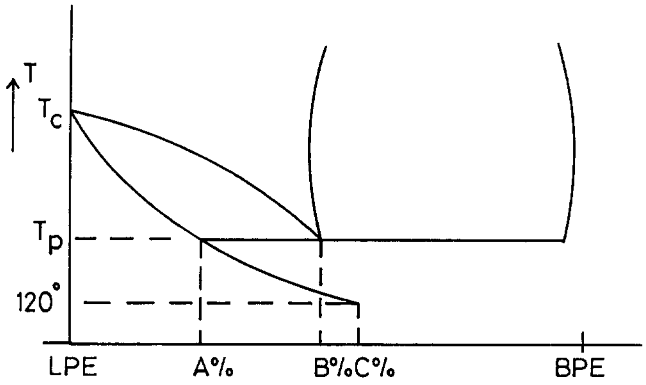

Figure 6 Sketch indicating some of the prominent features of the 'phase diagrams'. Values of the various parameters are given in *Table 2* for all blends studied

crystals and melt at T_p and that found in LPE-rich material crystallized at 120°C. The table should be read in the light of the explanatory sketch (*Figure 6*).

TEM results

TEM of quenched samples. The TEM results were in complete agreement with the d.s.c. results as in all our previous studies. All the blend pairs that showed single d.s.c. peaks on quenching had a single morphology when observed by TEM. All the blends that showed two d.s.c. peaks (after either quenching or isothermal crystallization) were seen to possess double morphologies.

Figure 7a shows a replica of a quenched 80% blend of linear Sclair 2907 with the branched Sclair 8105; only one morphology is visible, in agreement with the indications from d.s.c. (*Figure 2c*). All 2155/PN220

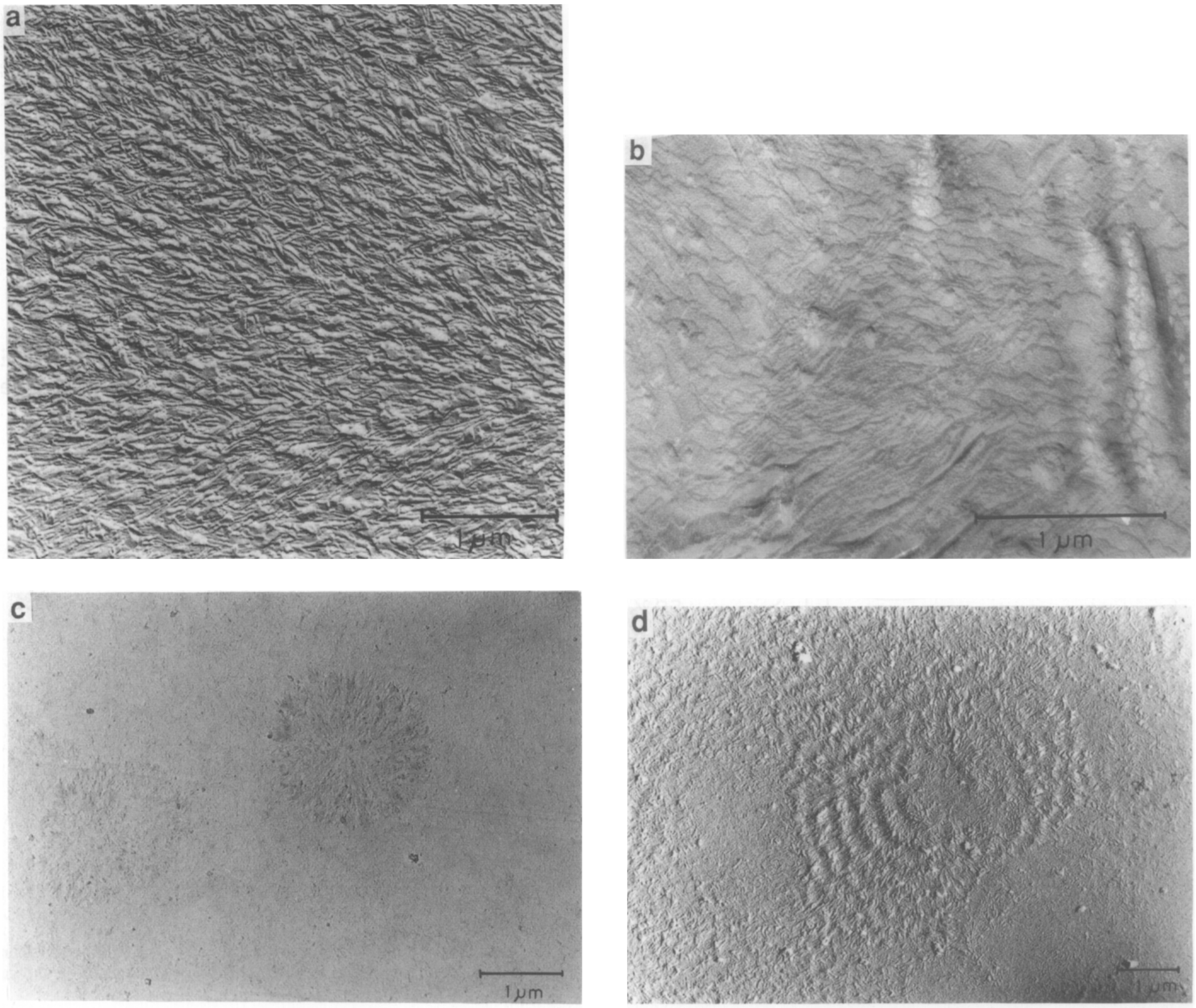

Figure 7 Transmission electron micrographs of replicas prepared from quenched blend melts. In all micrographs the scale bar represents 1 μm. (a) and (b) Examples of single morphologies after quenching: (a) is a replica of a blend of a quenched 80% LPE (Sclair 2907) with 20% BPE (Sclair 8105); (b) shows a blend of 10% LPE (2155) with 90% PN220. (c) and (d) Examples of double morphologies obtained after quenching: (c) shows a quenched blend of 1% LPE (R50) with PN220; (d) shows part of a replica made from a quenched blend with 10% 2907 and 90% 8105. (*Figures 7a* and *7d* courtesy of C. C. A. Rosney)

blends showed only one morphology, the 10% blend being shown as an example here (*Figure 7b*). On quenching, most blends of low LPE content showed double morphologies (in agreement with the double d.s.c. peaks obtained on melting those samples); the 1% R50/PN220 and the 10% 2907/8105 blends are shown here in *Figures 7c* and *7d* as examples. The LPE 2907 is the clearest because crystals containing 2907 twist, whereas those rich with other LPEs often do not; usually quenched BPE-rich lamellae are not twisted. However, two morphologies can still be identified, even when no twisting is present, by lamella thickness difference. All the replicas, obtained from all the quenched blends studied, fitted the same pattern, in full agreement with the d.s.c. results and with our previous work.

Isothermally crystallized samples. Very striking pictures can be obtained from replicas of isothermally crystallized samples. As with the pictures from quenched material, they fall into two groups – those crystallized from mixed melts and those from segregated melts. The pictures from replicas of fairly low LPE content are the most instructive since it is easier to detect segregation prior to crystallization.

Examples of crystallization from segregated melts are shown in *Figures 8a*, *8b* and *8c*, 1% blends of 15000/PN220 and DPE/PN220 crystallized at 122°C and a 25% blend of Hizex/PN220 crystallized at 126°C. In all these blends the linear-rich material has crystallized into lamellae that are, in most cases, organized into what must be, in three dimensions, roughly spherical groups, presumably corresponding to the segregated PLE-rich regions of the melt.

As explained above, it is clear from the d.s.c. that some blends remix at low temperature. It was shown in our earlier work that blends of 2907/PN220 crystallized from remixed melts have a characteristic appearance. We now find that these morphologies are again seen with most of the new blend pairs. *Figure 8d* shows a 1% blend of Hizex/PN220 crystallized at 118°C, from a melt that was

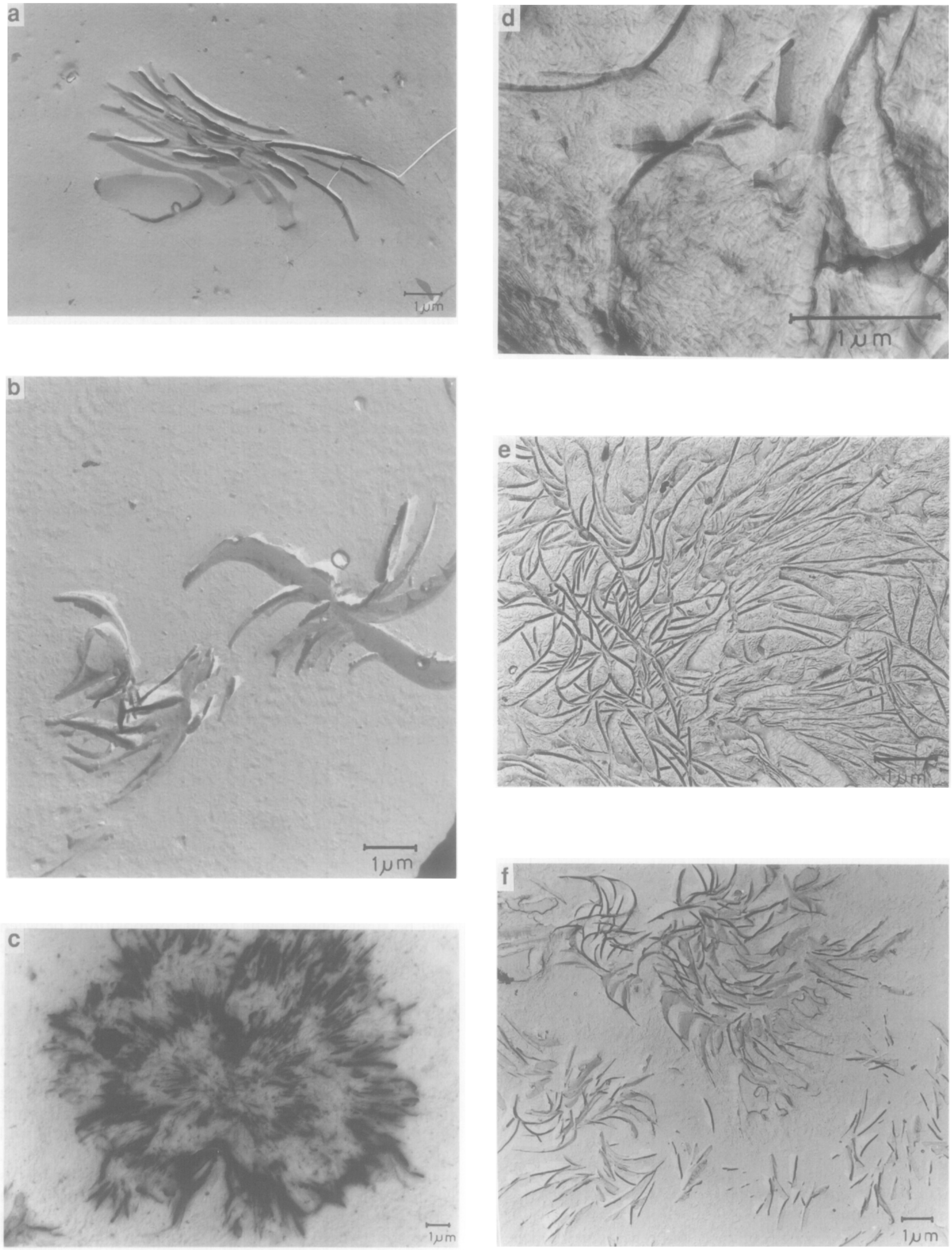

Figure 8 Transmission electron micrographs of replicas prepared from isothermally crystallized blends. In all micrographs the scale bar represents 1 μm. (a), (b) and (c) Examples of morphologies obtained after crystallizing from segregated melts: (a) shows the result of crystallizing a blend of 1% LPE (15000 fraction) with PN220 at 122°C; (b) shows a 1% DPE/PN220 blend crystallized at 122°C; and (c) a 25% Hizex/PN220 blend crystallized at 126°C. (d) and (e) Examples of morphologies obtained after crystallizing from mixed melts: (d) is part of a replica of a 1% blend of Hizex with PN220 crystallized at 118°C; (e) shows a replica of a 25% blend of 2155 with PN220 crystallized at 116°C. (f) A 1% R50/PN220 blend, which, we believe, crystallized as it mixed at 123°C

known to be remixed (see *Figure 3*). The LPE-rich lamellae are not found in clumps but crystallize individually, which we believe to be typical of crystallization from a mixed melt. The Hizex-rich lamellae are remarkably well formed considering the very high molecular weight of the LPE; lamellae of the Hizex homopolymer are not so regular. All 2155/PN220 blends are thought to be mixed in the melt; *Figure 8e*, which shows a 25% blend crystallized at 117°C, bears this out. The final picture in the group, *Figure 8f*, shows a 1% R20/PN220 blend crystallized at 123°C, where the LPE-rich polymer crystallized as it remixed, giving the characteristic appearance of loosely packed and disintegrating LPE-rich lamellar groups.

All the TEM results we have obtained are in full agreement with our previous work on the 2907/PN220 blends and with the d.s.c. results obtained from all the systems studied in this work. We have shown only a small selection here and have tried to choose a range of pictures covering all observed morphologies and all blend pairs. It is striking that all the LPE-rich lamellae appear very similar on isothermal crystallization – it would be hard to distinguish Hizex-rich lamellae (*Figure 8d*) from lamellae rich with very low-molecular-weight LPE (*Figure 8e*) in a blind test (although the crystalline homopolymers can be easily differentiated).

[Norton and Keller published the earliest work on PE blends from our laboratory. Their paper (ref. 8) shows d.s.c. traces and micrographs of replicas of 50% blends of Sclair 2907 with Sclair 8105. The quenched material gave a single-peaked d.s.c. trace and single morphology (Figures 2 and 4 of ref. 8). On isothermal crystallization at 124°C a segregated system developed by crystallization from the mixed melt. This was characterized by double d.s.c. peaks (Figure 2 of ref. 8) and two types of crystalline morphology (Figures 7 to 11 of ref. 8); in these micrographs of 50% blends, the LPE-rich lamellae are quite well separated, as would be expected from crystallization from a mixed melt. All this work is in complete agreement with the present study; it gives a detailed insight into the behaviour of one blend pair at one concentration and crystallization temperature.]

Phase diagrams

All the results obtained for all the blend pairs using both techiques are in agreement; they can be combined to give 'phase diagrams' for each LPE/BPE pair. In this work we have not reported experiments undertaken to determine the temperature of the top of the LLPS loops; we hope to publish this work separately in the near future. However, we have recorded the behaviour at lower temperatures for all blend pairs using our results obtained from d.s.c. and TEM. The results are shown in *Figure 9*.

DISCUSSION

D.s.c. from quenched blends – cases requiring ternary phase diagrams

The d.s.c. results obtained on reheating quenched blends of the linear DPE with branched PN220 and the linear Sclair 2907 with branched Sclair 8105 are detailed above. These systems showed single melting peaks for higher LPE contents (in both these cases down to 30%) and two peaks for lower LPE contents, as shown in *Figure 2c*. From this we suggest that LLPS occurs in these systems as it does with other LPE/BPE pairs. This is confirmed by the micrographs, which show two morphological components (see, for example, *Figure 7d*). However, in these two systems the temperature at which the higher of the two melting peaks occurs is not constant but decreases with increasing BPE content. This indicates that, if LLPS takes place in these systems, then the concentration of LPE in the LPE-rich phase decreases with increasing branched polymer content. This is not consistent with the picture we have used so far of a simple two-component system.

In order to interpret the data for these two cases, where the two homopolymers are less dissimilar and have become increasingly compatible, we must take into account the fact that neither of the homopolymers is in fact a single-component system. Indeed, our unpublished crystallization studies indicate the presence of two populations with differing branch content in the BPE Sclair 8105. Similar thermal behaviour has been seen in other BPEs[9], and some of these have been separated into more and less branched portions by crystallization and selective dissolution. Further, data such as that in *Figure 4a* suggest that some LPEs (DPE in this case) are not homogeneous.

The simplest way to consider these multicomponent systems is to approximate them as having three components. We consider these as the linear component (L) coming largely from the LPE; the intermediate component (I) from both the low-molecular-weight part of the LPE and the more linear parts of the BPE; and the most branched material (B). We show in *Figure 10* a sketch of a possible phase diagram for a three-component system showing how the observed melting behaviour could arise. Suppose the division of the LPE and BPE into the three components is such that the LPE contains 75% L with 25% I and the BPE 50% I with 50% B. Let us further assume that I and B are compatible in all proportions and L is compatible with I, but only partially miscible with B. If the 'plait point' is at P, then a series of tie lines would run as shown[10]. The possible compositions of the blends will all lie along the line YX. When the composition is between Y and R (e.g. at Q) then there will be a single-phase melt; accordingly a single d.s.c. peak and single morphology will be observed. There will be single-phase melts for all compositions between Y and R. But when the composition moves inside the region of LLPS (e.g. at S), two liquid phases will occur, as shown at S′ and S″; material of composition S′ will have a lower melting point than that of composition R, since it contains more of the branched component, B. It can be seen from the diagram, that as the composition of LPE is further changed by further decrease of the LPE content, say to T (with associated T′ and T″), the melting point of the LPE-rich material will continue to fall, while for this phase diagram that of the BPE-rich material will also fall. This is what we observe for 2907/8105 blends. The behaviour of quenched DPE/PN220 blends is slightly different in that the melting point of the BPE-rich peak changes less as the LPE content is reduced. This behaviour would follow from a similar phase diagram with a slightly wider LLPS region.

Thus, by quite a simple model, we can predict data similar to that shown in *Figure 2c*. However, this is a second-order effect and for most purposes the 'ternary' blends behave as the 'binary' ones. We should note that the ternary phase diagram we have drawn here is only

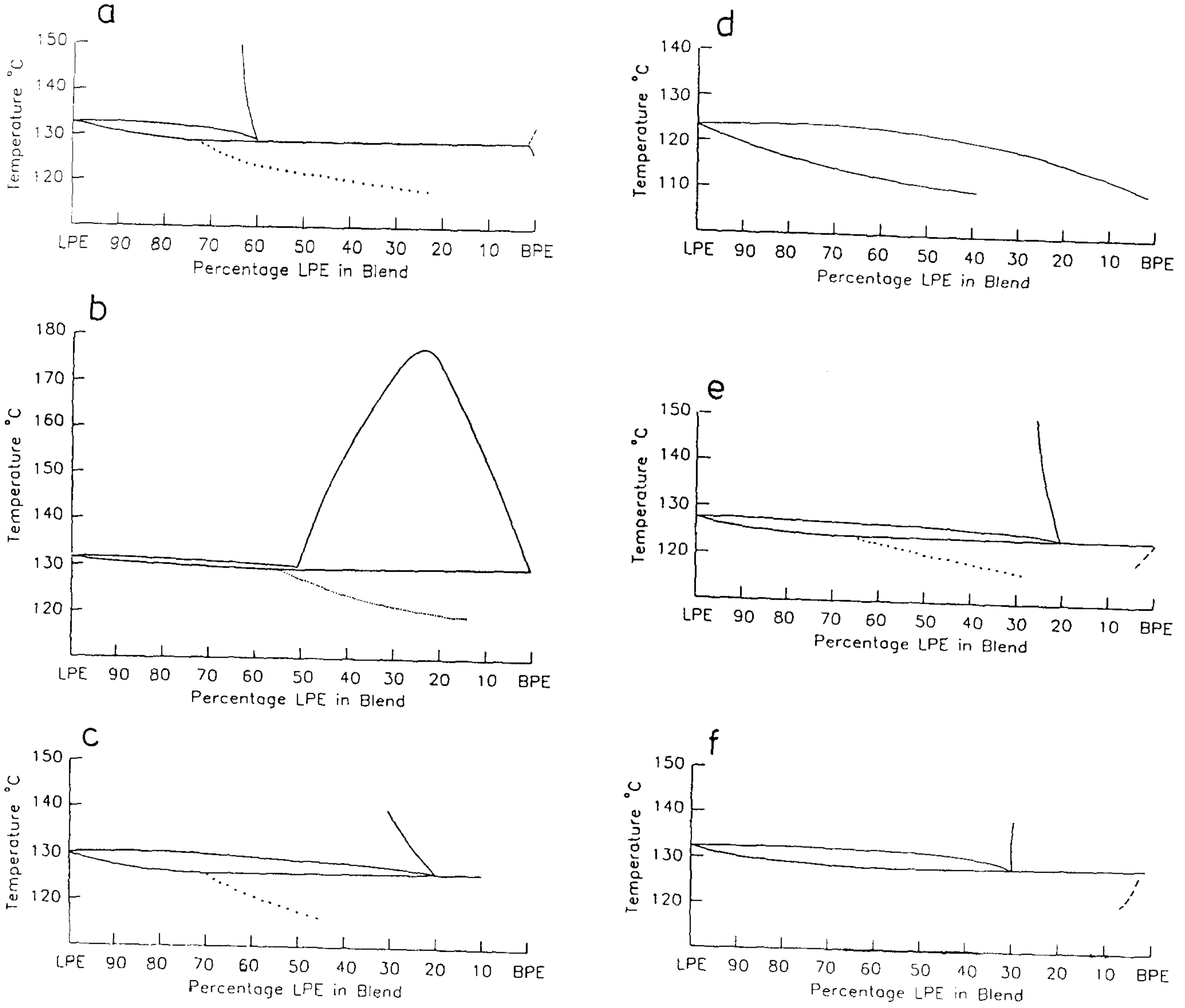

Figure 9 'Phase diagrams' for all the new systems discussed in this paper: (a) Hizex blended with PN220; (b) R50 blended with PN220; (c) fraction 15000 blended with PN220; (d) low-*MW* LPE 2155 blended with PN220; (e) DPE blended with PN220; (f) Sclair 2907 blended with Sclair 8105. Note that (a) to (d) show LPEs of diminishing *MW* blended with the same BPE

one of many possible diagrams that could explain our data.

Ternary phase diagrams are very difficult to calculate and are normally determined by experiment[10]. In our systems we are severely limited because we are unable to vary the relative proportions of the various components, as their ratio is fixed. Thus it is beyond the scope of this paper to do more than to show that the behaviour that we observed can be fully accounted for by a simple ternary phase diagram. In future, we hope to have access to better characterized, more uniformly branched materials. It will then be possible to mix three distinct components and determine diagrams of this type in full.

Comparison of the phase diagrams

It is clear from inspection of *Figure 1* and all parts of *Figure 9* that the 'phase diagram' found for the original LPE/BPE system of Sclair 2907 with BP PN220 is certainly not unique. All the 'phase diagrams' we have mapped out are fundamentally similar. The main features are as follows:

There is liquid–liquid phase separation (LLPS) in all systems except where the LPE is of very low molecular weight. [In ref. 11 Illers and Kohnlein claim that LPE/BPE melts are mixed. They conducted d.s.c. studies on an LPE/BPE blend crosslinked in the melt. They show that for their particular blend (a blend of 25% LPE of molecular weight 10^5 with 75% BPE of molecular weight 3.5×10^5 and 30 branches per 1000 C atoms) the melt is mixed at 175 and 200°C. However, they give no evidence for other blend concentrations or temperatures. There are other examples in the literature that indicate LLPS. In ref. 3 we cited the work of Mathot *et al.* on very low-density PE, which seems to be a blend in itself[9,12,13]. We have recently noted the work of Alamo *et al.*[14], who looked for co-crystallization in various PE blends, sometimes after quenching. They state that '... two pure species which have major differences in chain structure can co-crystallize with one another. However, co-crystallization is not universal and depends on the composition of the mixture and the crystallization conditions.' From the d.s.c. traces from quenched blends that they show in ref. 14 we would strongly suspect LLPS in the melt.]

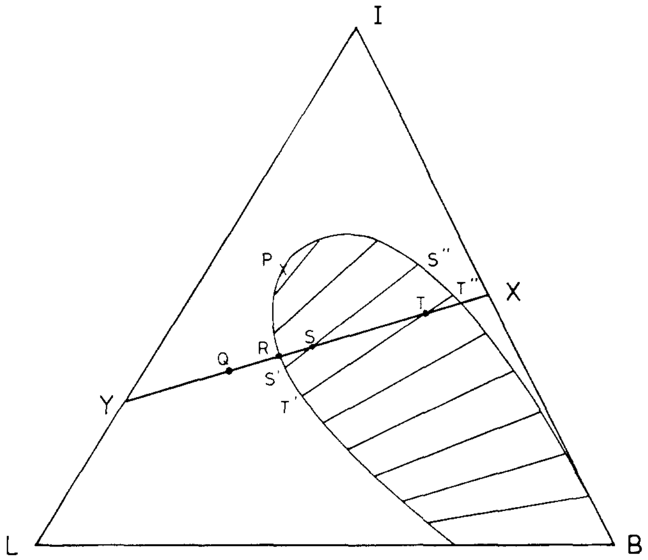

Figure 10 A possible ternary phase diagram that would account for effects such as are found on quenching blends of Sclairs 2907 and 8105. Here the system as a whole has three distinct components: L, the most linear material; I, intermediate material, probably the lowest-*MW* LPE together with the less branched BPE; and B, the most branched material. In the system pictured here, L mixes with I, and I with B, in all proportions, but L and B are only partially miscible. This is just one of many possible ternary phase diagrams that could account for the observations

The size of the LLPS region varies. From the results we have obtained to date it seems that the following conclusions can be drawn.

(i) The maximum width of the LLPS region (in concentration) is reduced as the LPE molecular weight is reduced. The blend containing very low-molecular-weight LPE, which does not show LLPS at all, is an example of the extreme case of this, where the LLPS region has been reduced to nothing.

(ii) From a comparison of the blends of the two different BPEs with the same LPE (8105 and PN220 with 2907), it seems that a higher branch content of the BPE leads to greater phase segregation. This is an effect that we intend to study in much more detail when suitable BPE materials become available.

(iii) The two cases where the molecular weights of both LPE and BPE are close (2907/8105 and DPE/PN220) fit into the general pattern, showing clear LLPS. This indicates that the LLPS effect must be primarily due to the difference in number of branches between the blend components rather than to molecular-weight differences between the LPE and BPE, as has been suggested in discussion with some of our colleagues.

(iv) Note that there is less segregation with DPE than would be expected with a blend containing LPE of equivalent molecular weight. It has been noted before that the behaviour of DPE is between that of LPE and BPE[15]. We note that our results are in agreement with this statement but have no explanation for it.

(v) In all the systems studied here considerable co-crystallization is observed on isothermal crystallization. Both the BPEs are co-crystallized into the products of isothermal crystallization at all temperatures. This is not surprising in the case of Sclair 8105, which we have found can, itself, partially crystallize at 128°C; it is, however, more surprising at first glance in the case of PN220, which does not itself crystallize above 114°C, but can be included in co-crystals at 128°C and even 131°C. The 'phase diagrams' of *Figures 1* and *9* show how this comes about.

(vi) The BPEs that we have examined crystallize as blends in themselves, i.e. under isothermal conditions, over a wide temperature range, part of the BPE will crystallize but the rest will not. This effect is present with PN220 but, fortunately, the temperature at which the more linear part of this BPE can crystallize is well below the temperature, T_p, at which the LLPS phase boundary meets the liquidus–solidus boundary for the blends with the LPEs we have used. Further, in PN220 the two components are present in such a concentration as to give a mixed melt and so a single melting peak after quenching – this is not always the case. Sclair 8105 itself gives a very broad melting peak after quenching (see *Figure 2c*); many other BPEs give double peaks. Indeed, all the homopolymers we have used are, in fact, multicomponent, the LPEs and all BPEs having a range of *MW*s in addition to the inhomogeneous branching present in the BPEs. Thus we should really use (at least) three-component rather than simple two-component phase diagrams. It is remarkable that binary, or at the most ternary, phase diagrams have been able to account for all the effects that we have seen.

This study gives us confidence in our assertion that 'phase diagrams' of this general type can commonly be obtained from blends of LPE with BPE. The results outlined here give a clear indication of the effect of the molecular weight of the LPE component on the 'phase diagram', and, particularly, on the size of the LLPS region. It is now clear that, where the molecular weight of the LPE is higher, the region of LLPS will be larger. The change is only slight at high molecular weight, but below a LPE molecular weight of about 20 000 the LLPS region rapidly decreases in size.

Further, we would like to stress the striking similarities of behaviour of all these blend systems. We have dwelt on the variations in 'phase diagrams' in some detail, but it is more important to stress their similarities. The morphologies are remarkably similar too; a casual observer would find it hard to tell, by inspection, which of the micrographs shown in *Figures 7* and *8* was obtained from a blend with Hizex or with the low-molecular-weight 2155, although the molecular-weight difference of these two LPEs is very great (see *Table 1*).

Finally we note that the apparent multicomponent nature of some of the blend phase diagrams suggests that under some circumstances certain unblended polymers can themselves undergo LLPS. We now suspect that many commercial polymers may behave in this way, and that LLPS may be responsible for some of the unusual morphologies and properties that have been observed.

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