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# Absence of phase separation effects in blends of linear polyethylene fractions of differing molecular weight

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Blends of linear polyethylenes of differing molecular weights (*MWs*) have been studied to try to determine whether there is any observable phase separation in the melt. Using four linear polyethylene fractions, of *MWs* between $2 \times 10^6$ and $2.5 \times 10^3$, blends were prepared and four blend systems investigated, the two high *MW* polymers being blended with each of the two lower *MW* materials in turn. The blends were studied by transmission electron microscopy and differential scanning calorimetry, techniques previously used to study blends of linear with branched polyethylenes. In these systems, for some compositions of blends of linear with branched polyethylene, quenched from some temperatures, phase separation on a scale of micrometres has been recorded. In contrast, no indications of phase separation were observed on examination of the blends of linear with linear polyethylenes. From this it follows that if there is any liquid–liquid phase separation in linear with linear polyethylene blends, taking place as a result of molecular weight differences, it cannot be detected by the methods used to detect liquid–liquid phase separation in linear with branched polyethylene blends; and, conversely, the phase separation observed in linear with branched polyethylene blend systems does not take place as a result of molecular weight difference alone.

**(Keywords: liquid–liquid phase separation; molecular weight; polyethylene)**

## INTRODUCTION

In the recent past we have published a number of papers relating to phase separation in melts of blends of linear with branched polyethylenes (LPEs with BPEs). We have found indications of liquid–liquid phase separation (LLPS) in many LPE/BPE melts[1–10]. Where the BPE was heavily branched we have observed extensive LLPS[8], as have other authors (see, for example, refs 11 and 12), but where the BPE has been only lightly branched, with less than 50 branches per 1000 backbone carbon atoms, we have observed LLPS of an unusual type. *Figure 1* shows the characteristic behaviour for LPE/lightly branched BPE blends; the phase-separated region is in the form of a closed loop found at low LPE content. To date we have observed this behaviour in more than 40 blend systems.

The polymers that we have used to make our LPE/BPE blends are very similar to each other in properties; as a result we have been unable to use traditional methods (such as light scattering) to detect phase separation and have had to develop a range of new (indirect) techniques to look for evidence of phase separation. We have used transmission electron microscopy (TEM) and differential scanning calorimetry (d.s.c.) to examine very rapidly quenched blends; these methods are described in detail in refs 1–5 and 13. Initially, we relied on the assumption that a rapidly quenched material cannot be very different in phase structure from the melt from which it was quenched; so that when large-scale phase separation is observed (and it is usually observed on a scale of micrometres) the separation cannot have taken place during the fraction of a second taken to achieve the quench[1–4]. We subsequently measured diffusion rates and have shown[5] that in our materials it would take tens of

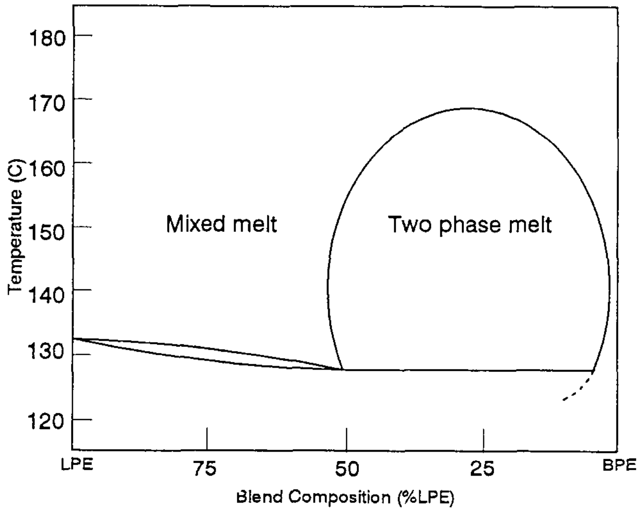

**Figure 1** Phase diagram showing the phase behaviour usually found when a LPE is blended with a lightly branched BPE. There is a region of LLPS at low LPE content and liquid–solid phase separation is found at high LPE content for temperatures in a narrow range (the leaf-shaped region on the left of the figure)

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**Table 1** Fractions used in this work

| Code | Origin | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| H | Fractionated from HIZEX® 240 at Bristol | $>2\times10^6$ | 13 |
| 127K | Fractionated at Bristol | $127\times10^3$ | 2.09 |
| 13K | Fractionated at Bristol | $13\times10^3$ | 2.0 |
| 2.5K | Polymer Laboratories' fraction 2155 | $2.5\times10^3$ | 1.1 |

minutes to achieve the large-scale phase separation that we see in quenched blends of low LPE content; the observed separation cannot have taken place during crystallization on quenching from mixed melts.

The normal Flory–Huggins models for liquid–liquid phase separation have been applied to mixtures of polymers differing only in their molecular weights (*MW*s). It has been shown that, at equilibrium, phase separation in the melt of such blends should be expected[14]. It is possible that such molecular weight effects may dominate the phase separation that we have observed in our LPE/BPE blend systems. Indeed, it has been suggested to us[15] that the separation that we observe may be a consequence of differences in molecular weight between the components, rather than of differences in branching. To see whether this could be the case, we have prepared four blend systems using pairs of linear polyethylenes of differing *MW*. We have examined these blends after quenching and after isothermal crystallization, using the same methods we used to examine our LPE/BPE blends, in order to try to detect any LLPS that may have occurred in the melt prior to quenching.

It is well known that phase separation can take place on crystallization as a result of molecular weight differences[16–18]. On isothermal crystallization or crystallization during slow cooling of a homopolymer of broad *MW* (or a blend mixed in the melt), the high *MW* material crystallizes first, and the lower *MW* material is separated during the crystallization process, eventually crystallizing in small groups of lamellae between spherulites of high *MW* polymer[19]. Using extraction techniques, Mehta and Wunderlich found that on isothermal crystallization at 120°C polyethylene of molecular weight 3700 and below was rejected from crystals, and that at 125°C polyethylene of molecular weight 4400 and below was rejected[20]. However, the appearance of material phase separated by molecular weight on crystallization is different, on a spatial scale, from that of a phase-separated LPE/BPE blend quenched from the melt. We are confident that we are able to distinguish between separation due to molecular weight effects, taking place on crystallization (on a scale of tenths of micrometres) and the separation found in LPE/BPE blends, which is on a scale of micrometres.

In summary, there are at least three different potential causes for the observation of phase separated regions in quenched blends. First, the blends may have been mixed in the melt, and have separated only on crystallization. In such cases we expect to see a very fine dispersion of the separated phases; diffusion studies have indicated that, in the time taken for crystallization on quenching, the molecules are unlikely to move more than a few tenths of a micrometre[4,5]. Secondly, the blends may have been phase separated in the melt. In these cases there are two possible effects that might have provided the thermodynamic driving force for separation: either it is the difference in branch content between the two components which is dominating the energy of mixing, or it is the difference in the molecular weights of the two components (although, possibly, both these things have to occur in combination). In this paper we address the question of whether it is possible to observe, by our techniques, LLPS due to differences in molecular weight alone.

## EXPERIMENTAL

The four linear polyethylenes used in this study were fractions, three prepared at Bristol and the fourth purchased from Polymer Laboratories. Details of these polymers are given in *Table 1*; *MW*s varied from 2500 to $2\times10^6$.

Our fractionation techniques used can be summarized as follows. First the high and low *MW* tails are removed. To do this the whole polymer is dissolved in xylene at 1% (w/v). The solution is heated to 130°C and stirred with a paddle stirrer until the polymer is dissolved (about 30 min). The solution is then cooled, very slowly (over some 12 h) to 70°C, the stirring continuing all the time. When the solution reaches 70°C the stirrer is removed. The remaining solution contains the lowest *MW* fraction, which is precipitated on cooling, harvested and dried. The stirrer is placed in fresh solvent which is gradually heated to 110°C and held there for about 15 min, stirring continuously throughout. After this process the top *MW* fraction still adheres to the stirrer and can be harvested and dried. The rest of the polymer, in solution, is then further fractionated by the method of fractionation by addition of non-solvent[21]; several fractionations are carried out to obtain successively lower molecular weights.

The fractionated materials were characterized by gel permeation chromatography (g.p.c.), using two 60 cm, mixed bed columns (from Polymer Laboratories) operating at 130°C, with infra-red detection.

Both of the higher *MW* fractions (which had been obtained and characterized by the above processes) were blended with each of the lower *MW* fractions. Four blend systems were studied in all. The polymers were blended by dissolving suitable weights of the components together in xylene and precipitating into acetone at its freezing point (we have always used this method in preparing LPE/BPE blends[1–3]). The blends were then dried and samples further prepared for d.s.c. or TEM. We looked at blends with 90, 70, 50, 30 and 10% of each component. We refer to a blend by citing the high *MW* polymer first and giving the composition by the percentage of this LPE, e.g. H/2.5 10% refers to a blend of 10% HIZEX® fraction with 90% 2.5K fraction.

Our d.s.c. methods are described and discussed in ref. 13. In brief, we take 2–3 mg samples in d.s.c. pans and hold them in the melt for about 30 min (it has been shown[4] that melt equilibrium is achieved within 20 min) before quenching very rapidly, by flicking into acetone at its freezing point. Samples are remelted at 10°C min$^{-1}$, under nitrogen, in a Perkin–Elmer DSC 7. For LPE/BPE blend samples, we have found that the observation of a single melting endotherm indicates a single crystal species, originating from a mixed melt. A double melting endotherm is indicative of two crystal species, originating from a phase-separated melt prior to quenching. A comparison of results obtained on heating at different rates has shown that the second peak is not due to annealing effects. Of course, the melting points of the quenched LPEs used here are closer than those of the LPE/BPE pairs that we have blended previously; this means that our d.s.c. method is not as sensitive in detecting phase separation in LPE/LPE blends as it was for LPE/BPE blends.

Our TEM methods, developed for observation of liquid–liquid phase separation in LPE/BPE blends, are described and discussed in refs 2–5. We examine surface replicas of drastically quenched blend samples. We look at surface replicas because the surface is the fastest quenched part of the sample and so nearest to the melt in phase structure. We have been able to see two clear crystal populations, separated on a scale of micrometres, in some quenched blends (those that show two melting endotherms) and only one crystal population in others (usually those that show only one melting endotherm). When the blend has been quenched through a temperature drop of 30°C or less we have always found complete agreement between TEM and d.s.c. (When the temperature drop during quenching was larger we sometimes have found discrepancies—in these cases TEM is more reliable than d.s.c.[13]. On isothermal crystallization from a phase-separated melt at a temperature at which one of the blend components will crystallize but the other will not, the species which crystallized isothermally is found in (usually spherical) crystal groups; where the melt was mixed before crystallization the isothermally grown crystals are found scattered about individually[1,5].

The LPE/LPE blends used for this study were all examined by d.s.c. and by TEM after quenching and after isothermal crystallization. Blends were quenched from 150°C for examination by d.s.c., and quenched from both 140 and 160°C for examination by TEM. All blends were crystallized isothermally at 125°C, where crystallization was so slow that any segregation on crystallization should have been apparent. Blends containing the 2.5K fraction were also examined after isothermal crystallization at 120°C.

## RESULTS AND DISCUSSION

The results from the four systems examined were, in many ways, similar and can be described together, with the HIZEX systems acting as examples.

### *Results obtained on quenching*

Single d.s.c. melting endotherms were obtained in all cases (there was a high melting shoulder on the endotherm from the HIZEX fraction itself, H, this was carried over in some of the high LPE content blends). *Figure 2a* shows the endotherms from the quenched H/2.5 system. There is a single peak in each case; note how the peak temperature falls linearly as more low molecular weight LPE is included in the blend. This was also the case in the other blend systems (see *Figure 3* where the peak temperatures are plotted). There was less difference in melting temperature when the low *MW* fraction was fraction 13K (indeed 13K and H have the same melting point after quenching). The heats of fusion rose with the content of low molecular weight fraction (*Figure 3*). The micrographs show no large-scale phase separation; in general a single morphology is seen (e.g. *Figures 4a–e*). Occasionally small (sub micrometre) groups containing a few thin lamellae are visible (*Figure 4c*), but these are nothing like the well separated, micrometre scale, regions of segregated lamellae regularly observed in LPE/BPE blends of low LPE content[1–6].

Apart from the presence of these very occasional small groups of fine lamellae (found only in H/2.5K blends of between 70 and 30% H content), the d.s.c. and TEM results are consistent and, by our previous criteria for judging blends, indicate co-crystallization after quenching from mixed melts. Using our standard methods, developed for use with LPE/BPE blends, we are unable to detect significant LLPS in these quenched LPE/LPE blends.

It is very striking that although the crystals obtained on quenching the H fraction are very ill formed (*Figure 4a*), the addition of a small quantity of the 13K or 2.5K fraction brings about a total transformation (*Figure 4b*). It is clear from the pictures of the 90% and 70% blends that the mixing is very good and co-crystallization is the

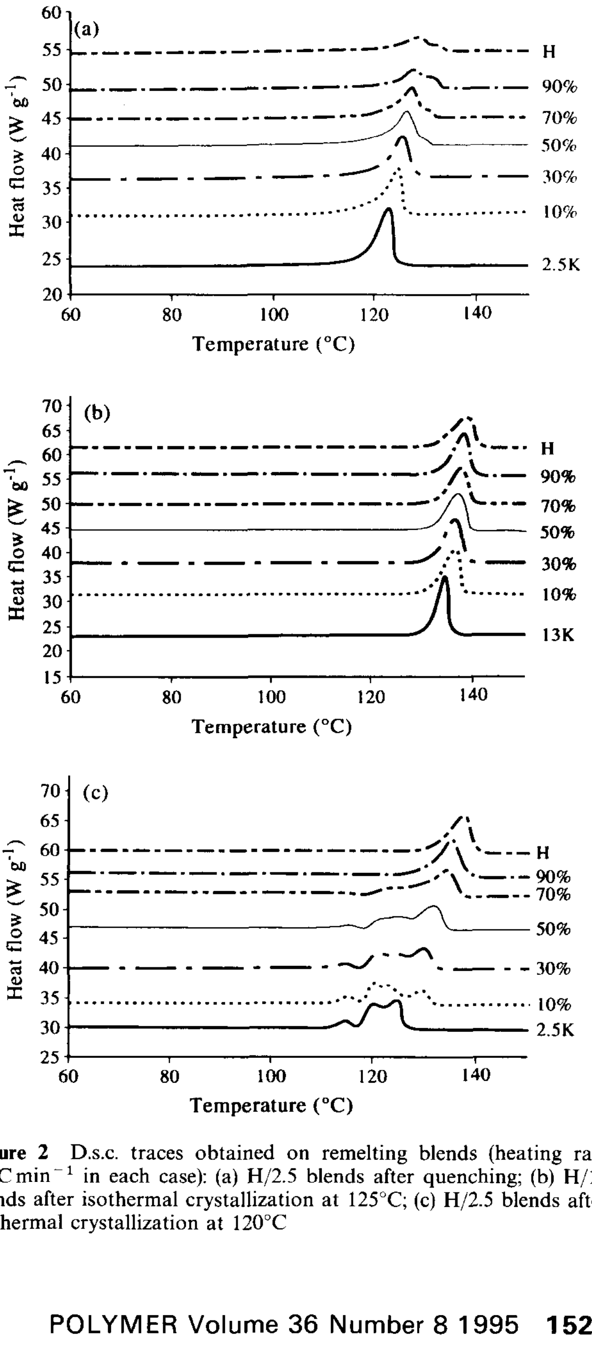

**Figure 2** D.s.c. traces obtained on remelting blends (heating rate 10°C min$^{-1}$ in each case): (a) H/2.5 blends after quenching; (b) H/13 blends after isothermal crystallization at 125°C; (c) H/2.5 blends after isothermal crystallization at 120°C

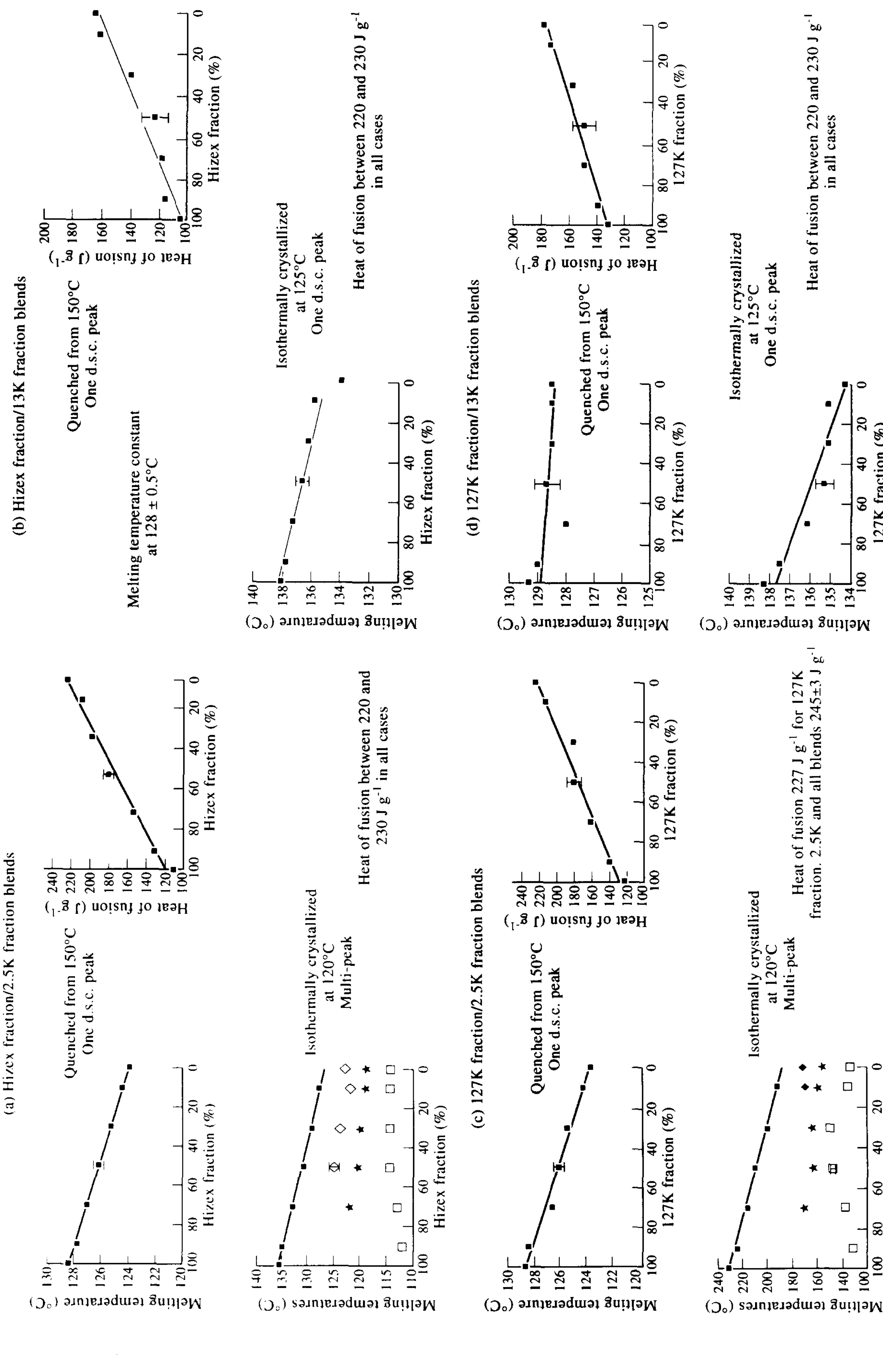

**Figure 3** Summary of all d.s.c. data, showing melting points and heats of fusion for quenched and isothermally crystallized blends (heating rate 10°C min⁻¹ in each case): (a) H/2.5 blends; (b) H/13 blends; (c) 127/2.5 blends; (d) 127/13 blends

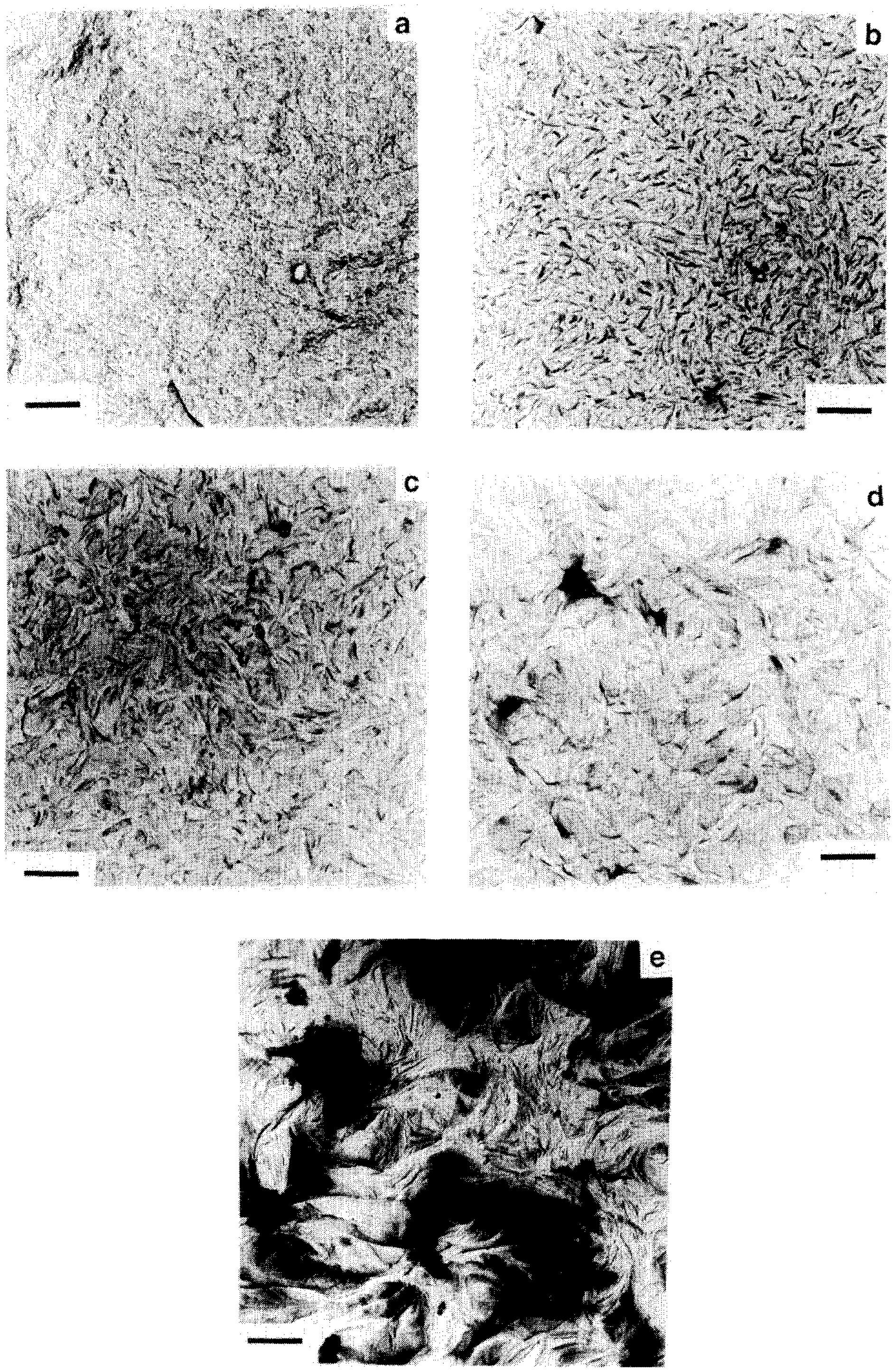

**Figure 4** Quenched blends from the H/2.5 system (all micrographs are of surface replicas of permanganically etched material; in each case the scale bar represents 1 $\mu$m). (a) HIZEX quenched from 140°C; the crystals are very small and poorly formed. (b) 90% H/2.5 quenched from 160°C; in spite of 90% HIZEX content, the crystals are much larger and look quite unlike those in *Figure 4a*. (c) 50% H/2.5 quenched from 140°C; groups of small, thin lamellae can be seen occasionally (there are some just above the right of the scale bar). (d) 30% H/2.5 quenched from 140°C; groups of small, thin lamellae can again be seen occasionally (there are some a third of the way up the right-hand edge). (e) 2.5K fraction quenched from 160°C; these low *MW* lamellae are rather longer than those of the blends. The dark material is detached polymer, adhering to the replica. The low *MW* materials very often detach in this way

rule. (If there were any phase separation, with pure HIZEX as a component, it would be easy to recognize by the characteristic appearance of the high *MW* polymer.) We believe that the improvement in crystal morphology on blending HIZEX can be explained, at least in part, by the realization that the very long chains in the HIZEX fraction are not very mobile and, on quenching, not able to move fast enough to re-organize into well formed crystals. The added low *MW* polymer in 90 or 70% HIZEX blends acts rather like a solvent, allowing much greater mobility for the long molecules, so that from the blend the HIZEX can form crystals of good appearance even on quenching. Note that although HIZEX crystals are ill formed when the polymer is

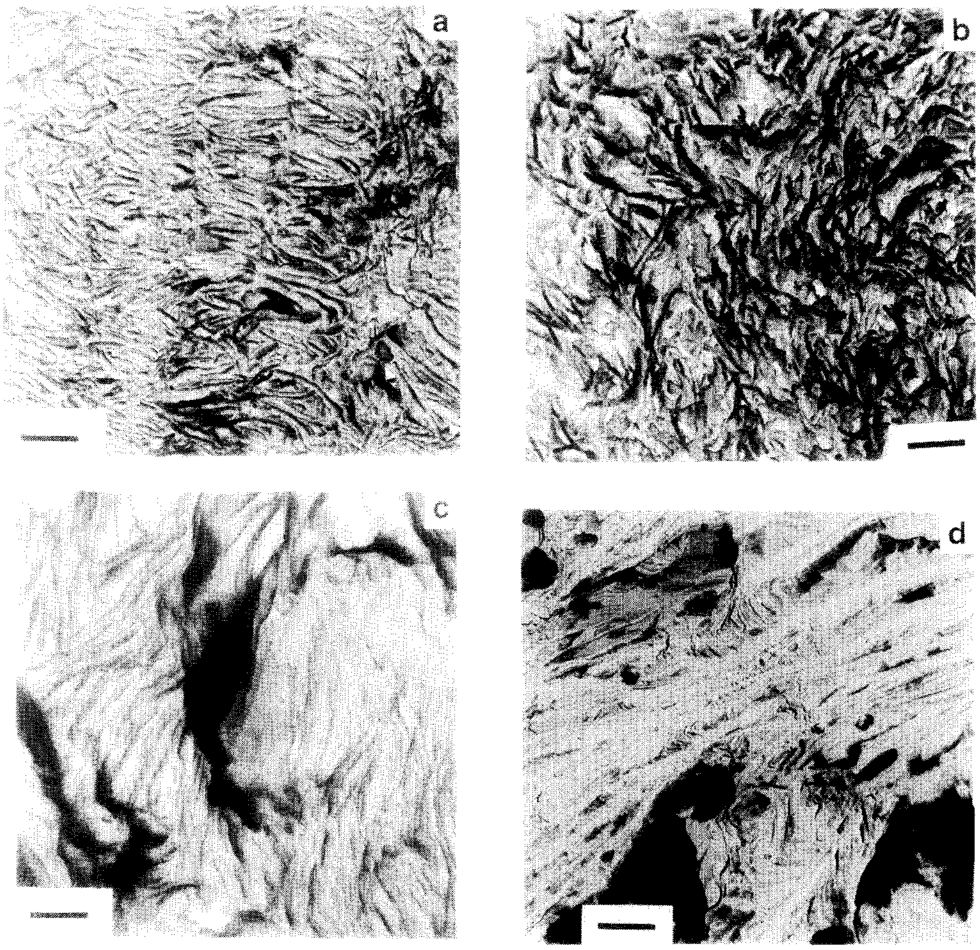

**Figure 5** Representative electron micrographs of blends from the H/13 system isothermally crystallized at 125°C (all micrographs are of surface replicas of permanganically etched material; in each case the scale bar represents 1 $\mu$m). (a) HIZEX crystallized isothermally at 125°C; these HIZEX crystals are well formed, presumably because of the very slow crystallization. There is considerable orientation in this particular region of the replica. (b) 70% H/13 blend isothermally crystallized at 125°C; the crystals here are rather longer than those in *Figure 5a*. There is some detached polymer adhering to crystal edges (very dark lines). (c) 30% H/13 blend crystallized isothermally at 125°C; the crystals, and the spherulites, are larger still. There is no sign of phase separation. (d) 2.5K fraction crystallized isothermally at 125°C; the morphology is typical of a low *MW* material crystallized isothermally

quenched, crystals of good appearance can be obtained without addition of lower *MW* material. On isothermal crystallization at 125°C, where the rate of crystallization is slow, the HIZEX fraction can form large crystals, see *Figure 5a*.

### *Results obtained following isothermal crystallization*

Again, all d.s.c. and TEM results are consistent. The blends containing the 13K fraction behaved differently from those containing the 2.5K fraction and will be discussed separately.

The blends containing 13K fraction (either with 127K or with H fractions) showed single d.s.c. peaks on remelting after isothermal crystallization at 125°C. The melting temperatures decreased linearly with increasing 13K content (*Figures 2b* and *3b* and *d*) and the heats of fusion were constant, within experimental error, for all blends. Micrographs showed one crystal type only, although the appearance of the crystals changed with blend composition (*Figure 5*).

It appears that fractions 13K, 127K and H can all crystallize completely at 125°C and that both the higher *MW* polymers co-crystallize with the 13K fraction. There is no sign of separation on crystallization or of separation in the melt before crystallization.

Separation was, however, seen when blends containing the 2.5K fraction were crystallized isothermally, both at 125°C and at 120°C. The 2.5K fraction itself crystallized partially at 125°C and largely at 120°C (*Figures 3a* and *c*). The melting point of the blend crystals with the higher melting temperature, found after crystallizing blends isothermally, dropped considerably as the 2.5K fraction content increased, indicating some co-crystallization. However, the presence of further melting endotherms at lower temperatures, even for the 70% blend, indicates a considerable degree of phase separation (*Figures 2c* and *3a* and *c*). Micrographs show two crystal types, with small (sub micrometre) groups of crystals of one type randomly interspersed amongst crystals of the other type (*Figures 6b–d*).

These studies of behaviour on isothermal crystallization indicate that the 13K fraction is completely miscible with the two higher *MW* fractions, and co-crystallizes with both of them even when crystallization is slow. On the other hand, the 2.5K fraction is, at least partly, found in separate crystals after isothermal crystallization (although it always co-crystallizes on quenching, see above). The fact that the low *MW* crystals are found randomly distributed, not grouped together, indicates that the separation took place on crystallization from a homogeneous melt.

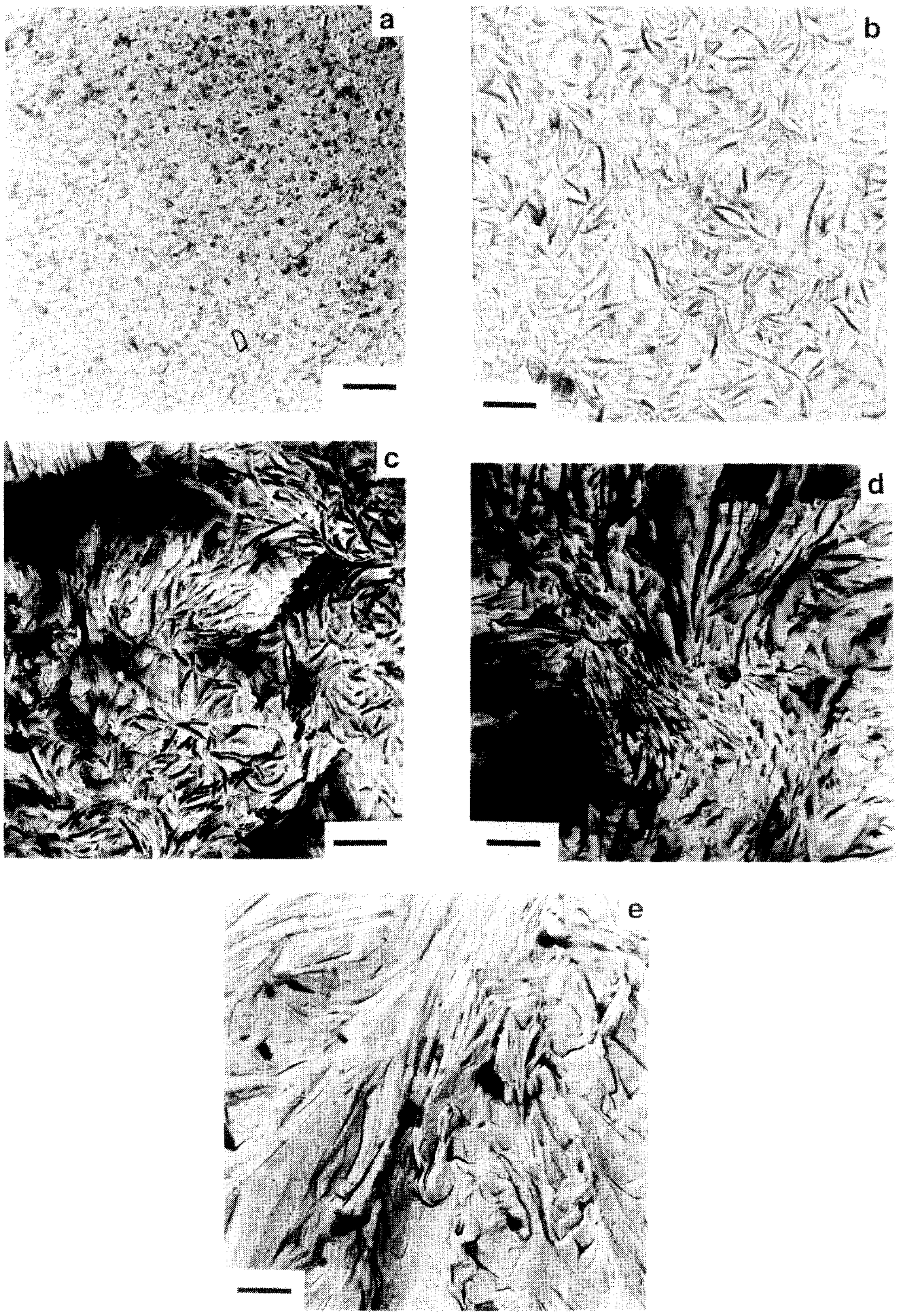

**Figure 6** Representative electron micrographs of blends from the H/2.5 system isothermally crystallized at 120°C (all micrographs are of surface replicas of permanganically etched material; in each case the scale bar represents 1 $\mu$m). (a) HIZEX crystallized isothermally at 120°C; these HIZEX crystals are not well formed (cf. *Figure 5a*) indicating that they crystallized quite quickly, probably on cooling between 125 and 120°C. (b) 90% H/2.5 blend crystallized isothermally at 120°C; there are some small, but distinctive groups of small crystals (there is a group half way up, above the right edge of the scale bar). (c) 50% H/2.5 blend crystallized isothermally at 120°C; again groups of small, separated crystals are visible (e.g. several small groups in the bottom left corner). There is also some detached material and etching debris in the picture. (d) 30% H/2.5 blend crystallized isothermally at 120°C; groups of small, separated crystals and detached material again visible (a group of small crystals can be seen on the left edge above the dark detached material). (e) Very large lamellae obtained on isothermal crystallization of 2.5K fraction at 120°C

Note that the 2.5K fraction consists of short molecules, about 23 nm in length. These would be unlikely to fold if incorporated into crystals of the thickness grown isothermally at 120 or 125°C (some 21–23 nm, ref. 22). Hence it is not surprising that many molecules are not trapped into co-crystals. Perhaps we should be more surprised that some molecules are trapped, considering the low driving force for crystallization and the high diffusion rate[5].

## CONCLUSIONS

We note that, throughout this study, all our d.s.c. and TEM results were consistent. When we observed two distinct morphologies we also found two d.s.c. endotherms; conversely, when we only observed a single endotherm in the d.s.c., we only observed a single morphology (except in the case of quenched 70–30% H/2.5K blends where minor separation was seen by TEM only). This consistency between the techniques lends weight to our further conclusions.

All four LPE/LPE blend systems studied here appear, by our previous criteria for judging LPE/BPE blends, to mix in the melt at all compositions, between 140 and 160°C. On quenching, only one crystal type could be detected in each case. No separation, on the micrometre spatial scale observed in many LPE/BPE quenched blends, can be seen in quenched LPE/LPE blends. We have found no evidence for any LLPS due to molecular weight effects. If any such separation does in fact occur then it is at a level below the resolution of our techniques.

We also failed to detect any phase separation during crystallization in blends of the high *MW* fractions with the 13K fraction. These blends always formed single populations of crystals when crystallized isothermally at 125°C, in any proportion. This result places some limits on the degree of phase separation that can be observed, by our techniques, purely due to crystallization; the difference between the two polymers must be larger than that used in these experiments.

When we looked at blends of the very low *MW* 2.5K fraction we found some phase separation, from both of the higher *MW* fractions, on isothermal crystallization at both 125 and 120°C. The TEM evidence indicates that the separation was not present on any large scale in the melt prior to crystallization. Our results on isothermal crystallization are consistent with those reported in the literature[19,20]. From the results of Mehta and Wunderlich, it would be expected that much of the 2.5K fraction would be unable to crystallize isothermally at both 125 and 120°C and, therefore, would be excluded from crystals forming from a mixed melt.

To summarize, as far as we can judge using our standard experimental methods, all LPE fractions mix in the melt in all proportions between 160 and 120°C. Phase separation does not take place on quenching, but some small-scale spatial separation can be observed on isothermal crystallization when the molecular weight difference between the two fractions is very large: we can see separation between 127K and 2.5K fractions, but not between H ($2 \times 10^6$) and 13K fractions. It seems that the lowest *MW* fraction is more inclined to separate out on isothermal crystallization – which seems reasonable in view of the greater mobility of short chains.

This work has important implications for our studies of LPE/BPE blends. We have been unable to detect any sign of LLPS (on the micrometre scale) in these quenched LPE/LPE blends using the standard methods that we have developed for use with LPE/BPE blends. The LPE/BPE blends used in our work on LLPS have molecular weights within the range of the fractions studied in the present work and have similar or broader molecular weight distributions. Hence we are strengthened in our view that the LLPS we have observed in LPE/BPE blend systems is a result of differences between the components as regards branch content, or branch content in association with molecular weight difference, but not as regards molecular weight alone.

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