polymer papers

Diffusion effects in blends of linear with branched polyethylenes

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In this paper a method of estimating diffusion rates in suitable polymer blend systems is described. Recent studies of blends of linear with branched polyethylenes have shown that in the melt the components mix under some conditions of temperature and composition, but segregate under others. In particular, for a large number of systems, blends with low linear content are demixed in the melt at the highest temperature at which crystallization is observed, but can be cooled into a metastable state in which the melt remixes before crystallization takes place. Such remixing is the subject of the present paper. The times of melt mixing were assessed from the thermograms and the distances over which the linear material diffused were assessed from electron micrographs of replicas. Combining this information, estimates were obtained for the diffusion rates of the various polymers (with molecular weights of between 2×10^6 and 2550) in the branched matrix. These diffusion rates vary with the inverse square of the molecular weight of the linear polymer, and are close to the self-diffusion rates expected from the Klein and Briscoe equation.

(Keywords: polyethylene; liquid–liquid phase separation; metastable remixing; diffusion; electron microscopy)

INTRODUCTION

In the course of our recent extensive work on liquid–liquid phase separation (LLPS) in blends of linear polyethylene (LPE) with branched polyethylene (BPE)[1–4], we have come to realize that it is possible to make order-of-magnitude estimates of the diffusion rates of the LPE in the BPE from observations of the morphology of the blends, and we have developed a method to do so. In this paper we introduce this technique for estimating diffusion rates in these systems. The method, described here for blends of LPE and BPE, could be applied to other blend systems. It involves studying the morphology of the blends prepared under conditions where we have established previously that the two blend components are in the process of mixing in the melt. The two components can be easily distinguished by transmission electron microscopy (TEM) when crystalline. Thus, with a knowledge of the remixing time, it is possible to obtain an estimate of the diffusion constant for the system under study by simple examination of the TEM images after crystallization.

In order to aid the understanding of this work, we shall begin by summarizing some of the salient features of our previous work[1–4]. We have found effects that we have only been able to explain by supposing that for those systems which we have studied there is a region of liquid–liquid phase separation (LLPS) in the melt. In these systems the LLPS regions are found at compositions where the LPE content is quite low (i.e. at high BPE content). In all the blends showing LLPS there is evidence that the LLPS region is a closed loop (e.g. ref. 2 figure 5 and ref. 3 figure 10a), but much of the lower-temperature part cannot be reached due to the onset of crystallization. We have proposed tentative 'phase diagrams' for the seven systems we have studied (e.g. ref. 3 figure 9 and ref. 4 figure 9); a generalized 'phase diagram', showing the features present in all the systems we have studied, is shown here as *Figure 1*. Note that this is not a true, equilibrium phase diagram, but a description of the state in which the system will be found after holding for some time under specified conditions of temperature and blend composition.

We have been able to obtain a very wide range of morphologies from these blends, a small selection of which appear in refs. 1–4. The morphologies are of four basic types, which occur because of differing crystallization processes; these are listed below and illustrated further in this paper, using selected examples from all the systems we have studied.

(1) Single morphology consisting of fine lamellae of one type only, resulting from crystallization on quenching homogeneous blends, e.g. quenching from α in *Figure 1* to give the morphology shown in *Figure 2a*; further illustrations may be found in ref. 1 figure 2, ref. 3 figures 1a, b and 4a, and ref. 4 figures 7a and b.

(2) Double morphology with regions of each of two distinct types of fine lamellar crystals resulting from crystallization on quenching segregated blends, e.g. quenching from β in *Figure 1*, shown here in *Figure 2b*. Further examples may be found in ref. 1 figure 3, ref. 3 figures 1c, 2d and e, and ref. 4 figures 7c and d.

(3) Groups of large, LPE-rich, crystals grown isothermally in a matrix of fine, BPE-rich crystals, which formed on subsequent quenching, e.g. quenching from γ or δ in *Figure 1*. This morphology is illustrated in *Figures 3a* and *3b* in the present paper and ref. 1 figures 4 and 5, ref. 3 figures 3b, 4a and b, and ref. 4 figures 8a and b.

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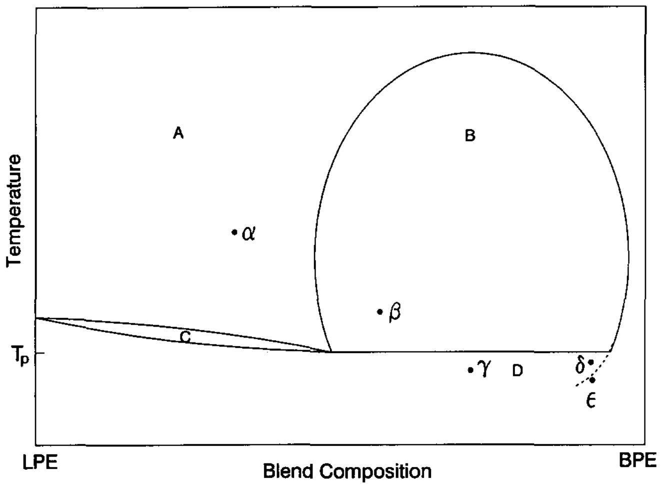

Figure 1 Generalized phase diagram showing the features we have found for LPE/BPE blends. The diagram has four regions: A, mixed melt; B, segregated melt; C, crystal and liquid; D, metastable region into which the melt can be cooled before crystallization. The dotted line (bottom right) is a continuation of the phase boundary between segregated and mixed melts. The points α, β, γ, δ and ε are typical points in the regions A, B, C and D

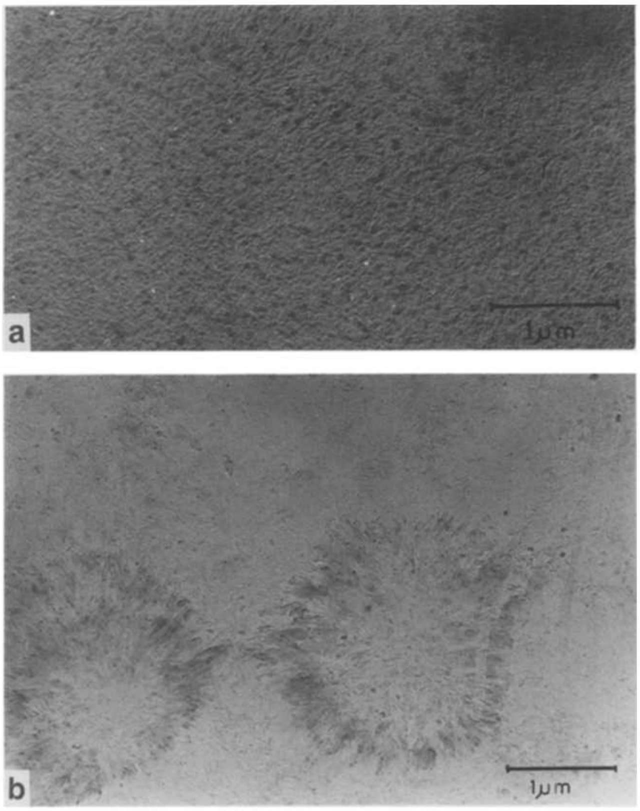

Figure 2 Electron micrographs of surface replicas from quenched blends. (a) 50% blend of DPE with BPE quenched from 150°C (mixed melt). (b) 10% blend of Rigidex 50 with BPE quenched from 150°C (segregated melt)

These morphologies occur on isothermal crystallization from segregated melts, crystallizing at temperatures where LPE-rich material can crystallize but BPE-rich polymer cannot.

(4) Individual large, LPE-rich, lamellae scattered randomly in a matrix of quenched BPE-rich crystals, e.g. quenching from ε in *Figure 1*, shown in *Figures 4a* and *4b* in the present paper. Further examples may be found in ref. 1 figure 6, and ref. 4 figures 8c and d. These morphologies occur on crystallization from mixed melts, crystallizing at temperatures where LPE-rich material can crystallize but BPE-rich polymer cannot.

Most of the work described in this present paper deals with the metastable region, which is found below the temperature at which the LLPS curve intersects the liquidus–solidus curve (region D in *Figure 1*). In this region the melt is metastable; it is only possible to obtain data on LLPS in this region because the slow crystallization of the LPE-rich polymer enables high supercoolings to be achieved.

Measurement of diffusion rates in blends

In most of the LPE/BPE blend systems we have studied it is possible to find blend compositions such that isothermal crystallization at one temperature gives regions of LPE-rich crystals grouped together (these are characteristic of crystallization from a segregated melt — crystallization from point δ on *Figure 1* would give this morphology); while crystallization at a lower temperature gives isolated, individual, LPE-rich crystals characteristic of crystallization from a mixed melt

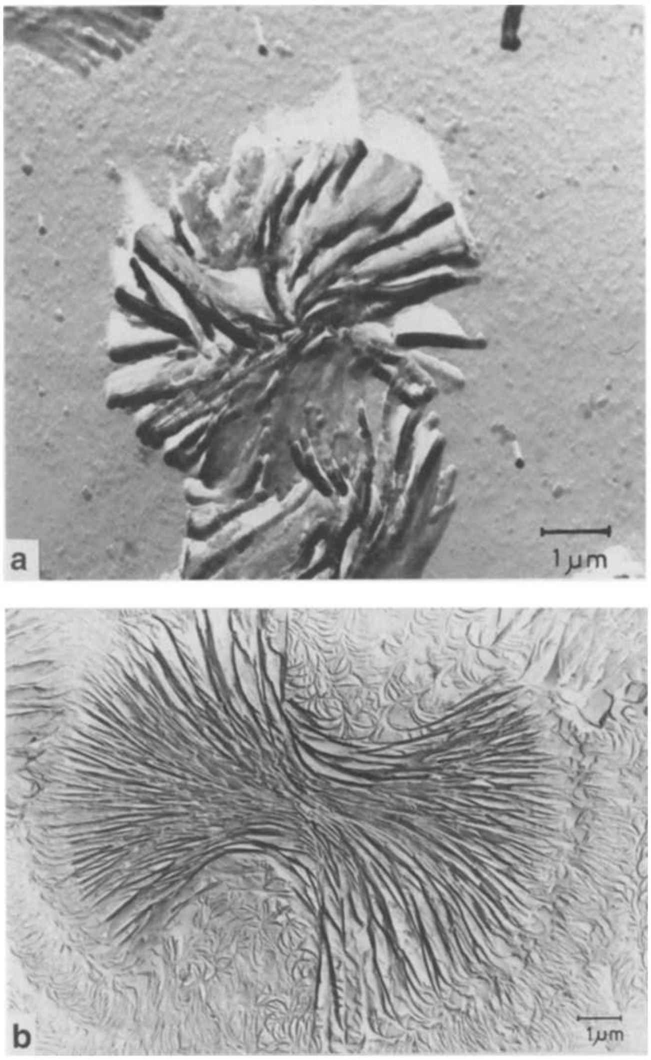

Figure 3 Electron micrographs of surface replicas from blends crystallized isothermally from segregated melts. (a) 1% blend of Rigidex 50 with BPE crystallized isothermally at 126°C. (b) 20% blend of Sclair 2907 with BPE crystallized isothermally at 126°C for 2 h before quenching

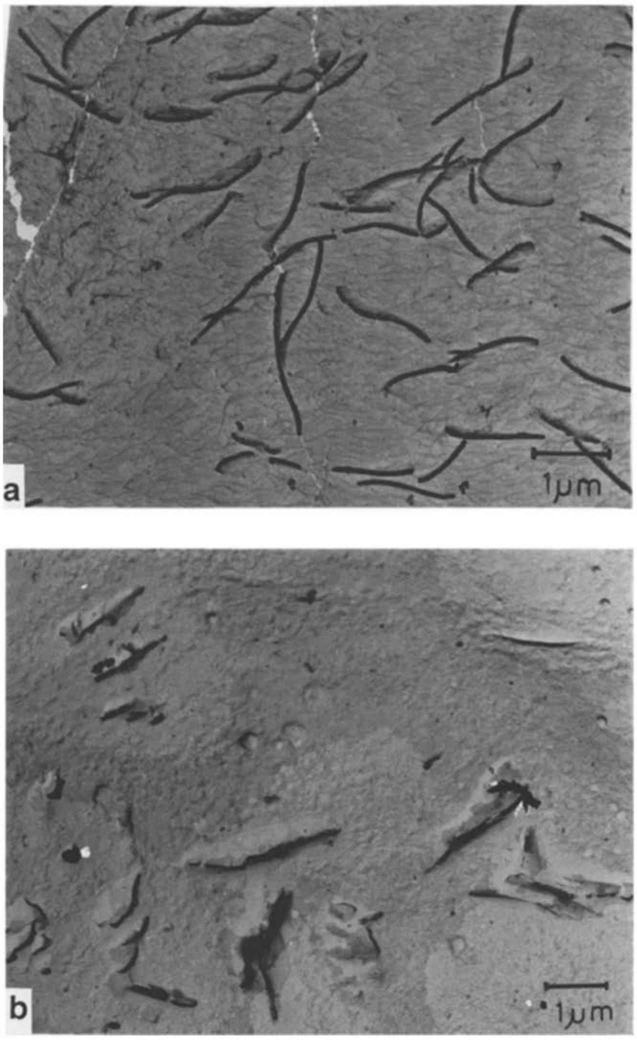

Figure 4 Electron micrographs of surface replicas from blends crystallized isothermally from mixed melts. (a) 1% blend of fraction 15000 with BPE crystallized isothermally at 117°C. (b) 1% blend of Hizex 240 with BPE crystallized isothermally at 126°C

(crystallization from point ε on *Figure 1*). It is in these cases that we can see diffusion effects.

For example, consider an experiment where the system is first allowed to equilibrate at δ (in a segregated state), after which the temperature is lowered from δ to ε. On passing into the mixed melt region (below the dashed line in *Figure 1*) the two components of the biphasic blend will begin to mix even as crystallization takes place. Rather loose groups of crystals will result. Some typical examples are shown in *Figure 5*. The 'looseness' of these crystal groups is apparent when we compare blends crystallized in the biphasic region (δ), *Figure 3*, with blends crystallized during remixing. *Figure 3a* shows the same blend as *Figure 5c* but was crystallized from the segregated region (δ). We are able to measure, from such micrographs, the distances over which the LPE-rich polymer has diffused and, from separate d.s.c. studies, we can estimate the upper limit of the time taken to diffuse that distance. By combining these two measurements, we can estimate the diffusion rates.

This morphological method provides a simple and direct way of observing diffusion in suitable polymer systems. The overall picture that emerges is that all the LPEs we have studied show similar diffusion effects when blended with our BPE (BP PN 220), but that the diffusion rates increase as the molecular weight of the LPE decreases. It has been argued that diffusion is difficult for branched polymers[5] in which case the LPE would be the main diffusing species in these LPE/BPE blends. We cannot support or deny this, but we do find that the distances diffused by the LPE molecules in the time available before crystallization are roughly in line with the simplest self-diffusion models. Even the highest-molecular-weight LPE that we have studied is able to change from a segregated to a mixed state prior to crystallization, given favourable conditions of composition and temperature. This material is relatively slow to crystallize, which allows time for diffusion, even at the slow diffusion rate observed (and expected) for this high molecular weight.

There is one further interesting aspect of diffusion, which can be seen in blends containing the lowest-molecular-weight LPE. Here we have no evidence of LLPS in the melt from either d.s.c., TEM of samples quenched into acetone at its freezing point[4] or melt rheology[6]. However, some micrographs obtained from blends with low LPE content do show unexpected grouping together of lamellar crystals. We will show below that this could be a result of the rapid diffusion rate in this material of very low molecular weight.

EXPERIMENTAL

The blend materials are listed in *Table 1*, where the molecular weights and, where relevant, branch contents are shown. The values are those provided by the manufacturers. The polymers were blended in solution, as described in ref. 1, where we showed that full blending can be achieved.

When crystallization was for a short period only, the polymer was placed between the thinnest possible cover slips wrapped in metal foil, melted and then held in a constant-temperature oil bath for the required time before quenching into acetone at its freezing point. Samples requiring long crystallization times were put into glass tubes, which were evacuated of air and refilled with argon before being sealed. The polymer was then melted and crystallized in the oil bath, as described above.

After crystallization, several 3 mg samples were removed for d.s.c. analysis. For the d.s.c. work we used a Perkin–Elmer DSC2 instrument, heating the samples at 10°C min^{-1}. A replica was made from the remaining material, using permanganic etching prior to replication[7]; we used a one-stage replication technique[8]. The replicas were examined in a Philips 301 transmission electron microscope.

Table 1

Polymer type	Polymer name	Molecular weight (weight-average)	M_w/M_n
LPE	Hizex 240	2×10^6	?
	Sclair 2907	10^5	3
	Rigidex 50	7×10^4	7
	Fraction 15000	1.5×10^4	1.4
	Polymer Labs 2155	2550	1.1
DPE[a]	MSD MD-775	2×10^5	2.2
BPE	BP PN 220[b]	2×10^5	8

[a] Deuterated linear polyethylene

[b] PN220 has 16 'short' and 10 'long' branches per thousand carbon atoms

RESULTS

D.s.c. traces

We have argued in our previous publications (e.g. refs. 1, 3 and 4) that melt remixing can be shown by d.s.c. Examples are to be seen in ref. 1 figure 7 (2907/220) and ref. 4 figure 3 (Hizex/220); we show here a further example of melt remixing, this time in the 15000/220 system (*Figure 6*). Several samples of the 1% blend were melted in d.s.c. pans in an oil bath at 150°C. Quenching after half an hour led to a trace with double peaks on remelting (*Figure 6* '0 min' trace). We argue that the presence of two melting peaks indicates that the melt was segregated at 150°C. Half the remaining blend samples were transferred rapidly, while still molten, to a second oil bath at 117°C. A sample quenched after 5 min at 117°C showed double peaks on remelting (*Figure 6* '5 min' trace) but with the higher melting peak shifted to lower temperature and decreased in size. On further storage at 117°C the higher peak further decreased and after 15 min had vanished completely (*Figure 6* '15 min' trace). We argue that the disappearance of this melting peak occurs because the originally biphasic melt has remixed. After 45 min of storage at 117°C a new, differently shaped, high melting peak appeared, which increased in relative size with time over some hours (*Figure 6* '2 h' and '20 h'). This new peak we attribute to the melting of LPE-rich material that had crystallized isothermally at 117°C. On repeating the experiment for isothermal crystallization at 122°C no sign of melt remixing was seen, as shown in *Figure 7*. The peak due to isothermal crystallization appeared after an hour and grew at the expense of the higher of the melting peaks due to material crystallized on quenching. (Further discussion of such experiments, including a consideration of annealing effects, is to be found in ref. 9.)

From experiments of this type we can estimate the time that the blend spends in the melt before crystallization occurs and the time it takes to remix. We do not wish to discuss the remixing times here in any detail. The mixing time depends on a number of factors in combination, of which we have identified three:

(1) The polymers themselves; as we shall show, the molecular weights influence the diffusion times.

(2) The temperature relative to the phase boundary. Mixing is slower very near the coexistence curve[9].

(3) The time for which the blend was held in the segregated melt. We have found (by TEM) indications that the sizes of the segregated regions build up with time (with a corresponding decrease in the number of segregated regions)[10]. LPE-rich material will obviously take longer to disperse completely (by diffusion) to produce a fully mixed melt where the segregated regions are very large.

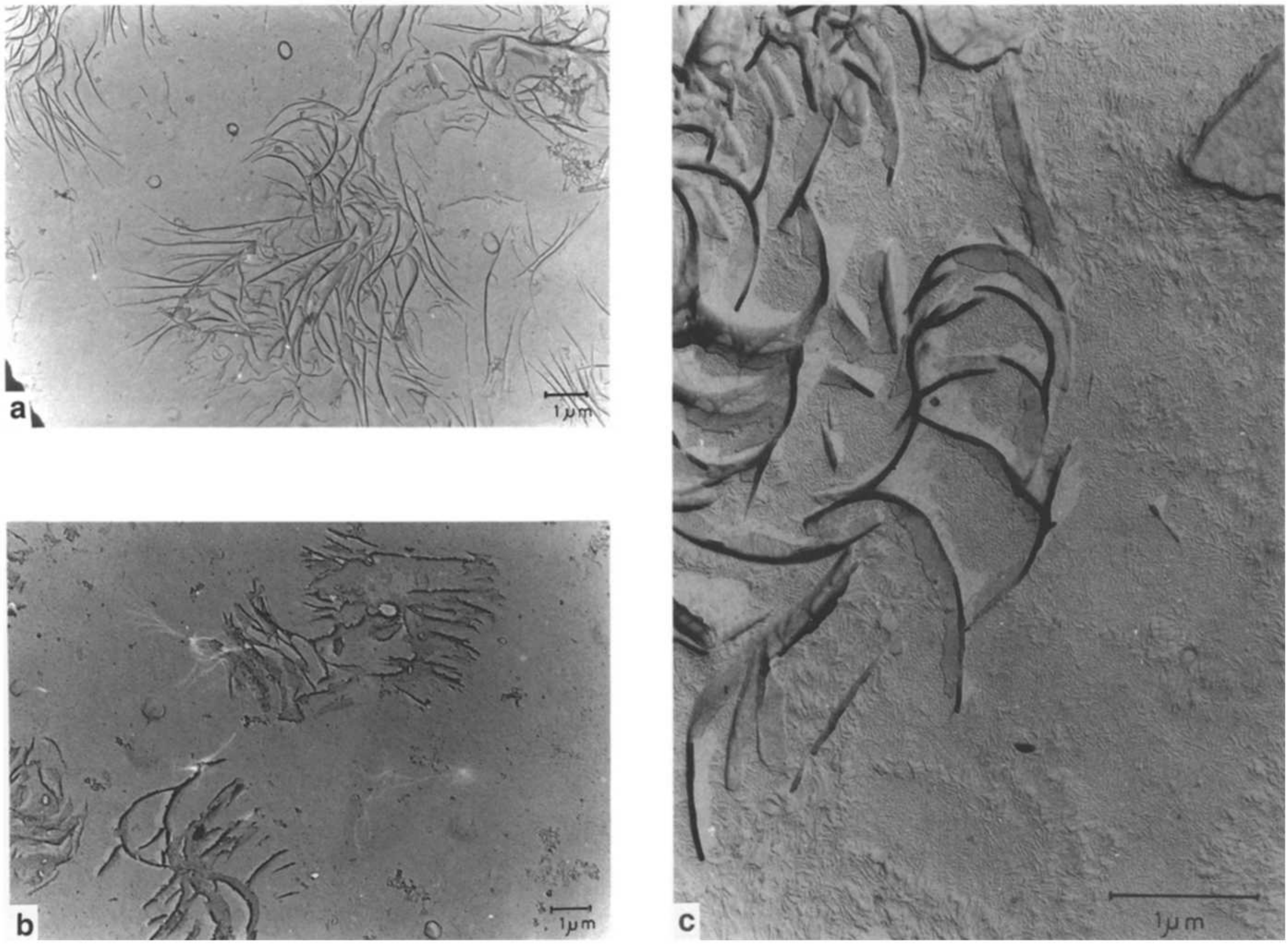

Figure 5 Electron micrographs of surface replicas from blends crystallized isothermally from melts that mixed as they crystallized. (a) 5% blend of fraction 15 000 with BPE crystallized isothermally at 118°C. (b) 2.5% blend of DPE with BPE crystallized isothermally at 117°C. (c) 1% blend of Rigidex 50 with BPE crystallized isothermally at 122°C

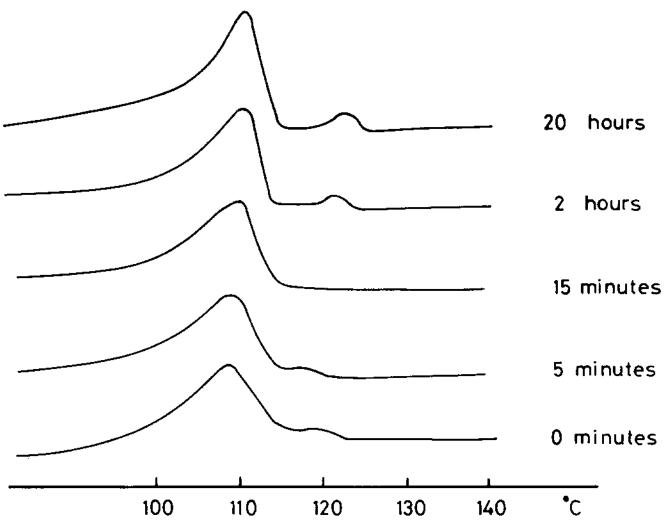

Figure 6 D.s.c. traces obtained on heating 1% blends of fraction 15000 with BPE at 10°C min^{-1}. The samples had been held at 150°C for 30 min and then quenched to 117°C and held there for the times indicated before further quenching into acetone at freezing point

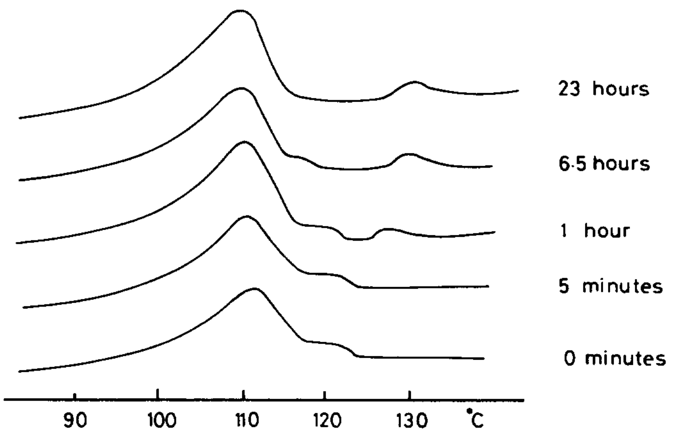

Figure 7 D.s.c. traces obtained from samples prepared as for *Figure 6*, but with the intermediate quench temperature at 122°C

The full study of remixing times is a large and complex one, which we have not carried out in detail. However, remixing times can be assessed for individual cases, and can be used to check if the observed diffusion rates are reasonable.

Electron microscopy

In *Figures 3* to *5* we present several electron micrographs showing the very different morphologies obtained on crystallizing from segregated and mixed melts respectively. We shall now discuss these in more detail. *Figure 3a* shows a replica obtained from a blend of 1% Rigidex 50 (R50) with 99% BPE (for details of the R50 see *Table 1*: the only BPE used in this study was BP PN 220). The segregated state of the melt on crystallization is clear from the way in which the isothermally crystallized LPE-rich crystals are grouped together in approximately spherical domains. *Figure 3b* shows a particularly striking morphology obtained from crystallizing a blend of 20% Sclair 2907 with 80% BPE for 2 h at 126°C (note that we term a blend containing 20% LPE and 80% BPE a '20% blend'). It has been shown by d.s.c. that in this 20% blend the LPE-rich material was not fully crystallized after 2 h; the elegant curling and tapering ends to the LPE-rich crystals crystallized on quenching[10].

Morphologies obtained on crystallizing the LPE-rich material from mixed melts can be seen in *Figure 4*. *Figure 4a* shows a replica of a 1% blend made from a fraction (15000 molecular weight) of R50 with BPE, crystallized for 3 h at 117°C. We know, from d.s.c. (*Figure 6*), that the melt was mixed prior to crystallization. The LPE-rich lamellae are randomly dispersed in the quenched BPE-rich matrix. In *Figure 4b* we show a replica of a 1% blend of Hizex 240 held at 126°C for a week before quenching. Again, the LPE-rich crystals are well dispersed, showing, as is confirmed by d.s.c.[10], that the LPE-rich polymer crystallized from a mixed melt.

We believe that the LLPS region is a closed loop (ref. 2 figure 5). We have found this region to be at its widest (in composition) at, or just above, the temperature (T_p) at which the LLPS intersects the liquidus/solidus coexistence curve (see ref. 4 figure 10). This means that melt mixing is most likely to be seen, prior to crystallization, at concentrations near to the LLPS boundary and at temperatures just below T_p. Because crystallization is slower for a blend of low LPE content than for a blend of high LPE content crystallizing at the same temperature, the best chance of observing melt remixing will occur on the lower LPE content side of the loop where the melt will have longer to mix before crystallization sets in. Owing to the asymmetry of the loop with respect to composition, the very lowest LPE content blends will be optimum, and these blends have the further advantage that crystallization from mixed melts is more easily detected where there are relatively few LPE-rich crystals.

In some cases we can see blends that seem to be 'caught in the act' of mixing when crystallization takes place. Three of these are shown in *Figure 5*; *Figure 5a* shows a blend of 5% LPE fraction, molecular weight 15000, with BPE, crystallized at 118°C; *Figure 5c* shows a 1% blend of R50 with BPE crystallized at 122°C; and *Figure 5b* a 2.5% blend of DPE with BPE. In all three cases (and there are others for the other LPE/BPE systems) the loose, apparently disintegrating groups of LPE-rich crystals indicate that crystallization took place before mixing was complete.

Diffusion rate estimates

The 1% R50/BPE blends give domains of crystals when crystallized at 126°C (*Figure 3a*) but when a similar blend is crystallized at 122°C the crystals are seen to be much less tightly grouped (*Figure 5c*) and we deduce that the melt is remixing as it crystallizes. We know, from separate d.s.c. measurements, the time taken both for mixing and for crystallization to set in. We can estimate, from the micrographs, the distance that the LPE-rich polymer in outlying lamellae has diffused from the original LPE-rich regions prior to crystallization.

Diffusion theory tells us that for self-diffusion (i.e. for a molecule diffusing in melt of similar material)[11]:

$$x^2 = 2D\Delta t \qquad \text{and} \qquad D = 14 \times 10^{-6} M^{-2}$$

where x is the mean diffusion length, D the diffusion rate, Δt the diffusion time and M the molecular weight. (Here we use the equation given by Klein and Briscoe; other measurements indicate that the diffusion constant may be a factor of 2 higher[12], if so x would be changed by the square root of 2.)

Table 2

Polymer	Molecular weight (weight-average)	'Mixing time' from d.s.c.	Calculated diffusion length (μm)	Measured diffusion length (μm)	Calculated time to diffuse 1 μm
Hizex	2×10^6	1–3 h (1% at 118°C)	0.2–0.3	0.5	40 h
		7–12 h (1% at 126°C)	0.4–0.6	1.0	
Sclair 2907	10^5	30 min (1% at 122°C)	2.0	2–3	6 min
Rigidex 50	7×10^4	45 min (1% at 122°C)	4.0	5.0	3 min
Fraction 15 000	1.5×10^4	25 min (1% at 117°C)	14	Homogeneous (several μm)	8 s
PL 2155	2550	Melt always mixed	N/A	N/A	0.2 s
DPE	2×10^5	30 min (2.5% at 118°C)	1.0	1–2	24 min

Putting the known molecular weight of the LPE into the self-diffusion equations, we find that in the 45 min before crystallization takes place the R50 molecules should be able to diffuse about 4 μm. The positions of outlying lamellae observed on the micrographs (see *Figure 5c* and ref. 4 figure 8f) indicate that the LPE has diffused a distance of about 5 μm, slightly further than expected.

Measured diffusion distances are compared with those predicted on this most simple model in *Table 2*. The measured diffusion distances quoted in *Table 2* were estimated by comparing the mean sizes of the expanded groups of LPE-rich lamellae in micrographs, such as those in *Figure 5*, with the original sizes of the LPE-rich crystal groups, such as those shown in *Figure 3*.

Where the molecular weight is higher the diffusion rate is reduced since D is proportional to M^{-2}. The LPE with the highest molecular weight among those we have studied is Hizex 240. We know from d.s.c. that the 1% blends slowly cooled from the melt and then crystallized at 118°C had about 1.5 h in which the melt could mix before the structure was frozen in by crystallization. In that time a diffusion of 0.3 μm could be expected, which is slightly less than the observed separation (0.5 μm, see *Table 2*). A larger separation is found on crystallizing 1% Hizex blends at 126°C — at this temperature the 1% composition melt is known to be mixed. There is considerable time for diffusion; 7 h elapse before crystallization of the LPE-rich polymer can be detected by d.s.c. and 12 h before quenched, segregated LPE-rich material is no longer visible in the d.s.c. trace[10].

The diffusion rate that we are measuring is not, strictly, that given by the equation above, which is applicable to a polymer molecule diffusing in its own melt. Our measurements are from diffusion of one species, LPE, in a matrix of a mixture of LPE and BPE, and hence do not strictly correspond to self-diffusion. In the case of diffusion in blends the situation is obviously more complicated; in particular, the role of the χ parameter becomes important[13,14]. However, in this simple system we believe the χ parameter to be very small, since the two polymers are very similar. A simple model that allows us to explain the phase separation with such a small χ parameter is to be published soon[15]. Here we only wish to demonstrate that our morphological TEM method gives an order-of-magnitude estimate of the diffusion constant. Although the system is not strictly at equilibrium, provided χ is small enough, the diffusion rate we estimate will approximate to that for self-diffusion. In the real, experimental situation, we have the more complicated case of diffusion of a polymer into a melt of changing composition and there is the further possibility that the BPE is restricted by the branches, and unable to diffuse[5]. We note that the product MD^2 should be independent of the molecular weight; in fact we find a value for this constant of $(1.4\pm0.3)\times10^{-5}$ for all our blends except those containing the Hizex, which give a somewhat higher value. Bearing all these uncertainties in mind it is, perhaps, surprising that we obtain such good agreement with the simple model.

Anomalous effects in (low-molecular-weight LPE)/BPE blends due to rapid diffusion

Polymers of low molecular weight can diffuse very rapidly; the estimated times for LPEs of various molecular weights to diffuse 1 μm are shown in *Table 2*. We believe that a rapid diffusion rate can lead to apparent segregation from mixed melts as a result of diffusion.

The evidence that we have from d.s.c., from TEM of quenched melts[4] and from rheology[6] indicates that the very low-molecular-weight LPE 2155 blended with BPE in all proportions gives mixed melts at all temperatures; we have never detected a segregated 2155/BPE melt. On the other hand, we have recently found that when blends of low LPE content are allowed to crystallize during slow cooling from the melt, the crystals do not appear randomly distributed, as would be expected, but are loosely grouped together, as shown in *Figure 8*.

As LPE-rich polymer crystallizes (at concentrations shown by the 'phase diagram' for the 2155/BPE system in figure 10 of ref. 4), local inhomogeneities will arise as LPE is removed from the melt, which will, consequently, become locally BPE rich around the LPE-rich crystals. LPE will diffuse in from the non-depleted melt to restore homogeneity. It is to be expected from the molecular weight of the 2155 that diffusion can be very rapid, certainly fast enough to compensate for the local

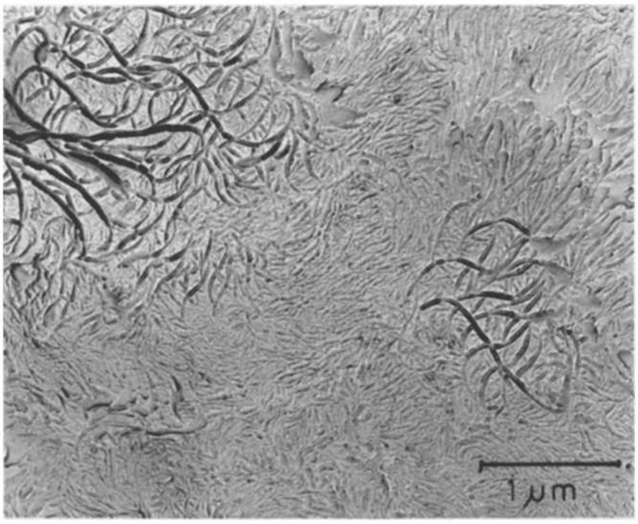

Figure 8 Electron micrograph of a surface replica from a blend of low molecular weight LPE (2155) with BPE. The blend had crystallized during slow cooling (cooling rate about 1°C $\rm min^{-1}$)

depletion of LPE due to crystallization. Where (LPE-rich) crystals are already present, these will provide nucleation sites for further crystal growth. Hence although the melt will maintain homogeneity, the blend sample as a whole (melt and crystal together) will not be homogeneous, but LPE will build up around those places where the first crystals grew. Thus loose clusters of LPE-rich lamellae are able to crystallize from mixed melts owing to the combined effects of availability of nucleation sites and rapid diffusion rate. In other blends, where the diffusion rate is slower, new LPE will not be in constant supply so that the growth of individual crystals will progressively slow down as the LPE in the nearby melt is exhausted.

CONCLUSIONS

A variety of morphologies have been obtained in LPE/BPE blends, the morphology depending on blend composition and temperature of crystallization. Previous work has shown how the behaviour observed can be described by phase diagrams, of which *Figure 1* is a typical example. We have shown, in this paper, examples of blends crystallized from both segregated and mixed melts in the metastable region shown on the phase diagram, below the temperature at which the LLPS loop intersects the liquidus/solidus curve ($T_{\rm p}$). Here, morphologies can be obtained that are characteristic of crystallization from either mixed or segregated melts. The former occur when crystallization is so slow that melt remixing (as indicated by the closed loop form of LLPS) is able to take place prior to crystallization. Conditions are particularly favourable where the concentration of LPE in the blend is low. It is even possible to observe remixing in blends of our highest-molecular-weight LPE (Hizex 240) because the very long time needed to crystallize LPE-rich material from this system allows appreciable diffusion, despite the low diffusion rate of the long molecules.

Where segregated melts have remixed prior to crystallization it is possible to make an estimate of the diffusion rates of the LPE from the experimental results, combining TEM with d.s.c., and to check them against diffusion theory. We find that for LPEs of molecular weight 15 000 and above, diffusion distances are of the order of magnitude of those expected from the molecular weight of the LPE alone. We realize that the rigorous theoretical treatment of diffusion will be very complex in a binary system where the two polymer components have differing molecular weight and one is a minority phase in the other; however, we are not attempting to argue in any detail here, merely to indicate that the diffusion times are of the order of magnitude that would be expected by the simplest possible treatment and thus to demonstrate this simple TEM method of estimating diffusion rates.

When any blend is slowly cooled from a mixed melt, crystallization of LPE-rich material leads to local inhomogeneities in melt composition. In the case of blends of the very low-molecular-weight LPE 2155 with BPE, rapid diffusion of 2155 molecules allows restoration of the homogeneity of the melt, so that the LPE-rich crystals continue to grow and branch. As a result, the sample as a whole (melt and crystal together) becomes locally rich in LPE and domains of crystals grouped together are observed, even though the original melt was fully mixed.

Thus, where the melt is in a metastable, supercooled state, diffusion effects often allow remixing before crystallization and so give rise to homogeneous distributions of LPE-rich crystals. On the other hand the grouping together of crystals can take place where the melt is mixed but the diffusion rate is very fast indeed. In each case the relative crystallization and diffusion rates determine the morphology that is observed.

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