Liquid–liquid phase segregation in blends of a linear polyethylene with a series of octene copolymers of differing branch content

M. J. Hill* and P. J. Barham
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

and J. van Ruiten
DSM Research PAC-CM, PO Box 18, 6160 MD Geleen, The Netherlands

A linear polyethylene (LPE) has been blended with a series of random ethylene–octene copolymers of differing octene content. Melts of blends containing the lowest octene contents (2, 3, 5 and 8 mol%) showed liquid–liquid phase separation at some temperatures and for some compositions. The phase-separated regions were in the shape of closed loops and asymmetrically placed at low LPE content. This behaviour has been found previously for LPE/branched PE blends. However, unexpectedly, the phase-separated loops became smaller as the octene content of the copolymer increased. Blends of LPE with a 12 mol% octene copolymer showed extensive separation and rather different morphologies.

(Keywords: phase separation; polyethylene; copolymers)

INTRODUCTION

In the course of recent, extensive work on blends of linear polyethylene (LPE) with branched polyethylene (BPE)[1–6], we have established that liquid–liquid phase separation (LLPS) can take place for blends of certain compositions held at particular temperatures. During the course of our studies, we blended one particular BPE (BP PN 220) with 6 LPEs of different molecular weight (MW), and one of the LPEs (Sclair 2907) with a second BPE[3,4]. We have found LLPS regions, always in the form of closed loops, in all blend systems except where the LPE was of very low MW (about 2500). The LLPS region varied in size, being larger when the LPE blended with PN 220 was of higher MW, but in every case the LLPS loop was found to be asymmetrically placed: LLPS always occurred where the LPE content of the blend was low. *Figure 1* shows a generalized phase diagram, indicating the salient features.

For some time we have wished to investigate the effect of the branch content of BPE on the phase diagram. However, we have not had suitable, randomly branched BPEs to work with. We have found that many commercial BPEs are bimodal in branch distribution, so that a ternary phase diagram is required to describe the behaviour when they are blended with an LPE; ref. 4 gives an example of this. Recently a series of octene copolymers has been made by DSM, with roughly equal MW but with differing branch content. In this paper we report the phase diagrams that we have obtained by

blending the same LPE with each of five 1-octene copolymers of differing branch content.

As for the previous systems we find LLPS in closed loop form and at low LPE content. However, the way in which the size of the loops varies with copolymer branching is entirely counter-intuitive. Where the molecular weights of the polymers are roughly equal, *the size of the LLPS region becomes smaller as the number of octene branches increases* from 2 to 8 mol% octene. The copolymer with 12 mol% octene, however, shows much more extensive LLPS when blended with the standard LPE.

The description of these new phase diagrams forms the basis of this paper. We have developed a tentative model to account for many of the features observed; however, this is not included here but is described separately in another paper[7].

EXPERIMENTAL

Homogeneous ethylene–1-octene copolymers with variation in 1-octene content and molar mass were obtained by polymerization with a (promoted) catalyst system[8], consisting of $VOCl_3$ and $Et_3Al_2Cl_3$. The 1-octene content was measured with FTi.r. and ^{13}C n.m.r. Gel permeation chromatography was used to measure M_n and M_w. Details of molecular weight and branch content of all the copolymers are listed in *Table 1*. Note that the copolymer with 2 mol% octene content is termed O(2), etc.

The experimental methods are those found to be successful in our previous studies of LLPS in blends of
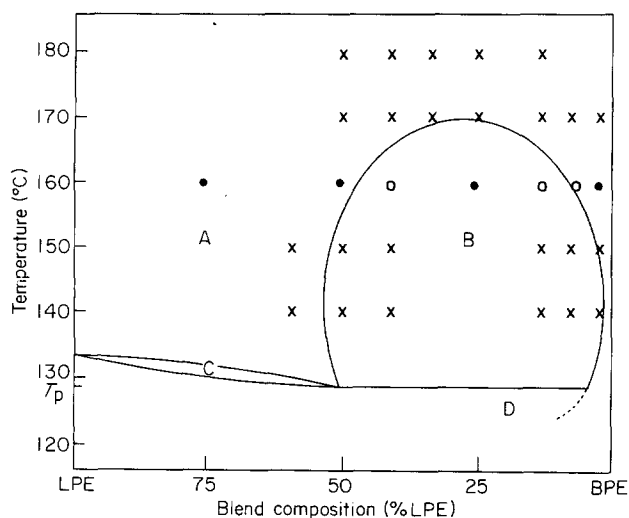
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*To whom correspondence should be addressed

Figure 1 Schematic phase diagram, showing the shape of LLPS loops found for LPE/BPE blend systems. 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 circles and crosses indicate a typical set of experimental sampling points (see details in the text)

Table 1 Molecular weights of polymers

Polymer	Octene content (mol%)	M_w	M_n
LPE	0	50×10^3	17.9×10^3
O(2)	2.1	51×10^3	23.2×10^3
O(3)	3.0	130×10^3	65.0×10^3
O(5)	5.2	37×10^3	18.5×10^3
O(8)	8.0	43×10^3	21.5×10^3
O(12)	11.8	46×10^3	23.0×10^3

LPEs with BPEs; details can be found in references 1–6, especially 1, 3 and 5. Here we will merely outline the methods and stress certain points of particular importance to this work.

The blends were all made by coprecipitation of the LPE and BPE from dilute solution in xylene by quenching into cold acetone. We have shown that this gives well-mixed blends[1,4].

The experimental methods routinely used for investigating our blends are d.s.c. of quenched samples and TEM, using surface replicas of quenched, and some isothermally crystallized, samples. We would stress that the components of our blends are very similar indeed, so that we have had to devise some special methods of investigation, of which the surface replica method has been particularly useful[5].

The chief aim of this work was to plot phase diagrams and, in particular, to look for LLPS loops. On initial investigation of a blend system, 75, 50, 25 and 1% blends were made (the percentage figure referring to the mass percentage LPE content of the blend, e.g. a 25% blend contains 25 wt% LPE). Samples (3 mg) of each blend were held at 160°C for 30 min before quenching into acetone at freezing point. These samples were heated at 10°C min^{-1} in a DSC 7. Surface replicas were also made of each blend quenched from 160°C. These initial points are indicated as solid circles on *Figure 1*.

Study of the d.s.c. traces and replicas (see below) indicated whether each melt was mixed or segregated at

160°C. Thus, from this preliminary investigation the extent of the LLPS loop at 160°C could be determined between certain limits. Further blends were then made to find the phase boundary at 160°C more precisely (open circles on *Figure 1*).

The final step in locating the LLPS loop was to determine the height (in temperature) of the LLPS region. This was done using surface replicas of very rapidly quenched samples[5]. Samples of chosen concentrations were quenched from temperatures differing by 10°C, to form a grid of sampling points (crosses on *Figure 1*). From these replicas the boundaries of the LLPS region could be determined, the blend being known to be either mixed or segregated at each grid point. Many replicas were made for each blend system; the LLPS loops shown later in *Figures 4A* and *B* were determined using between 25 and 36 replicas each.

The highest crystallization temperature of the LPE was found by investigating the d.s.c. traces of samples quenched after holding for several weeks at temperatures in the range 130–132°C; samples were held in sealed tubes under argon to prevent degradation. For each system the highest temperature at which any component of the 1% blend would crystallize isothermally (marked T_p in *Figure 1*) was determined by a similar method. Replicas of 1% blends crystallized isothermally at 127, 124 and 121°C were made for each blend system and used to determine the extent of LLPS at these compositions and temperatures.

RESULTS

We have long argued, and more recently shown by assessing diffusion rates in blends[6], that large-scale segregation takes some time to become apparent; if two crystal populations, separated on a scale of micrometres, are seen after quenching they must have come from two, distinct melt phases. Thus we can understand the state of the melt, prior to rapid quenching, from careful study of the quenched, crystalline material. As established previously[1,3], a single d.s.c. peak may be interpreted as being due to a single crystal population obtained from quenching a mixed melt, and double d.s.c. peaks are interpreted as being due to two crystal populations, obtained from quenching a segregated melt. So, from d.s.c., we are able to ascertain whether the melt was mixed or segregated at each of the initial points, marked by solid circles in *Figure 1*. In all our previous work we have found that, for prequench temperatures of 165°C and below, surface replicas of material quenched from the same points confirmed the d.s.c. results — crystals of two thicknesses were found wherever there were double d.s.c. peaks and a single morphology where there was only one d.s.c. peak. Note that it is important to take *surface* replicas since the interior of the (quite thick) samples required for replica making are cooled fairly slowly, due to the very poor heat transfer in PE samples, and segregation during quenching has been shown to take place[5,9]. We have found d.s.c. very reliable when samples are quenched from temperatures up to 35°C above the maximum crystallization temperature, but when quenching over a wider temperature range through the LLPS region, some segregation has been found to take place even on rapid quenching[1,5]. However, surface replicas are found to indicate the state of the melt reliably[5] even after quenching up to 80°C. Hence, using surface
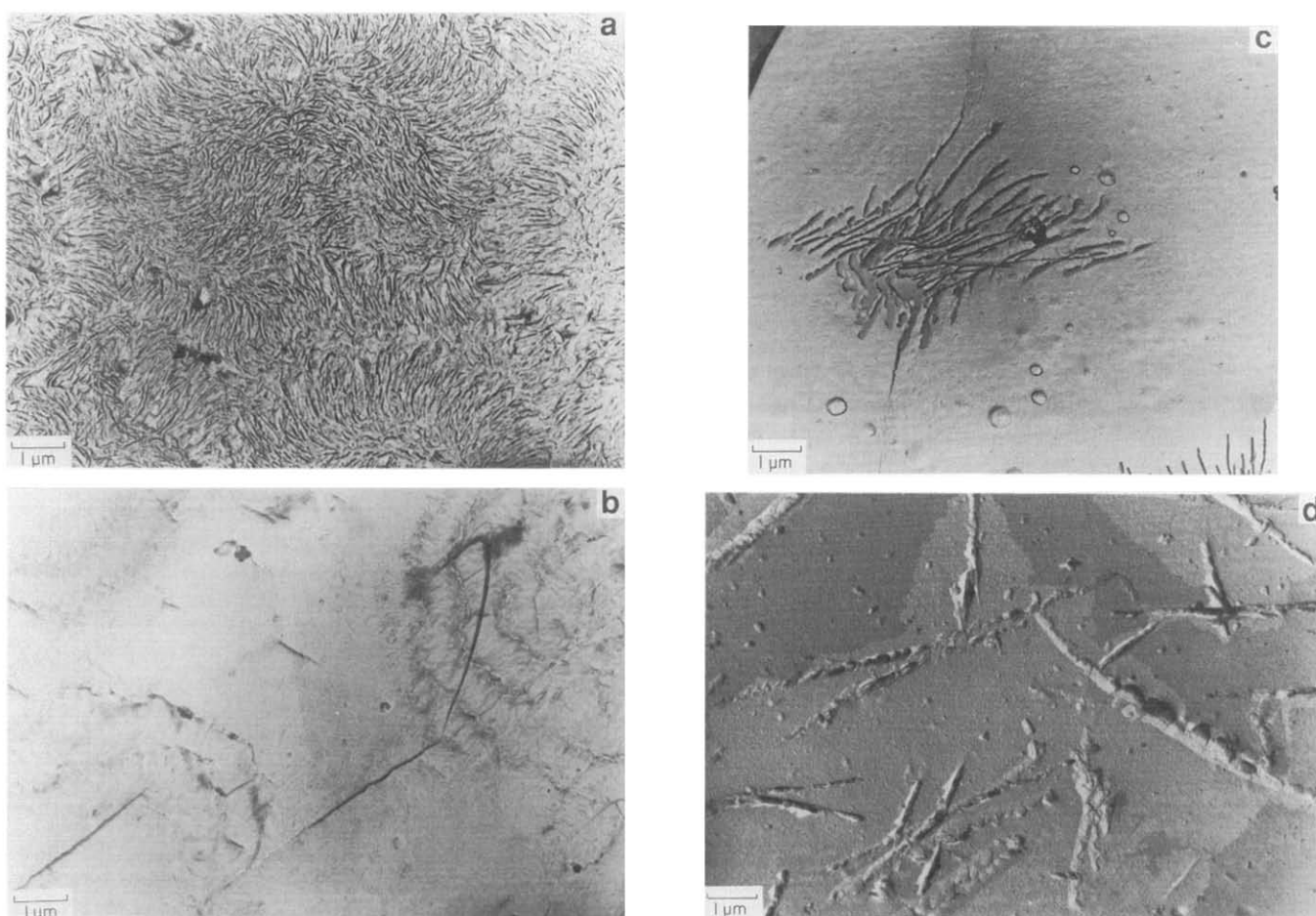
Figure 2 Examples of morphologies found in blends of LPE with the octene copolymers O(2), O(3), O(5) and O(8). All micrographs are of replicas made after permanganic etching. The samples were prepared as follows, before etching: (a) 50% LPE/O(5) blend, quenched into acetone at freezing point from 160°C, i.e. from a mixed melt; (b) 25% LPE/O(2) blend, quenched into acetone at freezing point from 150°C, i.e. from a segregated melt; (c) 1% blend of LPE/O(3) crystallized isothermally at 122°C, i.e. from a segregated melt; (d) 1% blend of LPE/O(8) crystallized isothermally at 122°C, i.e. from a mixed melt

replicas, the points such as those represented by crosses in *Figure 1* can all be determined as mixed or segregated.

For blends of LPE with O(2), O(3), O(5) and O(8) octene copolymers, the d.s.c. results from blends quenched from 160°C and below are, once more, in agreement with the morphologies obtained, double peaks corresponding to replicas showing two crystal morphologies etc. The replicas look very similar to those obtained from our other LPE/BPE systems[1-6]. A few typical examples of replicas of LPE/octene BPE blends from our extensive survey are shown in *Figures 2a–d*, which show, respectively, a blend quenched from a mixed melt, a blend quenched from a segregated melt and two 1% blends crystallized isothermally, one from a segregated melt and one from a mixed melt.

The d.s.c. results from LPE/O(12) blends show at least two peaks (indicating two or more crystal populations) over a wide composition range. However, the morphologies observed by TEM differ from those seen before. In some cases, when the d.s.c. indicates considerable numbers of BPE-rich crystals, two different morphological regions are clearly seen in the replicas. This is shown in *Figure 3a* for the 25% blend quenched from 160°C; a few typical regions of BPE-rich crystals are indicated. From the figure it is clear that the separation of the different crystal populations is on a much more intimate scale than seen previously (e.g. *Figure 2b*). It is thus

evident that the LPE/O(12) blends are rather different from all blends that we have studied previously.

At this stage we cannot be sure if this segregation is due to LLPS in the melt, as in all the other blend systems, or whether the segregation takes place during crystallization. The very fine scale of the segregation seen in the TEM (*Figure 3a*) is quite consistent with a model of segregation during crystallization. However, evidence for LLPS comes from a detailed examination of the d.s.c. traces, examples of which are shown in *Figure 4*. *Figure 4A* shows a trace obtained on reheating a sample of O(12) quenched from 160°C. Note two peaks, one at 32°C and a larger one at 65°C. *Figure 4B* shows a quenched 25% blend; note two peaks in the low-temperature region at 40 and 65°C, with the larger peak at 40°C. This could indicate that some of the higher melting component of the O(12) has cocrystallized with the LPE, thus altering the ratio of the peaks. *Figures 4C–F* show d.s.c. traces obtained on remelting 75% blends quenched from 180 to 140°C. In each case the whole trace is shown (*Figures 4C* and *E*), together with enlargements of the low-temperature region (*Figures 4D* and *F*). The fact that two clear crystal populations are obtained on quenching the 75% blend from 180°C, but only a trace of lower melting material on quenching from 140°C, suggests LLPS of the lower critical temperature (*LCT*) type at above 140°C. However, the evidence is not,
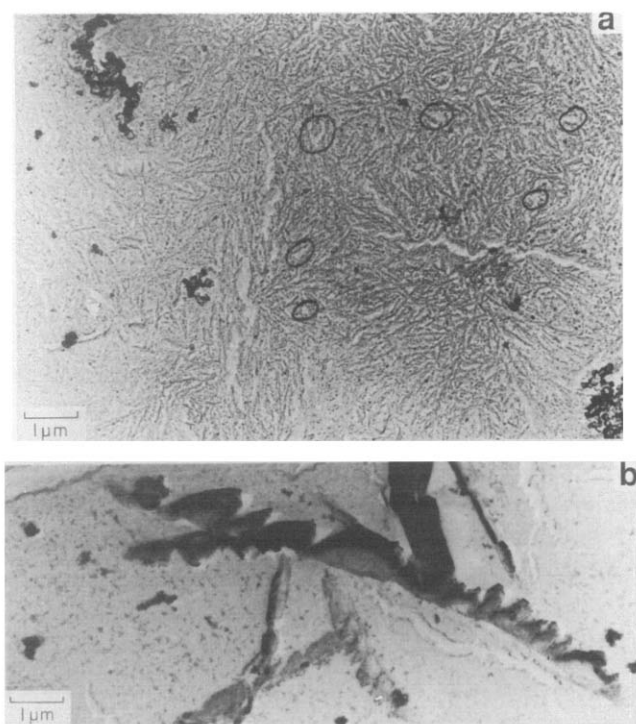
Figure 3 Examples of morphologies found in blends of LPE with the octene copolymer O(12). All micrographs are of replicas made after permanganic etching. The samples were prepared as follows before etching: (a) 25% LPE/O(12) blend, quenched into acetone at freezing point from 160°C. Rings enclose typical examples of small groups of thin crystals; (b) 1% blend of LPE/O(12) crystallized isothermally at 127°C
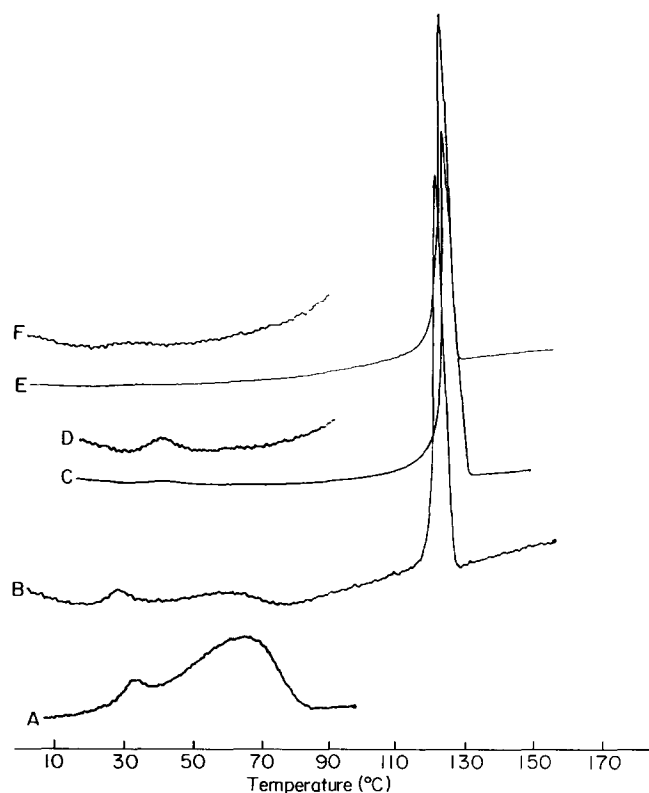

Figure 4 Examples of d.s.c. traces obtained from LPE/O(12) blends quenched from the melt into acetone at freezing point. Heating rate 10°C min⁻¹ in all cases. A, O(12) quenched from 160°C; B, 25% blend quenched from 140°C; C, 75% blend quenched from 180°C; D, 75% blend quenched from 180°C, enlargement of low-temperature region; E, 75% blend quenched from 140°C; F, 75% blend quenched from 140°C, enlargement of low-temperature region

at this stage, strong enough to be certain that there is LLPS in the LPE/O(12) system, although it is quite clear that the LPE/O(12) system is very different from all the others that we have studied.

In our previous work we have found that replicas of 1% blends crystallized isothermally at low temperatures show either grouped LPE-rich crystals (segregated melt) or isolated LPE-rich crystals (mixed melt)[1,3,4,6]. Where the melt remixes at low temperature, with a known upper critical temperature (*UCT*) LLPS region at higher temperature, a closed loop of LLPS is indicated[2–4,6]. Examples of 1% blends crystallizing from both mixed and segregated melts are found in the LPE/octene systems. (Arguments as to how the state of the melt, prior to crystallization, can be deduced from the crystalline morphologies are given in detail in references 1, 3 and, particularly, 6. *Figures 2c* and *3b* show grouped LPE-rich crystals, indicative of crystallization from segregated melts of LPE/octene copolymer blends. *Figure 2d* shows dispersed LPE-rich crystals, indicating crystallization from a segregated melt.) Note that where the BPE has a higher octene content, the LPE-rich crystals appear more ragged after etching. This is typical of these systems. Replicas of isothermally crystallized 1% blends of LPE/O(12) are similar to those from other systems; clear LPE-rich crystals are found, rather ragged in appearance (*Figure 3b*). These crystals are grouped after crystallization at 127°C, but separated after crystallization at lower temperatures. All the results obtained from isothermal crystallization of 1% blends are included in *Table 2*, M indicating that the melt was mixed at the temperature shown (indicated by isolated LPE-rich crystals), and S that the melt was segregated (indicated by grouped LPE-rich crystals). Where closed loops of LLPS are inferred, from observation of both *LCT* and *UCT* behaviour, this is noted.

The highest crystallization temperature for the DSM LPE was found to be between 131 and 132°C (the long-term temperature control of our oil baths did not permit greater accuracy). All the 1% blends (including that of LPE/O(12)) did not crystallize at all if held at 128°C or above, but did crystallize, in part, at 127°C. Thus it seems that the temperature T_p, at which the LLPS region intersects with the liquidus curve, is very similar for all these five systems; it is within 0.5°C of 127.5°C in each case. This is as expected since the liquidus is rather flat and the same LPE is used in each case.

Note that in this work we have concentrated on the extent of the LLPS loop only, and not investigated other features of the phase diagram. The high LPE-content side of the phase diagram has not been explored fully.

Table 2 Results from isothermal crystallization of 1% blends

Blend system	State of melt on isothermal crystallization as judged by morphology of 1% blend[a]			Loop present?
	127°C	124°C	121°C	
LPE/O(2)	S	S	(S)	Probably
LPE/O(3)	S	S	M	Yes
LPE/O(5)	M	M	M	Yes
LPE/O(8)	S	S	M	Yes
LPE/O(12)	S	M	M	Only LCT observed

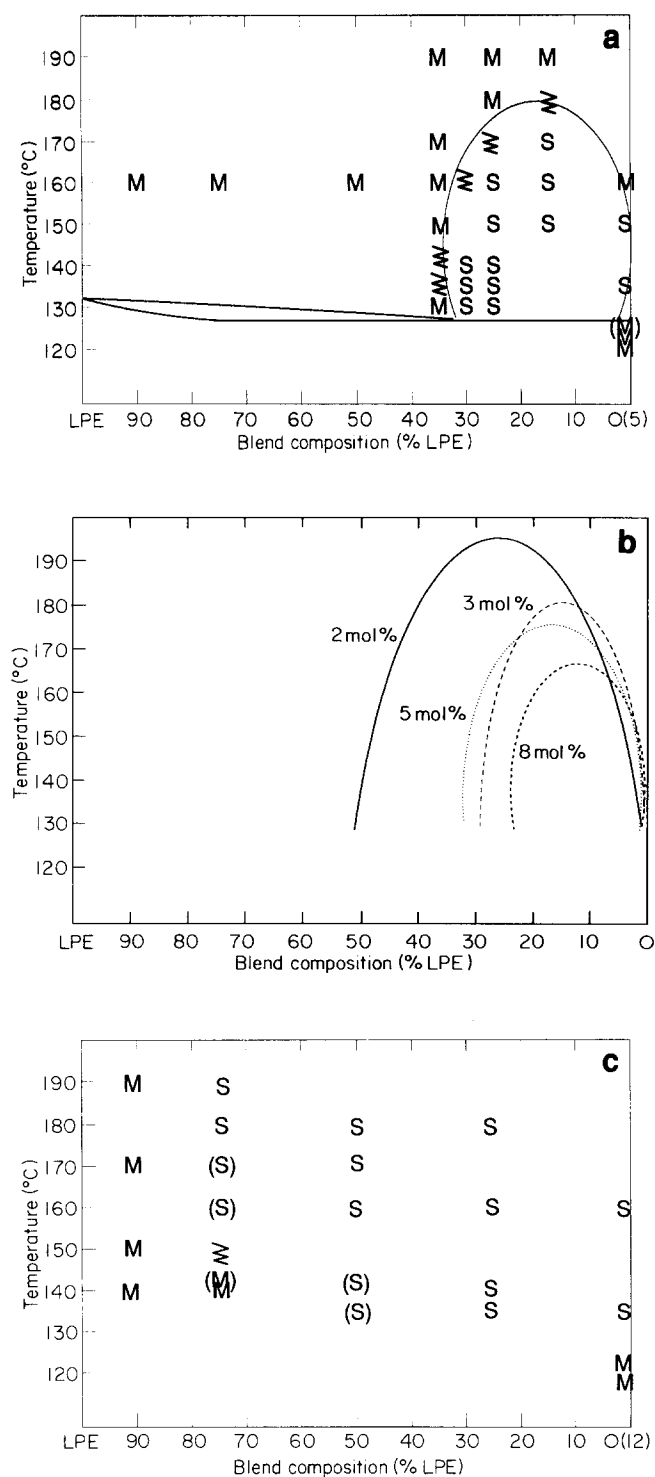[a] M, melt mixed at temperature indicated; S, melt segregated

Figure 5 Phase diagrams obtained for LPE/octene copolymer blend systems. Morphological and (for lower temperatures) d.s.c. data indicate a mixed melt where the symbol M is shown, a segregated melt where the symbol S is shown and ≳ for all border-line cases. (S) indicates only a little of the minority component, i.e. nearing the phase boundary. (a) LLPS loop obtained for the LPE/O(5) system, showing all the experimental points; (b) LLPS loops obtained for the blends of LPE with O(2), O(3), O(5) and O(8); (c) experimental points obtained for the LPE/O(12) system

Figure 5a shows, as a typical example, detailed results from the LPE/O(5) system, indicating the number of results and accuracy with which the LLPS loop can be drawn. All the LLPS loops deduced by the methods outlined above for blends of LPE with O(2), O(3), O(5) and O(8) are shown in *Figure 5b*. The following points

should be noted:

(i) all four blend systems shown here display LLPS;
(ii) in each case the LLPS is of closed loop form;
(iii) in each case the LLPS loop is found at low LPE content.

These three features are typical of LLPS loops found for LPE/BPE blends[3,4]. However, in *Figure 5b* we also see two new trends.

(iv) For BPEs of equal MW the LLPS loops become narrower and shift to lower temperatures as the branch content increases between 2 and 8 mol% octene.
(v) The octene copolymer O(3) has a higher MW than the rest of the series (see *Table 1*), thus it is not strictly comparable with the other three BPEs in this figure. However, the size of the loop can be taken to give some indication of the effect on the LLPS of increasing the MW of the BPE.

Due to the different morphology of the quenched LPE/O(12) blends the phase diagram here is less certain. *Figure 5c* shows the experimental points obtained from d.s.c. and TEM. There is no evidence, so far, of a *UCT* for this system, but, from the TEM of replicas of 1% blends crystallized isothermally, it seems probable that there is an *LCT*. We need to devise new methods of investigation for blends of this type, where segregation seems to be on a much smaller scale than seen before; however, it is already clear that this blend behaves essentially differently from blends of LPE with copolymers of lower octene content.

DISCUSSION

In this new work blending LPE with octene copolymers we have further evidence for the general occurrence of LLPS loops in blends of LPEs with BPEs. Where the branch content is 8 mol% octene or less, the LLPS regions are, as found previously, in the form of closed loops, and are, as previously, found at low LPE content. However, as stressed above, the way in which the sizes of the loops vary with frequency of branching (for blends of LPE with O(2), O(5) and O(8)) is not as we had expected. It is quite clear, from our present results, that for octene copolymers in this particular range of branching frequency, there is less LLPS as the branching increases. However, it appears that the LPE/O(12) system (O(12) being the BPE of highest branch content) is rather different from all systems that we have studied previously. A simple model that may account for this and for the (initially unexpected) trend as octene content is increased from 2 to 8 mol%, is indicated in reference 7.

We have previously shown that for a given BPE the size of the LLPS region decreases with decreasing LPE MW[4]. We would expect that increasing the MW of the BPE would have a similar effect to decreasing the MW of the LPE (this is argued in detail in reference 7). The narrower LLPS loop found when blending DSM LPE with O(3), compared with that predicted by extrapolation between LPE/O(2) and LPE/O(5), would fit in with this expectation since O(3) has a higher MW than the other BPEs in this series.

Blending the more highly branched O(12) with LPE gives rise to segregation on a much finer scale than we

have found previously and cannot be explored with complete confidence using the methods we have used to date. There is no firm evidence for a *UCT* for LPE/O(12), although there is some evidence for *LCT* behaviour. We suspect that this system is fundamentally different from all those we have studied previously, including the four others reported in this paper.

In summary, we have shown that blends of LPE with octene copolymers of differing branch content, up to and including 8 mol% octene content, give LLPS loops which are, to a first approximation, similar to those found in other LPE/BPE blends. Unexpectedly, the size of the LLPS loop decreases with increasing octene content for this branch range. However, there is evidence of rather different segregation behaviour for blends of LPE with the highest branched copolymer, O(12). Here extensive segregation is observed, but the segregated regions are at least an order of magnitude smaller in size than any we have seen previously.

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