

# Liquid–Liquid Phase Separation in Blends of a Linear Low-Density Polyethylene with a Low-Density Polyethylene

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**ABSTRACT:** A linear low-density butene copolymer, of overall branch content 3 mol %, has been blended with a low-density polyethylene. The low-density polyethylene has an overall branch content of 5 mol %, including both long and short branches. The two materials were blended in a wide range of compositions and the phase behavior investigated using indirect experimental methods, the examination of quenched blends by differential scanning calorimetry, and transmission electron microscopy. After quenching from temperatures up to 170°C, blends, of almost all compositions, show two crystal populations, separated on a micron scale. It is argued that this implies that the blends were phase separated in the melt before quenching. This behavior shows good agreement with predictions based on previous extensive studies of binary and ternary blends of linear with lightly branched polyethylenes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1921–1931, 1997

**Key words:** polyethylene blends; linear low-density/low density; phase separation

## INTRODUCTION

Linear low-density polyethylenes (LLDPEs) were first produced in the late 1970s. They were found to have good mechanical properties.<sup>1–3</sup> LLDPEs have frequently been blended with low-density polyethylenes, LDPEs. The superior mechanical properties of the LLDPEs are found to be retained, in combination with the easier processability of the LDPE.<sup>3</sup> Further advantages of the blends are given by Speed<sup>4</sup>: blending LDPE into LLDPE reduces haze and increases melt tension (to give a better bubble stability); blending LLDPE into LDPE improves melt drawdown properties as well as the toughness of the final polymer sheet.

The properties of LLDPE/LDPE blends must

be linked to the morphologies found in the blend samples; we show, in this article, that these morphologies can be quite complex. Biphasic morphologies are seen at room temperature in LLDPE/LDPE blends of most compositions, after a range of different thermal treatments. We believe that we can understand the origin of the observed morphologies by comparison with results obtained using blends of simpler materials.

In the recent past we have built up large body of evidence for liquid–liquid phase separation in blends of linear with lightly branched polyethylenes<sup>5–20</sup>; we now wish to see if these studies can help us to understand the more industrially important LLDPE/LDPE blends. To this end we have blended a well-characterized LLDPE with the LDPE that we used in much of our early work. We have produced a “map” showing morphologies obtained on quenching blends from various temperatures, this “morphology map” is of interest in itself. Further, following our previous practice, we have interpreted the morphology map as indicat-

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ing phase behavior in the melt, and we go on to show that the results can be interpreted with the aid of an appropriate ternary phase diagram. To put the present results in context we need to summarize some of the literature on LLDPEs and on LLDPE/LDPE blends, and the body of work dealing with phase separation in blends of linear polyethylenes with lightly branched copolymers.

## CONTEXT OF THE PRESENT WORK

### LLDPEs

It is clear that LLDPEs themselves are not simple materials; there is some evidence that they may phase separate in the melt. Mirabella et al.<sup>21</sup> and Debleik and Mathot<sup>22</sup> have shown that when highly branched materials are quenched from the melt, regions of differing crystallinity are manifest. Various authors have analyzed LLDPE materials by temperature-rising elution fractionation (TREF)<sup>23–25</sup> and have shown that LLDPEs contain molecules of very different molecular weights and branch contents. Wardaugh and Williams have suggested that there may be blockiness in branching, which may lead to phase separation in melts of some LLDPEs.<sup>26</sup> Mirabella et al.<sup>21</sup> and Channell et al.<sup>27</sup> have shown considerable morphological variations in LLDPE samples, and argued that phase separation may be the cause of the unusually high toughness of these polymers.<sup>1–3</sup> We have also detected phase separation in melts of several LLDPEs at some temperatures.<sup>14,18</sup> If LLDPEs can undergo phase separation in the melt it would not be surprising if blends of LLDPEs with other polyethylenes did so, too.

### LLDPE/LDPE Blends

There have been some studies on binary LLDPE/LDPE blends. Utracki and Schlund<sup>28</sup> looked at frequency relaxation spectra and rheological functions and deduced that the components of their system did not mix in the molten state. Other authors found that the addition of LDPE to LLDPE reduced the torque needed in processing<sup>29</sup> (thus saving on energy) and that the extensional flow behavior was modified.<sup>30</sup>

Studies of slowly cooled blends<sup>31,32</sup> showed that the LLDPE crystallized first, forming skeletal spherulites, within which the LDPE crystallized. Two endotherms were observed on remelting these slow-cooled blends. It has been suggested

that the high melting material is composed of the longest and least-branched molecules from each of the constituents.<sup>33</sup> TREF, on mixtures of LLDPE and LDPE fractions, indicated that miscibility is more likely where the branch contents are similar.<sup>34</sup>

Studies of the mechanical properties of a set of blends of a commercial LLDPE with a commercial LDPE<sup>35</sup> indicated that the components were mechanically compatible over the entire composition range. (These authors follow the definition of mechanical compatibility given by Utracki<sup>3</sup>: “if the mechanical properties of the blend conform to a rule of mixtures, or to positive deviations from it, then the system is said to be mechanically compatible.”) However, no data on the morphologies or phase behavior of these blends was available.

### Summary of Previous Work Using Blends of Simpler Materials

Recently, in Bristol, we have been studying the phase behavior of melts of blends of linear polyethylene with branched polyethylene (LPE/BPE), where the BPE is lightly branched (up to and including 8 mol % comonomer content).<sup>5–20</sup> Although physical properties of LPEs and lightly branched BPEs are too similar to enable the detection of phase separation directly in the melt (e.g., by light scattering), we have been able to observe biphasic structures in some rapidly quenched samples using both DSC and transmission electron microscopy, TEM; (our experimental methods are outlined below, and described in detail in references 5–9, 13, 19, and 20). The presence of a biphasic morphology is bound to effect the physical properties of the material. As a result, the “morphology maps” that we have produced must be of interest to those who use polyethylene blends. Further, we have interpreted these biphasic structures as clearly indicating liquid–liquid phase separation, LLPS, in the melts from which they were quenched.

We have looked at 65 binary systems to date. These include systems where molecular weight of the LPE has varied from  $2 \times 10^3$  to  $2 \times 10^6$ .<sup>7a,b</sup> We have used branched materials that are near random copolymers<sup>10,20</sup> and less well-defined commercial materials.<sup>5–9,13</sup> We have looked at ethylene–butene (EB) copolymers,<sup>14,18–20</sup> ethylene–octene (EO) copolymers,<sup>10,12,14,19,20</sup> and one ethylene–hexene (EH) copolymer.<sup>20</sup> We have looked at LPEs with polydispersity down to 1.1,<sup>18</sup> and at BPEs with polydispersity down to 2, looking at copolymers made by the single-site catalysis pro-

cess<sup>10</sup> and by the metallocene catalysis process.<sup>20</sup> In all cases, except one (where the molecular weight of the LPE was very low indeed,  $2 \times 10^3$ ,<sup>7</sup> we have found “morphology maps” that we interpret as indicating LLPS of a characteristic type. The blends mix in the melt (only one crystal type present on quenching from the melt) at high LPE content, but there is always a closed loop of LLPS (characterized by a biphasic morphology on quenching) at low LPE content. The phase separation is on a large spatial scale; typically, aggregates of minority crystals are some microns in diameter and separated on a similar scale, and we have shown that the diffusion rates are not large enough for this large-scale separation to have occurred during quenching from the melt.<sup>9,13</sup> Figure 1(a) shows an example of experimentally determined morphology map for a binary blend system. The extent of the LLPS region is dependent on the molecular weight of the LPE, but it only changes slowly for molecular weights of above about  $5 \times 10^4$ .<sup>7</sup> The composition range over which phase separation is observed is found to reduce as the branch density increases,<sup>10,12,14,18</sup> an observation that is, at first sight, surprising. For LPE/EO systems the characteristic closed loop of LLPS is found for copolymer contents of 8 mol % and less, and it becomes wider as the branch content of the EO copolymer is reduced (if the same LPE is used) [Fig. 1(b)]. However, when the octene content of the copolymer is 12 mol %, a completely different type of phase behavior is observed—the phase separation is then symmetric, wide-spread, but on a notably smaller spatial scale.<sup>10</sup> Where the branch content is 8 mol % or below, the extent of the phase separation observed for binary blends is the same, within the experimental errors, where the molecular weights of the two components and the branch densities of the copolymers are similar, whether the copolymers are EB, EO, EH, or have mixed branching. This important finding leads us to believe that it is the number of branches, rather than the branch type, that determines the phase behavior.<sup>14,18–20</sup> It has also been shown that where two near random copolymers of different branch content (both 8 mol % or less) are blended together the phase behavior is similar to that observed on blending an LPE with one near random copolymer.<sup>12,16,18</sup>

We have investigated ternary systems, as well as working with binary systems. We blended an LPE with two lightly branched EO copolymers<sup>12</sup> and an LPE with two lightly branched EB copolymers<sup>18</sup> to various compositions. Again, we plotted “morphology maps” and concluded that the phase

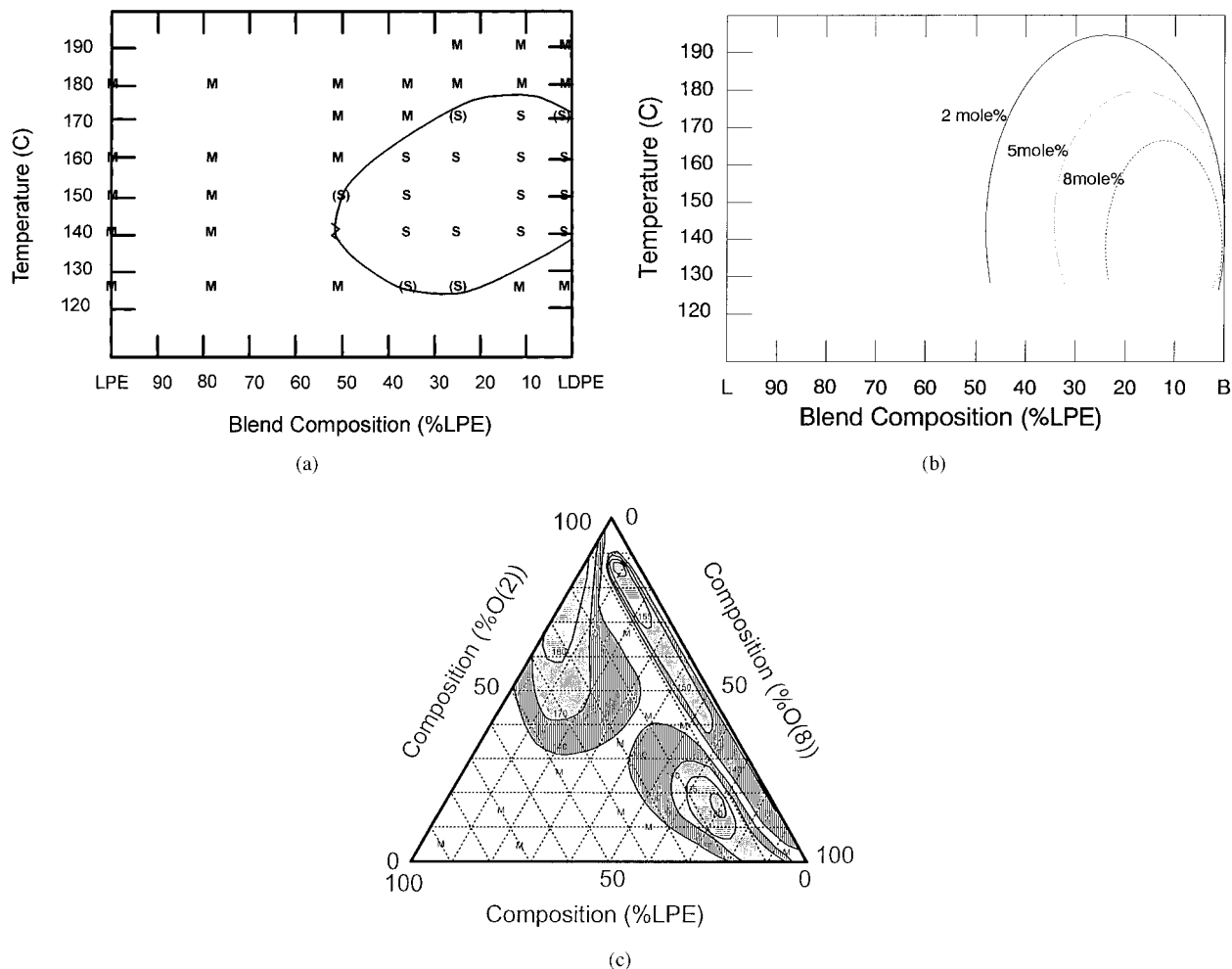
behavior of the LPE/EB/EB system was very similar to that of the LPE/EO/EO system where the branch contents were similar. Figure 1(c) shows the “morphology map” for our LPE/EO/EO ternary system. Our interpretation is that there are three regions of LLPS, all closed loops with respect to temperature. As in binary systems, the extent of phase separation increases as the branch content decreases, and, where the branch content at two of the apices is similar, or the branch content of two or more constituents is very low, the two larger regions of LLPS join up.<sup>12,18</sup> The behavior of binary systems can be seen to follow from that observed for ternary systems; each side of the ternary phase diagram represents a binary system.

We have published a simple model that enables us to predict the behavior that we expect on blending two or three polyethylenes of known branch content and molecular weight. (Details of the model can be found in ref. 11, with further expansion in refs. 12, 14, and 18.) Our model has enabled us to predict the (often quite complex) phase behavior of blends of LPEs with LLDPEs, and of near-random copolymers with LLDPEs, with reference to our ternary phase diagrams. LLDPEs are often bimodal in branch distribution.<sup>14,23–25</sup> If we regard an LLDPE as a mixture (in fixed proportion) of two copolymers of well-defined branch content, then the LLDPE can be represented by a point on a more branched/less branched BPE binary line. Blends of that LLDPE with an LPE will be represented by a line across an appropriate ternary phase diagram. The line will join the point representing the LLDPE, on one of the binary sides, to the opposite, LPE, apex.<sup>14,18</sup> Thus, the phase behavior of a set of blends of LPE with an LLDPE can be described by a cloud point curve that is a planar section across the relevant ternary phase diagram. We have found that all our results from blends of LPEs with LLDPEs can be interpreted in this way.<sup>14</sup> Similarly, when we have blended an LLDPE with a near-random branched copolymer, the phase behavior can be simply interpreted as a cloud point curve lying between the appropriate apex (random branched copolymer) and point on the opposite binary side (LLDPE).<sup>14</sup>

## EXPERIMENTAL

### Materials

The materials used in this study are listed in Table I. The EO LLDPE, EO'(3), has been the focus



**Figure 1** “Morphology maps” (i.e., phase diagrams as deduced by morphological means) of blend systems where the component materials were well characterized. (a) Morphology map of a binary system, obtained by examination of blends of the sharp, linear NIST fraction NIST119K with the LDPE PN220. NIST119K has an  $M_w$  of  $119 \times 10^3$ ,  $M_w/M_n$  of 1.1. “M” means that the blend of indicated composition, quenched from the temperature shown, showed a single crystal population (interpreted as indicating that the melt from which the blend was quenched was Mixed). “S” means that the blend of the indicated composition, quenched from the temperature shown, showed two well-separated crystal populations (interpreted as indicating that the melt from which the blend was quenched was phase Separated). (b) Morphology maps of binary systems obtained on blending an LPE with near random EO copolymers of branch content 2, 5, and 8 mol %. All four materials have  $M_w$  of about  $5 \times 10^4$  and an  $M_w/M_n$  of 2. Two clear morphologies are found within the loops at low LPE content. Data from ref. 10. (c) Morphology maps of a ternary system obtained on blending the LPE of (b), in various proportions, with the 2 and 8 mol % EO copolymers of the same figure; data from ref. 12. The blends quenched from within shaded regions show two clear morphologies, and the temperature contour lines indicate the extent of these regions at the temperatures shown. The points marked “M” are representative experimental points where a single crystal population was obtained on quenching from 140, and 160°C, and after isothermal crystallization at 126°C. Hence, the melt from which the blend was quenched was judged to be Mixed at all these temperatures.

**Table I** Details of the Polymers Used in this Research

	Branching (mol %)	$M_w$ (Uncorrected)	$M_w/M_n$
LLPDE, O'(3)	Overall 3 (components at 0.5, 4)	40 K	4.2
LDPE, PN220	5 (2 long, 3 short)	112 K	12

The LLDPE is bimodal in branch composition,<sup>14</sup> and the LDPE is reported (on the manufacturer's specification sheet) to have branches of two different lengths.

of a previous study in our laboratory.<sup>14</sup> We have analytical TREF data<sup>14</sup> showing that the branch distribution of this material is bimodal; the two components center on 0.5 and 4 mol % octene content. The LDPE, BP PN220, has been used extensively in our research.<sup>5-9,15,17</sup> It has both "long" and "short" branches, the overall branch content being 26 branches/1000 backbone carbon atoms (5.2 mol % overall comonomer content).

### Blending

The polymers were mixed in solution, the method has been described previously.<sup>6-9</sup> We label our blends by the LLDPE content; a 60% blend contains 60% LLDPE by weight. Blends were dried, mounted, either in DSC pans or between very thin glass microscope coverslips (for TEM), and then held at temperatures above the melting point for half an hour; we have previously established that this is long enough for blend melts to attain their equilibrium state.<sup>5-9</sup> The blends were then quenched into acetone at freezing point. We believe that, if there is clear evidence of large (micron) scale phase separation in quenched blends, the phase separation must have been present in the melt itself. We have shown that the diffusion rates are such that it is not possible for separation on a micron scale to take place during the short time of the quench.<sup>9,13</sup>

### Thermal Analysis

DSC was performed on 2 mg samples of quenched blends, heating at 10°C per minute, under nitrogen. Our DSC methods have been discussed elsewhere.<sup>13,19</sup> We have shown that the observation of two distinct melting peaks (with the ratio of the peaks independent of heating rate) is an indication of two crystal populations in the quenched melt, resulting from phase separation, in the liquid state, into LPE rich and LPE poor phases.

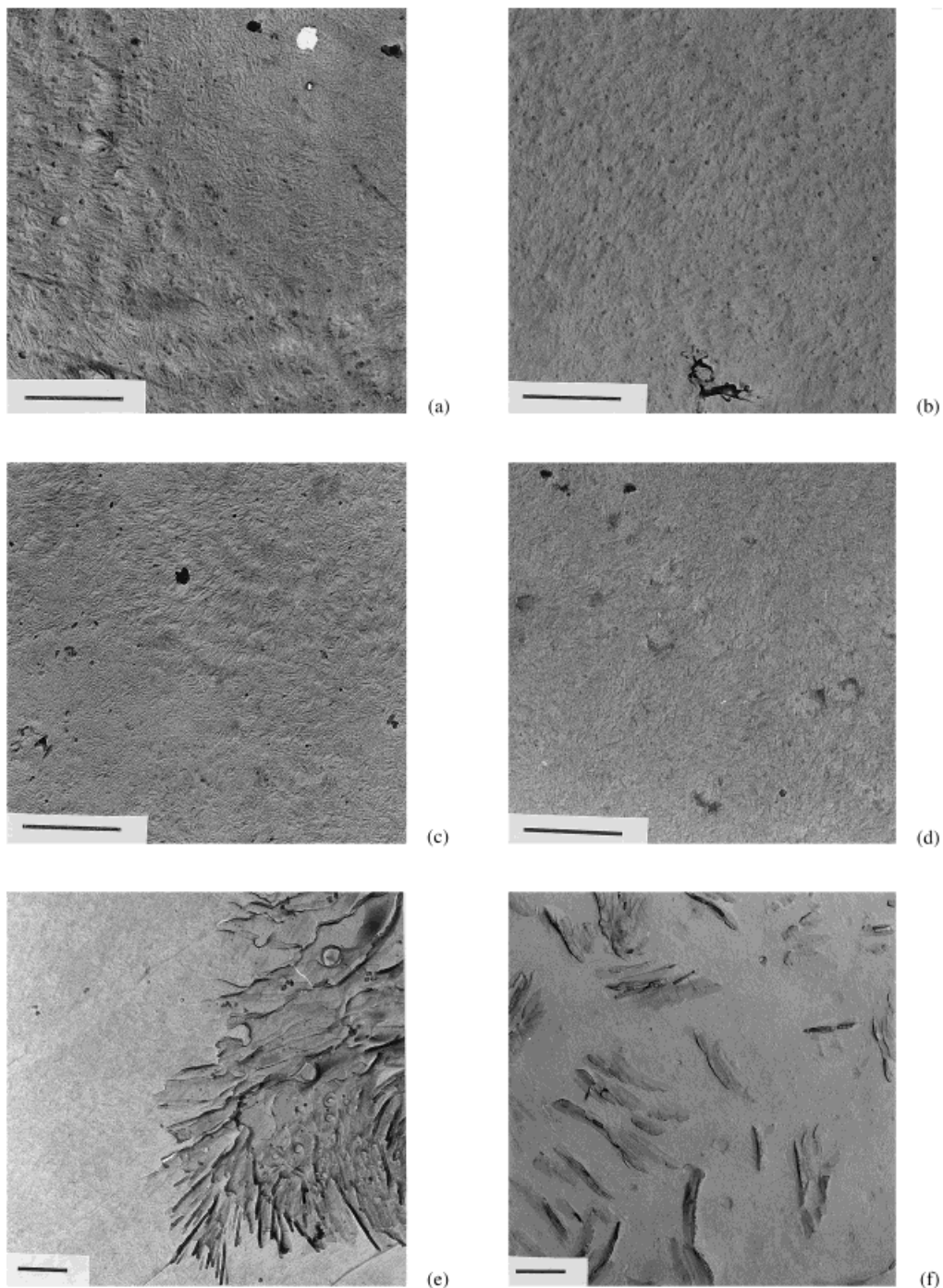
### Transmission Electron Microscopy

Surface replicas were made from samples of quenched blends, using the Bristol modification<sup>36</sup> of the permanganic etching technique.<sup>37,38</sup> We use surface replicas because the surface is the fastest quenched part of the sample, and so the nearest in phase structure to the melt from which it was quenched. Some of the replicas were examined in our Philips 301 TEM, operating at 80 kV and others in our Philips 400T TEM, operating at 100 kV. Each blend was also melted at 150°C, rapidly cooled to an isothermal crystallization temperature (in the range where the LPE rich material could crystallize, but the BPE rich material could not), and held at that temperature for 2 days; during this period any polymer that was able to crystallize isothermally could certainly do so. We believe that we can unambiguously distinguish materials that have crystallized isothermally from mixed melts and from phase separated melts.<sup>5,6,9</sup>

## RESULTS

### Transmission Electron Microscopy

Figure 2 shows micrographs of representative blends after various thermal treatments. Figure 2(a) shows an 80% blend, quenched from 160°C. There are two crystal types; thicker crystals, from two banded spherulites, and thinner crystals (right hand side) with no apparent overall ordering. We believe that such a morphology is indicative a phase separated melt prior to quenching. Note that the scale of the separation is large; in this sample the banded spherulites are some 5 microns across and the regions of thin lamellae several microns in size. Figure 2(b) shows a uniform morphology with one crystal type only; we associate this type of morphology with a mixed melt before quenching. Figure 2(b) was obtained after quenching a 20% blend from 190°C. In con-



**Figure 2** Electron micrographs of replicas of O'(3)/PN220 blends. In each case the scale bar represents one micron. (a) An 80% blend after quenching from 160°C. The micrograph shows parts of two banded spherulites containing thicker crystals (left side) and a region of thin crystals with no obvious overall order (right-hand side). We believe that such morphologies are indicative of a phase separated melt before quenching. (b) A 20% blend after quenching from 190°C. Only one type of (very thin) crystal can be seen. Blends quenched from high temperatures always have particularly thin crystals.<sup>8</sup> The uniform morphology indicates crystallization from a mixed melt. (c,d) Two different morphologies obtained on quenching a 10% blend from 140°C. Part (c) shows two crystal thicknesses (a group of thick crystals, top right, within a matrix of much thinner crystals—particularly clear at the bottom left). This morphology is again indic-

trast, the 20% blend displays a morphology of two crystal types after quenching from temperatures between 160 and 130°C. The morphology of a 20% blend, quenched from within this temperature range, is very like that seen in Figure 2(c). Figure 2(c) is actually a picture of part of a 10% blend quenched from 140°C. The 10% blend, when quenched from 140–130°C, shows some regions with two clear crystal types [thicker crystals, upper right, thinner lower left in Fig. 2(c)] and other regions with only one crystal type throughout [Fig. 2(d)]. This behavior is also observed for the 15% O'(3)/PN220 blend. In our experience, this is rare—usually the entire sample either looks like either Figure 2(c) or like Figure 2(d). This unusual behavior is discussed below.

Figure 2(e,f) shows 30% blends after isothermal crystallization, at 126°C [Fig. 2(e)] and at 120°C [Fig. 2(f)]. In Figure 2(e) the LPE-rich lamellae are grouped together, but in Figure 2(f) they are scattered individually. We have argued<sup>5-7a,9,13</sup> that the morphology in 2(e) implies that the LPE-rich material crystallized from a phase separated droplet, whereas the scattered, individual lamellae in 2(f) imply that the crystallization took place from a mixed melt. Thus, Figure 2(e) and 2(f) together indicate that the melt was separated over the period of crystallization (between 10 h and 2 days) at 126°C but remixed before crystallization took place (several hours) at 120°C; i.e., there is a phase boundary between these two temperatures. (On slow cooling the blend remixes as it crystallizes, to produce large, open spherulites as it does in other systems.<sup>6,20</sup> This is in agreement with the morphology deduced by Stein et al. from light-scattering results obtained from slowly cooled samples.<sup>31,32</sup> We believe that their observations indicate that the blend was remixing as it cooled during crystallization, in agreement with the present results from isothermal crystallization).

To sum up, we believe that the morphologies seen in Figure 2(a,c,e) are typical of crystallization from phase-separated melts, while those in Figure 2(b,d,f) are typical of crystallization from mixed melts. Figure 2(a–d) is of quenched

blends, and Figure 2(e) and (f) of isothermally crystallized blends. [Note that the magnification of Fig. 2(e,f) is half that of Fig. 2(a–d)—the isothermally crystallized LPE rich crystals are much larger than the quenched LPE rich crystals.]

### Thermal Analysis

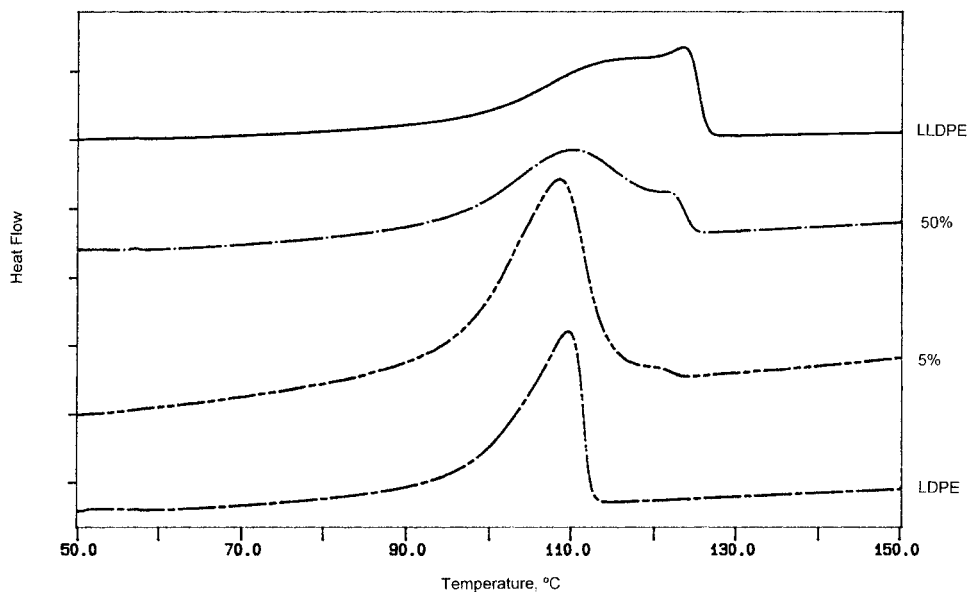
Figure 3(a) shows examples of normalized DSC traces obtained on reheating after quenching melts from 150°C. Note that the LLDPE itself shows two melting peaks, indicating a phase-separated blend before quenching, but the LDPE shows only one melting peak. In this blend system, where the lower peak of the LLDPE is quite close in temperature to the melting peak of the LDPE, the DSC results are not so striking as in other systems where the melting temperatures of the component materials are more widely separated. However, it is clear that the relative size of the top peak reduces with the LLDPE content [Fig. 3(a)] and, on close examination [Fig. 3(b), traces again normalized], we can also see that the high melting peak of the 10% blend is less than half the size of that of the 5% blend. (Six traces of each of the 30, 10, and 5% blends were run, using fresh samples each time. The high melting peak of the 10% blend was never completely absent, but always less than half the size of the high melting peak for the 5% blend. There was some variation in the size of the low melting peak of the 10% blend relative to that of the high melting peak. This, again, indicates some inhomogeneity in the phase structure of the 10% blend. In contrast, the relative sizes of the low and high melting peaks of the 5 and 30% blends did not vary outside the experimental errors of measurement. The 15% blend behaved very much like the 10% blend.)

### Phase Behavior

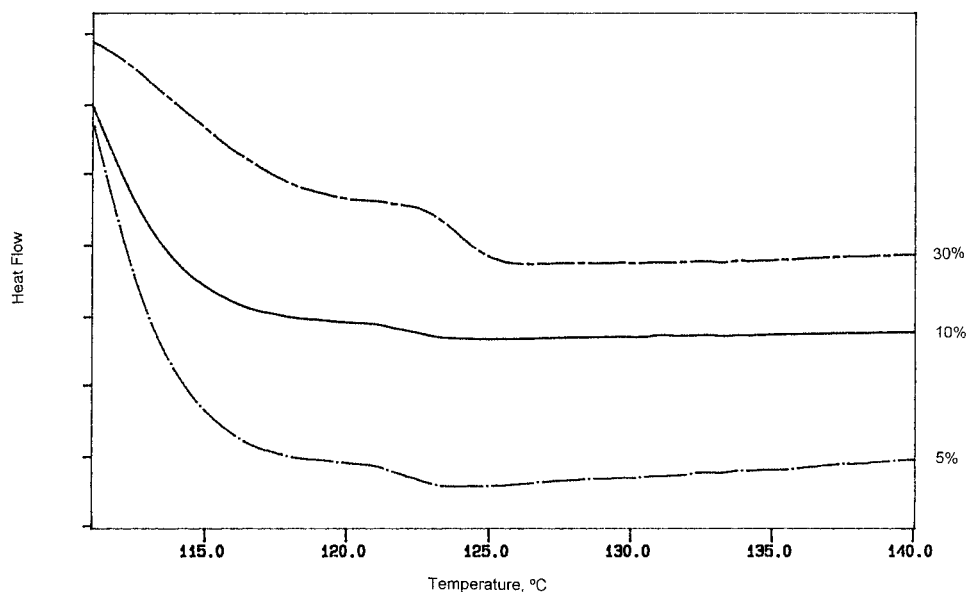
Figure 4 shows the state of the melt of a set of blends as determined by our indirect methods of DSC and TEM. “M” stands for uniform morphology after quenching, interpreted as indicating a Mixed melt prior to quenching. “S” stands for two

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ative of a phase-separated melt before quenching. Part (d) shows a uniform morphology with only one crystal type, thought to have been obtained by crystallization on quenching from a mixed melt. (e,f) Morphologies obtained on quenching a 30% blend after isothermal crystallization at 126°C (e) and 120°C (f). We believe that the thick, LPE rich crystals in (e) (right-hand side) crystallized from a LPE-rich droplet in a phase-separated melt, while the individual lamellae in (f) crystallized from a mixed melt.



(a)



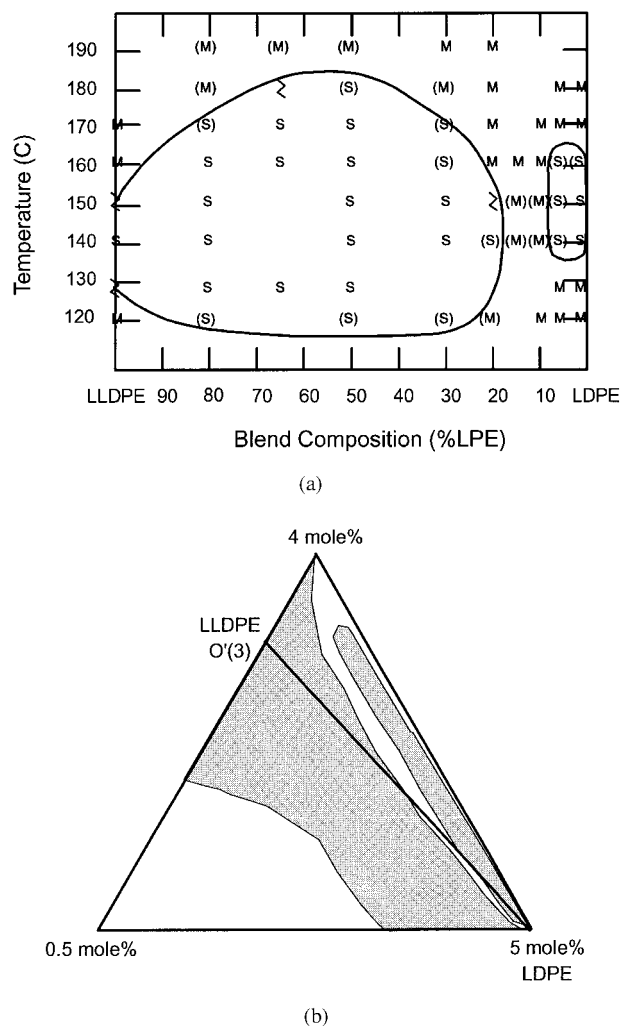
(b)

**Figure 3** DSC traces from a selection of blends from the O'(3)/PN220 system; all have been normalized. The traces were obtained by heating at 10°C/min; under nitrogen, after quenching from 150°C. Part (a) shows the melting behavior of the LLDPE and LDPE, together with the 50 and 5% blends. Part (b) shows part of the melting traces of the 30, 10, and 5% blends. Note that the higher melting peak is larger for the 5% blend than for the 10% blend, although the LLDPE content is lower.

clear crystal types after quenching, interpreted as indicating a Separated melt prior to quenching. It is clear that there is widespread phase separation in this system. Very few of the blends examined showed only one crystal population at any temperature between 125 and 170°C. However, the 10, 15, and 20% blends were mixed at

160°C and above and the 10 and 15% blends showed a tendency to mix at lower temperatures. The 10% blend will be discussed here, the 15% blend showed similar results. DSC traces of the 10% blend had small high melting peaks when compared to quenched 5% blends [Fig. 3(b)]. Further, replicas of the 10% blend, after quench-





**Figure 4** (a) Experimental results from O'(3)/PN220 blend system showing our findings for the state of selected melts at various temperatures. (b) A possible explanation for the results. If we are looking at the cloud point line indicated, running across the ternary phase diagram shown, we would expect the observed phase behavior.

ing from 140°C, showed single lamellar populations over substantial areas, although in each sample there were some regions where two lamellar populations were clearly seen. Ten percent blends quenched from 160°C always showed a single morphology (mixed melt), as did 15% blends. On the other hand the 1, 5, and 30% blends showed two distinct lamellar populations when quenched from 140°C, and the 30 and 1% blends showed two distinct lamellar populations when quenched from 160°C. Thus, both the DSC and the TEM indicate that 10 and 15% blends are less inclined to separate than the 30, 20, and 5% blends, and we conclude that there is either

a dip in the phase-separation contour in the region of 10–15% or two distinct regions of phase separation.

## DISCUSSION

The results are much as we would expect from a consideration of the relevant ternary phase diagram. From the TREF data (given in ref. 14) we can regard the octene LLDPE, O'(3), as a blend, in fixed proportion (roughly 1 : 3), of a 0.5 mol % EO copolymer with a 4 mol % EO copolymer. The LDPE, PN220, has behaved as a 5 mol % branched material in all our previous experiments.<sup>5–9</sup> In PN220, the branches are of unequal length, but we have shown that branch length is not a primary factor in determining phase behavior in blends containing lightly branched materials.<sup>14,18–20</sup> Hence, we would predict that the O'(3)/PN220 system would be well represented by a cloud point line across a ternary system with apices at branch contents 0.5, 4, and 5 mol %. The cloud point line would run from the 5 mol % (PN220) vertex to a point three-quarters of the way along the opposite binary side [O'(3)]. Because all the materials are quite lightly branched, and the components at two of the apices are close in branching (4 and 5 mol %), we would expect only two regions of phase separation; the regions of LLPS extending from the binary sides adjacent to the 0.5 mol % apex should have joined up. (Detailed arguments about the sizes of regions of LLPS in these systems can be found in refs. 11, 12, 14, and 18). Such a cloud point line, across a ternary system of the type we expect, is shown in Figure 4(b). Clearly, it would predict widespread LLPS in two regions, just as we observe. Our simple predictive scheme, derived from our considerable experience in looking at polyethylene blends, works perfectly in this case. The fact that our scheme works, even although one of the materials is an EO LLDPE and the other has more than one branch type, is a further indication that branch type is not of importance in determining the extent of phase separation. It is the number of branches that is of primary importance. We have previously examined the phase behavior of O'(3) blended with an LPE and, in a separate experiment, blended it with a near-random EO copolymer of 8 mol % octene content.<sup>14</sup> The morphology map obtained from the O'(3)/EO (8 mol %) system is very similar to that found in the present case of O'(3)/PN220 (5 mol %). The results obtained from both systems fit in with our predictive model.

From theoretical considerations<sup>11,12,18</sup> we would expect that the two phase-separated regions observed in the O'(3)/PN220 system would be completely separate, but experimentally we find some blurring of the phase boundaries at 10–15% concentration. On balance, the experimental evidence is that there are two regions, but they are not completely separate on an experimental scale, i.e., the 10% blend in a 2 mg DSC sample, after quenching from 140°C, is part mixed and part separated. We know, for previous studies<sup>7a,8</sup> that there are small fluctuations in concentration over any experimental solution blended sample. We estimate, from TEM studies of isothermally crystallized blends of low LPE content, that these fluctuations could be of up to about 3% LPE content. If this is the case, some parts of the nominally 10% sample could have compositions within the high PN220 concentration LLPS region of the phase diagram and others in a mixed region, as observed. Similarly, some parts of the 15% blend sample could have compositions within the lower PN220 concentration LLPS region of the phase diagram and others in a mixed region. Whatever is the cause, in practice we can see some tendency to mix at 10–15% LLDPE concentration, but we do not find complete mixing throughout any one experimental sample.

To sum up, we find that the phase behavior of the LLDPE/LDPE, O'(3)/PN220, blend system can be well understood in terms of our previous studies using simpler materials. We would expect other binary LLDPE/LDPE blends to behave in similar ways where the materials are lightly branched.

Other workers have assumed,<sup>40–42</sup> and some have argued on the basis of neutron scattering data,<sup>42</sup> that there is no phase separation in melts of blends of lightly branched polyethylenes; any separation observed at room temperature took place on crystallization. We are convinced that this is not the case; for instance, we have shown elsewhere that the average size of the minority, separated, regions ripens with storage time in the melt<sup>16</sup> and that neutron scattering results can be ambiguous.<sup>17</sup> The observed ripening is difficult to understand in terms of phase separation on crystallization.

We have observed two types of crystal, separated on a scale of microns, after quenching O'(3)/PN220 blends of most compositions from 130–170°C. The existence of such inhomogeneous morphologies must effect the physical properties of the blend. In addition if, as we firmly believe, there is liquid–liquid phase separation in melts

of these blends, it is very likely that the phase separation of the melt will effect the rheological properties. We have published very preliminary experiments that indicate that this may be the case.<sup>6</sup>

When applying of our findings to commercial materials, it should be remembered that the polymers in this study were mixed in solution. Commercial blends are made by melt mixing. In the past, we performed a limited set of experiments blending an LPE with the LDPE PN220 by melt mixing.<sup>15</sup> Blends of high LPE content showed a single lamellar population, proving that complete mixing was obtainable in a twin-screw extruder. Further, the phase behavior of melt mixed blends was the same, within the experimental uncertainties, as that of blends of the same composition after solution blending. However, the morphologies of the blends, following the two methods of mixing, were notably different. The morphologies of the melt mixed materials were dominated by shish-kebab crystals, whereas, following solution blending, the morphologies were spherulitic, as they are in this present work. We suspect that in melt mixed commercial blends the shish-kebab morphology could have as much, or more, effect on mechanical properties as the presence or absence of phase separation, particularly where the molecular weight of one or both of the components is high so that shish-kebabs are numerous.<sup>43</sup> It has been shown that the mechanical properties of blown films of 20% LLDPE/LDPE blends vary considerably with processing conditions and with the molecular weights of the components.<sup>44</sup> However, these mechanical properties have yet to be related to morphological observations and to phase behavior.

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