Liquid–liquid phase separation in melts of blends of linear with branched polyethylenes: morphological exploration of the phase diagram*

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The liquid–liquid phase separation in blends of linear and branched polyethylenes has been observed using a morphological technique. The results confirm our previous conclusion that the phase-separated region of the phase diagram has a closed loop shape. We have also been able to demonstrate that the phase separation occurs at the same temperature on heating and cooling and hence argue that it represents an equilibrium phase boundary. The process of phase separation has been studied by observing changes in the shape and sizes of the phase-separated regions with time. In some cases, we argue that it is possible to distinguish between morphologies caused by liquid–liquid phase separation which occurred through nucleation and spinodal decomposition.

(Keywords: polyethylene blends; morphology; liquid–liquid phase separation; phase diagram; spinodal decomposition)

INTRODUCTION

During our studies on blends of linear (LPE) with branched (BPE) polyethylene[1–4], we have established that there is extensive liquid–liquid phase separation (LLPS) in several LPE/BPE blend systems. We have used a variety of indirect experimental methods to show that these systems exhibit both upper and lower critical temperatures (*UCT* and *LCT*). The region of demixing appears on the phase diagram as a closed loop[2,3]. Such closed loop phase diagrams have been predicted theoretically[5,6] for polymer blends and solutions. They have been observed for solutions[7] and suggested in one other case for a polymer blend[8]. We have been able to show that this most unusual form of LLPS takes place, under specified conditions of temperature and composition, in all the LPE/BPE systems we have studied, unless the LPE is of very low molecular weight[4]. We have not yet looked at a BPE with <14 branches per thousand carbon atoms, or with a molecular weight $<10^5$. We have, however, found some evidence that size of the region of LLPS decreases with decreasing branch content[4].

The blend system that we have studied in the fullest detail is one of LPE Sclair 2907 with the BPE BP PN 220. The phase diagram for that system is given in reference 3. Here we reproduce, as *Figure 1*, Figure 10a from reference 3 showing the LLPS region of the phase diagram, which we determined experimentally. In blends of LPE with BPE the two components are physically very similar, and the usual, direct experimental methods such as light scattering, cannot be used. We deduced this diagram by combining the results from several indirect experimental techniques.

The present paper describes how morphological techniques have been used to improve our understanding of the phase diagram and to follow the process of phase separation. The basic assumption underlying this work is that at the surface of a rapidly quenched sample the molecules are unable to move significantly from the position they held in the melt before quenching. Thus the surface morphology of a rapidly quenched sample reflects the phase morphology in the melt. For example, we can start by quenching from a temperature where there is only one phase present and hence show that the melt was mixed. This is illustrated in *Figure 2a* for a blend containing 20% of the LPE. It can then be shown that after quenching the same melt from a lower temperature there are two distinct phases present. This is illustrated in *Figure 2b*, again for the 20% blend. Further, the development of the separating phases with time can be observed. Thus, when the original phases are seen as small circular regions of one phase embedded in another, it may be deduced that the phase separation involved nucleation. On the other hand when the beginning of phase separation is seen as a bicontinuous network, it is suggested that spinodal decomposition has occurred.

Several important results have emerged from this study. First, it has been possible to show clearly whether samples were mixed or segregated before quenching, e.g. from a comparison of *Figures 2a* and *b*. Secondly, by looking at blends after long storage in the melt it was possible to confirm the existence of LLPS in the particular blend system chosen. Thus, the coexistence curve could be drawn in greater detail. Thirdly, it was

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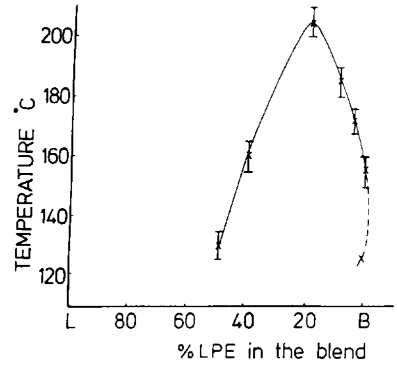

Figure 1 Data from reference 3 showing the extent of the liquid–liquid phase segregated region of melts of blends of Sclair 2907 (L) with BP PN 220 (B)

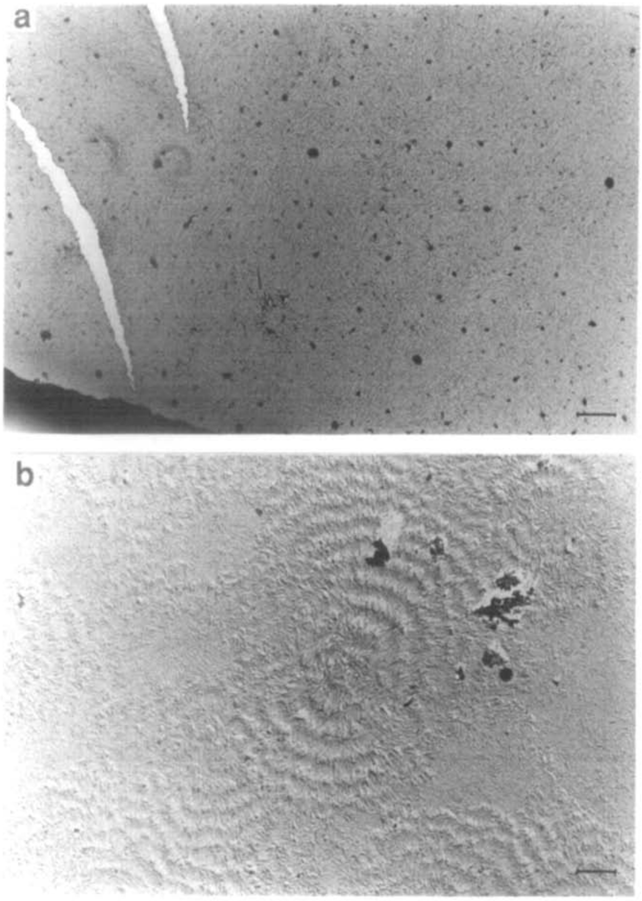

Figure 2 Transmission electron micrographs of surface replicas of 20% blends quenched from the melt. Blends quenched from (a) 230°C (where the melt was mixed) and (b) 150°C (where the melt was segregated). Scale bar = 1 μm

possible to show that the same phase boundary is found on cooling from a mixed melt to a segregated melt as on heating from a segregated melt to a mixed melt. Fourthly, by looking at the melts after short times at particular melt temperatures, some quantitative idea has been gained as to the times that the polymers take to mix and to segregate. Finally, it has been possible to observe the segregated regions change their size and shape as mixing (or segregation) progress. In a few cases, we believe that we can determine whether the segregation took place by a spinodal or by a nucleation mechanism. However, although some morphologies look as if they could have occurred by one mechanism and some by the other (examples are shown), we do not feel that a spinodal/nucleation boundary can be drawn with confidence until more experiments are performed.

EXPERIMENTAL AND RESULTS

Materials and blending

The polymers used were the LPE Sclair 2907 (molecular weight ~ 10^5) blended with the BPE BP PN220 (molecular weight 2×10^5, branch content 10 'long' and 16 'short' branches per thousand carbon atoms). These polymers have been used extensively in our previous work; reference 3 describes the properties of their blends in some detail.

The methods used to prepare the blends are described in detail in reference 1. The polymers were dissolved together in xylene and coprecipitated by pouring the solution into excess of a non-solvent (acetone) at 4°C. It has been shown in reference 1 that such a preparation method can lead to complete blending, i.e. complete cocrystallization can be obtained if the blend composition is suitable.

Blends of low LPE content were used in this study so that the LPE-rich regions were well separated. Samples ($\sim 2 \times 5 \times 0.5$ mm) were mounted between the thinnest possible coverslips and carefully wrapped in one thickness of aluminium foil. The wrapped samples were then placed in oil baths, at the desired temperatures and the various thermal treatments (see below) carried out.

In these experiments it was particularly important that the quench was as fast as possible and that the replicas showed the morphology of the surface, where the quench was fastest. Accordingly, quenching was carried out into acetone at its freezing point and, to obtain TEM samples, only very light permanganic etching was employed[9] using the 'Bristol recipe'[10], before replication. A single stage replication process[10] was used.

In the following, the blends are referred to by the percentage of LPE present; thus a 3% blend is one containing 97% BPE and 3% LPE. After several preliminary experiments to establish the best experimental conditions, 20%, 12% and 1% blends were quenched after treatment as detailed below. In all cases, segregated blends crystallized fully at 126°C were used for the starting materials. These samples had previously been studied extensively (e.g. ref. 3); they are known to crystallize from well segregated melts and the size and spatial distribution of the LPE-rich crystal groups have been fully documented (in unpublished work in association with ref. 3).

General experimental procedure

The experiments required particular care to be taken in several ways.

Degradation effects. PE specimens are liable to degradation if held at elevated temperatures. In reference 3 details are given of work on the present system, showing that blends with appreciable BPE content do not degrade significantly up to 200°C. Further work was done during the present study, where blends were held at 230°C for significant times and the surface—the region most likely to degrade—was the area of interest.

To check for degradation, samples were held at 230°C for various lengths of time before crystallizing isothermally at 126°C, where the morphology had been well documented. It was found that no observable change in crystalline morphology was found if blends had been stored at 230°C for 30 min, but if held at that temperature for >1 h changes in morphology were exhibited; the morphologies observed were those previously obtained for LPEs of lower molecular weight with BPE, i.e. segregation was less pronounced. When the blend had been held at high temperature for 2 h or more, segregation effects were no longer observed.

As a result of these checks, fresh blend samples were used for each experiment and no blend sample was held at 230°C for >30 min.

Temperature effects. In some temperature ranges the blend melt is very sensitive to temperature changes. In particular, for 1% blends it has been shown[3] that crystallization times and mixing times are similar at temperatures near 122°C. By varying the temperature slightly one can achieve (or not achieve) mixing before crystallization. It was not possible to control the temperature of the oil baths to better than half a degree, but 0.1°C can appreciably affect the crystallization time at temperatures near 122°C. To counteract this difficulty, groups of samples, which were to be compared, were all given the same thermal treatment together, throughout the experimental procedure. Thus specimens to be compared received the same thermal treatment, although the temperatures did not always correspond exactly between experiments. The behaviour of the blends is not so sensitive at higher temperatures.

Observations of size changes of the minority phase in 1% blends

In the first set of experiments, only samples containing 1% LPE were used. These were chosen because there is little LPE-rich material so that the groups of LPE-rich crystals are widely separated and hence easy to measure. Samples were held for various times at 150 and 175°C before they were quenched into acetone at its freezing point, washed and used to make surface replicas. The sizes of the LPE-rich crystal groups were then measured.

Some samples were held at 150 or 175°C for 30 min, then transferred to an oil bath at 122°C and held there for various times before quenching.

Figures 3a–d show a series of micrographs of 1% blends crystallized isothermally at 122 and 126°C. Micrographs such as these were used to obtain the sizes and spatial distribution of the LPE-rich crystal groups in the material used for subsequent experiments. All such measurements were carried out on replicas of the surface (rather than of the interior of the sample), since this is where the quenching rate is fastest. Hence the results are least affected by changes during quenching. However, it is clear from *Figures 3a* and *b* that there are differences between the surface and the interior of the samples*.

The results quoted below for sizes of LPE-rich crystal groups, in 1% blends, measured from surface replicas, were obtained from averaging measurements over 30 to 40 segregated regions. The results showed a quite wide distribution, as illustrated in *Figure 4*. This spread is inevitable since we are looking at sections through the (approximately) spherical segregated regions at all sorts of distances from the centre. Thus, a spread in apparent radius will be obtained from the true value (central section) downwards. However, the actual radius can be easily calculated from the average radius found on taking random sections.

Using the method outlined above, changes in the size of LPE-rich domains in the same samples used in *Figures 3* and *4*, could be seen clearly. At 150°C the LPE-rich domains decreased in size (from an average diameter of 1.4 μm to an average diameter of 1.0 μm) in the first 4 min; the domains then remained constant in size. On decreasing the temperature to 122°C (after first storing at 150°C for 30 min) the samples were able to crystallize. Before crystallization took place the size of the LPE-rich regions was seen to increase, until the material crystallized (after ~15 min) with a diameter of LPE-rich crystal region of 2.0–2.1 μm. The size changes of the LPE-rich regions are shown in *Figure 5*; *Figure 3c* shows a typical region after storage at 150°C followed by crystallization of LPE-rich material at 122°C before quenching.

Holding the same initial sample type at 175°C, the LPE-rich domains increased in size from 1.4 μm on average to 2.1 μm in the first 4 min. After that they continued to increase but the edges of the LPE-rich domains became indistinct as the two phases mixed. On decreasing the temperature to 122°C, after storage at 175°C for 30 min, the samples were again able to crystallize; when they did so, following storage at 175°C, the morphology was of well separated, individual lamellae (*Figure 3d*); indicating crystallization from a mixed melt[1,2].

Figure 3 also shows the results of quenching 1% blends from the melt. *Figure 3e* shows a replica obtained after quenching from 140°C. The two different crystal thicknesses indicate that the melt was segregated before quenching. *Figure 3f* shows a replica obtained following storage at 175°C, the single morphology indicates quenching from a fully mixed melt.

Mixing experiments (TEM) using 1, 12 and 20% blends

Samples were held for 20 min at 130, 150, 170, 190, 215 and 230°C before quenching into acetone at its freezing point.

It is not possible to show photographs of all the replicas here. In *Figure 6* examples are shown of replicas obtained from originally segregated 12% blends quenched after holding for 20 min at successively higher temperatures. Clearly at the lower melt temperatures the blends were still segregated. Two clearly different morphologies, with distinct crystal thicknesses are seen at 130 and 150°C; that quenched from 150°C is shown here (*Figure 6a*). At 170°C the structure is changed, although two types of crystal are still visible in the quenched blend

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*It has been observed, during this work, that there are distinct differences between the surface and the interior of 1% blend samples. No difference has been detected for the samples of higher LPE content. However, it appears that there are more crystal nuclei, and more LPE-rich material, at the surface of nominal 1% blends than in the interior. This difference is seen by comparison of *Figures 3a* and *b*. Note that the general morphology is the same (groups of LPE-rich crystals), but the number of groups per unit area is smaller in the interior (*Figure 3b*). The crystals in the interior are rather longer than those at the surface, but the crystal thicknesses are the same. By measuring many such photographs, we find that the LPE-rich material is three to four times denser in the surface layer. Thus the part of the nominal 1% blend that we observe may really be effectively a more concentrated blend since we are dealing with surfaces only. Similar effects have been observed by other authors[11,12].

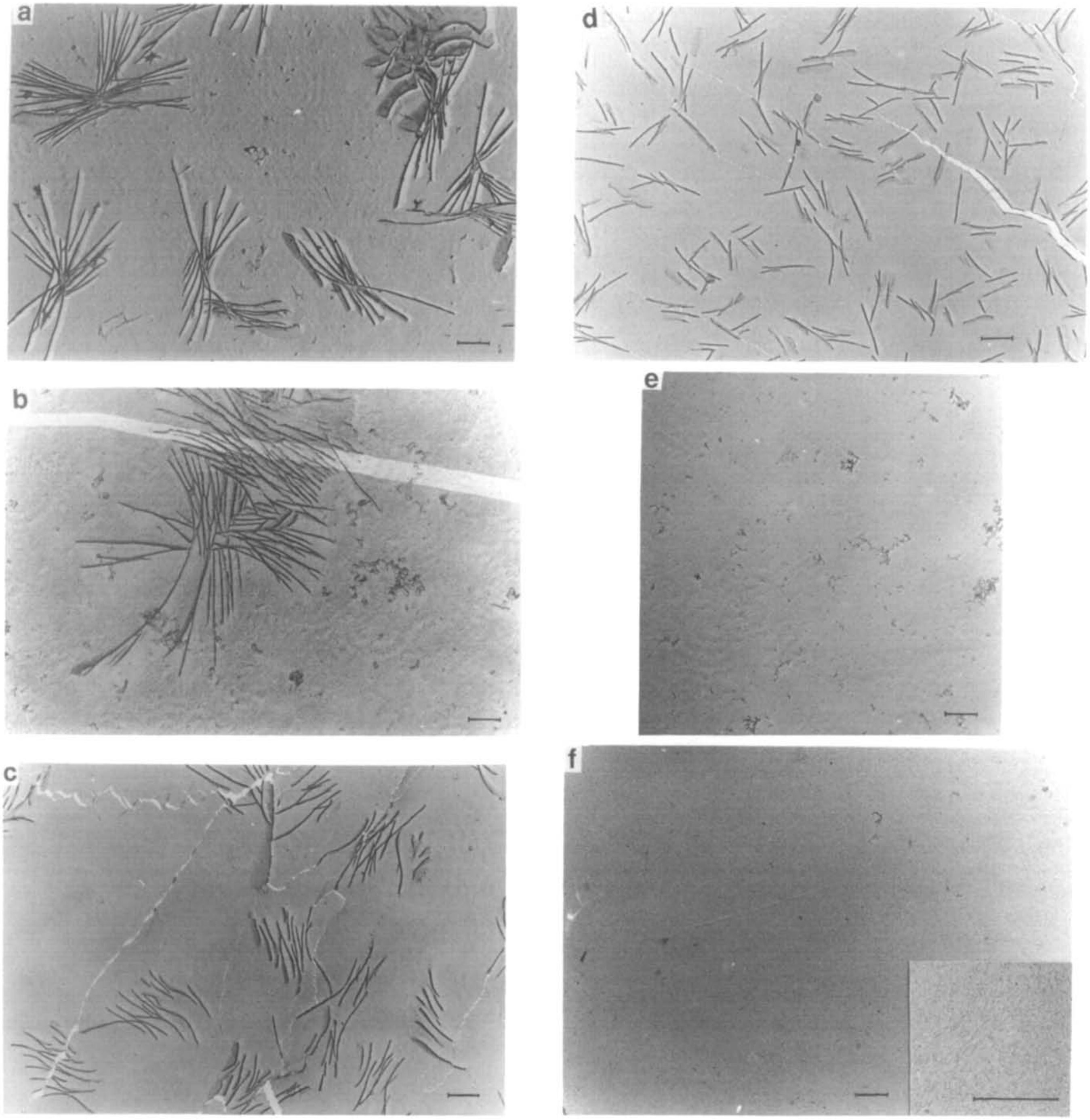

Figure 3 Transmission electron micrographs of replicas of 1% blends quenched after preparation as follows: (a) 1% blend melted at 160°C then cooled to 120°C and held at that temperature for 1 week before quenching. Surface replica; (b) as (a) but this replica was obtained from a surface cut from the centre of the sample after crystallization; (c) surface replica from a sample stored at 150°C for 1 h, then held at 122°C (whilst the LPE-rich material crystallized) and, finally, quenched; (d) as (c) but sample held at 170°C for 1 h before crystallization at 122°C; (e) 1% blend quenched directly after storage at 140°C (segregated melt); (f) as (e) but blend stored at 190°C (mixed melt) before quenching. Scale bar = 1 μm

(*Figure 6b*). However, at 190°C there is only a slight indication of a second morphology (*Figure 6c*), and only one type of crystal can be seen on quenching from 215 and 230°C; *Figure 6d* shows a replica of a blend quenched from 230°C.

The overall picture is shown schematically in *Table 1*, where M indicates a mixed melt and S a segregated melt. (S) indicates segregation, but not well developed—the sample was probably very near the coexistence curve. These results compare very well with those deduced in our previous work from d.s.c., rheology and other TEM methods (see ref. 3, Figure 10a, here *Figure 1*).

An additional feature that we have not commented on previously can be seen in *Figure 6*. The crystal sizes of the branch-rich material depend on the temperature from which they were quenched, higher melt temperatures leading to smaller crystals.

Segregation experiments (TEM) using 1, 12 and 20% blends

The blends were heated to 230°C, where all were known, from the experiments described above, to mix within 20 min. After 30 min the blends were quenched to storage temperatures at 130, 150, 170, 190 and 215°C;

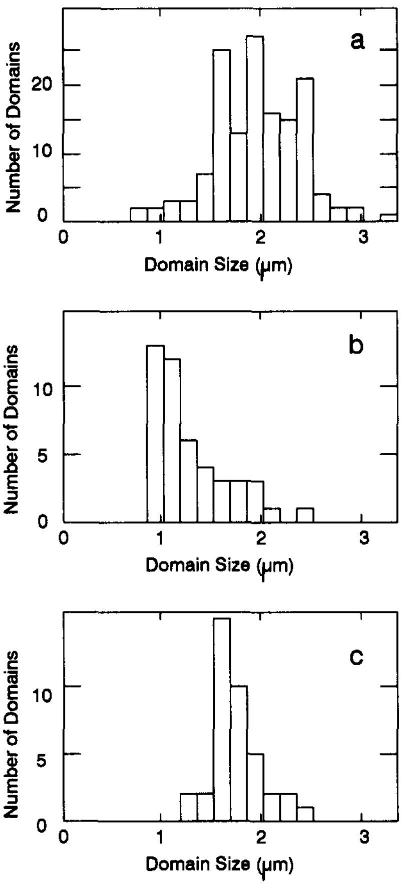

Figure 4 Examples of histograms showing the numbers of LPE-rich domains found with the diameters indicated: (a) samples crystallized at 122°C following storage for 20 min at 150°C; (b) samples crystallized at 126°C after storage at 160°C for 20 min; (c) samples quenched into acetone at its freezing point after holding in the melt at 175°C for 2 min

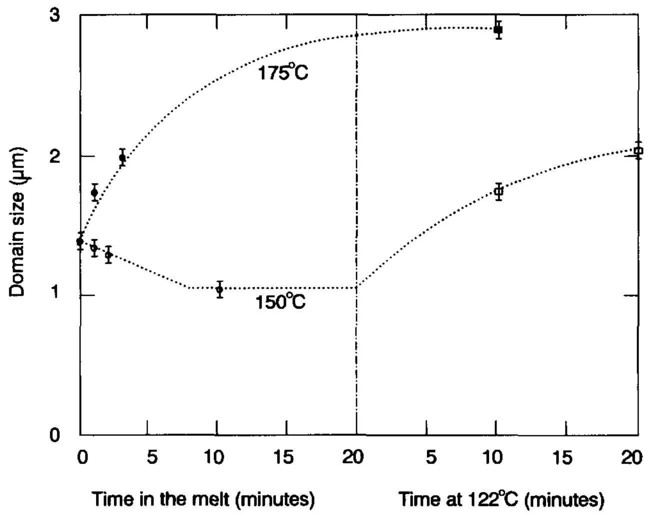

Figure 5 Results of four experiments to determine the changes in the sizes of the LPE-rich domains during storage in the melt. On the left are shown the domain sizes (filled symbols: stored at 150°C, i.e. inside the two-phase region; open symbols: stored at 175°C, i.e. outside the two-phase region). On the right we show how samples originally stored at 150 and 175°C for 30 min changed during subsequent storage at 122°C. For the sample originally stored at 150°C it is shown how the domain size increases. During storage at 122°C of the sample initially held at 175°C, isolated LPE-rich crystals grow from the mixed melt; the mean separation of these crystals is plotted

Table 1 State of mixing or segregation of the melt after holding for 20 min at the storage temperature, both on heating up from room temperature and on cooling from a mixed melt

Storage temperature (°C)	LPE concentration in blend (%)		
	20	12	1
230	M	M	M
215	M	M	M
190	S	(S)	M
170	S	S	M
150	S	S	S
130	S	S	S
122	S	S	M

It is only possible to observe the remixing of the 1% blend at 122°C on cooling from the melt

Table 2 State of mixing or segregation of the melt after holding at the storage temperature for 2 and 20 min after quenching from a mixed melt at 230°C

	After 2 min			After 20 min		
Storage temperature (°C)	LPE concentration in blend (%)			LPE concentration in blend (%)		
	20	12	1	20	12	1
215	M	M	M	M	M	M
190	M	M	M	S	(S)	M
170	(S)	M	M	S	S	M
150	S	(S)	M	S	S	S
130	S	S	S	S	S	S
122	S	S	S	S	S	M

two samples of each of the three blends were quenched to each temperature, one held for 2 min and the other for 20 min before further quenching into iced acetone. Replicas were then made.

A comparison of the 2 and 20 min storage results (*Table 2*) shows that there are variations in segregation rate. At any given temperature the blends with the highest LPE content segregate the fastest, and for any composition, segregation is faster at lower temperatures; i.e. segregation is faster the further away from the coexistence curve.

Samples can be produced that are well segregated (by crystallizing isothermally at 126°C) or well mixed (by melting at 230°C for 20 min). If such samples are then both held at a second temperature, it can be checked that they both show the same phase behaviour. This is illustrated by *Figure 7*, the 12% blend was held at 230°C for 20 min, then quenched to 150°C and held there for 20 min before quenching into cold acetone. Compare the morphology seen in *Figure 7* with that shown in *Figure 6a*, where the blend had been crystallized at 126°C, held at 150°C for 20 min and then quenched. The two morphologies seen in *Figures 6a* and *7* are essentially the same.

Morphologies as an indication of the phase separation mechanism

The morphology of phase-separated blends should reflect the mechanism of phase separation. If LLPS is controlled by nucleation, then we should expect to observe spheres of one phase in a matrix of the other; if there is spinodal decomposition we might expect to

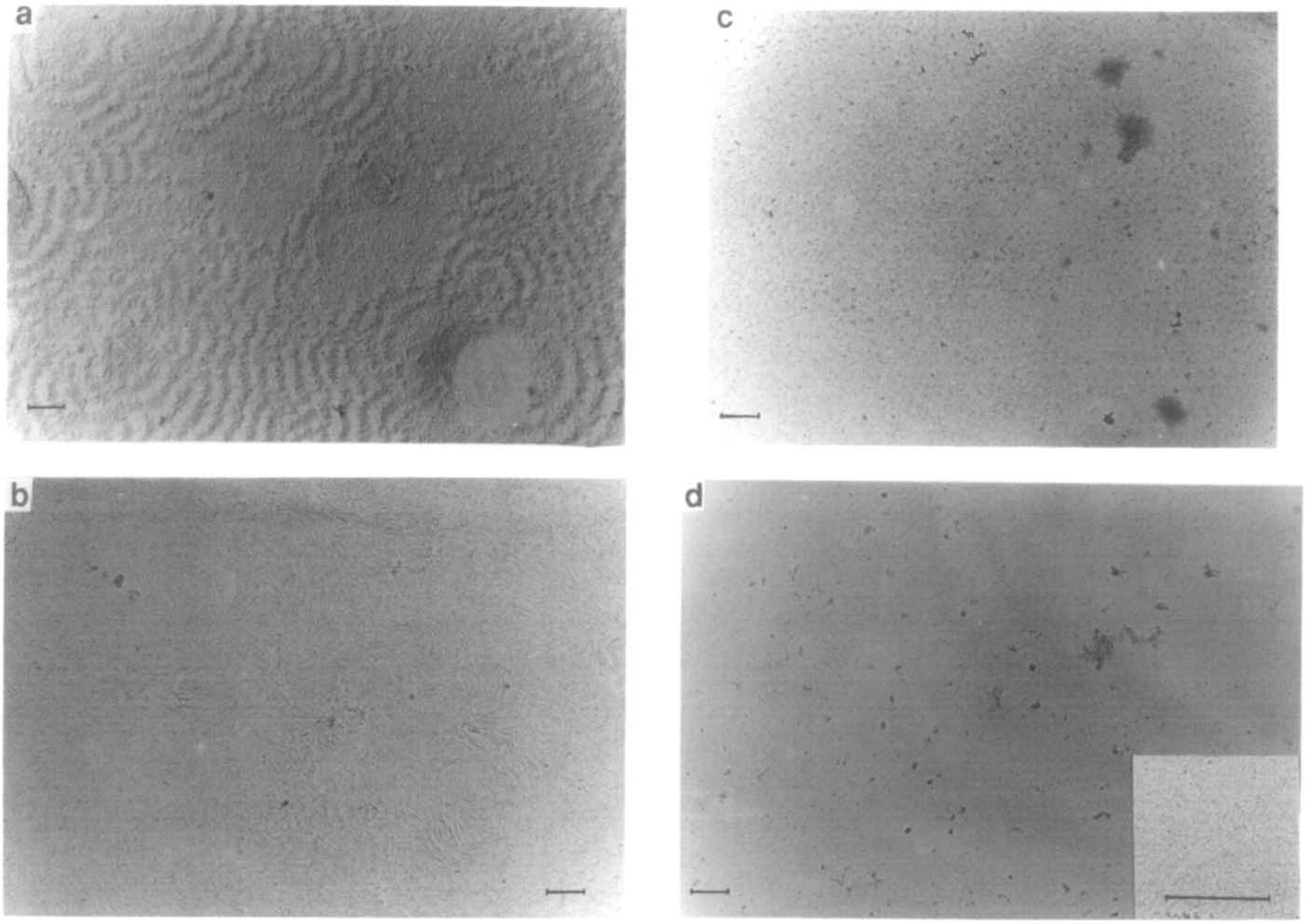

Figure 6 Transmission electron micrographs of surface replicas of 12% blends quenched from the melt. Blend quenched after 30 min at: (a) 150°C; (b) 170°C; (c) 190°C; (d) 230°C. Scale bar = 1 μm

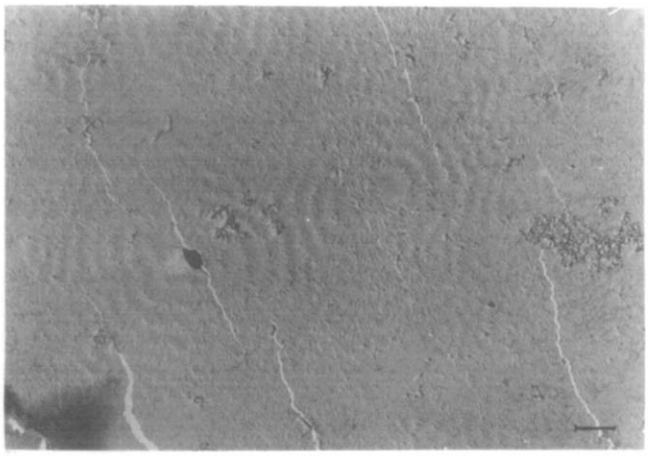

Figure 7 Transmission electron micrograph of surface replica of a 12% blend quenched from a melt which had been held first at 230°C for 20 min and then at 150°C for 20 min. Scale bar = 1 μm

observe a bicontinuous, fibrous network. During our studies, phase morphologies which answer each of these descriptions, have been observed.

An example of a phase morphology that could have arisen during spinodal decomposition is shown in *Figure 8a*, and one that could have arisen from nucleation in *Figure 8b*. In *Figure 8a* the two phases both appear to be continuous, as can be readily seen from the accompanying sketch outlining the two phases. In *Figure 8b* the LPE-rich phase is contained in approximately circular regions (shaded). The results we have obtained to date indicate that the demixing of 12% blends may be by the nucleation mechanism at 180°C and by the spinodal mechanism at 145°C. However, we have not yet obtained enough results at short segregation times to make any definite statement on the pattern of phase separation as a whole.

Parallel d.s.c. experiments looking at mixing and crystallization times

Very thin specimens of 1% blends previously crystallized at 126°C were placed in d.s.c. pans. Specimens were subjected to various heat treatments (as outlined below) and then examined in a Perkin Elmer DSC II heating at 10°C min^{-1}.

Several different sample preparation procedures were used. Some specimens were held at either 150 or 175°C for various times before quenching into acetone at its freezing point. Other samples were first held at 150°C (or 175°C) for 25 min, then at 122°C for various times before quenching into acetone at its freezing point.

The results are summarized in *Table 3*. When 1% blends had been held at 150°C, for any length of time, double d.s.c. peaks were obtained on reheating quenched specimens at 10°C min^{-1}. A typical d.s.c. trace is seen in

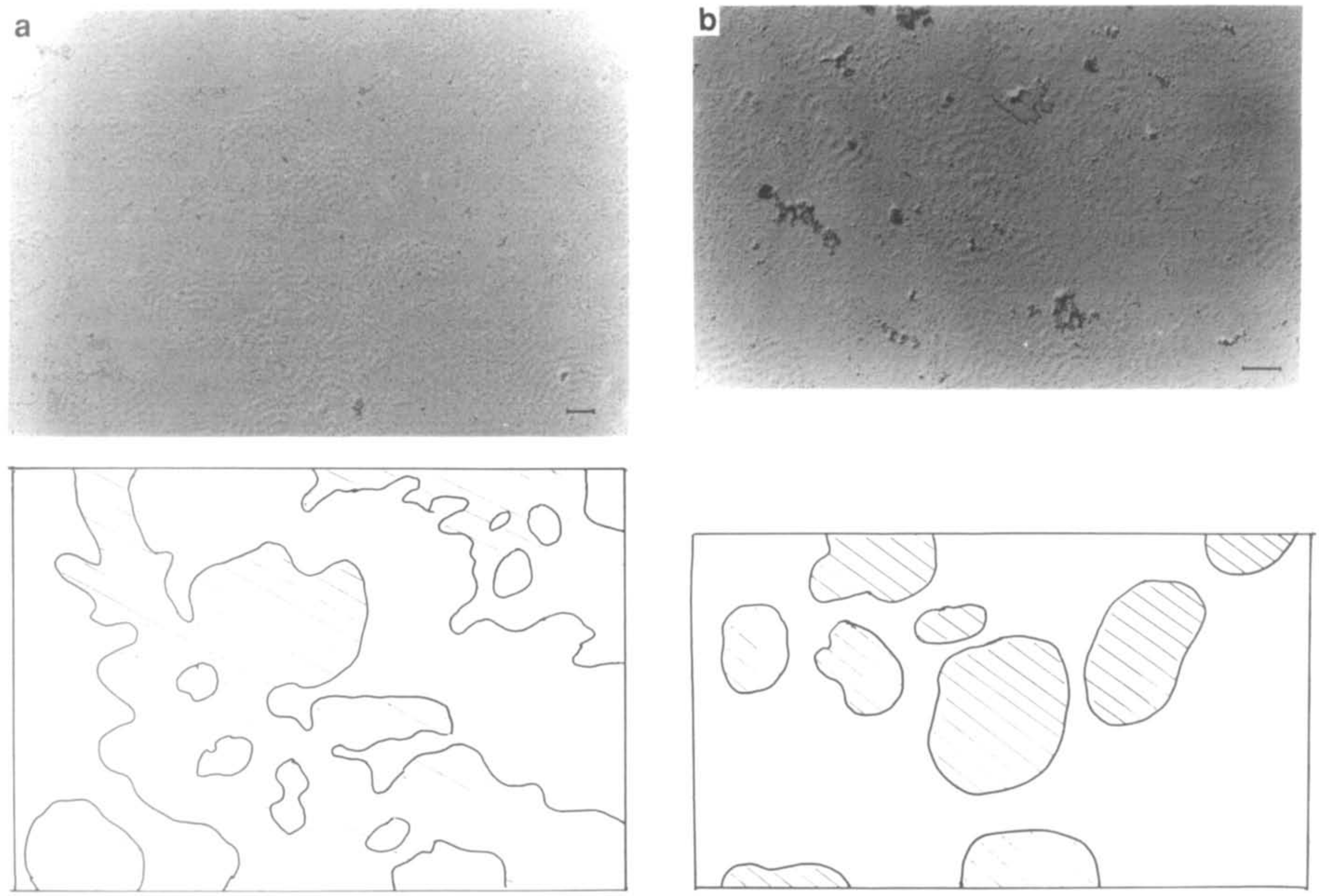

Figure 8 Transmission electron micrographs of surface replicas of 12% blends quenched from melts which show different segregation morphologies: (a) micrograph of an area whose appearance may indicate spinodal segregation. The sample had been held first at 230°C for 20 min and then at 145°C for 2 min; (b) micrograph of an area whose appearance may indicate nucleated segregation. The sample had been held first at 230°C for 20 min and then at 180°C for 4 min. For the sake of clarity, sketches are included of the two micrographs in which the phase-separated regions are outlined, with the LPE-rich domains shaded. Scale bar = 1 μm

Table 3 Summary of data from d.s.c. and TEM for 1% blends

	D.s.c. results			TEM results	
Sample preparation	Low melting peak (°C)	High melting peak	*Figure*	Morphology	*Figure*
Stored at 150°C then quenched	109	Broad peak up to 122°C	*9a*	Two types of lamellae both typical of quenched material	*3e*
Stored at 175°C for <20 min, then quenched		Result similar to *Figure 9a*; high temperature peak (reduces with time to look like *Figure 9b*)		Morphology much as in *Figure 3e* changing to *3f* over 20 min	
Stored at 175°C for >20 min, then quenched	109	No peak	*9b*	Single type of lamellae (quenched appearance)	*3f*
Stored at 150°C for 25 min, crystallized isothermally at 122°C	109	Sharp at 125°C (increasing to 127°C on storage)	*9c*	Groups of lamellar, LPE-rich crystals in BPE matrix	*3c*
Stored at 175°C for 25 min, crystallized isothermally at 122°C	109	Sharp at 125°C	*9d*	Isolated LPE-rich crystals in BPE matrix	*3d*

Figure 9a. However, when very thin film specimens were held at 175°C or above for times above 20 min, a single d.s.c. peak was obtained (*Figure 9b*). It could be shown that the single peak was not a product of degradation because a double peak was obtained again if, after storage at 175°C for 20 min, the temperature was reduced to 150°C for some time before quenching.

The 1% blend, mixed by holding at 175°C, appeared to segregate very quickly at temperatures between 140°C and 126°C. Although it was possible to obtain single

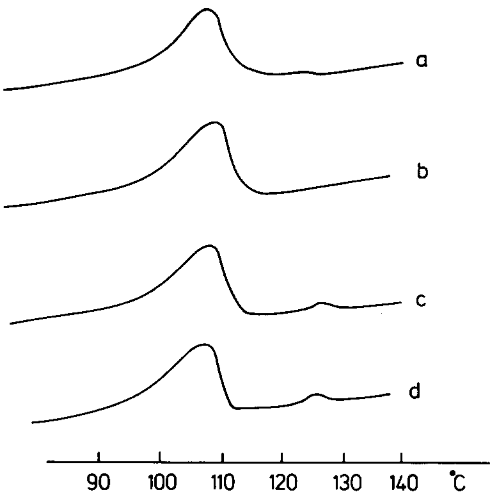

Figure 9 D.s.c. traces obtained by heating 1.5 mg samples of 1% blends at 10°C min^{-1} after preparation as follows: blend quenched after storage for 20 min at (a) 150°C; (b) 175°C; (c) 150°C followed by storage at 122°C overnight; (d) 175°C followed by storage at 122°C overnight

d.s.c. peaks on quenching very thin samples very quickly from 175°C into iced acetone, double d.s.c. peaks appeared on quenching less quickly, e.g. after quenching into oil at 122°C. Melts from 175 and 150°C both remixed if held at 122°C. The melt from 175°C remixed more quickly—presumably because the segregated LPE-rich domains were rather small having been produced during the quench. Typical times for remixing were 15 min for a blend previously held at 150°C and 7 min for one previously held at 170°C.

As explained above, crystallization and mixing times are very sensitive to temperature at ~ 122°C. It is possible to choose a temperature at which samples previously held in a segregated melt at 150°C do not have time to remix before crystallizing, but samples previously held in a mixed melt at 175°C (and slightly resegregated on quenching) do remix at 122°C before crystallization. Thus, it is possible to crystallize two groups of sample together—one (from storage in the melt at 150°C) crystallizing from a segregated melt and the other (from storage in the melt at 175°C) crystallizing from a mixed melt. In this experiment, d.s.c. indicates that the LPE-rich crystals crystallize significantly faster from the segregated melt compared with the mixed melt; crystallization times are very sensitive to exact crystallization temperature, one set of values obtained were 50 min for crystallization from a mixed melt and 30 min for crystallization from a segregated melt; at lower temperatures the times decreased, but the time to crystallize from the segregated melt was always significantly shorter.

Further, the LPE-rich crystals crystallized from segregated melts consistently show higher melting points than those crystallized from mixed melts when both were crystallized together in the same oil bath. If quenched immediately after crystallization both showed the same melting point, but when samples were held at the crystallization temperature for some 24 h after initial crystallization, the melting point of the LPE-rich material crystallized from the segregated melt was found to be up to 2°C higher than that of the LPE-rich material crystallized from the mixed melt.

We know, both from d.s.c. and from TEM, that when 1% blends are crystallized at 122°C after storage at 150°C they crystallize from a mixing, but still essentially segregated, melt. When they are crystallized at 122°C after storage at 175°C they crystallize from a mixed melt. TEM gives the additional information that the crystals from the segregated melt are seen to be grouped together (*Figure 3c*) whilst those from the mixed melt crystallize individually (*Figure 3d*). As a result we can suggest a reason why the melting points of the former (grouped) crystals are found to increase on long storage at 122°C whilst those of the latter (isolated) crystals do not. It has been observed that when lamellar crystals are well packed together they tend to thicken on annealing rather faster than isolated crystals[13]. Thus, we suggest that the higher melting points observed are caused by crystals having a greater thickness.

DISCUSSION

First, attention must be drawn to the advantages of this TEM experimental method. Although it is indirect, it gives clear results, which are in full agreement with those from other techniques. In references 1–4, particularly reference 3, we have shown the agreement between other experimental methods. In this work, the complete agreement with our d.s.c. results is clear, but the study of the replicas adds additional information to that which can be obtained by d.s.c.

The power of the TEM experimental method can be seen in the experiments concerning size changes on holding segregated 1% blends at 150 and 175°C. The decrease in size of the segregated regions during the first few minutes of storage at 150°C, contrasted with the increase on subsequent storage at 122°C or on holding at 175°C, is one of the clearest demonstrations of melt mixing and segregation that we have so far obtained.

We believe that the rapid decrease in size of the segregated domains of 1% blends, crystallized at 126°C and then held at 150°C, is a consequence of the crystal melting, as illustrated in *Figure 5*. Once the crystal is melted only a slight change in composition of the LPE-rich phase should be expected between 126°C and 150°C (if *Figure 1* is correct) and, consequently, little change in size of LPE-rich domains, as is observed. However, at 122 and 175°C complete mixing is expected for a 1% blend melt. We observe the LPE-rich domains getting larger, but less distinct, and eventually vanishing on storage at 175°C in accordance with this expectation (the mixing process is stopped by crystallization at 122°C). These results demonstrate, very elegantly, details of melt mixing and segregation.

It has been possible to show clearly that 20, 12 and 1% blends are mixed in the melt at high temperatures and segregated at lower temperatures. Note that the quenched, mixed, cocrystals of the 20% blend (*Figure 2a*) have a coarser texture than those of the quenched 12% blend (*Figure 6d*) which are, in turn, coarser than those of the quenched 1% blend (*Figure 3f*). This is expected from our previous work[3], where it was shown that the cocrystals obtained on quenching (under identical conditions) from mixed melts of higher LPE contents were progressively finer as the LPE content decreased. The quenched pure LPE gave the coarsest texture and the pure BPE the finest (see Figures 1 and 2 of ref. 3).

The coexistence curve obtained by this detailed study (indicated in *Table 1*) corresponds exactly with that obtained previously by other methods (Figure 1 from ref. 3). Further, the mixing/segregation process is reversible and the position of the coexistence curve, and the morphologies obtained, are the same on cooling from a mixed melt as on heating from a segregated melt (cf. *Tables 1* and *2* and *Figures 6a* and *7*). The fact that the phase boundary occurs in the same place on heating and cooling, with no hysteresis, indicates that the equilibrium phase boundary has been identified. The similarity of the morphologies obtained from samples which have never been fully mixed (*Figure 6a*) and those where LLPS occurred from a mixed melt (*Figure 7*) is striking. This similarity adds further evidence to our basic hypothesis that the morphology of rapidly quenched samples is characteristic of the melt itself and is independent of thermal history of the sample.

The potential of these morphological techniques to reveal details of the actual process of LLPS by following size changes with time in the melt permit further investigations into the mechanisms of phase separation itself. It should be noted that this is a very difficult system, where normal experimental methods, such as light scattering, cannot be used because of the great similarity between the physical properties of the two components of the blend, but it is possible to follow phase changes in surprising detail using the TEM method.

The times for segregation and remixing are indicated in *Tables 1* and *2* and by the d.s.c. results. Segregation times will be longer if the domain size is larger, but in our experiments we have carefully prepared our samples so that the domain size at the start of the experiment is of a known, standard distribution. It is found that mixing times are usually ~20 min, while segregation times vary between 20 min and a very short time. The segregation times are shorter where the storage temperature is further from the coexistence curve. The 1% blend seems to segregate unusually fast in the temperature range 140–126°C; it is not known why this is the case. (Indeed the 1% blend seems slightly anomalous in several ways. We suspect that in the 1% blend there is a manifestation of a type of behaviour that may require description by a ternary phase diagram for complete understanding[4].)

Some morphologies look as if they could have been the result of spinodal decomposition (*Figure 8a*) and some as if they were the result of nucleated decomposition (*Figure 8b*). For the 12% blend, the apparently nucleated morphology occurs at a higher temperature than the apparent spinodal morphology, as expected. However, there is some ambiguity with identification, since well advanced spinodal decomposition would be expected to look very like nucleated decomposition. Thus, a much more extensive study is needed of the development of morphology, especially at short times, before the full spinodal nucleation coexistence curve can be drawn with any certainty.

The question of spinodal or nucleation dominated segregation remains open, but we have been able to demonstrate the segregation and remixing of our particular LPE/BPE blends with remarkable clarity. We have obtained further evidence for LLPS in this system and have been able to demonstrate changes in the phase behaviour, both as a function of temperature and of time, in unexpected detail for 20, 12 and 1% blends.

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