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Ostwald ripening in polyethylene blends

Mary J. Hill* and Peter J. Barham
H.H. Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK
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The coarsening of phase-separated domains in a molten blend of two ethylene–octene copolymers has been observed by studying electron micrographs of rapidly quenched samples. Blends containing 10% of a 2 mol% ethylene–octene copolymer (with 90% of an 8 mol% ethylene–octene copolymer) were held in the melt for various times at a temperature at which phase separation was known to take place. The diameters of the regions rich in 2 mol% copolymer (the minority phase) were measured and shown to increase with the cube root of the time in the melt. It is argued that the coarsening occurs through the process of 'Ostwald ripening'. The results are similar to those previously reported by others on blends of polyethylene with hydrogenated polybutadienes and blends of polypropylene with ethylene–propylene rubbers. It is argued that the fact that coarsening is observed is strong confirmation that liquid–liquid phase separation does indeed occur in blends of linear with lightly branched copolymers. Hence, we conclude that the biphasic morphologies observed after quenching are not an artefact of crystallization but reflect genuine separation in the melt.

(Keywords: polyethylene; blends; Ostwald ripening)

INTRODUCTION

When a two-component system becomes unstable and begins to demix, small domains of one phase grow in a matrix of the other (provided of course that one of the components is dilute). The initial separation into domains may occur either by spinodal decomposition, or through a process of nucleation and growth. In any event, after some initial period the system will consist of an equilibrium concentration of small domains of one phase dispersed in a matrix of the other. Larger domains should grow, as time progresses, at the expense of smaller ones. This phenomenon of coarsening, or ripening, was originally described by Ostwald[1] and has been developed further by others[2–8]. The final equilibrium state of a blend which undergoes phase separation in the liquid state would consist of only two semi-infinite domains; however, in systems (such as polymers) with low diffusion constants this equilibrium is not approached within a realistic time-scale. In this paper we report on studies of the growth of phase-separated regions in molten polyethylene blends.

The phenomenon of ripening of phase-separated regions in polyolefin blends has been studied by Mirabella and co-workers[9–12]. They have developed experimental techniques in which the blends are held in the melt for various times to induce phase separation and then rapidly quenched to 'freeze in' the domains that have developed. The samples are then examined using electron microscopy and the sizes of the phase-separated domains measured. Mirabella and co-workers observe a steady growth of the larger phase-separated regions at the expense of smaller ones. In particular, they note that the mean size of the phase-separated domains increases with the cube root of time, in a manner characteristic of Ostwald ripening[1–8].

In a series of recent papers we have also used a morphological technique (studying rapidly quenched blends) to observe domains of apparently phase-separated material in a series of blends of polyethylenes with lightly branched copolymers[13–20]. We have interpreted our observations, of well separated domains of material containing more linear polymer in a matrix of material containing more branched polymer, as evidence for the occurrence of liquid–liquid phase separation in these systems. We have produced 'phase diagrams' of some 30 such systems. *Figure 1* shows a typical phase diagram, obtained using morphological techniques which are described in detail elsewhere (especially in refs 14 and 20). In one of our studies[15] we noted that the sizes of phase-separated domains observed in the blends, after quenching from the melt, increased with the time of storage in the melt. However, we have not previously made any detailed study of the rates at which the domains increase in size.

If our assertion that liquid–liquid phase separation occurs in the melt is correct then we should expect the phase-separated domains to increase in size during the time they are held in the melt, in exactly the same way that Mirabella has found in his similar systems. Indeed, we argue that if these systems do indeed exhibit Ostwald ripening, then the only explanation for the behaviour will be that they are phase-separating in the melt. In this paper we report studies of the increase in the sizes of the phase-separated domains in a blend of two homogeneous ethylene–octene copolymers containing 2 and 8 mol% octene (O(2) and O(8)) respectively; we have studied the

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* To whom correspondence should be addressed

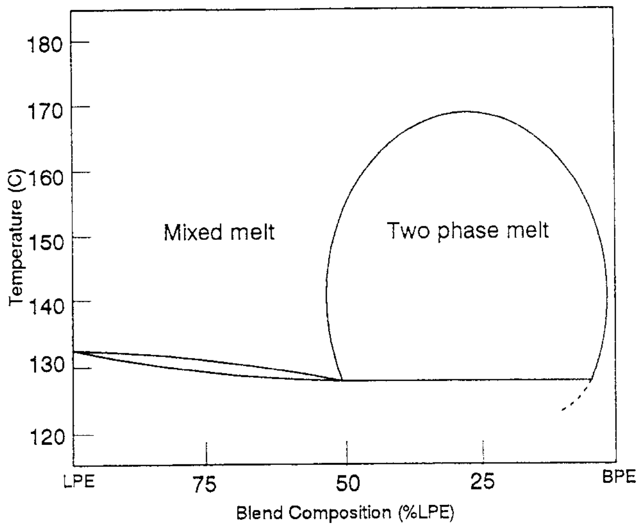

Figure 1 Schematic diagram showing the typical features of phase behaviour found in LPE/lightly branched BPE blend systems

phase behaviour of this system at short times in detail previously[18].

EXPERIMENTAL

The polymers used were two near-random octene copolymers, specially prepared for our earlier work by DSM[17]. The copolymers were blended in solution, by dissolving together in xylene and then precipitating rapidly by tipping into cold non-solvent. The details of this process have been described elsewhere[14]. For ripening experiments we used a blend containing 10% of the 2 mol% octene copolymer ($M_w = 51\,\mathrm{kg\,mol^{-1}}$, $M_w/M_n = 2.2$) with 90% of the 8 mol% octene copolymer ($M_w = 43\,\mathrm{kg\,mol^{-1}}$, $M_w/M_n = 2.0$), where M_w and M_n are the weight- and number-average molecular weights respectively; in our nomenclature this is termed a 10% blend.

After the blend had been harvested and dried, portions were placed between two thin glass cover slips and wrapped in thin aluminium foil. All samples were held in a silicone oil bath at 180°C for 30 min. Samples were then treated as follows. One sample was directly quenched from 180°C into acetone at its freezing point. A second sample was held at 180°C for a further 3 h before quenching. The remaining samples were transferred rapidly into a second oil bath at 137°C. Separate samples were subsequently quenched from 137°C into acetone at freezing point 1, 8, 27, 64, 125 and 225 min after transfer from the oil bath at 180°C. In a separate experiment we found that the time taken for a typical sample to reach 140°C, after transfer from an oil bath at 180°C to one at 137°C, was about 2 min. Accordingly we have taken the ripening times of the samples described above as 0, 6, 25, 62, 123 and 223 min.

In addition a further sample was prepared to check for reversibility in any ripening effects. This sample was held at 137°C for 240 min (after 30 min at 180°C) and was then reheated to 180°C for 30 min before being transferred rapidly into a second oil bath at 137°C where it was held for 8 min (corresponding to a ripening time of 6 min) before being quenched into acetone at freezing point.

After quenching, all samples were washed and used to make surface replicas suitable for transmission electron microscopy (TEM). Permanganic etching and replication were employed[21], using the Bristol recipe[22]. The replicas were examined using a Philips 301 TEM, operating at 80 kV. At least eight micrographs of each sample were taken; more were taken of the samples which had been ripened the longest because there were fewer separated domains per micrograph.

Both copolymers in the blends used for this study crystallize on quenching from the melt. The two crystal types can, however, be distinguished. We have shown in the past (e.g. refs 13–15, and, for octene copolymers, refs 17 and 18) that, where phase separation between less and more branched polyethylenes has taken place in the melt, groups of thicker crystals (rich in less branched polymer) in a matrix of smaller and thinner crystals (rich in more branched polymer) are observed. TEM hot-stage experiments have shown that LPE-rich crystals remain stable over a range of temperatures after BPE-rich crystals have melted[14]. In the 2 mol%–8 mol% octene copolymer blend system, crystals rich in 2 mol% octene copolymer are found to be considerably thicker (and usually larger in other dimensions) than those containing 8 mol% octene copolymer[18]. In 10% blends the phase rich in 2 mol% octene copolymer is the minority phase, and, accordingly, we measured the sizes of groups of thick crystals that were clearly visible in a matrix of thinner crystals.

The negatives were examined and phase-separated areas identified and measured. Between 85 and 300 areas were measured for each storage time. Some pictures were printed and the O(2)-rich phase-separated areas identified, cut out and weighed to get a measure of the volume fraction of this dispersed phase. The further treatment of the results obtained is detailed in the Results section.

EXPECTATIONS OF OSTWALD RIPENING

The process of Ostwald ripening consists of the growth of larger domains at the expense of smaller domains to reduce the total surface energy in a demixed system. Several authors have examined the problem and have, from their different perspectives, come up with similar results concerning the rate of growth of the domains, and the overall shape of the distribution of domain sizes. The various models and theories have been reviewed by Voorhees[6]; the most relevant results are summarized below.

The growth rate of the domains may be written in the form:

$$\bar{r}(t)^3 = \bar{r}(0)^3 + Kt \qquad (1)$$

where $\bar{r}(t)$ and $\bar{r}(0)$ are the number-average domain radii at times t and $t = 0$ (where zero time is defined as the time when the measurement of long-term coarsening begins) and K is a constant which, in the simplest theories[2], is independent of the volume fraction of the coarsening phase.

RESULTS

From the phase diagram of *Figure 2* it is apparent that a 10% blend of O(2) with O(8) should be expected to be mixed in the melt at 180°C but to exhibit phase

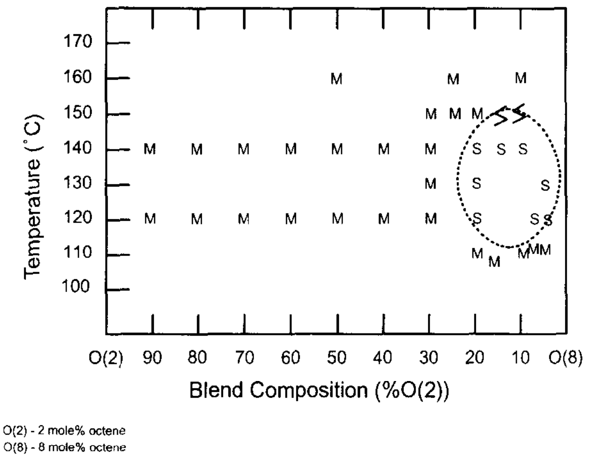

Figure 2 The 'phase diagram' established for melts of O(2)/O(8) blends[18]. M indicates a mixed melt (one morphological type found in rapidly quenched samples). S indicates a separated melt (two distinct morphologies found in rapidly quenched samples). $\lessgtr$ indicates an ambiguous result

Table 1 Mean diameters of domains in samples stored at 137°C

Time at 137°C (min)	Mean long diameter (μm)	S.d.	Mean short diameter (μm)	S.d.
6	0.36	0.10	0.24	0.13
25	0.67	0.16	0.50	0.27
62	0.77	0.19	0.57	0.28
123	0.97	0.20	0.75	0.29
223	1.27	0.29	0.97	0.35

separation in the melt at 137°C. We show, in *Figure 3*, electron micrographs illustrating the phase behaviour, previously determined for blends of O(2) with O(8)[18] and observed again in the present work. *Figure 3a* shows a 10% blend quenched from 180°C, and *Figures 3b* and *c* 10% blends quenched from 137°C after different times. It can be seen from *Figure 3a* that 10% blends quenched from 180°C after 30 min show a single-phase morphology, all the lamellae present have the same thickness; blends stored for 3.5 h at 180°C before quenching looked exactly the same. The sample quenched after 1 min in the oil bath at 137°C also has a single morphology (this sample would not have cooled to 137°C before it was quenched). However, as may be seen from *Figure 3b*, blends quenched from 137°C an estimated 6 min after reaching that temperature, showed large numbers of small phase-separated domains—regions where groups of thicker lamellae can be seen in a matrix of thinner lamellae. After longer storage at 137°C the blends appeared to be phase-separated. The O(2)-rich domains (regions of thicker lamellae) could be seen, even on a casual inspection, to increase in average size (and decrease in number) with storage time; one example is shown in *Figure 3c*. The phase-separated domains were often not circular but appeared elliptical in the micrographs; we believe this distortion may be introduced on crystallization. Measurements were made of both the long and short axes of the phase-separated domains. The results are summarized in *Table 1*. *Figure 4* shows histograms of the distributions of domain diameters measured after various times in the melt at 137°C. Note that the smallest domain size that could be unambiguously resolved was 0.15 μm; any smaller domains would be missed. Note also that at longer

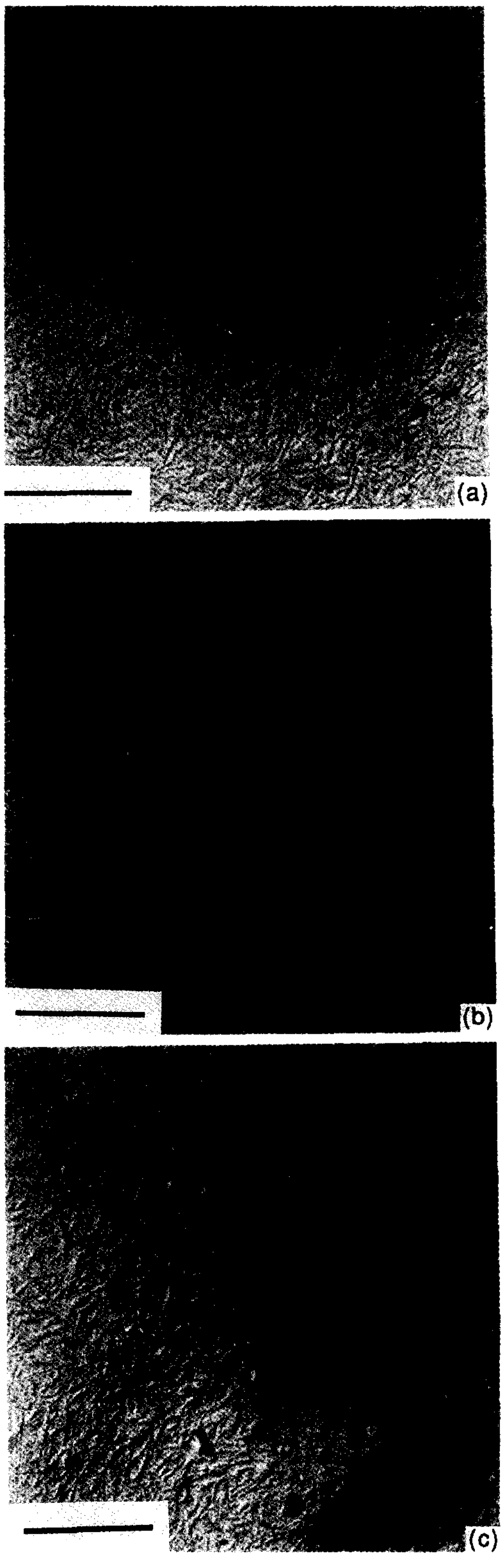

Figure 3 Transmission electron micrographs of surface replicas of 10% blends of O(2)/O(8). The small black dots are etching debris. Scale bars represent 1 μm. (a) Quenched after 30 min at 180°C. All the crystals in this micrograph are of the same thickness, indicating a mixed melt before quenching. (b) Quenched after 30 min at 180°C, followed by 6 min ripening at 137°C. Numerous small regions of thick lamellae are visible (typically the regions are 0.5 μm across, there are several such regions in the top left). This indicates that the sample contains small domains of phase-separated material. (c) Quenched after 30 min at 180°C, followed by 3.75 h at 137°C. A large group of thick lamellae is clearly visible near the centre, indicating that this sample contains large domains of phase-separated material

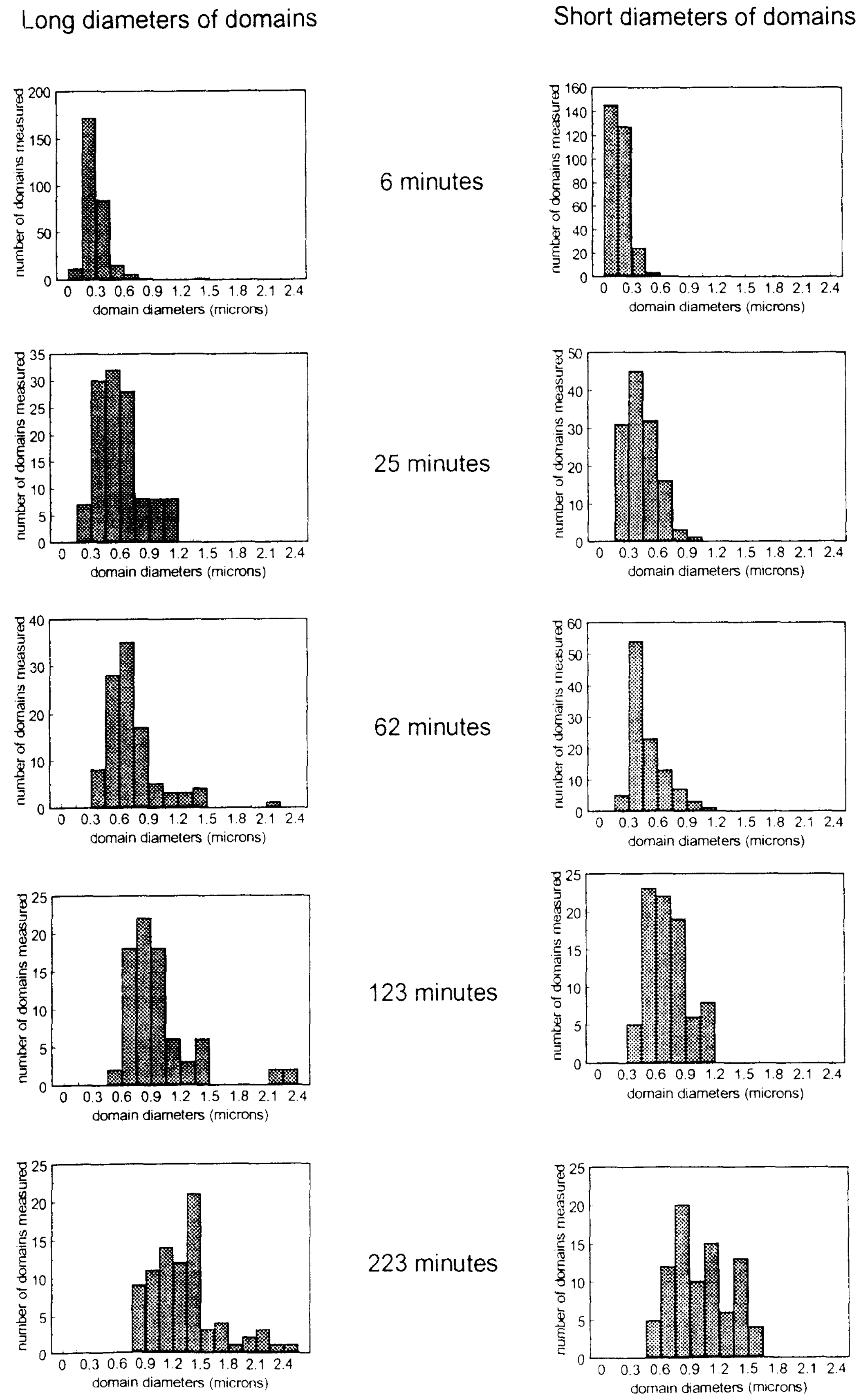

Figure 4 Histograms showing the spread of diameters of phase-separated domains after various ripening times at 137°C

times the distributions (especially the long diameters) begin to become bimodal. This is, we believe, due to the accidental merging of pairs of ripening domains; in these cases much larger ratios of long to short diameters were found. Accordingly we have ignored these data when calculating the means of the distributions.

If the data in *Figure 4* are fitted to Equation (1), a good fit is obtained (details of the slopes and intercepts are given in *Table 2*). We find that the constant $\bar{r}(0)$ is, within experimental error, zero. In *Figure 5* the number-average diameters (both larger and smaller) of the dispersed domains are plotted as a function of the cube root of the storage time in the melt. It is immediately clear that the relationship is linear, within experimental error. To compare our results with those of Mirabella a correction must be applied for the fact that the diameters are random cuts through three-dimensional objects. For simplicity, we shall use the same correction (multiplying by $4/\pi$) to the slope of the lines through the data in *Figure 5* as that used by Mirabella. This correction assumes that the measurements are from random cuts through spherical objects; the error introduced by the fact that, in our case, the domains are not spherical will remain unimportant providing the domains are ellipsoids with small eccentricity (in our measurements the eccentricity is typically 1.2). The corrected slopes are shown in *Table 3*. For ripening at 137°C we find a slope of 0.053 μm s$^{-1/3}$ for the short diameters and 0.065 μm s$^{-1/3}$ for the long diameters. Mirabella reported a slope of 0.0727 μm s$^{-1/3}$ for his analogous plot for a PP/EPR system[9] and 0.0336 μm s$^{-1/3}$ for a HDPE/HPB system[12].

The fractional areas of O(2)-rich LLPS material were assessed from the micrographs. In the cases that were measured accurately (after 6 and 223 min of ripening) the fractional area was found to be 12 ± 2%, indicating a volume fraction of the O(2)-rich phase of 12%. It is important to note that there is little, if any, change in the amount of the dispersed phase; again this is consistent with the interpretation of Ostwald ripening.

In addition to the experiments described above we also studied, in much less detail, the ripening of the blend at 142°C. The results are shown in the form of a plot of the mean diameters (corrected for random sections) as a function of the cube root of time in the melt at 142°C in *Figure 6*. The corrected slopes of these lines are 0.038 μm s$^{-1/3}$, for the short diameters and 0.067 μm s$^{-1/3}$ for the long diameters.

Finally it should be noted that the sample that was melted by holding at 180°C for 30 min, then quenched to 137°C and held for 240 min (when it would have had a morphology of a few large domains), then reheated to 180°C for 30 min and finally ripened at 137°C for 6 min, had the same morphology (many small domains) as samples prepared more directly by melting at 180°C for 30 min and then ripening at 137°C for 6 min.

DISCUSSION

Interpretation of the results as being due to phase separation in the melt

Before we can proceed to any analysis of our results we should first ensure that the domain structure observed in the solid samples after quenching is in fact due to a process of liquid–liquid phase separation in the melt and is not an artefact introduced during crystallization. It could be (and in one case[23] has been) argued that such separation can occur on crystallization from a mixed melt. We have previously countered such arguments by noting that the sizes of the phase-separated domains observed are large compared with the distances that molecules can diffuse during crystallization[16]. In addition, the phase morphology depends on the melt temperature, it being possible to produce a mixed morphology on quenching a blend from a high temperature but a separated morphology on quenching from a lower temperature[13,15].

The present results, which clearly show the growth of the phase-separated domains during storage in the melt, are a further strong counterargument. Indeed, we contend that the observation of any coarsening is unequivocal evidence of liquid–liquid phase separation,

Table 2 Results of fitting data on storage to Equation (1)

Storage temperature (°C)		Correlation coefficient	$\bar{r}(0)^3$	K
137	Long axes	0.980	−0.028	0.0089 ± 0.0007
	Short axes	0.982	−0.024	0.0040 ± 0.0003
142	Long axes	0.938	0.23	0.013 ± 0.002
	Short axes	0.814	0.18	0.006 ± 0.002

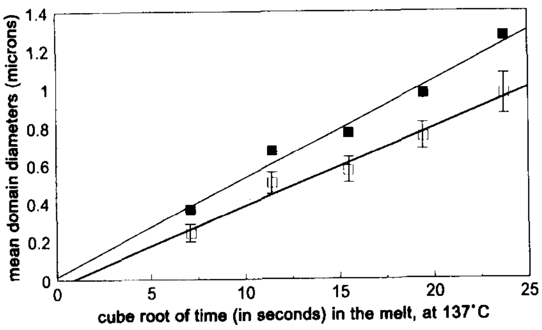

Figure 5 Dependence of average smaller diameters (□) and average larger diameters (■) on the cube root of time (s) for 10% O(2)/O(8) blends held at 180°C for 30 min and then quenched to 137°C. Error bars, corresponding to one standard deviation, are shown on the small diameter points. The scatter is exaggerated because we have taken random cuts through the domains

Table 3 Slopes of lines showing dependence of domain size on cube root of ripening time

Storage temperature (°C)		Uncorrected slope (μm s$^{-1/3}$)	Corrected slope (μm s$^{-1/3}$)
137	Long axes	0.051	0.065
	Short axes	0.041	0.053
142	Long axes	0.053	0.067
	Short axes	0.030	0.038

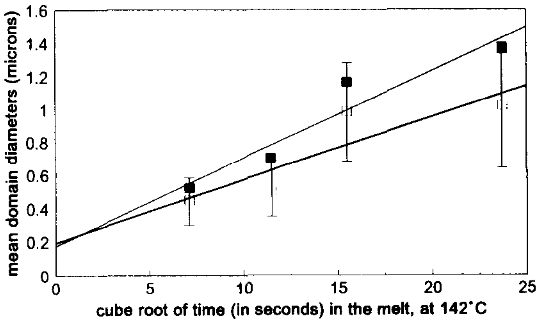

Figure 6 Dependence of average smaller diameters (□) and average larger diameters (■) on the cube root of time (s) for 10% O(2)/O(8) blends held at 180°C for 30 min and then quenched to 142°C

and that the fact that the coarsening evolves as expected by the theories of Ostwald ripening further strengthens the argument.

There remains one slight doubt that could be raised. It could be argued that there are some residual 'seeds' in the melt which act as nuclei for the growth of regions of high O(2) content crystals on crystallization from a mixed melt. The argument would then run that the number of such seeds remaining in the melt could decrease with the storage time in the melt, so accounting for the apparent increase in the sizes of the phase-separated domains in the quenched samples. However, we have performed an experiment which shows that this is not the case. We prepared one sample by first holding in the melt at 180°C for 30 min, then at 137°C for 240 min; samples quenched after this time would have a phase morphology of a few large domains. We then heated this sample directly from 137°C back to 180°C. At this temperature we have shown that the previously separated phases will mix within 30 min. The sample was then quenched back to 137°C and ripened there for 6 min before quenching into acetone at freezing point, prior to examination of the morphology. If the origin of the two phases was due to crystallization from a mixed melt and the increase in size a result of a reduction in the number of nuclei during storage in the melt, then this sample should show a morphology close to that obtained from samples stored at 137°C for long times and immediately quenched. Conversely, if we are correct, and the phase morphologies that we observe truly represent the structure in the melts prior to crystallization, then this sample should have a morphology closely similar to that of the samples ripened at 137°C for 6 min and immediately quenched (i.e. a large number of small domains). As noted in the Results section above, such a sample does indeed have a morphology of many small domains; thus the possible 'seeding' explanation can be eliminated.

Shapes of, and amount of material in, the phase-separated domains

Having demonstrated that the melts are separated into two distinct phases we realize that the smaller domains should in fact be spherical in shape. However, in the quenched samples the domains tend to have an elliptical appearance; this requires some discussion. We note that as the domains grow larger so they tend to become less anisotropic.

It is well known that when polymers crystallize from the melt they usually grow spherulites. At the centre of the spherulites is a 'sheaf' of lamellae which grow around a central screw dislocation and splay out and branch as they grow larger. Thus we expect the crystals that grow from the comparatively small phase-separated domains of O(2)-rich material to consist of such anisotropic sheaves; the shapes of the phase-separated domains may be distorted, by crystallization, from drops that were spherical in the melt.

The measurements of the amount of material in the O(2)-rich phase indicate that there is a volume fraction of this phase of about 12% at 137°C. If we were to assume that the phase diagram for the O(2)/O(8) system determined previously[18] and reproduced here as *Figure 2* represented a true binary phase diagram, then we could calculate the expected volume fraction of the O(2)-rich phase according to the lever rule. Making this assumption we would expect the volume fraction of the O(2)-rich phase to be some 30%. The fact that, in practice, we find a much lower volume fraction should not be a surprise since we are well aware that the components of our blend are not fully homogeneous. There is a distribution of molecular weights and of branch content in both of the polymers. Accordingly, the phase diagram of *Figure 2* is strictly a 'cloud point curve' indicating the compositions of blends in which we may expect to find phase separation, but not giving any information on the compositions of the separated phases.

Comparison with the results of Mirabella

Mirabella and his co-workers have studied ripening in blends of PP/EPR[9–11], and in blends of HDPE/HPB[12] using TEM of quenched materials. Their results are generally similar to ours but differ in certain details. It is clear that ripening takes place in all the systems studied. The diameters of the observed LLPS regions increase with the cube root of the storage time, and at rates of the same order of magnitude in all cases. Mirabella gives coarsening rates of 0.0336 μm s$^{-1/3}$ for his HDPE/HPB system and 0.0727 μm s$^{-1/3}$ for his PP/EPR system. These data should be compared with our results of between 0.038 and 0.067 μm s$^{-1/3}$ for the O(2)/O(8) blend system.

The rate of ripening can, in principle, give information about diffusion rates and surface energies. The rate constant K in Equation (1) is given (in the simplest theories) by

$$K = \frac{64 D \gamma \phi_e V_m}{9RT} \tag{2}$$

where D is the diffusion constant for the matrix phase, γ is the interfacial energy between the phases, V_m is the molar volume of the minor phase and ϕ_e is the molar fraction of the minor phase in the matrix phase, R is the gas constant and T the temperature. Mirabella[12] has made measurements of K in a blend of HPB with HDPE to compare with theoretical estimates deduced from calculations of D and γ. In these studies he found good agreement between calculated and measured values of K. We can make reasonable estimates of all the constants in Equation (2) (except D and γ). These estimates are generally similar to those used by Mirabella so that it is not surprising that we find similar slopes.

The main difference between our morphological observations and those of Mirabella is that Mirabella's phase-separated regions are spherical whilst ours are anisotropic. It is not surprising that Mirabella's domains, which do not crystallize due to the higher branch contents, should remain spherical after quenching. However, as we have explained above, it is possible that a distortion of the shapes of initially spherical domains is introduced by crystallization into lamellar structures.

CONCLUSIONS

First, and foremost, we have confirmed that phase separation occurs in melts of a system containing two octene copolymers of differing octene content by finding that the phase-separated domains in the system coarsen during storage in the phase-separated region of the phase diagram. Further, since the LLPS regions grow in such a way that the diameter of the separated region is proportional to the cube root of the time for which separation has been taking place, we conclude that the process of coarsening corresponds to Ostwald ripening.

In the octene copolymer blend system the rate of ripening is faster at 142°C than at 137°C, suggesting that at 142°C the system has a greater driving force for phase separation.

We believe that this coarsening is strong evidence for liquid–liquid phase separation. If, as has been suggested[23], the phase separation that we observe merely occurred on crystallization (from a mixed melt) there would be no reason for the LPE-rich regions to change in size with time of storage in the melt. The fact that the domain size observed on quenching increases with time of storage in the melt indicates that the melt was demixed.

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REFERENCES

1 Ostwald, W. *Z. Phys. Chem.* 1901, **37**, 385
2 Lifshitz, I. M. and Slyozov, V. V. *J. Phys. Chem. Solids* 1961, **19**, 35
3 Wagner, C. *Z. Elektrochem.* 1961, **65**, 581
4 Brailsford, A. D. and Wynblatt, P. *Acta Met.* 1979, **27**, 489
5 Glicksman, M. E. and Voorhees, P. W. Unpublished results (quoted in Ref. 6)
6 Voorhees, P. W. *J. Stat. Phys.* 1985, **38**, 231
7 Marquesee, J. A. and Ross, J. *J. Chem. Phys.* 1984, **80**, 536
8 Tokuyama, M. and Kawasaki, K. *Physica* 1982, **123A**, 386
9 Mirabella, F. M. Jr *Am. Chem. Soc. PMSE Prepr.* 1992, **Fall**, 371
10 Mirabella, F. M. Jr in 'New Advances in Polyolefins' (Ed. T. C. Chung), Plenum, New York, 1993, p. 225
11 Mirabella, F. M. Jr *J. Polym. Sci., Polym. Phys. Edn* 1994, **32**, 1205
12 Mirabella, F. M. Jr and Barley, J. S. *J. Polym. Sci., Polym. Phys. Edn* 1994, **32**, 2187
13 Barham, P. J., Hill, M. J., Keller, A. and Rosney, C. C. A. *J. Mat. Sci. Lett.* 1988, **7**, 1271
14 Barham, P. J., Hill, M. J., Keller, A. and Rosney, C. C. A. *Polymer* 1991, **32**, 2716
15 Hill, M. J. and Barham, P. J. *Polymer* 1992, **33**, 4099
16 Hill, M. J. and Barham, P. J. *Polymer* 1992, **33**, 4891
17 Hill, M. J., Barham, P. J. and van Ruiten, J. *Polymer* 1993, **34**, 2975
18 Thomas, D., Williamson, J., Hill, M. J. and Barham, P. J. *Polymer* 1993, **34**, 4919
19 Hill, M. J. and Barham, P. J. *Polymer* 1994, **35**, 1802
20 Hill, M. J., Barham, P. J. and Organ, S. J. *Thermochim. Acta* 1994, **238**, 17
21 Olley, R., Hodge, A. and Bassett, D. C. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 627
22 Norton, D. and Keller, A. *J. Mater. Sci.* 1984, **19**, 447
23 Alamo, R. G., Londono, J. D., Mandlekern, L., Stehling, F. C. and Wignall, G. D. *Macromolecules* 1994, **27**, 411

Note added in proof

Since submitting this paper we have seen a publication by B. Crist and A. R. Nesarikar (*Macromol.* 1995, **28**, 890) which reports on ripening in blends of linear polyethylene with highly branched polyethylene copolymers. The effects they report are similar to those we report in this paper.