polymer papers

Ambiguities in the interpretation of small-angle neutron scattering from blends of linear and branched polyethylene

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This paper describes the difficulties of interpretation of small-angle neutron scattering data from blends of linear with lightly branched polyethylenes. The expected 'phase diagram' for the blend system was determined using indirect techniques, i.e. differential scanning calorimetry and transmission electron microscopy. Two different blends have been examined by neutron scattering at temperatures well above the melting point of both components. The neutron scattering data from one blend (mixed according to the 'phase diagram'), containing 50% linear deuterated material and 50% branched polymer, showed it to be demixed. The phase sizes stayed constant at around 23 nm over 36 h. The scattering from the other blend (demixed according to the 'phase diagram'), containing 10% linear deuterated material and 90% branched polymer, could be interpreted in two different ways. The data are consistent with a homogeneously mixed blend, but can equally well be interpreted as coming from a system which is phase-separated with a large domain size, as seen in the electron micrographs. Crown copyright © 1996 Published by Elsevier Science Ltd.

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INTRODUCTION

The question of whether blends of linear polyethylenes with lightly branched polyethylenes (polyethylenes with less than about 50 short branches per 1000 backbone carbon atoms) can exhibit any liquid–liquid phase separation in the melt has become somewhat controversial in the recent literature. Most of the experimental evidence for any phase separation comes from indirect experiments in which rapidly quenched blend samples are studied in the solid state. The problem with obtaining direct experimental evidence for, or against, phase separation lies in the close similarity in physical properties of the two components of such blends. In particular, the refractive indices of linear and lightly branched polyethylenes are so close to one another that no light scattering experiments are possible. At first sight, neutron scattering experiments, using blends of a linear deuterated polymer with a hydrogenous branched polymer, should provide a way to investigate phase separation directly in the melt. However, as we shall show, there can be considerable ambiguities in the interpretation of the data from such experiments.

Several authors have recently investigated polyethylene

and blends of polyethylenes using techniques including neutron scattering[1-14]. Hydrogenous (HPE) and deuterated (DPE) polyethylenes are usually mixed together in various proportions and the scattering observed. The objectives have included determining the radii of gyration of the molecules, determining the χ parameter for interactions between HPE and DPE and studying the possibility of phase separation. In general any phase separation found has been interpreted as being due to isotope effects. Most of this work has only been concerned with linear polyethylenes.

In one particular paper[14] neutron scattering from blends of linear polyethylenes with lightly branched polyethylenes was studied. In this paper, Alamo *et al.* take issue with a body of work[15-33], mostly by ourselves, in which it has been argued, from indirect evidence, that such systems can undergo liquid–liquid phase separation in the melt at certain temperatures and blend compositions. Alamo *et al.*[14] suggested that their results demonstrated that the blends they studied were mixed in the melt at all compositions and temperatures, with any demixing being attributed to isotope effects introduced by the fact that the linear polyethylenes they used were deuterated.

In our earlier studies[15-20] we argued that the two distinct morphologies found in rapidly quenched blends of linear with lightly branched polyethylenes arose from some liquid–liquid phase separation in the melt prior to

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quenching. One of the most notable features of these samples was that the two morphologies were found in separate regions of the samples, with the regions typically being several micrometres across. The neutron scattering used by Alamo et al.[14] would, as they admit, be insensitive to phase separation on such a large distance-scale.

In this present paper we report on some neutron scattering experiments, similar to those of Alamo et al., that we have recently performed. In general, our results are in good agreement with those of Alamo et al. However, we show the data can be interpreted as being due to scattering from a melt consisting of two distinct phases, of sizes which are consistent with our indirect observations. In addition to the neutron scattering experiments, we also determined the 'phase diagram' of the same deuterated linear polyethylene (DLPE)/ hydrogenous branched polyethylene (BPE) blend system using indirect methods. Of the two blends studied by neutron scattering, one should have been fully mixed in the melt by our criteria, and the other should have been biphasic.

We found, in common with Alamo et al., that there is strong evidence for inhomogeneities in a 50:50 (DLPE: BPE) blend on a scale of around 40 nm (this sample, by our indirect methods, would be expected to be mixed in the melt). We further found that the size of the inhomogeneities did not change on prolonged storage in the melt.

The scattering from the 10:90 (DLPE:BPE) blend which (by our indirect methods) we would have expected to be separated into two distinct phases, namely domains of linear-rich material of diameter greater than $3\,\mu$m in a matrix of branched-rich material, can be fitted to the random phase approximation (RPA). However, this is not unambiguous evidence for the melt being homogeneous. The data may be just as easily interpreted as being due to a biphasic melt with a large phase size, as they are to a homogeneous melt.

THEORETICAL BASIS FOR THE INTERPRETATION OF THE NEUTRON SCATTERING DATA

It is well known that the scattering of a homogeneously mixed blend containing two kinds of molecules, A and B, can be calculated by using the random phase approximation (RPA)[34-36]. In the case where A and B have the same monomeric volume, the model function will be:

$$k_N \cdot \left(\frac{d\Sigma}{d\Omega}\right)^{-1} = \frac{1}{N_A \Phi_A S_A(q)} + \frac{1}{N_B \Phi_B S_B(q)} - 2\chi \quad (1)$$

here, $(d\Sigma/d\Omega)$ is the coherent cross-section, k_N is a constant and is defined by:

$$k_N = N_0 \cdot (b_A - b_b)^2 \quad (2)$$

with N_0 being the number of monomers per unit volume and b_i the scattering lengths of the different kinds of molecules. In equation (1), χ is the Flory–Huggins interaction parameter, N_A and N_B represent the degrees of polymerization and ϕ_A and Φ_B are the volume fractions of A and B in the blend; $S_i(q)$ is the single chain structure factor of each species. For random coil polymers; $S_i(q)$ is given by the Debye function[37,38], as

follows:

$$S_i(q) = \frac{2[R_{gi}^2 q^2 + \exp(-R_{gi}^2 q^2) - 1]}{R_{gi}^4 q^4} \quad (3)$$

where R_{gi} is the radius of gyration of the species A or B. This model described the scattering of a homogeneous mixture of two different molecules, where χ is below a value χ_{spin}[34], which gives the phase boundary of the stability region of the blend. This parameter is given by the following:

$$\chi_{spin} = \frac{1}{2}\left(\frac{1}{N_A \Phi_A} + \frac{1}{N_B \Phi_B}\right) \quad (4)$$

The above equation provides a critical value of χ for spinodal decomposition. If phase separation should occur through a nucleation and growth process then the critical value of χ will be reduced. For a polydisperse polymer blend system it is not a simple matter to calculate this critical χ.

If the blend is not homogeneous, but is demixed in two separate phases of random shape and size, the resulting scattering is usually described by the Debye–Bueche model[39-42], as follows:

$$\frac{d\Sigma}{d\Omega} = \frac{k\langle\eta\rangle^2 a_c^3}{(1 + a_c^2 q^2)^2} \quad (5)$$

where k is a constant, which depends on the radiation used and $\langle\eta\rangle^2$ represents the fluctuation of the scattering power of the system; a_c is the Debye–Bueche correlation length and can be regarded as a measure of the domain size. In concentrated systems the domain size is better represented by the average chord length l_c, which can be calculated from the correlation length and the volume fraction x_i of each phase by using the following:

$$l_{ci} = a_c/(1 - x_i) \quad (6)$$

However, if the sizes of the domains in a demixed blend are large compared with the scattering vector, i.e. $l_c \gg 1/q$, then the scattering within each phase should not be neglected. The simplest model to describe the total scattering (I_{tot}) of such a blend is obtained by considering each of the phases as scattering independently according to the RPA. A term corresponding to the Debye–Bueche model is added which represents the scattering resulting from the presence of two different phases in the system. Accordingly, if the blend demixes into two phases, 1 and 2, having the volume fractions x and $1 - x$, respectively, and if it is assumed that each phase i contains both kinds of molecules having the volume fractions Φ_{iA} and Φ_{iB} and a χ-parameter χ_{iAB}, the scattering of each phase $I_i(\Phi_{iA}, \Phi_{iB}, \chi_{iAB}, q)$ should be described by the RPA (equation (1)). The simplest such model, leaving out all cross terms, i.e. assuming the scattering from the two mechanisms is additive, is described by equation (7) as follows:

$$\left(\frac{d\Sigma}{d\Omega}\right)_{tot} = x[I_1(\Phi_{1A}, \Phi_{1B}, \chi_{1AB}, q)]$$
$$+ (1 - x)[I_2(\Phi_{2A}, \Phi_{2B}, \chi_{2AB}, q)]$$
$$+ \frac{k\langle\eta\rangle^2 a_c^3}{(1 + a_c^2 q^2)^2} \quad (7)$$

Table 1 Values of the molecular weight, molecular-weight distribution and degree of polymerization of the polyethylenes used in this study

Material	M_w (g mol^{-1})	M_w/M_n	DP
DLPE	200 000	2	12 500
BPE (PN220)	200 000	8	14 300
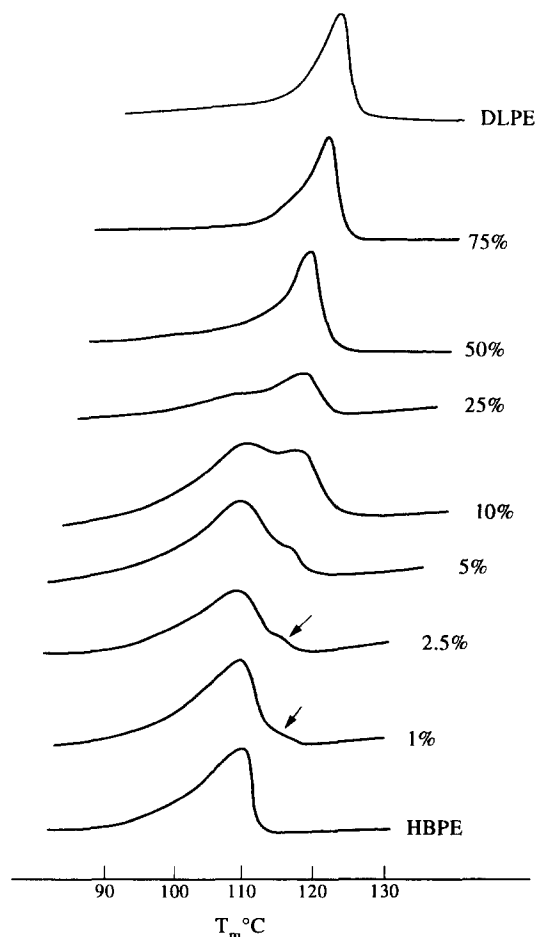
Figure 1 D.s.c. traces, recorded at a heating rate of 10°C min^{-1}, for DLPE/BPE samples quenched from 150°C into acetone at its freezing point

The functions $I_1(\Phi_{iA}, \Phi_{iB}, \chi_{iAB}, q)$ and $I_1(\Phi_{iA}, \Phi_{iB}, \chi_{iAB}, q)$ are the RPA contributions to the scattering and are given by the appropriate modifications to equations (1) and (2).

EXPERIMENTAL

Materials

The deuterated linear polyethylene was obtained from Merck, Sharpe and Dohme, while the protonated polyethylene was PN220 from BP; PN 220 has 10 long and 16 short branches per 1000 carbon atoms. Molecular weights and distributions were measured using gel permeation chromatography (g.p.c.) and are listed in *Table 1*. The preparation of the blends is described elsewhere[15-17].

Differential scanning calorimetry and transmission electron microscopy

Small blend samples were rapidly quenched, after 30 min equilibration in the melt, into acetone at its freezing point. The melting behaviour was determined using differential scanning calorimetry (d.s.c.); experiments were performed at a heating rate of 10°C min^{-1} using a Perkin-Elmer DSC7[28]. Samples for morphological examination by transmission electron microscopy (TEM) were prepared by permanganic etching, followed by a one-stage replication process[43,44]. Micrographs were obtained by using a Philips 301 electron microscope.

Neutron scattering

The experiments have been carried out using the V4 instrument at the Hahn-Meitner-Institut (HMI) in Berlin. Neutrons of wavelength of 0.75 nm ± 10% were used, with the sample to detector distance being 12.21 m. The correction of the data for detector response, transmission, reactor flux, the scattering of the sample environment, the radial averaging of the 2-D data and the calibration to absolute intensities were carried out by using the evaluation software of the HMI. The incoherent background was removed. During the experiment the samples were sealed in quartz cells under argon.

RESULTS

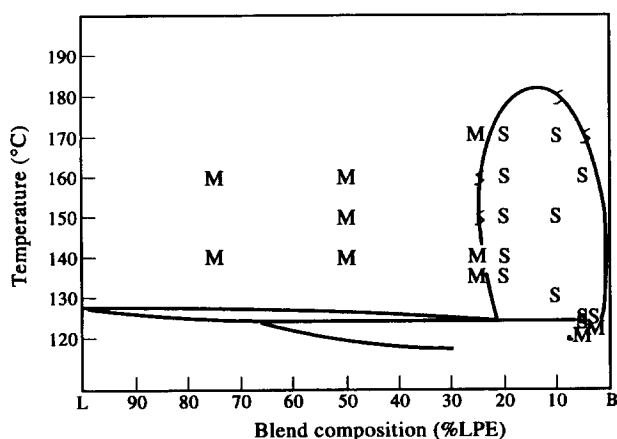### The d.s.c. and TEM determined 'phase diagram'

We used our usual d.s.c. and TEM methods[15,16,28] to determine whether rapidly quenched samples had a single, or a double, morphology as a function of the melt temperature and the blend composition. In accord with our earlier work, we deduce that a double morphology with spatially well separated domains is indicative of a biphasic melt. Hence we are able to estimate the position of the phase boundaries for the DLPE/BPE blend system. An incomplete version of this phase diagram has been published previously[17]. We performed some further experiments in order to determine the extent of probable phase separation at higher melt temperatures. Examples showing d.s.c. traces for several blends quenched from 150°C are shown in *Figure 1*; as described above we interpret the d.s.c. traces as indicating that the blend was mixed in the melt at 50% composition and above, but demixed at 25% composition and below. *Figure 2* shows typical morphologies of representative samples. The 50% blend (*Figure 2a*), quenched from 150°C, is judged as mixed because of the single morphology where all the lamellae have the same thickness. The 10% blend (*Figure 2b*) is judged as biphasic because of the clear micrometre-sized groups of thicker lamellae within the matrix of thin lamellae. Such results built up into the 'phase diagram', which is shown in *Figure 3*. The general appearance of this 'phase diagram' is similar to that previously reported for purely hydrogenous blends; the region of liquid–liquid phase separation (LLPS) is of a closed loop nature, and is asymmetrically placed at very low DLPE compositions. However, it is notable that the width of the region of LLPS is much narrower in the DLPE/BPE blend than in a blend of purely hydrogenous polymers with similar molecular weights; in addition, the height-to-width ratio is much greater in the DLPE/BPE blend[17,27].

Neutron scattering

Two different blends, one containing 50% deuterated linear polyethylene and 50% hydrogenated branched
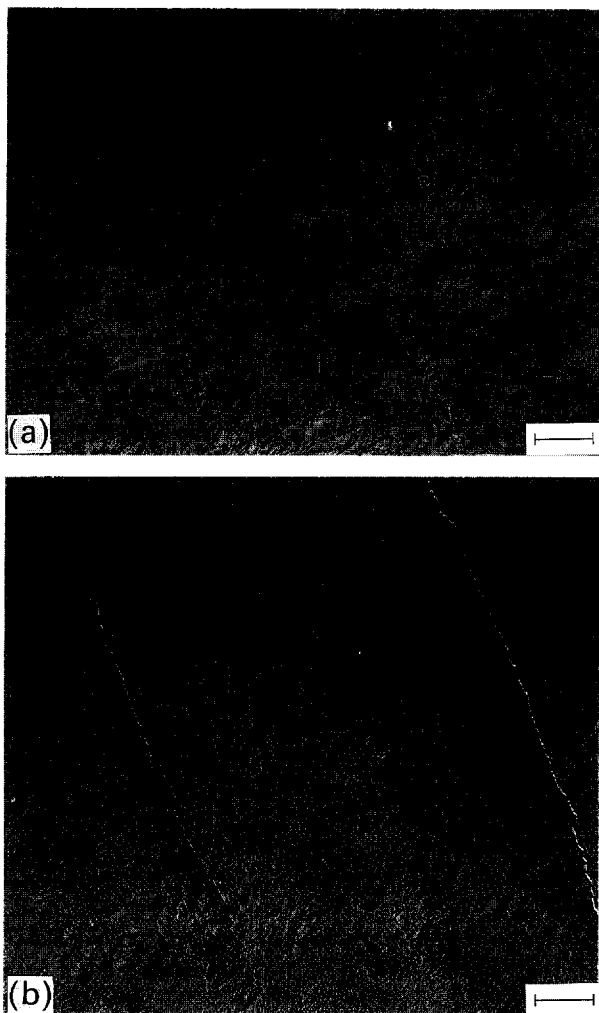
Figure 2 Transmission electron micrographs of replicas of DLPE/BPE samples; in (a) the 50% blend shows only crystals of a single size (the black spots are residues of the etching), whereas in (b) 10% blend crystals of two different sizes are visible (a group of the thicker crystals is visible at centre bottom). The scale bars represent 1 μm

Figure 3 The 'phase diagram' determined by d.s.c. and TEM, for the DLPE/BPE system used in this work; M refers to mixed melts, and S to separated melts and to cases where the melt phase structure is indeterminate

polyethylene (50% sample), with the other containing 10% deuterated linear and 90% hydrogenated branched material (10% sample), were chosen for study. Both samples were kept at 150°C, well above the melting
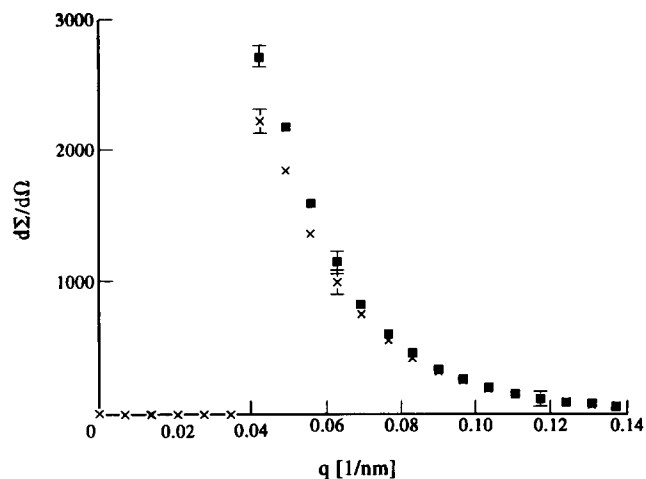
Figure 4 The scattering cross-section of neutrons scattered from the 50/50 blend as a function of the scattering vector, q, after reaching thermal equilibrium (×) and after 6 h (■) at 150°C. Error bars are shown on typical data points
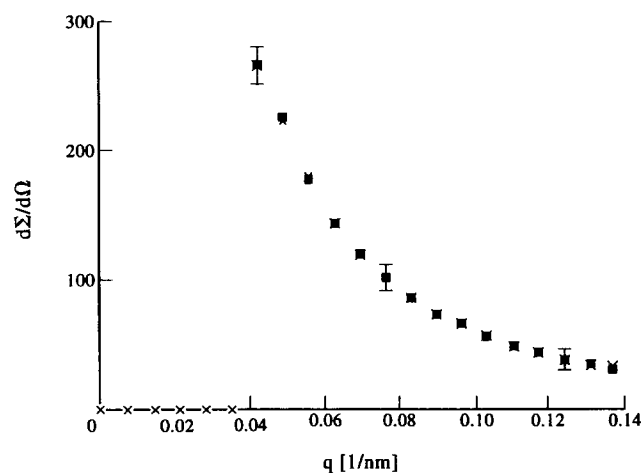
Figure 5 The scattering cross-section of neutrons scattered from the 90/10 blend as a function of the scattering vector, q, after reaching thermal equilibrium (×) and after 4.5 h (■) at 150°C. Error bars are shown on typical data points
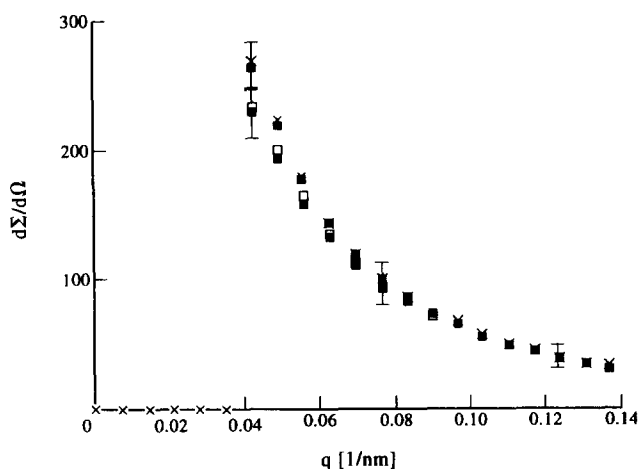
temperature of both materials, for 6 h. During this time the scattering was measured in frames of 10 min. After this the samples were examined at 190°C for 9.5 h in the same way. After measuring the scattering of the 10% sample for 2 h at 180°C both samples were measured again at 150°C for 4 h. The 50% sample was also examined at 100°C, which is below its melting temperature. At each temperature, the samples were allowed to equilibrate for 0.5 h before the measurements were started.

Figure 4 shows the scattering of the 50% blend at 150°C, immediately after equilibrating at this temperature, and at 6 h later. It is obvious that there is very little change in the scattering. No change of the scattering can be observed for the 10% blend (*Figure 5*).
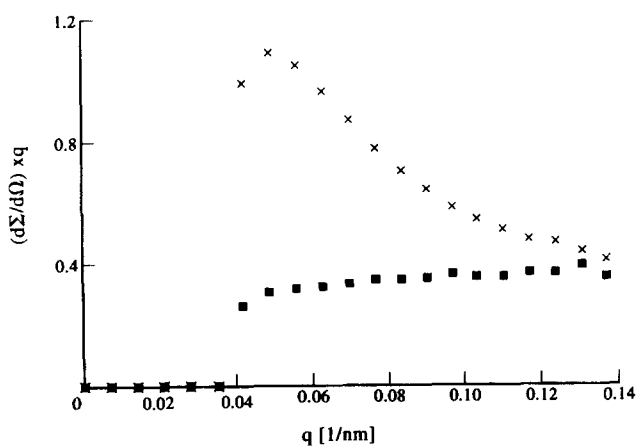
Figure 6 indicates that the changes in the scattering pattern due to the change of temperature are reversible. We are able to deduce that no decrease of the molecular weight occurred during the experiments.

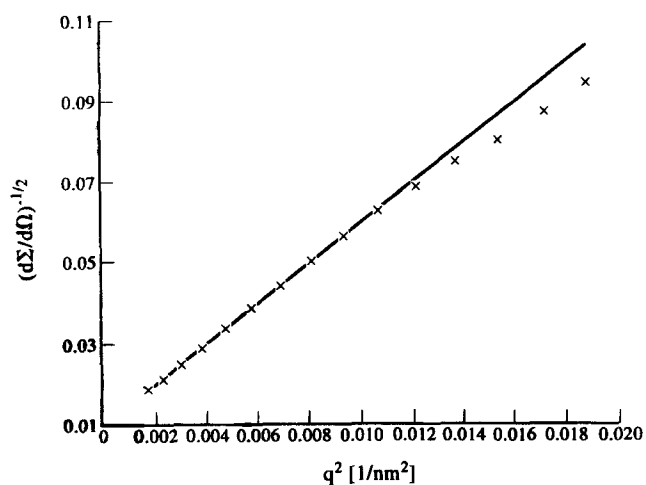*Interpretation of the neutron scattering data*

Multiplying the scattering intensities with q^2 (Kratky

Figure 6 The scattering cross-section of neutrons scattered from the 90/10 blend as a function of the scattering vector, q, at 150°C ($\times$), at 180°C ($+$), at 190°C (■), and again at 150°C (□). Error bars are shown on typical data points

Figure 7 Kratky plots of the 50/50 blend ($\times$) and the 90/10 blend (■) at 150°C

Figure 8 Debye–Bueche plot of the scattering of the 50/50 blend at 150°C

Table 2 Correlation chord lengths of the 50/50 blend at different temperatures

Temperature (°C)	a_c (nm)
150	20.2 ± 1
150[a]	22.8 ± 1
190	21.0 ± 1
150[b]	23.3 ± 1
100	8.1 ± 0.5

[a] After 6 h
[b] Measurement made for a second time

Figure 9 The scattering cross-section of neutrons scattered from the 50/50 blend as a function of the scattering vector, q, at 150°C ($\times$) with the fitted Debye–Bueche function (—). Note that only a few calculations were used at low q so that the shape of the curve as $q \to 0$ is only approximate

curves of the 50% blend were evaluated using the Debye–Bueche model, while those for the 10% blend were evaluated using both the RPA model, and according to the model of two large homogeneous phases, set out in equation (7).

In order to obtain the correlation length, a_c, the data of the 50% blend is presented in a Debye–Bueche plot in which q^2 is plotted against $\left(\frac{d\Sigma}{d\Omega}\right)^{-1/2}$. For a two-phase system this should give a straight line, and a_c can be calculated from its slope and intercept. A Debye–Bueche plot for the data obtained at 150°C is shown in *Figure 8*. The deviation from linearity at high q is due to problems of removing the background and to scattering of the phase boundaries. The values obtained for a_c are listed in *Table 2*. The Debye–Bueche model function, fitted to the scattering curve of the 50% blend at 150°C, is shown in *Figure 9*. Note that we find very little change in the scattering of this sample during melting at 150°C for 6 h; this implies that there is only negligible coarsening of the scale of the inhomogeneities seen in the scattering behaviour.

In order to fit the RPA model function to the experimental data of the 10% blend R_g and χ were varied in order to obtain a good fit; for simplicity we assume that both components were monodisperse and we took the molecular weights to be the weight averages. A change of 5% of the chosen value for R_g and of 2% for χ gives significant differences between the model function and the experimental scattering curve. For the degree of polymerization the g.p.c. values for the weight-average
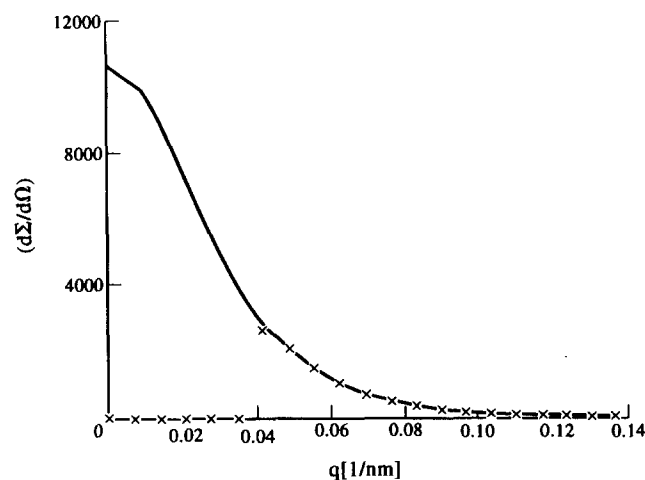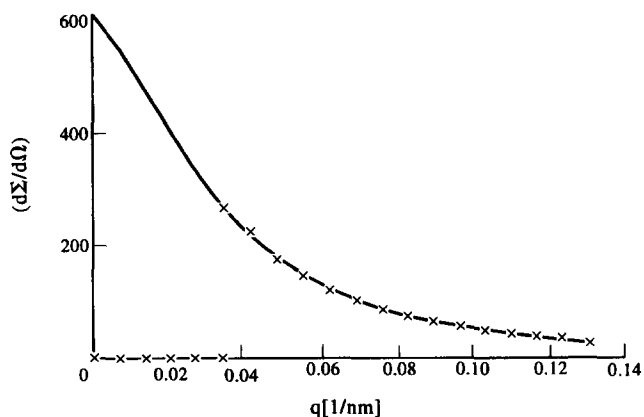
plot) shows that the shapes of the scattering curves of the samples are completely different (see *Figure 7*). While the curve of the 10% blend gives a plateau, indicating scattering from Gaussian coils[45], the curve of the 50% blend shows a maximum. Therefore, the scattering

Figure 10 The scattering cross-section of neutrons scattered from the 90/10 blend as a function of the scattering vector, q, ($\times$) and fitted RPA model (—) at 150°C. Note that only a few calculations were used at low q so that the shape of the curve as $q \rightarrow 0$ is only approximate

Table 3 Values of the χ-parameter and radius of gyration used for the best fit of the RPA function to the experimental data of the 90/10 blend at different temperatures

Temperature	$\chi \times 10^4$	R_G (nm)
150	4.02 ± 0.4	13.9 ± 0.5
180	3.90 ± 0.4	13.9 ± 0.5
190	3.87 ± 0.4	13.9 ± 0.5
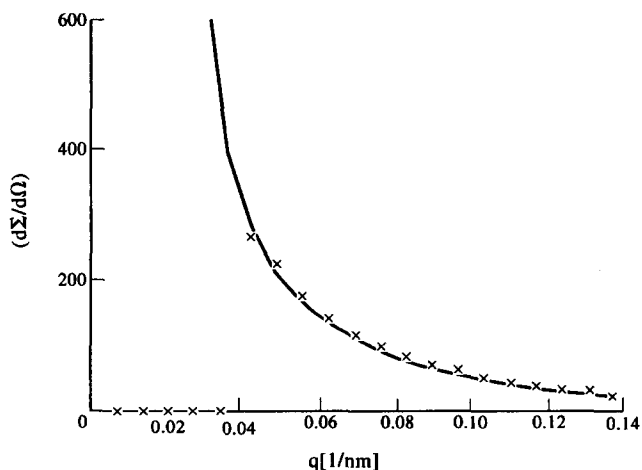
Figure 11 The scattering cross-section of neutrons scattered from the 90/10 blend as a function of the scattering vector, q, ($\times$) with the fitted model function combining the Debye–Bueche and RPA models

molecular weight were used. *Figure 10* shows the scattering curve and the fit obtained at 150°C. The values of R_g and χ that were used are listed in *Table 3*, although of course these values should be treated with caution because they are derived by using M_w, when the polymers are really polydispersed; furthermore, the extrapolation is over a large range of q.

The RPA model, which would indicate complete mixing, gives a good fit to the results from the 10% sample. However, it is also possible to fit equation (7), which is appropriate for a biphasic blend, to the experimental data, as shown in *Figure 11*. For this fitting we assumed that the blend does not demix into two phases of pure polymers, which is not very likely and

would not be indicated by the 'phase diagram' (*Figure 3*). Instead we calculated the scattering for a blend, demixed into two phases, with one having a volume fraction of the overall blend of $x_1 = 0.21$ (containing 60% branched polyethylene) and the other having a volume fraction of $x_2 = 0.79$ (containing 98% branched polyethylene). The correlation length, a_c, was taken as 3 μm, an average radius of gyration of 13.9 nm was assumed in both phases, and the values of k and $\langle \eta^2 \rangle$ were taken from the 50% blend. In order to obtain a good fit, a χ-parameter of 1.4×10^{-4} was chosen for the 60/40 phase; the value used for the 98/2 phase was 1.9×10^{-3}. The resulting theoretical curve (*Figure 11*) fits the experimental data points very well.

DISCUSSION

In general the results show a great similarity to those obtained by Alamo *et al.*[14]. It appears that the 50% blend is demixed and the 10% blend is either homogeneously mixed or is separated into large domains at all temperatures. Some other interesting information can be obtained from our experiments. Since there is no significant change in the scattering after the equilibration time, all changes in the blends take place during the first 0.5 h. This is especially remarkable for the 50% sample, because the phase size stays constant at ca. 22 nm and does not follow the classic Ostwald ripening growth[46]. This could be the result of the formation of a kind of micelle structure in the blend. It is also interesting that at 100°C the phases of the 50% sample have a correlation length a_{c12} of 8 nm, smaller than the length at 150°C (23 nm). This indicates that some mixing occurs during the crystallization of the blend.

Further questions are raised by the experiments. There are some clear differences between these results and those obtained by some of us in earlier experiments[15–28]. The neutron scattering experiment shows, very clearly, that the 50% sample contains inhomogeneities of a size of ca. 20 nm at all of the temperatures examined, while the morphological evidence is for complete mixing. However, it is unlikely that inhomogeneities on such a small scale would be picked up by a TEM experiment. This is a limitation of the TEM method. Most likely these inhomogeneities are caused by the isotope effect due to the deuteration of the linear polyethylene. However, the fact that the inhomogeneities do not coarsen on prolonged storage argues against any normal equilibrium phase separation mechanism being responsible. We can offer no explanation for this peculiar behaviour at this stage, but simply note that it appears to be somewhat more complex than that suggested by Alamo *et al.*, who argued that the phase separation is due to the deuteration of the linear chains[14].

The 10% sample may equally well be treated as consisting of a single homogeneous phase at both 150 and 180°C, or as being made up of two, large, homogeneous phases. However the (indirect) results from the electron microscopy and d.s.c. experiments (see *Figures 1* and *2*) are consistent only with the latter interpretation.

In order to find out which of the two models, biphasic on a large scale or completely mixed, describes the scattering curve of the 10% blend, measurements at smaller scattering vectors are needed. At this stage we

Table 4 Values of the χ-parameter used in fitting the neutron scattering data

Fraction of DLPE in the phase	χ (fit) at 150°C	χ (spinodal)[a]
10%[b]	4.02×10^{-4}	4.39×10^{-4}
40%[c]	1.40×10^{-4}	1.58×10^{-4}
2%[c]	1.90×10^{-3}	2.04×10^{-3}

[a] Calculated by using equation (4)
[b] From the RPA model
[c] From equation (6)

can only speculate. We find, whichever model we use, that the neutron scattering χ-parameters (see *Table 4*) are rather high and quite close to the critical χ-parameters for spinodal decomposition, calculated from the weight-average molecular weights (4.39×10^{-4}). Furthermore, the average radius of gyration of 13.9 nm, used to fit the experimental data, is much smaller than would be expected for a polyethylene of molecular weight 200 000[47–49]. The small value of the radius of gyration suggests that the coils of the components are collapsing and that branched polyethylene is, at best, a very poor solvent for DLPE.

CONCLUSIONS

We contend that the arguments we have presented in our past publications are sufficient to demonstrate that liquid–liquid phase separation does indeed occur in blends of linear with lightly branched polyethylenes. We further contend that the neutron scattering data that we present here for a 10% blend, and that of Almo *et al.*[14], may be equally well interpreted as being from a system that is phase-separated on scale which is large compared to the scattering vector as from a homogeneously mixed system. In view of the weight of evidence in favour of phase separation in similar systems, we suggest that such systems are more likely to be separated on a large scale than they are to be homogeneous.

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