Structural characterization of semicrystalline polymer blends by small-angle neutron scattering*

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A series of phase-separated polyethylene–polypropylene blends, which have undergone different thermal treatments, have been analysed by small-angle neutron scattering (SANS). The coherent scattering from normal hydrogenated blends is virtually zero, but strong contrast may be induced by partial or complete deuteration (labelling) of either phase. Here, the scattering from blends with complete labelling of the polyethylene phase was analysed to provide the domain dimensions by means of a theory due to Debye using an exponential correlation function. By this means the mean chord intercept lengths of both phases were shown to be in the range 1000–10 000 Å. The scattering from blends with partial labelling of the polyethylene was analysed to give the radius of gyration of the molecules in the polyethylene domains, which was found to be close to that measured in the homopolymer. For melt-quenched blends the deuterated polyethylene was shown to be statistically distributed in the polyethylene phase, whereas for slow-cooled blends, partial segregation of the labelled molecules occurred.

Keywords Small-angle neutron scattering; polyolefin; blend structure; semicrystalline polymer blends; polymer compatability

INTRODUCTION

Polymer blends ranging from completely compatible mixtures to phase-separated systems are gaining increasing commercial importance, though little information is available on how the configuration of individual molecules within the blend is perturbed from the configuration in the homopolymer. Furthermore, in cases where incompatibility of the components leads to phase separation, knowledge of the structural nature of the phase-separated domains is necessary if the observed properties are to be interpretable. Semicrystalline polymer blends are particularly difficult to characterize since the components may form lamella structures consisting of alternating regions of crystalline and amorphous materials in addition to phase separating into domains. Adding to this difficulty in some systems is the lack of electron density contrast between the phases, which limits the application of electron microscopy and optical techniques.

Blends of polyolefin homo- or copolymers are prime examples of these problems. Quantitative information about domain sizes and molecular characteristics are particularly difficult to obtain, and it is the object of this paper to demonstrate the application of small-angle neutron scattering (SANS) techniques to the solution of this problem.

SANS has been used increasingly for the study of chain configuration in bulk amorphous[1-3] and crystalline homopolymers[4,5] and many examples of the exploitation of this method are given in two recent reviews[6,7]. Samples analysed are made up of a host polymer matrix in which a fraction of isotopically-substituted (labelled) polymer molecules is dispersed. The difference in coherent scattering length between deuterium ($b_D = 0.667 \times 10^{-12}$ cm) and hydrogen ($b_H = -0.374 \times 10^{-12}$ cm) results in a marked contrast between hydrogenated and deuterated molecules.

Scattering theory has recently been developed[8-10] to the point where SANS can be applied to phase-separated systems. Here, we report experiments on model polyolefin blends. The blends are seen to form a phase-segregated domain structure and SANS provides a comprehensive analysis of the various levels of structure within the blend, including the domain dimensions of the phases, the dimensions of individual molecules within the domains and information on the intercompatibility of the different molecules within the blend. Complementary small-angle X-ray scattering (SAXS) measurements provide information on the lamella structures within each phase, and have been used to elucidate the contribution from these structures to the SANS patterns.

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THEORY

Jahshan and Summerfield[8], whose notation we adopt here, have shown that the single chain form factor, $S_S(K)$, which describes the configuration of an individual chain can be obtained from small-angle scattering measurements on labelled polymer blends. This was accomplished by adapting the expression for labelled polymer solutions[9] to polymer blends by treating one of the polymer species in the blend as a solvent in computing the contrast factors. A similar treatment has been given independently by Koberstein[10].

For an incompressible blend of two polymer species, designated P and S we assume that a fraction X of the P species has been labelled by substituting deuterium atoms for hydrogen. If a_H and a_D are the coherent neutron scattering amplitudes for the normal (hydrogenated) and deuterated monomer (repeat) units of the P species, a_S is the neutron scattering amplitude of the monomer unit of the S species, V is the total sample volume, V_P and V_S are the monomer specific volumes of the P and S species, then the coherent differential scattering cross-section per unit solid angle per unit sample volume, is given by:

$$\frac{d\Sigma}{d\Omega}(K,X) = X(1-X)(a_H - a_D)^2 N_P S_S(K) + \left[a_H(1-X) + a_D X - a_S\frac{V_P}{V_S}\right]^2 \frac{S_T(K)}{V} \qquad (1)$$

where:

$$S_S(K) = |\sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}|^2 \qquad (2)$$

$$S_T(K) = \langle|\sum_{M,j} e^{i\mathbf{K}\cdot(\mathbf{R}_M + \mathbf{r}_j)}|^2\rangle \qquad (3)$$

R_M is the centre of mass position of the P species chains, r_j is the monomer position relative to the centre of mass of the chain, $K = 4\pi\lambda^{-1}\sin\theta$, λ is the wavelength of the radiation and 2θ is the angle of scatter. $S_T(K)$ is proportional to the total scattering from a blend where the P species is fully labelled ($X = 1$), and may be analysed to give information on the phase structure and the dimensions of the individual phases. $S_S(K)$ is the single chain form factor of the P species and contains information on the configuration of the individual labelled chain, which may be characterized by the mean square radius of gyration, R_g^2.

In this work measurements were made on blends of polyethylene (P species) and polypropylene (S species) in which a fraction of the normal polyethylene (PEH) had been replaced by deuteropolyethylene (PED). Thus we may treat the polypropylene molecules as a 'solvent' for the polyethylene molecules in calculating the contrast factors. Taking the monomer (repeat) units of polyethylene and polypropylene as C_2H_4 and C_3H_6 respectively we have:

$$a_H = -0.166 \times 10^{-12}\,\text{cm} \qquad (4)$$

$$a_D = 3.998 \times 10^{-12}\,\text{cm} \qquad (5)$$

$$a_S = -0.249 \times 10^{-12}\,\text{cm} \qquad (6)$$

$$\frac{V_P}{V_S} = 0.62 \qquad (7)$$

Experiments were performed on blends with a 50:50 wt% ratio of polyethylene and polypropylene. $S_T(K)$ was obtained from measurements of the scattering cross-section, $d\Sigma(K)/d\Omega$, of a blend where all the polyethylene (P species) had been deuterated ($X = 1$), and thus the first term in equation (1) is zero. $S_S(K)$ was obtained from the scattering of a partly labelled ($X = 0.09$) blend after subtracting a term proportional to $S_T(K)$, which had already been determined.

Equation (1) is derived for an incompressible blend and hence neglects the scattering terms arising from the crystal–amorphous density fluctuations within each phase, which are known to produce strong SAXS scattering from polyolefin homopolymers and blends. However, the cancellation between the scattering lengths of carbon ($b_C = 0.665 \times 10^{-12}$ cm) and hydrogen ($b_H = -0.374 \times 10^{-12}$ cm) results in low values for a_H and a_S and hence masks the scattering from both the phase structure and internal density fluctuations, and this means that the coherent SANS scattering from an unlabelled blend is virtually zero (see below).

Similarly for low levels of deuteration of the P species ($X \leqslant 0.1$), the coherent scattering from the phase structure of the matrix (equation 1, term 2), and density fluctuations within each phase form only a small correction to the scattering from individual labelled molecules (equation 1, term 1), and this makes the determination of the single chain form factor relatively simple. However, no cancellation of scattering lengths occurs for a deuterated monomer unit, and hence the contrast between labelled and unlabelled phases is strong and the determination of the dimensions of the individual phases in a fully labelled system ($X = 1$) is also relatively straightforward. Mixed polyofin blends are therefore a favourable case for testing the applicability of SANS to phase-separated systems.

For a sample in which all the P species has been labelled ($X = 1$), the scattering cross-section is given by (equations, 1, 4–7):

$$\frac{d\Sigma(K)_{X=1}}{d\Omega} = \left[a_D - \frac{a_S V_P}{V_S}\right]^2 \frac{S_T(K)}{V} \qquad (8)$$

This cross-section arises from the fluctuations in scattering length density in the system and can be described generally by the theory first introduced by Debye and coworkers[11,12], which characterizes the fluctuations by a spatial two-point correlation function:

$$\gamma(r) = \langle\eta_A\eta_B\rangle/\langle\eta^2\rangle \qquad (9)$$

In terms of small-angle neutron scattering η_A and η_B are the local fluctuations in scattering length density at points A and B which are a distance r apart, and $\langle\eta^2\rangle$ is the mean square deviation over all points. For small-angle X-ray scattering (SAXS) η_A and η_B will be the corresponding fluctuations in electron density.

If the product of η_A and η_B depends only on the separation of the scattering elements, the scattering is proportional to $S_T(K)$ which is given by[7]:

$$S_T(K)=F\langle\eta^2\rangle\int_0^\infty \gamma(r)r^2\frac{\sin Kr}{Kr}\mathrm{d}r \qquad (10)$$

where F is a proportionality factor, with dimensions of length, which is effectively constant for all K.

At the levels of scattering encountered in this work equation (10) is rigorous. The problem is to determine the form of $\gamma(r)$ and relate it in a useful way to the structure of the blend. For a two phase system where the domains are randomly interdispersed, Debye *et al.*[12] have shown that $\gamma(r)$ should take the form of a simple exponential, $e^{-r/a}$, where a is a characteristic correlation length. Equation (10) then reduces to:

$$S_T(K)=\frac{2F\langle\eta^2\rangle a^3}{[1+K^2a^2]^2} \qquad (11)$$

and from equation (8), the differential scattering cross-section for this composition ($X=1$) is given by:

$$\frac{\mathrm{d}\Sigma(K)_{X=1}}{\mathrm{d}\Omega}=\frac{2F\langle\eta^2\rangle a^3[a_D-a_S V_P/V_S]^2}{V[1+K^2a^2]^2} \qquad (12)$$

It is easy to test whether experimental observations of $S_T(K)$ follow the form of equation (12), since a plot of

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(K)\right]^{-1/2} \text{ vs. } K^2$$

should give a straight line with ratio of slope/intercept $=a^2$.

Debye *et al.*[11,12] also demonstrated for their random two-phase model that the specific interphase surface per unit volume of composite, A_V, is given by:

$$A_V=\frac{4\varphi(1-\varphi)}{a} \qquad (13)$$

where φ = volume fraction occupied by phase 1. However, quite generally for any two phase structure[13]:

$$A_V=\frac{4\varphi}{L_1} \qquad (14)$$

where L_1 is the mean chord intercept length across continuous sequences of phase 1 when a straight line is drawn randomly through the structure. Thus it follows that:

$$L_1=\frac{a}{1-\varphi} \qquad (15)$$

Similarly the mean chord intercept length L_2 of phase 2 is given by:

$$L_2=\frac{a}{\varphi} \qquad (16)$$

Thus measurements of $\mathrm{d}\Sigma(K)/\mathrm{d}\Omega$ on a sample where the polyethylene species was completely deuterated ($X=1$), may be used to give the domain dimensions characterized by the mean chord intercepts L_1 and L_2, providing that plots of $[\mathrm{d}\Sigma(K)/\mathrm{d}\Omega]^{-1/2}$ vs. K^2 are linear. Similar information may be obtained from analogous SAXS experiments for systems with sufficient electron density contrast between the phases[13].

As described above, the single chain form factor may be obtained from the scattering of a partly labelled blend after subtracting off the scattering from the phase structure, $S_T(K)$, measured on a blend with a fully labelled P phase. The remaining scattering is given by the first term in equation (1), which in the Guinier region ($R_g{}^2K^2<1$) may be expanded to give:

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(K)\right]^{-1}=\frac{1}{K_N M_w}\left[1+\frac{R_g^2K^2}{3}\right] \qquad (17)$$

where K_N is a neutron calibration constant given by:

$$K_N=\frac{(a_H-a_D)^2N_0\rho X(1-X)}{M_P^2} \qquad (18)$$

N_0 is Avogadro's number; M_w is the molecular weight; ρ is the density; and M_P is the mass of a monomer unit of the P species. The above equations assume that the labelled molecules are fully deuterated which was the case for the present experiments. Otherwise the square of degree of deuteration should be included in K_N. Thus R_g and M_w may be obtained from the slope and intercept respectively of (Zimm) plots of $[\mathrm{d}\Sigma(K)/\mathrm{d}\Omega]^{-1}$ vs. K^2. Furthermore, the extrapolated forward scattering intercept has been shown to be a very sensitive indicator as to whether the labelled molecules are randomly or statistically distributed in the system. Any departure from a random distribution will lead to anomalous values of the molecular weight which in melt-crystallized polyethylene were interpreted in terms of small deviations (paraclusters) from a statistical distribution of labelled molecules[4]. Model calculations showed that the apparent molecular weight measured by SANS can exceed by many times the true molecular weight of the labelled molecules measured by g.p.c. prior to blending, with only slight deviations from statistical distribution of labelled molecules. Hence the SANS technique can provide valuable information on the compatibility of different molecular species in polymer blends[14-17].

EXPERIMENTAL

Polymer characterization

The polymers chosen for the blends were linear polyethylene and isotactic polypropylene. Marlex 6050 was used as the hydrogenated polyethylene (PEH), Prochem Ltd polyethylene-d_4 was used as the deuterated polyethylene (PED), and Hercules 6523 was chosen as the isotactic hydrogenated polypropylene polymer (PPH).

The molecular weights and molecular weight distributions of these polymers were determined by gel permeation chromatography (g.p.c.) by L. Westerman of Exxon Chemical Co.[18], using a Waters Model 200 GPC equipped with a Wilks infra-red detector. The C–H stretching frequency at 3.46 μm was employed for non-deuterated polyethylene and polypropylene, while the C–D stretching frequency of 4.55 μm was monitored for the deuterated polyethylene sample. The results are summarized in *Table 1* and *Figure 1*.

Table 1 Summary of homopolymer molecular weight characteristics

Material		$\langle M_w\rangle$*	$\langle M_w\rangle/\langle M_n\rangle$*
Marlex 6050	Hydrogenous polyethylene (PEH)	125 000	12.2
Prochem Ltd. polyethylene-d_4	Deuterated polyethylene (PED) (0.99/atom)	149 000†	9.6
Hercules 6523	Isotactic hydrogenous polypropylene (PPH)	411 000	8.3

* Determined by g.p.c. by L. Westerman, Exxon Chemical Co.
† Corrected for the difference in weight (16/14) of deuterated and hydrogenated monomer units

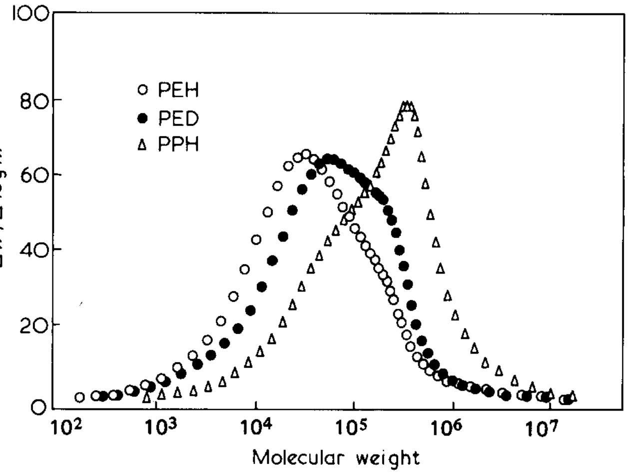

Figure 1 G.p.c. molecular weight distributions of the PEH, PED and PPH polymers

It should be noted that the PEH and PED have almost identical molecular weights, similar M_w/M_n values (*Table 1*), and overall distribution (*Figure 1*). This close similarity between the hydrogenated and deuterated samples should maximize molecular compatibility of the polyethylene.

Sample preparation and characterization

Two basic blend compositions were prepared. One was composed of a mixture of 5.6 wt% deuterated polyethylene (PED), 44.7 wt% hydrogenated polyethylene (PEH), and 49.6 wt% hydrogenated isotactic polypropylene (PPH). This composition ($X = 0.09$) would provide information about the molecular weight, coil dimensions and compatibility of PED in PEH. The second blend was 50.1 wt% PED and 49.9 wt% IPP. This blend ($X = 1$) would supply information about the domain dimensions and possibly the dimensions of the crystalline and amorphous component of the domain substructure.

A blend of 50.2 wt% PEH and 49.8 wt% PPH was also prepared to act as a blank for neutron scattering. Hereafter, the compositions of the blends are referred to as 50:50 or 45:5:50 for ease of nomenclature.

Samples were prepared by dissolving the weighed polymers in *o*-dichlorobenzene and stirring under reflux at 175°C. The blends were removed from solution either by rapid precipitation into methanol in an ice bath, or by allowing the solution to cool slowly to room temperature with the precipitate forming at ~85°C. Precipitates formed by both procedures were rinsed in methanol and dried overnight at 65°C. They were then cold-pressed at 10 000 psi at room temperature into discs ~1 mm thick and 19 mm dia. In addition, some of the cold pressed discs were melted at 200°C for ~7 min and then either quenched into ice water, or slow-cooled to room temperature at 5 K min^{-1}.

The samples were analysed by differential scanning calorimetry (d.s.c.) on a Perkin–Elmer DSC-1 using a sample weight ~10 mg and a scanning rate of 20 deg K min^{-1}. *Figure 2* shows the melting endotherm of a sample precipitated from solution into methanol. Two separate melting peaks, corresponding to the melting ranges of polyethylene and polypropylene, are observed even for this sample which had the most rapid crystallization conditions. Similar endotherms were observed for all other samples crystallized both from solution or from the melt. These indicate a phase-segregated morphology where a Debye analysis should be appropriate for measurement of domain dimensions.

Small-angle neutron scattering

Experiments were performed on a new SANS instrument at the Oak Ridge Research Reactor[19], using 4.8 Å neutrons and a two-dimensional position-sensitive detector. The scattering patterns from the labelled blends and the blank were each measured over a 32 x 32 array for a period of ~16 h. For each point of the data array, the scattering was corrected for background, sample thickness and transmission and the corresponding scattering from the polymer blank subtracted. The resulting two dimensional array of corrected data points was averaged over a ring of constant width as a function of radius from the centre of the beam, to obtain the intensity in the range of scattering vectors, 7×10^{-3} $\text{Å}^{-1} \leqslant K = (4\pi/\lambda)\sin\theta \leqslant 0.035$ Å^{-1}. These intensities were calibrated by comparison with scattering from water[20], and by direct measurements of the incident beam. By this means absolute values of $\mathrm{d}\Sigma(K)/\mathrm{d}\Omega$ were obtained.

Figure 3 shows the scattering cross-sections of a partly labelled blend (45% PEH: 5% PED: 50% PPH) both slow-cooled and quenched from the melt, together with that from a totally hydrogenated blank (50% PEH: 50% PPH). This shows the strong SANS contrast which is produced by deuterium labelling, and that the scattering from the

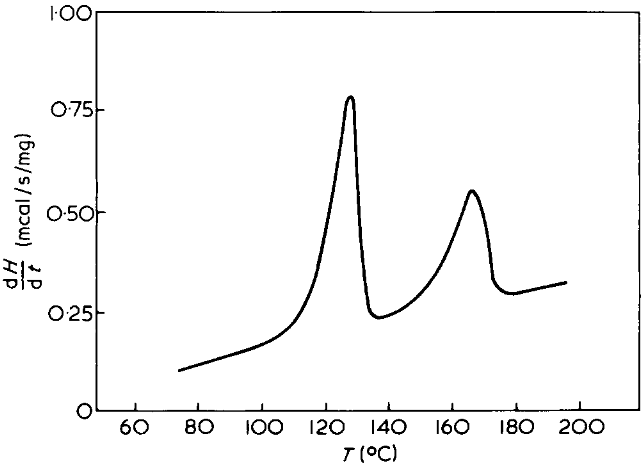

Figure 2 D.s.c. melting endotherm (20 deg K min^{-1}) for 50 : 50 polyethylene (PEH) and polypropylene (PPH) precipitated from solution into methanol

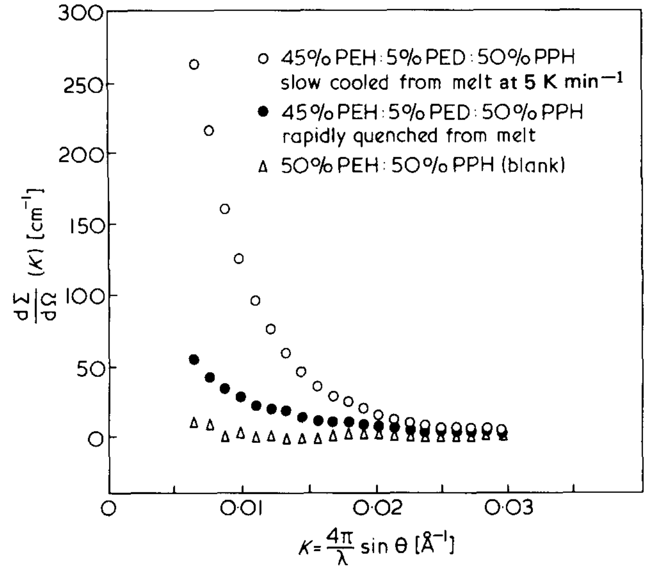

Figure 3 dΣ(*K*)/dΩ vs. *K* for melt-crystallized blends of polyethylene and polypropylene

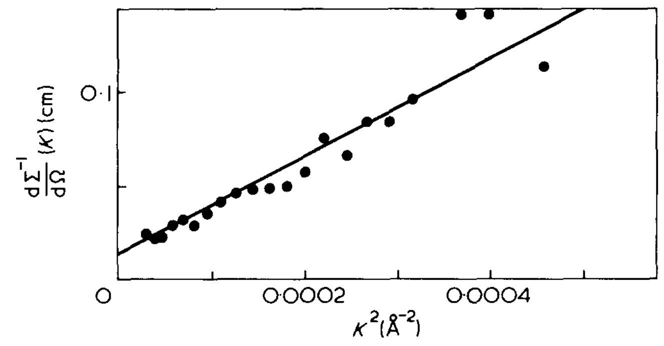

Figure 4 dΣ(*K*)/dΩ vs. K^2 for 5% labelled PED molecules in 50 : 50 polyethylene and polypropylene

labelled molecules is clearly visible over the background from the blank. This background scattering is due principally to incoherent scattering which was not included in the treatment of Jahshan and Summerfield[8], or in equation (1). However, this component is virtually independent of angle and is proportional to the number density of each atom multiplied by its incoherent scattering cross-section.

The dominant component of this scattering arises from ^{1}H nuclei and a correction was made for each sample by scaling from the level of the flat background scattering of the blank. The remaining coherent scattering from the labelled molecules can be analysed according to equation (1), and after subtraction of a term proportional to $S_T(K)$ determined from a fully labelled blank ($X=1$), the self-term $S_S(K)$ can be extracted and used to calculate the radius of gyration, R_g, and the molecular weight of an individual labelled molecule as shown in *Figure 4* for the melt-quenched sample. The data are plotted according to equation (17), and the value of R_g and $d\Sigma(0)/d\Omega$ calculated from the slope and intercept are 190 Å and 66.6 cm^{-1}, respectively. These values reflect the dimensions and molecular weight of the PED chains only if the labelled and unlabelled chains have the same molecular weight and distribution. While the g.p.c. traces from the two types of molecules are similar (*Figure 1*) they are not completely identical, and hence second order corrections must be made to take into account the differences in molecular weight distributions. These corrections have been developed by Boue *et al.*[21] who showed that if the weight-averaged (M_w) and z-averaged (M_z) molecular weights of the labelled (D) and unlabelled (H) chains are related by:

$$M_{wH}=M_{wD}(1+\Delta w) \tag{19}$$

$$M_{zH}=M_{zD}(1+\Delta z) \tag{20}$$

then equation (17) is modified to:

$$\frac{d\Sigma}{d\Omega}(K)=\frac{1+\Delta w(1-X)}{K_N M_{wD}(1+\Delta w)}\left[1+\frac{R^2_{g\mathrm{app}}K^2}{3}\right] \tag{21}$$

where $R_{g\mathrm{app}}$ is the apparent (z-average) radius of gyration of the deuterated molecules and is related to the real R_g by:

$$R_{g\mathrm{app}}=R_g\left[1+\frac{X\Delta z}{1+(1-X)\Delta w}\right] \tag{22}$$

Thus using values of $\Delta w=\Delta z=-0.16$ from the g.p.c. traces we calculate $M_{wD}=148\,000$ and $R_g=192$ Å. The virtually exact agreement between the molecular weights determined by SANS and g.p.c. (see *Table 2*) is probably fortuitous in view of the overall uncertainties (±20%) in both methods, though it clearly indicates that the PED molecules are statistically distributed in the phase-separated polyethylene phase in the blend, as expected for melt-quenched samples[4]. This result demonstrates that the SANS technique can provide information on compatibility of the components of blends and could be used to provide information in cases where the intercompatibility is less well understood (e.g. for ethylene–propylene copolymers in either homopolymer). The radius of gyration of the PED molecules measured in the blend ($R_g=192$ Å) represents a z-averaged value which may be approximately corrected to a weight-averaged value ($R_g=139$ Å) using the known polydispersity of the labelled molecules[22]. This value is of the same order as the radius of gyration of PED molecules in the quenched homopolymer where $R_g\simeq 165$ Å (weight-averaged) for $M_w=149\,000$[4], though the magnitude of the polydispersity correction precludes a more accurate comparison with values measured in the homopolymer.

For blends slow-cooled from the melt at 5 deg K min^{-1}, the scattering cross-section is much higher than for the melt-quenched material (*Figure 3*), and this leads to a much higher apparent molecular weight (>900 000), indicating that some paraclustering or partial segregation has occurred[4].

Table 2 Molecular weight correlation between g.p.c. and SANS for deuterated polyethylene

Processing conditions	$\langle M_w \rangle$	PED condition in PEH phase
G.p.c. of original PED	149 000 (g.p.c.)	
Melt quenched blend	148 000 (SANS)	Statistically distributed
Slow cooled from melt at 5 K min^{-1}	>900 000 (SANS)	Clustering or partial segregation

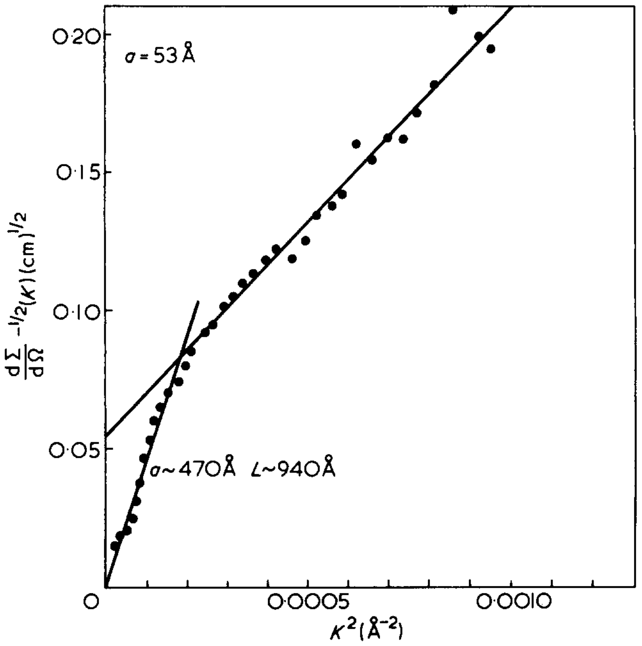

Figure 5 Debye plot for 50 : 50 melt-quenched polypropylene (PPH) and polyethylene (PED)

DISCUSSION

The SANS results from the 50% PED: 50% PPH materials ($X = 1$) are shown in the form of Debye plots in *Figures 5* and *6* for samples quenched and slow-cooled from the melt. The Debye theory (equations 11, 12) predicts that these plots will be linear in the low K region, and since this is true for the blends, an exponential correlation function appears to be a reasonable approximation for these systems.

The correlation length, a, can then be calculated from the ratio of the slope to intercept of this line (equation 12), and since the fraction φ of deuterated phase is known, the mean chord intercepts L_1 and L_2 of the polyethylene and polypropylene phases can then be calculated (equations 15,16). Since in this case, $\varphi = 0.47$, then $L_1 \simeq L_2$, and the correlation length, a, calculated from the ratio of the slope to intercept is in the range $a = 600 \pm 200$ Å. This indicates that the mean chord intercepts of the polyethylene and polypropylene phases L_1 and L_2 exceed 1000 Å.

Although to our knowledge domain sizes are not available for ethylene–propylene mixtures, domain dimensions have been reported[23] for a 70:30 EPM:IPP mixture by weight (here EPM is an ethylene–propylene copolymer of unknown composition). The mixture was examined in the electron microscope after dissolving out the EPM by solvent extraction and looking at the isotactic polypropylene left behind. Both phases were found to be continuous with domain sizes ranging from less than 1000 to 20 000 Å. Clearly, domain sizes of 1000 Å or greater obtained in the present study of polyethylene–isotactic polypropylene mixtures are consistent with the EPM–PPH results. The extreme conditions (solvent extraction) required to obtain information in the earlier EPM–PPH study emphasizes the great advantage of SANS for evaluating domain dimensions and relating these to the experimental conditions of sample preparation.

There was some indication that higher values of a were observed for blends slow-cooled from the melt. However, as the measured values approach the limit of resolution of this instrument, higher resolution experiments would be necessary to confirm this finding. Such studies are currently in progress on the ORNL double-crystal instrument[24] and preliminary experiments on a 50% PED:50% PPH sample slow-cooled from the melt indicate that the Debye theory fits the observed data down to $K \simeq 2 \times 10^{-3}$ Å^{-1} with a correlation length, $a = 580 \pm 50$ Å, consistent with the dimensions observed at higher K values (see *Figure 8*). Below $K = 2 \times 10^{-3}$ Å deviations from the Debye theory are observed, indicative of large domains with dimensions up to 10 000 Å.

In the higher K region ($K^2 > 0.0002$ Å^{-2}) of *Figures 5* and *6*, the data deviate from the simple Debye theory, and may be approximated by straight lines with correlation lengths (50–70 Å) much lower than those observed at lower K. This indicates that the scattering at large angles exceeds that which would be calculated from a simple domain structure of randomly interpenetrating homogeneous phases. A similar effect was observed by Stein *et al.*[25], who observed that the light scattering from polyethylene at large angles was too great to result from a simple structure of homogeneous spherulites, and attributed the excess scattering to the internal structure of the spherulites.

Following this approach the excess scattering observed in this work might be expected to originate from the internal scattering heterogeneities within the domains arising from the alternation of crystalline and amorphous lamellae within each semicrystalline phase. This component of the scattering was not included in equation (1), which gives the scattering for an incompressible blend, but Jahshan and Summerfield[8] have shown that it should introduce extra terms multiplied by the coefficients a_S and $(a_H(1-X)+a_DX)$. Due to the cancellation between the scattering lengths of hydrogen and carbon this component of the scattering is not observed in the SANS patterns of the unlabelled blend (*Figure 3*) or the

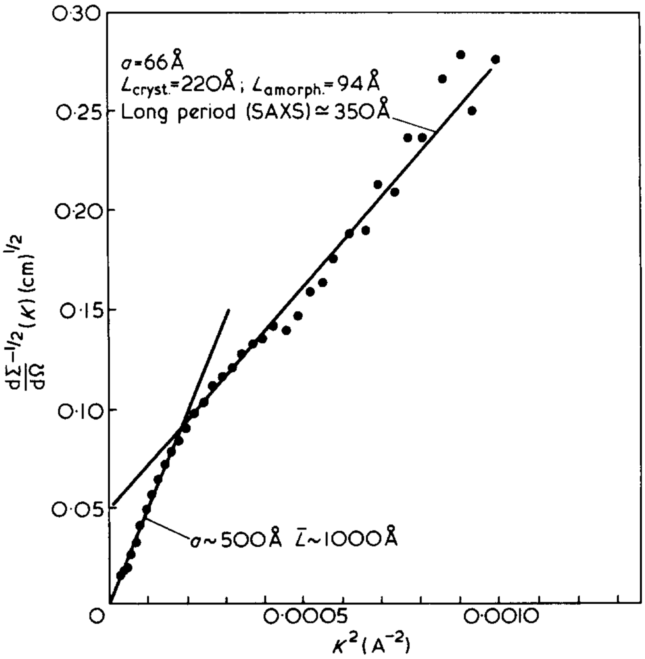

Figure 6 Debye plot of 50 : 50 polypropylene (PPH) and polyethylene (PED), slow cooled from the melt at 5 K min^{-1}

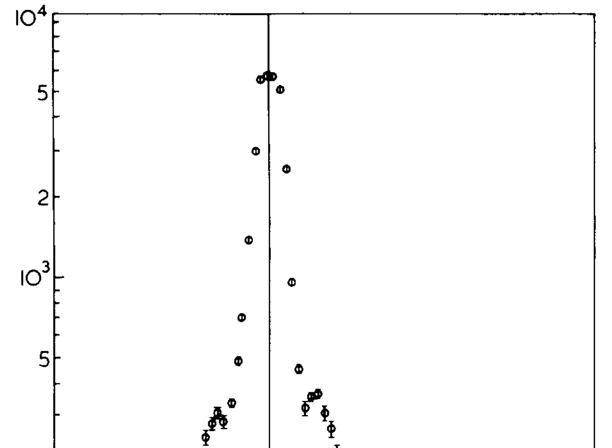

Figure 7 SAXS pattern for 50 : 50 polypropylene (PPH) and polyethylene (PED) slow-cooled from melt at 5 K min^{-1}

homopolymer[4]. Similarly, for low levels of deuteration ($X<0.1$) omission of these terms does not appear to lead to any appreciable error in the determination of individual chain dimensions as indicated by the excellent agreement between the g.p.c. and SANS determinations of the molecular weights of the labelled chains. However, for the fully labelled blend ($X=1$) there is no cancellation between the scattering lengths of carbon and deuterium and the density fluctuation scattering from the lamellar structure of the fully labelled (PED) phase can no longer be neglected, and this appears to be the origin of the departures from the simple Debye theory observed in *Figures 5* and *6*.

Lamellar structure is normally studied by SAXS and *Figure 7* shows a slice from a two-dimensional SAXS pattern of a slow-cooled blend taken on the ORNL 10 m SAXS camera[26]. This sample exhibited the largest lamella spacing (350 Å) as calculated from the SAXS peak at $K\simeq 0.02$ Å^{-1}; the smallest spacing (150 Å) was observed in the sample precipitated from solution into methanol. If we use the measured SANS correlation lengths and sample crystallinity to calculate the lengths of the crystalline and amorphous regions we obtain values of $L_{\mathrm{cryst}}=220$ Å and $L_{\mathrm{amorph}}=94$ Å from *Figure 6* using a crystal volume fraction, $\varphi=0.7$, typically measured on this type of blend by d.s.c. or wide-angle X-ray diffraction methods. Thus the long period calculated from the Debye plot ($L=314$ Å) compares with a value of $L=350$ Å measured by SAXS. The periodicity of the amorphous and crystalline regions is therefore of the correct order to produce an approximately linear Debye plot with the measured correlation length in the region $0.0002\leqslant K^2\leqslant 0.001$ Å^{-2}. This supports the suggestion that at lower K values the SANS data (*Figures 5* and *6*) of the fully labelled blend are dominated by the overall domain dimensions, whereas at higher K ($K^2\geqslant 0.0002$ Å^{-2}) the scattering is determined primarily by the internal domain structure.

To achieve more than semiquantitative analysis of the latter region, it would be necessary to utilize the individual crystallinities and long periods for each phase, rather than the average values for the whole sample used above.

To investigate whether the phase segregation observed in melt-crystallized and solution-precipitated samples persists in the molten state, one sample (50:50/PED:PPH) was examined at 200°C. The scattering cross-section observed (*Figure 8*) was strong compared with the scattering of statistically distributed molecules shown in *Figure 3* for the 45 PEH:5% PED:50% PPH sample quenched from the melt. This is indicative of phase segregation in the melt and the overall shape of the scattering curve suggested that the domain dimensions are of the same order as those observed in the melt crystallized blends. The results indicate that studies of melt domain kinetics are feasible.

The observed cross-section increases rapidly at low K for all the phase-segregated blends studied in this work, and this indicates the need for careful evaluation of the effects of multiple scattering on the data. Methods to evaluate such effects have recently been developed by Schelten and Schmatz[27] for samples for which scattering is confined to small angles ($\theta<0.1$) and for which scattering decreases rapidly with increasing K (e.g. as K^{-4}). As these conditions are fulfilled for samples for which the Debye theory is a reasonable approximation, these methods have been used to evaluate the effects of multiple scattering on the samples studied here.

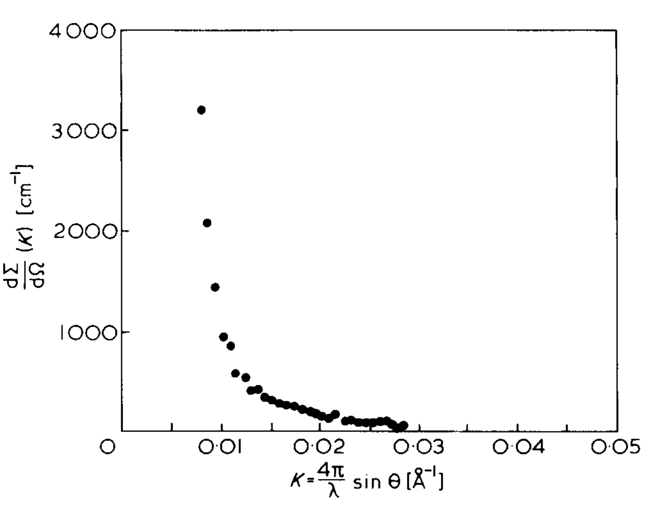

Figure 8 $d\Sigma(K)/d\Omega$ vs. K for 50 : 50 polypropylene (PPH) and polyethylene (PED) in the melt at $T=200$°C

Preliminary calculations[28] indicate that for the typical sample thicknesses measured (0.5–1.0 mm) where the extrapolated forward scattering, $d\Sigma(0)/d\Omega$ is in the range 2×10^5–5×10^5 cm^{-1}, the effects of multiple scattering on the measured correlation length and forward scattering are $<10\%$. When the scattering cross-sections are higher, the measured sample thickness should be reduced to an appropriate value to minimize the effects of multiple scattering. For phase-segregated systems with such high scattering cross-sections, the observed contrast is so strong that it should present little difficulty with regard to the measured signal-to-noise ratio.

In summary, the results of the present study of model blends demonstrate that isotopic labelling can produce strong SANS contrast in mixed polyolefin systems where the application of microscopy is limited due to lack of electron density contrast between the components. By appropriate labelling of the components SANS can be used to determine the domain dimensions and the dimensions of individual molecules within the domains.

SANS can also be used to study the blend structure in the melt and could yield important new information about the effect of different crystallization/processing routes on the domain character of the blend.

Finally, this technique should be applicable not only to homopolymer blends, as studied here, but also to copolymer–homopolymer blends, and should be an important new addition to the range of polymer characterization techniques currently available.

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