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Comments on 'Ambiguities in the interpretation of small angle neutron scattering from blends of linear and branched polyethylene'

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Small-angle neutron scattering has recently been applied to study liquid–liquid phase separation in blends of branched and linear polyethylenes. While experimental results from two groups are basically the same, interpretations differ strongly. The analyses of Schipp *et al.* (*Polymer*, 1996, **37**, 2291), which favour phase separation, are shown to be incorrect. There is no contraction of chain dimensions in blends of linear and branched polyethylene chains. The postulate that large domain sizes in two-phase blends obscure the presence of phase separation is correct in principle, but requires dimensions some ten times larger than the ~1 μm sizes reported for the systems in question. Thus, neutron scattering does not support liquid–liquid phase separation inferred from indirect studies of polyethylene blends. © 1997 Elsevier Science Ltd.

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Schipp *et al.*[1] recently discussed small angle neutron scattering (SANS) from molten blends of deuterated linear polyethylene (dPE) and branched polyethylene (BPE) having about 26 branches per 1000 carbon atoms. At issue is liquid–liquid phase separation (LLPS) inferred from the presence of two melting endotherms and regions of two lamellar thicknesses seen after quench crystallizing blends containing approximately 10% PE (or dPE) in BPE from melt temperatures of 130–180°C. Such studies by Barham, Hill and coworkers are given as refs 15–33 of Schipp *et al.*[1]. Almo *et al.*[2], on the other hand, had presented comprehensive SANS studies on a variety of dPE/BPE systems that indicate the *absence* of LLPS in BPE-rich blends of the sort claimed by Barham, Hill and coworkers. The paper in question addressed the Alamo work with experiments and analyses on blends with compositions of 10 wt% (volume fraction $\phi_d = 0.089$) and 50 wt% ($\phi_d = 0.467$) of dPE. The 10% blend gives (indirect) evidence of LLPS after quench crystallization, but the SANS pattern is consistent with a one-phase melt. Quite the opposite is seen with 50% blend, for which melting and morphology imply one liquid phase, but excess SANS demonstrates the presence of a two-phase melt. The foregoing discrepancies were ascribed to domain size effects in the liquid; Schipp *et al.*[1] suggest that phase domains in the 10% blend are too large to be seen by SANS, and that smaller ~50 nm 'inhomogeneities' in the 50% blend are irrelevant to quenched morphology used to infer LLPS.

These claims are contrary to work in this and other laboratories, where considerable excess SANS is seen at low q if and only if LLPS is present. Most published experiments are on one-phase mixtures because interpretation of patterns in phase separated mixtures is difficult and generally unrewarding. However, Lohse's pioneering work with SANS showed very large intensity unambiguously associated with phase domains as large as 10 μm[3]. Balsara *et al.*[4] worked with model ethylene copolymers and confirmed with light scattering the presence of two macroscopic phases when excess SANS is present, and the absence of two macroscopic phases when SANS indicates only one phase.

We examine here the proposals of Schipp *et al.*[1] (hereafter referred to as Schipp), concentrating on the molten 10% blend at 150°C. Of interest is the coherent SANS cross section per unit volume I as a function of the magnitude of the scattering vector q. $I(q)$ is readily calculated for a one-phase blend of two polymers with the random phase approximation expression:

$$\frac{1}{I(q)} = \frac{1}{K}\left(\frac{1}{\phi_d N_d P_d} + \frac{1}{\phi_h N_h P_h} - 2\chi\right) \tag{1}$$

The contrast factor for dPE/BPE blends is $K = 0.291\ \text{cm}^{-1}$, evaluated from melt density and scattering lengths of the repeat units, C_2H_4 for BPE and C_2D_4 for dPE. Volume fractions are $\phi_{d,h}$, $N_{d,h}$ are (weight-average) degrees of polymerization, $P_{d,h}$ are normalized scattering factors for the polymer molecules, and χ is the Flory–Huggins parameter for interactions between two-carbon units in the labelled and unlabelled chains.

The structure of equation (1), together with $P^{-1} \propto (qR_g)^2$, suggests analysis in the format of $1/I(q)$ *versus* q^2. Schipp's data are so plotted as symbols in *Figure 1*, and the solid line is a linear least squares fit. Using molecular weights published by Schipp ($\bar{N} = 6320$ C_2H_4 groups), the intercept and slope of this line respectively yield $\chi = 8.4 \times 10^{-4}$ and z-average radius of gyration $\langle R_g^2 \rangle_z^{1/2} = 26.1$ nm. These results are reasonable, with χ (attributed almost exclusively to H-D isotope effects) of the same size having been measured on similar blends[2,5]. Following the usual correction for polydispersity, the weight average radius of gyration is $\langle R_g^2 \rangle_w^{1/2} = 21.3$ nm, which conforms to the ratio $R_g/M^{1/2}$ established with other studies of linear and lightly branched polyethylene[6–8].

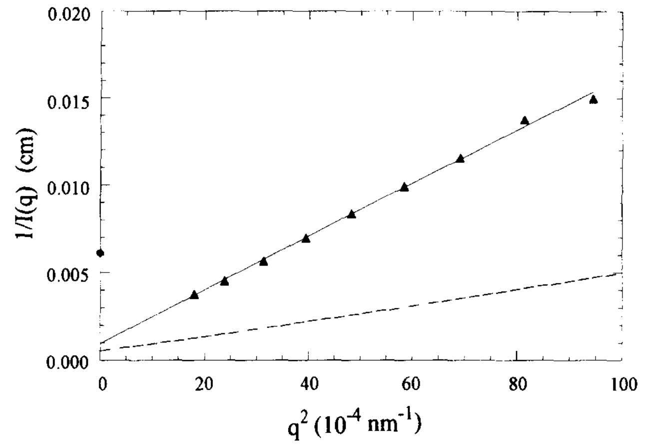

Figure 1 SANS data (▲) for the 10% dPE/BPE taken from Figure 5 of ref. 1 and plotted as $1/I(q)$ *versus* q^2. The solid line is a least squares fit to the data and the dashed line is calculated from equation (1) with the parameters reported by Schipp *et al.*[1]. The symbol (●) on the ordinate is $1/I(q = 0)$ calculated for an ideal solution having $\chi = 0$

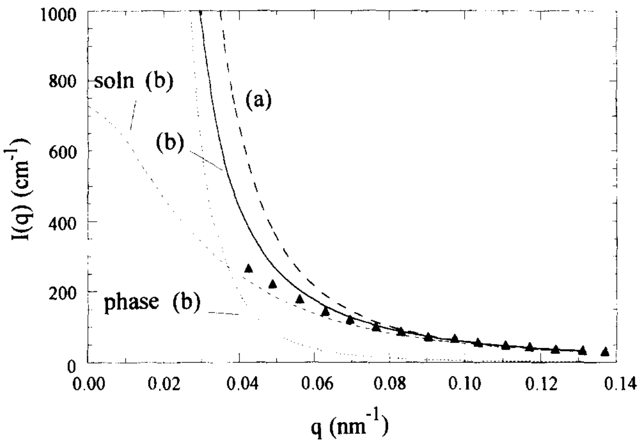

Figure 2 The same data as in *Figure 1* plotted as $I(q)$ vs q. Lines (a) and (b) are calculated $I(q)$ for two-phase models; neither fits the observed intensities. Dashed curve (a) has phase compositions $\phi_d^\alpha = 0.40$ and $\phi_d^\beta = 0.02$ and other parameters reported by Schipp *et al.*[1]. Solid line (b) is for phases with $\phi_d^\alpha = 0.25$ and $\phi_d^\beta = 0.02$ and other parameters given in the text. The contributions from solution and interphase scattering are shown for case (b)

The dashed line in *Figure 1* is calculated for the same molecular weights with parameters ($\phi_d = 0.10$, $\chi = 8.0 \times 10^{-4}$, $R_g = 13.9$ nm) reported by Schipp. This model is clearly incorrect, predicting $I(q)$ that is a factor of three times too large. The interaction parameter $\chi = 8.0 \times 10^{-4}$ is close to that obtained above, but the apparent chain dimension R_g is egregiously small. Agreement with the data can be achieved by multiplying the dashed line by 3, effectively increasing R_g from 13.9 nm to $13.9\sqrt{3}$ nm = 24.1 nm, which is close to $\langle R_g^2\rangle_z^{1/2}$ determined above. Schipp's claim that the small (but incorrect) value of R_g suggests that '...branched polyethylene is, at best, a very poor solvent for [dPE]'[1] is unwarranted.

Schipp further asserted that the experimental intensity $I(q)$ of the 10% blend may also be fit to a model with two liquid phases of compositions $\phi_d^\alpha = 0.4$ and $\phi_d^\beta = 0.02$. Analysis of the two-phase blend is done by summing solution scattering from within each of the two phases and the intensity scattered by the two-phase microstructure:

$$I(q) = \Omega_\alpha I^\alpha(q) + \Omega_\beta I^\beta(q) + I_2(q) \tag{2}$$

$\Omega_{\alpha,\beta}$ are volume fractions of the two phases, and $I^{\alpha,\beta}(q)$ are from equation (1) with parameters replaced by phase-specific compositions and χ, e.g. ϕ_d^α, ϕ_h^α and χ^α for the α phase. Scattering from contrast between the two phases is given the Debye–Bueche equation:

$$I_2(q) = \frac{8\pi\bar{\eta}^2 a^3}{(1 + a^2q^2)^2} \tag{3}$$

Here a is the correlation length of the two-phase structure and the mean square fluctuation of scattering length density is $\bar{\eta}^2 = \Omega_\alpha\Omega_\beta((b/v)_\alpha + (b/v)_\beta)^2$; scattering length densities $(b/v)_{\alpha,\beta}$ are readily calculated from phase compositions $\phi_d^{\alpha,\beta}$. Mass conservation governs the relations between phase compositions, which establish the magnitudes of the solution scattering $I^{\alpha,\beta}(q)$, and $\bar{\eta}^2$, which together with a sets the magnitude of interphase scattering $I_2(q)$.

Figure 2 presents experimental and calculated intensities $I(q)$ for the 10% blend. The dashed curve (a) is for a two-phase model with parameters used by Schipp: $\phi_d^\alpha = 0.40$, $\chi^\alpha = 2.8 \times 10^{-4}$, $\Omega_\alpha = 0.21$; $\phi_d^\beta = 0.02$, $\chi^\beta = 38 \times 10^{-4}$, $\Omega_\beta = 0.79$, and $a = 3\,\mu$m. R_g for all solution components was set at 24.1 nm, because the smaller value reported by Schipp cannot even approximate the data. Calculated intensity is clearly greater than experimental values for $q < 0.09\,\text{nm}^{-1}$, contrary to Figure 11 of ref. 1. This particular choice of phase compositions is curious, because $\phi_d^\alpha = 0.4$ is well into the 'mixed' or one-phase region of the 'phase diagram' established by Schipp for the dPE/BPE system. We therefore recalculated $I(q)$ for two phases consistent with the 'phase diagram' at 150°C having the following parameters: $\phi_d^\alpha = 0.25$, $\chi^\alpha = 2.8 \times 10^{-4}$, $\Omega_\alpha = 0.35$; $\phi_d^\beta = 0.02$, $\chi^\beta = 38 \times 10^{-4}$, $\Omega_\beta = 0.65$, and $a = 3\,\mu$m. The resulting curve is labelled (b); also shown are the contributions from solution scattering $\Omega_\alpha I^\alpha + \Omega_\beta I^\beta$ within the two phases and the interphase scattering I_2. Total intensity (b) is lower than (a) because the I_2 term is reduced by smaller differences in phase composition, but it still exceeds the experimental values.

We have shown that correctly calculated intensities for two-phase models do not reproduce the experimental $I(q)$ for the 10% dPE/BPE blend, contrary to the contention of Schipp. The only way to force agreement is to reduce the interphase contribution $I_2(q)$. One approach is to lessen further the 'miscibility gap' $\phi_d^\alpha - \phi_d^\beta$, but this violates the spirit of the phase behaviour postulated by Schipp. Another tactic is to increase the correlation length a, since $I_2(q = \text{const}) \propto 1/a$ for $aq \gg 1$. Rising a to 10 μm will indeed achieve the agreement claimed by Schipp, but with different parameters. In this case the domain sizes are $a/\Omega_\beta = 30$ nm for BPE-rich α phase, and $a/\Omega_\alpha = 15$ nm for the dPE-rich β phase, easily an order of magnitude greater than seen by microscopy on this and similar blends[1,9]. It goes without saying that a similar analysis with $a = 0.5\,\mu$m, which corresponds to the $\sim 1\,\mu$m domains actually observed by microscopy, would result in $I_2(q)$ far in excess of observed $I(q)$.

Some comments on scattering from the 50% dPE/BPE blend are in order. Intensity is much larger than predicted for a single phase, and $I(q)$ indeed conforms to the Debye–Bueche expression (equation (3)) with a correlation length $a = 24\,\text{nm}$. This interphase scattering decays relatively slowly and masks the weaker solution terms in equation (3). Schipp is uncomfortable with this manifestation of two-phase behaviour because differential scanning calorimetry (d.s.c.) and microscopy on the same blend indicated a 'mixed' or one-phase state. A solution to this apparent dilemma can be had by considering the magnitude of $I(q=0) = 10^4\,\text{cm}^{-1}$ from Figure 8 of ref. 1, which directly yields $\bar{\eta}^2 = 3.3 \times 10^{19}\,\text{cm}^{-4}$. This fluctuation may arise from equal volume fractions ($\Omega_\alpha = \Omega_\beta = 0.5$) having similar compositions $\phi_d^\alpha = 0.42$ and $\phi_d^\beta = 0.58$, which would be difficult to distinguish by either microscopy or d.s.c. We note that the latter method should not be limited by $\sim 50\,\text{nm}$ domain sizes which certainly complicate microscopy. While this estimate should not be taken as a complete description of the system, it should be clear that SANS can easily detect concentrations fluctuations accompanying LLPS that are difficult to observe by other methods.

We conclude by reiterating that the 'ambiguities' suggested by Schipp *et al.*[1] in interpreting SANS from the 10% dPE/BPE blend result from incorrectly calculated $I(q)$ for both the one-phase and two-phase states. Chain dimension R_g is not anomalously small, and hence there is no indication of coil contraction from strong repulsive interactions. It is possible that domain sizes in a two-phase melt become so large that the characteristic intense forward scattering decays to insignificant levels for $q > 0.04\,\text{nm}^{-1}$, but we are aware of no independent reports of such behaviour. Correct calculations show that this may happen for the blend in question when the correlation length a exceeds $10\,\mu\text{m}$. Aside from the fact that implied domain sizes are an order of magnitude larger than observed, the calculation ignores imperfect resolution of the SANS instrument. The sharply peaked function $I_2(q)$ will certainly be broadened by instrumental effects[10], leading to a slower apparent decay of interphase scattering and more 'interference' with solution scattering than indicated in *Figure 2*. We see no reason to accept the proposition that SANS from the 10% dPE/BPE blend is consistent with two liquid phases. It is certain that $I(q)$ is exactly that expected for a one-phase blend with conventional chain dimensions and χ dominated by H-D isotope effects. These SANS experiments, and the similar results of Alamo *et al.*[2], are thus taken as evidence *against* LLPS of the type advocated by Barham and Hill. Similar conclusions, arrived at by different considerations, have recently been set forth by Alamo *et al.*[11].

The 50% dPE/BPE blend is phase separated at 150°C. A simple SANS analysis indicates small domains with similar compositions, which may elude detection by indirect methods. Here LLPS is unambiguous and driven by well-documented isotope effects[2,5]. For unlabelled components one estimates that $\chi \leq 1 \times 10^{-4}$ at this level of branching[12,13], hence the comparable 50% PE/BPE blend would be single phase. In this lone conclusion do we concur with the arguments of Schipp *et al.*[1].

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