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In a previous paper we have shown how small-angle neutron and x-ray scattering (SANS, SAXS) can be used to determine the melt compatibility of different polyolefins, including high-density (HD), low-density (LD), and linear low density (LLD) polyethylene. Such blends have attained widespread commercial applications, though the understanding of the mechanical and melt-flow properties of such blends has hitherto been handicapped by the absence of a consensus concerning the degree of mixing of the components, both in the melt and solid states. Recent SANS data indicate that for HDPE/LDPE blends, the melt is homogenous for all compositions after proper accounting for H/D isotope effects.¹ In this publication we use complementary SANS, DSC, and SAXS to examine the types of morphologies and the different degrees of phase separation which may arise via crystallization effects on cooling from a homogenous melt.

SAMPLE PREPARATION AND DATA ANALYSIS

The mixtures were prepared by dissolving deuterated linear polymer (HDPE-D), and branched (LDPE-H or LLDPE-H) protonated polymer in ortho-dichlorobenzene, rapidly quenching into chilled methanol and pressing into discs ~1-mm thick via compression molding. The sample concentrations were (wt%) 80/20, 70/30, 50/50, 23/77, and 10/90 (HDPE-D/LDPE-H). Absolute SANS data were collected as described previously¹ as a function of the scattering vector (Q) in the range $0.003 < Q = 4\pi \lambda^{-1} \sin \theta < 0.04 \text{ \AA}^{-1}$, where 2θ is the angle of scatter and $\lambda = 4.75 \text{ \AA}$ is the neutron wavelength. For 2-phase systems, Debye, Bueche (DB), et al.²⁻⁴ proposed that the cross section has the form:

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{8\pi a_1^3 \phi_1 \phi_2 [SLD(1) - SLD(2)]^2}{(1 + Q^2 a_1^2)^2} \quad (1)$$

where a_1 is a length characterizing the spatial dimensions via an exponential correlation function.²⁻³ The volume fractions are ϕ_1 and ϕ_2 , and SLD(1) and (2) are the scattering length densities of the two phases.

RESULTS AND DISCUSSION

(A) Slowly Cooled Blends

Figure 1 shows typical DB plots for samples with 80/20 and 70/30 wt% blends of HDPE-D and LDPE-H slowly cooled from the melt at $0.75^\circ\text{C}/\text{min}$ and the fits for these (and all other) are reasonably linear. Assuming complete separation of the components (i.e., $\phi_1 = \phi_D$; $\phi_2 = \phi_H$), the cross sections calculated from eq. (1) at ($Q = 0$) are shown in Table 1 along with the experimental SANS results. The agreement with the DB theory is excellent for blends with high concentrations of linear polymer ($\phi_D \geq 0.5$). SAXS data were also collected on these samples and for predominantly linear blends ($\phi \geq 0.5$) two "peaks" or modulations are clearly seen in Lorentz-corrected plots ($Q^2 d\Sigma/d\Omega$ vs Q), whereas for the predominantly branched samples only one feature is observed. The "peak" positions (Q^*) were converted to length scales representing the lamella spacings or "long periods" ($D = 2\pi/Q^*$) and are shown in Table 1. It is interesting to note that the measured and calculated SANS intensities are in good agreement where two SAXS "peaks" are observed, whereas the calculations overestimate the measured cross sections by a factor (~3) when only one feature is present in the SAXS data. This suggests that in HDPE-rich blends ($\phi \geq 0.5$), the components are segregated into separate HD- and LDPE lamella stacks, each with its own characteristic spacing. For LDPE-rich blends, there is only one long period and this implies that the components are dispersed in a common lamella stack with

mixed HDPE and LDPE lamellae. The difference between the measured and calculated intensities further imply that the components are not completely separated and there must be some mixing of the two species within each lamella. However, the incorporation of as little as 15–20% LDPE within the HDPE phase (and vice-versa) would be enough to bring the experimental and calculated intensities into agreement. Thus, HDPE/LDPE blends are either completely ($\phi \geq 0.5$) or almost completely ($\phi < 0.5$) phase separated into separate HDPE and LDPE lamellae over the whole compositional range after slow cooling from the melt.

B. Rapidly Quenched Blends

SANS data were also collected on blends of HDPE-D/LDPE-H, quenched from the melt into dry ice/acetone at -78°C , though these samples gave qualitatively different spectra at the LDPE-rich and HDPE-rich ends of the composition range. For LDPE-rich blends (10/90 and 23/77 wt%), a monotonic fall-off is observed as a function of Q and the data approach the Q^{-2} asymptote, as opposed to the Q^{-4} behavior observed for slowly cooled blends [eq. (1)]. This suggests that the scattering arises from individual molecules as opposed to separate phases with sharp boundaries. When the data are replotted in the Zimm or Ornstein-Zernicke format [$d\Sigma/d\Omega^{-1}(Q)$ vs. Q^2 , the ($Q = 0$) calculated cross section is close to the measured value from the extrapolated intercept (Fig. 2). The radius of gyration ($R_g \approx 140 \text{ \AA}$) is similar to the molecular dimensions measured in the solid state for HDPE-D/HDPE-H blends. For all blends, SAXS shows only one feature in the Lorentz-corrected data indicating that there is a single lamellar stack. Thus, for LDPE-rich blends, the deuterated linear polymer seems to be extensively cocrystallized with the branched molecules in the lamellae.

For HDPE-rich mixtures, the form of the scattering is apparently different at first sight as indicated in Fig. 3. Data for the 80/20, 70/30, and 50/50 blends exhibit inflections, which seem to reflect the peak in the HDPE scattering. A component of the scattering from the periodic lamellar structure is always present in the blend data, though if the D-labeled and protonated molecules are randomly mixed, it normally forms a minor correction to the data. However, if the protonated molecules were preferentially located in the interlamellar amorphous regions, this would enhance the scattering length density contrast between the crystal and amorphous regions and the overall lamellar periodicity would therefore show up much more strongly in the blend cross section. For example, assuming an overall crystallinity index of ~33% for the 80/20 blend, if the average concentrations in the crystal and amorphous regions were 90/10 and 75/25 respectively, the blend cross section would contain a component of 450% (~4.5 ×) the fully deuterated "blank" cross section, which would cause observable inflections in the slope as observed in Fig. 3. Figure 4 shows the corrected signal after subtracting $5 \times$ the PED SANS cross section. The Zimm plot is now linear with good agreement between the measured (644 cm^{-1}) and calculated (612 cm^{-1}) cross sections. Thus, the blends are again extensively cocrystallized, though the branched molecules seem to be preferentially contained in the amorphous regions. The perturbation of the SANS pattern by such an excess concentration of LDPE would be much less for predominantly branched materials, as the SLD difference between the crystal and amorphous is much smaller, so no such feature is observed (Fig. 2). Thus, for rapidly quenched blends, the components are extensively cocrystallized for all concentrations. Experiments are currently in progress to explore the solid state morphology of blends of HD and LDPE as a function of quench rate, and these studies are also being extended to HD/LLDPE systems.

REFERENCES

1. R. A. Alamo, J. D. Londono, L. Mandelkern, F. C. Stehling, and G. D. Wignall, *Macromol.* **27**, 411 (1994).
2. P. Debye and A. M. Bueche, *J. Appl. Phys.* **20**, 518 (1949).
3. P. Debye, H. R. Anderson, and H. Brumberger, *J. Appl. Phys.* **28**, 679 (1957).
4. A. M. Fernandez, G. D. Wignall, and L. H. Sperling, *ACS Advances in Chemistry Series*, **211**, 1534 (1986).

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TABLE 1. Measured and Calculated Cross Sections for HDPE/LDPE Blends Slow Cooled (0.75°C/min) From the Melt

Nominal Wt% (HDPE/LDPE)	Correlation Length (Å)	$10^3 d\Sigma/d\Omega(Q=0)(\text{cm}^{-1})$ (expt)	(calc)	Long Period (Å)
80/20	63	7.6	6.9	299/125
70/30	77	15.5	16.6	292/125
50/50	92	28.4	34.3	285/114
23/77	114	15.6	45.0	180
10/90	107	6.9	19.1	139

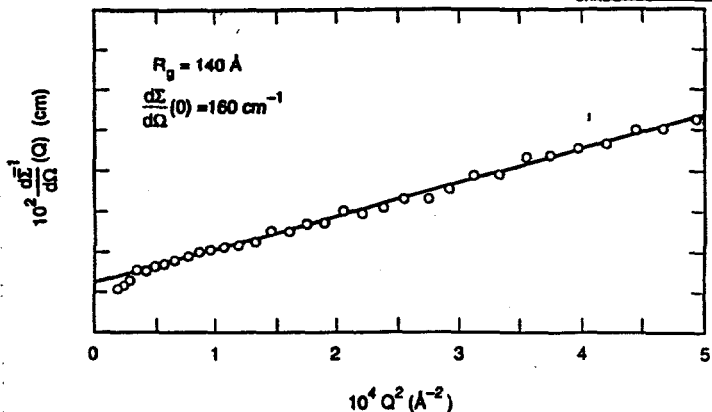


Figure 2
 $\frac{d\Sigma}{d\Omega}(Q)$ vs Q^2 for 10/90 Sample of HDPE-D/LDPE-H

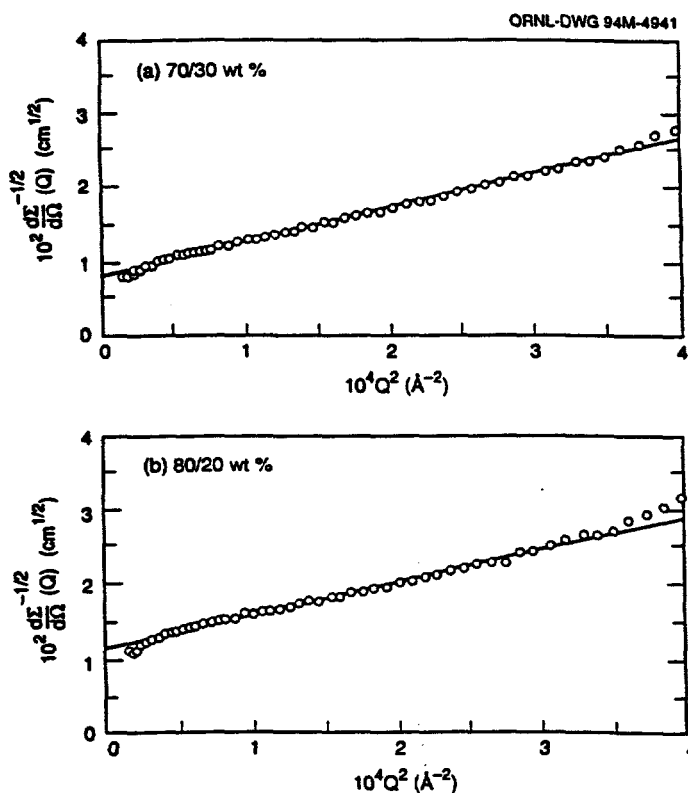


Figure 1
Debye-Bueche Plots for (a) 70/30 and (b) 80/20 wt % Blends of HDPE-D and LDPE-H Slow Cooled from Melt 0.75°C/min

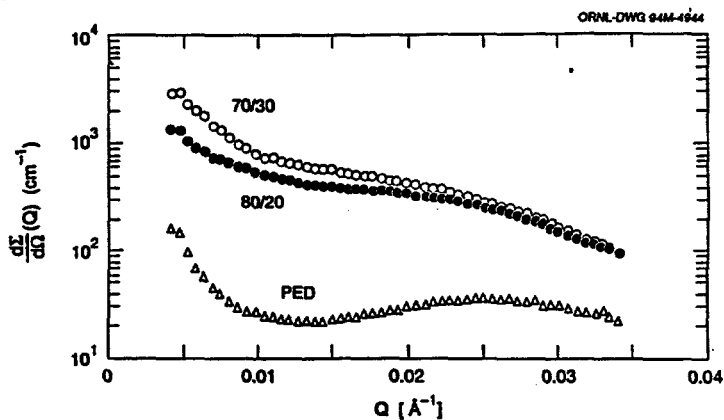


Figure 3
 $\frac{d\Sigma}{d\Omega}(Q)$ vs Q for PED and PED-RICH Blends of HDPE-D/LDPE-H

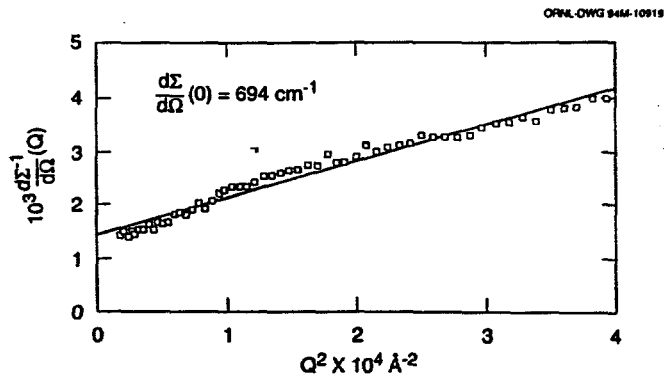


Figure 4
 $\frac{d\Sigma}{d\Omega}$ vs. Q^2 FOR RAPIDLY QUENCHED 80/20 BLEND OF HDPE-D / LDPE-H AFTER BACKGROUND CORRECTION BASED ON THE ASSUMPTION THAT THE LDPE RESIDES PREFERENTIALLY IN THE AMORPHOUS REGION