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Small-Angle Neutron Scattering Investigations of Liquid−Liquid Phase Separation in Heterogeneous Linear Low-Density Polyethylene

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ABSTRACT: The issue of multiple equilibrium phases in compositionally heterogeneous random copolymers has been addressed by a series of small-angle neutron scattering (SANS) experiments. An ethylene−hexene (EH) copolymer, representative of many linear low-density polyethylenes (LLDPE) has been shown to contain a dispersed minority phase (volume fraction, $\phi \sim 0.02$) consisting of highly branched, amorphous material. The dispersed phase is eliminated to a good approximation by xylene extraction, which removes the low molecular weight and highly branched molecules. The extracted material contains a much higher fraction of branched molecules and hence has a greater proportion of the dispersed phase ($\phi \sim 0.2$). These findings support the prediction of liquid−liquid phase separation for compositionally polydisperse LLDPEs, whereby the more highly branched molecules in the distribution may phase segregate, even if the overall branch content is low.

Introduction

It is now well established[1−8] that small-angle neutron scattering (SANS) can be used to determine the melt compatibility of mixtures of linear and branched polyolefins, including high-density (HD), low-density (LD) and linear low-density (LLD) polyethylenes. HDPE is the most crystalline form of polyethylene (PE) because the chains contain very little branching. LDPE contains some short chain branches (typically 1−3 per 100 backbone carbon atoms), as well as a few long chain branches (typically 0.1−0.3 per 100 backbone carbon atoms). Linear low-density polyethylene (LLDPE) is produced by catalytically copolymerizing ethylene with an α-olefin such as butene, hexene, or octene. LLDPEs can have a wide range of branch contents, depending primarily on the type of catalyst and concentration of added comonomer, with a homogeneous side (short) branch length. SANS data indicate that for HDPE/LDPE blends with molecular weights $\sim 10^5$, the melt is homogeneous for all compositions after proper accounting for H/D isotope effects.[1,2] Similarly, SANS indicates[3−6] that mixtures of HDPE and LLDPE are homogeneous in the melt when the branch content is low (i.e. <4 branches (br)/100 backbone carbons). However, when the branch content is higher (>10 br/100 C), the blends phase separate.[5,6]

In previous SANS experiments,[3−6] the LLDPE's were simulated by hydrogenated (or deuterated) polybutadienes, because these materials may be prepared as nearly monodisperse ($M_w/M_n < 1.1$) molecules with a homogeneous branch distribution within each chain. Thus, these studies were not affected by polydispersity effects, in either the branch content or molecular weight. However, for typical LLDPEs prepared with heterogeneous-type Ziegler−Natta catalysts, it is well-known that the multisite nature of catalysts typically used in the preparation of such materials leads to a wide distribution of chain compositions.[9] The branch content and molecular weight are strongly correlated and the low molecular weight chains exhibit the most branching.[10,11] Thus, a heterogeneous LLDPE may be thought of as a "blend" of different species and when the composition distribution is broad, the multicomponent system can, in principle, phase separate.

This raises the intriguing prospect that even when the average branch content is low (e.g. 1−3 br/100 C), there should be a small fraction of highly branched chains (e.g. >10 br/100 C), which are incompatible with the lightly branched molecules and will thus phase separate. To our knowledge, this was first suggested by Mirabella and co-workers,[11,12] based on scanning electron microscopy (SEM) investigations of the solid state. Subsequently, Nesarikar and Crist[13] performed a thermodynamic calculation of the equilibrium melt state using a distribution of chain branching estimated from temperature-rising elution fractionation.[12,13] The calculations predicted a small fraction of a second phase consisting of highly branched amorphous material, and the predicted volume fraction ($\phi \sim 10^{-2}$) was in reasonable agreement with the SEM findings.[12,13]

However, studies in the solid state do not necessarily reflect the structure of the melt, as crystallization can produce phase segregation in mixtures of linear and branched molecules, even if the melt is homogeneous.[1] It is the purpose of this investigation to examine the structure of the liquid directly to complement the solid state SEM studies. Because the linear and branched molecules have virtually the same scattering power, there is no contrast between the phases and the melt structure would not be manifested via X-ray or light scattering. We have therefore added a fraction of

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Table 1. Characterization of Original Polydisperse Ethylene−Hexene-1 Copolymer and Its Fractions

sample	$10^{-3}M_w$	$10^{-3}M_N$	br/100 C or mol % butyl br	T_m (°C)	crystallinity $(1-\lambda)_{\Delta H}$
original EH	120	30	1.7	124	0.29
high-M_w fraction	124	37	1.4	123.5	0.27
low-M_w fraction	53	8.5	3.1	55−65	0.05
deuterated HDPE	139	23		123.1	0.42

deuterated linear polymer (20%) and examined the blends by neutron scattering. On the basis of previous studies, the linear material should be incompatible with the minority phase but should mix homogeneously with the predominantly low-branched matrix. Thus, the addition of HDPE-D should provide SANS contrast between the phases (and also between the protonated and deuterated molecules within the majority phase), without perturbing the predicted two-phase morphology.

Sample Preparation and Characterization

(a) Extraction Process. A commercial ethylene−hexene-1 (EH) copolymer, prepared with a Ziegler−Natta catalyst, was dissolved in *p*-xylene (1 wt/v %) at 170 °C during approximately 2 h under N_2 purge. The heat source was removed, and the solution was allowed to cool to room temperature. During this process the high molecular weight, lightly branched material crystallizes out of the solution. These crystals were filtered out, washed with methanol, and dried under vacuum. The lower molecular weight, more highly branched component (≃8%) was recovered from the filtrate by evaporating the solvent and drying at 50 °C in vacuum over 2 days.

The molecular weight and butyl branching composition were analyzed by conventional GPC and ^{13}C NMR techniques. The melting temperatures and degrees of crystallinity $(1-\lambda)_{\Delta H}$ were obtained by differential scanning calorimetry (DSC) on rapidly quenched samples.[1] These data are listed in Table 1. Also listed is the deuterated linear HDPE used to provide SANS contrast.

(b) Blend Preparation. Mixtures of the original EH copolymer and the two fractions each with 20% deuterated linear polyethylene were prepared by dissolving the initial components in 125 mL of *o*-dichlorobenzene (total weight ≈ 300 mg) stirring at 178 °C for 15 min. The solution was rapidly quenched into 2 L of chilled methanol (≈−60 °C), and after filtering and washing with methanol, the crystals were dried overnight in a vacuum oven at 60 °C. Disks ≈1 mm thick were obtained via compression molding in a Carver Press at 190 °C and quenching into ice water. Single melting peaks and degrees of crystallinity similar to the protonated species found for the 80/20 blends of the original and high molecular weight fraction were consistent with a high amount of cocrystallization of both species. However, double peaks with melting temperatures corresponding to the initial components were found in the blend of the deuterated HDPE with the low molecular weight fraction.

Small-Angle Neutron Scattering: Data Collection

The data were collected on the W. C. Koehler 30 m SANS facility[14] at the Oak Ridge National Laboratory via a 64 × 64 cm^2 area detector with cell (element) size ~1 cm^2 and a neutron wavelength (λ) of 4.75 Å. The sample−detector distance was 14 m, and data were corrected for instrumental backgrounds and detector efficiency on a cell-by-cell basis, prior to radial averaging to give a Q range of $0.004 < Q = 4\pi\lambda^{-1} \sin\theta < 0.04$ Å^{-1}, where 2θ is the angle of scatter. The measured intensities were corrected for the efficiency variation of the detector, instrumental (beam blocked) backgrounds, and also the intensities of the corresponding sample cells with quartz windows, which formed only a minor correction (<5%) to the sample data. The net intensities were converted to an absolute (±3%) differential cross section per unit sample volume [$d\Sigma/d\Omega(Q)$ in units of cm^{-1}] by comparison with precalibrated secondary standards, based on the measurement of beam flux, the scattering from water, vanadium, and other reference materials.[15] Details of transmission measurements, data collection, and correction procedures for instrumental and incoherent backgrounds have been given previously.[16,17]

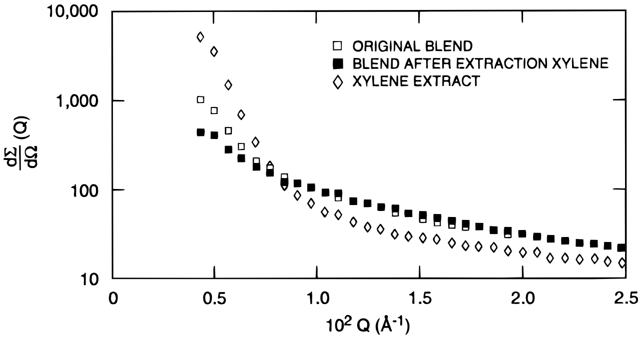

Figure 1. $d\Sigma/d\Omega(Q)$ for heterogeneous ethylene−hexene LLDPE copolymer blended with 20 wt % (deuterated) HDPE before and after xylene extraction.

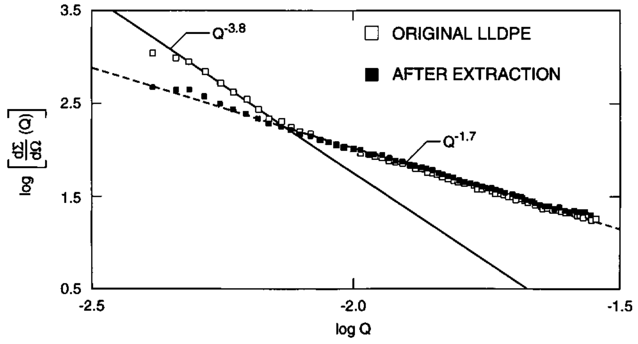

Figure 2. log−log plot for compositionally heterogeneous ethylene−hexene copolymer before and after xylene extraction (both samples blended with 20 wt % HDPE-D to provide SANS contrast).

Small-Angle Neutron Scattering: Data Analysis

Figure 1 shows the cross section in the melt (T = 160 °C) for the original ethylene−hexene LLDPE, along with the same sample after xylene extraction, and also the extracted material. All samples were blended with 20 wt % linear HDPE-D (to provide SANS contrast). The existence of multiple phases should be reflected in the SANS data and the original blend clearly exhibits two regions where the scattering varies as $Q^{-3.8}$ and $Q^{-1.7}$ (Figure 2) for the lowest and highest Q values, respectively. These exponents are close to the Porod limit (Q^{-4}, expected for separate phases with sharp boundaries[18]) and Gaussian (Debye) coil limit (Q^{-2}, expected for individual random coil molecules[19,20]). It may be seen that the extraction procedure, which is expected to remove the highly branched and low molecular weight components, only changes the scattering at the lowest Q values and that the data superimpose over most of the range (Q > 0.01 Å^{-1}). Xylene extraction effectively removes the component, which varies with the Porod exponent (−4).

The original LLDPE has an average branch content (Table 1) of 1.4 mol % butyl branches (or ~1.4 br/100 C), though a small fraction of the distribution will be highly branched, and chains with >10 br/100 C should phase separate from the lightly branched matrix. As the disperse phase (volume fraction, $\phi \sim 10^{-2}$) is incompatible with lightly branched chains, it is to be expected that it is also incompatible with the linear (deuterated) material which is added to provide SANS contrast. If these domains consisted of particles with relatively sharp boundaries, this would naturally give rise to the Q^{-4} variation observed in the low-Q (Porod) limit. Conversely, it is well-known[1−5] that lightly branched material is compatible with linear HDPE-D, so the matrix should consist of a homogeneous mixture of HDPE-D and LLDPE-H chains, and such a morphology would also give rise to the observed Q^{-2} variation over most of the Q range. Thus the two-phase hypothesis[12,13] accounts qualitatively for the general features of the scattering, and a more quantitative analysis is given below.

For a homogeneous blend of two polymer species, one of which is deuterium labeled, the coherent cross section is given[1] by

$$\frac{d\Sigma}{d\Omega}(Q) = V^{-1}(a_H - a_D)^2 S(Q) \quad (1)$$

where a_D is the scattering length of the repeat unit (segment) of the labeled species (HDPE-D in this research), a_H is the scattering length of the unlabeled species (LLDPE-H), $S(Q)$ is the structure factor, and V is the segment volume. Assuming that the polymer constituents can be treated as ideal (Gaussian) coils, unperturbed by the weak interactions between monomers, $S(Q)$ is given by[21]

$$S^{-1}(Q) = [\phi_D N_D P_D(QR_{gD})]^{-1} + [(1-\phi_D)N_H P_H(QR_{gH})]^{-1} - 2\chi \quad (2)$$

where ϕ_D is the volume fraction of the labeled species and R_{gD}, R_{gH}, N_D, and N_H are the radii of gyration and polymerization indices of the two species, with intrachain functions $P_D(QR_{gD})$ and $P_H(QR_{gD})$ represented by Gaussian (Debye) linear coils[19−22]

$$P(Q,R_g) = 2[R_g^{\,2}Q^2 + \exp(-R_g^{\,2}Q^2) - 1]/(R_g^{\,4}Q^4) \quad (3)$$

When $QR_g \gg 1$, the homogeneous RPA scattering is dominated by $P(Q,R_g)$, which varies as Q^{-2} in this limit (eq 3).

χ is the Flory−Huggins interaction parameter, and for mixtures of protonated and deuterated linear HDPEs, the interaction arises from isotope effects,[2] with $\chi \simeq \chi_{HD} \simeq 4 \times 10^{-4}$, which is relatively independent of concentration for $0.2 < \phi_D < 0.8$. Similarly, for mixtures of linear and lightly branched molecules (<3 br/100 C), one of which is deuterated (e.g. HDPE-D/LDPE-H), only the isotopic interaction parameter is observed via SANS.[1] However, where the branch content of one species is appreciable, there is another contribution to the interaction parameter.[3−5] Crist and co-workers[5] have estimated an interspecies interaction parameter between ethyl-branched and linear molecules as $\chi_{inter} \simeq CY_{br}^{\,2}$, where Y_{br} is the fraction of branched (C_4H_8) units and $C \sim 0.02$ (or 0.01 for the C_2H_4 unit used in this work). Similar magnitudes for the interspecies component of χ have been estimated independently via SANS.[3,4]

At small Q, eqs 1 and 2 reduce to the Ornstein−Zernicke (O−Z) form,[1,2]

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{d\Sigma}{d\Omega}(0)/(1 + Q^2\xi^2) \quad (4)$$

$$\frac{d\Sigma}{d\Omega}(0) = \frac{V^{-1}(a_H - a_D)^2}{(\phi_D N_D + \phi_H N_H - 2\chi)} \quad (5)$$

where ξ is the composition fluctuation correlation length. Figure 3 shows an O−Z plot [$d\Sigma/d\Omega(Q)^{-1}$ vs Q^2] for the LLDPE-H/HDPE-D sample, where linear regression omits the lowest Q region of the data. The extrapolated ($Q = 0$) intercept is positive, as expected for a homogeneous mixture. Depending on the “cutoff” point chosen between the Porod and Debye regions of the data, the value is in the range $330 < d\Sigma/d\Omega(0) < 470$ cm^{-1}, compared to ≃400 cm^{-1} calculated from eq 4 with $\chi \sim \chi_{HD} \sim 4 \times 10^{-4}$. This supports the postulate that the vast majority of the sample forms a homogeneous mixture. The volume fraction of the disperse phase can be estimated[23] from the SANS invariant

$$Q_0 = \int_0^\infty Q^2 d\Sigma/d\Omega(Q)\, dQ = 2\pi^2\phi_1\phi_2[\rho_{1n} - \rho_{2n}]^2 \quad (6)$$

where ϕ_1, ϕ_2 and ρ_{1n}, ρ_{2n} are the volume fractions and neutron scattering length densities of the two phases, respectively.

The scattering from the minority (disperse) phase is manifested (Figures 1 and 2) below $Q \simeq 0.01$ Å^{-1}, where it is superimposed on the cross section of the majority of the sample consisting of a homogeneous mixture of HDPE-D and LLDPE-H. We have removed this coherent “background” by subtracting the cross section of the xylene-extracted material, which superimposes on the scattering of the original blend for $Q > 0.1$ Å^{-1}. Below this limit, the cross section of the extracted material varies as Q^{-2} (Figure 2) and is therefore a reasonable approximation for the homogeneous RPA scattering in the low-Q limit. As the original and xylene-extracted materials have the same isotopic ratio, subtracting this component will also remove the incoherent background (∼1 cm^{-1}).

The net scattering is given in Figure 4 which shows a Kratky plot [$Q^2 d\Sigma/d\Omega(Q)$ vs Q], and in order to estimate the portion of the area below the minimum observable $Q_{min} \simeq 0.004$ Å^{-1}, we rely on the fact that the curve must pass through the origin at $Q = 0$. We assume that the missing low-Q data follow the Guinier approximation, to give an integrated area of $Q_0 \simeq 3.3 \times 10^{-5}$ cm^{-1} Å^{-3}.

Assuming that the disperse phase consists of protonated material in a matrix which is a blend of protonated LLDPE and 20 wt % HDPE-D, this leads to $\phi \simeq 0.021$ via eq 5. This is close to previous estimates[12,13] for the volume fraction of the phase-separated regions in a typical heterogeneous LLDPE, though exact agreement is not expected as the comonomers were different for the two polymers (butene as opposed to hexene).

Figure 5 shows a Kratky plot [$Q^2 d\Sigma/d\Omega(Q)$ vs Q] of the material extracted by xylene extraction. As this formed 8% of the original polymer, 2% of which was phase separated, we might expect that the volume fraction of the disperse phase in the xylene extract would be $\phi \sim 0.20$, when blended with 20% HDPE-D. Invariant analysis leads to $\phi \simeq 0.20$, after correction for the coherent “background” from scattering from the homogeneously mixed material. The close agreement between these estimates is probably fortuitous in view of the fact that the scattering from particles with

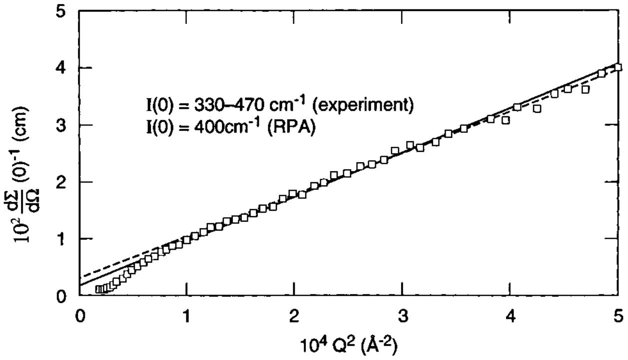

Figure 3. Ornstein–Zernicke plot for heterogeneous ethylene–hexene LLDPE copolymer blended with 20 wt % (deuterated) HDPE.

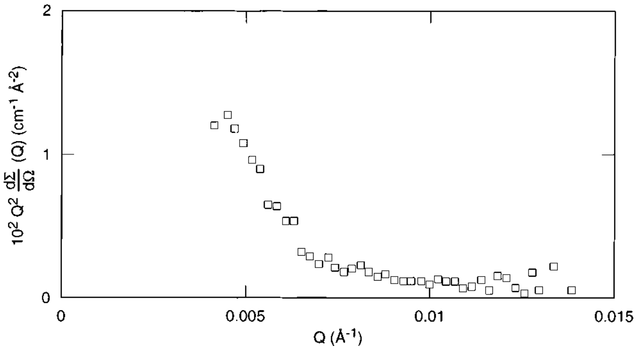

Figure 4. $Q^2 d\Sigma/d\Omega(Q)$ versus Q for the low-Q region of SANS data of heterogeneous LLDPE-H blended with 20 wt % HDPE-D.

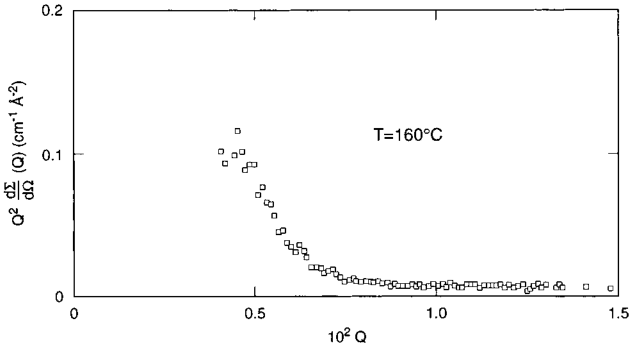

Figure 5. SANS invariant for xylene extract of LLDPE-H blended with 20 wt % HDPE-D.

dimensions >2000 Å appears at Q values <0.004 Å^{-1}, which is beyond the resolution limit of the experiment (Figures 4 and 5). This region has to be estimated in the invariant analysis, by the approximations described above, leading to an uncertainty of ±20% in ϕ. However, within the experimental errors, the SANS data strongly support the hypothesis that the highly branched molecules in LLDPEs can phase segregate and form a disperse phase.[12,13]

This research is relevant to the understanding of the melt phase behavior of ethylene copolymers having wide composition distributions. These results support the view, previously presented by others,[11−13] that such LLDPEs can form two phases in the melt. The relationship of these results to the fracture toughness of LLDPE has to be established by independent studies.

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