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Small Angle Neutron Scattering Investigations of Melt Miscibility and Phase Segregation in Blends of Linear and Branched Polyethylenes as a Function of the Branch Content

R. G. Alamo,[†] W. W. Graessley,[‡] R. Krishnamoorti,[§] D. J. Lohse,[⊥] J. D. Londono,[||] L. Mandelkern,[∇] F. C. Stehling,[#] and G. D. Wignall*,[||]

Department of Chemical Engineering, Florida Agricultural and Mechanical and Florida State University College of Engineering, Tallahassee, Florida 32310-6046, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544, Department of Materials Science and Engineering, Barb Hall, Cornell University, Ithaca, New York 14853-1501, Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801, Oak Ridge National Laboratory,[¶] Oak Ridge, Tennessee 37831-6393, Department of Chemistry, Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306-3015, and Plastics Technology Division, Exxon Chemical Company, Baytown, Texas 77522

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ABSTRACT: We have performed a series of small angle neutron scattering (SANS) experiments on blends of linear and branched polyethylenes to investigate the level of branching that is required to phase separate the system. These results confirm that the mixtures are homogenous for all compositions when the branch content is low (i.e., <4 branches/100 backbone carbon atoms for molecular weight $M_w \sim 10^5$). However, when the branch content is higher (typically ≥ 8 branches/100 backbone carbons), the blends phase separate. Segregation can also be driven by isotope effects, when the molecular weight is sufficiently high so that the product of the polymerization index and the H^1/D^2 interaction parameter ($N\chi_{HD}$) > 2. In each case, the resolution of conventional SANS pinhole cameras ($Q_{min} \sim 10^{-3}$ Å^{-1}) is adequate to determine the state of mixing, even for systems with large domains.

Introduction

Polyethylene is produced in many forms, each of which has different properties resulting from variations in structure. The melting temperature depends on both the molecular constitution and crystallization conditions. High-density polyethylene (HDPE) has linear chains with a (peak) melting point in the range 130 °C $< T_m <$ 135 °C. Low-density polyethylene (LDPE) contains both short and long chain branches, formed through intramolecular and intermolecular hydrogen transfer reactions, respectively, and has a melting point typically 108 °C $< T_m <$ 115 °C. Linear low-density polyethylene (LLDPE) is produced by copolymerizing ethylene with an α-olefin such as butene, hexene, or octene. The melting point, which is intermediate between HDPE and LDPE, is a strong function of the amount of comonomer incorporated.

The properties of the individual species can be altered by mixing the components, and blends of HDPE, LDPE, and LLDPE are widely used commercially. However, understanding of the mechanical and melt flow properties of such blends is handicapped by the absence of a consensus concerning the melt miscibility of the components. For example, different views have been expressed in the literature ranging from liquid−liquid phase segregation[1−3] to complete homogeneity in the melt[4,5] for HDPE/LDPE mixtures. Small angle neutron scattering (SANS) can supply information on melt homogeneity of polymer blends via the contrast achieved by deuterating one of the components, as there are large differences, in both the shape and the absolute magnitude of the scattering, between phase-separated and homogenous systems.[4−8]

In the latter case, the SANS technique permits the measurement of the Flory−Huggins (FH) interaction parameter (χ) and molecular dimensions (radius of gyration, R_g) via the deGennes random phase approximation[9−11] (RPA). The RPA is based on the assumption that the polymer constituents can be treated as ideal (Gaussian) coils, unperturbed by the weak interactions between the segments. SANS experiments[4,5] have shown that mixtures of HDPE and LDPE exhibited a scattering cross section that was well described by the RPA in the melt for (weight-averaged) molecular weights, $M_w \sim 10^5$, and it was therefore concluded that the blends were homogenous for all compositions. The only phase segregation phenomena that were observed were attributed to H/D isotope effects,[4,6] due to the interaction parameter $\chi_{HD} \simeq 4 \times 10^{-4}$ between deuterated (C_2D_4) and protonated (C_2H_4) monomer units. Thus, when the product of the polymerization index (N) and χ_{HD} exceeds 2 (for 50/50 mixtures), isotope-driven phase separation[4] is expected, even between compatible species such as HDPE/LDPE, and may also be observed in isotopic mixtures of the same species.[6,7,12]

However, it has been asserted[13] that these experiments do not provide unambiguous evidence for a one-phase (homogenous) melt and that the data might also be interpreted as arising from a biphasic melt with a very large particle size. The experiments[4,6] were performed with a minimum value of the momentum transfer, $Q = 4\pi\lambda^{-1} \sin \Theta \simeq 0.004$ Å^{-1} (where λ is the wavelength and 2Θ is the angle of scatter), so the maximum spatial resolution is therefore $D \sim 2\pi/Q_{min}$

[†] Florida Agricultural and Mechanical and Florida State University College of Engineering.

[‡] Princeton University.

[§] Cornell University.

[⊥] Exxon Research and Engineering Co.

[||] Oak Ridge National Laboratory.

[∇] Florida State University.

[#] Exxon Chemical Co.

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~ 1500 Å. Thus, if the domains had dimensions ~ 1 μm, much of the scattering from the different phases would be exhibited at Q-values < 10^{-3} Å^{-1}.

We have addressed this hypothesis by a series of further investigations on a wide assortment of mixtures of branched and linear polyethylenes. The experiments confirm that blends are homogenous in the melt when the branch content is low (i.e., <4 branches/100 backbone carbons for MW ~ 10^5). However, when the branch content is higher (typically >8 branches/100 backbone carbons), the blends phase separate. When the dimensions of the domains are beyond the resolution limit of conventional pinhole SANS cameras, the cross section generally contains a strong component of Porod scattering from the interfaces [$d\Sigma/d\Omega(Q) \sim Q^{-n}$] in the Q-range 10^{-3}−10^{-2} Å^{-1}, with an exponent, $n \sim 4$. This scattering is over 1 order of magnitude higher than the cross section of randomly mixed molecules in a homogenous blend and is easily observed, even if the domains are large. In addition, critical opalescence is expected near the phase boundary, and segregation can be observed[6,14] via a "neutron cloud point", which can also be examined with modest resolution ($Q_{\min} \sim 5 \times 10^{-3}$ Å^{-1}). At higher Q-values (10^{-2}−10^{-1} Å^{-1}), the scattering arises from labeled molecules within the domains, and while it has the general **shape** ($d\Sigma/d\Omega \sim Q^{-2}$) of the cross section of a one-phase system, it is a complicated function of the volume fractions and compositions of the phases. In general, absolute magnitude of the scattering is quite different for phase-separated and homogenous systems, and it will be shown that SANS can also distinguish these cases (see below).

It has also been shown[15] that for heterogeneous LLDPEs with a wide range of branch contents, a fraction of the highly branched chains (e.g., >8 branches/100 backbone carbons) can phase separate from the lightly branched majority, even when when the average branch content is low (e.g., 1−2 branches/100 backbone carbons). Thus the question is not simply whether linear and branched molecules are miscible, because it is evident that there will be miscibility when the branch level is very low and immiscibility when it is high.[5,18−20] Rather, the question at issue is the level of branching that is required to phase separate the system.

Experimental Section

Sample Preparation and Characterization. A wide range of blends of linear and branched polymers were studied, including both long and short chain branching. The HDPEs and LDPEs had relatively high polydispersities with M_w/M_n in the range 1−6 for the HDPE and 5−17 for LDPE. In addition we have studied blends of hydrogenated and deuterated polybutadienes made by anionic polymerization of butadiene in the presence of different modifiers followed by catalytic hydrogenation (or deuteration) in cyclohexane in the temperature range 70−85 °C with H_2 or D_2 pressures of 300−500 psi. The resultant copolymers are virtually monodiserse (M_w/M_n < 1.07) model LLDPEs, which have been the subject of extensive SANS and thermodynamic studies.[8,17−20]

The blends were fabricated as described previously,[4,6,15,17−20] and Table 1 shows the molecular weights, degrees of deuteration (X_D), and polydispersities of the components. It will be seen that the phase stability of the blends is independent of the polydispersity in chain length (MW) to a good approximation.

Table 1. Molecular Weights, Polydispersities, Degree of Deuteration, and Branch Content of Blend Components

	10^{-3} M_w	M_w/ M_n	X_D	branches/ 100 backbone carbons long[a]	branches/ 100 backbone carbons short[b]
		Low-Density PEs			
LDPE-2H	212	17.2	0	0.25	1.6
LDPE-3H	136	11.0	0	0.28	1.31
		High-Density PEs			
HPDE-D	146	1.1	1.0	0	0
HPDE-1D	201	3.4	1.0	0	0
HPDE-2D	101	2.9	1.0	0	0
HPDE-3D (ISO)	138	6.0	1.0	0	0
HPDE-H	146	1.1	0	0	0
HPDE-2H (SNPA)	94	1.03	0	0	0
		Hydrogenated Polybutadienes			
HPB-D08	67	<1.07	0.44	0	2.1
HPB-H17	123	<1.07	0	0	4.6
HPB-H25	96	<1.07	0	0	7.1
HPB-H32	96	<1.07	0	0	9.5
HPB-D35	78	1.1	0.35	0	10.6
HPB-H35	78	1.1	0	0	10.6

[a] Branches containing >8 carbon atoms. [b] Branches containing ≤8 carbon atoms.

Small Angle Neutron Scattering: 1. Data Collection. The data were collected on the W. C. Koehler 30m SANS facility[21] 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 [$d\Sigma/d\Omega(Q)$, cm^{-1}] by comparison with precalibrated secondary standards, based on the measurement of beam flux, vanadium incoherent cross section, and the scattering from water and other reference materials.[22] Further details of transmission measurements, data collection, and correction procedures for instrumental backgrounds, incoherent scattering, etc., have been given previously.[4,6,15]

2. Data Analysis. For a homogenous blend of two polymer species, one of which is deuterium labeled, the coherent cross section is given[4,6,23] by

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

where a_D and a_H are the scattering lengths of the repeat unit (segment) of the labeled and unlabeled species, respectively, which were assumed to have the same segment (C_2H_4) volume (V). Assuming that the polymer constituents can be treated as ideal (Gaussian) coils, unperturbed by the weak interactions between monomers, the structure factor $S(Q)$ is given by

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

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 $P_H(QR_{gH})$ represented by Gaussian (Debye) coils.[4,6,9,10] The values of the N and χ are defined with respect to the volume of a C_2H_4 segment.

At small Q, eqs 1 and 2 reduce to the Zimm or Ornstein−Zernike (O−Z) form[4,6,23]

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{d\Sigma}{d\Omega}(0)/(1 + Q^2\xi^2) \tag{3}$$

$$\frac{d\Sigma}{d\Omega}(0) = \frac{V^{-1}(a_H - a_D)^2}{[(\phi_D N_D)^{-1} + (\phi_H N_H)^{-1} - 2\chi]} \tag{4}$$

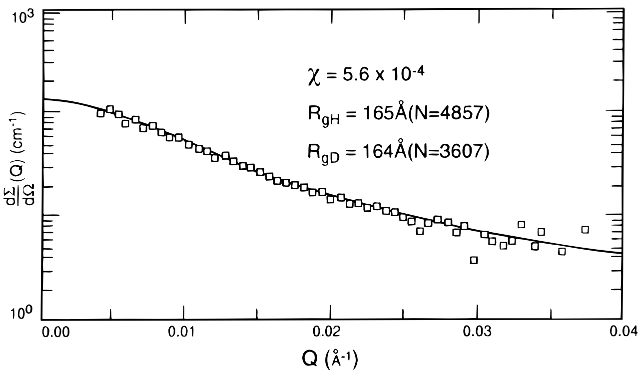

Figure 1. Fit to random phase approximation for a blend of LDPE ($\phi_H = 0.91$) and deuterated HDPE ($\phi_D = 0.09$) at 143 °C.

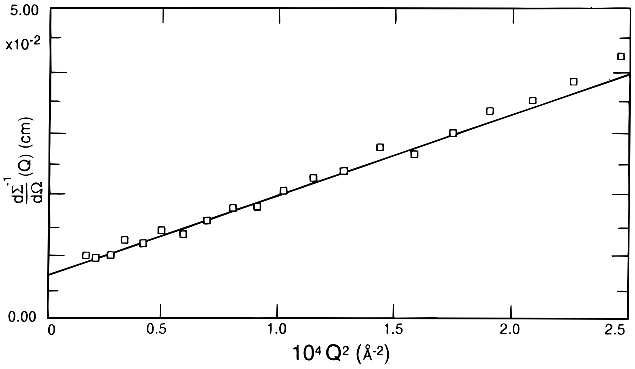

Figure 2. Ornstein–Zernike plot of SANS from a blend of branched HDPE ($\phi_H = 0.91$) and linear HDPE ($\phi_D = 0.09$) at 143 °C.

where ξ is the composition fluctuation correlation length. R_g and N are weighted by the ratio of the z- and w-averages of the distribution, respectively. Equations 1 and 2 may be applied to analyze SANS data from hydrogenated polybutadienes as model LLDPEs with χ as the only fitting parameter. Not only are isotope effects minimized, but SANS can give independent estimates of the degrees of polymerization and segment lengths [$a = (6/N)^{0.5}R_g$] via experiments on isotopic mixtures of the same species.[18–20]

SANS data from HDPE/LDPE and HDPE/HPB mixtures may also be analyzed via eqs 1 and 2, though the degrees of polymerization (molecular weights) for HDPE and LDPE must be determined independently via chromatography. The segment length (a) is well known from the literature both for linear HDPE[6,10] and for HPB as a function of branching[20] (falling by ~7% as the branch content increases from 0 to 10 branches/100 backbone carbons). The segment length is not as well known for long chain branched molecules (e.g., LDPE) and must therefore be used as a fitting parameter.[4] However, the χ-value is largely determined by the low-Q portion of the data, which is insensitive to this variable. Thus, the interaction parameter is virtually the only unknown in the analysis, and phase separation and homogeneity are easily distinguished in both types of blends.

Results and Discussion

Figures 1 and 2 show SANS data[4] from mixtures of LDPE-H ($M_w \simeq 136$ K; $\phi_H \simeq 0.91$) and HDPE-D ($M_w \simeq 101$ K; $\phi_D \simeq 0.09$), where the linear component is fully deuterated. The data are well described by the RPA formalism (Figure 1) in terms of a homogenous mixture, despite the fact that the polydispersity is high ($M_w/M_n \sim 3-11$). The interaction parameter is virtually the same as the χ_{HD} measured[6] in mixtures of linear HDPE-D and HDPE-H, as expected[4] when the level of branching is low (<2 branches/100 backbone carbons). The O–Z (Figure 2) plot has a positive intercept characteristic of a one-phase system, though for mixtures with higher molecular weight ($M_w > 200$ K), $N\chi_{HD}$ exceeds 2.0 and a 50/50 mixture phase separates, giving a dramatically different plot (Figure 3) with a negative intercept.

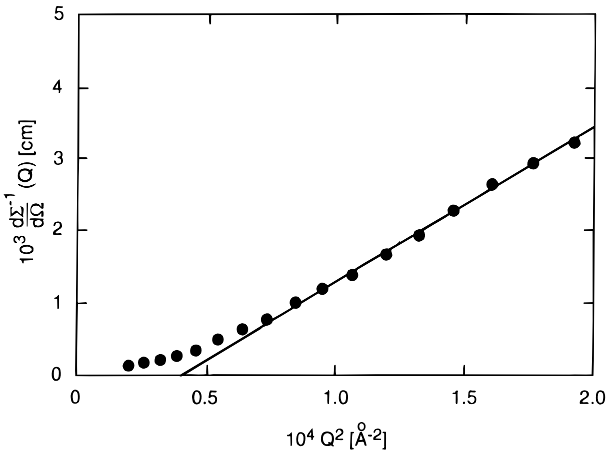

Figure 3. Ornstein–Zernike (Zimm) plot for a mixture of linear (HD) PED ($M_w = 210 \times 10^3$) and branched (LD) PEH ($M_w = 212 \times 10^3$) at 165 °C.

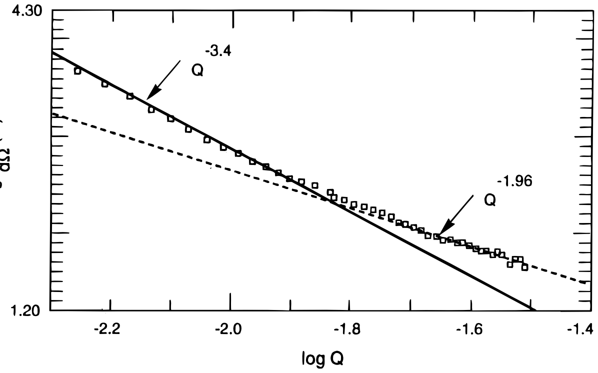

Figure 4. Log–log plot of SANS from a mixture of linear (HD) PED ($M_w = 210 \times 10^3$) and branched (LD) PEH ($M_w = 212 \times 10^3$) at 165 °C.

Schipp and co-workers[13] have interpreted data from a sample similar to that shown in Figure 1 via an equation derived for a biphasic melt, as a function of the volume fractions, compositions, χ-parameters, and domain dimensions of the phases. However, several of the fitted parameters are different to those generally reported in the literature. For example, the reported radius of gyration (139 Å) and molecular weight (200 000) of the linear component led to $R_g/M_w^{0.5} \cong 0.31$, compared to the generally accepted[10,20,24,25] value of $R_g/M_w^{0.5} \cong 0.45 \pm 0.01$. Similarly, the fitted χ-parameters are generally high (up to 19×10^{-4} for a CH_2 segment, or 38×10^{-4} for the C_2H_4 segment used in this work). To our knowledge this is 1 order of magnitude greater than previously reported[4,18–20,26–27] values for systems with such low levels of branching (1 long chain and 1.6 short chain branches/100 backbone carbon atoms). No Porod regime ($d\Sigma/d\Omega \sim Q^{-4}$) was reported[13] for this sample, though in our experience this is generally observed for phase-separated systems.

For example, Figure 4 shows a log–log plot of the data of Figure 3, which clearly exhibits two different regions, with an exponent $n \sim 2$ observed for $Q > 0.015$ Å^{-1}. In this range, SANS probes length scales <400 Å and is therefore sensitive to the contrast between the H- and

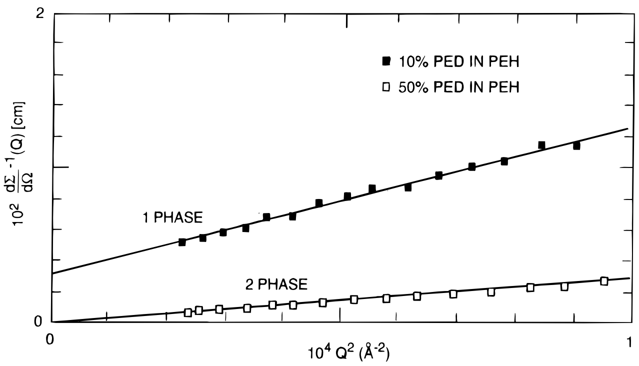

Figure 5. Ornstein–Zernike plots for mixtures of linear PEH and PED ($N_H = N_D = 5200$).

D-labeled molecules within the phase-separated regions. The domain dimensions cannot be resolved with $Q_{min} \simeq 0.004$ Å^{-1}, and the Guinier range[28] of the scattering is close to the transmitted beam or hidden behind the beam stop. However, the Porod region,[29] arising from the interphase boundaries, is clearly visible, and departures from an exponent (n) of 4.0 indicate that the phase boundary is not sharp. Such deviations can be used to extract the dimensions of the interface, as shown by Bates and co-workers, who studied phase segregation in isotopic mixtures of H- and D-labeled polybutadienes, with a similar division into "Porod" and "Debye" regions of the SANS data.[7]

These effects are independent of the level of branching, which is sufficiently low that virtually the same phase behavior is exhibited by mixtures of protonated and deuterated linear (HDPE) molecules.[6] This is illustrated in Figure 5 for a 50/50 blend of HDPE-H and HDPE-D (each with $M_w \simeq 146$ K; $M_w/M_n \simeq 1.1$), so $N\chi$ is very close to 2.0, and the mixture is just below the critical point for phase segregation.[6] For asymmetrical mixtures (e.g., 10/90 HDPE-D/HDPE-H), $N\chi_s \sim 5.5$ at the spinodal,[7,12] so the blend of the same (linear) species with a different concentration of D-polymer is clearly homogenous (Figure 5). Thus, phase segregation is quite observable via SANS in this Q-range for both strongly (Figure 3) and weakly (Figure 5) segregated blends of either monodisperse or polydisperse molecules.

In the above experiments, the main contribution to the measured interaction parameter arises from isotope effects, as the level of branching is low. However, where the branch content becomes appreciable, there is another contribution to χ. Crist and co-workers[26,27] have estimated an interspecies interaction parameter between ethyl-branched and linear molecules as

$$\chi_{\text{inter}} \simeq C Y_{\text{Br}}^{\;2} \qquad (5)$$

where Y_{Br} is the fraction of branched (C_4H_8) units and $C \sim 0.01$ for C_2H_4 segments. Complementary SANS studies[18–20] of ethylene–butene (EB) model copolymers over a wide range of compositions from polyethylene to polybutene indicate that C is a strong function of Y_{Br} but confirm that $C \simeq 0.01$ when the branch content is ≤10 branches/100 backbone carbons.

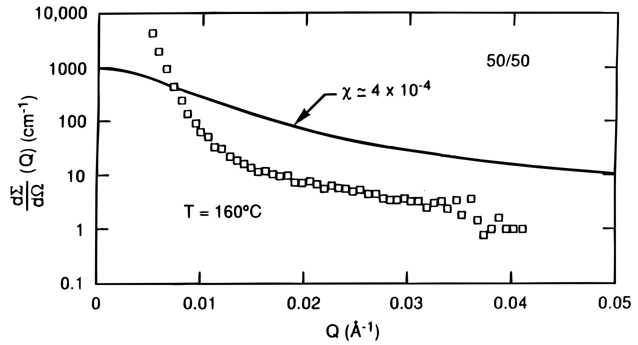

Figure 6. Fit to random phase approximation for a 50/50 phase-separated blend of deuterated HDPE ($M_w \simeq 138 \times 10^3$) and hydrogenated polybutadiene ($M_w \simeq 78 \times 10^3$) with 10.6 branches/100 backbone carbon atoms.

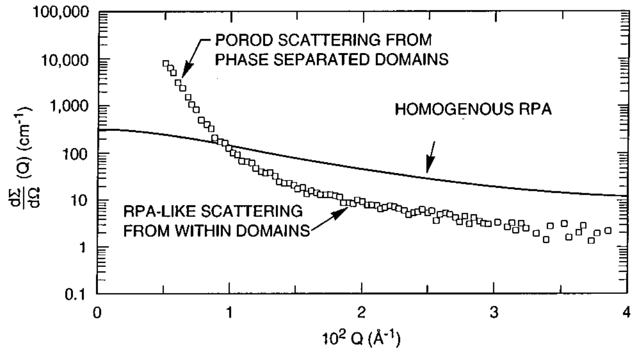

Figure 7. dΣ/dΩ(Q) for a 75/25 blend of linear HDPE-D and hydrogenated polybutadiene (10.6 branches/100 backbone carbon atoms) compared to homogenous (RPA) function (T = 160 °C).

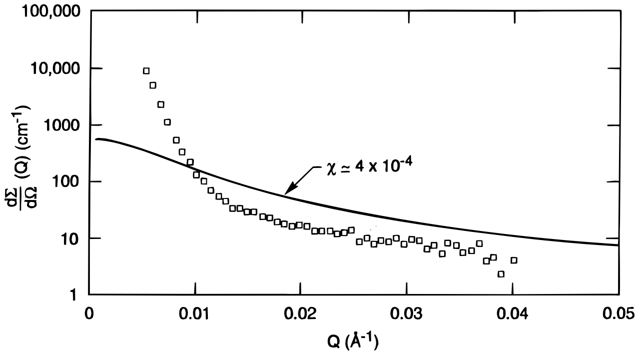

Figure 8. Fit to random phase approximation for (phase-separated) blend (25/75) of deuterated HDPE ($M_w \simeq 138 \times 10^3$) and hydrogenated polybutadiene ($M_w \simeq 78 \times 10^3$) with 10.6 branches/100 backbone carbon atoms.

For HDPE/LDPE mixtures (Figures 1–4) the level of branching is low[4] and $\chi_{inter} \sim 0.3 \times 10^{-4}$, which is only a minor perturbation on the isotopic parameter ($\chi_{HD} \sim 4 \times 10^{-4}$). Figure 6 shows the SANS data from a 50/50 blend of HDPE-D and HPB and also the theoretical (RPA) curve expected if the only interaction between the species arose from isotope effects. The HPB has a large branch content (10.6 branches/100 backbone carbons) and contributes an extra component in addition to χ_{HD}, which is sufficient to cause demixing. Figures 7 and 8 show data from the same blend components in other regions of the phase diagram (25/75 and 75/25 HDPE-D/HPB). All three data sets are clearly characteristic of a phase-separated blend with both "Porod" ($n \sim 4$) and "Debye" ($n \sim 2$) regions of the scattering arising from the interphase boundaries and the molecules within the domains, respectively. This is illustrated in Figure 9, which shows a log–log plot of the data of Figure 8. In the O–Z representation, the plots are similar to Figure 3 with negative intercepts.

The phase segregation phenomena exhibited in Figures 6–9 are caused by a combination of both isotope and branching effects, each of which contributes to the interaction parameter, thus raising it above the critical

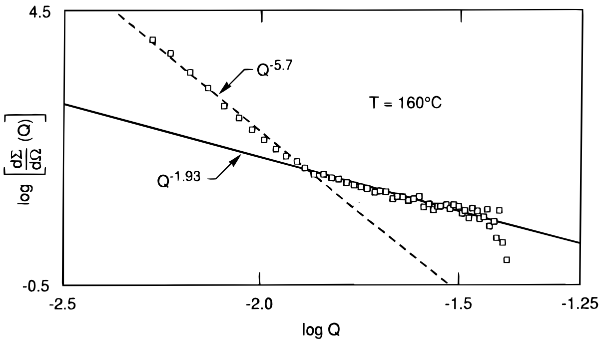

Figure 9. Log–log plot of SANS data from (phase-separated) blend (25/75) of deuterated HDPE ($M_w \simeq 138 \times 10^3$) and hydrogenated polybutadiene ($M_w \simeq 78 \times 10^3$) with 10.6 branches/100 backbone carbon atoms.

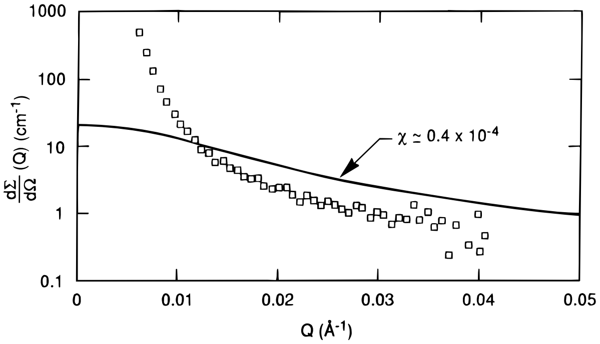

Figure 10. Fit to random phase approximation for (phase-separated) blend of HDPE ($M_w \simeq 91 \times 10^3$) and partially deuterated (~35%) polybutadiene ($M_w \simeq 78 \times 10^3$; 10.6 branches/100 backbone carbon atoms).

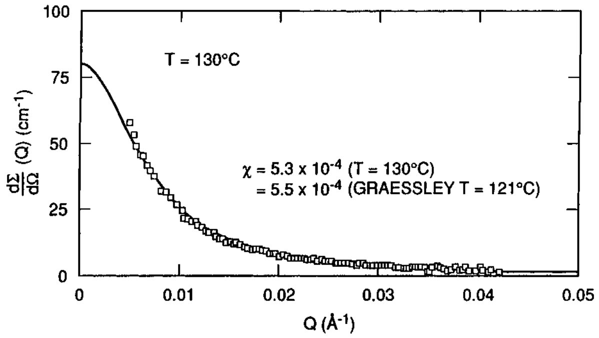

Figure 11. Fit to random phase approximation for a 50/50 blend of partially (43%) deuterated ($M_w \simeq 67 \times 10^3$; 2.1 branches/100 backbone carbon atoms) and hydrogenated ($M_w \simeq 96 \times 10^3$; 7.1 branches/100 backbone carbon atoms) polybutadienes.

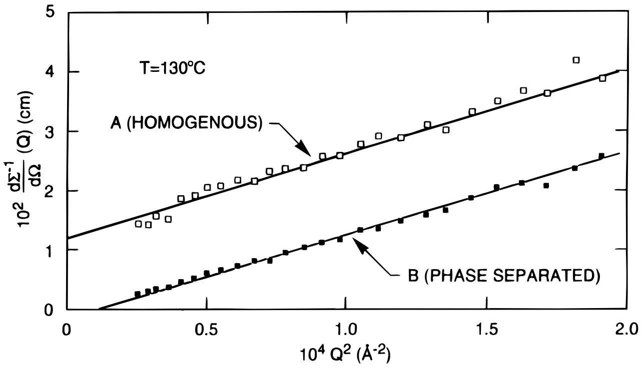

Figure 12. Ornstein–Zernike plots for 50/50 blends of hydrogenated polybutadienes (HPB): (A) HPB-H ($M_w = 123 \times 10^3$; 4.6 branches/100 backbone carbon atoms)/HPB-D ($M_w = 67 \times 10^3$; 2.1 branches/100 backbone carbon atoms) and (B) HPB-H ($M_w = 96 \times 10^3$; 9.5 branches/100 backbone carbon atoms)/HPB-D ($M_w = 67 \times 10^3$; 2.1 branches/100 backbone carbon atoms).

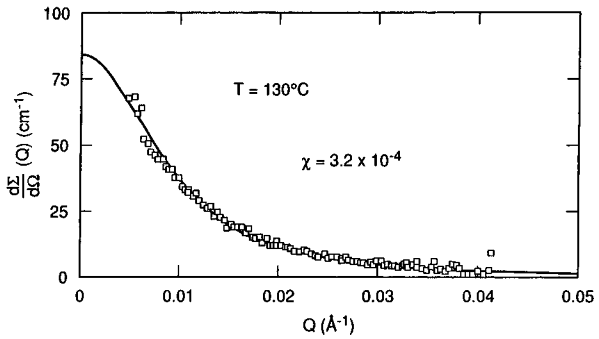

Figure 13. Fit to random phase approximation for a 50/50 blend of hydrogenated ($M_w = 123 \times 10^3$; 4.6 branches/100 backbone carbon atoms) and partially deuterated (43%) ($M_w = 67 \times 10^3$; 2.1 branches/100 backbone carbon atoms) polybutadienes.

level for demixing, χ_{crit}. Although SANS from D-labeled mixtures has provided a wealth of new information on polymer–polymer thermodynamics, the isotope effect is clearly a complicating factor in these examples. All commercial polymer blends are made from protonated (undeuterated) species, and in order to predict their phase behavior it is necessary to separate these contributions. This can be done to a good approximation by using *partially* deuterated material, as $\chi_{HD} \sim X_D^2$, where X_D is the fractional degree of deuteration.[30,31] Thus blends of hydrogenated and deuterated HPBs are ideal model systems[8,18–20] to study the phase behavior of HDPE/LLDPE blends and mixtures and LLDPEs with different branch contents. As the labeling level produced by deuterating HPBs is ~30–45%, χ_{HD} for these systems is typically $<1 \times 10^{-4}$, which is the same order as the uncertainty in the χ-determination. Accordingly, the measured interaction parameter is dominated by the interspecies contribution.

Figure 10 shows the SANS data from a blend of protonated (linear) HDPE-H and partially ($X_D \simeq 35\%$) deuterated polybutadiene with 10.6 branches/100 backbone carbons. Even though the M_w of both components is $<10^5$ and the isotopic contribution to χ is $<0.5 \times 10^{-4}$, the system has clearly phase separated and shows the same general features as Figure 6–9. Thus, a level of 10.6 branches/100 backbone carbons is sufficient to phase separate the system for $M_w \sim 78–91$ K, even in the absence of isotope effects. Figure 11 shows the SANS data for a blend of two HPBs, one of which is partially ($X_D \simeq 43\%$) deuterated. The level of branching is low, and the system is clearly homogenous. The RPA fit gives $\chi = 5.3 \times 10^{-4}$, in good agreement with a value of 5.5×10^{-4}, measured independently[20] by one of us at a slightly lower temperature ($\chi \sim T^{-1}$). Figure 12 shows O–Z plots from two 50/50 mixtures of HPBs, one of which has a sufficiently low difference in branch contents (3.5 branches/100 backbone carbons) between the species that the system is homogenous. When the differential is raised to 7.4, the system phase separates, as indicated by a negative intercept on the ordinate. Figure 13 shows the RPA fit to the (homogenous) data set (A) of Figure 12.

These results and others in the literature[4–6,18–20,26,27,32,33] confirm that mixtures of linear and branched polyethylenes are homogenous for all compositions when the branch content is low (i.e., <4 branches/100 backbone carbons for MW ~ 10^5). However, when the branch content is higher (typically ≥8 branches/100 backbone carbons), the blends phase separate. Segregation can also be driven by isotope effects, when the molecular weight is sufficiently high that $N\chi_{HD} > 2$. In each case, the resolution of SANS pinhole cameras ($Q_{min} \sim 10^{-3}$ Å^{-1}) is sufficient to determine the state of mixing, even for systems with large domains. Not only is strong Porod scattering clearly detectable, but the high-Q portion of the data does not fit the homogenous RPA function for phase-separated systems (Figures 6−8,10). This scattering arises from labeled molecules within the domains, and while it has the general **shape** ($d\Sigma/d\Omega \sim Q^{-2}$) of the cross section of a one-phase system, it is a complicated function of the volume fractions and compositions of the phases.[7,12]

Consider a two-phase binary polymer blend, in which the components occupy overall volume fractions ϕ_1 and ϕ_2 and the phases occupy volume fractions ϕ' and ϕ''. The composition of each phase is determined by the shape of the coexistence curve in composition−temperature space. The various volume fractions are denoted by ϕ_i^j, where $i = 1$ or 2 refers to the components and $j = '$ or $''$ refers to the phases. These volume fractions must add to unity:

$$\sum_{i=1,2} \phi_i = 1$$

$$\sum_{j=','',} \phi^j = 1$$

$$\sum_{i=1,2} \phi_i^j = 1 \qquad (6)$$

Denoting the structure factor for the two-phase binary blend by $S_S(Q)$ and for a homogenous blend of the same overall composition by $S_H(Q)$, the following relations hold[7] in the limit $R_gQ \gg 1$:

$$S_H(Q) = \frac{12}{a^2Q^2}\phi_1\phi_2$$

$$S_S(Q) = \frac{12}{a^2Q^2}\sum_{j=','',} \phi^j\phi_1^j\phi_2^j \qquad (7)$$

where a is the segment length. In this case it may be shown that,

$$S_H(Q) - S_S(Q) = \frac{12}{a^2Q^2}\phi'\phi''(\phi_1' - \phi_1'')^2 \qquad (8)$$

which is always positive, so the intensity at high Q for a two-phase binary mixture will always fall below that of a homogenous mixture of the same overall composition (see Figures 6−8, 10). Thus, the absolute magnitude of the scattering is quite different for phase-separated and homogenous systems, and SANS can distinguish these cases in the Q-range (10^{-1}−10^{-2} Å^{-1}), even when the domain dimensions are large.

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