PHASE BEHAVIOR OF BLENDS OF LINEAR AND BRANCHED POLYETHYLENES VIA SMALL- AND ULTRA-SMALL ANGLE NEUTRON SCATTERING

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It is well established [1-9] 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 (1-3 per 100 backbone carbon atoms), as well as long chain branches (0.1-0.3 per 100 backbone carbon atoms). Linear low density polyethylene (LLDPE) is produced by co-polymerizing ethylene with an alpha-olefin such as hexene and can have a wide range of branch contents, depending on the catalyst and concentration of added comonomer. SANS data [2] indicate that for HDPE/LDPE blends with molecular weights ~ 10^5, the melt is homogenous, after accounting for H/D isotope effects [3]. Similarly, mixtures of HDPE and LLDPE are homogenous in the melt [4-6] when the branch content is low (i.e. < 3 br./100 backbone carbons). However, when the branch content is higher (> 10 br./100 C), the blends phase separate (9).

In previous SANS experiments [4-6], the LLDPE's were simulated by hydrogenated (or deuterated) polybutadienes, because these materials may be prepared as nearly monodisperse molecules with a homogenous branch distribution within each chain. Thus, these studies were not affected by polydispersity effects, either in the branch content or molecular weight. However, for LLDPEs prepared with heterogeneous-type Ziegler-Natta catalysts, the multi-site nature of catalysts leads to a wide distribution of chain compositions, with the low molecular weight chains exhibiting the most branching. Heterogeneous LLDPE may therefore be thought of as a "blend" of different species and when the composition distribution is broad enough the multicomponent system can, in principle, phase separate. Thus, even when the average branch content is low, a fraction of highly branched chains (> 10 br./100 C), which are incompatible with the lightly branched molecules may phase separate, as first suggested by Mirabella and co-workers [10], based on scanning electron microscopy (SEM) investigations of the solid state. Subsequently, Nesarikar and Crist [11] performed a thermodynamic calculation of the equilibrium melt state as a function of the distribution of chain branching, which predicted a second phase consisting of highly branched amorphous material. The volume fraction ($f \sim 10^{-2}$) was in reasonable agreement with the SEM findings [11].

Previous SANS [1] studies examined the structure of the liquid directly, and because the linear and branched molecules have virtually the same scattering power, a fraction of deuterated linear polymer (20%) was added in order to manifest the melt structure. Based on 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, without perturbing the predicted two-phase morphology.

Details of sample preparation and sample characterization have been given previously [1]. Mixtures of the original ethylene-hexene (EH) copolymer, the xylene extract and filtrate (each with 20% deuterated linear polyethylene) were prepared by dissolving the components in o-dichlorobenzene. After washing with methanol, the samples were dried overnight in vacuum oven and pressed into disks ~ 1 mm thick. Pinhole SANS data were collected on the 30m SANS facility at Oak Ridge National Laboratory as described previously [1-3] in the Q-range $0.004 < Q = 4\pi\lambda^{-1}\sin\theta < 0.04$ Å^{-1}, where $\lambda = 4.75$Å is the wavelength and 2θ is the angle of scatter. The USANS measurements were carried out on the Bonse-Hart Double-Crystal Diffractometer equipped by triple-bounce Si(111) channel-cut crystals, which have been modified by adding a cadmium absorber [12]. This reduces the wings of the rocking curve and improves the sensitivity by two orders of magnitude, thus allowing the determination of phase dimensions up ~ 30 μm.

Fig. (1) shows a log-log plot of the cross section [$d\Sigma/d\Omega(Q)$ in units of cm^{-1}] in the melt (T = 160°C) for the original ethylene-hexene LLDPE, along with the same sample after xylene extraction (after blending with 20 wt.% linear D-HDPE to provide SANS contrast). The existence of multiple phases is reflected in the two regions where the scattering curve varies as $Q^{-3.8}$ and $Q^{-1.7}$ for the lowest and highest Q-values respectively. These values are close to the Porod limit (Q^{-4}), expected for separate phases with sharp boundaries, and to the Gaussian coil limit (Q^{-2}), expected for random coil molecules [1].

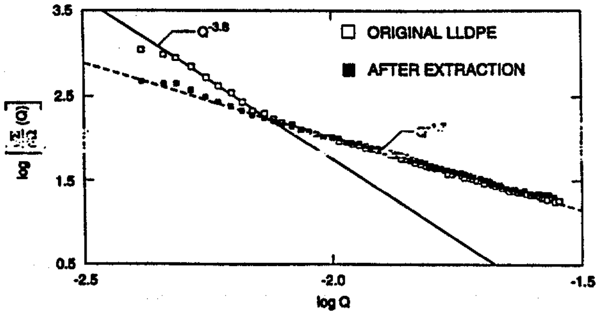

Fig. (1). Log-log plot for compositionally heterogeneous ethylene-hexene copolymer before and after xylene extraction.

It may be seen that the extraction procedure, which removes 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}). Thus, xylene extraction effectively removes the component, which varies as Q^{-4}. The original LLDPE has an average branch content of 1.4 mole % butyl branches (or 1.4 br./100 C), though a small fraction of the distribution will be highly branched, and chains with > 10br./100 C should phase separate from the lightly branched matrix. As the disperse phase (volume fraction, $f \sim 10^{-2}$) 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 [1-3] that lightly branched material is compatible with linear HDPE-D, so the matrix should consist of an homogenous 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 2-phase hypothesis [1], accounts qualitatively for the general features of the scattering.

The volume fraction of the disperse phase can be estimated [13] from the SANS invariant:

$$Q_0 = \int_0^\infty Q^2 d\Sigma/d\Omega(Q)dQ = 2\pi^2\varphi_1\varphi_2[\rho_1 - \rho_2]^2 \quad (1)$$

where φ_1, φ_2, ρ_1 and ρ_2 are the volume fractions and neutron scattering length densities of the two phases respectively. The scattering from the minority (disperse) phase is manifested below Q ~ 0.01 $Å^{-1}$, where it is superimposed on the cross section of the majority of the sample consisting of a homogenous 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 > 0.01 $Å^{-1}$. In order to estimate the portion of the area below the minimum Q-value (0.004 $Å^{-1}$), we assumed initially [1] that the missing low-Q data follow the Guinier approximation, to give an estimate of f = 0.021 for the original sample via the equation (1).

The xylene-extract formed 8% of the original polymer, 2% of which was phase separated, and thus we might expect that the volume fraction of the disperse phase in the xylene extract would be f ~ 0.20, when blended with 20% HDPE-D. Invariant analysis leads to f ~ 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 dimensions > 2000 Å appears at Q-values below the resolution limit of the experiment. However, USANS allows us to fill in the missing portion of the data and improve the estimate of f. Figure (2) shows the overlap of the pinhole SANS and USANS data and invariant analysis of the combined curve leads to a volume fraction of the disperse phase of f = 0.30. This may be compared with the previous determination (f ~ 0.20), derived from the pinhole SANS data. Thus USANS substantially improves the estimate of f by filling in the previously inaccessible portion of the SANS invariant.

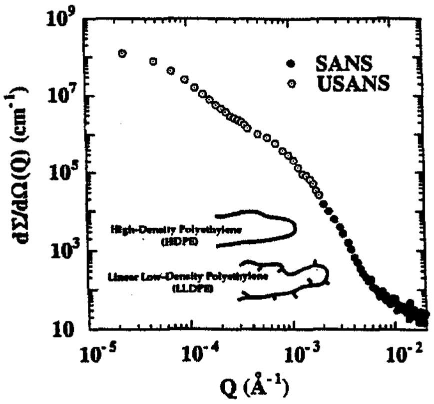

Fig. 2. Overlap of SANS and USANS data obtained for 20% linear HDPE-D blended with branched LLDPE-H at T = 160°C.

In addition, it has recently been asserted [14] that pinhole SANS experiments [2] do not provide unambiguous evidence for a 1-phase (homogenous) melt in HDPE/LDPE mixtures, and that the data might also be interpreted as arising from a bi-phasic melt with a very large particle size. As described above, the SANS experiments had a minimum value Q = 0.004$Å^{-1}$, so the maximum spatial resolution is therefore D ~ $2\pi/Q_{min}$ ~ 1500Å. Thus, if the domains had dimensions ~ 1μm, 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 pinhole-SANS investigations on a wide assortment of mixtures of branched and linear polyethylenes[9], which confirm that blends are homogenous when the branch content is low (< 4 br./100C). When the branch content is higher (> 10 br./100 C), the blends phase separate. While 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 [dΣ/dΩ(Q) ~ Q^{-n}] in the Q-range 10^{-3}-10^{-2} $Å^{-1}$, with an exponent, n ~ 4. This scattering is over an 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 [9]. In addition, critical opalescence is expected near the phase boundary and segregation can be observed via a "neutron cloud point", which can also be examined with modest resolution (Q_{min} ~ 0.004 $Å^{-1}$). 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** (dΣ/dΩ ~ Q^{-2}) of the cross section of a 1-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 1- and 2-phase systems and it has been shown that SANS can also distinguish these cases [9].

In addition, USANS experiments are currently in progress on these systems in the melt state, which will be capable of resolving phases with dimensions up to 30mμ and the results of these new investigations will be presented. Finally, we have explored the effect of the polydispersity in chain length (molecular weight). As mentioned above, in many previous SANS experiments [4-6], the LLDPE's were simulated by monodisperse hydrogenated polybutadienes. Thus, it was not necessary to apply corrections for polydispersity when extracting the Flory-Huggins interaction parameter (χ) via the de Gennes random phase approximation (RPA). However, when analyzing SANS data from mixtures of polydisperse and monodisperse molecules, allowance must be made for such effects [15]. We have therefore reformulated the RPA on the assumption that the molecular weight distribution can be described via a Schultz distribution and examples of this modified data treatment will be presented.

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REFERENCES

1. Wignall, G. D., et al., Macromolecules, 29, 5332 (1996).
2. Alamo, R. G., et al., Macromolecules, 27, 411 (1994).
3. Londono, J. D., et al., Macromolecules, 27, 2864 (1994).
4. Krishnamoorti, R., et al., Macromolecules, 27, 3073 (1994).
5. Graessley, W. W., et al., Macromolecules 26, 1137 (1994); 27, 2574 (1994).
6. Nicholson, J. C., et al., Macromolecules, 24, 5665 (1991).
7. Bates, F. S., et al., Macromolecules, 25, 5547 (1992).
8. Tashiro, K., et al., Macromolecules, 28, 8484 (1995).
9. Alamo, R. G., et al., Macromolecules, in press.
10. Mirabella, F. M., & Ford, E.A., J. Polym. Sci., Polym., Phys., Ed., 25, 777 (1987); J. Polym. Sci., B26, 1995 (1988).
11. Nesarikar, A., & Crist, B., J. Polym. Sci., B32, 641 (1994).
12. Agamalian, M., M. et al., J. Appl. Cryst., 30, 345 (1997).
13. Wignall, G. D., "Neutron and X-Ray Scattering", Polymer Properties Handbook, ed. J.E. Mark, AIP Press, 299 (1996).
14. Schipp, C. et al., Polymer, 37, 2291 (1996).
15. Weimann, P. et al., Macromolecules in press.