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Neutron Scattering Studies of a Semicrystalline Homopolymer and Copolymer Blend

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ABSTRACT: A system consisting of polyethylene blended with a branched ethylene/ethyl acrylate (EEA) copolymer (18 wt % EA) is studied by the technique of neutron scattering. We find that an analysis using the two-parameter Debye−Bueche model allows determination of blend morphology both above and below the melt temperature. Above the melt temperature, this blend is inhomogeneous at all compositions, with the EA groups within the copolymer associating on length scales of approximately 30−40 Å. Below the melt temperature, we determine the thicknesses of the polyethylene crystalline (δ_c) and amorphous (δ_a) regions, finding $\delta_c = 140$ Å and $\delta_a = 110$ Å with little variation with composition or temperature. Finally, we determine the structure of the blend during the melt−crystalline transition, allowing us to gain insight into the crystalline phase growth mechanism.

1. Introduction

Due to its simple structure and ubiquity in commercial applications, polyethylene (PE) is probably most notable of that class of polymers which forms a partially ordered structure at moderate temperatures. In fact, it is this semicrystalline nature of PE that makes it ideal for a number of applications that take advantage of the melt transition to obtain multiple order of magnitude changes in electrical properties. To do so, however, requires the addition of conductive fillers to the PE matrix. Copolymers, including ethylene/ethyl acrylates, ethylene/butyl acrylates, and ethylene/vinyl acetates (EEAs, EBAs, and EVAs, respectively) are often blended with PE in these and other systems to improve filler interactions as well as modify other physical properties, though the morphology of these blends is often poorly understood. One would like to develop a thorough understanding of the microstructure in these systems because of its influence on both macroscopic structural properties and the dispersion of materials added to the blend.

Characterization of blend morphology on these small length scales can be very difficult however. Many polymers have similar indices of refraction, making visible microscopy and other light scattering characterization techniques problematic. In addition, X-ray scattering techniques are hindered by the fact that most polymers have similar densities, giving rise to little electron contrast. In the past 10 years however, neutron scattering has become increasingly available as a characterization tool to those interested in polymer systems. Small-angle neutron scattering (SANS) is extremely useful in the study of such systems because one can substitute an analogous deuterated polymer to obtain the required contrast and determine the relative dispersion of polymers within the blend. Because of the similarity in chemical structure of the components and the resulting difficulty in characterization through other means, a blend of polyethylene (PE) and a branched copolymer of ethylene and ethyl acrylate (EEA copolymer) was chosen for our study.

In previous years, PE has been studied extensively by neutron scattering. Much work has been aimed at determining chain conformation in both crystalline[1,2] and melt[3,4] phases. In the past, blend studies have focused on determining the thermodynamic interactions between *noncrystalline* polyolefins, having either different structure or isotopic components.[5−9] Because of the additional complication that crystallization adds to the analysis of scattering data, there has been relatively little study of blends of semicrystalline materials via neutron scattering. Some early work[10,11] showed that isotopic substitution gave strong contrast in polyolefin systems and that structural information, including domain and individual molecule sizes, could be determined via the neutron scattering technique. In recent years, semicrystalline blends have been increasingly studied[12−16] and the techniques required for examining such systems further refined. We will take advantage of these techniques to study the morphology of a blend of two polymers, both of which have a crystalline phase at moderate temperatures.

In fact, it is of interest to characterize the behavior of blends over a wide variety of temperatures, both above and below the melt temperature. Many blends such as those studied here are exposed to a variety of temperatures during processing ranging from relatively high temperatures (~200 °C) to even higher temperatures (such as 250 °C) for short periods of time. Ideally, one would like to predict both the behavior of these blends at extreme processing conditions and when these materials are cooled through their crystalline transition. Issues regarding the significance of the morphological changes during such transitions have large implications in determining the mechanical and electrical properties of the final material.

2. Experimental Section

We begin by characterizing the deuterated polyethylene (dPE), obtained from Lawrence Livermore National Laboratories, and a hydrogenated EEA copolymer obtained from Union Carbide (DPD-6169). Differential scanning calorimetry (DSC)[17] scans were performed on the individual polymers, and gel permeation chromatography (GPC)[18] was used to characterize their molecular weights. Also, for comparison to DSC results, the density of the polymer was determined via pycnometry[19] (giving 1.08 g/cm^3 and corresponding to a crystallinity of approximately 62%) and X-ray diffraction (XRD), where a crystallinity of 69 ± 2% was obtained.[20] Branch content of the individual polymers was determined via solid-state NMR,[21] and the results are summarized with the other data in Table 1. Past studies[2] have shown lower

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Table 1. Polymer Properties

	T_{melt} (°C)	T_{cryst} (°C)	M_w	M_w/ M_n	~N	% cryst (DSC)	SCB[a]/100 carbons
dPE	125	110	100 000	4.0	6300	60	~0
EEA copolymer	100	85	81 000	3.5	4500	25	0.9

[a] SCB = short-chain branching.

crystallization and melting temperatures for dPE than for its hydrogenated counterpart. This, in combination with the above data, indicates that the dPE can be characterized as a material somewhere between a typical high- and low-density polyethylene.

For neutron scattering experiments, we prepared a number of dPE/EEA copolymer blends of varying composition for study at a variety of temperatures. Preparation involved dissolving the polymers into a cosolvent at elevated temperatures (*m*-dichlorobenzene at ~160 °C) and solvent casting onto the copper scattering cells. The solvent was then removed at temperatures of ~90 °C under vacuum and the procedure repeated until a polymer film approximately 0.5 mm thick had been built up. The final samples were left under vacuum at elevated temperatures for another day to remove any residual solvent.

All neutron scattering experiments were conducted at the National Institute of Standards and Technology (NIST) on the 8 m beam line using neutrons of wavelength λ = 9 Å. Scattering intensities were measured at a sample to detector distance of 3.6 m from which we obtained data over the range $0.007 \leq q \leq 0.08$ Å^{-1}, typically collecting total scattering counts of ~5×10^5. After correcting for empty cell scattering, detector inefficiency, and background scattering, conversion to absolute scattering intensity was done using a silica standard (SIL-A3) of well-characterized scattering intensity supplied by NIST. Being isotropic, the patterns were subsequently radially averaged and converted to absolute scattered cross section $\mathrm{d}\Sigma(q)/\mathrm{d}\Omega$ vs scattering vector q, where $q = (4\pi/\lambda)\sin(\theta/2)$.

Once the data has been converted to absolute scattering cross section, it must be corrected for the incoherent scattering contribution caused by the presence of hydrogen. There are various ways of doing this, including taking data from a pure sample of the EEA copolymer, determining the incoherent contribution, and then subtracting a volumetrically weighted isotropic intensity from the blend experimental data. However, to do this properly would have required that we subject the pure EEA copolymer to all of the same experimental conditions as the blend data (each experiment lasting perhaps an hour due to the low contrast in a homogeneous sample). Since data was taken at many different temperatures, this would have taken a great deal of scattering time. In addition, since we were varying the temperature in these experiments, we need to account for the contribution from thermal fluctuations to the scattered intensity. Contributions due to thermal fluctuations and incoherent scattering can be determined simultaneously by plotting[14]

$$q^4\frac{\mathrm{d}\Sigma(q)}{\mathrm{d}\Omega} \text{ vs } q^4 \tag{1}$$

at large scattering vector q. Such a plot emphasizes large q where the scattering is dominated by isotropic contributions. The slope of this plot is the sum of the incoherent and thermal scattering contributions and can be subsequently subtracted from the data. Magnitudes of the background for all samples were small and approximately 1–2 cm^{-1}.

3. Results

3.1. Melt Studies. Once the thermal and incoherent scattering contributions are subtracted, we are ready to fit the data to a model. Generally, for homogeneous blends one can apply the random phase approximation (RPA)[22] to determine information about the interaction parameter χ and the individual polymer radii of gyration. This analysis has been successfully applied to mixtures of polyethylenes[23] and has shown these systems to form single phases in the melt at all concentrations. This suggests that the RPA could be used as a test for the state of homogeneity in the dPE/EEA copolymer system. In fact, this model does not fit our melt data, indicating the blends studied here are inhomogeneous in the melt and are a good candidate for application of two-phase methods, such as the Debye–Bueche model, applicable to such systems. Direct comparison to the data on mixed polyethylenes also suggests that the interactions are dominated by the acrylate in the copolymer.

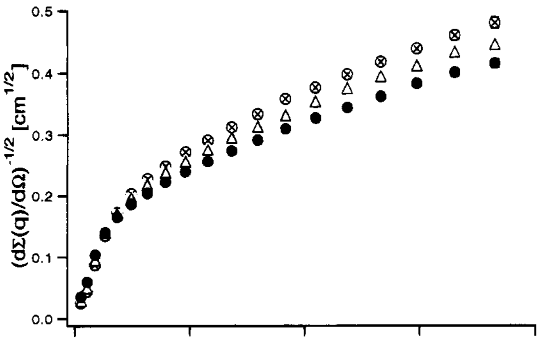

Figure 1. Debye–Bueche plot of scattering data at 47 wt % dPE: (●) 210 °C; (△) 150 °C; (⊗) 110 °C.

The Debye–Bueche model can be used to describe a random two-phase system and is based on a simple correlation function γ where

$$\gamma(r) = \exp\left(-\frac{r}{a_c}\right) \tag{2}$$

with a_c the correlation length. After Fourier transforming, one obtains intensity vs q as

$$I(q) = \frac{I(0)}{(1 + q^2{a_c}^2)^2} \tag{3}$$

One can now see that plotting $I^{-1/2}$ vs q^2 yields the correlation length as (slope/intercept)$^{1/2}$. In Figure 1 we show typical scattering from a dPE/EEA copolymer mixture above the melt. It is apparent from this that a simple one correlation length model will not fit due to the nonlinear behavior over a large q range.

For systems that do not follow linear Debye–Bueche behavior, a modified version known as the two correlation length model has been developed[24] and recently used[15,25] in the analysis of neutron scattering data on semicrystalline blends where

$$\gamma(r) = f\exp\left(-\frac{r}{a_1}\right) + (1-f)\exp\left(-\frac{r^2}{{a_2}^2}\right) \tag{4}$$

and

$$I(q) = \frac{A_1}{(1 + q^2{a_1}^2)^2} + A_2\exp\left(-\frac{q^2{a_2}^2}{4}\right) \tag{5}$$

where $I(0) = A_1 + A_2$ and

$$f = \frac{A_1}{A_1 + \frac{8}{\pi^{1/2}}\left(\frac{a_1}{a_2}\right)^3 A_2} \qquad (6)$$

Here f is the fractional contribution of the first term to the total scattering and has been equated with the sample amorphous content in studies of semicrystalline polymers.[15] It is this two-parameter model that we will primarily use to extract information on the blends studied. To curve fit data, we perform a weighted least squares fit to the four parameters a_1, a_2, A_1, and A_2, accounting for the error associated with each data point. The errors in the absolute intensity are generated along with intensity and q in the original corrected data files from NIST.

A typical graph of scattering cross section vs q as well as the two correlation length model fits to the data is shown in Figure 2. We can see that the data are fit rather well by the model and that the blend morphology remains relatively unchanged over the entire temperature range. The Debye–Bueche fit parameters are summarized for this sample in Table 2.

A similar analysis was applied to the other samples and the results summarized in Figure 3, where it is seen that the two correlation length model yields more than one distinct length scale. The smaller length scale a_1 remains constant with respect to composition over the conditions studied and is roughly 35 Å in size. The large length scale a_2, however, increases with increasing dPE concentration and covers the range of approximately 250–300 Å in size. It is interesting to note that there is, in general, little variation of the determined size for both correlation lengths with temperature over the range studied here, $110 \leq T \leq 210$ °C.

Interpretation of these measured correlation lengths is somewhat difficult due to the immiscibility of the blend. It is interesting, however, to compare the larger length scale to the size of the individual polymer molecules within the blend. Previous authors have correlated molecular weight M_w and radius of gyration R_g in experiments on polyethylene, finding that $R_g = 0.46M_w^{1/2}$.[4,26] Using a M_w of 10^5 from Table 1, we expect $R_g^{PE} \sim 145$ Å; assuming a similar relationship for the copolymer yields $R_g^{EEA} \sim 130$ Å. These values are comparable to the measured length scales shown in Figure 3, indicating that domains consist of very few polymer molecules and that there may exist some level of miscibility between polymer species. Note that a_2 increases as the amount of dPE (the larger of the two components) within the blend is increased, indicating a strong correlation to the sizes of the individual polymer species.

The other length scale is of a size much smaller than the polymer physical dimensions. We believe, however, that a_1 corresponds to an association of the ethyl acrylate groups within the copolymer. One expects that acrylate of sufficient size to be detected by neutron scattering will be observable because oxygen has a similar scattering length to deuterium.[26] A carbon/oxygen-rich region would therefore show a large amount of contrast if embedded within a carbon/hydrogen-rich matrix (for a comparison of neutron scattering length densities of the systems studied here, see Table 3). We have attempted to predict the size of an individual ethyl acrylate group within the copolymer and find the length from the tip of the EA group to the polymer backbone is only about 5 Å. This indicates that either an association of polar groups is made up of many individual molecules or the polymer is significantly reorienting itself to accommodate the interactions between acrylate groups.

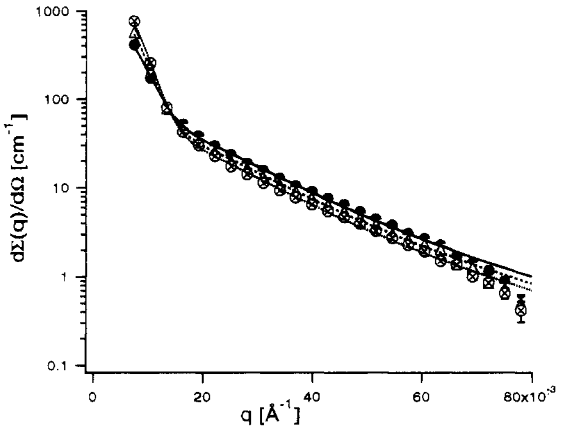

Figure 2. Example two-parameter Debye–Bueche fit at elevated temperatures: (●) 210 °C; (△) 150 °C; (⊗) 110 °C.

In Figure 4 we show the variation of f, the fractional contribution of the small length scale contrast to the total scattering, as a function of concentration. We can see that it decreases significantly as the amount of dPE is increased as one would expect from the overall decrease in the amount of acrylate in the blend. In fact, the curve tends toward zero at 100% dPE, indicating that this scattering arises from the copolymer component of the blend. With the information determined here, we believe that one can develop a picture of the microstructure of the blend above the melt. Because the size of the small correlation length does not vary over a wide range of compositions and the large length scale is not greater than approximately the size of one copolymer molecule, the association of ethyl acrylate (EA) groups is likely intramolecular in nature. We must point out that a polar association on such small length scales may have little effect on the macroscopic properties of the final blend except in a bulk, mean-field way.

3.2. Crystalline Regime. Once the temperature in the blend drops below the melting point, we would expect a strong change in the scattering pattern as the blend components orient into crystalline domains. In fact, we do see a large change, in both the scattering profile and intensity. Interestingly, the data can now be relatively well fit with the one-parameter Debye–Bueche model (i.e., a plot of $I^{-1/2}$ vs q^2 gives a reasonably straight line). This is not true at all temperatures, however; deviations from straight line behavior are most apparent at higher temperatures (i.e., 105 °C) where the system has not yet fully crystallized. We will therefore continue to use the full two correlation length model to do the analysis. We show results for the "short" correlation length a_1, the "long" correlation length a_2, and the single-parameter a_c Debye–Bueche fit to the data at 70 °C in Figure 5. We can see that the data vary little as one increases the amount of dPE, though there is a trend toward decreasing size. Also note that the one-parameter fit lies between the long and short correlation lengths in all cases, indicating that it is simply some combination of the two.

Figure 6 shows f at various compositions and for a variety of temperatures where it remains relatively constant over the entire range. As mentioned previously and discussed by other authors in studies of semicrystalline polymer blends,[15] f has been correlated with the amorphous content in the sample. In order to

Table 2. Debye–Bueche Model Fits (29 wt % dPE)

temp (°C)	a_1 (Å)	a_2 (Å)	A_1 (cm^{-1})	A_2 (cm^{-1})	f
110	36.0 ± 0.2	294.0 ± 1.8	59.9 ± 0.7	2169.5 ± 71.5	0.769 ± 0.021
130	35.3 ± 0.2	292.7 ± 1.9	61.6 ± 0.7	1835.7 ± 60.2	0.809 ± 0.020
150	35.0 ± 0.2	287.2 ± 1.9	64.9 ± 0.7	1490.7 ± 46.5	0.842 ± 0.018
170	34.6 ± 0.2	282.0 ± 1.9	67.5 ± 0.7	1242.6 ± 37.9	0.867 ± 0.016
190	34.1 ± 0.2	276.1 ± 1.9	69.4 ± 0.7	1041.2 ± 30.8	0.887 ± 0.015
210	34.5 ± 0.2	274.4 ± 2.0	73.5 ± 0.8	909.8 ± 26.6	0.900 ± 0.015

Table 3. Neutron Scattering Length Densities (SLD)

	SLD (×10^{-10} cm^2)
dPE	7.1
polyEA (100 wt % EA)	1.0
EEA copolymer (18 wt % EA)	−0.26

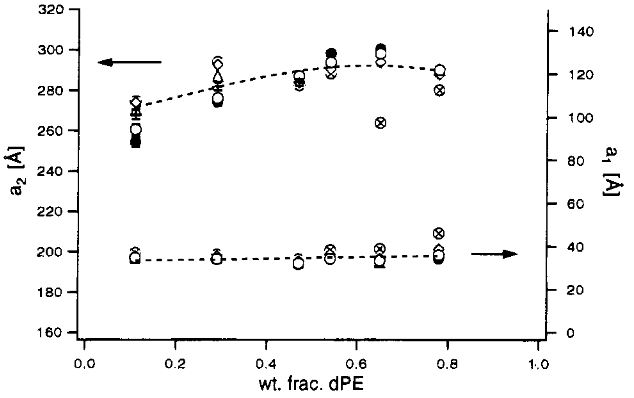

Figure 3. Correlation lengths determined for melt samples at various temperatures: (●) 210 °C; (○) 190 °C; (△) 150 °C; (◇) 130 °C; (⊗) 110 °C.

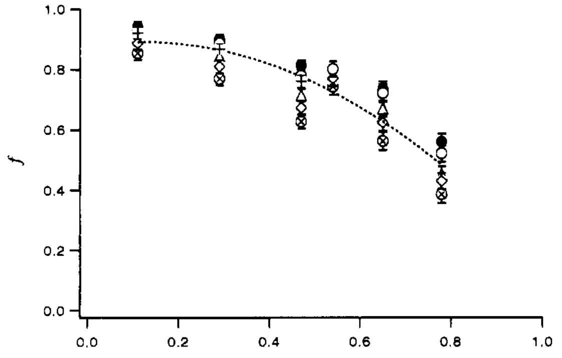

Figure 4. f for melt samples: (●) 210 °C; (○) 190 °C; (△) 150 °C; (◇) 130 °C; (⊗) 110 °C.

better understand our observed behavior in f, it is useful to present data on the heats of crystallization as a function of blend composition. Figures 7 and 8 show the cooling and heating curves as measured by DSC, with the measured transition heats and approximate crystallinities summarized in Figure 9 (a value of 289 J/g was used as the dPE melt/crystalline enthalpy and an equivalent value was assumed for the copolymer). Despite this approximation, it is quite apparent from Figure 9 that the total sample crystallinity varies significantly over the compositions studied, a fact not reflected in our measured values of f.

In the context of neutron scattering, one would expect contrast between phases of dPE and EEA copolymer (should separate phases exist) and between the crystalline and amorphous regions within phases of dPE because of its high scattering length density (see Table 3). Scattering between crystalline and amorphous regions within the hydrogenated phase would give rise to little contrast and would therefore not be observed.

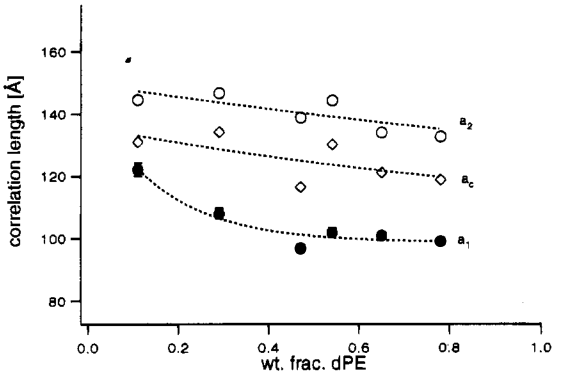

Figure 5. Calculated correlation lengths at 70 °C: (●) a_1; (○) a_2; (◇) a_c.

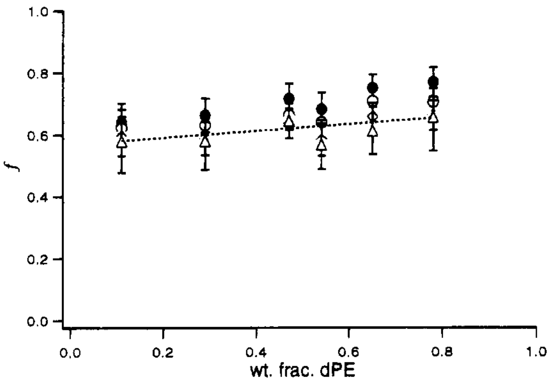

Figure 6. Two-parameter Debye–Bueche f parameter results (●) 70 °C; (○) 85 °C; (◇) 95 °C; (△) 105 °C.

If, during the crystallization process, the copolymer regions were excluded to a large extent and formed phases larger than accessible with neutron scattering, then the contrast observed would be due entirely to crystallization within dPE. In this case, f would correlate with the crystallinity (or amorphousness) within the dPE phase and the measured size scales in Figure 5 would correspond to the dPE amorphous and crystalline domains.

In support of this picture, we compare our results to the longitudinal acoustic mode (LAM) Raman studies on linear polyethylene of Mandelkern et al.[27] In this study, thicknesses were found for the core crystalline (δ_c) and interlamellar (δ_a) regions as a function of molecular weight. At molecular weights of ~10^5, corresponding to the dPE investigated here, they find thicknesses of $\delta_c \approx 140$ Å and $\delta_a \approx 110$ Å. These values are in extremely good agreement with the values we measure (see Figure 5), indicating that a_2 corresponds to the crystalline domain size, a_1 corresponds to the amorphous domains, and f correlates with the dPE phase "amorphousness". We can roughly estimate the dPE phase crystallinity by taking the data of Figure 9 and assuming the EEA copolymer crystallinity varies little over the range of compositions. We plot the resulting estimate for the dPE crystallinity as well as f at the lowest temperature investigated in Figure 10,

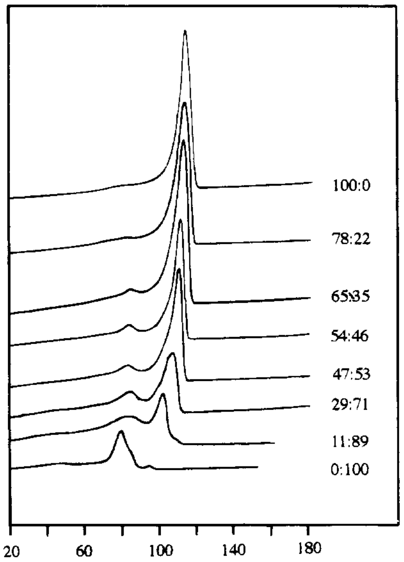

Figure 7. DSC exotherms at various dPE:EEA copolymer compositions (10 °C/min, cooling cycle). The dPE peak remains nearly constant at 109–110 °C until low concentration (11 wt %), where the crystallization temperature drops to ~100 °C.

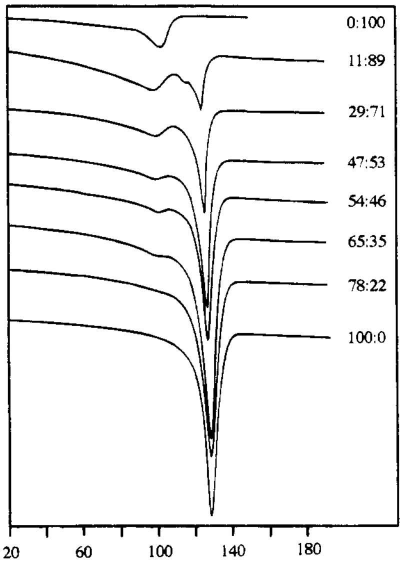

Figure 8. DSC endotherms at various dPE:EEA copolymer compositions (10 °C/min, 2nd heats). The dPE peak position shifts slightly from 122.0 °C at 11:89 to 126.7 °C at 100:0.

where one can see that the two measures both remain relatively constant over the entire composition range.

3.3. Melt/Crystalline Transition. In order to properly determine a model for the structure within the semicrystalline polymer blend, it is useful to observe how the correlation lengths vary as one makes the transition from melt to solid. In Figure 11, we show the variation of both short and long correlation lengths as a function of temperature for all compositions studied, and in Table 4 we list the fit parameters for an example composition. These samples were taken initially to melt temperatures (~150 °C) and then slowly cooled (~2 °C/min) through the crystallization transition. Each sample was held at measurement temperatures for times varying from 0.5 to 2 h before data were taken, and all samples were held for a minimum of ~2 h at each temperature before being cooled to the next point.

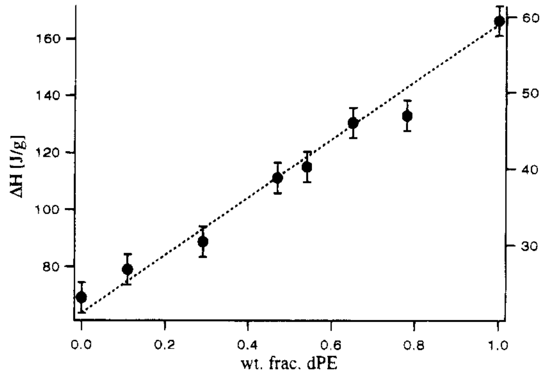

Figure 9. Variation of the melt transition enthalpies with blend composition.

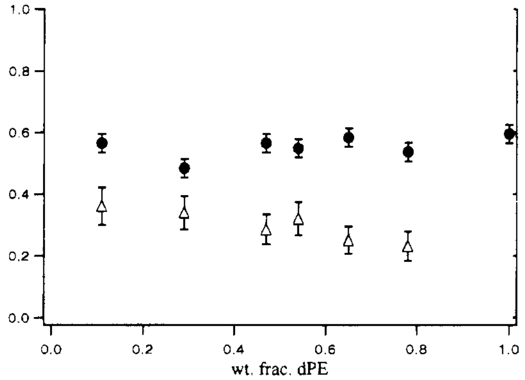

Figure 10. Estimated fraction dPE crystallinity (●) from transition heat measurements compared with (1 − *f*) at 70 °C (△).

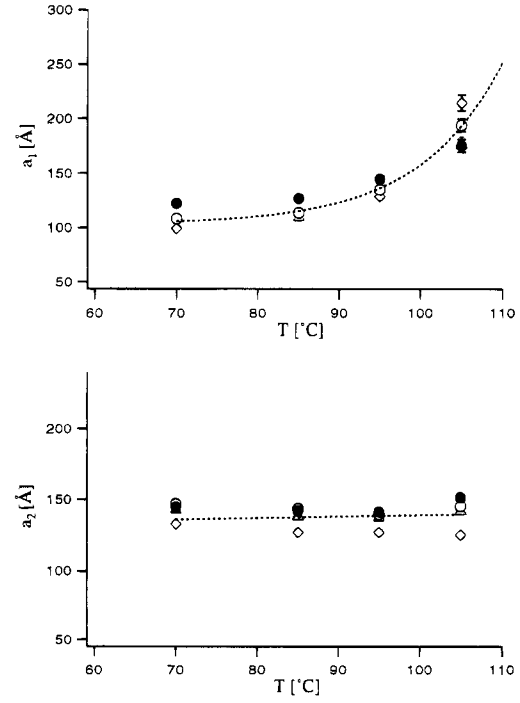

Figure 11. Determined correlation lengths through crystalline transition: (●) 11 wt % dPE; (○) 29 wt % dPE; (△) 54 wt % dPE; (◇) 78 wt % dPE.

The most striking observation one can make with these two figures is the different behaviors of the two length scales. The "long" length scale, attributed to the crystalline core thickness in the sample, varies little as the temperature is first lowered past the crystallization point of the dPE (~110 °C) and then the EEA copolymer (~80–85 °C). However, the "short" length scale, at-

Table 4. Debye–Bueche Fit Results (29 wt % dPE)

temp (°C)	a_1 (Å)	a_2 (Å)	A_1 (cm^{-1})	A_2 (cm^{-1})	f
105	193.7 ± 5.8	145.2 ± 0.6	5774.2 ± 621	388.8 ± 6.9	0.580 ± 0.092
95	134.6 ± 2.2	139.4 ± 0.5	2487.6 ± 144	428.5 ± 7.4	0.588 ± 0.053
85	113.4 ± 1.7	143.5 ± 0.6	1645.5 ± 86.6	434.6 ± 9.7	0.630 ± 0.038
70	108.0 ± 1.6	146.6 ± 0.7	1479.4 ± 77.4	417.7 ± 10.8	0.662 ± 0.054

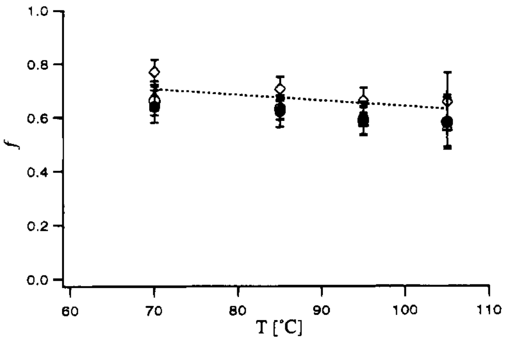

Figure 12. *f* through the crystalline transition: (●) 11 wt % dPE; (○) 29 wt % dPE; (△) 54 wt % dPE; (◇) 78 wt % dPE.

tributed to an amorphous contribution to the scattering, shows a marked but smooth drop as the melt to semicrystalline transition is made.

The behavior of the long length scale structure suggests that its morphology is locked in very near the crystallization temperature. The core crystalline regions of the dPE lamellae are initially formed and vary little as the temperature is further lowered. It is probable that an annealing of the samples below the melt would lead to thicker crystalline regions but such a heat treatment was not carried out in this study.

As discussed in section 3.2, the short length scale corresponds to the amorphous component of the dPE within the blend. If we extrapolate the measured size scale to the melting temperature, we approach the large length scale determined earlier in the melt studies. As the temperature is lowered, however, and the copolymer begins to crystallize, we see a decrease in the size of the amorphous, or interlamellar, region. It is clear by comparing Figure 11 to the crystallization curves of Figure 7 that the short length scale is monitoring the evolution of the amorphous regions as the polyethylene component crystallizes. From these figures one can see that both the decrease in the short correlation length and the crystallization of the polyethylene component of the blend are completed by $T = 85$ °C, long before the EEA copolymer has completed its crystallization. Once again, lack of contrast within the crystallizing EEA copolymer has left the short correlation length unaffected by its morphological transitions as the temperature is further lowered. Interestingly, we would expect the value of *f* to decrease through the transition as the crystallinity increases, however, we see little variation in Figure 12.

As the sample is cooled below the melt, we no longer observe length scales corresponding to an association of ethyl acrylate groups. It is possible that the scattering is simply being masked by other more strongly scattering features, but there is some support for the picture that the EA groups within the copolymer are incorporated within the lattice and do not associate in the solid phase. The scattering cross section is relatively small in pure EEA copolymer; there is very little contrast to give rise to scattering. If we apply the two-parameter Debye–Bueche analysis to this sample at 21 °C, we find that $a_1 = 118.2 \pm 5.4$ Å, $a_2 = 69.7 \pm 4.2$ Å, $A_1 = 138.1 \pm 15.6$ cm^{-1}, $A_2 = 1.0 \pm 0.3$ cm^{-1}, and $f = 0.865 \pm 0.1671$. The scattering observed here is due to the difference in densities between the amorphous and crystalline regions in the sample. If EA groups were associating, there would be more scattering, and one would very likely see EA size scales comparable to those in the melt. As before, with semicrystalline polymers, the "long" correlation length corresponds to the core crystalline thickness and the "short" correlation length the thickness of the interlamellar region. These conclusions are supported by the agreement between the calculated *f* and the approximate crystallinity of 25% for EEA copolymer from Table 1.

4. Discussion

As a result of our analysis and as predicted from molecular weight correlations, we know the size of the polymer molecules investigated here is relatively large with $R_g \sim 150$ Å. This, in combination with the *q* range examined here, limits analysis of the data to non-Guinier approaches as $qR_g > 1$. Plots of $(d\Sigma(q)/d\Omega)^{-1}$ vs q^2 are linear only over very small ranges at the smallest *q*, making fitting the data problematic and leaving polymer conformation undetermined via such standard approaches. This motivates our use of the two-parameter Debye–Bueche model, allowing determination of morphology over a large *q* range. Because of this broad applicability, we have been able to use the same model to examine our blend system above, below, and through the melt transition. Such an ability is important in that we are interested in the behavior of this system over a wide range of temperatures.

It is difficult to predict, *a priori*, the phase behavior of this system over the temperature range studied here. One expects that the ratio of ethyl acrylate to ethylene groups within the copolymer will have a significant influence on the interactions and the subsequent phase behavior in this system. In the limit of zero EA content, we expect complete miscibility as indicated by studies[12,23] of HDPE and LDPE showing no phase separation over a wide range of temperatures in the melt. As one increases the EA content, however, the interactions will be progressively modified and the polymers less compatible in nature. At exactly what point the interactions are strong enough to induce phase separation remains to be determined. One normally predicts the point of phase separation with knowledge of the Flory–Huggins parameter χ by determining if $\chi N > 2$.

We must concern ourselves first with phase separation due to isotopic substitution because the polymers are of relatively high M_w in our studies. Using a value of $\chi_{hd} = 2.5 \times 10^{-4}$ for the interaction between deuterated and hydrogenated polymer[2] and a geometric average for the effective number of repeat units N_{eff} in the blend, we find $\chi N_{eff} \sim 1.3$. This indicates that a blend of the pure hydrogenated LDPE analog of the EEA copolymer and the dPE studied here would not phase separate, and any phase separation that did occur in our studies with the copolymer would be caused, at least partially, by the presence of the EA groups. Our results within the melt indicate the dominance of the interactions due to the acrylate in this system.

An interesting study would be to vary the percentage of EA in the EEA copolymer (various copolymers are commercially available). One could conceivably extract the influence of EA content on χ and predict the concentration required for the onset of phase separation in the melt. As evidenced by the inability to fit the scattering data to the RPA, we have observed phase separation with the current copolymer (18 wt %). We would assume though, that as the overall polarity of the copolymer is decreased, we would, at some point, see the onset of blend miscibility. The experiments carried out here, however, do not allow for the extraction of the χ parameter. Traditionally one determines χ through studies of polymers in dilute solution. Studies of polymer blends, however, are better done at high concentration.[30] It has been shown[31] some time ago that a modified Zimm analysis can be used to determine interaction parameters in concentrated polymer solutions by varying the amount of deuteration of one component while keeping the overall composition of chemically dissimilar polymer species constant. Such a study should yield information on the temperature dependence of the χ parameter, allowing one to predict the entire phase diagram as a function of both temperature and copolymer composition.

To this point we have not addressed the question of the influence of kinetics on the results presented. None of the samples studied here were held more than a few hours at the temperatures reported. For studies above the melt, one expects that diffusion is fast enough (even for the relatively high M_w polymers studied here) that we would see an increase in the measured correlation lengths over the time scales of the experiment if the blend were unstable. In the semicrystalline regime, however, the structure of the system will be highly dependent on its thermal history as evidenced by other studies.[2] We would expect that allowing the samples to anneal at elevated temperature would lead to a growth in the core crystalline sizes as often seen previously with polyethylene. However, what makes the current study interesting is not only the specific values obtained for the blend physical parameters but also that this technique and the two-parameter model allows us to, in fact, extract these values. In addition, we have been able to monitor the structure during the crystallization process, allowing one to study questions regarding the influence of polymer interactions on transition morphology.

5. Summary

We have used the technique of small-angle neutron scattering to determine the morphology of a blend of dPE and an EEA copolymer over a temperature range of 70–210 °C. Above the melt, the interactions due to the acrylate dominate and the mixture is two phase but shows little variation in domain size with temperature or composition. The length scales observed in the analysis correspond well to the size of the individual polymer molecules. In addition, we interpret observed scattering corresponding to a length scale of order 35 Å as an association of the ethyl acrylate within the copolymer. As might be expected, we see a drastically different microstructure as the temperature is lowered below the crystallizing temperature (~110 °C). We find length scales of approximately 100 and 140 Å, both depending little on the composition of the blend. These were interpreted as the size of the crystalline core and the interlamellar amorphous regions within polyethylene. Results for the correlation lengths through the melt/crystalline transition indicate that the size of the crystalline region is locked in early during cooling while the interlamellar thickness undergoes a more continuous transition in size.

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