

# Small-angle neutron scattering of partially segregated blends of polyethylene and deuteropolyethylene\*

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A previous paper described work in which polyethylene (PEH) blended with 4.3 vol% deuterated polyethylene (PED) was annealed and plastically deformed at different temperatures. The most prominent change resulting from the deformation is a significant reduction in the apparent molecular weight measured from the extrapolated small-angle neutron scattering (SANS) data. The model adopted in the data analysis was based on a heterogeneous distribution of the centres of mass of the labelled (PED) chains which form a two phase system of enriched and depleted regions described by a Debye-like correlation function. A comparison between this model and alternative approaches based on the correlation network and random phase approximation will be delineated. The results from these models lead to the conclusion that for typical melt crystallized samples the centres of mass of the labelled chains are only slightly perturbed from a random distribution. Plastic deformation of the blends tends to lessen the degree of segregation of the PED molecules and the results suggest that a portion of the specimen must undergo a melting and recrystallization mechanism during deformation.

(Keywords: neutron scattering; blends; polyethylene; deformation; melting; recrystallization)

## INTRODUCTION

In a previous paper we have shown that plastic deformation of a partially segregated PE/PED blend resulted in a significant reduction of the apparent molecular weight ( $MW$ ) measured using the SANS technique<sup>1</sup>. Based on earlier observations that such a reduction in the apparent molecular weight also took place during melting and recrystallization of the partially segregated blends<sup>2</sup>, it was concluded that a portion of the crystalline phase must melt and recrystallize during the plastic deformation process. It is noteworthy that the type of deformation used in the previous work was a pure shear, as the SANS measurements were carried out along the axis where the macroscopic strain is zero. Any changes in either the shape of individual chains or the distribution among the centres of mass (CM) of these chains along the other two axes did not have any affect on the scattered intensities measured.

A set of Zernicke-Prins (Z-P) type equations was derived to relate the scattered intensities and the extent of heterogeneity of the labelled chains distribution<sup>3</sup>. These equations were derived from a two-phase, geometrical

model based on the assumption that some regions are completely depleted of PED chains. The remainder of the volume consists of a PED enriched phase within which the CM of PED chains are randomly distributed. Such a model originated from a consideration of crystallization kinetics and was first proposed by Sadler and Keller<sup>4</sup>. The enhancement of the scattered intensities at small-angle due to the labelled chain segregation results in a significant increase in the apparent  $MW$  and the radius of gyration ( $R_g$ ) obtained from a Guinier or Zimm plot. Frequently, the enhancement in  $MW$  and  $R_g$  can be as large as several orders of magnitude<sup>2,4</sup>. Based on the previously derived equations<sup>3</sup>, the size, the volume fraction of the PED enriched domains, as well as the labelled chain concentration within these domains can be deduced from the scattered intensities. Only the magnitude of the enhancement in both  $MW$  and  $R_g$  measured in SANS is required to calculate a set of parameters which specifies the structure of these partially segregated blends. Using these equations, the structural changes due to plastic deformation can then be studied quantitatively. Alternative models have also been developed<sup>5,6</sup> to account for the enhancement in  $MW$  and  $R_g$  and we will outline their relationship to the two-phase geometrical model<sup>3</sup> described above. Schelten *et al.*<sup>5</sup> gave a theoretical treatment of a paraclustering model based on the assumption of interconnections between the labelled chains which formed a correlation network and supported this concept by

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SANS measurements as a function of crosslinking introduced by  $\gamma$  irradiation<sup>7</sup>. de Gennes<sup>6</sup> applied the random phase approximation (RPA) to obtain an equation which relates the magnitude of the scattered intensities to the Flory interaction parameter  $\chi$  between two different species of molecules. While mixtures of normal and deuterated polymers have generally been considered ideal ( $\chi=0$ ), recent calculations<sup>8</sup> have indicated the possibility of an ultra-weak interaction between H and D molecules and that  $\chi$  might be finite ( $10^{-4}$  to  $10^{-3}$ ). It has been suggested<sup>6,9</sup> that this might give rise to incipient liquid-liquid phase separation near the spinodal leading to anomalous values of  $MW$  and  $R_g$  in scattering measurements. In general anomalous SANS effects have only been reported to date for solid semicrystalline polymers and seem to arise from differential crystallization effects due to the different melting points of H and D molecules. While we are not aware of any reports of anomalous scattering arising in the melt or glassy state we will include a discussion of this possibility via the RPA equation which relates to the magnitude of scattered intensities to the assumed interaction parameter  $\chi$  between the labelled chains and the regular molecules. Although the equations derived from the above models are based on different geometric and thermodynamic assumptions, it is the object of this work to demonstrate that under certain conditions the resulting equations are very similar. The limit beyond which the equation derived from RPA is not applicable will also be addressed.

### SCATTERED INTENSITIES FROM PARTIALLY SEGREGATED BLENDS

The scattered intensities from a molecular weight matched PED/PE blend containing  $\bar{N}_D$  PED chains with a degree of polymerization,  $n$ , has been derived using a Z-P approach for the two phase geometrical model<sup>3</sup> and the resultant formula is

$$\frac{I(Q)}{I_0(Q)} \simeq X_D n (1 + K(1-\phi)^4 Y) \left[ 1 - Q^2 \left( \frac{R_g^2}{3} + \frac{2K(1-\phi)^4 Ya^2}{1 + K(1-\phi)^4 Y} \right) \right] \quad (1)$$

where  $K$  equals  $8\pi$ ,  $R_g$  is the radius of gyration of the labelled chains,  $Q$  is the magnitude of the scattering vector,  $\phi$  is the volume fraction occupied by clusters or domains within which the labelled chain are randomly distributed,  $Y$  is the average number of labelled chains per cluster,  $a$  is the correlation length of the partially segregated system and  $X_D$  is the volume fraction of PED chains. The cord length  $l_c$  of the clusters is related to  $\phi$  and  $a$  through the well known Porod relation<sup>10</sup>

$$l_c = \frac{a}{1-\phi} \quad (2)$$

Furthermore, the quantity  $Y$  is defined in terms of the other variables by

$$Y = \frac{\bar{N}_D l_c / \phi V}{a^3 \bar{N}_D} = \frac{1}{V \phi (1-\phi)^3} \quad (3)$$

where  $V$  is the scattering volume.

The assumptions made in the derivation of equation (1) are: (1) the centres of mass of the labelled chains are depleted completely in certain regions and randomly distributed outside those regions; (2) the correlation function describing the geometric arrangement of the PED containing phases or clusters is of the Debye-type<sup>11</sup>, i.e., of the form  $e^{-r/a}$ ; and (3) the labelled chain concentration is low. While the depleted domains do not contain the centres of mass of PED molecules, they may contain segments of these molecules whose CM lie outside the domain. For example, if the value of  $a$ , the correlation length, is of the same order of magnitude as  $R_g$  in a partially segregated blend, PED segments can be located throughout the whole volume with a finite probability. Regions completely depleted of PED segments start to appear only as the value of the correlation length grows beyond that of  $R_g$ .

The scattering equation<sup>6</sup> derived from RPA in a matched molecular weight blend is

$$\frac{I(Q)}{I_0(Q)} = \frac{X_D X_H g_D(Q)}{1 - 2\chi X_D X_H g_D(Q)} \quad (4)$$

where  $X_D$  and  $X_H$  are the volume fractions of PED and PE chains respectively,  $\chi$  is the interaction parameter between D and H chains and  $g_D(Q)$  is the scattering factor of a single chain. In the present case,  $g_D(Q)$  can be approximated as

$$g_D(Q) \simeq n \left( 1 - \frac{Q^2 R_g^2}{3} \right) \quad (5)$$

Strictly speaking, equation (4) is only applicable under the condition that phase separation does not occur. This restriction is a direct consequence of the approximation used during the derivation of this equation. In other words, the value of  $\chi$  in equation (4) is bounded by

$$\chi < \frac{1}{n} \frac{1}{1 - 2X_D} \ln \left( \frac{1 - X_D}{X_D} \right) \quad (6)$$

The right hand side of equation (6) simply denotes the value of  $\chi$  on the coexistence curve from a mean field approach<sup>12</sup>. In the present case, the value of  $X_D$ , the volume fraction of PED chain, is 0.043. Accordingly, the upper limit of the term  $2\chi n X_D X_H$  is about 0.28 which is much less than unity. Consequently, equation (4) can be approximated as

$$\frac{I(Q)}{I_0(Q)} = X_D X_H g_D(Q) (1 + 2\chi X_D X_H g_D(Q)) \quad (4')$$

After combining equations (4) and (5), one has the following relation

$$\frac{I(Q)}{I_0(Q)} = X_D X_H n (1 + 2\chi n X_D X_H) \quad (7)$$

$$\left[ 1 - Q^2 \left( \frac{R_g^2}{3} + \frac{2\chi n X_D X_H R_g^2}{3(1 + 2\chi n X_D X_H)} \right) \right]$$

where the term  $X_H X_D$  can be approximated by  $X_D$  since  $X_H$  is close to unity in the present case. The similarity

between equations (1) and (7) is rather striking in view of the fact that these two equations are derived from completely different viewpoints. By comparing these two equations one has

$$K(1 - \phi)^4 Y = 2\chi n X_D X_H \quad (8)$$

$$6a^2 = R_g^2 \quad (9)$$

Equation (8) simply means that the extent of labelled chain segregation,  $K(1 - \phi)^4 Y$ , is directly proportional to the multiple of the polymerization index  $n$  and the interaction parameter  $\chi$ . Equation (9) indicates that the extent of segregation within which equation (4) is applicable is rather limited; the correlation length  $a$ , between the segregated domains is smaller than the  $R_g$  of an individual chain. Under such circumstance the term segregation might better be replaced by concentration fluctuation. Thus according to the RPA treatment the positions of the CM of the PED molecules are only slightly perturbed from a random distribution and since the correlation length is less than the value of  $R_g$ , the segments of the labelled chain are still distributed throughout the whole scattering volume with finite probability as discussed in the earlier portion of this work.

The above rationale demonstrates that in the single phase region equation (1) and equation (4) are basically the same; one expresses the scattered intensities in terms of the thermodynamic parameters and the other is in terms of the geometric arrangement of the molecules. As the blend starts to segregate into real phases, or as the correlation length  $a$  increases beyond the value of  $R_g$ , equation (4) is no longer applicable. For the present work with  $X_D = 0.043$ , the maximum value of the term  $2n\chi X_D X_H$  of equation (4) is 0.28 as already mentioned. By substituting this value into equation (4) and allowing  $Q$  to approach zero, the corresponding limit for molecular weight enhancement is 1.39.

The values of both  $MW$  and  $R_g$  measured from SANS of the annealed and deformed specimens are listed in Table 1. As the molecular weight enhancement is far beyond the factor of 1.39, the data from these specimens cannot be interpreted using equation (4). This indicates that the RPA with the values of  $\chi$  assumed<sup>7,8</sup> does not provide a reasonable description of the anomalous SANS effects observed in mixed PED/PE systems and supports the view that these are due to kinetic or differential crystallization effects.

Given the value of  $n$  is  $6.9 \times 10^3$  from gel permeation chromatography (g.p.c.) and the corresponding value of  $R_g$  is  $121 \text{ \AA}$ , the values of  $Y$ ,  $l_c$  and  $\phi$  can be calculated using equation (1) and the data in Table 1. The results for

the correlation length  $a$ , the average chord length  $l_c$  of the PED enriched domain and its volume fraction  $\phi$ , are shown in Figures 1 and 2 and Table 2. The size of the PED enriched domain is in the range of  $10^4 \text{ \AA}$  except for an annealing temperature of  $126^\circ\text{C}$ . It is noteworthy that the value of  $10^4 \text{ \AA}$  does not reflect the resolution of the SANS equipment which is in the range of  $10^3 \text{ \AA}$ . What is measured directly from the scattering curves is the value of the correlation length  $a$  which is  $\sim 200\text{--}300 \text{ \AA}$ . The values of  $l_c$  are calculated from  $a$  and  $\phi$  according to

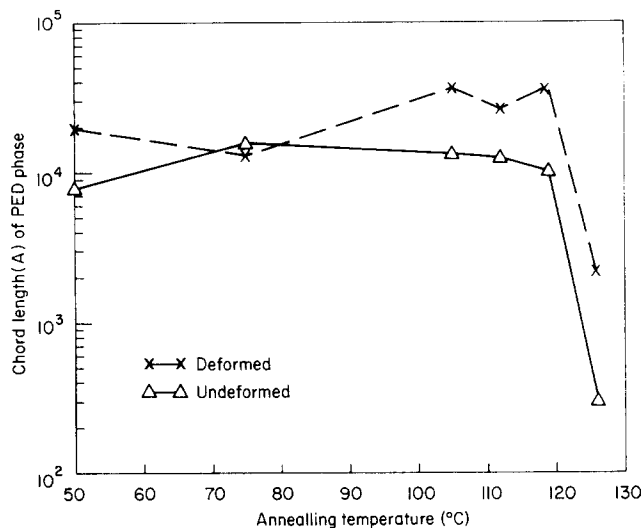


Figure 1 Effect of deformation on the distribution of molecules in PED/PEH blends. 4.3% vol PED

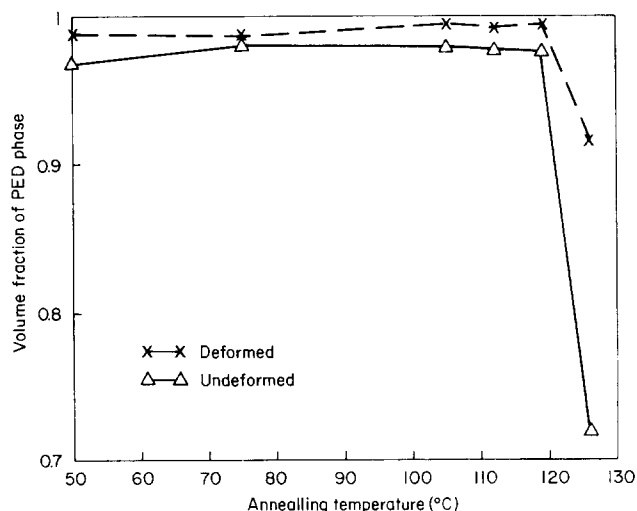


Figure 2 Effect of deformation on the distribution of molecules in PED/PEH blends. 4.3% vol PED

Table 1 Apparent SANS molecular weights and radii of gyration of labelled D chains in oriented and unoriented samples

Annealing temperature (°C)	Unoriented		Oriented	
	$M_{wD} \times 10^{-3} \text{ g}$ (weight-averaged)	$R_g$ (Å) (z-averaged)	$M_{wD} \times 10^{-3} \text{ g}$ (weight-averaged)	$R_g$ (Å) (z-averaged)
20	1395	288		
50	1382, 1347	362, 365	313	317
75	1560, 1638	439, 462	245	255
105	1162, 1343	385, 405	241	283
108	1105	346	251	
112	1338, 1513	408, 498	233, 182	270
119	1042, 938	356, 383	175	259
126	618	163	1120	260

**Table 2** Values of the correlation length,  $a$ , volume fraction  $\phi$ , and chord length,  $l_c$  of the PED rich domains

Annealing temperature (°C)	Unoriented			Oriented		
	$a$ (Å)	$\phi$	$l_c$ (Å)	$a$ (Å)	$\phi$	$l_c$ (Å)
50	249	0.968	7790	228	0.988	19600
75	306	0.980	15500	182	0.986	12800
105	282	0.979	13100	219	0.994	36000
112	284	0.977	12400	205	0.992	26100
119	246	0.976	10100	206	0.994	36900
126	83.8	0.72	800	169	0.916	2020

equation (2). The extent of segregation seems not to change much over the temperature range from 50°C to 119°C within the 30 min used in these experiments. A dramatic reduction in  $\phi$  or a growth of the PED depleted region occurs as the annealing temperature reaches 126°C which is fairly close to its melting point. A reduction in the average size, hence the chord length  $l_c$ , of the PED enriched region is also observed resulting from the high annealing temperature.

Based on the above results, one reaches the conclusion that most segregation processes take place over the temperature range close to the melting point. Furthermore, the segregation process can be specified as an increase in the volume fraction of the PED depleted region and a decrease of the cord length of the PED containing domains. Such features are not obvious from the raw SANS data of *Table 1*. If one simply takes either the apparent molecular weight or the radius of gyration measured from SANS as an indicator of segregation, an opposite conclusion could be drawn regarding the influence of annealing temperature on the extent of segregation.

The average cord length of the PED depleted regions is given by  $a/\phi \approx a$  as  $\phi \approx 1$ , and thus for samples annealed below 119°C the depleted regions occupy only a few per cent of the total volume and have dimensions just slightly larger than the  $R_g$  of the individual labelled chains. Thus the two-phase geometrical model leads to a similar conclusion as the RPA in the distribution of centres of mass of the labelled chains is only slightly perturbed from a random distribution as also envisioned in the correlation network or paracluster model. This provides yet another alternative description of the anomalous SANS scattering effects where segregation has not yet proceeded to the point where the size of PED depleted regions exceeds  $R_g$ . The model leads to an equation<sup>5</sup> very similar to the RPA

$$\frac{I(h)}{I_0(h)} = \frac{X_D X_H g_D(Q)}{1 - Z \alpha g_D(Q)} \quad (10)$$

where  $\alpha$  is a parameter which describes the probability of finding a deuterated repeat unit in the  $Z$  nearest neighbours around a given deuterated unit. For a statistical distribution of labelled and unlabelled molecules  $\alpha = 0$ , and  $\alpha > 0$  implies an enhanced probability of contacts between labelled units ( $CD_2$  in this study) leading to the formation of a correlation network<sup>2,10</sup>. Thus all three models lead to very similar equations for the scattering although they are based on quite different assumptions. The RPA treats anomalous SANS effects in terms of a thermodynamic parameter  $\chi$ , whereas the correlation network and two phase geometrical models assume different distributions of labelled molecules arising from differential crystallization or kinetic effects. As stated

above there is no actual evidence for the existence of a finite value of  $\chi$  between PED and PE though the evidence for differential crystallization effects is well established<sup>13</sup>, and for this reason we will not proceed further with the RPA. The two remaining models lead to a similar conclusion that the CM of the labelled molecules are only slightly perturbed from a statistical distribution and we will restrict our discussion to the two-phase geometrical model which can be more easily adapted to our original objective of the study of plastic deformation mechanisms.

#### EFFECT OF PLASTIC DEFORMATION ON CHAIN SEGREGATION

Plastic deformation tends to smear out the PED labelled chains distribution. This is evident from the increase both in the cord length and the volume content of the PED containing phase at all temperatures. It should be noted that the smearing phenomenon of the PED labelled chains was measured along the axis of zero macroscopic strain. Only the positions of the centres of mass of PED chains projected on this specific axis are reflected in the scattering intensities measured. It is also interesting to note the increase in the volume fraction of the PED containing phase resulting from the deformation. This small amount of increase in  $\phi$  is calculated from the pronounced change in the observed value of  $R_g$  and  $MW$  using equation (1). The values of both  $l_c$  and  $\phi$  presented in *Figures 1* and *2* are surely model-sensitive. If one alters the assumption regarding the distribution of the centres of mass of PED chains, different values of  $R_g$  and  $MW$  will result. For example, if one discards the assumption that there are regions completely depleted of the CM of PED chains, instead, one can assume that there is a fluctuation in the distribution of the CM of PED chains. Let the magnitude of the fluctuation be  $\Delta c$ , and the correlation function still be  $e^{-r/a}$ . What one can calculate from the SANS result is the values of the scattering invariance  $\Delta c^2 \phi(1 - \phi)$  and  $a$ ; no detailed calculations of  $\phi$  and other quantities is possible unless an additional assumption is made. In the present work, we simply let the lower limit of the PED fluctuation reach zero; consequently a relationship between  $\Delta c$  and  $\phi$  is implicated. Such a hypothesis seems to be a reasonable one in light of the 5°C difference in the melting point of PED and PE chains. PEH chains will crystallize ahead of the deuterated species and result in some regions of low PED content.

#### DEFORMATION MECHANISMS AND THE CORRESPONDING CHANGES IN SCATTERED INTENSITIES

It was shown in our previous paper that the extent of

randomization of the labelled chains on orientation, and the consequent fall in the apparent SANS  $R_g$  and  $MW$  are consistent with a partial melting and recrystallization mechanism. We now wish to use the geometrical model described above to examine how far the SANS observations are consistent with other deformation models. According to the deformation mechanisms proposed by Peterlin<sup>14,15</sup> for polyethylene and other crystalline polymers, the deformation consists of a lamellae to fibrils transformation and an interfibrillar shear process.

In the following, we will proceed with the assumption of no melting and recrystallization during deformation processes and examine the consequence of this assumption on the scattered intensities. Rearrangement of the PED chains can easily be visualized by this purely mechanical mechanism along these two principal strain axes where the deformation ratio are 13 and 1/13 respectively. However, the rearrangement or the homogenization of the PED chains along the zero strain axis is the object of our SANS measurements and the focal point of this discussion. It is conceivable that a certain amount of rearrangement could still occur during the deformation processes mentioned above. For example, several PED chains belonging to different lamellae might be recombined into a single microfibril and give rise to some rearrangement of the PED chains along the zero strain axis. For this type of rearrangement, PED chains can best be described as a randomization process since the possible role of the interaction parameter  $\chi$  between the D and H chains is not included. The effect of a randomization process on the scattered intensities of a partially segregated blend will be addressed as follows.

Let the position of the CM of a PED chain be moved from its original position by a distance  $r$ . Let the magnitude of  $r$  follow a Gaussian distribution  $h(r)$  with the variance  $\sigma^2$  as in a random walk process. The distribution of the CM or PED chains after the randomization process can be expressed as  $\rho(\bar{R}_i) * h(r)$ , where  $\rho(\bar{R}_i)$  is the distribution function of the CM of PED chain  $i$  before randomization and  $*$  denotes folding or convolution.

The scattered intensities of a system before randomization can be expressed as<sup>3</sup>

$$I(Q) = I_0(Q) \left[ N_D g_D(Q) + \frac{N_D^2}{V} g_D(Q) F(\rho(\bar{R}_i) * \rho(\bar{R}_j)) \right] \quad (11)$$

where  $g_D(Q)$  is the single chain form factor of molecular weight  $n$ ,  $F$  denotes Fourier transform and  $N_D$  is the number of PED chains within the scattering volume  $V$ . After randomization the scattered intensities change to

$$I'(Q) = I_0(h) \left[ N_D g_D(Q) + \frac{N_D^2}{V} g_D(Q) F(\rho(\bar{R}_i) * \rho(\bar{R}_j)) (Fh(r))^2 \right] \quad (12)$$

Since  $h(r)$  is a Gaussian distribution function with variance  $\sigma^2$ , the term  $(Fh(r))^2$  can be expressed explicitly as  $\exp\{-\sigma^2 Q^2\}$  for an isotropic case. Equation (12) can then be rewritten as

$$I'(Q) = I_0(Q) \left[ N_D g_D(Q) + \frac{N_D^2}{V} g_D(Q) \exp\{-\sigma^2 Q^2\} F(\rho(\bar{R}_i) * \rho(\bar{R}_j)) \right] \quad (13)$$

It is important to notice that the limit of  $\exp\{-\sigma^2 Q^2\}$  is unity as the value of  $Q$  approaches zero. Accordingly, the extrapolated value of scattered intensities at zero angle, or the SANS molecular weight, will not change as a result of this type of randomization process. From an experimental viewpoint, the above statement is true as long as the magnitude of variance  $\sigma^2$  is not much greater than the quantity  $Q_0^{-2}$  where  $Q_0$  is the resolution of the scattering equipment used. In present cases the corresponding value is about 260 Å denoted as  $\sigma_0$ . If the amount of randomization or the average distance of the movement of the CM of these PED chains along the zero strain axis is less than  $\sigma_0$ , the SANS molecular weight should stay the same. The amount of randomization based on the deformation mechanism mentioned above is expected to be only a fraction of the width of a microfibril which is 100 Å wide. Figure 3 shows the effect of such a randomization mechanism on the observed scattering data (taken from ref. 1, Figure 4) which are shown in the form of a Zimm plot. The solid lines represent typical scattering data for unoriented and oriented samples and show that both  $R_g$  and  $\frac{d\Sigma}{d\Omega}(0)$ , from which the apparent SANS-MW is

calculated, fall on orientation. The dotted lines show the way the scattering curves may be expected to change if the CM of the PED molecules are randomized according to equation (11) for various values of  $\sigma$ . For a typical  $\sigma \approx 100$  Å corresponding to a fibril width of 100 Å, it is clear that such a randomization process cannot reproduce the observed data. Indeed if a straight line were drawn through the line for  $\sigma \approx 100$  Å in the measured  $Q^2$  range  $0.15 \times 10^{-4}$  to  $1 \times 10^{-4}$  Å<sup>-2</sup>, this would lead to an apparent increase in  $\frac{d\Sigma}{d\Omega}(0)$ , rather than the decrease by a

factor  $\sim 4-5$  which is actually observed. Thus the experimental findings cannot be explained by a randomization process for a microfibrillar deformation scheme based on equation (12). As pointed out by Peterlin<sup>14,15</sup> the energy input during deformation processes is insufficient to raise the temperature of the whole spectrum above its melting point. However, a partial melting and recrystallization process is still possible. Such a partial melting process might presumably occur during the lamellae to fibrils

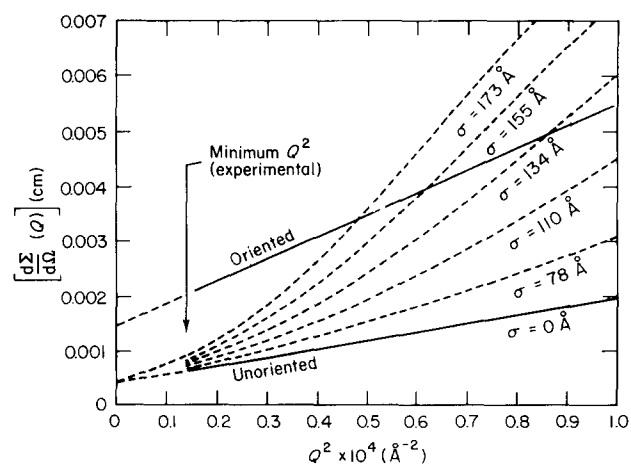


Figure 3  $\left[ \frac{d\Sigma^{-1}}{d\Omega}(Q) \right]$  vs.  $Q^2$  for typical oriented and unoriented experimental samples (solid lines) and unoriented data with CM of labelled molecules randomized according to equation (12) for various values

transformation stage. Thus the results of the present work may be incorporated into the deformation model of Peterlin after making allowance for a partial melting mechanism.

## CONCLUSIONS

The scattering equation derived using a Zernicke-Prins approach is very similar to that of the random phase approximation in the single phase region defined by the mean field approach, and also with the equation derived from a correlation network model. The SANS data of PED/PE blends were interpreted using the Zernicke-Prins type formula and the results can be summarized as follows:

(1) The degree of segregation remained unchanged until the annealing temperature approached the melting point, thereafter the extent of segregation was significantly enhanced.

(2) An enhancement in segregation can be characterized as a decrease in the cord length and the volume fraction of PED containing phase.

(3) Plastic deformation tends to lessen the degree of segregation, and the results suggest that a portion of the specimen must undergo a melting and recrystallization process during deformation.

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