

Small-angle neutron scattering by semicrystalline polyethylene

D. Y. Yoon* and P. J. Flory†

(Received 1 October 1976)

The angular dependence of the intensity of neutron scattering by deuterated polyethylene chains (PED) dispersed in the protonated host (PEH) in the semicrystalline state has been computed over the scattering range $0 < \mu < 0.2 \text{ \AA}^{-1}$, where $\mu = (4\pi/\lambda)\sin(\theta/2)$, for various morphologies that differ according to the mode of chain re-entry into the crystalline lamellae. The scattering functions vary strongly with the tendency for adjacent re-entry. The intensity in the range $0.04 < \mu < 0.10 \text{ \AA}^{-1}$ is 30–40% greater for the regularly folded morphology than for the 'switchboard' model. Calculations for the latter approximate the experimental results of Schelten *et al.* Optimum agreement with their scattering intensities, and the chain dimensions and degree of crystallinity as well, is achieved by a statistical model in which the chain preferentially re-enters the crystalline layer with a probability of about 0.7. Re-entry, when it occurs, is not required to be adjacent to the preceding sequence.

INTRODUCTION

The methods of small-angle neutron scattering (SANS), so strikingly successful in characterizing the configurations of polymer chains in the amorphous state, have recently been applied to semicrystalline polyethylene by Schelten *et al.*¹ Special procedures were devised to assure molecular dispersion of the deuterated polyethylene chains (PED) in the protonated (PEH) host. To overcome the tendency of the solute to undergo aggregation during crystallization, occurrence of which appears to have invalidated previous experiments on mixtures of PED and PEH², the samples were rapidly cooled from the melt. That molecular dispersion was achieved by this procedure was attested by determination of the weight-average molecular weight of the PED by extrapolation of the SANS data.

The principal results of Schelten *et al.*¹ may be summarized as follows: (i) the mean-squared radius of gyration $\langle s^2 \rangle$ obtained by extrapolation of the intensity I_θ plotted against the magnitude of the scattering vector, $\mu = (4\pi/\lambda)\sin(\theta/2)$, virtually coincides with the value for the polymer in the amorphous state, or in a Θ -solvent³, and (ii) their Kratky plot of $I\mu^2$ vs. μ at large μ is difficult to reconcile with the form factor for a planar sheet in which the PED chain is regularly folded with adjacent re-entry. The difficulty (ii) is compounded by measurements on PED samples differing in chain length which would require the breadth-to-length ratio of the sheets in which the chains are folded to be independent of chain length. Since the length of the fold is effectively fixed by the matrix (PEH) and, thus, is independent of the chain length of the tagged molecule (PED), the width of the sheet would be required to remain constant as the molecular weight varies. Schelten *et al.*¹ concluded therefore that their results are irreconcilable with a model in which the chains are regularly folded.

Against the contention that the results of Schelten *et al.* are peculiar to rapidly cooled specimens, it should be ob-

served that the thickness of their samples, ~ 1 mm, precluded quenching of the interior of the sample upon subjecting the exterior to ordinary temperature. The exothermal heat of crystallization must have moderated the actual cooling rate considerably. Moreover, small-angle X-ray diffraction revealed presence of the lamellar morphology which has been widely accepted as *prima facie* evidence of regular folding of chains with adjacent re-entry. The lamellar repeat distance was $\sim 250 \text{ \AA}$. According to the investigations of Mandelkern and coworkers^{4,5}, the temperature within the sample during crystallization is reliably indicated to have been in the range 114° – 120°C . We conclude, therefore, that the samples prepared by Schelten and coworkers¹ are representative of melt crystallized polyethylenes having the characteristic lamellar morphology.

In this paper we present calculations of scattering functions for models of semicrystalline polymers in which the arrangement of the molecule is varied between the extremes of regular folding and random ('switchboard')^{6,7} re-entry in the crystalline lamella.

THEORY AND COMPUTATIONAL PROCEDURES

The scattering function $F_x(\mu)$ is defined for chains of $x + 1$ identical units by^{8,9}:

$$F_x(\mu) = (x + 1)\mu^2 P_x(\mu) \quad (1)$$

where $P_x(\mu)$ is the ratio of the intensity scattered at an angle θ to the scattered intensity at $\theta = 0$. It is proportional therefore to the Kratky function $I\mu^2$, where I is the intensity at angle θ . The scattering function thus defined is given by^{8,9}:

$$F_x(\mu) = \mu^2 + 2\mu^2(x + 1)^{-1} \sum_{t=1}^x (x + 1 - t) \left\langle \frac{\sin(\mu r_t)}{\mu r_t} \right\rangle \quad (2)$$

where r_t is the distance between scattering centres separated by t units, and angle brackets denote the statistical mechanical average over all configurations of the chain.

* IBM Research Laboratory, San Jose, California 95193, USA

† Department of Chemistry, Stanford University, Stanford, California 94305, USA

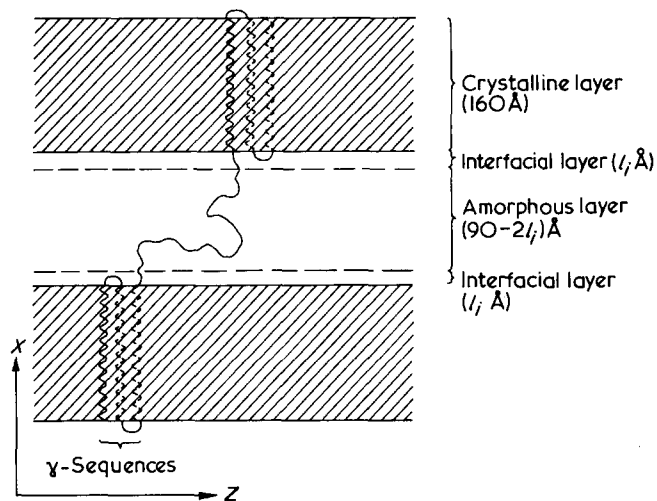


Figure 1 Representation of the lamellar structure of semicrystalline polyethylene. The chain backbone is shown schematically; its carbon atoms occur in XY planes perpendicular to the diagram

In order to simplify the computation, every fifth carbon atom was taken as the point scatterer representing five CD_2 groups. The effect of this simplification is insignificant for $\mu < 0.15 \text{ \AA}^{-1}$, which includes the range of interest. Accordingly, we define x as the number of 'units' consisting of five CD_2 groups; i.e. $x = (n + 1)/5$, where n is the number of skeletal bonds. For polydisperse samples, the weight-average \bar{x}_w is required.

The semicrystalline state was represented by an array of alternating crystalline and non-crystalline layers as in Figure 1. The degree of crystallinity was $\sim 65\%$ according to both X-ray diffraction and density measurements. In view of the layer repeat spacing of $\sim 250 \text{ \AA}$ (see above), we therefore take the thickness of the crystalline and amorphous layers to be 160 and 90 \AA , respectively.

The quantities $\langle (\mu r_t)^{-1} \sin(\mu r_t) \rangle$ in equation (2) were evaluated as the averages over sets of Monte Carlo chains (PED) that pass successively through crystalline and amorphous layers, the paths of the chains at the interface being dependent on the model considered. Monte Carlo chains consisting of 3500 bonds (i.e. $x = 700$ 'units'), corresponding to a molecular weight of 56 000, were generated.

The length of the C-C bond and the supplement of the CCC skeletal bond angle were assigned the values $l = 1.53 \text{ \AA}$ and $\theta = 68^\circ$, respectively. Within the crystalline lamellae all bonds were required to assume the *trans* conformation. Outside the lamellae the chains were allowed to take on the conformations represented by three rotational isomeric states: *trans*, *gauche*⁺, and *gauche*⁻, located at $\phi = 0, 120, -120^\circ$, respectively^{3,10}. The statistical weight matrix used previously for the representation of the polymethylene chain was employed with first and second order statistical weights assigned the values $\sigma = 0.54$ and $\omega = 0.088$, respectively¹⁰. The conformation of each bond outside the lamellae was assigned from computer generated random numbers with ranges apportioned according to conditional probabilities $q_{\xi\eta;i}$ for bond i in state η when bond $i - 1$ is in state ξ ¹¹. These conditional probabilities were calculated from the *a priori* probabilities $p_{\xi\eta;i}$ and $p_{\xi;i-1}$ according to the relation³:

$$q_{\xi\eta;i} = p_{\xi\eta;i} / p_{\xi;i-1} \quad (3)$$

The *a priori* probabilities were evaluated from the statistical weight matrix³.

MODELS AND NUMERICAL RESULTS

A Cartesian coordinate system is adopted with its X -axis along the crystal c -axis perpendicular to the plane of the lamella, and the Y -axis in the CCC plane; the Z -axis perpendicular to this plane completes a right-handed Cartesian system. In all the models considered here the crystalline sequences for a given $-(CD_2)_n$ -chain occur in parallel XY planes, successive planes being displaced by 5 \AA (see below).

Adjacent re-entry models

We start with an all *trans* crystal sequence that passes through a crystalline layer 160 \AA in thickness. This requires 126 bonds. For the first series of models, the chain re-enters the same lamella at adjacent sites consecutively γ times. The location of the re-entry site is separated by 5 \AA in the positive Z -direction from the emerging site of the preceding crystalline sequence. After γ consecutive passes through the same lamella in this manner, the chain enters the non-crystalline layer. In this layer the chain assumes the conformations assigned by the Monte Carlo procedure described above until it reaches either the upper lamella or the lower one. At the point of this contact the chain adopts the all-*trans* conformation with its backbone in the XY plane and its axis of propagation normal to the lamellar surface. After traversing the lamella, the chain re-enters at the adjacent site, etc. until another set of γ sequences is generated, whereupon the chain again enters the amorphous layer. This process is repeated until the 3500 skeletal bonds of the chain are exhausted.

The values of $(\mu r_t)^{-1} \sin(\mu r_t)$ were computed for sequences of t units at ten different, randomly selected locations within each Monte Carlo chain. Averages over 100 Monte Carlo chains for each value of t up to $t = 500$ (2500 bonds) were taken in order to compute the scattering function $F_x(\mu)$ according to equation (2). This function $F_x(\mu)$ was multiplied by 5 to yield the scattering function $F_n(\mu)$ for chains consisting of $n + 1$ CD_2 units defined by⁸:

$$F_n(\mu) = (n + 1)\mu^2 P_n(\mu) \quad (4)$$

Scattering functions $F_n(\mu)$ thus evaluated for chains of $n = 2500$ bonds* are presented in Figure 2 for numbers γ of consecutive crystalline sequences equal to 1, 3, 5, 7 and 28. For even numbers, $\gamma = 2, 4$, etc., the entire chain is contained within the domain of two lamellae and the non-crystalline region between them. These cases were not considered, with the exception of $\gamma = 28$ where the entire molecule is committed to a single succession of crystalline sequences. For the case $\gamma = 1$, in which adjacent re-entry is excluded, the scattering function $F_n(\mu)$ in the range $\mu > 0.06 \text{ \AA}^{-1}$ is slightly lower than for the experimental curve, also shown in the same Figure. On the other hand, for $\gamma = 3$ adjacent crystalline sequences it is higher by 30–40% than for the experimental curve. As the number γ of adjacent crystalline sequences is increased to higher values, the scattering function increases further for $\mu < 0.06 \text{ \AA}^{-1}$. It shows a maximum near $\mu = \sim 0.04 \text{ \AA}^{-1}$ for $\gamma > 5$, but beyond $\mu = 0.06 \text{ \AA}^{-1}$ it is little changed from the curve for $\gamma = 3$.

The mean-squared radii of gyration (s^2) were evaluated from the same Monte Carlo chains that were generated to compute the scattering functions. The characteristic ratios C_n calculated from (s^2) by the relationship:

* The choice of $n = 2500$ is arbitrary over the range of μ of interest. $F_n(\mu)$ is independent of n for $n \geq 2000$.

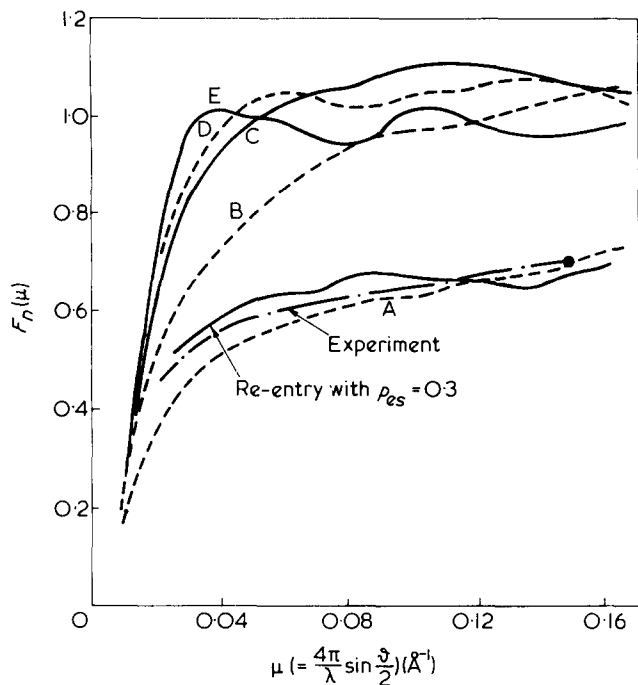


Figure 2 The scattering functions $F_n(\mu)$ for PED chains of 2500 bonds dispersed in the semicrystalline PEH matrix. Curves were computed for the adjacent re-entry model with curves A, B, C, D and E calculated, respectively, for $\gamma = 1, 3, 5, 7$ and 28 consecutive sequences traversing the crystalline lamella. The experimental curve is from Schelten *et al.*¹. The curve labelled ' $p_{es} = 0.3$ ' is for the irregular re-entry model, taken from Figure 4

$$C_n = \frac{5\langle s^2 \rangle}{nl^2} \quad (5)$$

for $n = 1500, 2500$ and 3500 are given in Table 1 for $\gamma = 1, 3, 5$ and 28. The average fraction f_c of units located in the crystalline layer are also given in Table 1.

The average length of the amorphous sequence leading from one succession of γ crystalline sequences to the next comprises 130 ± 20 bonds, as may be deduced from the data in Table 1. For $\gamma > 1$, the deuterated chain tends to confine itself to an average of about three crystalline lamellae. In those instances where the amorphous sequence re-enters the crystal lamella from which it emerged, the mean displacement between points of exit and of re-entry should be $\sim 30 \text{ \AA}$, which is much beyond the displacement for adjacent re-entry.

According to the calculations presented in Figure 2 and Table 1, this model with $\gamma = 1$ gives a scattering curve close to that observed, a characteristic ratio that is too large and a degree of crystallinity that is too low. For $\gamma = 3$, the calculated characteristic ratio and degree of crystallinity are acceptable, but the scattering function is incompatible with experiment.

These models are deficient in failing to take into account the attrition in the flux of chains passing from the crystal face to the amorphous zone, this being an inevitable consequence of the spatial requirements of the random chains, as previously discussed⁷. The following models afford a better representation in this respect.

Irregular re-entry models

In the second series of models, the non-crystalline layer was further divided into a central amorphous layer and two interfacial layers. The latter were assigned thicknesses $l_i = 5, 10$ and 15 \AA , the thickness of the amorphous central

layer being $90 \text{ \AA} - 2 l_i$. In these models *immediate* re-entry is disallowed after each traversal of the crystalline layer, the chain being required to enter the interfacial layer. A fraction p_{es} of the chains reaching the boundary between the amorphous and the interfacial zones escape into the amorphous layer; the remaining chains are forced to assume conformations that do not cross this boundary. This increases the number of chains that re-enter the crystalline lamella without entering the amorphous layer, but *the sites of re-entry are not specified*. For the chains that reach the boundary of either interfacial zone from the amorphous layer, the probability p_{en} of entry upon contact at the interfacial zone was assigned the value $1 - p_{es}$.

The scattering functions $F_n(\mu)$ were first calculated for $l_i = 5 \text{ \AA}$ following the procedure described above. Values of $\langle (\mu r_t)^{-1} \sin(\mu r_t) \rangle$ were taken as averages over ten different locations of sequences of t units within each of 100 Monte Carlo chains (3500 bonds) with $t = 1 - 500$. Escape probabilities $p_{es} = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were chosen. Results of these calculations are shown in Figure 3. For $p_{es} < 0.2$, the scattering functions show maxima at $\mu \approx 0.06 \text{ \AA}^{-1}$. These maxima are broader than the one for $\gamma = 28$ (adjacent re-entry) in Figure 2. For $p_{es} > 0.2$, the scattering functions increase monotonically and level off beyond $\mu > \sim 0.05 \text{ \AA}^{-1}$.

Table 1 Characteristic ratios C_n and fractions f_c of the chain in crystalline layers for adjacent re-entry models

γ	C_n			f_c
	$n = 1500$	$n = 2500$	$n = 3500$	
1	15.4	14.9	13.7	0.48
3	9.3	8.6	7.6	0.72
5	6.3	5.4	4.6	0.85
28			2.7	1.00

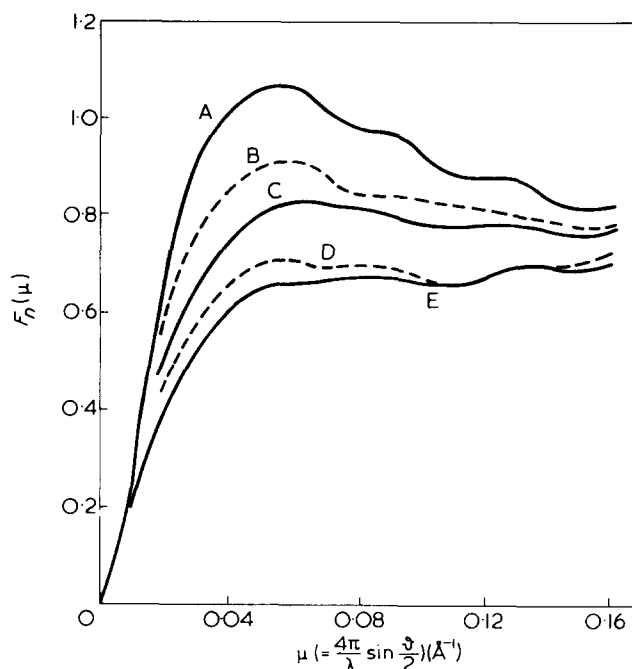


Figure 3 The scattering functions $F_n(\mu)$ for PED chains of 2500 bonds dispersed in the semicrystalline PEH matrix, computed for the irregular re-entry model with interfacial zones 5 \AA in thickness. Values chosen for the probability p_{es} of escape into the amorphous layer upon contact from the interfacial zone are 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 for curves A, B, C, D and E, respectively

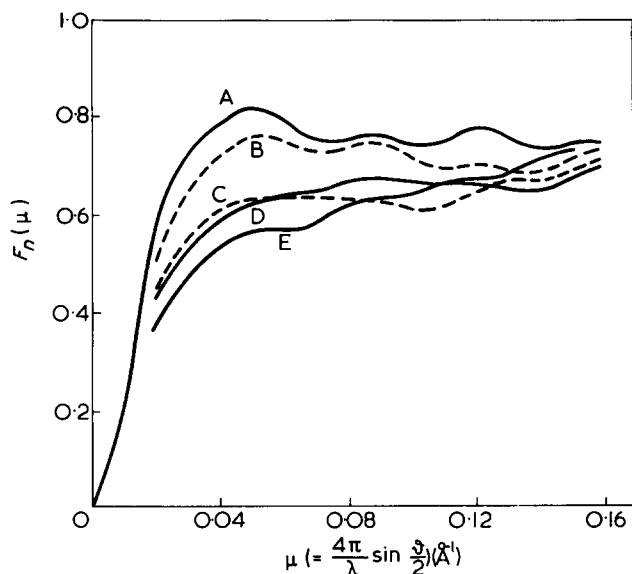


Figure 4 The scattering functions $F_n(\mu)$ for PED chains of 2500 bonds computed for the irregular re-entry model with interfacial zones of 10 Å thickness; see legend to Figure 3. p_{es} values: A, 0.0; B, 0.1; C, 0.2; D, 0.3; E, 0.4

Calculations similarly carried out for $l_i = 10$ Å are shown in Figure 4. These scattering functions are less dependent on the escape probability than those in Figure 3. When the average separation of the site of chain re-entry from the site of emergence is increased further by taking $l_i = 15$ Å, the scattering functions (not shown) converge to that for $\gamma = 1$ in Figure 2, regardless of the value of p_{es} . The dependences of the scattering functions on the thickness of the interfacial layer are most significant for $p_{es} < 0.2$. For $p_{es} > 0.2$, they become negligible.

The corresponding characteristic ratios C_n computed according to equation (5) from the mean-squared radii of gyration, and the fractions f_c , f_i and f_a of the units in the crystalline, interfacial and amorphous layers, respectively, are shown in Table 2 for $l_i = 5$ and 10 Å.

The results obtained by Schelten *et al.*¹ are represented by the dash-dot curve in Figure 2. Their relative intensity scale was converted to $F_n(\mu)$ by normalizing to the experimental point at $\mu = 0.15$ Å⁻¹ (●, Figure 2), which was computed from the experimental value of $\langle s^2 \rangle_w \mu^2 P_n(\mu)$ (at $\mu = 0.15$) = 2.4 together with $\langle s^2 \rangle_w^{1/2} / \bar{M}_w^{1/2} = 0.46$ ¹. The experimental curve is matched closely over the range $0.02 < \mu < 0.15$ Å⁻¹ by the one calculated for the irregular re-entry model with $p_{es} = 0.3$ and $l_i = 10$ Å, also shown in Figure 2. The characteristic ratio $C_n \approx 9.1$ and the degree of crystallinity $X_c \approx 0.66$ (obtained from $f_c + \frac{1}{2}f_i$ in Table 2) calculated for this model agree satisfactorily with the experimental values of $C_n \approx 8.7$ and $X_c \approx 0.65$ ¹.

DISCUSSION

No attempt was made to adjust the approximate models used for the calculations presented above so that they would conform quantitatively to the crystal structure and chain conformation in melt crystallized, semicrystalline polyethylene. That precise duplication in detail is not required will be apparent from the fact that the scattering function depends on the distribution of distances, or correlations, within the range determined by the value of μ . For $\mu = 0.1$, distances less than ~ 30 Å are decisive; for $\mu = 0.04$ the range extends to ~ 75 Å. Regular folding clearly augments the

numbers of pairs of units at distances less than the fold length. Increases in the scattering function calculated for the models of the first kind with increase in γ (see Figure 2) are readily comprehended on this basis. Because of the average length of the amorphous sequence between two sets of γ passages through the layer, these sets, even if they occur in the same lamella, will generally be separated from one another by distances commensurate with those quoted. Hence, pairs of units in different sets of crystalline sequences contribute little to the scattering function.

In models of the second kind, a chain that does not escape from the interfacial layer frequently will return to the crystal at a site near the one from which it emerged, although not necessarily adjacent to it. The average displacement for chains thus 'reflected' increase with the thickness of the interfacial layer. For thicknesses l_i of 5 and 10 Å, the effect of such return on the scattering function may resemble that of adjacent re-entry. The scattering function must fail to discriminate between the adjacent re-entry dictated by the regularly folded model and re-entry at a nearby site as the irregular re-entry models require for chains that do not escape from the interfacial layer. Those chains that enter the amorphous zone from this layer rarely re-enter the crystal near their point of departure, and hence do not enhance the sum in equation (2). The comparison of model calculations to observations clearly shows that neither adjacent nor nearby re-entry is the overwhelmingly predominant mode. Of the emergent chains a large fraction re-enter at sites well removed from the site of emergence. The neutron scattering results of Schelten *et al.*¹ cannot otherwise be explained.

It is noteworthy that the value $p_{es} = 0.30$ found to give best agreement with experiment is consistent with the previous estimate of the attrition of the flux of chains emanating from a crystalline lamella in polyethylene⁷. The adoption of a discrete thickness for the interfacial zone is an artifice introduced for convenience in carrying out the present calculations; it has no precedent in the earlier discussion of molecular morphology in semicrystalline polymers⁷.

The absence of a significant alteration of the measured average radius of gyration upon crystallization implies that crystallization is too rapid to allow relaxation of the mole-

Table 2 Characteristic ratios C_n and fractions of the chain in crystalline (f_c), interfacial (f_i) and amorphous (f_a) layers for irregular re-entry models

p_{es}	C_n			f_c	f_i	f_a
	$n = 1500$	$n = 2500$	$n = 3500$			
$l_i = 5$ Å						
0.0	5.4	3.6	2.7	0.85	0.14	0.01
0.1	7.1	5.9	5.5	0.76	0.13	0.11
0.2	9.8	8.6	7.9	0.67	0.11	0.22
0.3	10.9	9.6	9.2	0.59	0.09	0.31
0.4	11.8	11.3	10.8	0.54	0.08	0.37
0.5	12.8	12.1	11.1	0.46	0.07	0.47
$l_i = 10$ Å						
0.0	7.0	5.0	3.9	0.75	0.23	0.02
0.1	9.3	7.1	6.1	0.69	0.20	0.11
0.2	12.4	10.5	9.2	0.62	0.18	0.20
0.3	11.1	10.0	9.1	0.57	0.17	0.26
0.4	13.8	12.9	12.6	0.49	0.15	0.36

cule as a whole during its incorporation in the lamellae. The stochastic models here employed do not take this constraint into account. Their deficiency in this respect should be inconsequential except insofar as the calculated characteristic ratios fail to reflect this circumstance. For this reason, the computed characteristic ratios should not be given undue weight.

CONCLUSIONS

Our analysis of the scattering functions for various models of the molecular arrangement in a semicrystalline polymer formed from the melt confirms the conclusions reached by Schelten *et al.*¹ that the results of their carefully executed investigations of small-angle neutron scattering by samples of PED dispersed in a PEH host are incompatible with the regularly folded morphology that has gained widespread acceptance. Their results are consistent with models in which a major fraction of the chains emanating from a crystalline layer escape therefrom instead of re-entering the layer at the adjacent lattice site. The molecular arrangement of those chains that re-enter the crystal from the interfacial region is reminiscent of the 'switchboard' model^{6,7}.

The results of SANS on polyethylene corroborate the large body of evidence gathered and evaluated by Mandel-

kern and coworkers¹², showing the regularly folded model to be untenable for bulk crystallized polymers.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation, Grant No. DMR-73-07655 A02.

REFERENCES

- 1 Schelten, J., Ballard, D. G. H., Wignall, G. D., Longman, G. W. and Schmatz, W. *Polymer* 1976, **17**, 751
- 2 Schelten, J., Wignall, G. D. and Ballard, D. G. H. *Polymer* 1974, **15**, 682
- 3 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
- 4 Mandelkern, L., Posner, A. S., Diorio, A. F. and Roberts, D. E. *J. Appl. Phys.* 1961, **32**, 1509
- 5 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964, p 297
- 6 Fischer, E. W. and Schmidt, G. *Angew. Chem.* 1962, **74**, 551
- 7 Flory, P. J. *J. Am. Chem. Soc.* 1962, **84**, 2857
- 8 Fujiwara, Y. and Flory, P. J. *Macromolecules* 1970, **3**, 288
- 9 Yoon, D. Y. and Flory, P. J. *Polymer* 1975, **16**, 645
- 10 Abe, A., Jernigan, R. L. and Flory, P. J. *J. Am. Chem. Soc.* 1966, **88**, 631
- 11 Yoon, D. Y. and Flory, P. J. *J. Chem. Phys.* 1974, **61**, 5366
- 12 Mandelkern, L. *Prog. Polym. Sci.* 1970, **2**, 165; *J. Polym. Sci. (C)* 1975, **50**, 457; *Acc. Chem. Res.* 1976, **9**, 8