

polymer papers

A neutron scattering study of slowly crystallized bulk polyethylene

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(Received 17 November 1983)

Neutron scattering measurements on polyethylene slowly crystallized from the melt give similar results, in the q range $0.1\text{--}0.4\text{ \AA}^{-1}$, to melt-quenched material. This indicates a similar type of folding, at least as concerns structure on a scale of about 10 \AA . It is anticipated that some degree of demixing of isotope species will have occurred during these experiments; this has been minimized by a light crosslinking procedure. Several arguments are advanced to suggest that in this q range any demixing does not affect the scattering: in particular the normalized intensities are independent of the isotope concentration. The samples have been extensively characterized to assess the effects of slow crystallization (as opposed to quenching) and crosslinking, both separately and in combination. Slowly crystallized samples are similar whether crosslinked previously or not, the principal difference being changes in the way different lamellae stack together. In both cases the morphology is completely different from that of quenched material, as indicated by much larger lamellar thicknesses. Hence, in these experiments there is enough molecular mobility for stems (chain traverses of lamellae) to be much longer than in the case of quenching; the fold type (as assessed by stem separation) is however, similar to the quench case. This conclusion is discussed in the light of a new proposal for equilibrium roughness on the crystal growth surfaces.

(Keywords: neutron scattering; folding; adjacency; polyethylene; slow crystallization)

INTRODUCTION

Neutron scattering of isotopic blends has enabled conformations in polymer crystal lamellae to be studied in more detail than was previously possible. Several reviews exist¹⁻³, so that only a short summary will be given here for melt grown crystals of polyethylene.

In contrast to solution grown crystals⁴, values of radii of gyration (R_g) for crystals grown by quenching from the melt are very similar to those for the melt⁵. There have been extensive discussions of the local conformation in these crystals. In spite of a divergence in nomenclature, there appears now to be a consensus that there are groups of stems (these are the chain sequences traversing the lamellae) that are separated by small multiples of the nearest neighbour separation between stems⁶⁻¹⁰. Several models also have in common that each group ('subunit') consists of a straight row of stems. Although this is not highly 'adjacently re-entrant' folding, neither is it 'random'. 'Nearby re-entrant' is probably the best description. Joining the subunits there are long random loops which may involve the molecule going from one lamella to another.

The interpretation of these models has tended to turn on the speed of crystallization: in one way or another the molecules have been thought of as being 'trapped' by the quenching process. A new approach to polymer crystallization¹¹ has been based on the possibility that for high temperatures of crystallization (as for nearly all crystal growth from the melt) the crystal growth surface has a roughness of an equilibrium type. This idea would imply that there is another reason for lack of highly adjacent folding: re-entrant corners will be fairly plentiful, leading to the same molecule attaching at several points along the growth face independently.

Slow crystallization and demixing

The reason for this type of experiment not being usual is that the isotopic blends give scattering at very low q (below about \AA^{-1}) additional to that expected for random mixtures of the isotopic species^{5,12}, and the scattering is in this sense 'anomalous'. It is generally accepted that in these cases the centres of gravity of the two isotopic species are not distributed at random and that there are intermolecular terms in the scattering (a more detailed discussion is given in ref. 3). Under these conditions it cannot be assumed *a priori* that neutron scattering experiments would be interpretable. However, it has been established⁵ that intensities at 'large' q (e.g. $q > 0.1\text{ \AA}^{-1}$) are the same independently of whether the low q anomaly is present (at least to a moderate degree). It is also possible to minimize the anomaly by lightly crosslinking in the quenched state prior to slow crystallization¹². Our approach has been to make use of the crosslinking technique and to see if self-consistent results can be obtained at large q (up to 0.4 \AA^{-1}) for slow crystallization. The principal test of consistency¹² is the coincidence of the normalized scattering for different isotope concentrations. If any anomalies, from whatever origin, existed in this q range, their dependence on concentration would almost certainly not be the same as for the desired signal. The interpretation in the case of a favourable outcome is that on a local scale the isotopic mixing is fairly random. Although some demixing of isotopes ('fractionation' or 'clustering') is probably present, the mixing is probably much nearer to random than it is to complete phase segregation. The small angle anomaly was not measured directly since the majority isotope was deuterium, where the coherent scattering background is very high, so parallel results for samples with hydrogen as the majority isotope

are invoked in the interpretation.

In using crosslinking we have unfortunately introduced a source of uncertainty since this itself may affect the conformations. This is discussed in the following section.

Influence of crosslinking

Extensive work has been carried out (e.g. refs. 14 and 15) on the effects of irradiation, especially on the properties of the material which involve molecular motion (melting, recrystallization). One principal conclusion is clear: the polymer retains a substantial ability for molecular reorganization in spite of constraints imposed by cross linking. In particular, in experiments involving melting and recrystallization, the lamellar thickness is not restricted to the values existing in the state in which the sample was crosslinked¹⁶; this is further borne out in our present experiments. Melting properties are influenced, but since the direction of change depends on the morphology at the time of crosslinking¹⁵, subtle effects concerned with chain motion are likely to be the cause. Density is also affected, as is to be expected since high crystallinities will be less easily attained.

Since the implications of our results depend on whether crosslinking is fundamentally influencing molecular conformation, a full range of techniques has been used on the samples used for these measurements.

As will be discussed below, there is no positive evidence that the effects of crosslinking extend beyond the arrangement of crystallites (on a scale of 1000 Å) and the limitations on crystallinity.

Sample preparation

Blends of 3–10% of hydrogenous polyethylene (PE) fractionated by gel permeation chromatography or liquid–liquid separation were made with unfractionated deuterated polymer (PED) by boiling in xylene. Crystallization was then, by pouring into thin walled tubes, held at room temperature. The crystals were filtered, washed in acetone, and dried, giving a granular consistency. These were then melted and quenched into water at room temperature. Apart from control samples, the sheets were sealed in vacuum and irradiated by ⁶⁰Co radiation to 50MRad (by Dr Fydeler of the Royal Military College, Shrivenham). Still in vacuum, the sheets were melted at 160°C, and cooled relatively quickly to 135°C. They were then cooled by 1°C per day to about 120°C. Isothermal crystallization was not attempted since, if crystallization were to be slow, a substantial fraction of polymer would remain molten at the crystallization temperature. For comparison, unirradiated samples were made in 3 ways: (a) by cooling at 1°C per day; (b) by cooling at 10°C per minute; and (c) by quenching from the melt into water.

Sample characterization

D.s.c. A Perkin Elmer DSC2 calorimeter was used to obtain melting endotherms. A heating rate of 2.5°C per minute was employed. Samples were cooled at 40°C per minute after melting and the heating cycle was repeated.

D.s.c. traces for samples with and without radiation treatment before crystallization on cooling at 1°C/day are shown in *Figure 1*. Corresponding curves obtained after cooling at 40°C/minute appear in *Figure 2*. Heats of fusion were calculated using an Indium sample for calibration and sample crystallinities by using a value of 67.14 cal g⁻¹ for the crystal heat of fusion¹⁷. The results are sum-

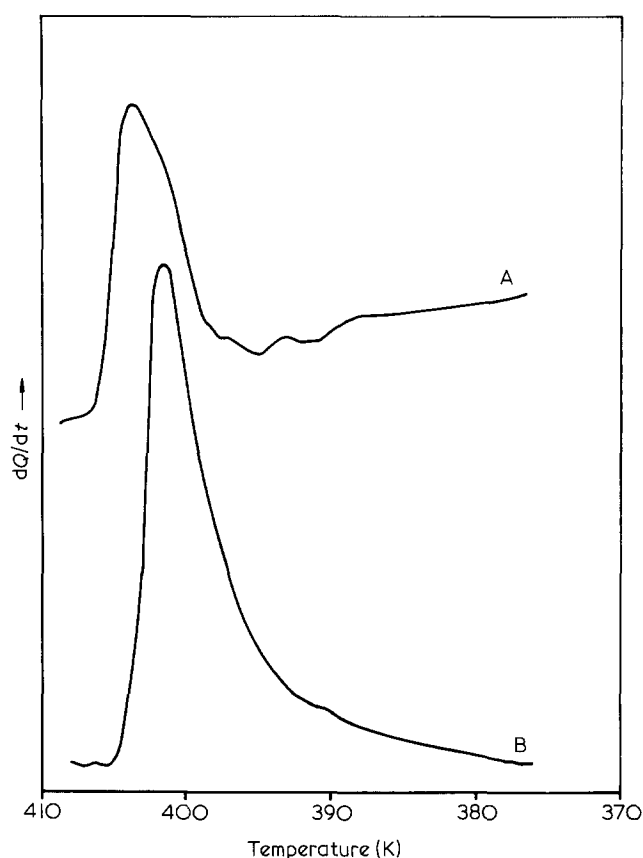


Figure 1 D.s.c. traces for an unirradiated PED sample (A) and an irradiated sample containing 10% PEH (B). Both were crystallized by slow cooling (1°C/day). The curves are displaced vertically for clarity, with an arbitrary vertical scale

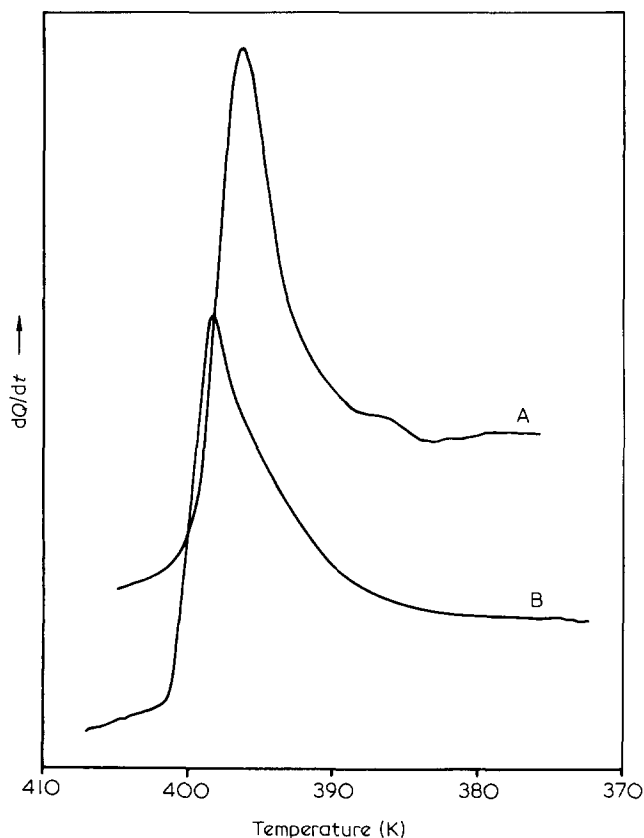
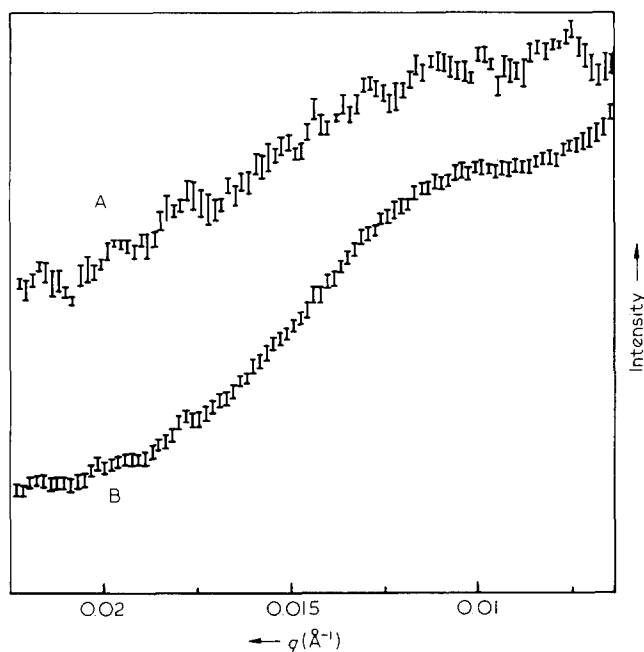


Figure 2 D.s.c. traces for the same samples as in *Figure 1*, after melting in d.s.c. (*Figure 1*) and cooling. The curves are again displaced vertically

Table 1 D.s.c. results from Figures 1 and 2

	Initial d.s.c. run		Second d.s.c. run	
	Melting peak position (K)	Crystallinity (%)	Melting peak position (K)	Crystallinity (%)
Irradiated 10% PEH sample	402	68.5	398.5	56
Unirradiated PED sample	403.5	69	396	62

**Figure 3** Small-angle X-ray scattering curves for irradiated (A) and unirradiated (B) samples of PED, crystallized by slow cooling. The curves are displaced vertically, with arbitrary intensity scale

marized in Table 1, and indicate close similarities in both peak positions and crystallinities, irrespective of radiation treatment. It is noted that the initial crystallinities for PED or PED matrix samples are considerably lower than a typical figure of $\sim 85\%$ for PEH crystallized under the same conditions. The reason for this difference is currently being investigated. The reduction in melting points on recrystallization was anticipated¹⁵, although the small change in the initial peak position on irradiation is in the opposite direction to that previously reported¹⁵. This may be partially due to the small difference in isotopic content in the samples, but is likely to be primarily influenced by the exact crystallization conditions: these were earlier shown to affect the direction of change¹⁵. The position of melting peak on the second heating cycle is lower for the unirradiated sample, although the crystallinities for the two samples are in the opposite order to that predicted from melting temperatures. Again, this may be partly due to an isotope effect.

X-ray diffraction. Small-angle X-ray diffraction patterns were obtained using the small angle scattering facility at the S.R.S. (Daresbury). A sample-detector distance of 220 cm was used, with a wavelength of 1.608 Å. With photographic detection, exposure times of about 1 min were adequate. Films were scanned using an

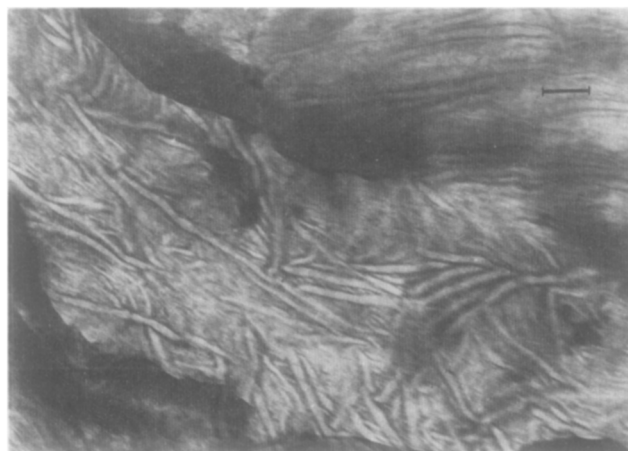
Optronics P1000 microdensitometer with a raster size of 100 μm . After locating the centre of the diffraction patterns, the intensities were averaged across a vertical strip of width 500 μm , passing through the centre. An empty cell run of the same duration as the sample runs was found to give intensities negligible in comparison.

Data for two PED samples crystallized by cooling at 1°/minute from the melt, both with and without prior irradiation, are illustrated in Figure 3. Each pattern shows a broad feature at small scattering vectors, although the inflexion (around 600 Å equivalent spacing) in the case of the unirradiated sample is more clearly defined. In the region of $q = 0.01 \text{ \AA}^{-1}$, the absolute intensity for the unirradiated sample (curve B) is approximately 50% larger than for the irradiated sample, whereas at the largest q values the intensities are similar.

Electron microscopy. Transmission electron microscopy was carried out on samples prepared using the technique of Kanig¹⁸. Samples were left in chlorosulphonic acid at room temperature for 6 days. After thorough washing with acetone and distilled water, sections were cut using an ultramicrotome with a diamond knife. The sections were left for half an hour in a 0.7% aqueous solution of uranyl acetate. These were washed with distilled water and dried before viewing in the electron microscope.

Representative electron micrographs for PED crystallized by cooling at 1°C per day are shown in Figures 4 and 5 for samples with and without prior irradiation. The bright cores of lamellae are bordered by dark boundaries in the unirradiated sample (Figure 5), which also shows longer continuous lamellae. The stacking may be responsible for the clearer small angle X-ray peak in the case of unirradiated material (Figure 3).

To summarize the results of sample characterization, the samples crystallized following irradiation show a more disorganized arrangement of lamellae, which broadens the X-ray diffraction peaks. However, the morphology is clearly closer to that of samples crystallized by slow cooling without irradiation than to samples quenched from the melt. In the latter case, X-ray small-angle peaks and Raman LA modes are sharper and more clearly defined, giving spacings of typically 250 Å for PED, the exact value depending on the effective crystallization temperature. These spacings should be compared with a figure of at least 600 Å for irradiated slowly crystallized

**Figure 4** Electron micrograph of a stained section of irradiated PED, crystallized by slow cooling. Scale bar represents 0.1 μm

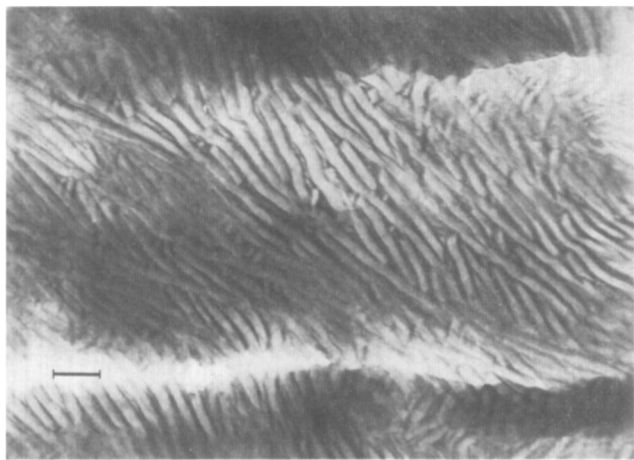


Figure 5 Electron micrograph of a stained section of unirradiated PED, crystallized by slow cooling. Scale bar represents 0.1 μm

material (see Electron microscopy section above). This confirms that the crosslinking, although reducing the large scale chain mobility, does not preserve the chain configurations characteristic of the melt quenched crystals.

Neutron scattering measurements

Samples were mounted in aluminium holders with 7×20 mm apertures, and with aluminium foil holding them in place. Cadmium on the sample support shielded the aluminium holders to within 1 mm of the samples. The D17 instrument at I.L.L. (Grenoble) was used for these measurements in the intermediate angle range ($0.4 \geq q \geq 0.1 \text{ \AA}^{-1}$). Count rate measurements were made on the blends, pure PED, pure PEH of several different thicknesses, an empty holder and a holder containing cadmium. The sensitivities of the counters in the detector were normalized using a run with thick PEH (nearly all incoherent scattering). Radial regrouping of the count rates from different cells¹⁹ resulted in sets of intensity *versus* q data. Prior to the operations to be described in the next section, intensities from an empty cell were subtracted from sample intensities, with allowance for the attenuation of the incident beam by the specimen.

Methods of analysis

The basic theory is given elsewhere. A brief description of the results is given here, following the formalism in ref. 3.

Each hydrogen atom in the blend may be allocated a scattering length, b_i , which is the average over both isotopes in the blend ($\langle b \rangle$), modified by the addition of a positive contribution (in the case of deuterium atoms) or a negative contribution (for hydrogen atoms):

$$b_i = \langle b \rangle + \delta b_i$$

The contribution from $\langle b \rangle$ will lead to a coherent background, $|A_0(q, \langle b \rangle)|^2$ (similar in nature to that for X-ray scattering). The terms δb_i will result in a signal related to the molecular form factor, $P(q)$, with, in the ideal case, no contributions from intermolecular interference. The results for the coherent differential cross-section is:

$$|A(q)|^2 = |A_0(q, \langle b \rangle)|^2 + \sum_i \delta b_i^2 (n^2 (P_i(q)) N_i) \quad (1)$$

where n is the number of hydrogen atoms per molecule and N_i is the number of molecules of isotope i .

The subtraction procedures are in two stages: firstly the removal of incoherent scattering from the data and then the subtraction of the term $|A_0(q, \langle b \rangle)|^2$ in equation (1). Finally, checks are made that the difference intensity goes to zero at high q values beyond the ones used to calculate $nP(q)$. $I(q) = nP(q)$ (primarily for PEH molecules).

Because of multiple scattering, incoherent scattering does not increase linearly with the thickness of PEH. The dependence was measured experimentally and the PEH spectrum used for incoherent scattering subtraction was chosen to give about the same incoherent scattering.

The coherent diffuse background (the first term in equation (1)) is assumed to depend on the square of the average scattering length density of the polymer, the density being proportional to the fraction of PED in the sample blend. A scaling factor derived in this way was applied to the signal from the PED specimen in order to subtract the coherent diffuse contribution from the sample. In order to make the remaining difference intensity go to zero at $q > 1.5 \text{ \AA}^{-1}$ ²⁰ the scaling factor was adjusted finally to 0.55 for a PEH proportion of 0.1. This adjustment should improve the precision of the subtractions, though in practice it does not materially affect the results in this case.

As in previous work²⁰, the data are presented in terms of $I_c(q)$, where $I_c(q) = I(q)/C(q)$ and $C(q)$ is the calculated ratio of scattering from a real stem to the scattering from an infinitely thin stem. A convenient way of representing the data then involves plotting $I_c(q)q^2$ against q . An arrangement of isolated stems would produce a straight line plot passing through the origin.

RESULTS AND DISCUSSION

Neutron scattering results are shown in *Figures 6 to 9*. *Figure 6* shows the concentration dependence of scattering for irradiated samples recrystallized by slow cooling. As was mentioned in the introduction, the independence of the normalized signal on concentration (as in *Figures 6–11*) is strong evidence that the isotope mixing is random enough for there to be no significant anomalies in this q

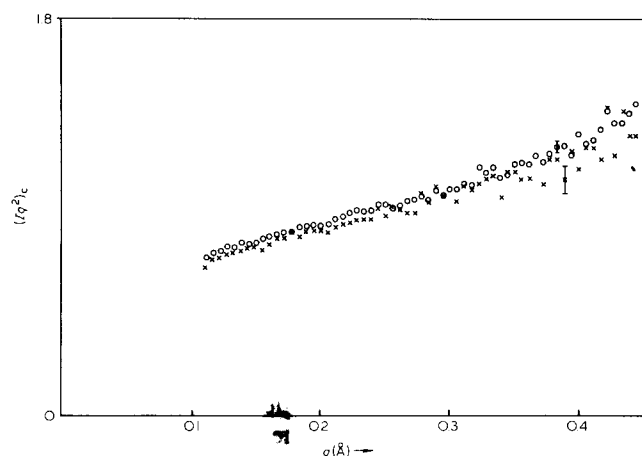


Figure 6 Example of the concentration dependence of the intermediate angle neutron scattering (IANS) from polyethylene slow cooled after irradiation. Guest PEH ($M_w = 28600$) 5% (x) and 10% (O). Neutron wavelength (λ) = 8.0 \AA

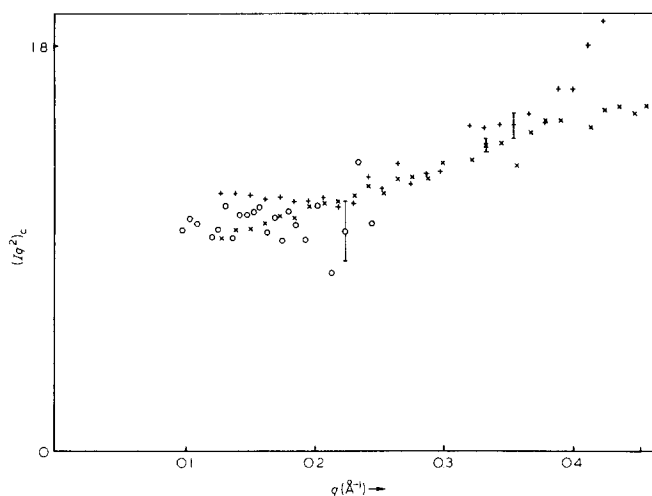


Figure 7 IANS data for 3% PEH samples ($\bar{M}_w = 224\,000$) quenched from the melt (O) crystallized on cooling at $1^\circ/\text{minute}$ (+) and crystallized on cooling at $1^\circ/\text{day}$ (x). Only the last sample has received prior irradiation. Typical long spacings for samples of types (O) and (x) are 250 and 600 Å respectively. $\lambda = 7.8$ Å (+ and x); 7.9 Å (O)

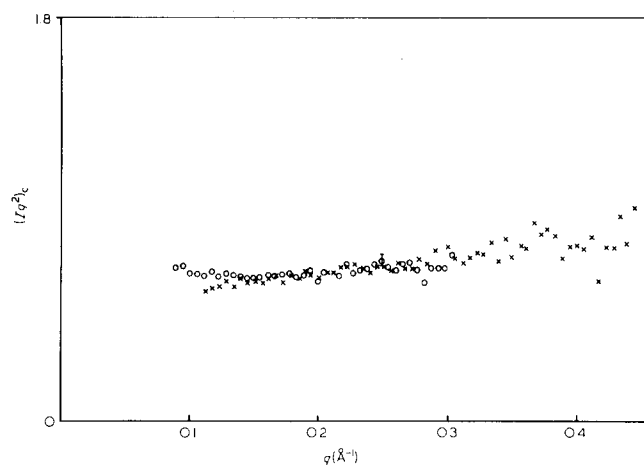


Figure 8 IANS data for 5% PEH crystallized on cooling at $1^\circ/\text{day}$ after irradiation (x) and 10% PEH quenched from the melt without irradiation (O). $\bar{M}_w = 50\,000$, $\lambda = 8.0$ Å (x); 8.2 Å (O)

range. It seems reasonable to proceed to treat the data in *Figures 6–11* as representative of the molecular form factor, enabling crystal stem arrangements to be studied.

The small q anomaly almost certainly involves intermolecular contributions to the scattering, and it is very unlikely that the molecular form factor and the anomaly should scale with isotope concentration in the same way, even if in some sense the origin of the anomaly was independent of isotope concentration. (For anomalies to exist in the data in *Figures 6–11*, the 2 signals would have to scale similarly with concentration). The anomaly has been interpreted as the consequence of fractionation^{3,12}, arising from different crystallization rates for the two isotopes. It was found^{12,28} that the degree of fractionation calculated from the small q anomaly was highly variable, and in particular increased with PED concentration. This is further evidence that if anomalies were to exist in the data in *Figures 6–11* they would lead to a significant concentration dependence.

Figures 7, 8 and 9 show comparisons between three sample types: (a) blends irradiated and recrystallized by slow cooling ($1^\circ/\text{day}$); (b) blends not irradiated, but

crystallized by cooling at $10^\circ\text{C}/\text{minute}$; and (c) un-irradiated blends crystallized by quenching from the melt into water at room temperature. For reasons stated earlier, it is preferable not to study with this technique samples prepared by slow cooling ($1^\circ/\text{day}$) without prior irradiation. Samples (b) and (c) correspond to those previously studied⁹, with the chain conformations now determined⁹. Type (b) samples represent an intermediate situation. The scattering curves clearly show close similarities throughout the angular range. Small differences at q values below about 0.2 \AA^{-1} show that the scattering for samples of types (b) and (c) is somewhat larger than for type (a). It should be noted, however, that in no case can the scattering be described by a straight line passing through the origin of these plots. Even at the lowest molecular weights used, there is a small excess of intensity at the smallest angles above that expected from isolated single stems.

In order to extract at least some information from this technique for the interesting conditions of slow crystallization, it has been necessary to concern ourselves with whether anomalies which have been found at small q may also be present in some degree at large q . Irradiation was used for this reason, but any additional complications introduced by the sample irradiation need to be assessed. The results of sample characterization, discussed earlier, are reassuring in this respect. In addition the negative result, namely that the large q scattering depends little if at all on the rate of crystallization, provides further confidence that the experimental results can be analysed in the usual way, without complicating side-effects from the irradiation. Another possibility, that the local stem arrangement is 'locked in' by the irradiation, can be excluded since the lamellar morphology (thickness in particular) changes very substantially in spite of irradiation.

We are drawn towards a model for the stem arrangement in type (a) samples which is very similar to that already proposed for type (b)⁹. In fact, the differences in scattering intensity mentioned above are probably too small to make confident assertions of any significant difference in models. In *Figure 10* we therefore reproduce previous calculations from a model developed to fit scattering data for melt crystallized PE (*Figure 6f* of ref. 9). Also shown is the experimental scattered intensity for a

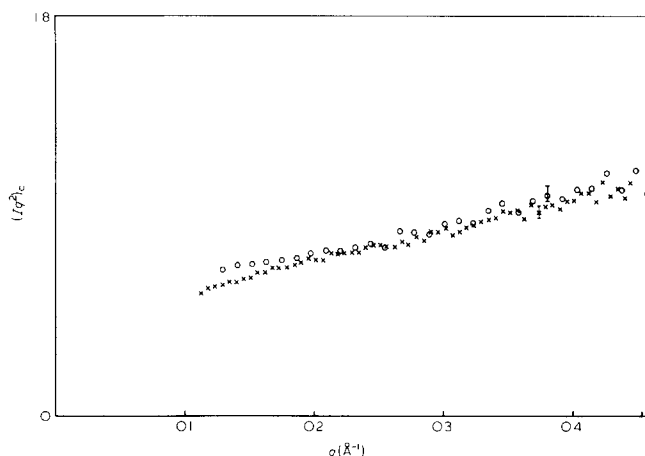


Figure 9 IANS data from 10% PEH, $\bar{M}_w = 15\,000$, crystallized by cooling at $1^\circ/\text{day}$ after irradiation (x) and quenched from the melt without irradiation (O). $\lambda = 8.0$ Å (x); 7.8 Å (O)

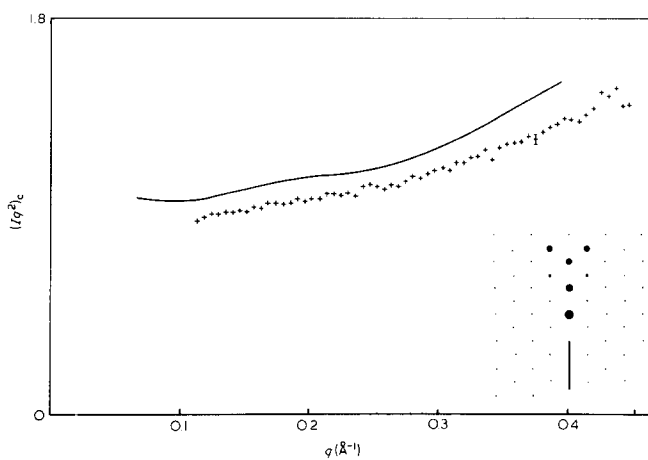


Figure 10 IANS data for a sample of 10% PEH, \bar{M}_w 90000, crystallized on cooling at $1^\circ\text{C}/\text{day}$ after irradiation. Continuous curve represents calculations derived from the model in the lower right hand corner (see Figure 6f of ref. 9). Stem projections in the (001) plane are shown, with the vertical line representing an existing (labelled) stem. The areas of the larger spots indicate the probabilities of successive stems occupying each site. $\lambda = 8.0 \text{ \AA}$

sample irradiated and recrystallized by cooling at $1^\circ\text{C}/\text{day}$ (i.e. type (a)) and with a molecular weight (\bar{M}_w) of 90000. The agreement is good, as is expected from the discussion above.

The molecular model, from which the calculated scattering curve in Figure 10 was derived, is shown schematically in that Figure. In more detail, this model involves a sub-unit of about 4 stems, with a preference for a straight row of stems but quite possibly with an occasional stagger away from the row. The proportion of adjacent folding is below 50%, with a progressive decrease in the probability of longer folds. Over larger dimensions, a three-dimensional Gaussian probability distribution was inferred for the chain conformation⁹. In the present case, the large scale mobility of polymer chains is inhibited by crosslinks and we anticipate that the larger scale conformation is correspondingly modified. The angular range studied here is primarily influenced by the conformation on a local level, and not by the structure on the scale of the radius of gyration. Our use of the model presented in ref. 9 is therefore limited to a description of the local conformation in slowly crystallized samples.

Scattering data for irradiated, slowly crystallized samples (type (a)) are shown in Figure 11 as a function of molecular weight. The level of intensity increases with increasing molecular weight. Two possible explanations for this behaviour are suggested, both involving an increase in the average size of the subunit. Firstly, the proportion of adjacent folding may rise with increasing molecular weight, resulting in a lengthening of the subunit. Secondly, the subunit may start to occupy nearby fold planes. This second possibility has attractions by analogy with the superfolded model proposed for solution grown crystals²⁰. However, in the absence of data over a wider angular range, it is difficult to differentiate between these models.

It may seem very surprising that changing the speed of crystallization by a factor of more than about 10^5 should not have induced modifications to the (local) conformation as tested by neutron scattering. The consensus, forming at the time of the Faraday Discussion (1979) and developing since, is that crystallization rate is certainly

very important, even if there is disagreement as to whether it is overwhelmingly so. A more 'perfect' kind of adjacency of folding was anticipated if more time were to be available: one would have anticipated that 'nearby' re-entry would be replaced by a higher degree of truly adjacent re-entry. (By 'adjacent', we mean folds connecting neighbouring stems, with separations of 4.4 \AA or 4.9 \AA .) This appears not to be the case, even though we must bear in mind the differences between irradiated and unirradiated specimens, which may not be entirely negligible even for local conformations. It should be mentioned that this paper is primarily concerned with testing the importance of crystallization rates for conformations. We are less concerned with crystallinity *per se*, although the slowly crystallized samples do have slightly higher crystallinities than quenched samples (Table 1).

The recent new approach¹¹ places much less reliance on crystallization rate being a crucial factor. Differing degrees of adjacency follow from the different degrees of roughness which may exist on the growth face. A brief summary of the idea will now be given.

Recent theoretical developments concerned with crystal surfaces^{22,23} have predicted a transition from a faceted to a non-faceted (rounded) surface at a temperature T_R . Recent observations on ^4He crystals²⁴ clearly demonstrate the applicability of these ideas. The origin of the transition is a surface disorder, leading to a surface entropy, which can be pictured as a 'crenellation' or roughness involving unmade bonds parallel to the crystal surface. The equilibrium surface roughness increases fairly steeply with temperature above $T \approx 0.6 T_R$, but does not increase abruptly as in the case of the melting of a (three dimensional) crystal. Although the connectedness along the polymer chain is no doubt important, calculations of the type developed for crystals of atoms²² give an idea of the roughness and the number of re-entrant corners (Figure 12). The first stage in the application of these ideas to polymer crystals¹¹ started with the recognition that a crystal face which is rounded on the scale of electron microscopy cannot be smooth on a molecular scale. It was then shown that the range of crystal morphologies observed in polyethylene is consistent with T_R at about 383 K (110°C). At this stage it seems

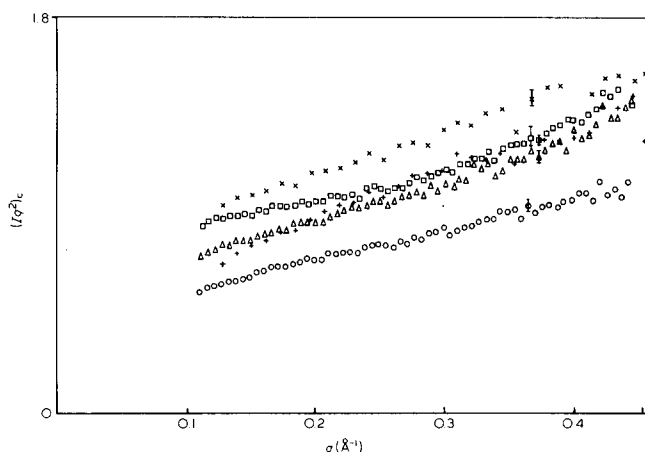


Figure 11 IANS data from samples crystallized by cooling at $1^\circ\text{C}/\text{day}$ after irradiation; 10% PEH, $\bar{M}_w = 15000$ (\circ); 3% PEH, $\bar{M}_w = 15400$ ($+$); 10% PEH, $\bar{M}_w = 28600$ (\triangle); 10% PEH, $\bar{M}_w = 90000$ (\square); 3% PEH, $\bar{M}_w = 224000$ (\times), $\lambda = 8.0 \text{ \AA}$ (\square , \triangle and \circ); 7.8 \AA ($+$ and \times)

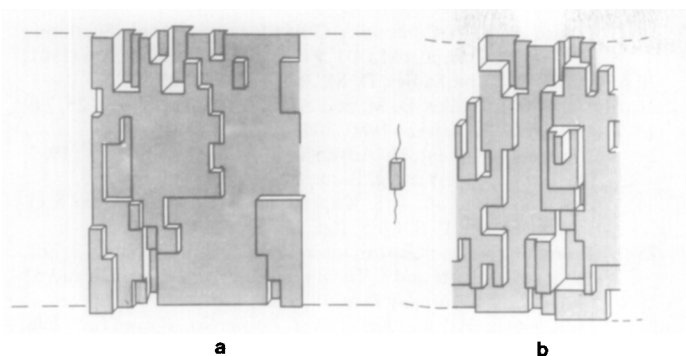


Figure 12 Schematic representations of possible roughness on the growth surface of a lamellar crystal. Parts (a) and (b) correspond to $kT/\varepsilon_1=0.5$ and 0.65 respectively. (ε_1 =energy of bonds parallel to surface). For further details see ref. 11

unnecessary to postulate kinetic in addition to equilibrium factors. The explanation of the origin of lamellae and of the observed growth kinetics consistent with this model is the subject of work in press²⁹. It will simply be pointed out here that a rough surface will lead to a molecule being attached independently at several places on the growth face. As the attachment points lengthen into stems, unless some of these attached stems are removed altogether, a folded structure will result.

It is clear that the type of folding will be strongly dependent on the degree of growth surface roughness³. Below T_R (Figure 12a), there will be a definite preference for adjacency during attachment in the same way as has long been envisaged for smooth surfaces. (This is certainly true for dilute solution growth, and may also be true in some degree for melt growth.) At T_R (Figure 12b) and above, the structure is rougher and the preference for adjacency will be less. All melt crystallization is expected to be under these conditions, and it may be that purely rate effects are much less important than had been supposed previously. The degree of non-adjacency is limited, as inferred from neutron scattering, and this has been explained in terms of the spacefilling restrictions in the fold surface^{10,25,26}.

All the samples show similar scattering patterns in the region of $q \approx 0.2 \text{ \AA}^{-1}$; hence the correlations between different stems are similar. (The latter can be obtained from the former by Fourier transformation.) It is probable that the conformation is also similar, though in principal different structures could coincidentally give the same correlations. This is reasonable if what controls the local conformation is spacefilling in the fold surface. The new model for growth face structure now suggests that even for very slow crystallization rates spacefilling remains dominant, and that there is no *additional* driving force for adjacency arising, for example, from nucleation of new layers on the crystal. The situation is quite different for solution growth where the temperature is below T_R and where there should be an enhancement of adjacency.

If this interpretation is accepted, there is the possibility that crosslinking might after all be expected, in some circumstances, to affect the fold patterns. It is known that branching modifies the morphology of polyethylene²⁷. It is possible that branching can have the effect of roughening the growth surface, though the morphological evidence is not straightforward. Crosslinking might be expected to have the same effect. It would not have been surprising therefore if the folding pattern for even lightly

crosslinked polyethylene were to be more random than linear polyethylene. There seems to be no evidence for this. One could speculate that the reason is that the actual observed folding patterns in both quenched linear and slowly cooled irradiated polyethylene are the *most* random possible, given the space filling constraints at the fold surfaces. Once this degree of randomness is achieved, perhaps further changes in (growth) surface roughness can have no effects on fold randomness. See also ref. 30 on a slightly branched type of polyethylene.

CONCLUSIONS

Experiments and calculations on neutron scattering of melt-crystallized linear polyethylene have previously been restricted almost entirely to quench conditions; and it has become increasingly desirable to test the supposition that slow crystallization would produce entirely different molecular conformations. The results ($q=0.1-0.4 \text{ \AA}^{-1}$), using cross-linking prior to slow crystallization, are self-consistent using the criterion of the independence of the (normalized) scattering on isotope concentrations. This agrees with previous findings that crosslinking minimizes anomalies that would otherwise be found at small q ($\leq 0.1 \text{ \AA}^{-1}$), and that even when such anomalies are present to a moderate degree, they do not extend to the q range used here. Extensive characterization studies show that in spite of the crosslinking the morphology is entirely different from the quench case. (Consequences of the crosslinking are restricted to effects such as the stacking of different lamellae with which we are not here primarily concerned.) However, the scattering data are remarkably insensitive to the rate of crystallization, which may be presumed to be entirely different for quenching or cooling at $10^\circ \text{ min}^{-1}$ or 1° day^{-1} . The clear inference is that the range of interstem separations is similar in all these cases of melt crystallization, in spite of enough freedom for conformational change to give large changes in stem lengths. The proposal that equilibrium roughness may exist on the crystal growth surfaces is relevant here: this results in a degree of adjacency which is the minimum compatible with spacefilling requirements.

ACKNOWLEDGEMENTS

Support from the SERC for S.J.S. is gratefully acknowledged. We would like to thank Professor A. Keller for critical comments and encouragement. We are indebted to Dr M. J. Hill for doing the electron microscopy, to Dr P. Fydeler (Royal Military College, Shrivenham) for irradiating the samples, to the staff of I.L.L. (Grenoble) for assistance with neutron scattering experiments and to the staff at the S.R.S. (Daresbury) for assistance with X-ray measurements.

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