Neutron scattering studies of semicrystalline polymers in the solid state: The structure of isotropic polyolefins

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It has been shown that on solidification from the melt, the radius of gyration (R_w) of organic polymers does not change significantly. This shows that any conformational changes occurring involve only fragments of the polymer chain, and these are distributed throughout several lamellae in space. It is not always possible to differentiate between a coil or an array of sets of stems since at high molecular weight, for both structures, R_w shows an $M_w^{1/2}$ dependence. At low molecular weight, the length of the stems which constitute the array can be recovered. In polypropylene and quenched polyethylene this is shown to be approximately equal to twice the X-ray lamellar thickness (d) showing that rods which constitute the array contain two stems d and $2d$ in length. The latter act as tie molecules between lamellae. The structure is supported by chemical etching experiments which can differentiate between the tie molecules and folds in the amorphous phase (*Figure 6b*) and show the presence of two stems d and $2d$ in length in polypropylene and polyethylene. Finally polypropylene, which is crystallized by 'seeding', folds fully in such a way as to preserve the tie molecules and the chain occupies two lamellae. Polyethylene crystallized under high pressure on the other hand, in which $d \simeq$ 2000 Å, is fully folded and each lamella contains complete polymer molecules. No evidence has been obtained for the nature of the re-entry in any of these structures.

INTRODUCTION

The use of the large difference in neutron scattering cross-section between hydrogen atoms and atoms such as deuterium, carbon, oxygen etc. for the study of organic polymers in the solid state has been described in several publications. The credibility of this technique for determining dimensions of a linear macromolecule in the amorphous state rests on three experiments. The first relates to the measurement of the dimensions of protopolymethylmethacrylate molecule in a deuteropolymethylmethacrylate matrix[1]; the second relates to the measurement of the dimensions of protopolystyrene molecule in a deuteropolystyrene matrix[2] and in the third the dimensions of a deuteropolystyrene molecule in a protopolystyrene was measured[3].

In each study the molecular weights (M_w) of the tagged molecules measured in the solid state agreed with those measured in solution by conventional methods; the radius of gyration ($R_w = \langle s^2\rangle_w^{1/2}$) of the tagged macromolecule varied with the M_w over a range 6×10^3 to 2×10^6 and the ratio $R_w/M_w^{1/2}$ was close to the value determined for macromolecular molecule in a θ-solvent; R_w was found to be almost independent of the concentration of the tagged molecules in the matrix showing that the second virial coefficient was finite but close to zero. Subsequently it was shown that amorphous polystyrene[2] and polyethylene[6,10] in the melt and at high molecular weights had similar dimensions to that found in the solid state. This observation implies that the macromolecule retains approximately its Gaussian distribution of chain elements about the centre of mass of the molecule on solidification.

Although small angle scattering techniques are able to give information about the dimensions of the macromolecule as a whole the nature of this data is limited since it is confined to R_w. It must be combined with other information if structural data of value are to be obtained. It can be particularly useful in comparing structural models when these are sufficiently different to give a characteristic dependence of R_w on the length of the molecule. A particularly successful example is the light scattering studies of α and β-poly-γ-benzyl-L-glutamate in solution[4].

Semicrystalline polyolefins have been variously representted structurally since the early X-ray measurements on polyethylene by C. H. Bunn. Subsequent small angle X-ray scattering techniques (SAXS) showed that there were reflecting planes at distances 100–500 Å (d-spacing) apart showing the presence of much larger crystalline regions than had previously been suspected. The next major observation was the isolation of discrete crystals of polyethylene by Keller and others and subsequently similar crystals for other polymers; this led to the ideas of chain folding. *Figure 1* illustrates the basic types of model discussed in the literature[5].

In *Figure 1a* the polymer chains are approximately normal to the X-ray reflecting planes. The model approximates

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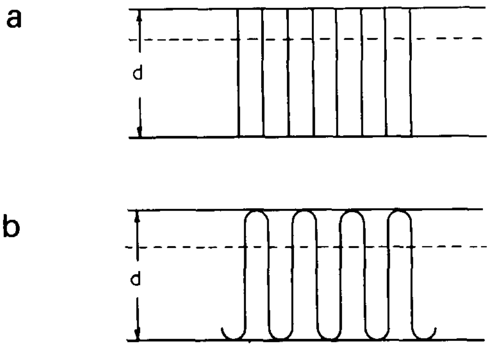

Figure 1 The organization of a macromolecular fragment between the lamellae planes according to various models proposed for the structure of polyolefins. The dotted lines represent the boundaries of the amorphous regions

to a random array one molecule thick of rods in space connected by a random coil fragment. If the chain re-enters the lamellae it is a statistical event. The radius of gyration of such a system with reference to the centre of mass of the set of rods is given by:

$$R_w^2 = \frac{l^2}{12n} + \frac{l^2(n-1)}{6} \qquad (1)$$

if there is no preferred orientation of the rods. In equation (1) l is the length of the rod and n the number of such rods. Since $n = L/d = \alpha M_w/d$ at large values of n the value of R_w closely approximates to:

$$R_w = (l^2 n/6)^{1/2} = (\alpha l^2/6d)^{1/2} M_w{}^{1/2} = \beta M_w^{1/2} \qquad (2)$$

where α is a constant proportionally relating the length of the molecule (L) to its molecular weight. The real system, however, consists only of 50–80% crystalline material; each stem is, therefore, connected by a fraction of randomly organized molecule. It will be shown experimentally that the latter contributes only a minor component to the scattering intensity.

It is evident from equation (2) that R_w is proportional to $M_w^{1/2}$ provided the molecular weight is high enough for the number of stems to be large. *For this reason it is not possible, at high molecular weights, to differentiate between the scattering from an array of coils and an array of sets of stems.*

In *Figure 1b* the surface of the crystal is the sum of the fold surfaces of the molecule and the radius of gyration is given by:

$$R_w^2 = \frac{l^2}{12} + \frac{w^2}{12} = \frac{l^2}{12} + \frac{(\eta_s - 1)^2 a^2}{12} \qquad (3)$$

$$\alpha M_w = d\eta_s + (\eta_s - 1)a$$

$$\eta_s \simeq \alpha M_w/d$$

where w is the thickness of the folded molecules, η_s is the number of stems per lamella and a their distance apart. In *Figure 1b* $l = d$ but in other structures to be discussed l may be greater than d. In known systems d is 100–2000 Å depending on the material studied. If a is the same as for adjacent chains in the unit cell of the crystal we have 'adjacent re-entry'; if a is greater than this we have the 'switch board' or nearby re-entry models. In practice, the chain can fold many times without increasing the thickness of the stem significantly in relation to its length and the scattering in these circumstances is from a rod of length l and for all molecular weights we have the condition:

$$w^2/12 \ll l^2/12$$

and therefore

$$R^2 = \frac{l^2}{12} \qquad (4)$$

It should be noted that the centre of mass of the molecule in equation (3) lies within the set of stems which constitute the whole molecule whereas equation (4) refers to an array of discrete stems and the centre of mass of the molecule is at $l/2$.

It is possible, therefore, for the crystallization from the melt to cause two extreme conditions to arise each represented by equations (2) and (4). In exploring the change in R_w with molecular weight both situations may be encountered. At high molecular weight each molecule consists of a three-dimensional set of stems whereas at low molecular weights each molecule can consist of a single stem. Since the system is polydisperse, scattering will occur from an admixture of both geometrical arrangements of the molecule and R_w is therefore given by:

$$R_w^2 = \frac{l^2}{12} + \beta^2 M_w \qquad (5)$$

Equations (1), (3), and (5) show that extrapolation to low molecular weights produces a situation where the radius of gyration becomes independent of molecular weight and enables the stem length l to be determined. This is independent of the precise description of the behaviour of R_w with M_w at higher molecular weights. Previous studies with pressure crystallized polyethylene showed this behaviour[6] and the stem length derived agreed with that obtained by other measurements. Recent studies on isotropic polypropylene[7] have shown that some departure at low molecular weight from the simple $M_w^{1/2}$ rule is evident.

We have carried out neutron scattering studies at low molecular weights in the case of polypropylene and quenched polyethylene and compared the changes of R_w with molecular weight in this region with amorphous polystyrene. This has given valuable information about the structure.

EXPERIMENTAL

The synthesis and characterization of polypropylene[7] and polyethylene[8,9] samples were carried out as described in previous publications. Low molecular weight samples were obtained by fractionation of the deutero and protopolymers to give the appropriate molecular weights with as narrow a molecular weight distribution as possible. For polyolefins the polydispersity was $1.5 \leqslant M_w/M_n \leqslant 2.0$

The mixtures of matrix and tagged molecules were prepared and then crystallized using the appropriate conditions[7,8,9]. In the case of polypropylene the tagged molecules do not cluster. It has been possible to produce four types of isotropic sample in which the X-ray long spacing (d)

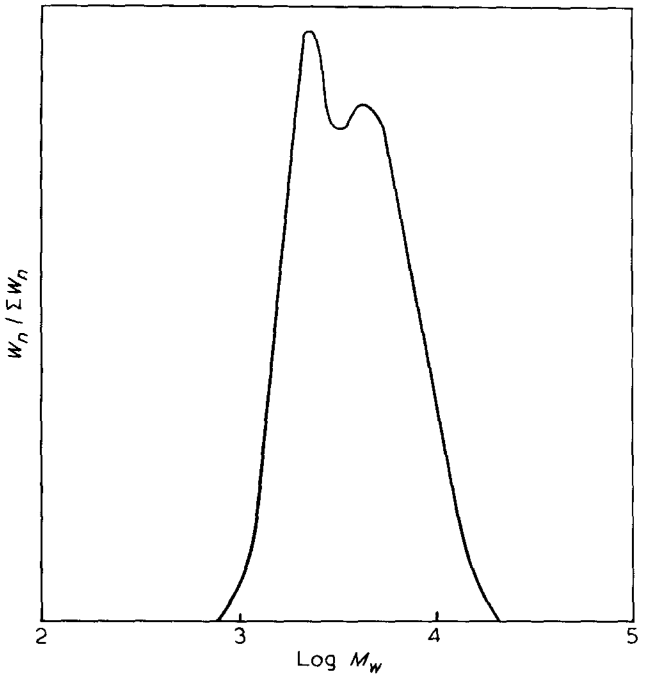

Figure 2 The weight fraction (W_n) of a polymer molecule of size n versus M_w (g.p.c. curve) for isotropic polypropylene etched under standard conditions

varied between 122 and 345 Å. These were obtained by quenching the samples from the melt in ice–water mixtures, then annealing the quenched samples for 24 h at 120°C; annealing quenched samples for 7 days at 165°C: the fourth sample was heated above the melting-point and then crystallized by slow cooling just below the melting point. One anisotropic sample of polypropylene has also been studied which was obtained by biaxially orienting the film and has a *d*-spacing of 380 Å; no neutron scattering studies have been carried out, however. The tagged molecules in isotropic polyethylene do not cluster when the sample is quenched in ice–water mixtures; a full study of this system is therefore possible.

Additional studies have been carried out on polyethylene crystallized at 6–9 k bars pressure[10] ($d \simeq 2080$ Å) in which the molecular weight of the tagged molecules was varied over a much wider range. In these studies the molecular weight of the matrix was maintained at M_w = 81 500–86 000 and the molecular weight of the tagged molecules was varied from M_w = 23 000–250 000. In previous studies[6] the tagged molecules were limited to molecular weight 54 000 in the same matrix.

For comparison of neutron scattering behaviour at low molecular weights, radii of gyration of polystyrene were measured. These polymers were prepared by alkali metal initiation in the range M_w = 2800–215 000. At the lower molecular weight M_w/M_n = 1.08 increasing to 2.00 at the high end. Matrix (PSD) and tagged (PSH) molecules had closely similar molecular weights. Measurements were carried out on samples which were heated above T_g at 6 kbars and cooled to ambient temperature at 6 kbars. Measurements were carried out at atmospheric pressure.

X-ray and neutron scattering studies were carried out in the manner described previously[7,8,9].

Plaques similar to those used in neutron scattering measurements were etched using 70% nitric acid (Analar Grade) at 100°C. The samples (~0.4 g) were submerged, by glass probes, in 30 ml of the acid contained in glass tubes held in a temperature controlled oil bath. The etched samples were removed from the acid, washed with distilled water and then allowed to soak in water for 24 h before being re-washed and vacuum dried at 60°C.

Gel permeation chromatography (g.p.c.) analyses of the etched samples were made on the CL-R developed instrument using *o*-dichlorobenzene as solvent at 135°C. A standard Styragel column set of porosities 10^6, 10^5, 10^4 and 10^3 Å as supplied by Waters Associates was used. A shifted polystyrene standard calibration supported by low molecular weight hydrocarbon data was used in the calculation of the molecular weights of the etched samples.

Isotropic samples of polypropylene and polyethylene when etched using the above conditions for moderate times show the presence of two peaks. In a typical example etching polypropylene for 8 h produce the g.p.c. curve shown in *Figure 2*. The high molecular weight peak was very persistent but could be removed by oxidizing the samples for addition times in excess of thirty hours. To produce these two stems from isotropic polymers with the range of *d*-spacings quoted in *Table 1* was extremely easy. A wide variety of oxidizing conditions could be employed but in all cases studied long relative reaction times were required to remove the high molecular material. The sharpness of the resolution on the g.p.c. persisted over many hours showing that oxidation readily converted the solid into two dominant molecular weight fractions.

The stem length quoted in *Table 1* were derived from the molecular weight obtained from g.p.c. measurements on samples where the degree of etching corresponds to equal weight of the polymer fractions in the solid.

It should be noted that the pressure crystallized polyethylene and biaxially oriented polypropylene which were etched under similar conditions only showed the presence of one molecular weight fraction in the etched solid.

RESULTS AND DISCUSSION

Neutron scattering

Extending the previous studies of slow cooled polypropylene[7] we have carried on measurements of R_w at values of M_w as low as 21 600 in the solid state. These results are plotted in *Figure 2* and it is evident that values of R_w do not decrease with M_w in this region but tend to a constant value. Equation (5) is found to fit this data reasonably well with the values of β = 0.38 and l = 450 Å and also the polypropylene data for quenched and annealed samples.

A similar study at low molecular weights has been carried out on quenched polyethylene. We have succeeded in obtaining sharp fractions at molecular weights as low as 4600 with very little clustering. It was found that R_w changes very little up to a molecular weight of 17 000 and was independent of the number of molecules in a cluster within the range 1–6 molecules. This is typical behaviour of an array of stems. The variation in R_w over the entire M_w range is summarized in *Figure 4*. Equation (5) fits this data closely and the extrapolated value for the stem length l = 294 Å was obtained.

In order to ensure that this tendency to asymptotic value of R_w at low molecular weight was associated with the stem-like structure of crystalline polyolefins we carried out a similar set of measurements on atactic polystyrene in the solid state down to a molecular weight of 2800. Moreover, we carried out these measurements on polystyrene which has previously been heated above the glass transition temperature pressurized to 6 kbars, cooled to ambient temperature.

Table 1 Summary of data for crystalline polyolefins

Polymer	Type of treatment	Stem length measurement using chemical etching/g.p.c. (Å) Smaller stem length	 Longer stem length	 Ratio of lengths Long to short stems	SAXS Measurement of *d* (Å)	SANS Measurement of *l* (Å)	*l*/*d*
Polyethylene	Crystallized at pressures of ≃ 5 kbars	1880	Nil	–	2000[a]	2080	1.0
	Quenched[b]	120	207	1.7	178	294	1.7
	Annealed[b]	221	393	1.8	260	–	
	Slow cooled[b]	173	342	2.0	220	–	
Polypropylene	Quenched	130	205	1.6	122	250	2.0
	Annealed 24h	191	341	1.8	202	350	1.7
	Annealed 1 week	342	745	2.2	345	690	2.0
	Slow cooled	220	390	1.8	245	459	1.8
	Biaxially oriented	440	Nil	–	380	–	

[a] Electron microscope measurements on fracture surface (ref 7)

[b] Data on these samples refers to branched polyethylene used to match the melting point of the tagged molecules hence lower values obtained on etching (see ref 6 and 11)

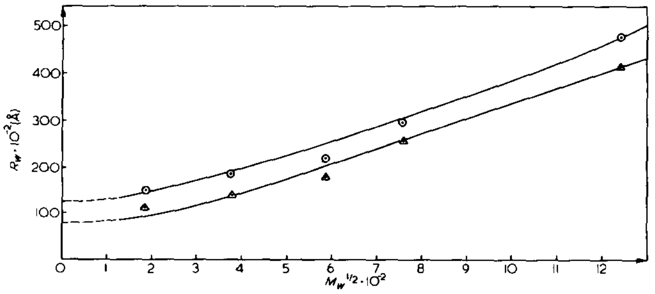

Figure 3 The radius of gyration of polypropylene in the semi-crystalline state produced by quenching (Δ), and slow cooled (○) as a function of the square root of molecular weight M_w in comparison with calculated model functions according to equation (5) with l = 250 Å, β = 0.33 for Δ and l = 450 Å, β = 0.38 for ○

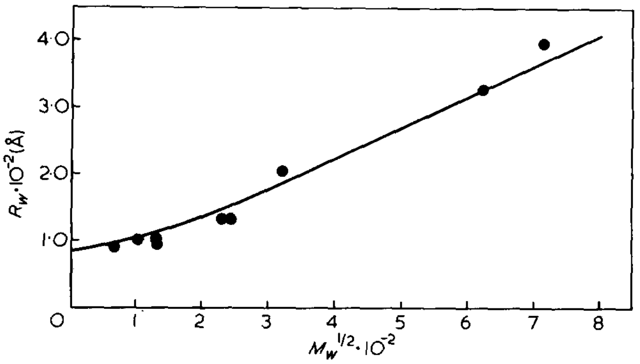

Figure 4 The radius of gyration of polyethylene in the semi-crystallized state produced by quenching. Comparison with calculated model functions according to equation (5) with l = 294, β = 0.50

This type of treatment in the case of polyethylene and polypropylene leads to an increase in the stem length. The results are summarized in *Figure 5*. It is evident that the $M_w^{1/2}$ law is strictly obeyed down to the lowest molecular weights. *This shows experimentally there is a fundamental difference between amorphous and semicrystalline materials* and the behaviour of the latter is consistent with an array of stems. We compute from the polystyrene data that there are no stems in this polymer longer than 30 Å.

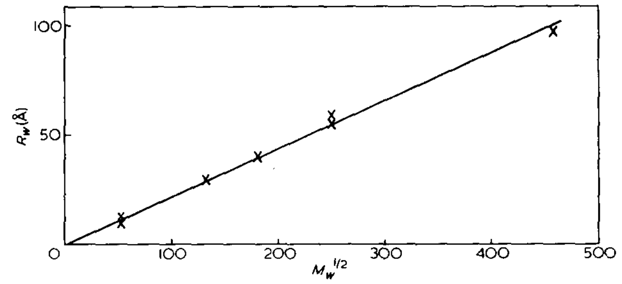

Figure 5 The radii of gyration of polystyrene measured at 23°C at a pressure of 1 bar. Sample previously heated above T_g at 6 kbars are cooled below T_g at the same pressure

Quenched polyethylene and slow cooled polypropylene are the best examples we have for the independence of R_w from M_w at low molecular weight. In the case of the latter polymer we have succeeded in changing the *d*-spacing from 122 to 345 Å and although the data is less complete it is good enough to give a value for the scattering stem length *l*. This data is summarized in *Table 1* and the ratio of the SANS to the SAXS stem length (*l*) are compared in the last column. We see that this ratio is on average about 1.8.

It is evident that the structure in *Figure 1a* and *1b* both require that this stem length *l* should be equal to the *d*-spacing. The neutron scattering data, therefore, does not support either of these structures.

The structure displayed in *Figure 6* can explain the neutron scattering data. At high molecular weights the neutrons see an array of rods approximately twice the *d*-spacing in length and of negligible thickness, this is represented by *Figure 6a*. The chain as a whole has approximately the same disposition in space as a Gaussian coil and reflects the organization possessed by the molecule in the melt[8,9,10,12,13]. It is for this reason that the value of β in equation (5) is close to, but not identical with, the melt value for this parameter.

It must follow that if the surface of the lamellae corresponds to the fold surface of the macromolecule, and the chain crystallizes locally, whilst retaining the same overall dimensions as in the melt then a structure similar to *6b* follows. This requires a long stem which connects adjacent lamellae and is approximately 2*d* in length. The simplest type of

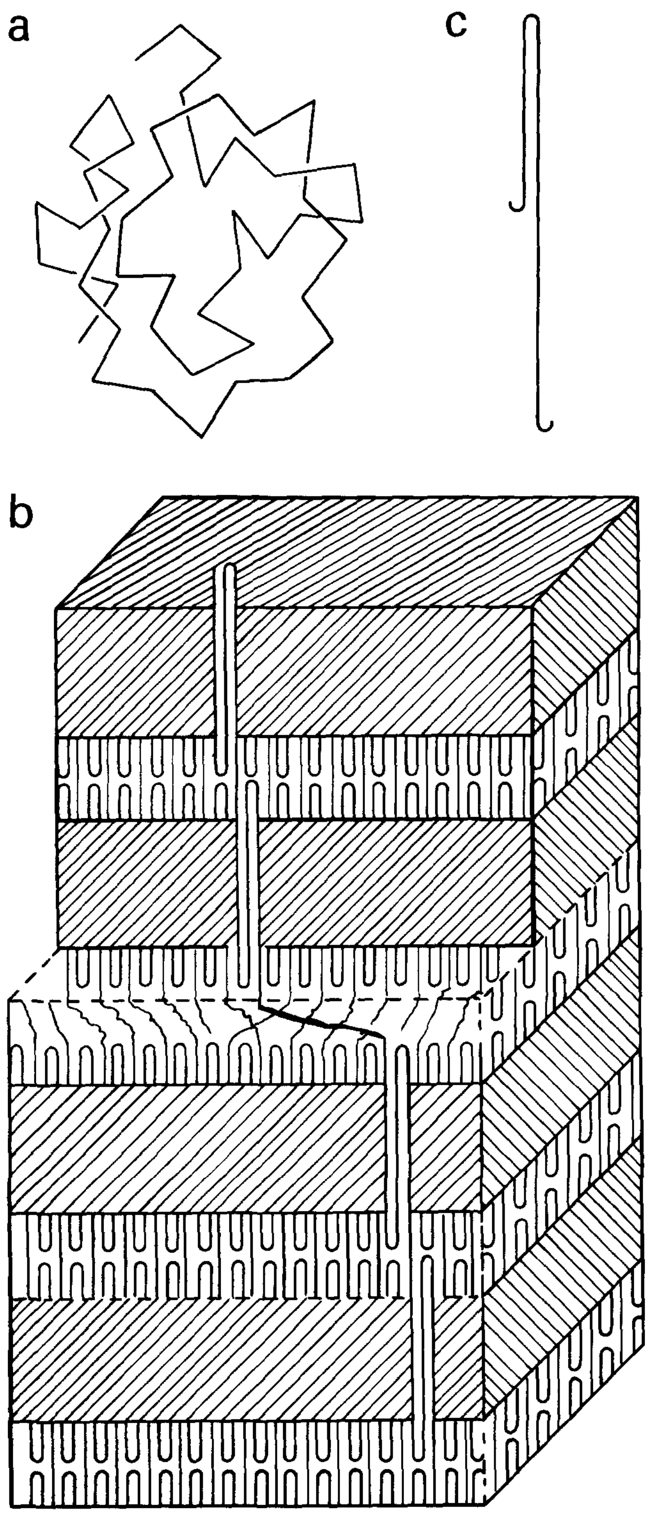

Figure 6 (a) represents a three dimensional random array of rods $2d$ in length with a Gaussian distribution around the centre of mass. (b) shows the construction of a chain from the simplest composite rod. (c) structure of one of the many types of composite stems. It should be noted that adjacent re-entry or 'switch-board' re-entry are possible. The thickness of composite rod (6c) can be at least 10% of its length

element from which the structure is built is shown in *6c* and consists of two stems d and $2d$ in length joined together by a fragment of chain of as yet undefined length. The neutron scattering characteristics of such a structural element would be such that the longest stem would dominate. This accounts for the fact that at low molecular weights we see stem length approximately $2d$ in length.

It should be noted that no comment can be made about the nature of the re-entry since only the length of the stem is measurable.

It is not possible to study annealed or slow cooled polyethylene because the tagged molecules cluster together in large numbers and interpretation is ambiguous. Polyethylene crystallized at 5 kbars has a d-spacing of approximately 2000 Å. In these circumstances the stem length is so long that even at high levels of clustering the scattering element always behaves as a thin rod of length l and diameter D which contains η_c molecules with η_s stems per molecule. In these circumstances we amend equation (3) to give:

$$R^2 = \frac{l^2}{12} + \frac{D^2}{8} \cong \frac{l^2}{12} \qquad (6)$$

where $D = 4.8\,(\eta_s \cdot \eta_c)^{1/2}$.

Initial studies on this system[6] showed that at two molecular weights corresponding to one stem length and 2.5 stem lengths of 2000 Å, R_w was independent of molecular weight and the number of molecules in the cluster. In fact the second term of (8) never exceeds *one per cent* of the first. The calculated value of l deduced from the extrapolated value of R_w agreed with the stem length obtained by other means. We have now extended the molecular weight range of the tagged molecules to 250 000 and measured the radius of gyration in a PEH matrix of approximately 84 000 molecular weight. The results are summarized in *Figure 7* and show that the radius of gyration is still independent of the molecular weight. The scattering behaviour corresponds to a single stem 2080 Å in length. The only possible explanation is that the molecule folds into a single lamella as shown in *Figure 1b*. A remarkable feature is that the thermodynamics of the crystallization process are such that the macromolecule prefers to fold approximately eleven times into the same lamella and has little tendency to occupy adjacent crystalline regions. This is reflected in the crystallinity of this system which can be greater than 98%.

An additional observation about this system is that if the samples of polyethylene are heated in the neutron spectrometer to 145°C the radius of gyration falls from 684 Å to 151 Å within a few minutes. The latter value is close to that previously measured in the melt. There seems to be no tendency for the structure of the type in *Figure 1c* to persist above the melting point.

It is evident that only neutron scattering could give such unambiguous information on the folding of the macromolecules. However, it is not possible to make any comment on distance between stems of the same macromolecules in the

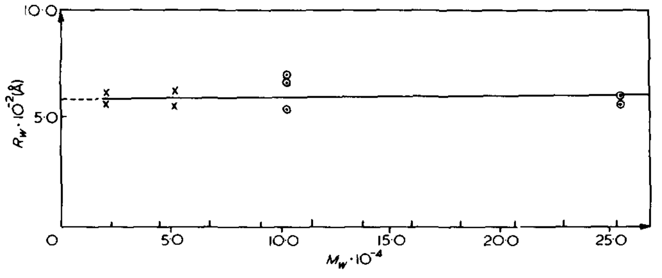

Figure 7 Pressure crystallized polyethylene experimentally determined values of the radius of gyration (R_z) plotted against the molecular weight PED matrix M = 80 000–86 000 M_w/M_n for PED molecules varies between 2.2 and 1.6, ref. 7. X and O denote two independent sets of experimental data

Table 2 Neutron scattering of annealed polypropylene samples which have been etched to give discrete composite stems. R_z is the radius of gyration of the macromoelcule and R of the array of stems found on etching

Initial M_w	R/R_z
34 000	0.91
140 000	0.85
340 000	0.90
575 000	0.82

crystallite. Even allowing for the high crystallinity, the folding pattern could be such that stems of the same macromolecule could be more than 40 Å apart. This would allow structure from adjacent re-entry to nearby re-entry to be possible.

Chemical etching in structural studies of crystalline polyolefins

An important feature of the studies carried out on the pressure-crystallized polyethylene was the good agreement between the three techniques. The technique of measuring stem lengths within the crystalline regions by removing the surrounding amorphous part of the matrix by chemical oxidation was particularly successful. In this process the amorphous regions are selectively dissolved away by chemical oxidation at the same time cutting the folds at the surface of the crystalline lamellae to give molecular fragments of a length related to the thickness of the latter. These chain lengths and their distribution are readily measured using the gel permeation chromatography technique. Careful control of the etching procedure enables the population of various stem lengths to be measured and how these change with time of etching to be determined.

Using this technique it is evident on comparing *Figure 1a* and *1b* that it would not be possible to differentiate between them since both would yield the same stem length.

The results given in *Table 1* for pressure crystallized polyethylene are particularly important because only one stem is isolated equal in length to the *d*-spacing determined in the electron microscope. Since SANS has shown that this structure is folded it is evident that the chains are uniformly cut and no stems equal in length to 2*d* are present. It has been suggested previously[11] from a study of single crystals that etching of a chain folded structure would produce, for statistical reasons, an average of stem lengths equal to *d* and 2*d*. The reasons why single crystals produce these two stem lengths is not known but from the experiments with pressure crystallized polyethylene it is evidently not due to the fact that the chain is folded.

Etching isotropic polyethylene and polypropylene, however, does show the presence of two stems equal to *d* and 2*d* in length. Using standardized conditions, degradation of the polymer is complete within 2–3 h and on dissolving in an organic solvent the matrix gives a mixture of short and long stems (*Figure 2*). The origin of these two stems is now evident from the neutron scattering studies and derives directly from the oxidation of structure *6b*. The reason that two stems can be identified is that the initial attack of the oxidant takes place at the interface of the folds where neutron scattering studies show voids of the order of 100 Å to be present. The oxidant obtains ready access via the latter severing the folds and thereby giving a mixture of short and long stems. This happens after modest reaction times and with only 10–15% of the polymer being removed. A more severe oxidation and requiring five times this reaction time is necessary before the long stems are attacked and converted into short stems.

In *Table 1* are summarized all the etching data for isotropic samples of polyethylene and polypropylene and the ratio of long to short stems is seen to be approximately 1.8 and compares favourably with the ratio *l*/*d* obtained by SANS and SAXS measurements. It should also be noted that indrawn systems such as biaxially oriented polypropylene etching reveals only one stem equal in length approximately to the *d*-spacing.

Mathematical expressions for the variations in radius of gyration with molecular weight of a polymer

In equations of the type (2) and (5) scattering is considered to be from a set of rods arranged in space, each set having its own centre of mass. This is at best an approximation since in reality the rod is generated from a single molecule by discrete regions folding and crystallizing. It is possible, however, to remove part of the chain in the amorphous regions and thereby generate a discrete array of stems occupying the same positions in space as they were when part of a macromolecule. If the assumption underlying the use of equations (2) and (5) is correct, namely, that the stem in each set is the dominant scattering entity then there should be little change in the radius of gyration. In *Table 2* is shown the effect on the radius of gyration in the solid state of cutting the macromolecule into discrete stems by oxidizing the same until the molecule was reduced to fragments similar in composition to the system shown in *Figure 2*.

This shows that the contribution to the overall scattering by random elements, which link the stems, is small, in agreement with expectation. An additional feature is that the scattering by the discrete stems follows equation (5) namely at low molecular weight R approaches asymptotically $l^2/12$ and at high molecular weight $\beta M_w^{1/2}$ or more precisely:

$$R^2 = \frac{(565)^2}{12} + (0.41)^2 M_w \qquad (7)$$

The significance of the β term in equation (5) has not been discussed. It is evident that the value of β tends to be approximately the same as for the melt, for both the macromolecule and discrete stems and lies between 0.3 and 0.5. This is equivalent to the statement that the disposition of the stems in the solid follows the contours the macromolecule possessed in the melt.

If there is any gross movement of the chain on crystallization then equation (5) would not be valid. This is very easy to prove experimentally by carrying out a 'seeded' crystallization of polypropylene. A polypropylene sample which had

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Since the paper was written new information has become available concerning the organization of macromolecules in polyethylene crystals grown from solution. Neutron scattering studies show that the radius of gyration is independent of the molecular weight and the stem length is approximately twice the thickness of the lamellae 'We can attribute this to some chains crystallizing partly in neighbouring lamellae or between three with the central lamellae containing most of the chains' – D. M. Sadler and A. Keller to be published in Science.

The etching g.p.c. data is therefore seen to give accurate information about the presence of long stems in all systems studied. The long stem or tie molecule is, therefore, a significant structural entity in semicrystalline polyolefins.

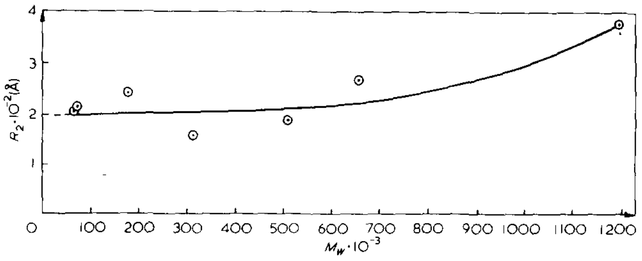

Figure 8 'Seeded' crystallized polypropylene values of the radius of gyration (R_z) plotted against the molecular weight. Matrix (PPH) and tagged molecules (PPD) have approximately the same molecular weights. d = 345 Å and the PPD molecules are unclustered

been previously crystallized by slow cooling in the manner previously described was heated at a rate of 30°C/h from 120 to 165°C; the melt was then immediately cooled at 6°C/h to room temperature. The crystallization which occurs does so in the presence of nuclei remaining from the previous crystallization processes. It is seen from *Figure 8* that the radius of gyration is now independent of the molecular weight over the range 60000 to 500000. The behaviour is similar to that previously observed for pressure crystallized polyethylene but in the absence of clustering we can use equation (3) directly and over the range of molecular weights quoted R is given by equation (4). The macromolecule is folded into a rod of length $l = \sqrt{12} \times 200 = 692$ Å. As the length of the chain is increased the number of stems increases and the macromolecule generates more folds, but, because the thickness is small compared to the length, the radius of gyration is unchanged. Above 500000 the thickness of the rod becomes comparable with its length and the radius of gyration increases. The X-ray d-spacing for these samples was 345 Å and therefore $l/d = 2$. This shows that the crystallization has taken place to preserve the long stem and that each macromolecule occupies a pair of lamellae. It is clearly possible to write down a very large number of folded structures which will comply with this condition.

It will be noted that the data in *Figures 3* and *4* has been corrected for polydispersity whereas in *Figures 7* and *8* values for R_z are quoted. It should be evident in the latter examples that the length of the scattering stem is in no way related to molecular weight but determined by the morphological characteristics of the system. This should be obvious since the d-spacing and hence the long stem is independent of molecular weight[7].

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REFERENCES

1 Kirste, R. G., Kruse, W. A., and Schelten, J. *Makromol. Chem.* 1972, **162**, 299

2 Ballard, D. G. H., Schelten, J., and Wignall, G. D., Symposium on Molecular Weight Characterization of Industrial Polymer, National Physical Laboratory, (Eds. J. H. S. Green and R. Dietz) Transcription, London, 1973; *Eur. Polym. J.* 1973, **9**, 965

3 Benoit, H., Cotton, J. P., Decker, D., Farnoux, B., Higgins, J. S. Jannick, G., Ober, R., and Picot, C. *Nature* 1973, **245**, 13

4 Doty, P. D., Bradbury, J. H. and Holtzer, A. M. *J. Am. Chem. Soc.* 1956, **78**, 947

5 Wunderlich, B., Macromolecular Physics Vols. 1 and 2, Academic Press, New York, 1973. A comprehensive review of structures of polyolefins is given in this text

6 Ballard, D. G. H., Schelten, J. and Cunningham, A. *Polymer* 1977, **18**, 259

7 Ballard, D. G. H., Schelten, J., Cheshire, P. and Longman, G.W. *Polymer* 1978, **19**, 379

8 Schelten, J., Wignall, G. D. and Ballard, D. G. H., *Polymer* 1974, **15**, 682. Schelten, J., Wignall, G. D., Ballard, D. G. H., Longman, G. W. *Polymer* 1977, **18**, 1111

9 Ballard, D. G. H., Schelten, J., Wignall, G. D., Longman, G. W. and Schmatz, W. *Polymer* 1976, **17**, 751

10 Lieger, G., Fisher, E. W. and Ibel, K. *J. Polym. Sci. (B)* 1975, **13**, 39

11 Ward, F. C., and Williams, I. M. *J. Polym. Sci. A2,* **6**, 1357. Williams, T., Blundell, D. J., Keller, A., Ward, I. M. *J. Polym. Sci. A2,* **6**, 1613. Keller, A., Martuscelli, Priest, D. J. and Udagawa, Y. *J. Polym. Sci. A2,* **9**, 1807

12 Herchenroder, P., Dettenmair, D., Fischer, E. W., Wegner, G., Pieke, B. in press

13 Allen, G. and Tanaka, N. *Polymer* 1978, **19**, 271