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# Conformation of the molecules in drawn polypropylene revealed by neutron scattering studies†

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It has not been possible previously to do a complete study of drawn polyolefins using SANS techniques because of void scattering. In the case of polypropylene this can be reduced sufficiently to permit measurements with the *Q*-vector perpendicular and parallel to the draw direction. A complete analysis has been carried out with a draw ratio 8:1 in which the PPD molecules of narrow molecular weight distribution and molecular weights in the range 390 000 to 50 000 are molecularly dispersed in a drawable PPH matrix. The dimensional changes on drawing are to extend the molecule by a factor of 2 with a corresponding reduction in diameter to a maximum of 40%. We have interpreted the data at high *Q* on the basis that the molecule is not uniformly distributed but the majority is folded into sub-units and the number of these is proportional to the molecular weight of the polymer. A further feature of the sub-units structure is that its length is approximately two lamellae thick, this dimension is similar to the SANS scattering length ($l_n$) identified in the study of isotropic material. The double stems belonging to the same molecule have been concentrated by the drawing process some 16 times and a consequence of this is to markedly change the Kratky curves from the isotropic case. Notwithstanding, this increase in the packing of the molecule, the stems are still, on average, some 40 Å apart and surrounded by many stems belonging to other macromolecules. Similarly, each sub-unit is surrounded by sub-units belonging to neighbouring molecules.

**Keywords** Conformation; drawn polypropylene; small-angle neutron scattering; dimensional changes

## INTRODUCTION

In a previous publication we described the first experiments on drawn polypropylene in which small angle neutron scattering (SANS) was able to give information about the molecular dimension at right angles to the draw direction. This study revealed that examination of the dimension of the molecule parallel to the draw direction was seriously impeded by the presence of voids which scatter neutrons and obscured the scattering by the tagged molecules. This problem has been encountered by groups seeking to study hot stretched amorphous polymers[2]. Similar difficulties are associated with small angle X-ray studies (SAXS) which have limited investigation at very low angles.

It has been found in the Corporate Laboratory, that by careful sample preparation, drawn polypropylene can be obtained in which the interference due to void scattering can be reduced to an insignificant level. This feature combined with the fact that deuteropolypropylene (PPD) tags do not aggregate in the protopolypropylene (PPH) matrix makes this system ideal for studying conformational changes occurring on drawing. Moreover, because high draw ratios can be studied for the first time it is possible to explore the changes at the molecular level when a thermoplastic 'necks'.

From studies of isotropic systems it is known that due to the spherical averaging valuable details of the molecular conformations remain undetectable. Studying highly oriented systems has the advantage that a more detailed picture of the molecular conformation can be deduced from scattering patterns. As an example, for drawn polymers one determines two components of the radius of gyration, one parallel and one perpendicular to the draw direction instead of just one average value as in the isotropic cases.

## EXPERIMENTAL

Polypropylene samples were prepared and characterized using techniques described in previous publications[6,10].

Hot drawn samples were prepared from rapidly quenched ($\chi = 55\%$, $d = 135$ Å) polypropylene samples shaped to permit mounting in an Instron Tensiometer. They were drawn at 145°C at a rate of 1 cm min$^{-1}$ and at constant load. The extension obtained with these conditions was equivalent to a draw ratio of 8:1. The dimensions of the PPD tags are given in the Tables listing the SANS data. The PPH matrix had a molecular weight and polydispersity to permit facile drawing and to minimize the formation of voids $M_w = 263\,000$,

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In our previous publications we have used $\kappa$ to describe the scattering vector $(4\pi \sin\theta)/\lambda$ where $\theta$ is half the scattering angle and $\lambda$ is the wave length of the radiation. In this paper $\kappa$ is replaced by Q to conform with a more widely used notation.

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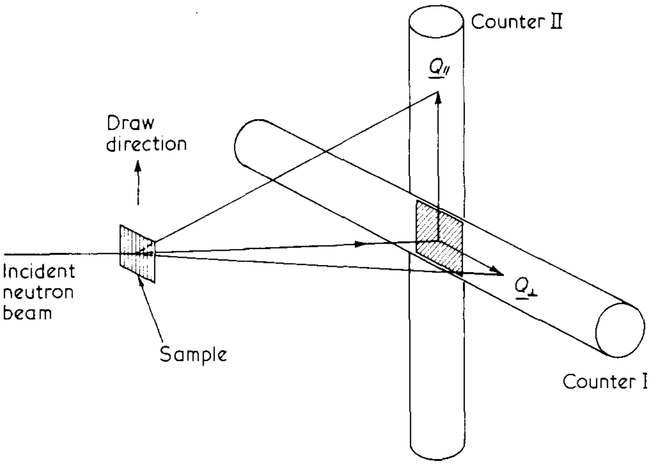

*Figure 1* Diagramatic representation of the experimental arrangement used to study drawn polypropylene. Note that the two detectors allow the simultaneous measurement of scattering curves with the *Q*-vector perpendicular and parallel to the draw direction in the sample

$M_w/M_n = 6.0$. The SAXS value of the d-spacing increased to 240 Å. The drawn samples were cut into 3 cm lengths, and pieces of equal thickness and similar crystallinity and d-spacing assembled between silica slides to give a sample of dimension $3 \times 2 \times 0.05$ cms.

SANS experiments were carried out on the Julich spectrometer which has been described in our previous papers. *Figure 1* shows the orientation of the position-sensitive detectors with respect to the draw direction ($Z$) of the samples. Information is obtained simultaneously with $Q$-vectors parallel ($Q^{\parallel}$) and at right angles ($Q^{\perp}$) to the Z-direction. Three detector distances were used which are given in the Tables together with the incident neutron wavelengths.

In isotropic systems previously studied the radius of gyration ($R_z = \langle s^2 \rangle_z^{1/2}$) and the molecular weight ($M_w$) of the PPD molecules in a PPH matrix are obtained by plotting the reciprocal of $(\mathrm{d}\Sigma/\mathrm{d}\Omega)(Q) = I(Q)$, the differential scattering cross section per cm$^3$, against $Q^2$ ($Q = 4\pi(\sin\theta)/\lambda$ when $\theta$ is half the angle subtended at the detector at which the intensity is measured. For small $Q$ we have:

$$\frac{C_D.C_H.K_N}{I(Q)} = \frac{1}{M_w}[1 + \alpha R_z^2 Q^2] \qquad (1)$$

$c_D$ is the concentration of PPD (tagged) molecules and $C_H$ the matrix molecules;

$$K_N = \rho.\mathrm{N}\left[\frac{v.X.(b_D - b_H)}{M}\right]^2$$

where $\rho$ is the density of the polymer, $X$ is the degree of deuteration, N is Avogrado's number, $M$ is the molecular weight of the repeat unit of the tagged molecules $b_D$ and $b_H$ are the scattering lengths of deuterium and hydrogen and $v$ is the number of replaceable hydrogen atoms in the repeat unit. For the isotropic case $\alpha = 1/3$. The applicability of equation (1) to non spherical particles and the validity of the concept of the radius of gyration in such circumstances has been discussed at length by Guinier[3]. This equation is modified for narrow cylinders, the geometry to which the scattering envelope of the drawn molecule approximates. In these circumstances $R_z$ is replaced by $R^{\perp}$ and $R^{\parallel}$ and the value of $\alpha$ put equal to 0.5 and 1.0 for $Q^{\perp}$ and $Q^{\parallel}$ data respectively.

It has been recognised for some time that the values of $R$ in isotropic systems were insensitive to the concentration of tagged molecules in the range $C_D = 0.3$–5%. Recently[4,5], it has been shown that provided the matrix and tagged molecules are similar in molecular weight the values of $R$ are unchanged even for equimolecular mixtures of deutero and proto-species.

We have used this information to increase the scattering intensity at low $Q$ by increasing the tagged molecules to 10% concentration. It is impractical to match $M_w$ and $M_w/M_n$ ratios for tag molecules with the matrix. It is necessary to have some breadth to the distribution of the matrix polymer to achieve drawability whereas the tag molecules should ideally be monodispersed. We have chosen the molecular weight for the matrix polymers to be in the middle of the range covered by the tagged molecules. It can be shown, using similar arguments to those deployed to discuss equimolar concentrations of tagged and matrix molecules[4,5] that this introduces negligible error to the low $Q$ data at 10% concentration of PPD molecules. *Table 2* confirms this analysis since the molecular weight of the PPD molecule in the low $Q$ range agree with those obtained from solution measurements. Moreover, a comparison of radii of gyration at 3% concentration in *Table 1* at the highest molecular weight studied show reasonable agreement with data obtained at 10% concentration of tagged molecules. We, therefore, consider this to be a valid procedure.

A final feature to these studies is that the scalar product $Q.R$ is, in a few instances, comparable to unity as is the case with most SANS studies in the solid state. It can be shown, however, that values of $M_w$ and $R$ obtained in those circumstances using the first two terms of Guinier's approximation are close to the values recovered using a complete Debye function. The latter is fitted to experimental data by a weighted least square fit. This is shown in *Figure 2* for isotropic polypropylene in which the conventional line obtained by plotting the reciprocal of $I(Q)$ vs. $Q^2$ is close to that obtained using the Debye function without approximation.

## RESULTS AND DISCUSSION

In *Figure 3* is shown typical scattering curves for polypropylene, with and without the tagged molecules, in which the void population has been significantly reduced. The effectiveness of the sample preparation technique is clearly demonstrated. It is evident, however, that at very low $Q$ a large background scattering is still present. This phenomena is common to crystalline substances, in general, including single crystals. In order to determine the significance of this residual background scattering, the measured differential scattering cross-section can be compared with the incoherent scattering from the hydrogen atoms in polypropylene. The latter is independent of $Q$ and has a value of 0.5 cm$^{-1}$; this is a quarter of the background cross-section at the largest $Q$-values in *Figure 3*. Similarly, comparing with expected cross-section assuming 1000 Å voids are present at one per cent volume fraction. The former is proportional to $Q^{-4}$ provided $Q.R \geqslant 2$. Therefore, at $Q = 0.002$ the cross-

*Table 1* Results of SANS experiments on drawn polypropylene

| | | | | $Q^{\perp}$ Draw direction | | | | $Q^{\parallel}$ Draw direction | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Low $Q$ | | High $Q$ | | Low $Q$ | | High $Q$ | |
| % PPD molecules | Incident neutron wavelength $\lambda$ (Å) | G.p.c. $10^{-3} \times M_w$ | Sample-detector distance (m) | $10^{-3} \cdot M_w$ | $R^{\perp}$ (Å) | $10^{-3} \cdot M_s$ | $R_s^{\perp}$ (Å) | $10^{-3} \cdot M_w$ | $R^{\parallel}$ (Å) | $10^{-3} \cdot M_s$ | $R_s^{\parallel}$ (Å) |
| 3 | 6.68 | 390 | 5 | – | – | 51 | 51 | – | – | 58 | 169 |
| 3 | 6.70 | 390 | 17.6 | 390* | 231 | – | – | 390* | 590 | – | – |
| 10 | 6.67 | 390 | 5 | – | – | 62 | 53 | – | – | 61 | 183 |
| 10 | 7.11 | 390 | 17.6 | 426 | 216 | – | – | 411 | 706 | – | – |
| 10 | 7.13 | 390 | 6 | – | – | 74 | 54 | – | – | – | – |
| 10 | 7.13 | 195 | 6 | – | – | 63 | 60 | – | – | 53 | 160 |
| 10 | 7.12 | 195 | 17.6 | 217 | 113 | – | – | 195 | 367 | 67 | 154 |
| 3 | 6.68 | 165 | 5 | – | – | 38 | 47 | – | – | 36 | 145 |
| 8 | 7.13 | 118 | 6 | – | – | 37 | 39 | – | – | – | – |
| 8 | 6.74 | 118 | 17.6 | 113 | 124 | – | – | 118* | 255 | – | – |
| 3 | 6.70 | 50 | 5 | 45 | 71 | 30 | 39 | 50* | 156 | 25 | 87 |

* Indicates intercept fixed at this $M_w$

Data taken with the scattering vector $Q$ either perpendicular or parallel to the draw direction

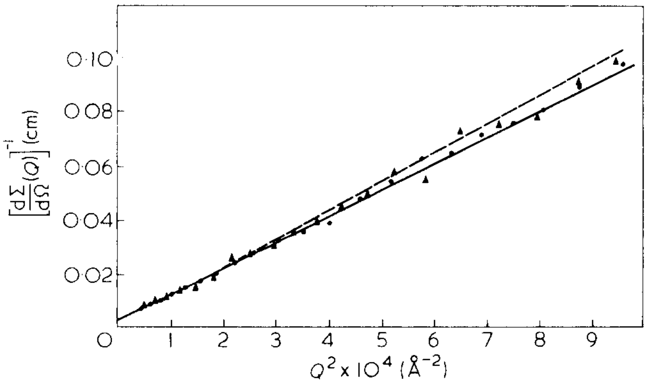

*Figure 2* Comparison of a Guinier's approximation of obtaining $R_z$ and $M_w$ with that using the Debye Function without approximation. Sample undrawn polypropylene containing 10% PPD in a PPH matrix, $M_w$ = 390 000. The full line is the best straight line and the dashed line is a computed fit of a Debye function to the same data

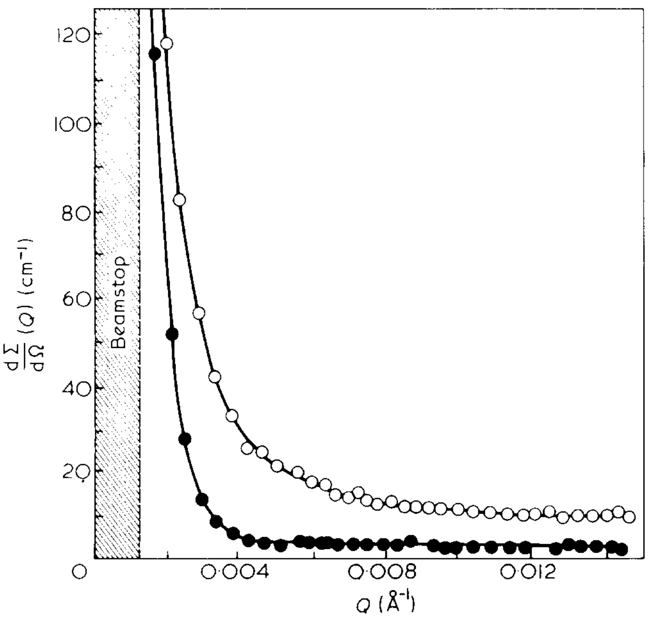

*Figure 3* The measured scattering intensity as a function of $Q$ for samples of drawn polypropylene containing a reduced population of voids. Sample distance 17.6 m, $\lambda$ = 7.1 Å. ● PPH matrix only; ○ matrix + 10% PPD ($M_w$ = 390 K)

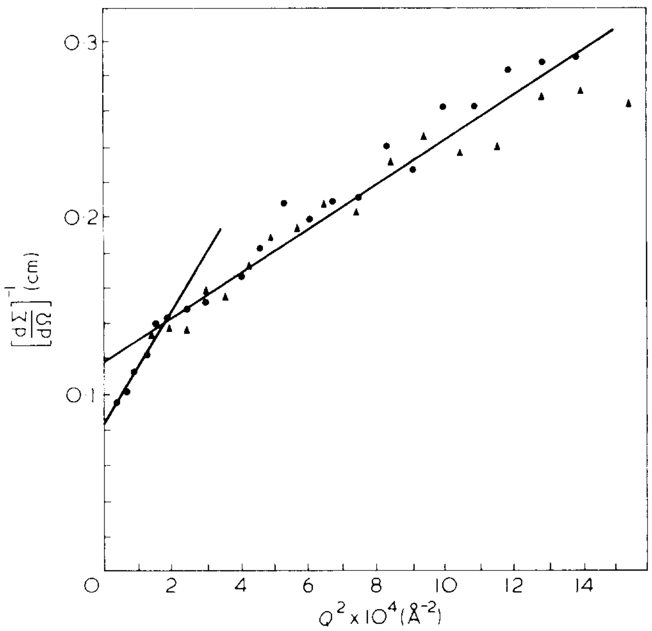

*Figure 4* Guinier plot of Data $Q$-perpendicular to draw direction. Sample drawn polypropylene containing 3% PPD; $M_w$ = 50 000

section expected is 13 cm$^{-1}$. This is an order of magnitude lower than the experimental values. Since neither of these effects are sufficiently large to account for the residual background scattering.

Plotting the data in accordance with equation (1) gives *Figure 4* and the slope and intercept gives values for $\alpha R^2$ and $M_w$. In the case of the drawn systems with $Q^{\perp}$ and $Q^{\parallel}$ *Figure 4* is typical of the type of curve obtained. The tangent to the curve at low $Q$ as $Q \rightarrow 0$ gives values of the intercept close to the value corresponding to the molecular weight of the tagged molecules and the slope refers to a component of the radius of gyration of the whole molecule in the direction of the $Q$-vector. At the higher $Q$-values the tangent to the curve gives an intercept when extrapolated to $Q \rightarrow 0$, as shown in *Figure 4*, corresponding to an entity of lower molecular weight and the slope refers to a component of its radius of gyration in the direction of the $Q$-vector. It has been shown[1] that this is typical of the behaviour of a macromolecule in which

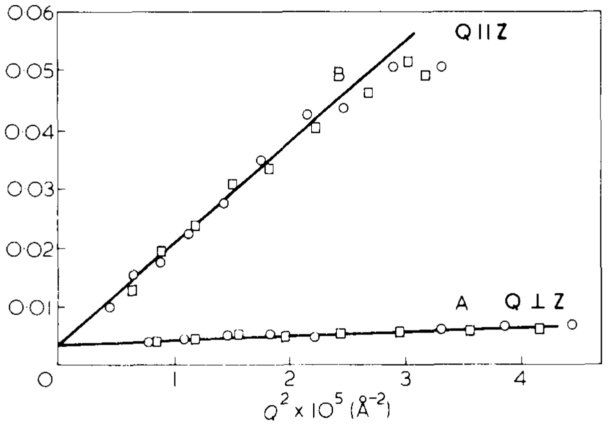

*Figure 5* Guinier plot of data obtained for low *Q*. (A) *Q*-vector perpendicular and (B) *Q*-vector parallel to draw direction. Sample polypropylene containing 10% PPD, $M_W$ = 390 000

the conformation is such that several sub-units of high scattering intensity are separated by molecular fragments of relatively low scattering intensity. In the case of isotropic polypropylene crystallized to 80% crystallinity it was shown that scattering considerations required the separation of the sub-units to be such that, at the appropriate *Q*-range, they behave as discrete scattering entities. In the isotropic case in which the phenomenon was first observed, the sub-units were separated by 150 Å and the radius of gyration for the whole molecule was 60% greater than that observed for the molten polymer[1].

It is experimentally convenient to cover the *Q* range using measurements at different detector distances as shown in *Figures 5* and *6*.

Alternative methods of analysis were tried using computer curve fitting techniques to the complete scattering curves shown in *Figure 3*. It was found that curves could not be fitted using a simple scattering law, assuming one type of scattering particle was present. The types of functions explored using the damped least squares fit included combinations of Gaussian, Debye and Lorentzian. However, by combining the scattering from two particles containing different amounts of scattering material and radii of gyration the whole *Q* range would be covered. A combination of two Gaussian funcions of the type:

$$F^2(Q)=\frac{A}{B}\exp(-Q^2.R^2.\alpha)$$

where *A* is a constant and *B* is a function of the amount of scattering material within the particle. The computer was able, using a least square fitting procedure, to identify values of *B* and *R* which gave the best fit to the curves. These corresponded approximately to the values found using the Guinier approximation in the different *Q*-ranges. An improved procedure was to reduce the number of variables by putting in the molecular weight for the complete molecule. Finally, it can be shown that a Gaussian function for the sub-units approximates to a straight line on extrapolation to relatively low *Q* in the appropriate *Q*-region as is found for the Gaussian function for the whole molecule. Support for the sub-unit analysis of the data is the fact that the molecular weights of the sub-unit for $Q^{\perp}$ and $Q^{\parallel}$ are the same, as shown in *Figure 6*.

Extremely high resolution was required to measure the forward scattering for drawn polypropylene with large molecular weights of the tagged molecules. Typical examples of these curves are shown in *Figure 5* for polypropylene tagged molecules of molecular weight 390 000 in which the *Q*-vector is perpendicular and parallel to the draw direction. In both instances the correct value for the molecular weight of the whole molecule is obtained. These results are summarized in *Table 1* and show that the molecular weights obtained in the drawn system agree reasonably well over the range 50 000 to 390 000 with the known values for the tagged molecules. In particular the data for the *Q*-vector parallel to the draw direction is unambiguous showing that the improved sample preparation techniques are successful.

It is evident that with the detector at 17.6 metres the spectrometer is measuring the dimensions of the whole molecule in both directions. For a further interpretation of the scattering data, as stated previously, we assume as a first approximation that a tagged polymer molecule is distributed over a cylinder with diameter *D* and length *L*. In this case the deduced mean square distances for *Q* parallel and perpendicular to the draw direction determine the cylinder dimensions:

$$D^2=8.(R^{\perp})^2\ ;\quad L^2=12.(R^{\parallel})^2 \qquad (2)$$

The average values $R^{\perp}$ and $R^{\parallel}$ from *Table 1* are listed in *Table 2* for the low *Q*-region and the calculated values of *L* and *D* given.

In *Figure 6* are shown typical curves obtained with these samples with detector distances of 5 or 6 metres. In this part of the *Q*-range intercepts correspond to the amount of scattering material contained within the sub-unit, we represent this quantity by $M_s$. The average values at each molecular weight is summarized in *Table 3*. Comparison with values of $M_s$ previously obtained[1] for draw ratios of 6.0:1 over a similar molecular weight range show that the values of $M_s$ are similar and independent of the draw ratio.

Analysis of the slopes of the curves in *Figure 6* closely follows that previously discussed for the low *Q*-range and

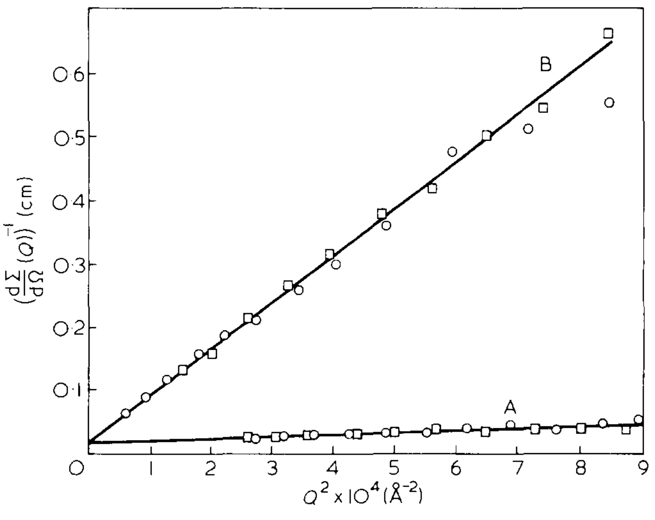

*Figure 6* Zimm representation of data obtained at high *Q*.
(A) *Q*-vector perpendicular to draw direction. (B) *Q* - vector parallel to draw direction. Sample 10% PPD in PPH matrix $M_W$ = 390 000

*Table 2* Summary of SANS and SAXS data obtained at low $Q$ structural information for complete PPD molecule

| Solution data for PPD molecules | | SANS Undrawn | | SAXS Undrawn | SANS Drawn $Q^{\perp}$ to $Z$ | | SANS Drawn $Q^{\parallel}$ to $Z$ | | SAXS Drawn | | Dimensional changes on drawing | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^{-3} \cdot M_w$ | $M_w/M_n$ | $M_w \cdot 10^{-3}$ | $R_z$ (Å) | $d$ (Å) | $10^{-3} \cdot M_w$ | $R^{\perp}$ (Å) | $10^{-3} \cdot M_w$ | $R^{\parallel}$ (Å) | $d$ (Å) | $M_w/M_s$ No. of sub-units | $\frac{R^{\perp}}{R_z}$ | $\frac{R^{\parallel}}{R_z}$ | $D$ (Å) | $L$ (Å) | $\frac{L}{d}$ |
| 390 | 1.60 | 406 | 260 | 135 | 426 | 216 | 411 | 672 | 240 | 6.3 | 0.85 | 2.6 | 622 | 2328 | 9.7 |
| 195 | 1.95 | 222 | 207 | 135 | 217 | 113 | 195 | 367 | 240 | 3.1 | 0.60 | 1.8 | 320 | 1271 | 5.3 |
| 118 | 1.55 | 113 | 155 | 135 | 113 | 124 | 118 | 255 | 240 | 3.2 | 0.80 | 1.7 | 351 | 883 | 3.68 |
| 50 | 2.40 | | 110 | 135 | 45 | 71 | 50 | 156 | 240 | 1.67 | 0.65 | 1.42 | 301 | 540 | 2.25 |

Draw temperature, 145°C; Draw ratio, 8 : 1

we write for the radius of gyration:

$$D_s^2 = 8.(R_s^{\perp})^2 \ ; \quad L_2^s = 12.(R_s^{\parallel})^2 \qquad (3)$$

The calculated values of $D_s$ and $L_s$, the diameter and length of the cylinder enclosing the fragment of the tagged molecule which constitutes the sub-unit, are listed in *Table 3*.

*Conformation of the molecular fragment within the sub-unit*

Comparison of the length of the sub-unit ($L_s$) with SAXS value for the d-spacing in the drawn polymers which is 240 Å, shows that the molecular fragment is folded between two lamellae. This structural feature has been identified in all examples of isotropic polypropylene[6-8] and derives from the requirement for the molecule to fold and yet inhabit many lamellae. This produces a molecular fragment which connects adjacent lamellae. The neutron scattering length, $l_n$ determined from analysis of the SANS data for the isotropic systems is given in *Table 4*. It is evident that $L_s$ and $l_n$ and the ratios $L_s/d$ and $l_n/d$ are similar. In the isotropic samples the values of $l_n$ were obtained by extrapolation to low molecular weights except for the highly annealed sample where $R$ becomes independent of molecular weight over a wide range of molecular weights and equal to $l_n/\sqrt{12}$. This quantity has now been obtained with the drawn samples over a range of molecular weights. These results confirm the existence of this connecting fragment as a basic structural feature of crystalline polyolefins.

The diameter of the sub-unit allows an estimate to be made of the average distance between the stems ($W$) within it. If $N$ is the number of stems equal to the lamellae thickness by SAXS, $X$ is the crystallinity of the sample, then from the total length of the molecule within the sub-unit we have:

$$L(M_s) = d.X.N + (N-1).S(W)$$
$$L(M_s) = 0.0517.M_s \qquad (4)$$

where $W$ is the average length of the molecule connecting stems. Also from the cross-sectional area of the sub-unit we have the relationship:

$$\frac{N.\pi.W^2}{4} = \frac{\pi D_s^2}{4} \qquad (5)$$

Equation (4) takes into account that the thread length $s(W)$ between two consecutive stems separated by a distance $W$ perpendicular to the cylinder axis, can vary. If the next stem jumps into a neighbouring lamella $s(W)$ is $d(1-x) = 108$ Å or if there is adjacent reentry $s(W)$ is about 8 Å. If the reentry place is determined by a random walk in the amorphous layer $s(W)$ can be much larger than $d(1-x)$. Density arguments for the amorphous layers lead to $s(W) \simeq d(1-x) = 108$ Å as an average value. With this assumption one calculates from (4) and (5) $N$ and $W$ and these values are listed in *Table 3*. The $W$ values are typically 40 Å, i.e. stems belonging to the same molecule are separated by 5 to 8 stems which belong to other chain molecules. In *Figure 7(a)* a projection at right angles to the draw direction showing a matrix of stems belonging to other macromolecules. In *Figure 7(b)* is a projection in the draw direction of the sub-unit showing

*Table 3* High $Q$ data structure of the sub-unit
Draw temperature, 145°C, draw ratio, 8 : 1, d spacing, 240 Å

| G.p.c. | $Q \perp Z$ | | $Q \parallel Z$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $M_w \times 10^{-3}$ | $10^{-3} \cdot M_s$ | $R_s^{\perp}$ (Å) | $M_s \cdot 10^{-3}$ | $R_s^{\parallel}$ (Å) | $D_s$ (Å) | $L_s$ (Å) | $W$ (Å) | $N$ | $L_s/d$ |
| 390 | 62 | 53 | 55 | 178 | 150 | 519 | 38 | 15 | 2.1 |
| 195 | 63 | 60 | 60 | 157 | 170 | 588 | 43 | 15 | 2.45 |
| 165 | 38 | 47 | 36 | 145 | 132 | 457 | 47 | 9 | 1.9 |
| 118 | 37 | 39 | – | – | 110 | 386 | 35 | 9 | 1.6 |
| 50 | 30 | 39 | – | – | – | – | 40 | 7 | – |
| Drawn at ambient temperature (21°C). Draw ratio 6 : 1, d-spacing 145 Å | | | | | | | | | |
| 389 | 55 | 61 | – | – | 172 | – | 47 | 13 | – |
| 165 | 38 | 51 | – | – | 144 | – | 47 | 9 | – |
| 116 | 32 | 47 | – | – | 133 | – | 47 | 8 | – |

*Table 4* Value of the SANS scattering length ($l_n$) for isotropic polypropylene

| Type of crystallized condition | Crystallinity (%) | SAXS $d$ (Å) | SANS $l_n$ (Å) | $l_n/d$ |
|---|---|---|---|---|
| Quenched[6] | 54 | 122 | 250 | 2.0 |
| Annealed 24 h[6] | 63 | 202 | 350 | 1.7 |
| Slow cooled[6] | 70 | 245 | 459 | 1.8 |
| Prolonged annealing | 80 | 345 | 690 | 2.0 |

all the stems with their connecting fragments.

Finally, it is of value to compare the data for the sub-unit when the material has been hot drawn with that previously obtained for the cold drawn sample[1]. The latter data is reproduced in part in *Table 3* and is restricted to information obtained with the $Q$-vector at right angles to the draw direction. This being the only information available at the time. It is evident that the sub-unit is of similar cross-section and the length of polymer chain folded to produce the sub-unit is of similar dimension. Also both of these quantities show a small dependence on the molecular weight of the whole macromolecule.

We have investigated the possibility that the dimensions of the sub-unit might be related to the crystallite size determined using WAXS. This was found to be close to the predicted value obtained from the d-spacing and the crystallinity. The crystallite size in these samples varies between 135 and 165 Å in thickness.

### *Analysis of the low Q-data*

The scattering data at low $Q$ refers to the total macromolecule. Comparison of the molecular weight in this region with those for the PPD values determined in solution confirm this. *Table 2* summarizes this information for undrawn and drawn samples. The agreement with $Q$-vector parallel and at right angles to the draw direction is excellent under the circumstances. It is interesting to compare the dimensional changes on drawing as shown by the ratios $R^{\perp}$ and $R^{\parallel}$ to the undrawn molecule $R_z$. Surprisingly, the elongation of the molecule is modest compared to the 8 times extension of the material. This is similarly matched by only an equally small contraction of the molecules perpendicular to $Z$ of 15–40%.

The whole molecule may be considered as being contained within a cylinder of length $L$ and diameter $D$ the values of which are computed from the components of its radius of gyration. These two quantities are highly sensitive to the molecular weight of the polymer. Similarly the number of sub-units obtained from the ratio of $M_w/M_s$ is also directly related to the molecular weight of the polymer.

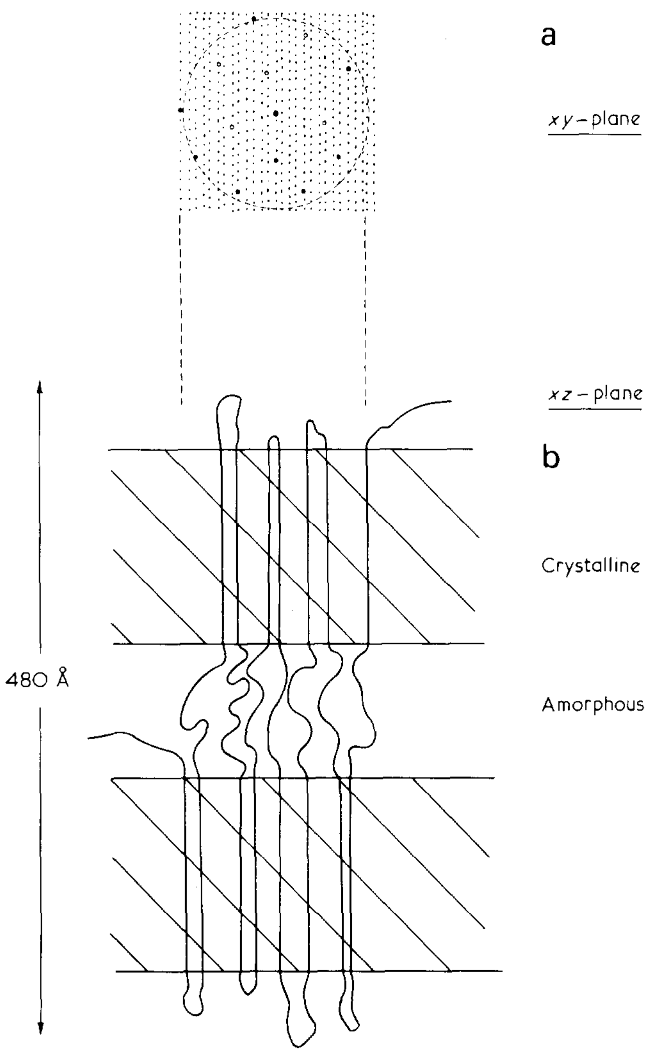

*Figure 7* Organization of stems in the crystalline regions derived from data at high $Q$. (a) Shows the possible relative position of stems in the plane of the lamellae ($xy$), $Q^{\perp}$ data. The smallest dots represent stems of other molecules; ■ stems in lower lamellae; ○ stems in upper lamellae

It is necessary that the arrangement of the sub-units

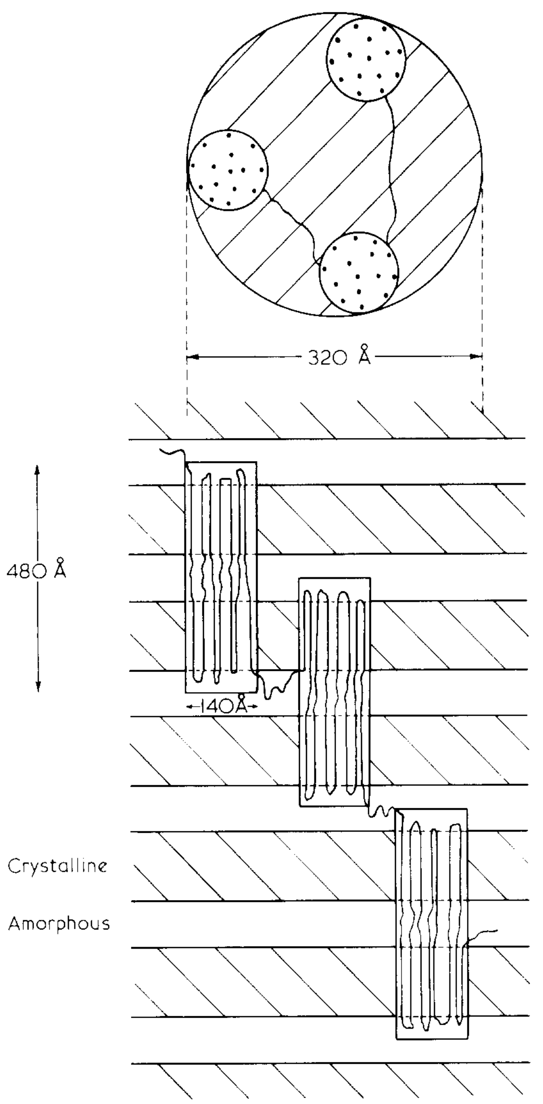

*Figure 8* Organization of sub-units derived from data at low *Q*. (a) Shows possible relative position of sub-unit in the *xy* plane. (b) Shows two possible ways sub-units are connected as a projection in the *xz* plane

within the space described by the dimensions $D$ and $L$ should be such that they are separated sufficiently to be 'seen' as discrete entities at the higher $Q$ values. If $\delta$ is the average distance between the centres of the neighbouring units perpendicular to the draw direction. Then we have:

$$r\left(\frac{\pi\delta^2}{4}\right)=\frac{\pi D^2}{4} \tag{6}$$

where $r = M_w/M_s$ the number of sub-units per polymer molecule leads to values of $\delta$ of 200 Å. It has been shown previously[1], that in the isotropic case, a separation of 150 Å was sufficient for the centres to scatter as discrete entities. The data is, therefore, consistent with this requirement.

The number of lamellae in the $Z$-direction over which the sub-units are distributed is the ratio $(L/d)$ and values are listed in *Table 2*. This information enables the arrangement of the sub-units with respect to one another to be described.

The overall organization of the macromolecules with respect to each other is therefore seen to be the sum of two interpenetrating structural systems, in which each lamellae of the sub-unit is joined to its neighbour by much longer tie fragments of macromolecules. Thus two types of connective molecular fragments, present in the amorphous regions, are involved in joining the crystalline domains together. It should be pointed out that in a previous publication[1] it was considered that only one type of tie molecule was present and the sub-units were one lamellae thick. In the absence of data with $Q^{\parallel}$ to $Z$, due to the presence of voids, this was the simplest structure to choose. It is now seen, that at the higher molecular weights, the molecular organization is more complex. However, at molecular weights below 100 000 there appears to be structural differences imposed by the shorter molecule. The data at $M_w = 50\,000$ in *Table 2* suggests that only one sub-unit is present at these molecular weights. It must be remembered that the PPD molecule of $M_w = 50\,000$ inhabits a similar PPH matrix to the higher molecular weight species and that it will adopt a conformation consistent with the latter. It is unlikely that any further separation of lamellae will occur. The data in *Table 2*, in fact, shows that all the molecule is contained within a sub-unit. Further work is planned at these lower molecular weights in order to follow the conformation changes resulting from shortening of the molecule.

### *Kratky representation of high* Q*-data*

In *Figure 9* the Kratky plots for the same samples before and after drawing are shown. It is evident that there is a significant difference with the $Q$-vector perpendicular and parallel to the draw direction. These are the largest changes produced in curves of this kind. No other physical treatment is known which influences the magnitude of the assymptotic value of $I(Q).Q^2(=G)$ in this way. Previous studies on isotropic systems showed that $G$ was independent of the molecular weight, crystallinity, and d-spacing. A possible explanation for the large difference between $G^{\perp}$, $G^{\parallel}$ and $G^{i}$ is as follows.

We modify the Debye function to apply it to anisotropic systems:

$$F_n(Q)=\frac{2N}{y^2}(e^{-y}-1+y)=\begin{cases} N \text{ for } y=0 \\ \dfrac{2N}{y} \text{ for } y \gg 1 \end{cases} \tag{7}$$

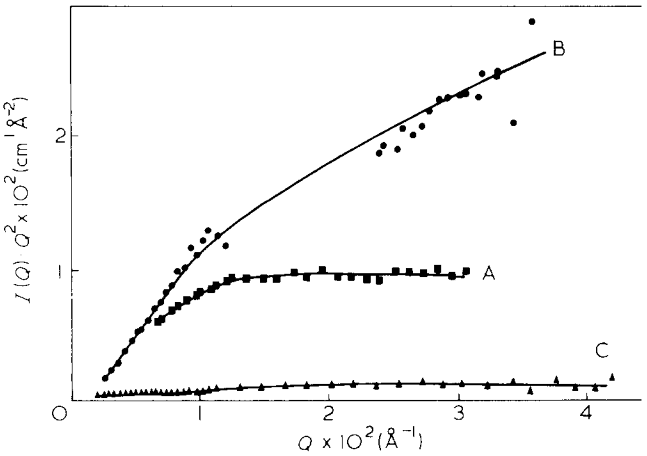

*Figure 9* Plot of $I(Q).Q^2$ against $Q$ for polypropylene containing 10% PPD. (A) Undrawn, $d$ = 135 Å. (B) Drawn with $Q$-vector perpendicular to draw direction. (C) Drawn with $Q$-vector parallel to draw direction. Draw ratio 8 : 1 $M_W$ = 390 000 and $d$ = 240 Å

*Table 5* Concentration of deuterated monomer belonging to the same macromolecule units found for different conformation of macromolecules

| Arrangement | $10^6$ $\bar{n}$ Monomer units (Å)$^{-3}$ |
|---|---|
| Isotropic quenched | 8.6 |
| Adjacent stems in crystal lattice<br>No amorphous | 1410.0 |
| Sub-unit of drawn molecule | 136 |

$$y=\tfrac{1}{2}aN.Q^2 \qquad (8)$$

The anistropy of the scattering function is allowed for by assigning different values to the coefficients $\underline{a}^2$for the different $Q$ directions. This is achieved with the equation

$$(\underline{r}_{ee}\hat{Q})^2=a^2.N \;;\quad \hat{Q}=\frac{Q}{|\underline{Q}|} \qquad (9)$$

where $\underline{r}_{ee}$ is the end to end distance vector and $\hat{Q}$ the unit vector of $Q$ in the $Q$ direction. For large $y$, $G$ is given by:

$$G=\{2/(\tfrac{1}{2}a^2)\}=\frac{2N}{3.S^2(\mathrm{N})} \qquad (10)$$

where $S^2(N)$, is the component in the Q direction of the mean square distances of $N$-segments with respect to their centre of mass. The scattering function $F_n(Q)$ is proportional to the number of coherent scattering segments. At small $Q,y \ll 1,F_n(Q)=\text{const.}\ N$, $N$ being the number of bonds in the whole molecule and at large $Q$ it is equal to $\underline{b}$ where the latter is defined by:

$$\tfrac{1}{4}a^2.b=\left(\frac{1}{Q}\right)^2 \qquad (11)$$

and

$$F_n(Q)=\text{const.}\,b=\text{const.}\frac{4}{a^2Q^2} \qquad (12)$$

where $b$ is the number of redefined scattering segments.

It has been shown that for isotropic polypropylene

$$G^i=\frac{2N}{R_z^2} \qquad (13)$$

it follows from equation (11) that in general

$$G=\frac{2N}{3.\alpha.R} \qquad (14)$$

The ratios of the assymtotic values of $F_n|Q|.Q^2$ are:

$$G^{\perp}{:}G^{i}{:}G^{\parallel}\frac{4{\cdot}N}{(R^{\perp})^2}{:}\frac{6N}{(R_z)^2}{:}\frac{2N}{(R_{\parallel})^2} \qquad (15)$$

$$=3{:}1{:}0.12$$

values of $N$ are obtained from $M_w$ for the isotropic case and $M_s$ for the drawn samples. Using these values and the appropriate values for the radii of gyration we obtain the ratios of $G$'s consistent with the maximum intensities observed.

The lower scattering intensity in the $Q$-parallel direction is accounted for by the fewer number of segments required to traverse a distance related to $1/Q$. In this direction the segment length is proportional to the d-spacing and $b$ is therefore small. In the case of the $Q$-perpendicular direction the segment length is the distance between stems which is much smaller and therefore $b$ is proportionally larger.

### *Physical changes occurring on 'necking' of a thermoplastic*

In *Table 5* are compared the value of $\bar{n}$, the number of monomer units per unit volume for the sub-unit given by:

$$\bar{n}=(M_s/M)/(L_s.\pi.D_s^2/4) \qquad (16)$$

with that for the undrawn material. The latter was calculated assuming that the arrangement of deuterated stems is close to a Gaussian distribution. The formation of the sub-unit on drawing has resulted in a 16-fold increase in the value of $n$ which is comparable with the draw ratio of 8:1. In *Table 5* the value of $n$ for a pure crystal of deuterostems with no amorphous material is also given.

It is evident from *Table 5* that the formation of the sub-unit has resulted in a major concentration of the stems of the same molecule within the lamellae.

### *Polyethylene*

Preliminary studies show that on drawing the sub-unit is formed. Curves similar to *Figure 1* are obtained with the $Q$-vector perpendicular to the draw direction. However, the elimination of voids in the case of polyethylene is more difficult and no data is available with the $Q$-vector parallel to the draw direction.

## CONCLUSIONS

(1) The overall dimensional changes occurring on drawing polypropylene at a draw ratio of 8:1 are modest. An extension of between 1.7 and 2.5 times from what it was in the melt, with a contraction perpendicular to the draw direction of 20 to 40%. The length of the cylinder containing the whole molecule is 10–20% of the length of the molecule in the fully extended form. The polymer chain must, therefore, be folded up 5–10 times.

(2) It is our interpretation of the data at higher $Q$ that the chain is non-uniformly distributed within the cylinder and that there are clusters of stems connected by molecular fragments. Support for this view is that the scattering curves cannot be fitted by any reasonable scattering law for a single particle; the amount of scattering material contained within the sub-unit determined with $Q^{\perp}$ and $Q^{\parallel}$ to $Z$ are similar; the dimensions of the sub-unit are independent of the molecular weight of the polymer; the Kratky plot for $Q^{\perp}$ can be explained by an increase in concentration of stems compared to the isotropic system.

(3) The double stem present in the isotropic material persists in the drawn state since the sub-unit is approximately two lamellae in length.

(4) The effect of drawing is to increase, up to 16 times,

the number of double stems belonging to the same macromolecule per unit volume compared to the undrawn material. However, each stem is approximately 40 Å from its nearest neighbour and is surrounded by the stems belonging to other molecules.

(5) The sub-units are not aligned and are displaced approximately 200 Å from each other. Each sub-unit is surrounded by sub-units belonging to other molecules connected by long molecular fragments which scatter neutrons relatively little.

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## REFERENCES

1 Ballard, D. G. H., Burgess, A. N., Nevin, A., Cheshire, P., Longman, G. W. and Schelten, J. *Macromolecules* 1980, **13**, 677
2 Picot, C. *et al.*, *Macromolecules* 1977, **10**, 436; Clough, S. B., Maconnachie, A. and Allen, G. *Macromolecules* 1980, **13**, 774
3 Guinier, A. and Fournet, G. 'Small Angle Scattering of X-rays', Chapman and Hall Ltd., London, 1955, p 26
4 Tangari, C., Summerfield, G. C., King, J. S., Berliner, R. and Miloner, D. F. R. *Macromolecules* 1980, **13**, 1546
5 Akcasu, A. Z., Summerfield, G. C., Jahshan, S. N., Han, C. C., Kim, C. Y. and Yu, H. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 863
6 Ballard, D. G. H., Longman, G. W., Crowley, T. L., Cunningham, A. and Schelten, J. *Polymer* 1979, **20**, 399
7 Ballard, D. G. H., Schelten, J., Longman, G. W., Crowley, T. L. and Burgess, A. N. *Faraday Discussion* 1979, **68**, 279
8 Stamm, M., Schelten, J. and Ballard, D. G. H. *Colloid Polym. Sci.* 1981, **259**, 286
9 Natta, G. and Corradini, P. *J. Polym. Sci.* 1959, **39**, 239
10 Ballard, D. G. H., Cheshire, P., Longman, G. W. and Schelten, J. *Polymer* 1978, **19**, 379
11 Yoon, D. Y. and Flory, P. J. *Polymer* 1977, **18**, 509
12 Stamm, M., Fischer, E. W., Dettanmaier, M. and Couvert, P. *Faraday Discussion* 1979, **68**, 263