

Small-angle neutron scattering studies of isotropic polypropylene

D. G. H. Ballard, P. Cheshire and G. W. Longman
ICI Corporate Laboratory, The Heath, Runcorn, Cheshire, UK

and J. Schelten

Institut für Festkörperforschung der Kernforschungsanlage Jülich, West Germany
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Small-angle neutron scattering studies have been made of molten and crystalline polypropylene using samples containing small amounts of deuterated polypropylene in a protonated polypropylene matrix. The specimens were characterized by small- and wide-angle X-ray scattering to determine the d -spacing and the degree of crystallinity χ and by gel permeation chromatography to determine molecular weight, M_w , and molecular weight distribution. The degree of crystallinity was varied from 0.5 to 0.7, the d -spacing from 120 to 250 Å and the molecular weight from 34 000 to 1 540 000. Clustering was not observed. The radius of gyration $\langle s^2 \rangle_w^{1/2}$ of the tagged molecules was approximately proportional to $M_w^{1/2}$ and almost independent of d and χ . In the melt similar values were obtained which are, within experimental uncertainties, the same as in a θ -solution. For $\langle s^2 \rangle_w \kappa^2 \gg 1$ the scattering law approaches a κ^{-2} dependence. The results are discussed with reference to the chain-folded model but a fit cannot be obtained over all molecular weights. A simple random coil model fits the neutron scattering data partly but this does not explain the origin of the d -spacing.

INTRODUCTION

Small-angle neutron scattering (SANS) from polymer molecules tagged by deuteration has proved successful in studying amorphous polymers in the solid state¹⁻³ and more recently polyethylene in the molten and crystalline states⁴⁻⁶. Several experimental problems have been identified in the study of crystalline polymers. These include void scattering, which was overcome, by using deuterated polyethylene (PED) in a protonated polyethylene (PEH) matrix, and clustering phenomena of the PED molecules on crystallization. The latter was avoided by matching melting points between PEH and PED molecules and by improving mixing, but it was only possible to study samples which had been crystallized by rapidly quenching or the molten polymer. In both cases⁵ it was shown that the radius of gyration ($\langle s^2 \rangle_w^{1/2}$) was related to the molecular weight by an identical relationship and similar to that found by light scattering for polyethylene dissolved in a θ -solvent.

These experiments have since been repeated⁷ and the most likely structure, therefore, for the molecules is an unperturbed coil. However, with such a conformation it is difficult to imagine how the chain is organized in the crystalline regions to give the long spacing. As already stated, slow crystallization or annealing leads to clustering of the PED molecules and it was not possible to comment unambiguously on their structure because of this. Crystallization to 5 kbars also gave clustered PED molecules but here conformational interpretation was possible for polymer molecules whose stretched length was comparable with the large lamellae thickness produced (2000 Å)⁶. In these experiments⁴ it was shown for the first

time that polyethylene can, in fact, fold in bulk crystallized isotropic samples.

These experiments leave unanswered the question, do polyolefins crystallize with chain-folding when the polymer is slowly cooled or annealed at ambient pressures? It has been found that polypropylene (PPH) differs from polyethylene in that clustering of the deuteropolypropylene (PPD) occurs less readily and samples of slowly cooled and annealed polypropylene can be obtained in which the PPD molecules are statistically distributed in the matrix. In this paper we give an account of the neutron scattering studies with this polymer.

EXPERIMENTAL AND RESULTS

Polypropylene and deuteropolypropylene were synthesized using organometallic polymerization catalysts with special features that give polymers with very high tacticities compared with conventional Ziegler systems. The polymers were freed from catalyst impurities and atactic material by conventional means.

The tacticity of the protopolymer was determined by ¹³C n.m.r. and found to be 97–99% isotactic in all cases. It was fractionated into five fractions with molecular weights (M_w) 46 000 to 1 135 000 and melting points 163° to 166.5°C, measured at 5°C/min. Hot *ortho*-dichlorobenzene (ODCB) was used as solvent for the fractionation by the co-precipitation technique with triethylene glycol as non-solvent. Molecular weights were measured by gel permeation chro-

matography in ODCB as solvent and National Physical Laboratory Standard polypropylene samples were used for calibration. The molecular weight polydispersity can be described by a log normal distribution function with M_w/M_n values as given in Table 2. According to this distribution function weight-average values were calculated from measured z-average radii of gyration.

The level of deuteration in deuteropolypropylene was obtained by integrating the n.m.r. trace obtained on a 220 MHz machine for the protopolymer and comparing this with a PPD solution of the same concentration, run under the same conditions. The fractions examined were at least 95% deuterated. The same fractionation procedure was used to give fractions with values of M_w between 34 000 to 1 540 000 and values of T_m ($5^\circ\text{C}/\text{min}$) between 161° and 164°C . Comparison of values of T_m for PPD and PPH obtained on annealed samples as well by crystallization measurements at $0.62^\circ\text{C}/\text{min}$ using a Perkin-Elmer DSC-2 shows no measurable difference in thermal behaviour bet-

ween these polymers. In this respect polypropylene differs from linear polyethylene where a 6°C difference in melting temperature was detected between deuterated and protopolymers.

The components of blends were chosen to match crystallization temperature and molecular weight as closely as possible from the available fractions. Components were mixed as powders and the mixture dissolved in ODCB and precipitated in methanol, washed and dried in a vacuum oven. Samples were compression moulded to give plaques 1 mm in thickness and quenched into cold water; these samples are identified in the Tables as quenched samples. Some of these were annealed by heating to 137°C and maintaining this temperature for 24 h; these samples are identified in the Tables as annealed samples. Finally, quenched samples were heated well above the melting point and then cooled at 139°C in order to crystallize them slowly and isothermally; these are identified in the Tables as isothermally crystallized.

Crystallinities were derived from relative areas under the defraction peaks obtained with a Philips diffractometer used in the transmission mode ($\text{CuK}\alpha$ radiation). Measurements of the low-angle spacing were carried out with a Kratky camera fitted with a graphite monochromator using $\text{CuK}\alpha$ radiation. The intensity data (I) were desmeared using standard computer techniques and the low-angle X-ray scattering obtained from a plot of $I(\kappa)$ vs. κ , where $\kappa = 4\pi\sin\theta/\lambda$. As a typical result, a desmeared X-ray small-angle scattering pattern is shown in Figure 1a, in which the first maximum is well resolved. In Figure 1b the same scattering data, but plotted in the form $\kappa^2 I(\kappa)$ vs. κ , is shown. From the maximum positions of such curves the d -spacings given in Table 1 were calculated using Bragg's law.

The extrapolated forward scattering cross-section, measured in absolute units is a very sensitive indicator as to whether the PPD molecules are clustered or statistically distributed. Only for statistical distribution the following relation holds:

$$\frac{1}{cK_N} \left(\frac{d\Sigma}{d\Omega} \right)_{\kappa=0} = \frac{1}{M_w} \quad (1)$$

where

$$K_N = \rho N \left[\frac{vy(b_D - b_H)}{M\alpha} \right]^2 \quad (2)$$

where M is the mass of the chain segment $\text{C}_3\text{D}_{6,y}\text{H}_{6(1-y)}$, y is the degree of deuteration, $v (= 6)$ is the number of H places of a chain segment, N is Avogadro's number, b_D and b_H are the scattering lengths of D and H atoms, ρ is the density of the polymer and c the concentration of tagged mole-

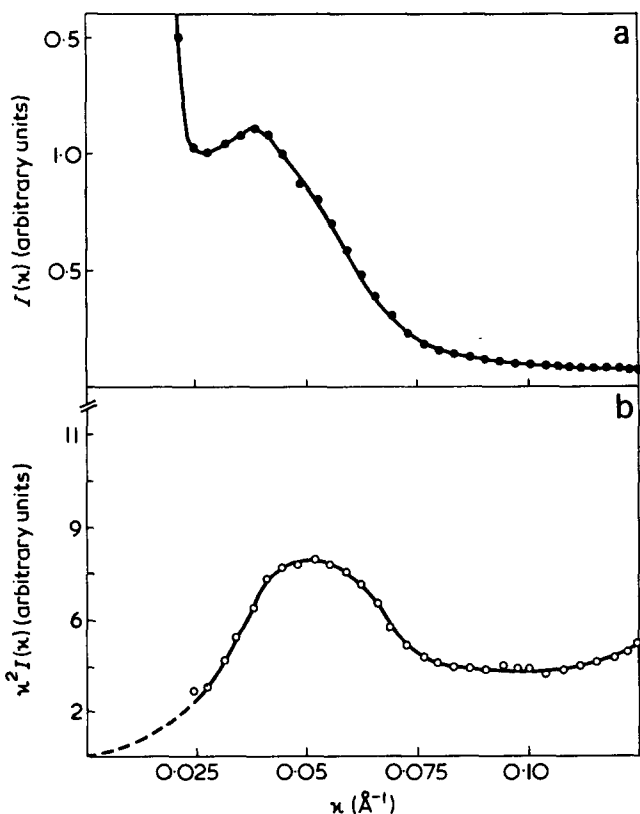


Figure 1 Small-angle X-ray scattering pattern from quenched polypropylene (PPQ2) $d = 117 \text{ \AA}$

Table 1 Low-angle spacings (d) (\AA) and crystalline fraction (χ) of polypropylene samples containing 3% PPD molecules

Sample	Quenched		Annealed		Crystallized	
	d	χ	d	χ	d	χ
1	120	0.54	190	0.62	239	0.69
2	117	0.56	189	0.63	239	0.68
3	130	0.55	198	0.61	246	0.70
4	130	0.58	239	0.64	276	0.69
5	—	0.59	—	—	—	—
6	114	0.54	198	0.61	245	0.67

cules. The extrapolated forward scattering cross-section is obtained from the usual linear plots $1/(d\Sigma/d\Omega)$ vs. κ^2 . Where there is no clustering, M_w , determined from neutron measurements [equation (1)], should equal the known molecular weight of the tagged molecules previously determined by other means prior to blending. Where clustering does occur, curves obtained by plotting $1/(d\Sigma/d\Omega)$ against κ^2 are still linear⁴ but the value of the intercept now gives the molecular weight of the cluster $(M_w)_{app}$. The ratio $(M_w)_{app}/M_w$ is a measure of the number of molecules in the cluster and has been used diagnostically to determine the absence of clustering⁵. A typical plot of the scattering data used to obtain values of M_w and the radius of gyration $\langle s^2 \rangle_w^{1/2}$ is shown in Figure 2 and all the results of this analysis are in Table 2.

Measurements were also carried out at higher angles similar to those reported for polystyrene^{2,3} and polyethylene⁵. A typical curve obtained for all molecular weights, except the lowest, is shown in Figure 3 and is similar to those obtained with the quenched and annealed samples. Unclustered polyethylene samples give identical curves⁵. When clustering does occur, as is indicated from the extrapolated forward scattering for the specimen with the lowest molecular weight,

a maximum in the Kratky plot is obtained identical to that observed with the clustered polyethylene samples⁵.

At higher κ values the cluster effect disappears and therefore the quantity Q defined by:

$$Q = \frac{\kappa^2 \langle s^2 \rangle_w (d\Sigma(\kappa)/d\Omega)}{cK_N M_w} = \kappa^2 \langle s^2 \rangle_w [F(\kappa)]^2 \quad (3)$$

becomes a molecular parameter where $[F(\kappa)]^2$ is the form factor of the polymer molecules. From the Kratky plots (see Figure 3) it is indicated that the scattering function approaches a κ^{-2} dependence i.e. the values of Q as given in Table 2 are independent for κ values larger than 0.025 Å. For a Gaussian chain, for which Debye's scattering law is an excellent approximation, a κ^{-2} dependence is obtained for $\kappa^2 \langle s^2 \rangle_w \gg 1$ with $Q = 2$. The values of Q as given in Table 2 are on average close to 2.

It is evident from Figure 4 that the data given in Table 2 fit a Gaussian distribution of scattering segments except for the lowest molecular weight. The quenched and annealed samples give almost identical data despite the fact that

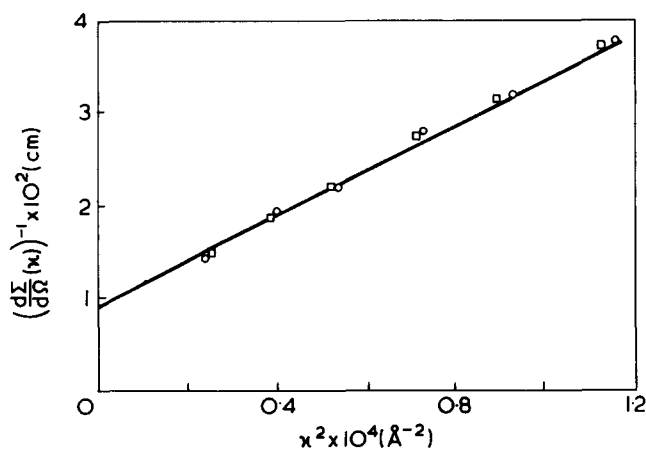


Figure 2 Plot of $d\Sigma/d\Omega$ vs. κ^2 for sample PPC3. $M_w = 334\,000$, PPH matrix plus 3% PPD isothermally crystallized. PPH/3% PPD; $M_w = 340\,000$, crystallized

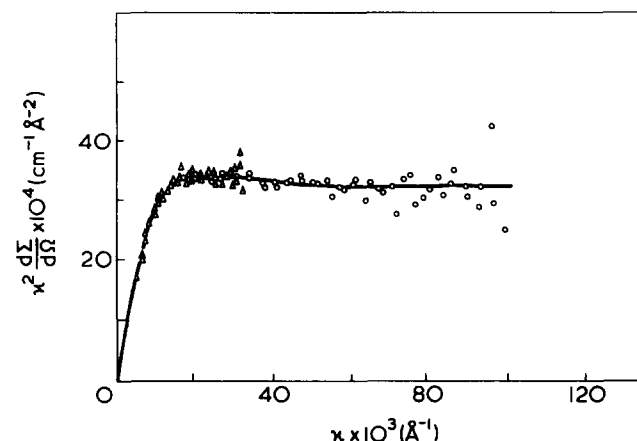


Figure 3 Kratky plot for scattering from 0.03% PPD. Isothermally crystallized polypropylene. Sample PPC3, $M_w = 340\,000$, PPH/3% PPD crystallized

Table 2 Neutron scattering data for polypropylene with PPH matrix and PPD tagged molecules. The concentration of the latter is 0.03 g/g. measurements at 23°C

Sample No.	PEH $M_w \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	$(M_w)_{app} \times 10^{-3}$	$\frac{(M_w)_{app}}{M_w}$	$\langle s^2 \rangle_w^{1/2}$ (Å)	$\langle s^2 \rangle_w^{1/2}$ (Å)	$\frac{\langle s^2 \rangle_w^{1/2}}{M_w^{1/2}}$	Q
Quenched:									
PPQ1	46	34	2.52	64	1.88	180	113	0.61	4.1
PPQ2	46	140	1.68	118	0.84	180	139	0.37	
PPQ3	56	340	2.02	299	0.88	255	179	0.31	2.17
PPQ4	105	575	1.56	529	0.92	320	256	0.34	
PPQ6	114	1540	1.48	1480	0.96	503	413	0.39	1.7
Annealed:									
PPA1	46	34	2.52	74	2.17	180	113	0.61	3.3
PPA2	46	140	1.68	122	0.87	190	147	0.39	
PPA3	56	340	2.02	299	0.88	265	186	0.32	2.4
PPA4	105	575	1.56	587	1.02	347	278	0.37	
PPA6	114	1540	1.48	1509	0.98	514	423	0.40	1.7
Isothermally crystallized:									
PPC1	46	34	2.52	240	7.1	235	148	0.8	1.7
PPC2	46	140	1.68	185	1.32	235	181	0.48	
PPC3	56	340	2.02	347	1.02	290	218	0.37	2.5
PPC4	105	575	1.56	667	1.16	368	296	0.39	
PPC6	114	1540	1.48	2002	1.30	580	477	0.38	1.8

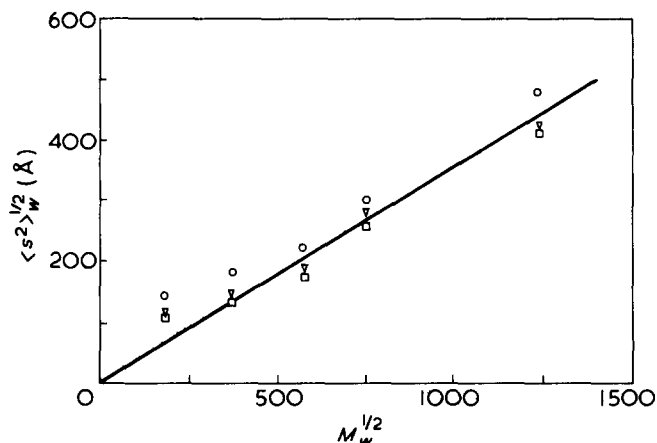


Figure 4 Plot of $\langle s^2 \rangle_w^{1/2}$ versus M_w of data in Table 2. PP: □, Quenched; △, annealed; ○, isothermally crystallized

there is a major increase in d -spacing as a result of differing thermal treatments. With the isothermally crystallized samples there is some scattering in results but the discrepancies are not significant and the law is followed reasonably well.

A particularly important feature to all the results in Table 2 is that, despite the fact that the d -spacing has increased by more than a factor of 2, by isothermally crystallizing the samples the values of $\langle s^2 \rangle_w^{1/2}$ for a particular molecular weight are similar.

Furthermore, the values of Q are of the order of 2 and there is no significant difference between quenched, annealed or crystallized samples.

Specimens PP Q 1-6 were finally heated up to temperatures of 200° and 220°C, which are beyond the melting point, and measurements carried out at these temperatures for several hours in the molten state.

During this heat treatment in some instances there was a loss of material due to decomposition of the sample material. This effect caused some uncertainty in how to correct for background scattering. In addition, because of this loss of material during the measurement it was not possible to determine in absolute units the forward scattering cross-section and, therefore, measurement of the molecular weights in the melt was not possible. Furthermore, it was virtually impossible to obtain reliable scattering data in the higher κ region, where data must be collected for a very long time and where precise background scattering measurements are necessary.

The scattering patterns in the molten state were similar to the patterns in the crystalline state. The radii of gyration $\langle s^2 \rangle_w^{1/2}$ calculated from these scattering curves, measured in the molten state are compared with those in the crystalline state at 150° and 23°C are plotted versus $M_w^{1/2}$ in Figure 5. It is shown in this Figure that within the experimental uncertainty the radii of gyration do not depend on temperature and obey the $M_w^{1/2}$ law. The experimental uncertainties are, to a large extent, caused by the uncertainty for the background correction because of degradation of some samples. In Figure 5 the straight line $\langle s^2 \rangle_w^{1/2} = 0.34 M_w^{1/2}$ is drawn, which describes the molecular weight dependence of the radius of gyration for isotactic polypropylene in a θ -solution.

The main conclusions derived from these neutron scattering experiments are that in the molten state and in θ -solution the same radii of gyration are obtained; also the

radii of gyration are only slightly affected by going from the molten to the crystalline state.

DISCUSSION

The simplicity of the above results enable some rather clear conclusions to be drawn concerning the relationship between the morphology of isotactic polypropylene and the conformation of the chain. It is evident that the different thermal treatments which cause a change in the d -spacing from 120 to 250 Å have no significant effect on the conformation of the chain as a whole. Moreover, the disposition of chain segments around the centre of mass, is independent of the degree of crystallinity and d -spacing.

The dilemma of trying to reconcile these observations with models which postulate the presence of crystalline regions with thicknesses comparable with the measured d -spacing has already been discussed in our previous paper with reference to quenched polyethylene⁵. It now seems that when the polymer chain has sufficient time to diffuse and take up a thermodynamically acceptable conformation the situation is not changed. Moreover, we now have the additional information that increasing the value of the d -spacing of the matrix does not affect the chain conformation. It is worthwhile discussing the new observation with reference to the chain-folded model for polymers and then to consider alternative structures.

CHAIN-FOLDED MODEL

Let us consider the idealized diagrammatic representation of the chain-folded structure shown in Figure 6. Then the

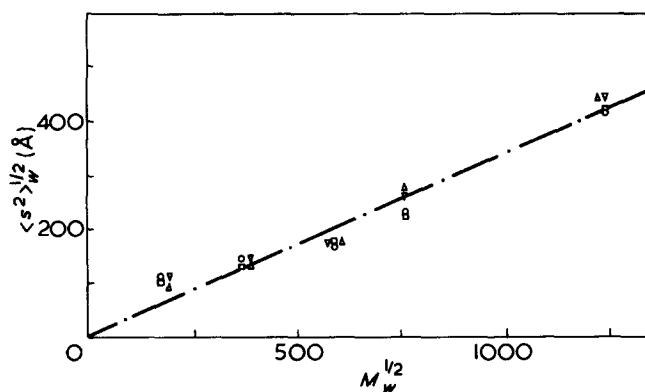


Figure 5 Plot of $\langle s^2 \rangle_w^{1/2}$ versus M_w for PPQ1-6 measured in the melt at 200° and 220°C and in the solid state at 150° and 23°C. (---), $\langle s^2 \rangle_w^{1/2} = 0.34 M_w^{1/2} = 0.34 M_w^{1/2}$, PP melt

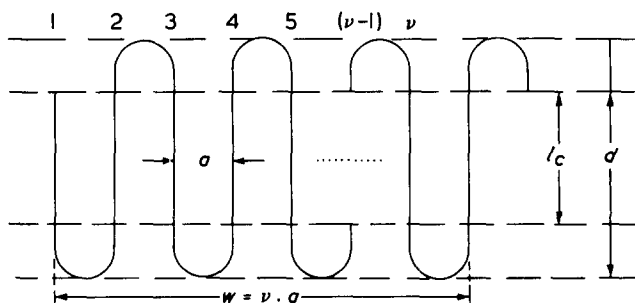


Figure 6 Dimensions of a polymer molecule with idealized structure according to the chain-folded model

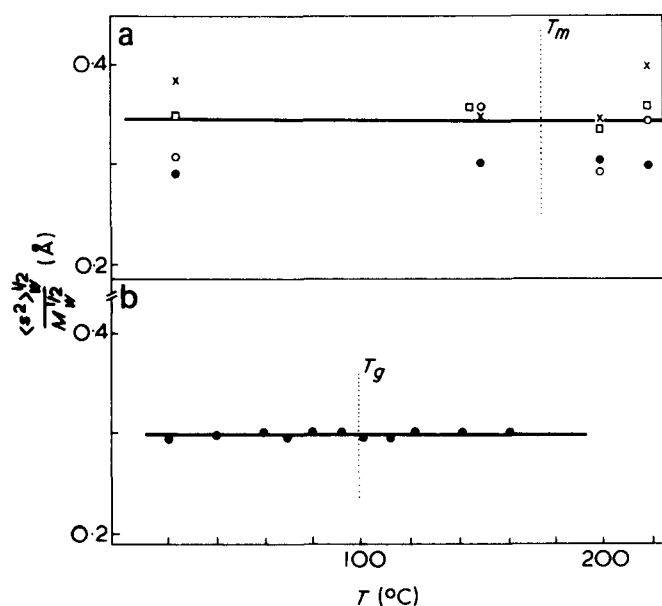


Figure 7 Polymer chain dimensions as a function of temperature above and below the transition temperatures. (a) PP crystalline polypropylene, M_w values: \square , 1 500 000; \circ , 575 000; \bullet , 345 000; \times , 145 000. (b) PS crystalline polystyrene: $M_w = 98\,000$, data from ref 2

length of the molecules (L) to be distributed over (n) lamellae of thickness (d) and in which the chain folds ν times in each lamella is given by:

$$L = l_c n \nu + l_a n = 0.0517 M_w \quad (4)$$

where

$$l_a = d(1 - \chi) \text{ and } l_c = d\chi \quad (5)$$

and l_a and l_c have the values shown in Figure 6. It is necessary to state that $n > 1$ and $\nu > 3$. The latter condition is necessary because the lamella surface corresponds to the fold surface and two folds are necessary to define the upper and lower surfaces as shown in Figure 6. As thermodynamic equilibrium is approached, in going from the quenched to the isothermally crystallized states, there is an increase in the values of the d -spacing and crystallinity and these changes are represented in the model by changes in the values of ν and n in accordance with equation (4). It must be evident that if the $M^{1/2}$ relationship is going to persist down to the lowest molecular weights that these changes must compensate for the change in the d -spacing.

Let us consider the situation at high molecular weights, in which if the model is correct, the molecule will be equivalent to an array of rods of length d and thickness $w = \nu a$ where a is the average distance between folds and $w \ll d$. If we now apply the random flight concept we can write:

$$\langle s^2 \rangle_w = \frac{n \cdot d^2}{6} \quad (6)$$

$$\begin{aligned} \langle s^2 \rangle_w^{1/2} &= \left\{ \frac{0.0517d}{6[(\nu-1)\chi+1]} \right\}^{1/2} M_w^{1/2} \\ &= \beta M_w^{1/2} \end{aligned} \quad (7)$$

where β is the slope of the lines in Figures 4 and 5.

From equations (4), (6) and (7) we can derive values of n and ν which satisfy these equations:

$$n = \frac{6\beta^2 M_w}{d^2} \quad (8)$$

$$\nu = \left(\frac{0.0517d}{6\beta^2\chi} - \frac{1}{\chi} + 1 \right) \quad (9)$$

Equation (9) gives the number of stems corresponding to the values of d and χ . Equation (8) defines the number of lamellae over which the molecule is distributed. The value of n and ν computed from the data in the Tables and using $\beta = 0.35$ from Figure 4 are summarized in Table 3. These are the numerical values which would enable $\langle s^2 \rangle_w^{1/2}$ to be dependent on (d) yet give an $M_w^{1/2}$ relationship. They constitute a severe criticism of this model for the following reasons.

(a) The number of lamellae over which the molecule is distributed is too small in number, except at the highest molecular weights, to permit the random flight concept to be applied⁸. Equation (6) cannot be used uniformly over the total molecular weight range and its use in the above discussion is questionable.

(b) The numerical values of n derived when $M_w < 140\,000$ are less than unity implying that at these molecular weights the structure crystallizes as a single rod. Neutron scattering studies of such systems⁶ show that $\langle s^2 \rangle_w^{1/2}$ is independent of M_w and related to d only. If the chain-folded model was correct, therefore, one would expect a break in the $\langle s^2 \rangle_w^{1/2}$ vs. $M_w^{1/2}$ curves at the molecular weight at which this occurred.

(c) Since polypropylene has a random coil structure in the melt crystallization at molecular weights where $n \sim 1$ would result in a reduction in values of $\langle s^2 \rangle_w^{1/2}$ due to chain folding into a single lamella.

Further problems arise with the chain-folded model in trying to account for the κ^{-2} behaviour of the scattering law indicated by measurements in the region of higher κ values shown in Figure 3. For the simple model of thin rods consisting of ν stems of length l_c interconnected by a one-dimensional random walk one calculates for the scattering law:

$$S(\kappa) = \left\langle D(z) \left[\frac{\sin \kappa l_c / 2}{\kappa l_c / 2} \right]^2 \right\rangle_{\hat{k}} \quad (10)$$

Table 3 Number of lamellae n occupied by a single chain and the number of stems ν per lamella from equations (8) and (9)

		ν		
		Quenched	Annealed	Crystallized
		15	22	25
		n		
Sample	$10^3 M_w$	Quenched	Annealed	Crystallized
1	34	1.5	0.2	0.5
2	140	7	3	1.5
3	340	17	6	4
4	575	28	11	7
6	1540	76	28	18

where $D(z)$ is the Debye function with the argument $z = 3\langle s^2 \rangle \hat{k}_{\parallel}^2$, with \hat{k}_{\parallel} the components of \hat{k} in the stem direction, and $\langle \rangle_{\kappa}$ indicates an average over all orientations of the scattering vector. This averaging is equivalent to the following integration:

$$S(\kappa) = \frac{1}{\kappa l_c} \int_{\kappa l_a/2}^{\kappa l_c/2} d\xi D \left[\frac{3\langle s^2 \rangle}{(l_c/2)^2} \xi^2 \right] \left(\frac{\sin \xi}{\xi} \right)^2 \quad (11)$$

This expression indicates that for $\kappa l_c > 1$, $S(\kappa)$ becomes proportional to κ^{-1} and demonstrates that the model does not agree with observation.

One possible modification we have considered is to replace the rods with plates. Assume that the molecule is folded ν times along a plane so that a plate of height l_c and width w is formed, consisting of ν equally spaced stems. Such plates within the lamellae are again interconnected according to a one-dimensional random walk in the stem direction with step sized as was discussed for the rods. Furthermore, it is assumed that there is no orientation correlation between consecutive plates. Certainly the plates do not have random orientation since their normal is always perpendicular to the uniform stem direction.

With this modified model the same parameters given in Table 3 are calculated but only if the contribution of a plate to the radius of gyration of the long chain molecule can be neglected, i.e.:

$$\frac{1}{12}(l_c^2 + w^2) \ll \langle s^2 \rangle_w \quad (12)$$

This inequality holds only if w is of the same order of magnitude as l_c . For a molecule folding with an adjacent or nearly adjacent re-entry the spacing between two consecutive stems is less than 10 Å. This gives, with the ν values from Table 2, values of w of 150, 202 and 250 Å for the quenched, annealed and crystallized specimens, respectively. Thus, the condition for the inequality [equation (12)] would be fulfilled and the calculated model parameters n and ν from Table 3 can be used also for the plate model.

The scattering function for plates of dimensions l_c and w with random orientation approaches a κ^{-2} dependence if κl_c and κw become larger than unity. This situation is realized in the plate model since coherent interference of the scattering from both plates belonging to the same chain molecules and to different chain molecules does not occur. The reasons for this are that orientation correlations between plates belonging to the same chain are not present and the tagged molecules are statistically distributed. For the scattering cross-section of the tagged molecules one obtains in the high κ region:

$$\frac{d\Sigma}{d\Omega}(\kappa) = N_T n (\nu l_c \bar{b})^2 \frac{12k}{(l_c^2 + w^2)} \kappa^{-2} \quad (13)$$

where N_T is the number of tagged molecules per unit volume, \bar{b} is the scattering length per unit length of a tagged molecule and k is a numerical value which depends essentially on the ratio w/l_c (see ref 5, Figure 9). In the low κ region the scattering cross-section of the tagged molecule is

$$\frac{d\Sigma}{d\Omega}(\kappa) = N_T n^2 (\nu l_c \bar{b})^2 [1 - \frac{1}{3} \kappa^2 \langle s^2 \rangle_w] \quad (14)$$

with $\langle s^2 \rangle_w$ given in equation (6).

With equations (13), (14) and (6) one obtains for the quantity Q defined in equation (3):

$$Q = \frac{2d^2}{l_c^2 + w^2} k = \frac{2k}{\chi^2} \cdot \frac{l_c^2}{l_c^2 + w^2} \quad (15)$$

Inserting into equation (15) $\chi = 0.65$, $w = l_c$ and $k = 1$, the value of Q obtained is 2.4 which can be compared with the experimental Q values given in Table 2.

It is evident that even this solution is extremely restricted since it requires that the inequality [equation (12)] be valid over the whole molecular weight range and this cannot be the case as shown in Table 3. Also the comments (a), (b) and (c) relating to the low κ region apply equally to the high κ region and undermine the validity of the derived equation.

ALTERNATIVE MODELS

Reference to Figures 4 and 5 for values of $M_w > 140\,000$ shows that the configuration of the polymer in the solid state is such that the distribution of tagged polymer segments about the centre of mass is not dissimilar from that found in the melt or in solution in a θ solvent. It should be clear at the outset that this can only be at best an approximation since in the latter situation the chain is free to adopt a random coil configuration without any constraints imposed by this crystal lattice. It is known from studies carried out by us and others that removal of the amorphous fraction of polypropylene by etching with nitric acid followed by measurement of the dimensions of polymer fragments within the crystalline phases that a majority of the polymer consists of stems of length at least equal to the d -spacing measured using SAXS techniques. What these results show, therefore, is that the statement that ' $\langle s^2 \rangle_w^{1/2} \propto M_w^{1/2}$ means that the structure is a random coil' is not a true generalization. However, the distortion imposed by the crystallization process is modest and that no major reorganization such as that represented by the structure shown in Figure 6 has occurred. Since, as already stated such a conformational change would be accompanied by a transition to a condition where $\langle s^2 \rangle^{1/2} \propto d$ and be independent of the molecular weight; the values of d have been changed by a factor of two without exhibiting this behaviour; therefore we conclude that the 'jumping cracker' model does not obtain in this instance.

The best approximation, therefore, is that of a random array of rods, where each rod is related in length to the crystalline lamella thickness. A random fragment connects the rods and constitutes the amorphous region. It may be shown that such an array can be represented by equations of the type:

$$\langle s^2 \rangle_w = \frac{l^2}{12n} + \frac{\alpha l^2 (n-1)}{6} \quad (16)$$

where l is the length of the rod, n is the number of rods and α is a proportionality constant. It is evident that $n \propto M_w$ and, therefore, at large values of n , $\langle s^2 \rangle_w^{1/2} \propto M_w^{1/2}$. At lower values of M_w , however, where the population of rods becomes small there is a departure from the simple $M_w^{1/2}$ relationship; eventually the radius of gyration is proportional

to the rod length only. It is evident from *Figure 4* that our data is sufficiently accurate to observe such changes and the values of $\langle s^2 \rangle^{1/2}$ for $M_w = 140\,000$, although unclustered show a measureable departure from the θ line. With the information available so far it is not possible to define the structure further.

We are presently using a combination of etching experiments together with further neutron scattering studies at a spacing of $d = 400 \text{ \AA}$ with the intention of defining the structure of the individual rods which constitute the array.

It should be emphasized that the structure described relates to a polymer which is only 50–65% crystalline. In one particular instance we have clearly identified the 'jumping cracker' structure. This is in pressure crystallized polyethylene⁶, where the crystallinity is greater than 95%. More recent work on this system has shown that $\langle s^2 \rangle_w^{1/2}$ is proportional to d and independent of M_w , even when the molecular weight is such that the molecule has folded eleven times. At the other extreme we have the observation⁹ that solid amorphous polyethylene crystallizes at -120°C . At such temperatures the viscosity of the medium precludes the migration of the chain to allow the formation of a structure analogous to *Figure 6*. It is evident, therefore, from these observations that polyolefins have more than one conformation in the solid state.

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