Small-angle neutron scattering studies of polyethylene crystallized at high pressure

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(Received 27 September 1976)

The technique of small-angle neutron scattering (SANS) has been used to study the chain configuration in pressure crystallized polyethylene. Two narrow molecular weight fractions of deuterated molecules (PED) of M_w 23 000 and 54 000 were solution blended with a protonated matrix polymer of M_w 81 500. Although pressure crystallization was shown to have produced a clustering of the PED molecules, the radii of gyration $\langle S^2\rangle_z^{1/2}$ were, nevertheless, shown to be consistent with a model in which the PED molecules possessed rod-like configurations. The predicted rod lengths were in close agreement with the molecular stem lengths of the PEH matrix polymer, which were independently determined by nitric acid etching. Furthermore, a doubling of the PED molecular weight produced no change in the value of $\langle S^2\rangle_z^{1/2}$. This was interpreted in terms of a chain folding mechanism in which a molecule is bounded by the surfaces of a lamellar block and is therefore unable to increase its' rod length.

INTRODUCTION

In recent publications[1,2] we have described the problems of using small-angle neutron scattering (SANS) techniques to study crystalline polyethylene and how these problems may be overcome. It has been shown that when clustering of the deutero-polyethylene (PED) in a polyethylene (PEH) matrix is avoided in rapidly quenched polyethylene, the SANS data is readily interpretable in terms of a structural model in which the polymer chain adopts a similar configuration to that of the random coil. In such a model the chain meanders from one lamellar to another and is spatially distributed over many lamellae.

When polyethylene is slowly crystallized, either by directly cooling from the melt or by annealing, clustering of the PED molecules occurs and the interpretation of the data is consequently ambiguous. More recently we have studied pressure crystallized polyethylene in which the lamellar thickness increased to several thousand angstroms. Deutero-polyethylene molecules with fully extended lengths comparable to the lamellar thickness were chosen as tagged molecules. As was expected, clustering of the tagged molecules to a large extent was detected by neutron small-angle scattering. Despite this effect it was, however, possible to obtain information on molecular folding in pressure crystallized polyethylene. This paper reports these results and how they have been derived.

EXPERIMENTAL

Sample preparation for neutron scattering experiments

The matrix polymer (PEH) was blended with the tagged molecules (PED) by dissolving both polymers in *o*-dichlorobenzene and precipitating into methanol. The powder was washed with methanol to remove all traces of the higher boiling solvent and then dried thoroughly. Plaques (15 mm x 32 mm x 1 mm) were moulded at a temperature of 190°C and under a pressure of 0.7 kbars finally cooling in a cold press.

Details concerning the molecular weight and molecular weight distribution of the fractionated tagged molecules and the proto matrix are given in *Table 1*. The two narrow deutero molecular weight fractions were used with the same proto matrix polymer and have weight-average chain lengths $\langle L\rangle_w$ in the fully extended form of 2091 Å (TCl series) and

Table 1

	Matrix parameters					Tagged molecules			After etching at 60°C				SANS predicted stem length
Sample series	M_w	M_w/M_n	Density (g/cm^3)	Crystallinity (%)	M.p. (°C)	M_w	M_w/M_n	$\langle L\rangle_w$ (Å)	M_w	M_w/M_n	$\langle l_s\rangle_w$ (Å)	$\frac{\langle L\rangle_w}{\langle l_s\rangle_w}$	$\langle l_s^2\rangle_z^{1/2}$ (Å)
TC1	81 500	8.2	0.992$^{(o)}$ ± 0.0005	95	139.5 ± 0.1	23 000	1.8	2091	22 650 ± 2000	3.0	2060 ± 200	1.0 ± 0.1	2053 ± 200
TC2	81 500	8.2	0.992$^{(o)}$ ± 0.0005	95	139.5 ± 0.1	54 000	1.6	4909	18 650 ± 2000	2.8	1700 ± 200	2.9 ± 0.3	2053 ± 200

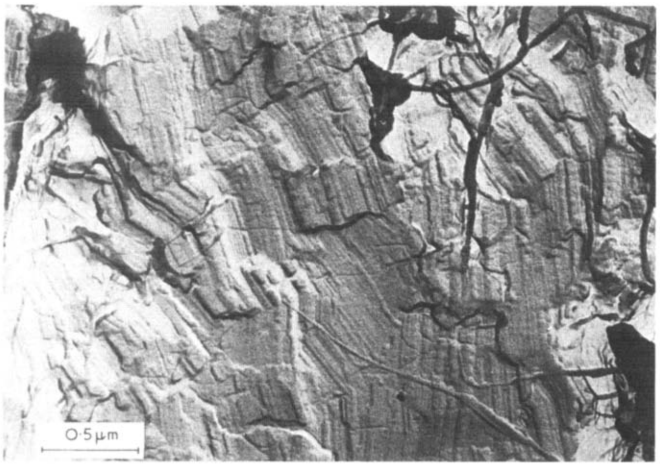

Figure 1 Fracture surface electron micrograph of sample TC1A

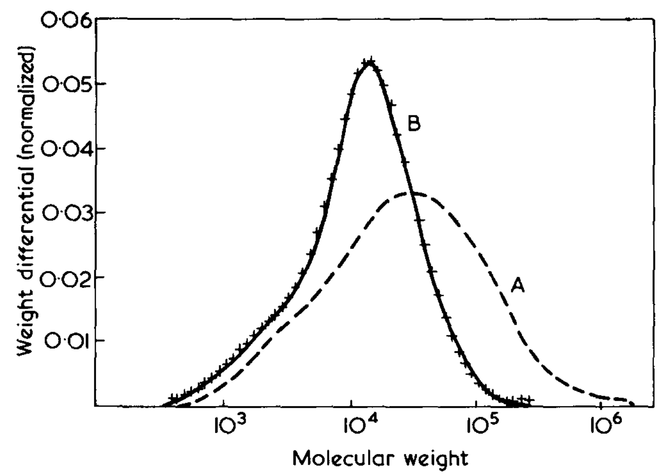

Figure 2 G.p.c. analysis of sample TC1A. A, Before etching; B, after etching at 60°C for 3 days (curves are normalized)

4909 Å (TC2 series). Measurements were carried out with loadings of 3 and 6% by wt of deutero polymer.

Eight samples were simultaneously annealed at 5.1 ± 0.2 kbars at a temperature of 250° ± 3°C for approximately 30 min[3]. They were then cooled slowly whilst under pressure to room temperature. The melting point, as determined by d.s.c., and the densities of the samples were also measured and an approximate degree of crystallinity calculated. Average values of this information are listed in *Table 1*. In addition, an electron micrograph of a typical fracture surface is shown in *Figure 1*. The samples are, therefore, seen as typical of high pressure annealed polyethylene.

Structural studies of PEH matrix

The molecular stem lengths (l_s) were measured by oxidizing the surfaces of the lamellae with nitric acid and determining the molecular weight of the chain fragments remaining. The temperature of etching was fixed at 60°C. Recent work by Bassett *et al.*[4,5] has shown that the g.p.c. M_w values obtained from samples etched at this temperature correlate well with independent fracture data. A typical sample determination is as follows.

A sample (50 mg) was sealed in a glass tube in the presence of excess fuming nitric acid and heated at 60°C for 3 days and finally washed with water and dried. The molecular weights and molecular weight distribution was determined in *o*-dichlorobenzene as solvent at 130°C in the g.p.c. unit designed in the Corporate Laboratory equipped with i.r. detector and previously calibrated by established techniques.

Figure 2 shows the type of curve obtained. The molecular weight data is summarized in *Table 1*, together with the weight-average stem lengths $\langle l_s \rangle_w$ obtained from the M_w values of the etched samples.

Clustering of the PED molecules

It has been shown that the forward scattering cross-section, measured in absolute units, is very sensitive to the degree of clustering of the PED molecules. Using the latter measurements an indication of the average number of molecules in a cluster can be obtained from the molecular weight of the cluster $(M_w)_{\mathrm{app}}$:

$$\frac{1}{cK_n}\frac{(\mathrm{d}\Sigma)}{(\mathrm{d}\Omega)_{\kappa=0}} = (M_w)_{\mathrm{app}} \tag{1}$$

with

$$K_n = \rho\left[\frac{2x(b_{\mathrm{D}} - b_{\mathrm{H}})}{M_{\mathrm{CH_2}}}\right]^2 N \ \mathrm{cm}^{-1}$$

where ρ is the density of the sample, x is the degree of deuteration of PED chains, $M_{\mathrm{CH_2}}$ is the mass of a chain segment, N is Avogadro's number, b_{D} and b_{H} are the scattering lengths of deuterium and hydrogen respectively and c is the percent concentration in g/g. The extrapolated forward scattering cross-section is obtained from the plot of $\ln(\mathrm{d}\Sigma)/(\mathrm{d}\Omega)$ vs. κ^2. If there is no clustering $(M_w)_{\mathrm{app}} = M_w$, the molecular weight of the PED molecules determined by g.p.c. prior to blending. When clustering does occur curves obtained by plotting $\ln(\mathrm{d}\Sigma)/(\mathrm{d}\Omega)$ vs. κ^2 are still linear over a wide range as can be seen in *Figure 3*, but the values of the intercept and slope are changed. By extrapolation to $\kappa = 0$ $(M_w)_{\mathrm{app}}$ the average molecular weight of the cluster, is obtained, and the ratio $(M_w)_{\mathrm{app}}/M_w = n_w$, indicates the average number of molecules. Values for the radius of gyra-

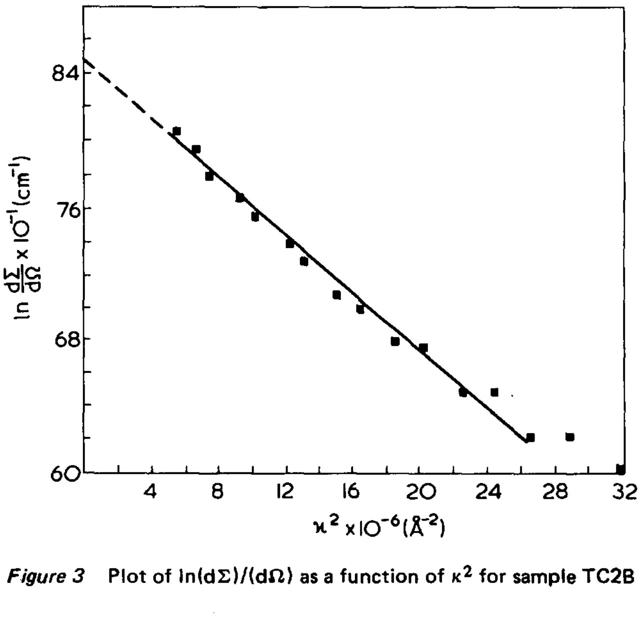

Figure 3 Plot of $\ln(\mathrm{d}\Sigma)/(\mathrm{d}\Omega)$ as a function of κ^2 for sample TC2B

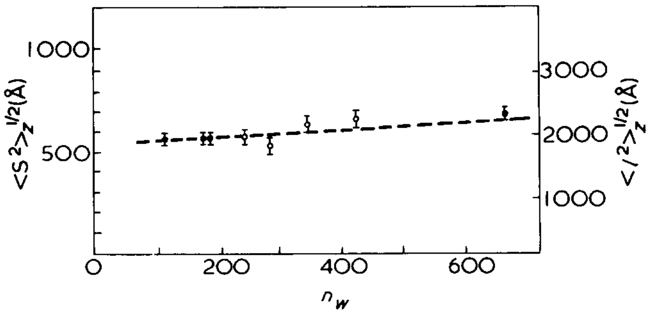

Figure 4 Radius of gyration $\langle S^2\rangle_z{}^{1/2}$ as a function of the number of tagged molecules n_w per cluster. $\langle l_s{}^2\rangle_z{}^{1/2}$ is the length of rods of equivalent radii of gyration. ○, M_w = 23 000; ●, M_w = 54 000

tion were obtained from the slopes of the curve shown in *Figure 3*, in the manner described previously for single molecules.

RESULTS AND DISCUSSION

In *Figure 4* the radius of gyration of the tagged clustered molecules are plotted *versus* the average number of molecules per cluster. One sees that between 100 and 6000 molecules belong to a cluster. Despite this large variation of n_w the radii do not change more than ±10% and the straight line correlation indicates that the slight change of $\langle S^2\rangle^{1/2}$ is approximately linearly related to the cluster size. In addition, it is noticeable that the radii of gyration for the TC1 series and TC2 specimens are the same within the mentioned ±10% although the molecular weight of the tagged molecules has been changed by about a factor of 2.5 going from TC1 to TC2. Finally, attention should be paid to the observation that a thin rod or stem of length equal to the stem length $\langle l_s\rangle_w$ of the matrix molecules has the measured radius of gyration.

Because of these observations we propose the following structural model in which the tagged molecules cluster to form a collection of fully extended rods of mean length equal to the weight-average stem length $\langle l_s\rangle_w$ of the etched matrix polymer. Each cluster is visualized to be bounded in its length direction by the surfaces of a lamellar block. The radius of gyration for an isotropic distribution of such clusters, each of diameter D is given by:

$$\langle S^2\rangle_z^{1/2} = \left[\frac{\langle l_s^2\rangle_z}{12} + \frac{\langle D^2\rangle_z}{8}\right]^{1/2} \qquad (2)$$

If we assume a dense packing of stems of tagged molecules within the cluster the diameter is given by:

$$D = 4.8 n_w^{1/2} (\text{Å}) \qquad (3)$$

With this assumption the width term in equation (2) contributes at the most only 0.2% to the radius of gyration. In addition there is also no way to account for the observed n_w dependence of $\langle S^2\rangle_z^{1/2}$ by assuming less dense packed clusters. It is, however, more likely that the effective length of the cluster rods increase slightly with increasing number of molecules per cluster. Nevertheless, we have a structural system for which the problems associated with clustering have, to a large extent, been eliminated and the radius of gyration is within an accuracy of ±10% a configuration parameter of the tagged molecules.

By comparing the rod length $\langle l_s^2\rangle_z$ as determined by neutron scattering (see *Figure 4*) with the independently determined stem lengths $\langle l_s\rangle_w$ and the calculated fully extended lengths $\langle L\rangle_w$ (see the last three lines of *Table 1*) it is apparent that the tagged molecules of the TC2 series are folded within the same lamellar. Had the tagged molecules of TC2 passed into more than one lamellar block there would have been a substantial increase of more than a factor of 2 in $\langle S^2\rangle_z^{1/2}$.

It is not possible, however, to comment on the nature of the re-entry into the lamellae so that in this respect the structure is incompletely defined.

CONCLUSION

It is evident from this study that an important feature to chain folding in the present system is that the radius of gyration is unrelated to molecular weight, possibly up to a maximum value $M_{\max}$, where $M_{\max} > 54\,000$. This feature does appear to manifest itself in clustered polyethylene slow cooled from the melt at atmospheric pressure, where the radius of gyration appeared not dependent on molecular weight up to the maximum investigated (350 000). We will be discussing these results in subsequent papers. By studying higher molecular weight polymers it is evident that the pressure crystallized system offers the possibility of studying the folding of the chain within the lamellae and determining the number of folds occurring before the chain prefers to enter a second lamellar.

ACKNOWLEDGEMENTS

We wish to thank G. W. Longman, T. L. Crowley, R. T. Murray and G. D. Wignall for discussions.

REFERENCES

1 Schelten, J., Wignall, G. D. and Ballard, D. G. H. *Polymer* 1974, **15**, 682
2 Schelten, J., Ballard, D. G. H., Wignall, G. D., Longman, G. W. and Schmatz, W. *Polymer* 1976, **17**, 751
3 Bassett, D. C. and Carder, D. R. *Phil. Mag.* 1973, **28**, 513
4 Bassett, D. C., Khalifa, B. A. and Olley, R. H. *Polymer* 1976, **17**, 284
5 Bassett, D. C., Khalifa, B. A. and Olley, R. H. *J. Polym. Sci. (A-2)* to be published