Small-Angle Neutron Scattering from Solution-Crystallized and Melt-Crystallized Polyethylene*

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Results are presented and analyzed for mixtures of normal and deuterated polyethylene. Some of the results are used to determine single-chain radii of gyration in bulk polyethylene. The radii of gyration are found to be smaller for solution-crystallized samples than for melt-crystallized samples and smaller for slowly crystallized samples than for rapidly crystallized samples. Although the data are not always consistent, comparison of Kratky plots in the higher-Q region with Yoon-Flory model calculations suggests that the solution-grown samples show adjacent reentry whereas melt-crystallized samples do not.

Introduction

Experiments have been performed on mixtures of small amounts of completely deuterated polyethylene in a matrix of normal polyethylene. The chains marked with deuterium scatter neutrons substantially differently than the normal chains and one should be able to measure the characteristics of a single, deuterated chain by performing small-angle neutron scattering experiments from these mixed samples. This technique has been used to determine single-chain radii of gyration in bulk polystyrene (Cotton et al., 1974) and polymethyl methacrylate (Kirste, Kruse & Ibel, 1975; Kirste & Lehnen, 1976). Attempts at similar measurements in polyethylene (Schelten, Wignall & Ballard, 1974; Schelten, Ballard, Wignall, Longman & Schmatz, 1976; Sadler & Keller, 1976) have met with difficulties due to void-scattering background and different crystallization characteristics of the marked and unmarked chains.

By way of introduction, let us rederive the scattering form factor for a mixture of marked and normal polymer. Define the position of the jth monomer of the mth chain to be \( \mathbf{R}_{jm} = \mathbf{Q}_m + \mathbf{R}_j \), where \( \mathbf{Q}_m \) is the position of the center of mass of the mth chain and \( \mathbf{R}_j \) is the monomer's position relative to the center of mass. Then the scattering form factor for neutrons is

\[
S(Q) = \left\langle \left\{ \sum_{m,j} a_m \exp(i(Q \cdot \mathbf{Q}_m) \exp(i(Q \cdot \mathbf{R}_j))^2 \right\}^2 \right\rangle.
\]

where Q is the neutron wave-vector transfer, \( \langle \ldots \rangle \) indicates an ensemble average, and \( a_m \) is the neutron scattering length for a single monomer of the mth chain. It is convenient to introduce several probabilities here. Let \( P_{mHmH} \) be the probability that both the mth and m'th polymers are normal; \( P_{mDmD} \) the probability that both are deuterated, and \( P_{mHmD} \) that m is normal and m' is deuterated. With these probabilities \( S(Q) \) can be written as follows for marked and normal chains that are of the same molecular weight:

\[
S(Q) = \sum_{m,m'} \langle a_m P_{mHmH} + 2a_m a_{m'} P_{mHmD} + a_{m'}^2 P_{mDmD} \rangle \exp \left[ i(Q \cdot (\mathbf{R}_j - \mathbf{R}_{j'}) \right] \exp \left[ i(Q(\mathbf{Q}_m - \mathbf{Q}_{m'})) \right] \right\rangle.
\]

If the normal and marked chains are uniformly and randomly mixed, \( S(Q) \) can be evaluated using the following expressions for the probabilities

\[
P_{mDmD} = c \delta_{mm'} + c^2 (1 - \delta_{mm'})
\]

\[
P_{mHmD} = (1 - c) \delta_{mm'} + (1 - c)^2 (1 - \delta_{mm'})
\]

\[
P_{mHmH} = c (1 - c) (1 - \delta_{mm'})
\]

where \( \delta_{mm'} \) is the Kronecker delta and c is the number concentration of deuterated chains. Using these values of the probabilities in (2) gives

\[
S(Q) = Nc (1 - c) (a_H - a_D)^2 S_{sH}(Q) + \{c a_D + (1 - c) a_H\}^2 S_{sD}(Q),
\]

where \( N \) is the total number of chains, and where \( S_{sH}(Q) \) is the single-chain form factor:

\[
S_{sH}(Q) = \left\langle \left\{ \sum_j \exp(i(Q \cdot \mathbf{R}_j))^2 \right\} \right\rangle.
\]

This is of course what we wish to measure. \( S_{sD}(Q) \) is the total sample form factor

\[
S_{sD}(Q) = \left\langle \left\{ \sum_{m,j} \exp(i(Q \cdot \mathbf{R}_j) \exp(i(Q \cdot \mathbf{Q}_m))^2 \right\} \right\rangle.
\]

For non-crystalline polymers, \( S_{sD}(Q) \) becomes very small for clean samples at small Q. This near vanishing of \( S_{sD}(Q) \) is the reason that the experiments in the amorphous polymers are successful. For crystalline polymers on the other hand, \( S_{sD}(Q) \) is very large at small Q owing to the lamellae and voids.

However, we should note the difference in sign between \( a_H \) and \( a_D \) for polyethylene, \( a_H = -0.003 \times 10^{-2} \text{ cm} \), \( a_D = 2.000 \times 10^{-2} \text{ cm} \). This would indicate that the coefficient of \( S_{sH}(Q) \) in (6) should be small and in fact should vanish at \( c \approx 3.8\% \).

II. Analysis

If all of the assumptions made above were true, the extraction of \( S_{sD}(Q) \) from SANS experiments should be quite simple. One should be able to measure \( S_{sD}(Q) \) by performing a SANS experiment on a blank sample of normal polyethylene with no marked polymer, and subtract that contribution from the mixed sample with the use of (6).

The experimental results are considerably more complicated than this. The scattering from the blank is relatively small. The scattering from the mixed samples does not, in general, admit to the easy determination of \( S_{sD}(Q) \). For example, one would expect \( S_{sD}(Q) \) to equal the square of the number of monomers per chain. Some experiments have given an effective weight from measured S(0) almost two orders of magnitude larger than the known molecular

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weight of the marked polymer (Schelten et al., 1974, 1976). Furthermore, there seems to be a sometimes random variation of the measured scattering from factors of different samples. One would expect the variation in observed intensity with concentration to be always systematic. This has not generally been observed. It has thus been difficult, in general, to determine the correct $S_d(Q)$ from SANS experiments for polyethylene.

The inability to extract $S_d(Q)$ easily from experiments clearly indicates that one of the assumptions made in deriving (6) is wrong. Most workers agree that the suspect assumption is that of random and uniform mixing. Models of clusters of marked molecules have been invoked to explain the difficulties (Schelten et al., 1976). We feel that such models are neither required nor valid.

Let us consider the methods of manufacture of mixed samples. All the methods that have been used involve dissolving the marked and unmarked polymers in a good solvent such as xylene. Subsequently the 'mixed' polymer solution is precipitated by a variety of techniques, some involving magical incantations.

It has been known for years that the precipitation rate of crystalline polymers from solution is a strong function of molecular weight, increasing by about a factor of two going from molecular weights of several tens of thousands to several million (Stehling, Ergos & Mandelkern, 1971). It is also a strong function of temperature, changing by several orders of magnitude between 75 and 91°C. Finally, it is a strong function of temperature, changing by several million (Stehling, Ergos & Mandelkern, 1971).

The relative rates of precipitation of the marked and normal polymers from the xylene solutions. In no experiment performed to date, including these, was any attempt made to match the rates of precipitation of the two components.

We do however have some knowledge of the contributions to $S(Q)$. In the blank scattering, we measure the shape of $S_r(Q)$. Also, we know that $S_d(Q)$ is given by

$$S_d(Q) = n^2 \left( 1 - \frac{Q^2 R_s^2}{3} + xQ^4 \right)$$

for small $Q$, where

$$R_s^2 = \frac{1}{2n^2} \sum_{\langle RJ \rangle} \langle |\mathbf{R}_j - \mathbf{R}_j'|^2 \rangle$$

and $n$ is the molecular weight divided by the monomer weight.

Then $S(Q)$ is related to the scattering from the blank $S_d(Q)$ and the radius of gyration as follows

$$S(Q) = \beta S_d(Q) + Nc(1-c)(a_d-a_n)^2n^2 \left( 1 - \frac{Q^2 R_s^2}{3} + xQ^4 \right),$$

where

$$\beta = \frac{\langle \mathbf{R}_d(1-c)a_n \rangle^2 + (a_d-a_n)^2 \delta^2}{a_n^2}.$$  

III. Experiments

All of the experiments were performed on the D-11 small-angle scattering facility at the Institut Laue-Langevin, Grenoble, France. The samples were prepared by codissolving protonated polyethylene (this is called the matrix) and deuterated polyethylene in boiling xylene. The solutions were then cooled so that the mixed polyethylene precipitated out of solution. Two matrix polymers were used in different samples. The first is denoted SRM and has $M_w = 52,700$, $M_w/M_n = 2.93$. The second is denoted EHM and has $M_w = 78,700$ and $M_w/M_n = 5.76$. Seven deuterated polymers were used. These had the following values of $M_w$ and $(M_w/M_n)$: 97,140 (1.61), 39,170 (1.56), 25,870 (1.53), 17,420 (1.52), 8,730 (1.41), 5,840 (1.31) and 2,910 (1.34).

Two methods were used to obtain the initial mixed precipitates. First a boiling xylene solution of SRM and the marked polymer was simply allowed to cool to room temperature. The samples were labelled C and B. Second the self-seeding technique (Blundell & Keller, 1968) was followed, in which the solution of SRM and marked polymer is cooled to 80°C, held at that temperature for several hours, heated to 97°C for 30 min and then added dropwise to cold methanol to form the precipitate. This procedure produces rapid precipitation and supposedly better mixing of the matrix and the marked polymers. These samples are labelled P and M. The C and P samples, which were in powder form, were then used to perform SANS experiments after they had been moderately compressed between glass slides. The B and M samples were melted in an evacuated mold, pressed to a thickness of 0.1 cm and rapidly cooled by dropping into cold water. Samples labelled PE and ME were made by using the self-seeding procedure but with a matrix of EHM. The ME samples were melted and cooled as for the B and M samples. The samples labelled PP were
Table 1. Radii of gyration for solution-precipitated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>Initial mixing method</th>
<th>Matrix</th>
<th>PED concentration $F_c$</th>
<th>$R_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>97 140</td>
<td>Self-seed and quench</td>
<td>SRM</td>
<td>1:28 0.020</td>
<td>124</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td>1:27 0.015</td>
<td>139</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td>1:40 0.010</td>
<td>138</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td>1:51 0.005</td>
<td>136</td>
</tr>
<tr>
<td>$PE$</td>
<td>97 140</td>
<td>Self-seed and quench</td>
<td>EHM</td>
<td>1:04 0.020</td>
<td>106</td>
</tr>
<tr>
<td>$PE$</td>
<td></td>
<td></td>
<td></td>
<td>1:17 0.015</td>
<td>98</td>
</tr>
<tr>
<td>$PE$</td>
<td></td>
<td></td>
<td></td>
<td>1:13 0.010</td>
<td>106</td>
</tr>
<tr>
<td>$PE$</td>
<td></td>
<td></td>
<td></td>
<td>1:14 0.010</td>
<td>118</td>
</tr>
<tr>
<td>$PP$</td>
<td>97 140</td>
<td>Self-seed and quench</td>
<td>EHM</td>
<td>1:00 0.020</td>
<td>119</td>
</tr>
<tr>
<td>$PP$</td>
<td></td>
<td></td>
<td></td>
<td>1:09 0.015</td>
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<td>$PP$</td>
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<td>1:05 0.010</td>
<td>127</td>
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<td></td>
<td></td>
<td>1:05 0.005</td>
<td>113</td>
</tr>
<tr>
<td>$C$</td>
<td>97 140</td>
<td>Slow cool</td>
<td>SRM</td>
<td>1:07 0.010</td>
<td>97</td>
</tr>
<tr>
<td>$C$</td>
<td></td>
<td></td>
<td></td>
<td>1:06 0.007</td>
<td>86</td>
</tr>
<tr>
<td>$C$</td>
<td></td>
<td></td>
<td></td>
<td>1:08 0.007</td>
<td>91</td>
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<tr>
<td>$C$</td>
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<td></td>
<td></td>
<td>1:04 0.004</td>
<td>101</td>
</tr>
<tr>
<td>$C$</td>
<td></td>
<td></td>
<td></td>
<td>1:08 0.002</td>
<td>104</td>
</tr>
<tr>
<td>$C$</td>
<td>39 170</td>
<td>Slow cool</td>
<td>SRM</td>
<td>1:33 0.010</td>
<td>59</td>
</tr>
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<td>$C$</td>
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<td>1:36 0.010</td>
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<td>1:38 0.007</td>
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<td>1:33 0.002</td>
<td>63</td>
</tr>
<tr>
<td>$P$</td>
<td>25 870</td>
<td>Self-seed and quench</td>
<td>SRM</td>
<td>1:62 0.020</td>
<td>129</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td>1:34 0.015</td>
<td>87</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td>1:92 0.005</td>
<td>75</td>
</tr>
<tr>
<td>$P$</td>
<td>8 730</td>
<td>Self-seed and quench</td>
<td>SRM</td>
<td>1:35 0.020</td>
<td>38</td>
</tr>
<tr>
<td>$P$</td>
<td></td>
<td></td>
<td></td>
<td>1:87 0.015</td>
<td>33</td>
</tr>
</tbody>
</table>

To summarize $C$, $P$, $PE$, and $PP$ are solution-precipitated samples, while $B$, $M$, and $ME$ are melt-crystallized samples. Within these two sets, differences are due to initial mixing procedure and to choice of matrix. A number of deuterated chain concentrations were prepared, ranging from 2% to 0.2% (weight fractions). The sample label, $M_w$, concentration, matrix, and method of initial mixing are given in Table 1 for solution-precipitated samples and in Table 2 for melt-crystallized samples.

The SANS data from these samples were analyzed by extracting the absolute coherent-scattering component from marked sample and blank, and inserting these as $S(Q)$ and $S_b(Q)$ in equation (15). $\beta$, $R_g$, and $\kappa$ were treated as unknown parameters, and all other constants in (15) were known. $n^f$ was taken from the GPC molecular weights, quoted earlier. $\beta$, $R_g$, and $\kappa$ were then adjusted to give a best fit to all data within the $Q$ interval 0.0075 to 0.041 $\AA^{-1}$. The procedure was considered acceptable if the extrapolation of $S(Q) - \beta S_b(Q)$ to $Q = 0$ gave a molecular weight differing from the GPC molecular weight by a factor less than two. This condition was met for about 60% of the runs and these are listed in Tables 1 and 2.

We should point out here that the failure to meet this condition indicates that $S(Q)$ has a substantially stronger variation with $Q$ than would be indicated by (15) with the measured $S_b(Q)$. It might be that a more accurate determination of the form of $S_b(Q)$ would rectify this difficulty. $S_b(Q)$ is measured for a completely hydrogenated sample which is dominated by incoherent scattering. A better result might be obtained on a completely deuterated sample or by using SAXS. In these cases, $\beta$ would be given by expressions different than (16). The ratio of extrapolated $M_w$ to GPC $M_w$ is called $F$, and this is given along with $R_g$ in the tables. These ratios tend to approach unity for the highest $M_w$ samples and deteriorate as $M_w$ is lowered. This we attribute to the dominating effect of void scattering at the lower $M_w$. Failure of the criterion for the remaining 40% of the data is attributed to the same cause, predominantly, since all but two samples in this group are of lower $M_w$. Of course, the single-chain scattering increases relative to the void scattering as the molecular weight increases.

In spite of sample inconsistencies, we feel that there are sufficient systematic variations in the data shown to draw some very tentative conclusions at both low and intermediate $Q$. As Tables 1 and 2 show, radii of gyration are systematically lower for solution-crystallized samples ($P$, $PE$, $PP$, $C$) than for melt-crystallized samples ($ME$, $M$, $B$). This is not surprising and is consistent with (1) greater confinement of chains to single lamellae, and (2) a greater degree of adjacent reentry for the solution-grown samples. There is also indication that the more rapid the rate of crystallization the larger the radii of gyration for solution-precipitated samples. Again, this is not surprising.

In the intermediate-$Q$ regime, small-dimension correlations are expected to be sensitive to chain-folding geometry in the lamellae, as discussed by Yoon & Flory (1977). In Fig. 1 we have superposed our results for 1% concentration, $M_w = 97 140$ samples representing melt-crystallized ($ME$), solution-crystallized ($PE$), and solution-crystallized, pressed ($PP$) cases, against the Yoon–Flory model curves for 1, 3, 5, and 7 adjacent stem reentry ($T_1$, $T_2$, $T_3$, $T_4$ respectively in Fig. 1; the curve for 28 adjacent stems is only slightly higher than the model curve).
than for 7 stems, Yoon & Flory, 1977). A Gaussian curve calculated for $R_g = 140$ Å is also included for comparison. The ordinate $Y(\mu)$ is the Yoon–Flory ordinate $F_2(\mu)$, which differs by a constant $nN(1-c)(a_H-a_D)^2$, from a Kratky ordinate $S(Q)Q^2/c$. That is, we take

$$Y(\mu) = \frac{Q^2S(Q)}{c(1-c)nN(a_H-a_D)^2}.$$  \hspace{1cm} (17)

We emphasize that our data are absolute scattering results so that no normalization has been applied between model and experiment. At the highest $Q$ shown there appears to be a regular tendency for melt-crystallized samples $(E_1)$ to coincide with random reentry $(T_1)$ whereas the solution-precipitated results, for unpressed $(E_3)$ or pressed $(E_2)$ samples more nearly agree with substantial adjacent reentry. Others of our experimental results show the same tendency, although the scatter in our present data allows only this qualitative observation.

From our results here and from the results of other experiments on crystalline polymers, we must conclude that it is vital to insure a complete uniformity in technique when the mixed samples are made. Small changes in technique seem to produce enormous changes in the mixed samples. Subsequent experiments must be performed with stringent controls on all aspects of sample preparation. It is very important to demonstrate that samples which have had similar histories give similar SANS results. This seems to us to be a more important first step than inventing new schemes to eliminate ‘segregation’ and $\delta^3$. Thereafter, we can seriously begin to discuss the details of precipitation rates and the resultant fluctuations in the concentration of marked chains.

References


A Dynamic Study of the Crystallization of Polyethylene from the Melt*

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Crystallization of a linear polyethylene from the melt was followed in situ with the ORNL 10-meter SAXS camera [Hendricks (1978). J. Appl. Cryst. 11, 15-30]. Specimens were rapidly cooled in the X-ray beam in tandem birdcage furnaces from $\sim 180$ °C to temperatures between 115 and 126 °C, and scattering patterns were recorded for 30 s in 50 s intervals. Because of this relatively high-speed data acquisition rate, it was possible to obtain data in time periods which were short compared to the rate of change of the scattering patterns. The SAXS curves showed shapes which changed continuously during crystallization. The scattering curves are the superposition of a zero-angle peak and a Bragg maximum. Guinier plots of the zero-angle peak manifest scattering by lamellae of constant thickness. The thickness value is nearly that expected for crystallites at these crystallization temperatures. A model in which skeletal spherulites form and then later fill in is consistent with these results. Decreasing SAXS intensity and changing Bragg peak intensities indicate crystal thickening during cooling to room temperature.

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Reference