

## Temperature-Dependent Small-Angle X-Ray Scattering from Polyethylene

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(Received July 6, 1976)

**ABSTRACT:** Temperature-dependent small-angle X-ray scattering from polyethylene is analysed using a correlation function technique. It is found that the correlation function gives two maxima corresponding to long periods of 163 Å and 205 Å at room temperature. These must correspond to different morphological structures. These long periods remain almost constant up to the crystallization temperature and after that they merge into a single long period which increases with increasing temperature.

**KEY WORDS** Correlation Function / Crystallinity / Long Periodicity / Lorentz Correction / Fourier Transformation /

The small-angle X-ray scattering (SAXS) from a semicrystalline polymer is usually characterized by the appearance of one and sometimes several intensity maxima. Straightforward application of Bragg's equation to the angular positions of these maxima leads to the periodicities of the order of a few hundred angstroms. This simple approach has led to inconsistencies. It is found that the sizes calculated by the Bragg's method do not match with other experimental methods, notably with electron microscopy data. By way of example, the SAXS results obtained by Geil<sup>1</sup> are not in agreement with his electron microscopic measurement. In addition polyethylene, polypropylenes and polyoxymethylene frequently show two SAXS maxima which are apparently not first- and second-order scattering maxima from the same structure.<sup>1-3</sup> These two effects, which have been reviewed by Geil,<sup>1</sup> Kavesh and Schultz,<sup>4</sup> and Burmester,<sup>5</sup> have led a number of authors to consider refinements of a simple two-phase model. Tsvankin<sup>6</sup> included a transition zone between crystalline and amorphous regions as a modification to a two-phase model. The exact size of this transition zone, which is characterized by a linear density profile, apparently has little effect on the first- and second-order

maxima, provided its size is not zero.<sup>7</sup> Recently, Blundell<sup>8</sup> has calculated small-angle X-ray scattering curves assuming a transition-zone model in the electron density distribution. He has shown that this trapezium profile has a small effect only on the position and intensity of the second-order maximum arising from a two-phase model with symmetric Gaussian distributions of crystal and amorphous lengths. On the other hand, Strobl and Müller<sup>9</sup> in their new method of a direct analysis for SAXS have shown the validity of the two-phase model for polyethylene.

In a different approach, Vonk and Kortleve<sup>10,11</sup> have analyzed the SAXS from various polyethylenes in terms of a discrete two-phase model with asymmetric length distributions. In their analysis they Fourier transformed the scattering curve to obtain the correlation function. They report satisfactory agreement between the average period of the model and the first maximum of the correlation function.<sup>11</sup> The method of correlation functions has also been used by Deopura and Gupta.<sup>12</sup> It is found that this method gives an accurate value of the long period<sup>13</sup> and a true estimation of crystallinity.<sup>14</sup>

The present publication gives an analysis of temperature dependent SAXS from polyethylene

using the correlation function technique. The SAXS curves used are temperature dependent, as reported by Schultz, *et al.*,<sup>15</sup> for fractionated polyethylene of molecular weight 36,500 crystallized at 123°C. Most of the earlier SAXS of polyethylene has been done side the higher molecular weight on. The present analysis takes care of scattering intensities at the tail end of the experimental curve. It is seen that for polyethylene the scattering does not drop to zero in the wide-angle region. This is due to the fact that there is an overlap of small- and wide-angle X-ray scattering curves. The tail of the scattering curve considerably affects the correlation function.<sup>10</sup> Kortleve and Vonk,<sup>16</sup> in their analysis of SAXS using the correlation function method, shifted the base line upwards until it became tangent to the experimental curve at the point of minimum intensity. We have extrapolated the scattering curve in the tail part of the SAXS, assuming Porod's relationship.<sup>17</sup> This is the theoretical asymptotic form of SAXS valid for crystalline particles of any shape in the two-phase structure.

#### EXPERIMENTAL CORRELATION FUNCTION

The intensity of small-angle X-ray scattering from a single region of parallel layers along the normal direction is represented by an intensity function  $i(s)$  in reciprocal space. This is given by

$$i(s) = 2\bar{V} \int_0^\infty \gamma'(x) \cos 2\pi xs ds \quad (1)$$

where

$$\gamma'(x) = \int_0^\infty \eta(\xi - x) \eta(\xi) d\xi \quad (2)$$

and

$$s = (2 \sin \theta) / \lambda,$$

$\bar{V}$  = irradiated volume of the region under consideration,

$x$  = coordinate perpendicular to the layer,

$\theta$  = half angle of diffraction,

$\lambda$  = wavelength of X-rays, and

$\eta(\xi)$  = local fluctuations of electron density around the average value.

From eq 1 we get

$$\gamma'(x) = \frac{1}{2\bar{V}} \int_0^\infty i(s) \cos 2\pi xs ds \quad (3)$$

and

$$\gamma'(0) = \langle \eta^2 \rangle = \frac{1}{2\bar{V}} \int_0^\infty i(s) ds \quad (4)$$

where  $\langle \eta^2 \rangle$  is the average of the square of the electron density fluctuations.

The correlation function as defined by Debye and Bueche<sup>18</sup> is

$$\gamma(x) = \frac{\langle \eta_1 \eta_2 \rangle}{\langle \eta^2 \rangle} = \frac{\gamma'(x)}{\gamma'(0)} (-1 \leq \gamma(x) \leq +1) \quad (5)$$

where  $\eta_1$  and  $\eta_2$  are the electron density fluctuations at the positions separated by a distance  $x$ .

The experimental scattering intensity is corrected for slit height as suggested by Chu and Tencretti.<sup>19</sup> If  $I(s)$  is the experimental scattering intensity and  $i(s)$  is the Lorentz corrected scattering intensity, then they are given by the following relationship:

$$I(s) \propto i(s) s^{-2} \quad (6)$$

The relation between  $\gamma(x)$  and the experimental scattering curve obtained from eq 3 to 6 is given by

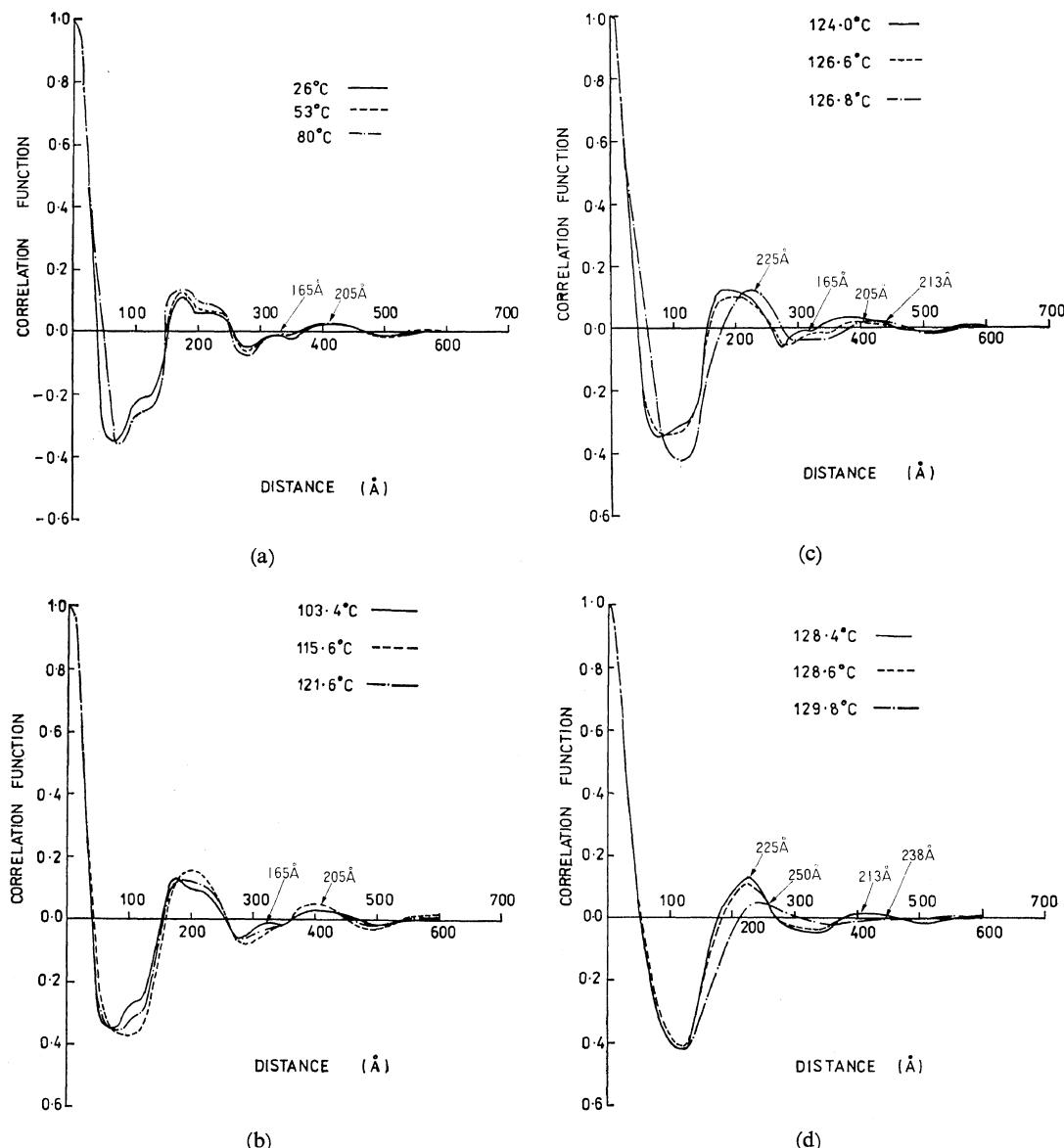
$$\gamma(x) = \frac{\int_0^\infty I(s) s^2 \cos 2\pi xs ds}{\int_0^\infty I(s) s^2 ds} \quad (7)$$

Equation 7 has been used in the calculation of the distance correlation function in this work. The total small-angle scattering curve is obtained by smoothly extrapolating the observed curve to zero angle, and to the tail end of the scattering curve from the point of inflection of the observed curve based on Porod's law.

#### RESULTS AND DISCUSSION

The temperature-dependent scattering curves for a polyethylene sample of molecular weight 36,500 (shown in Figure 2 in Schultz, *et al.*'s paper<sup>15</sup>) are used. After being corrected for slit-smearing, correlation functions are obtained for all these curves. The characteristics of the correlation function are shown in Figure 1a, b, c, d. It is found that the first broad maximum is not single but double. This is also the same for the first minimum. These two maxima are the result of two morphological structures in the sample. The two morphological structures

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**Figure 1.** (a) Correlation function for polyethylene at 26, 53, and 80°C with long periodicities of 165 and 205 Å. (b) Correlation function for polyethylene at 103.4, 115.6, and 121.6°C with long periodicities of 165 and 205 Å. (c) Correlation function for polyethylene at 124, 126.6 and 126.8°C with long periodicities of 165 and 205 Å, 213 Å, and 226 Å, respectively. (d) Correlation function for polyethylene at 128.4, 128.6, and 129.8°C with long periodicities of 213 and 225 Å, 213 and 225 Å.

are consistent with several earlier reports of SAXS of polyethylene.<sup>20,21</sup> The long periods at room temperature obtained from half of the distance between the origin and the second maxima are 163 and 205 Å. Such long peri-

odicities for polyethylene have been reported earlier. In fact, a plot between the number average molecular weight and long periodicity (the result reported by Kortleve and Vonk<sup>11</sup>) shows that the long periodicity for 36,500

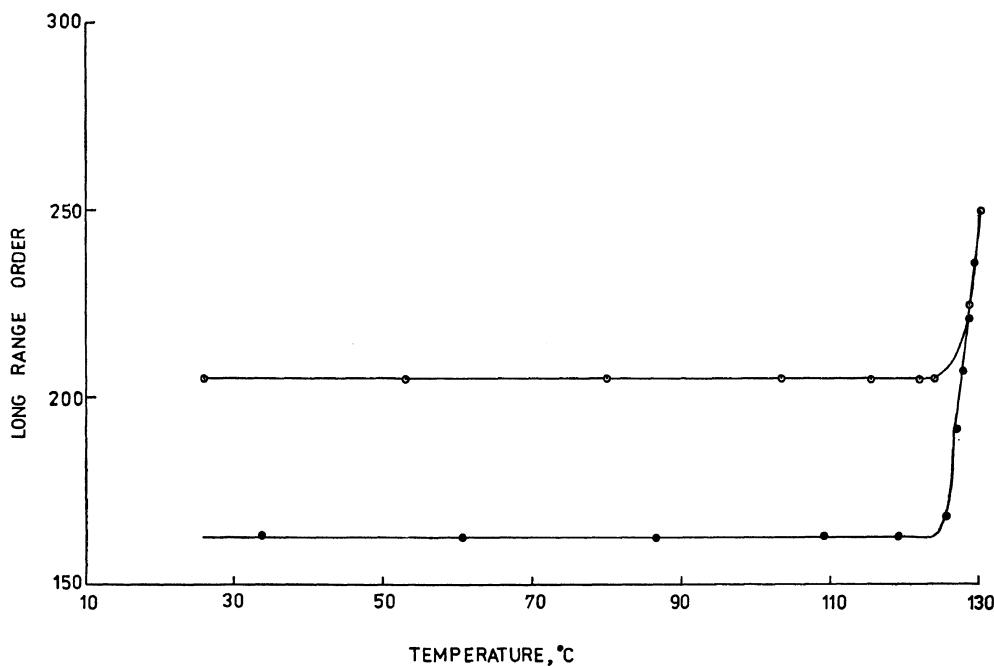


Figure 2. Long periods as a function of temperature.

number-average molecular weight is between 175 Å and 250 Å, approximately. This long periodicity is nearer to our results of periodicity of 205 Å. The two periodicities plotted as a function of temperature are shown in Figure 2. With increasing temperature the long periods remain almost constant up to a temperature of approximately 123°C.

Beyond the crystallization temperature of 123°C, the chain mobility increases due to the greater freedom on the internal rotation around single bonds. The larger crystals grow at the expense of smaller ones. In other words, the crystal size distribution shifts towards larger values. At around 127°C both the long periodicities merge into a single periodicity, as seen in Figure 2. The rate of increase of periodicity is extremely fast around these temperatures. The correlation function obtained for the scattering curve at 129.8°C is shown in Figure 1d. A very poor correlation shows that most of the crystalline part of the sample is melted at this temperature.

The correlation function can also be used to obtain a rough estimate of the degree of order.

This is related to the depth of the first minimum.<sup>10-12</sup> In the present analysis there are double minima instead of a single one. A rough estimate of the crystallinity has been obtained by using the weighted average of the crystallinity values ( $\phi_1$  and  $\phi_2$ ) determined from the depth of the two minima. The weight factors are equal to the reciprocal of the area under the two minima of the correlation function. In addition, crystallinity values have also been obtained by assigning the following weight factors  $C_l$  ( $l=1, 2$ ), corresponding to the two scattering species:

$$C_l = \frac{\int i_l(s) ds}{\int i(s) ds}$$

where  $i(s)=i_1(s)+i_2(s)$  is the total scattering intensity. With these weight factors the crystallinity index is given by

$$\phi = \frac{c_1 \phi_1 + c_2 \phi_2}{c_1 + c_2}$$

The results obtained from these two approaches are shown in Table I and they are in close

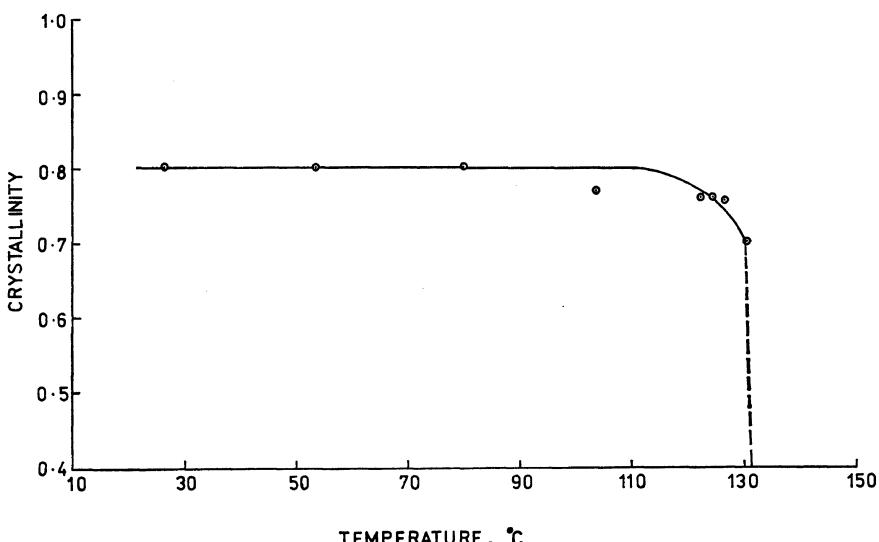
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**Table I.** Crystallinity values obtained from two different methods

Temperature, °C	Crystallinity from first approach	Crystallinity from second approach
26.0	0.80	0.79
80.0	0.80	0.79
103.0	0.78	0.76
121.8	0.76	0.76
124.0	0.76	0.75
126.6	0.76	0.75
126.8	0.7	0.7
128.4	0.7	0.7
128.6	0.7	0.7
129.8	0.7	0.7

A word about the calculation of a correlation function from an experimental curve will be appropriate here. The full small angle scattering curve is obtained by extrapolating the observed curve to  $S=0$ . But it is found that neither the position nor the height of the first maximum are seriously affected by the method of extrapolation. But the extrapolation at the tail end of the scattering curve affects the correlation function considerably. As we have used the Porod's relationship for this extrapolation, our results are believed to be appropriate.

The parameter obtained in the present analysis can be used in relation to the analysis of semicrystalline polymers by making use of the



**Figure 3.** Average crystallinity as function of temperature.

agreement. A graph has been plotted between the crystallinity values so obtained and the temperatures, and is shown in Figure 3. It is found that with increasing temperature the crystallinity remains almost constant up to the crystallization temperature of 123°C and then decreases continuously. Combining the results of long period and crystallinity above 123°C would essentially point to a much faster increase in the size of the amorphous regions. This could be expected because of the fact that these temperatures are beyond the crystallization temperature of the sample.

mathematical methods of Markoff chains.<sup>22-23</sup> Thus the transition probability of various stages can be calculated. It should then be possible to relate these probabilities with the nature of the potential barrier around single bonds.

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