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Crystallization of polymers. Part II: Fractionated polyethylene quenched from the liquid state

E. Robelin,
Institut Textile de France, Boulogne, France

F. Rousseaux, M. Lemonnier
L.U.R.E. Université Paris-Sud, 91405 Orsay, France

and J. Rault
Physique des Solides, Université Paris-Sud, 91405 Orsay, France

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Résumé. — Par diffusion centrale à l'I.T.F. et à Lure, nous avons mesuré les longues périodes $L$ du polyéthylène (P.E.) monodisperse et polydisperse en fonction de la masse moléculaire $M$. Les échantillons portés un certain temps à la température $T$ au-dessus de la température de cristallisation $T_c$, étaient trempés rapidement à l'azote liquide.

On distingue trois types de comportement :

1. $M < M_1$, $L \sim M$ (1)
2. $M_1 < M < M_2$, $L \sim M^{1/2}$ (2)
3. $M > M_2$, $L \sim M_2^{1/2}$ (3)

$M_1$ est la masse moléculaire critique au-dessous de laquelle la chaîne liquide n'a pas un comportement gaussien, c'est typiquement la masse d'une portion de chaîne comprise entre deux enchevêtrements.

La loi (2) est nouvelle, nos résultats mettent en évidence une masse critique $M_2$ au-delà de laquelle la longue période et l'épaisseur des lamelles cristallines sont indépendantes de la masse moléculaire.

L'existence de ce régime où la longue période est comparable à la taille des pelotes dans le fondu, conduit à préciser le processus de cristallisation.

Les grandes périodes dépendent de la température du fondu $T_i$, les variations observées sont reliées à la variation de la taille des pelotes dans la phase liquide, et confirme avec une plus grande précision les résultats de la 1ère partie.

Abstract. — We have measured by low angle X-ray scattering (SAXS) the long period of fractionated polyethylene (P.E.) quenched from the melt. The P.E. samples were annealed at different temperatures $T_i$ above the melting temperature and for a time greater than the relaxation time defined in Part I. As for polydispersed material, the long period is given by the relationship $L(T_i) = L(T_o) (1 + \alpha(T_i - T_o))$ : $\alpha$ is equal to $\beta/2$, $\beta$ being the temperature coefficient of the ideal chain in the liquid state.

Three types of behaviour are distinguished according to the value of the molecular weight $M$ of the fractionated samples :

1. $M < M_1$, $L \sim M$ (1)
2. $M_1 < M < M_2$, $L \sim M^{1/2}$ (2)
3. $M > M_2$, $L \sim M_2^{1/2}$ (3)

$M_1$ is the critical molecular weight, above which the chain has a Gaussian behaviour in the liquid state. $M_2$ is of the order of the molecular weight $M_s$ of a portion of chain between two entanglements.

The scaling law (2) is new, the long period varies like the end to end distance of the coil in the melt. Our results indicate the necessity of introducing a critical value $M_2$ for the molecular weight, above which the long period is constant.

From WAXS and SAXS measurements the crystalline core lamella thickness $l_c$ is found to be constant, of the order of 170 Å, the distance between two consecutive entanglements along a chain.

The experimental scaling laws giving $L$ and $l_c$ give information about the process of crystallization of fractionated P.E.
1. Introduction. — The so-called kinetic theories of crystallization of polymers [1, 2] cannot explain various features of the lamellar structure observed in semi-crystalline polymers crystallized from dilute solution [3, 11], from the melt and from the solid amorphous phase [3]. The study of polydispersal materials shows that the long period, measured by low angle X-ray scattering, is a complex function of the molecular weight distribution. For such complicated systems it has not been possible to find out a relationship between the long period and the molecular weight.

In order to understand the crystallization process of polymers, we have studied monodisperse polyethylene fractions crystallized by quenching the melt at temperature $T_i$ to liquid nitrogen temperature. This method of crystallization has several practical and theoretical advantages.

a) The initial state of the chain in the melt is the ideal state: macromolecular chains have the unperturbed dimension $<r_0>$ because inter-chain and intra-chain interactions cannot be differentiated.

b) The dimension $<r_0>$ varies with the temperature $T_i$ of the melt [5], and the annealing time $t$ at that temperature. The quenching of samples previously annealed at different temperatures $T_i$ allowed us to establish correlations between the rigidity of the chain in the liquid state and the lamellae thickness in the solid state (Part I [6]).

c) The quenching in liquid nitrogen prevents the annealing process. Lamella thickening [1, 2, 7], involving cooperative movements of large parts of the chain, is not operative. The morphology of the semi-crystalline material depends essentially on the liquid state, and not on the temperature of crystallization [6]. During the quenching process the cooling rate is the same for all our samples and is about $10^{-2}$ to $10^{-1}$ s$^{-1}$, which is as we will see later on, greater than the deformation rate of the coils in the liquid state when the temperature is changed.

In this note we report the relationship between the long period and the molecular weight for monodisperse polyethylene (P.E.) material. This relationship is at variance with what is observed in Polydisperse P.E. (Part I) [6]. We give also the relationship between the long period and the molecular weight for monodispersed ethylene fractions crystallized by quenching the melt at temperature $T_i$ of the melt. This result confirms the result of Statton [8a] since the index is a relative number, precision is more important than accuracy. The reproducibility of index measurements of same samples crystallized in the same manner is about 1% [8a, c] this is the precision of the measurements on the surface area ratio $A_c/A_s + A_a$, $A_c$ and $A_a$ being the crystalline peaks and amorphous halo surfaces.

2. Experimental study. — Polyethylene fractions were provided by SNPA (France).

The weight-average and number-average molecular weights $M_W$ and $M_N$ and the polydispersity $I$ are:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$m_4$</th>
<th>$m_5$</th>
<th>$P_1$</th>
<th>$P_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_W$</td>
<td>9.950</td>
<td>30.700</td>
<td>59.000</td>
<td>112.000</td>
<td>246.000</td>
<td>11.000</td>
<td></td>
</tr>
<tr>
<td>$M_N$</td>
<td>10.480</td>
<td>32.200</td>
<td>61.600</td>
<td>118.000</td>
<td>264.000</td>
<td>90.000</td>
<td>$\sim 10^4$</td>
</tr>
<tr>
<td>$I$</td>
<td>1.1</td>
<td>1.10</td>
<td>1.19</td>
<td>1.10</td>
<td>1.15</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

Samples $P_1$ and $P_2$ are two commercial samples (Manolene M.N.P.E. and Hoescht) with high polydispersity.

Small-angle X-ray diffraction patterns were obtained using synchrotron radiation of Lure ($\lambda = 1.8 \AA$ and a 110 cm sample-to-counter distance). This experimental setup gives a good accuracy of the small angle X-rays scattering.

The samples were 0.1 to 0.3 mm thick. The long period was determined according to the procedure given in Part I [6] without Lorentz correction and background correction.

Crystallinity measurements was deduced from the wide angle X-ray scattering [8]. The crystallinity index $\chi$ is $(1 + KA_a/A_c)^{-1}$, in which we put $K = 1$ because we are mostly interested in the variations of the crystallinity index, and less in the absolute values. As noted by Statton [8a] since the index is a relative number, precision is more important than accuracy. The reproducibility of index measurements of same samples crystallized in the same manner is about 1% [8a, c] this is the precision of the measurements on the surface area ratio $A_c/A_s + A_a$, $A_c$ and $A_a$ being the crystalline peaks and amorphous halo surfaces.

3. Results and discussion. — 3.1 Long periods. —

3.1.1 Variation of $L$ with the temperature of the melt. — As in Part I we have measured for fractionated P.E. the relationship between the long period and the temperature of the melt. The annealing time of the melt was greater than the relaxation time. Figure 1 shows the intesity curve as a function of the scattering angle. Unlike polydisperse polymer (see for example Fig. 1, Part I), P.E. fractions exhibit symmetric intensity peaks having a gaussian shape and a smaller width. The two SAXS curves shown in this figure correspond to a P.E. fraction of molecular weight $6 \times 10^4$ which have been annealed in the liquid state at 150°C and 230°C and then quenched to liquid nitrogen.

The width of the two peaks with median lines $M$ and $M'$ are equal. The displacement of the angular position of the maximum gives the variation of the long period, using Bragg’s law. This figure shows clearly that the precision on the difference in Bragg’s spacing is about 2 Å.

Figure 2 shows for a fraction of molecular weight $6 \times 10^4$ the measured variation of $L$ with the temperature $T_i$ of the melt. This result confirms the result of Part I with a higher accuracy. The experimental relation is:

$$L(T_i) = L(T_0)(1 + \alpha(T_i - T_0))$$

(1)

where $\alpha = 0.5 \times 10^{-3}$, $\alpha$ is equal to the half value of the temperature coefficient $\beta$ giving the variations of the unperturbed dimensions of the coil $r_0$ [5]:

$$\beta = - \frac{\partial \log r_0}{\partial T} = - 1 \times 10^{-3}.$$  

(2)
Fig. 1. — SAXS of fractionated P.E. samples of molecular weight $6 \times 10^4$. The two samples have been annealed at 150 °C and 230 °C and then quenched to liquid nitrogen. Synchrotron radiation wavelength $\lambda = 1.8 \text{ Å}$. The Bragg's long periods are respectively 274 Å and 265 Å.

Fig. 2. — Variation of the long period $L$ of fractionated P.E. of molecular weight 60 000 with the temperature of the melt $T_i$.

Eq. (1) can be written:

$$\alpha = \frac{\delta \log L}{\delta T} = \frac{\beta}{2} = \frac{1}{2} \frac{\delta \log r_0^2}{\delta T},$$

which leads to the scaling law:

$$L \sim r_0 \sim \sqrt{C \cdot M} \quad (3)$$

where $C$ is the rigidity $r_0^2/Na^2$ of the chain. The scaling law giving $L$ is different from that giving the crystalline lamella thickness $l_c$. Proposed in reference [3].

The following table gives the difference $\Delta L$ of the long period of samples $m_1$, $m_2$ and $m_3$ crystallized (by quenching) from the melt in the equilibrium state at 150 °C and 230 °C. The annealing in the liquid state prior to crystallization has been checked to be greater than the relaxation time defined in Part I. $\Delta r_0$ is the difference between the unperturbed dimensions of the chains at these two melt temperature. $\varepsilon$ is the accuracy on $\Delta L$, due to the localization of the maximum of the intensity curve $I = f(\theta)$. $\Delta \alpha$ is the maximum error for $\alpha$ (see Fig. 2).

<table>
<thead>
<tr>
<th>$\Delta r$ (Å)</th>
<th>$\Delta L$ (Å)</th>
<th>$\frac{\Delta L}{L} \cdot \frac{1}{\Delta T}$ (Å)</th>
<th>$\varepsilon$ (Å)</th>
<th>$\Delta \alpha$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 K</td>
<td>$m_1$ 4.1</td>
<td>3.3  $-0.20 \times 10^{-3}$</td>
<td>2</td>
<td>0.25 $\times 10^{-3}$</td>
</tr>
<tr>
<td>30 K</td>
<td>$m_2$ 7.1</td>
<td>8    $-0.44 \times 10^{-2}$</td>
<td>2.5</td>
<td>0.26 $\times 10^{-3}$</td>
</tr>
<tr>
<td>60 K</td>
<td>$m_3$ 10.1</td>
<td>11   $-0.50 \times 10^{-2}$</td>
<td>3</td>
<td>0.27 $\times 10^{-3}$</td>
</tr>
</tbody>
</table>

In spite of the great in accuracy on $\Delta L$, the observed variations $\Delta L$ are proportional to $\Delta r$ as predicted by relation (3). In the next section the experimental variation of $L$ with the molecular weight will confirm this law.

3.1.2 Variation of $L$ with the molecular weight.

The long periods as a function of the square root of the molecular weight are given in figure 3. Two behaviours are observed depending on the value of the molecular weight.

Fig. 3. — Long period of monodisperse ($m$) and polydisperse ($p$) polyethylene as a function of $\sqrt{M}$. $l_c$ is the crystalline lamella thickness and $\langle r_0 \rangle$ the non perturbated end-to-end distance of the chain in the melt [5]. The long period was measured on samples annealed in the liquid state 230 °C and quenched to liquid nitrogen.

In spite of the great in accuracy on $\Delta L$, the observed variations $\Delta L$ are proportional to $\Delta r$ as predicted by relation (3). In the next section the experimental variation of $L$ with the molecular weight will confirm this law.

3.1.2 Variation of $L$ with the molecular weight.

The long periods as a function of the square root of the molecular weight are given in figure 3. Two behaviours are observed depending on the value of the molecular weight.

- $M_1 < M < M_2$.

For polymer chains smaller than $M_2 = 10^5$ the long periods vary as the unperturbed dimensions of the coils, with the molecular weight.
It is worthwhile noting that the line $L = f(M)$ intersects the line $L = 170 \text{ Å}$ for $M_i - M_e = 1900$. In the next paragraph we note that this critical weight $M_i$ is the molecular weight between two entanglements in the liquid state. According to Smith and Manley [14], quenched P.E. fraction of molecular weight 2000 presents long period of 173 Å, and the chains are extended. Analysing other fractions, and blends of fractions these authors arrive at the conclusion that below 2000, the long period is proportional to the molecular weight, the chains are extended. The molecular weight $M_e$ separates the two domains of crystallization of polymers and oligomers.

In the domain $M_e < M < M_2$ the amorphous phase increases with the molecular weight and the long period obey to the relation:

$$L = l_e + l_a = l_e + \gamma \sqrt{M} \tag{4}$$

where $\gamma = 0.54$ and $l_e = 170 \text{ Å}$.

This long period must be compared to the unperturbed dimension [4, 5]: $<r_o>_M = 0.9 \sqrt{M}$, dashed line in figure 2.

As noted in Part I [6] Bragg's law should not be used in such disordered systems: the 2nd order of the small angle reflexion is not observed. A more sophisticated analysis of the intensity curve like the Tsvansk analysis, must be used. The average long period $L_{av}$ deduced from this analysis is related to the long period $L$ deduced from the Bragg's law by the relation

$$L_{av} = xL$$

where the parameter $x$ [$1 < x < 1.5$] depends on the distribution of the thickness $l_a$ and $l_e$, and on the crystallinity. In the case where $x = 1.5$ the slope of the straight line $L_{av} = f(\sqrt{M})$ would be equal to 0.75, of the same order of magnitude as the slope of the straight line $r_o = f(\sqrt{M})$.

In conclusion, relation (4) gives the relationship between the long period and the unperturbed dimension of the coils just before crystallization. Any variation of the rigidity of liquid chain will involve variation of the long period in the semi-crystalline phase. The scaling form of relation (4) is equivalent to that of relation (3). The slope of the line $L = f(M)$ is temperature dependent, as predicted by relation (3). In figure 3 we have shown the value of the long period of the polydisperse sample $P_1$, it corresponds to a monodisperse sample of molecular weight $M_w + M_n/2 \approx 53000$.

We cannot at present give a physical interpretation to this result. In order to study the influence of the polydispersity, a study of mixtures of monodispersed fractions has been undertaken, and will be reported in a forthcoming paper.

b) $M > M_2$. — For monodisperse and polydisperse samples of molecular weight greater than 100 000, the long period and the crystalline lamellar thickness are constant. $L \approx 2 \times l_c$. It is to be noted from some results not reported in figure 2 that every mixture of monodispersed fractions of $10^5$ and $2.6 \times 10^5$ give the same value $L \approx 300 \text{ Å}$. We conclude that the limiting value $L_c$ is again a characteristic of the material, depending only on the nature of the ideal chain as the limiting lamellar thickness in solution grown crystals [3].

### 3.2 Crystalline lamella core thickness $l_c$.

#### 3.2.1 Variations with the molecular weight.

The following table gives the value of the crystallinity $\chi$ and the crystalline lamella thickness $l_c$. The thicknesses of the crystalline and amorphous phases are deduced from the relations:

$$L = l_a + l_c \chi = \frac{\rho_z l_c}{\rho_p l_a + \rho_z l_a}, \tag{5}$$

$\rho_a$ and $l_c$ being the specific mass and the lamella thickness of the amorphous layer. Distortion in the crystalline phase and the presence of an intra-lamellar amorphous phase (grain boundary) are neglected. As noted by Capaccio [9a, b] this assumption of infinitely wide lamellae leads to an underestimated of $l_c$. The value of $l_c$ determined by X-Ray is about 20% smaller than the value obtained by low frequency Raman Spectroscopy and G.P.C. The following table gives the values of the crystallinity and the deduced of $l_c$.

<table>
<thead>
<tr>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$m_4$</th>
<th>$m_5$</th>
<th>$P_1$</th>
<th>$P_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>0.53</td>
<td>0.54</td>
<td>0.52</td>
<td>0.46</td>
<td>0.55</td>
<td>0.44</td>
</tr>
</tbody>
</table>

$\chi = 0.68$, $0.53$, $0.54$, $0.52$, $0.46$, $0.55$, $0.44$.

A correction of 20% of that value would give a value of 160 Å very near the G.P.C. values. In figure 3 the dashed line represent the $l_c$ corrected values. It intersects the line $L = l_e + \gamma \sqrt{M}$ for the value $M = M_e$ as expected.

In solution grown crystal the long period and therefore the crystalline lamella thickness ($L \approx l_c$) is found to be independent of the molecular weight. In quenched samples from the melt the situation is not so clear because of the difference in $l_c$ values obtained by SANS, Raman scattering (R.S.) and Gel Permeation Chromatography (G.P.C.) [9]. Nevertheless, when we compare the values obtained by the same technique R.S. and G.P.C. for polydisperse P.E. of molecular weight less than 260 000 we can conclude that the thickness $l_c$ is not dependent on the molecular weight. For higher molecular weight the wider distribution of transverse chains in crystalline layers probably hinders any comparison with low molecular weight samples.

The following table compares the $l_c$ values in Angelströms obtained by Capaccio et al. [9] by the three techniques

<table>
<thead>
<tr>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$D$ SANS</th>
<th>$D$ Raman</th>
<th>$D$ G.P.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>67 000</td>
<td>13 000</td>
<td>131</td>
<td>161</td>
<td>174</td>
</tr>
<tr>
<td>126 000</td>
<td>6 000</td>
<td>153</td>
<td>169</td>
<td>174</td>
</tr>
</tbody>
</table>
As noted by these authors the SAXS estimate of crystal thickness is the less reliable. From our work, in spite of some scatter in the data shown in figure 3, we conclude that in monodisperse P.E. the crystalline core thickness can be considered as a constant independent of the molecular weight. Therefore, as in solution grown crystals, \( l_e \), in quenched P.E. from the melt is a characteristic of the chain, dependent only on its nature. For solution grown crystal a physical interpretation of \( l_e \) has been given \([3-10]\). In polymers crystallized from the melt, an important question arises as to why the value of \( l_e \) is about twice the value observed in solution grown crystals? We suggested an explanation based on the two stages model of crystallization \([7, 11]\) pictured in figure 4. Let us assume that crystals grow with a constant thickness (for example, comparable with \( l_e \sim 70 \text{ Å} \), length of a chain having a gaussian character) and then that thickening proceeds during crystallization. This second stage should stop because of the presence of entanglements which hinder the diffusion of the chains. The values of the crystalline core thickness and the distance between two entanglements must be compared.

![Diagram](image)

Fig. 4. — Two stage process of crystallization \([7]\) : conformation of the chain in the melt (a). The contour length \( MN \) is about \( 170 \text{ Å} \). The two entanglements \( M \) and \( N \) move aside during thickening (b). This second process stops when \( l_e = MN \approx 170 \text{ Å} \) (c).

The difference in behaviour of short and long chains is well known in rheology. The zero-shear viscosity of melt polymer is:

\[
\eta \approx M \quad M < M_e \\
\eta \approx M^{3.4} \quad M > M_e.
\]

The critical mass \( M_e \) is the mass above which the entanglements are operative. \( M_e \) separates the both domains of polymer and oligomers. According to Bueche \( M_e \) is related to the average molecular weight \( M_e \) between two entanglements, approximately \( M_e \approx 2 M_e \) \([12]\). For P.E., \( M_e = 1900 \); this weight corresponds to a chain length of \( 170 \text{ Å} \). This is exactly the value of the crystalline thickness measured by Raman spectroscopy and G.P.C. \([9]\). \( l_e \) values given by SAXS and WAXS measurements are lower, because this method rests on the assumption of infinite lateral dimension of lamella. We conclude that in P.E. crystallized from the melt, the crystalline lamellae thickness is the average distance between entanglements. The process of crystallization pictured in figure 4 shows a portion of a chain between two entanglement points which crystallizes. Then \( l_e \) obtained at the end of the thickening is equal to the contour length \( MN \), if the entanglement points do not move along the chain \([11]\).

3.2.2 Variation with the temperature of the melt \( T_i \). — It is obvious that the distance between entanglements is proportional to \( C \). Extended chains in the liquid do not entangle. Therefore, if the temperature of the melt is varied, \( C \) and \( l_e \) vary in the same way. This feature is experimentally observed.

(a) By low frequency Raman spectroscopy \([13]\) Hendra has measured directly the variation of \( l_e \) with temperature \( T_i \). The coefficients \( \beta \) and \( \alpha = \frac{1}{l_e} \frac{\partial l_e}{\partial T} \) are of the same order of magnitude, thus bearing out the correlation between \( C \) and \( l_e \).

(b) There is no measurable difference in crystallinity between two samples quenched from two different temperatures of the melt \((T_i = 150 ^\circ \text{C} \text{ and } 230 ^\circ \text{C})\). The expected variation of crystallinity from relation (5) with \( \rho_e \sim \rho_e \) is:

\[
\frac{\Delta l}{\Delta T} = \chi \left( \frac{1}{l_e} \frac{\Delta l_e}{\Delta T} - \frac{1}{L} \frac{\Delta L}{\Delta T} \right).
\]

A constant value of \( l_e \) would lead to a difference of crystallinity of:

\[
\Delta \chi = \chi \cdot \Delta T \cdot \frac{\Delta L}{L},
\]

which is of the order of 0.3, for \( \Delta T = 80^\circ \), \( \chi \approx 0.60 \), \( \alpha = 0.5 \times 10^{-3} \).

We estimate that a variation of 0.01 of the crystallinity index is measurable by our method \([8]\). The absence of any measurable variation of the crystallinity implies therefore that \( l_e \) varies with the temperature in the same way as \( L \), and with the same order of magnitude.

4. Conclusion. — The variation of the long period with the temperature of the melt and with the molecular weight are explained by the law \( L \sim (C.M.)^{1/2} \). This law is valid for molecular weights greater than the molecular weight between two entanglements \( M_e \), and smaller than a critical molecular weight \( M_2 \). The long period in this range of molecular weight depends on two intrinsic parameters, the rigidity of the chain and the molecular weight. In polydisperse P.E. (Part I) the long period would be given by an average value of the coil dimensions, depending therefore on the molecular weight distribution. This explains why in commercial P.E. having similar weight distribution
there is not much difference in the long period values. Unlike the long period, the crystalline lamella core thickness \( l \) is found to be molecular weight independent. This parameter, which is characteristic of the semi-crystalline phase, has been related to the entanglement distance in the melt. The correlation between the crystalline lamella core thickness and the rigidity of the liquid chain just before crystallization [3] explains the variations of \( l \) with the temperature of the melt found by Hendra [13].

References

[1] See for example