Molecular model of partial crystallization of branched polyethylene

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A model is proposed which considers various cases of arrangement of crystallizable chain elements of branched polyethylene in lamellar crystalline elements. On the bases of statistical calculations, relationships between crystallinity and long spacing of the lamellar structure are derived. Calculated relations are compared with experimental crystallinity and long spacing values determined for polyethylene samples crystallized under various cooling conditions.

Keywords Chain branches; lamellar structure; crystallinity; long period; molecular model; polyethylene

INTRODUCTION

Crystallization of molecules containing small amounts of non-crystallizable units is an old problem as it still involves controversy both about the nature of the crystalline state and the nature of partial melting, commonly observed for such polymers. The first controversy, if non-crystallizable units are included in the crystalline regions or excluded from them, will not be discussed in this paper. In most opinions expressed recently, and related to branched polyethylene, even short branches are thought to be located within interlamellar regions[1,2] and this will be accepted here also.

The partial melting of low density polyethylene is well documented experimentally but the nature of it is still under discussion. Two main points of view have been given. According to the first, the melting is related to different stabilities of lamellae which melt selectively according to their size[3,4]. In the contrary view, the melting is related to the partial melting of lamellae and successive increase in the thickness of interlamellar amorphous layers[5]. In a recent paper by Strobl *et al.*[6] basic geometrical principles according to which the lamellae can fill up the space in a crystallizing polymer are proposed. This very general concept applies well for a qualitative explanation of experimentally observed phenomena during the partial melting of low density polyethylene as for example reversible changes of long spacing[6,7]. However it does not consider explicitly the molecular structure of the polymer as well as possible arrangements of molecular segments in crystalline elements.

In this paper we propose models of detailed arrangements of molecules in lamellar elements which on the basis of statistical calculations lead to relationships between morphological parameters and molecular structure of branched polyethylene.

Results of calculations are compared with experimental data of crystallinity and long spacing determined for samples crystallized under different conditions.

THE MODEL

It is assumed here that branches (or non-crystallizable units in more general case) are randomly distributed along the polymer chains. This involves particular distribution of lengths of chain segments between neighbouring branches. If the mean density of branches is given by probability p of finding a branch on a carbon atom of the main chain (p = number of branches/number of carbon atoms in the main chain) then the probability distribution of lengths x of chain segments between neighbouring branches is given by

$$p(x) = p\,\mathrm{e}^{-px} \tag{1}$$

where x is expressed in units of distance between two carbon atoms as measured along the chain axis.

This should satisfy the following condition

$$\int_0^\infty p(x)\mathrm{d}x = 1 \tag{2}$$

By introducing infinity as the upper limit of the integral we neglect the finite length of chains. It simplifies expressions and is not important when the concentration of chain ends is small in comparison with the concentration of branches.

We will further assume that the growth of lamellae in such a molecular system is controlled by segmental nucleation at the growing crystal side and that a certain minimal length, a, of the segment is needed for an effective nucleation step at a given temperature. According to this any segment shorter than this critical nucleus length will have to stay in the melt.

If one permits a complete spatial fractionation of segments with respect to their lengths, all those longer than the critical length will crystallize in lamellae of different thicknesses. In such a case the ratio of the integral fraction of segments longer than the critical length to the overall portion of the crystallizing material

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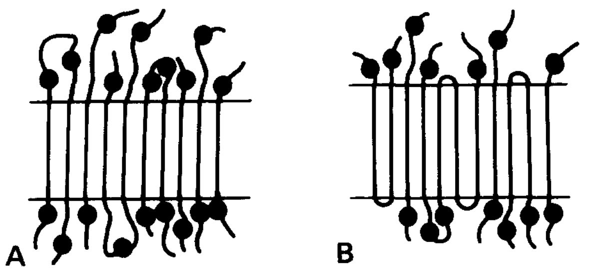

Figure 1 Schemes of models of molecular arrangement in lamellar structure (for description of models see the text)

can be interpereted as a potential crystallinity and can be calculated as follows

$$w_0 = \frac{\int_a^\infty x p(x) \mathrm{d}x}{\int_0^\infty x p(x) \mathrm{d}x} \tag{3}$$

where a is the critical nucleus length (in the same units as x). There is no doubt that this value of potential crystallinity cannot be achieved in real crystallizing systems because of unrealizable complete fractionation strongly hindered by segmental diffusion and intramolecular connections between segments of different lengths.

Two other more realistic models of formation of lamellae from molecular segments are proposed here. They are schematically illustrated in *Figure 1*.

In the first case (model A) it is assumed that chain segments of length greater than the critical length enter the crystalline phase without fractionation in such a way that only a part of segment related to lamellae thickness contributes to crystallinity while the remaining parts of segments contribute to amorphous phase. Under the assumption that branches are completely rejected from the crystalline phase the lamella thickness in such a case will be determined by the length of the shortest segments and therefore will be equal to the value of a. According to this, each segment will contribute to crystallinity exactly with length a and the expected crystallinity will be calculated as follows

$$w_1 = \frac{a \int_a^\infty p(x) \mathrm{d}x}{\int_0^\infty x\, p(x) \mathrm{d}x} \tag{4}$$

In the second case (model B) it is assumed that chain segments much longer than the critical length can be folded entering the crystalline phase with adjacent re-entry folds so that they give maximal contribution to the growth of lamellae of thickness a. In this case crystallinity expected in the system is given by

$$w_2 = \frac{\sum_n na \int_{na}^{(n+1)a} p(x) \mathrm{d}x}{\int_0^\infty x\, p(x) \mathrm{d}x} \tag{5}$$

where $n-1$ is the number of folds in the folded segment.

For the distribution $p(x)$ given by equation (1) respective crystallinity values can be expressed in simpler form

$$w_0 = (1 + pa)\mathrm{e}^{-pa} \tag{6a}$$

$$w_1 = pa\,\mathrm{e}^{-pa} \tag{6b}$$

$$w_2 = pa \sum_n \mathrm{e}^{-npa} \tag{6c}$$

Functions described by these equations are plotted in *Figure 2* for the value of $p = 0.035$ characteristic for the polymer studied in the experimental part of this paper. In the calculations of w_2 it was assumed that for every fold of the chain inside the segment three $-CH_2-$ groups are lost which do not contribute to crystallinity.

The results show a considerable difference in crystallinity values between the models introduced in this paper and the model in which segmental fractionation is assumed, especially at low values of a. The models introduced are regarded as extremes of non-effective and effective arrangement of segments in crystalline lamellae and the gap between w_1 and w_2 values is expected to cover the real cases.

Having the crystallinity values determined and the lamellar thickness related to critical segment length it is possible to calculate the mean long spacing of the lamellar

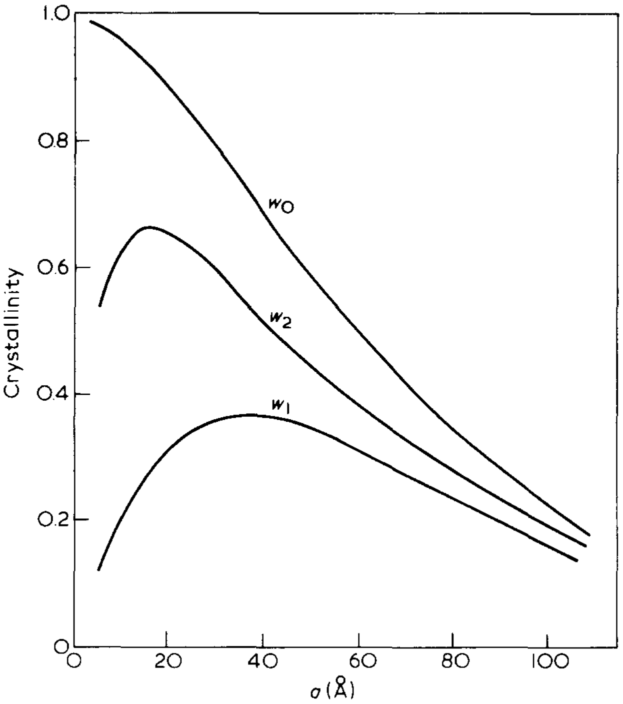

Figure 2 Calculated dependencies of crystallinity on critical nucleus size according to various models

structure by means of the following approximate relation

$$L=\frac{a[wv_c+(1-w)v_a]}{wv_c} \tag{7}$$

where w is the crystallinity, v_a and v_c are the specific volumes of amorphous and crystalline regions respectively. *Figure 3* shows the values of L as a function of crystical nucleus size calculated assuming w equal to w_1 and w_2 respectively for models A and B. Both dependencies are regarded again as limits for expected values of long spacing. The straight line in this Figure represents the values of a assumed to be the thickness of the lamellae.

In this way the model is described by two independently measurable parameters the crystallinity and long spacing which are interrelated by the value of the critical nucleus size. Therefore the model is suitable for direct comparison with experimental data.

In the calculations the constant value of a was assumed which means that expressions obtained interrelate the finite crystallinity and long spacing values at a given temperature of crystallization T_0 in isothermal conditions. Usually, after crystallization at constant temperature the sample is cooled to ambient temperature. During this cooling the value of critical nucleus size decreases. The portion of material initially excluded from the crystalline phase formed at T_0 can therefore further crystallize at lower temperatures forming lamellar elements of smaller thicknesses and distributed between lamellae which were formed at T_0. This will change the crystallinity and long spacing of the system. The geometrical principles of space filling by lamellae described by Strobl are applicable in this case. According to this the sample at room temperature will have a crystallinity and long spacing other than that at the temperature at which it was initially crystallized.

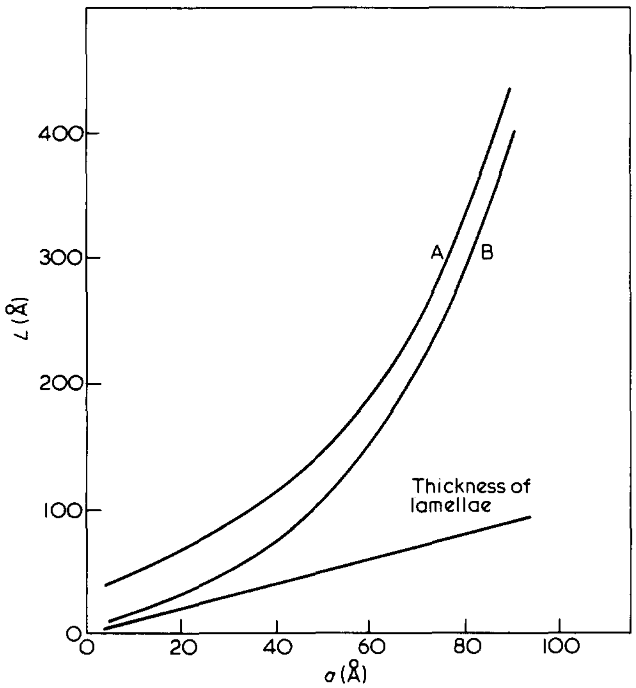

Figure 3 Calculated dependences of long spacing on the critical nucleus size according to models A and B

EXPERIMENTAL

Lupolen 1800S (BASF) with a molecular weight of ($\bar{M}_v$) 28 000 containing 35 methyl groups per 1000 carbon atoms was used. Thin films were prepared by press moulding at 130°C and subsequent cooling of polymer melt in water at temperatures 0°, 25°, 50°, 70°, 80° and 90°C. The process of sample cooling and studies of the resultant spherulite growth kinetics have been described in detail elsewhere[8]. During the cooling of each sample the temperature change was recorded by a thermocouple immersed in the sample. Simultaneously the spherulite growth was observed by small angle light scattering technique. Both sets of information have shown that in all samples growth of spherulites proceeds with such rate that samples become spherulitic in a narrow temperature interval dependent on the temperature of the cooling bath. This makes it possible to assume, with some approximation, that the crystallization related to spherulite growth was not far away from isothermal conditions. The middle value of the temperature interval at which spherulite growth was observed was therefore assumed as the crystallization temperature. After 20 seconds immersion in the cooling bath the samples were brought up to room temperature by subsequent immersion in water at 25°C. *Table 1* shows the main relevant parameters for the cooling process and the supermolecular structure formed in the samples. The values of crystallinity and long period given in the Table are those which were measured at room temperature by X-ray diffraction and small angle X-ray scattering, respectively.

The melting behaviour of these six samples was studied by differential scanning calorimetry (d.s.c.) as described elsewhere[9] and by small angle X-ray scattering at successively increasing temperature.

Intensity distributions of small angle X-ray scattering were recorded by means of Kratky camera with a

Table 1 Characteristics of cooling process and morphology of samples

Sample	Temperature of cooling bath (°C)	Temperature interval of spherulite growth (°C)	Mean crystallization temperature (°C)	Volume average spherulite radius (μm)	X-ray crystallinity (%)	Long period (Å)
1	0	72.2–75.2	73.7	1.83	43.2	103
2	25	73.2–76.5	74.8	1.98	43.4	106
3	50	74.8–78.6	76.7	2.16	43.5	109
4	70	78.0–81.5	79.7	2.28	44.2	109
5	80	82.0–85.0	84.5	2.43	45.2	111
6	90	90.5–91.5	91.0	2.84	45.6	113

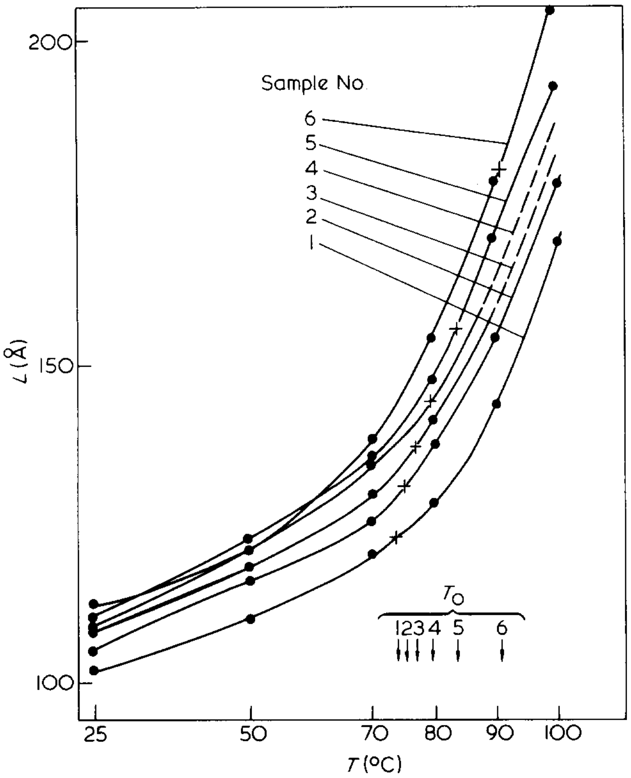

Figure 4 Temperature dependence of long spacing for samples 1–6 determined by small angle X-ray scattering

proportional counter. The samples with uniform thickness were successively heated up to the temperature of measurement in an evacuated heating chamber in which the temperature during the measurement was kept constant. The long period values at a given temperature were determined from $I(s)s^2$ scattering curves obtained by application of desmearing procedure elaborated by Strobl[10]. The results are shown in *Figure 4*.

The values of long spacing increase considerably with temperature for all samples. However, it was observed that this change is completely reversible only if the sample was not heated up above the temperature of the initial crystallization and was subsequently cooled down in a water bath. For sample No. 5, when heated up to 80°C and cooled down quickly the long spacing has only changed to 113 Å in comparison with the original value of 111 Å (both measured at room temperature). For the same sample, when heated up to 100°C, the long spacing values measured at room temperature were 121 and 130 Å dependent on the fast or slow cooling respectively.

The above observations make it possible to assume that from dependencies in *Figure 4* we can determine values of long spacing $L(T_0)$ characteristic for the structure formed at the temperature of crystallization. The value of long spacing for each sample was determined from the respective $L(T)$ dependence at the temperature assigned as the mean crystallization temperature (compare *Table 1*). Respective points are shown in *Figure 4* by crosses.

To determine the values of crystallinity at temperatures at which the samples were crystallized use was made of melting thermograms recorded by d.s.c.[9]. Assuming that $\frac{dH}{dT} \sim -\frac{dw}{dT}$, we have corrected crystallinities measured at room temperature (values given in *Table 1*) according to the following equation

$$w(T_0) = w_x\left(1 - \frac{\Delta H(T < T_0)}{\Delta H_f}\right) \qquad (8)$$

where w_x is the value of crystallinity determined at room temperature from X-ray diffraction, ΔH_f is the overall heat of fusion of the sample and $\Delta H(T < T_0)$ is the heat of fusion measured up to the temperature at which the sample was originally crystallized. Both ΔH quantities are represented by respective areas under the melting d.s.c. trace as shown schematically in *Figure 5*.

In this way both crystallinity and long spacing values were determined as characteristic for temperatures at which the samples were crystallized. Such data are now suitable for comparison with dependences predicted by the models introduced in this paper.

The comparison was made in the following way: Values of $L(T_0)$ were used for determination of lamellar thicknesses according to dependences plotted in *Figure 3*. Respective long spacing value for each sample determines the range of lamellar thicknesses Δa lying between extremes predicted by the models A and B as shown in *Figure 6a*. The crystallinity values $w(T_0)$ are then related to respective Δa values as shown in *Figure 6b*. A three percent error Δw in determination of the absolute values of crystallinity was assumed here. The results show that the data for all samples fall exactly between dependencies of w_1 and w_2 predicted by the models. They cover, however, a narrow range of theoretical dependencies. A wider range of crystallization temperatures of samples would extend the comparison.

An attempt has been made to compare the models with results obtained by Strobl *et al.*[6] for the same polymer crystallized at 100°C. The values of long spacing $L = 267$ Å, lamellae thickness $d = 60.5$ Å and crystallinity $w = 0.195$ were obtained by these authors from small angle X-ray scattering. The comparison has not shown good agreement between these results with the dependencies predicted by the models. For a lamellae thickness of 60 Å the models predict crystallinity values ranging from 0.30 to 0.35 which are much higher than the value determined experimentally. Such discrepancies for higher crystallization temperatures have been, however,

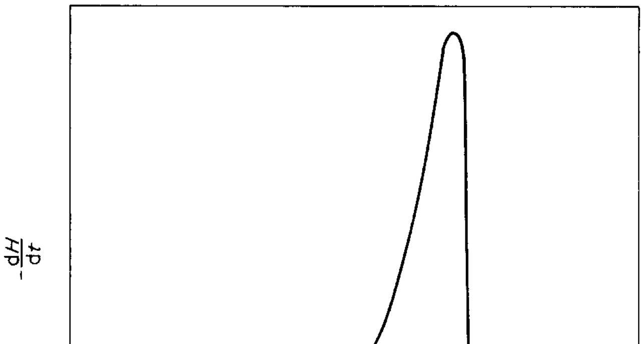

Figure 5 Illustration of evaluation of $\Delta H(T < T_0)$ from d.s.c. thermogram

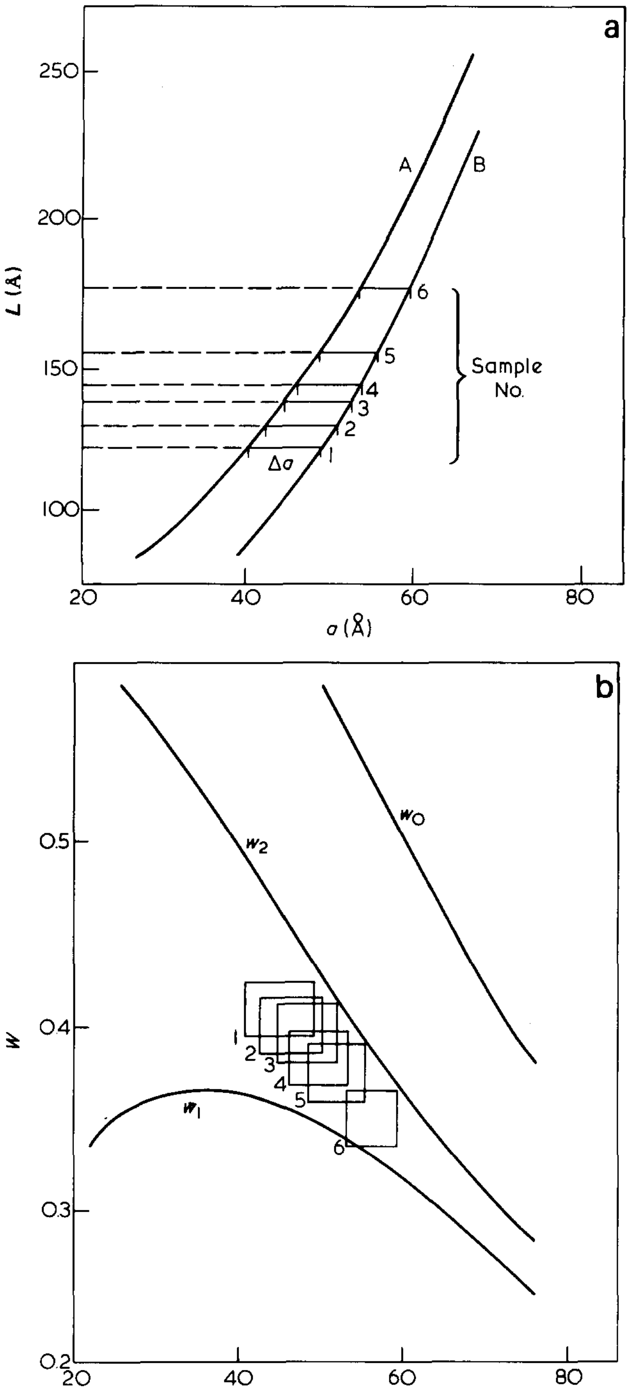

Figure 6 Comparison of (a) experimental long spacing and (b) crystallinity values with those predicted by models (For detailed description see the text)

expected for two reasons: (1) the models in actual form assume that all chain segments longer than the critical length can contribute to the crystalline phase, and such an assumption is non-ralistic when the critical length becomes large and consequently the concentration of longer chain segments becomes low as it takes place at temperatures close to melting point of the polymer, and (2) the chain axes in lamellae can be tilted with respect to the lamellar basal planes as observed in oriented samples of branched polyethylene annealed at higher temperatures[11]. In the latter case chain segments in the lamellae are longer than the lamellae thickness. Assuming for example the tilt through an angle of 40° and the thickness of lamellae of 60 Å we get the length of chain segments $a \approx 80$ Å. This, according to the models, gives crystallinity values ranging from 0.23 to 0.25 which are much closer to the value determined by Strobl *et al.*[6].

CONCLUSIONS

The results obtained in this study for samples crystallized at temperatures below 90° are in satisfactory agreement with theoretical predictions. This leads to the conclusion that the correlation between morphological parameters (crystallinity and long spacing) determined by the molecular structure of the polymer containing non-crystallizable units is predicted on the basis of realistic models of molecular arrangement inside lamellae. The models need however further consideration to be consistent with structure of samples crystallized at higher temperatures.

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REFERENCES

1 Keller, A. and Priest, D. J. *J. Polym. Sci. B* 1970, **8**, 13
2 Kawai, T., Ujihara, K. and Maeda, H. *Macromol. Chem.* 1970, **132**, 87
3 Flory, P. J. *Trans. Faraday Soc.* 1955, **51**, 848
4 Kilian, H. G. *Kolloid Z.u.Z. Polym.* 1969, **231**, 534
5 Fischer, E. W., Martin, B., Schmidt, G. F. and Strobl, G. IUPAC Toronto 1968, Preprints A-6, No. 17
6 Strobl, G. R., Schneider, M. J. and Voigt-Martin, I. G. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1361
7 Pope, D. P. and Keller, A. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 821
8 Pakula, T. and Kryszewski, M. *Eur. Polym. J.* 1976, **12**, 47
9 Pakula, T. in preparation
10 Strobl, G. R. *Acta Cryst. A* 1970, **26**, 367
11 Hay, I. L. and Keller, A. *J. Mat. Sci.* 1966, **1**, 41; *ibid.*, 1967, **2**, 538