Equilibrium shapes of microparacrystals in chain hydrocarbons and ammonia catalysts*

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The linear relationship between the unit cell cross-section *ab* and the reciprocal of lamellae thickness *H*, first experimentally observed by Davis *et al.* for melt- and solution-crystallized linear polyethylene (PE) and paraffins and now also shown to apply for branched materials, can be theoretically derived if one makes use of the presence of microparacrystals. The existence of microparacrystals involves two kinds of novel phenomena: (1) liquid-like lattice distortions which are both limiting the size of the crystallites and sometimes provoking a volume expansion of the lattice; (2) the formation of an equilibrium shape of the microparacrystals. Kinks, branches and thermally-induced rotational distortions give rise to different typical slopes of the linear plots for chain molecules. The slope of the plot for the ammonia catalyst is zero, because no volume increase occurs on the inclusion of $FeAl_2O_4$ motives within the lattice.

INTRODUCTION

The so-called 'crystalline phase' of melt- and solution-crystallized chain polymers consists of mosaic blocks with liquid-like lattice distortions, which can be defined as microparacrystals (*mPCs*)[1]. These distortions are produced by kinks, branches and other conformational variations[2]. The *mPCs* in melt-crystallized branched PE reach an equilibrium shape after stretching to the natural draw ratio[3,4]. All branches are segregated outside of the newly formed *mPCs* up to branching ratios $\epsilon = 1.3\%$. The cross-section *ab* of a lattice cell and the paracrystalline distortions concurrently increase when ϵ becomes larger than 1.3%. Davis *et al.*[5] investigated orthorhombic paraffins of different chain lengths and linear PE, crystallized under different conditions from solution and melt. These authors found a linear dependence of *ab* on the reciprocal of the lamellar thickness *H*. It was proposed that slope differences should be correlated to differences arising in surface effects such as fold interactions, methyl interactions, fold packing, etc. Furthermore, the variation of cell dimensions with lamellar thickness led to a quadratic term – lying scarcely outside the experimental error – in the variation of density with long period.

In the present study the coherent height *H* of the crystals in chain direction will be calculated from the SAXS long period *l* reduced by the volume fraction of crystallinity, because *H* depends solely on the properties of the crystalline phase and not on the thickness of the amorphous interlayers. The same linear relationship between *ab* and the value of $1/H$ can be found for commercial PE within a wide range of chain defects from $\epsilon = 0.17\%$ up to 6.9%[6,7]. The fraction of defects incorporated into the lattice did not exceed 20% of the total number of defects. A quantitative connection between the concentration γ of chain defects within the lamellae and the size of *ab* important for the following conclusions, was derived.

In *Figure 1* the averaged data of Davis *et al.*[5] for melt- and solution-crystallized PEs and for paraffins of different molecular weights are depicted as full and broken lines respectively. The experimental data of Baltá-Calleja *et al.*[6] and Martinez de Salazar *et al.*[7] at 296K for branched PE slowly

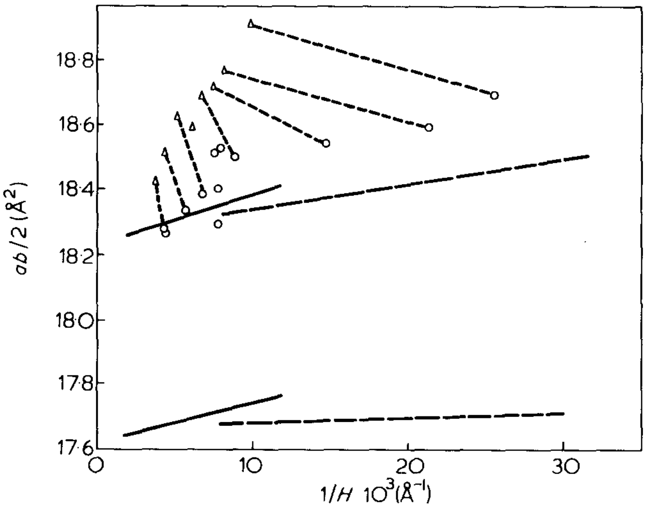

Figure 1 The $\Delta\ 1/H = K\ \Delta\ ab/2$ plot of melt-crystallized PE under slow cooling (○) and 10°C below the melting point (△) with nine different branching ratios between $\epsilon = 0.17\%$ and 6.9%. The dotted lines connect samples of the same ϵ. Here *ab* increases with increasing size *H* of the *mPCs*. The full lines are the averaged values of Davis *et al.*[5] for melt- and solution-crystallized linear PE. The broken lines represent the values for paraffins at 296K (above) and 153K (below)

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*Dedicated to Professor Dr W. Gerlach on the occasion of his 90th birthday.

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Table 1 The reciprocal of the slope value, K. $10^2(\text{Å}^{-3})$

Samples	153K	296K
n-paraffins	61 ± 15	13 ± 1.5
Linear PE solution-crystallized	7.9 ± 1	6.8 ± 1
Linear PE melt-crystallized	9 ± 2	6 ± 1
Branched PE melt-crystallized with 1°C/min cooling	–	6 ± 1
Branched PE isothermically melt-crystallized at $\Delta T = 10^\circ\text{C}$	–	1.5 ± 1
Ammonia catalyst	–	∞

cooled (1°C/min) and isothermally crystallized 10°C below the melting point are also drawn. The former data scatter considerably (correlation factor = 0.59), but furnish, indeed, a slope similar to that for linear PE with an intercept of about 18.23 Å^2. The latter values offer a much larger slope with a better least square fit and a much smaller factor $K \sim 1.5 \times 10^{-2}$ Å^{-3}. From all these data the relation

$$\Delta(1/H) = K\Delta\left(\frac{ab}{2}\right) \qquad (1)$$

is straight forwardly derived.

The reciprocals K of the slope values from *Figure 1* are collected in *Table 1*. This table also contains the infinitely large K-value for the ammonia catalyst[10]. Though the errors of experiment are relatively large, specially at 153K, the rough linear relationship[1] can be immediately observed for all PE and paraffin data.

The purpose of this paper is to show that the linear dependence between unit cell dimensions and reciprocal crystal thickness can be simply explained, if the stacks of lamellae are considered to be sheets of *mPCs*. The abnormally small K-value of branched PE melt-crystallized 10°C below the melting point and the extremely large K-value of paraffins at 153K will be explained in terms of specific properties of the chain conformation. The infinitely large K-factor of the ammonia catalyst will also be justified.

Paracrystallinity features relating to microstructure

The presence of liquid-like distortions within the lattice, mathematically defined by the theory of paracrystals[8], is closely connected with the concept of the free surface energy of the lateral boundaries of the microparacrystals. The latter are generated when a minimum concentration of statistically distributed point defects within a lattice limits the crystal coherence to a certain number of lattice planes. An important consequence of paracrystallinity is that for the melt- and solution-crystallized polymers so far investigated, the ammonia catalyst and many other colloidal systems, the relation

$$N = D/\bar{d} = (\alpha^*/g)^2 \qquad (2)$$

always holds[9]. This equation relates the number, N, of lattice planes, the crystal size, D, orthogonal to the hkl direction divided by the lattice spacing, d, with the reciprocal squared paracrystalline standard deviation of the lattice spacing,

$$g = (\overline{d^2} - \bar{d}^2)^{1/2}/d \qquad (3)$$

and $\alpha^* \sim 1/6$ for PE[9]. Thus, the higher the concentration of defects, the greater the g-value obtained and consequently the larger the inner surface according to equation (2). $\bar{d}$ averaged for the observed (200) and (110) reflection of PE has a value of ~4 Å. Equation (2) is of fundamental importance for the thermostability of all colloidal systems and catalysts[10].

The paracrystalline lattice distortions in chain polymers are admittedly mostly generated by the presence of kink isomers mainly 2gl in the PE lattice[2]. These chain conformers do not efficiently fit into the lattice thus producing a cell expansion preferentially along the (110) direction which is approximately of 50% with respect to the undisturbed zig-zag interchain separation. If dR/R is the relative thickening of the chain (R being the radius of the molecular cross-section normal to c) provoked by the creation of a 2gl kink in the (110)-direction and γ is the number concentration of kinks, then the value of the distortion, g, produced will be[1]:

$$g = [\gamma(1-\gamma)]^{1/2}\, dR/R \qquad (4)$$

In the case of kinks in PE, dR/R has a value ~0.5, as mentioned above. The formation of each kink concurrently reduces the length of the chain by a $c/2$ unit and enlarges the interchain separation in such a way that each $-CH_2-$group is replaced by a conformational detail with a $\delta V = 60$ Å^3 larger volume[2]. Since each lattice cell contains four monomers, a concentration, ϵ_c, of chain defects incorporated in the lattice produces an increase of the averaged volume $\bar{\nu}$ of all paracrystalline lattice cells by

$$\epsilon_c = \frac{\bar{\nu} - \nu_0}{4\delta V} \qquad (5)$$

where ν_0 is the volume of the undisturbed lattice cell. One of us (FJBC)[6,7] has recently shown that ϵ_c and γ are identical quantities within the error of experiments for both, branched, melt-crystallized under slow cooling (1°C/min), and isothermally crystallized PE. Thus

$$\epsilon_c \sim \gamma \qquad (6)$$

A further consequence of paracrystallinity is the large mobility of the macromolecules within the *mPCs*. The lateral boundaries between *mPCs* presumably contain a variety of kinks and other conformational defects. Renecker[11] suggested that pairs of kinks in a chain generate 'caterpillars' by means of inner rotations around the c-axis. These can rearrange if the material is annealed and/or deformed to *mPCs* of a specific lateral size with a minimum free surface energy given by equation (2). For instance, cold drawn PE with different branching concentrations suffers a rearrangement in such a way that Wulff's rule holds[4]:

$$D = \zeta H \qquad (7)$$

thus, relating the microparacrystallite size for the normal, D, and the parallel, H, direction. The coefficient ζ exhibits values[12] which lie between 1 and 2 depending on the lateral direction.

We wish next to illustrate how the above phenomena of paracrystallinity lead to the same conclusions drawn by Davis *et al.*[5]. Namely, that surface effects play an important role in simultaneously defining both the size of H and the unit cell cross-section, *ab*: (i) through the presence of three-dimensional distortions of a new type previously unknown in crystallography and (ii) by means of the concept of lateral crystal boundaries mostly ignored in current papers of polymer physics[13].

Derivation of equation (1)

Combination of equations (2) and (7) leads to

$$\Delta\left(\frac{1}{H}\right)=\frac{\zeta}{d}\Delta\left(\frac{1}{N}\right) \tag{8}$$

From equation (3) one obtains

$$\Delta\left(\frac{1}{H}\right)=\frac{\zeta}{d\alpha^{*2}}\Delta(g^2) \tag{9}$$

Equation (4) leads to

$$\Delta\left(\frac{1}{H}\right)=\frac{\zeta}{d}\left(\frac{dR}{\alpha^*R}\right)^2\Delta\gamma$$

Using now equation (6) and taking into account that the lattice parameter c remains constant ($c = 2.54$ Å), the increase of the average volume $\bar{v}$ of a lattice cell will be:

$$\Delta\bar{v}=2c\Delta\left(\frac{ab}{2}\right) \tag{10}$$

then

$$\Delta(1/H)=K_{theor}\Delta\left(\frac{ab}{2}\right)$$

where

$$K_{theor}=\frac{\zeta}{d}\left(\frac{1}{\alpha^*}\frac{dR}{R}\right)^2\frac{2c}{4\delta V} \tag{11}$$

By substituting the above collected numerical values for linear PE ($d \sim 4.0$ Å; $\alpha^* = 1/6$; $dR/R = 0.5$; $c = 2.54$ Å; $\delta V = 60$ Å^3; $\zeta = 1.5$), one obtains

$$K_{theor}=\sim 7.2\times10^{-2}\ \text{Å}^{-3} \tag{12}$$

value which is in fair agreement with the K experimental ones of the linear PE samples collected in *Table 1*. It is interesting to note that this K-value also agrees for the branched PE samples, cooled down from the melt at 1°C/min. Obviously $(\Delta R/R)^2/\delta V$ has here a similar value as that for linear PE, solely distorted by kinks. This value is four times smaller for branched PE crystallized 10°C below the melting point. A pertinent explanation for this discrepancy is offered later on.

DISCUSSION

The above results suggest that the experimental linear relation found between $1/H$ and $ab/2$ for the PE samples, paraffins and ammonia catalyst under discussion is in fact directly in favour for the existence of microparacrystals in polymers. The surface energy part certainly plays an important role as pointed out by Davis *et al.*[5]. The surface effects of the lamellae seem, however, to be not the only ones exclusively responsible for this behaviour. The three-dimensional distortions embedded within the so called crystalline phase are evidently influencing the $1/H$ and ab values. Furthermore, the presence of paracrystalline distortions prevents the formation of unbounded lamellae with negligible lateral surface energies. Thus, in addition to the fold surface, the lateral boundaries, hitherto neglected[12], have to be also taken into account. The above deviation of K_{theor} suggests that the thickness of the lamellae is correlated to the cross-section dimensions of the unit cell by means of the boundary surface energy. The paracrystalline distortions, hence, induce an enlargement on the one hand of the ab dimensions (equations (5) and (10)) and on the other a decrease of the lateral size D of the *mPCs* (equation 2). The latter effect influences, in addition, the H size of the *mPCs* in chain direction by means of Wulff's relationship (equation 7). In conclusion, the contribution of the above discussed physical effects furnishes a satisfactory explanation for the experimental findings of Davis *et al.*[5] and the data of Baltá-Calleja *et al.*[6,7] in *Figure 1*.

The other interesting result is that equation (1) also is valid for n-paraffins. Obviously paraffins consist also of *mPCs* though the g-values could not previously be measured because they lie beyond the resolution power of the available diffraction techniques. The large temperature-dependent value of K suggests that here the distortions are thermally induced rotational conformations (the so called rotons). Their $(dR/R)^2/\delta V$-value is, according to equation (12), two-(ten) times larger at 296K (153K) than for PE and proves the thermally induced character of this distortion. The anharmonic component of the rotations is small at small oscillation amplitudes. δV increases therefore appreciably only at higher temperatures. $(dR/R)^2$ is, on the other hand, proportional to the square of this amplitude and hence proportional to the temperature. $(\delta R/R)^2/\delta V$ consequently increases in a characteristic way with decreasing temperature.

The extremely small K-value of PE melt-crystallized 10°C below the melting point indicates that $(\delta R/R)^2/\delta V$ is four times smaller than for the other PE-samples. The most reasonable explanation for such a low K-value is that during this slow and cautious crystallization process the branches have enough time to become embedded into the *mPCs* with a minimum of strain fields. This process resembles the above mentioned mechanism occurring during stretching of branched PE[3,4]. There the branches are totally segregated outside of the newly formed PE-*mPCs* up to branching ratios $\epsilon = 1.3\%$ providing, in addition, evidence for the liquid-like mobility of the chains caused by caterpillars etc.[11]. Another striking difference between the behaviour of branched PE and melt- and solution-crystallized linear PE is that for the former ab increases (instead of decreasing) with decreasing $1/H$ (see the dotted lines in *Figure 1*), if the crystallization is carried out isothermally. The explanation is that the branches are situated at fixed positions along the chains whilst the kinks are able to displace themselves. The slower and the more cautious is the crystallization contributing to larger *mPCs*, the larger will be the number of short segments ($<H$) between adjacent branches, which must be built in, to the crystals. The averaged size ab of a lattice cross-section therefore increases. δV in equation (11) is negative, because when $1/H$ increases the mean increase $\Delta\, ab/2$ of the lattice cell cross-section is

negative. This is due to the fact that only longer chain segments are required. In branchless PE and paraffins, on the other hand, the distortions have more possibilities to be removed under slow crystallization and, as a result, *ab* decreases with increasing *H*.

We mentioned above that equation (2) is of fundamental importance for all colloidal systems. A last example is offered in *Table 1* for the ammonia catalyst. In this case the *mPCs* are evidently not built up by chain molecules, but by metallic α-Fe-atoms. Instead of conformational defects of the chain segments here the motives ($Fe^{++}Al_2^{+++}O_4^{--}$) are statistically embedded within the Fe-lattice[10]. These defects occupy the same volume as that replaced by seven Fe-atoms. Hence $\delta V = 0$ and $K = \infty$ (*Table 1*). In chain molecules the branches are fixed and the kinks cannot emigrate by annealing[14]. Thus, the thermal induced rotons are in an equilibrium state. However, in case of the ammonia catalyst, the $FeAl_2O_4$ motives migrate by annealing at temperatures $T > 400°C$. Hence $ab/2$ is independent of H and H increases according to the α^*-law of equation (2).

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