Structure of crystalline polymers produced by rapid cooling of their melts:
1. Polyethylene

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The influence of the structure of motlen high density polyethylene on that of the crystalline material produced by rapid cooling of this melt has been investigated by Raman spectroscopy. It is shown that a relationship exists between the characteristic dimensions of a molecule in the molten phase and the length of the all *trans* linear sequences present in the subsequent crystalline material. The observations reported here are shown to be incompatible with the folded-chain lamellar structure often proposed for melt crystallized material; and an alternative model, in which the chains meander through neighbouring lamellae, is supported.

INTRODUCTION

Most current textbooks make it clear that the structure of melt-crystallized linear polymers, crystallized in conditions close to isothermality, can be best described by a spherulitic morphology containing a chain-folded lamellar structure. Justification for this view exists on theoretical[1] and experimental[2] grounds.

It is also apparent that linear polymers crystallized rapidly from their melts are spherulitic and also lamellar. It has therefore been widely, but not universally, assumed that their structure is also based on folded-chain lamellar units. In some quarters, this hypothesis has been contested since its original proposition[3,4]. Recently, neutron scattering data have been published which suggest that the radius of gyration of linear polyethylene and polypropylene in their melts is essentially the same as that in the solid produced by cooling them[5,6]. This analysis is interpreted to indicate that the chains lie in approximately the same position after crystallization as they did in the melt; and hence that chain-folding cannot occur during crystallization. In our Note on the Raman spectra of quenched melts of polyethylene[7] we reached essentially the same conclusion, and it is the purpose of this paper to elaborate on this point.

Recently, we have become interested in the processes occurring during rapid cooling of melts and have been successful in producing a glass of linear polyethylene for the first time[8]. A surprising characteristic of this material is that it is only stable at cryogenic temperatures and, in fact, crystallizes rapidly near 170K. We considered that it was unlikely that a glassy phase at such a temperature could permit sufficient flexibility in its constituent molecules for them to rearrange themselves during crystallization into folded-chain lamellae.

We therefore initiated a study of the structure of linear polyethylene rapidly cooled from the melt. Whilst the most rapid cooling experiments described in this paper are strictly atypical of commercial production practice, some of the data presented and our conclusions clearly have immediate relevance to the structure of commercially-produced films, fibres and mouldings.

Experimental data already in the literature which support current polymer structure theories have been obtained for very small or negligible cooling rates. In this paper, we propose that the more widely accepted current theoretical models may be inappropriate when rapid cooling conditions are encountered.

EXPERIMENTAL

Samples of commercial linear polyethylene (Rigidex 9 and 50) were kindly supplied in pellet form by British Petroleum Ltd. Rigidex 9 was used for the majority of the experiments reported here, but some were repeated using Rigidex 50 or a very high molecular weight linear polyethylene. This sample was kindly supplied by Professor R. N. Haward of the University of Birmingham. The samples have been characterized as shown in *Table 1.*

Raman Spectroscopy

The lamellar thickness of polyethylene as a function of the crystallization conditions was monitored using Raman

Table 1 Some characteristics of the polyethylenes used in this study

Grade characteristic	Rigidex 9	Rigidex 50	High molecular weight P.E.
M_n	9.8×10^3	7.4×10^3	260×10^3
M_w	179×10^3	96×10^3	1.9×10^6
M_w/M_n	18.2	13	7.3
Methyl groups per 10^3C atoms	0.1	2	1
Melt index (g 10 min^{-1})	0.9	5.5	–
Density	0.962	0.966	–

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spectroscopy[9,10]. The longitudinal vibrations of the linear all *trans* sequences present in the cores of the crystalline lamellae give rise to a low energy Raman active vibration, the longitudinal accoustic mode (*LA* mode). The frequency of vibration of this mode is inversely proportional to the length of the linear sequences according to:

$$\nu = \frac{m}{2L}\left\{\frac{E}{\rho}\right\}^{1/2} \qquad (1)$$

where ν is the frequency (Hz); m is the mode order; E is the Young's modulus of the chain (Pa or $\mathrm{Nm^{-2}}$); ρ is the crystalline density ($\mathrm{kg\,m^{-3}}$) and L is the length of the all *trans* sequence in m.

We have used the value of $E = 3.4 \times 10^{11}$ Pa proposed by Schaufele and Shimanouchi[11] in deducing the values of the lamellar core thicknesses presented in *Tables 2* and *3*.

Raman spectra were recorded at room temperature using a Cary 82 (triple monochromator) Raman spectrometer powered by a Coherent Radiation model 52B argon ion laser operating at 514.5 nm. The laser power was limited to ~100 mJ $\mathrm{s^{-1}}$ to prevent any sample decomposition.

The Raman band due to the *LA* mode is superimposed on a steeply rising background (*Figure 1*). In order to determine the position of the band head, the spectrum was deconvoluted using a Dupont A 310 curve analyser. Both the vibrational band and the background were approximated by Gaussian curves. A typical recording and deconvolution of the *LA* mode is shown in *Figure 2*. In the experiments reported here, the error in measurement of the band head frequency was estimated to be ~0.2 $\mathrm{cm^{-1}}$. On repeating the experiment, values were obtained within 0.2 $\mathrm{cm^{-1}}$ of the mean value. Combining these figures we have, with due caution, quoted the band head frequencies to the nearest 0.5 $\mathrm{cm^{-1}}$.

Thermal treatments

Samples of polyethylene (5–10 mg) contained in an aluminium sample pan were heated in a Perkin–Elmer DSC-2B differential scanning calorimeter to a predetermined temperature. When equilibrium had been established, the samples were removed and, still in their aluminium cans, quenched into a refrigerant. The d.s.c. was also used to provide a controlled cooling rate when required.

Table 2 Effect of melt temperature and molecular weight on the LA mode of some polyethylenes quenched into liquid nitrogen

Melt temperature (K)	LA mode frequency ($\mathrm{cm^{-1}}$) [Lamellar thickness (nm)]		
	Rigidex 9	Rigidex 50	High mol wt PE
473	17.5 [17.4 ± 0.5]	17.5 [17.4 ± 0.5]	18.5 [16.4]
573	18.5 [16.4 ± 0.5]	19.0 [16.0 ± 0.4]	19.5 [15.6]
673	20.5 [14.8 ± 0.4]	20.0 [15.2 ± 0.4]	20.0 [15.2]

One experimental parameter requires immediate justification. All samples cooled from the melt were kept at a particular melt temperature T_m for approximately 60 s before quenching. It is desirable that polymer samples be kept hot for as short a time as possible; on the other hand they must be allowed to equilibrate at the selected T_m. Samples were studied after they had been heated to 573K for either 1, 5 or 10 min before quenching into liquid nitrogen. *LA* modes of 18.2, 18.3 and 18.5 $\mathrm{cm^{-1}}$ were obtained. Clearly then, equilibrium has occurred after about 1 min.

X-ray diffraction

Photographs of the diffraction patterns of the samples (~40 μm thick) were taken using nickel-filtered CuKα radiation (0.154 nm). Radial X-ray diffractograms were obtained from the photographs using a Joyce–Loebl microdensitometer. X-ray crystallinities were then calculated using the straight ratio method.

Optical microscopy

Spherulitic structures in polymer films give rise to a characteristic 'Maltese Cross' pattern when viewed with polarized light. To determine spherulitic size, quenched films of approximately 30 μm were observed with a Vickers M10 petrographic microscope using X400 magnification.

POLYETHYLENE CRYSTALLIZED FROM THE GLASS PHASE

Assuming that gross rearrangement of the molecules is unlikely to occur either during the production of a glass, or subsequently during low temperature crystallization, then it is reasonable to assume that the structure of the crystalline solid so produced, in this somewhat esoteric manner, will be related to that of the melt.

Flory *et al.*[12] have investigated the effect of melt temperature on the structure of the melt. They found that the unperturbed mean square end-to-end distance for the molecules decreases with increasing melt temperature according to:

$$\frac{\langle r^2(T_2)\rangle_0}{\langle r^2(T_1)\rangle_0} = \exp[-1.2 \times 10^{-3}(T_2 - T_1)] \qquad (2)$$

Table 3 Effect of melt temperatures, quenching agent and cooling rate on the LA mode of Rigidex 9. Data taken from ref 7

Melt temperature (K)	LA mode frequency ($\mathrm{cm^{-1}}$) [Lamellar thickness (nm)]			
	Quenched in			Cooled at 320 K $\mathrm{min^{-1}}$
	Liquid N_2	CO_2/acetone	Ice/water	
473	17.5 [17.4 ± 0.5]	17.0 [18.4 ± 0.5]	16.5 [18.4 ± 0.5]	15.0 [20.3 ± 0.5]
523	18.0 [16.9 ± 0.4]	18.5 [16.4 ± 0.5]	17.5 [17.4 ± 0.5]	–
573	18.5 [16.4 ± 0.4]	19.0 [16.0 ± 0.4]	18.5 [16.4 ± 0.5]	15.5 [19.6 ± 0.5]
623	19.5 [15.6 ± 0.4]	20.0 [15.2 ± 0.4]	20.0 [15.2 ± 0.4]	–
673	20.5 [14.8 ± 0.4]	21.0 [14.5 ± 0.4]	20.5 [14.8 ± 0.4]	16.5 [18.4 ± 0.5]

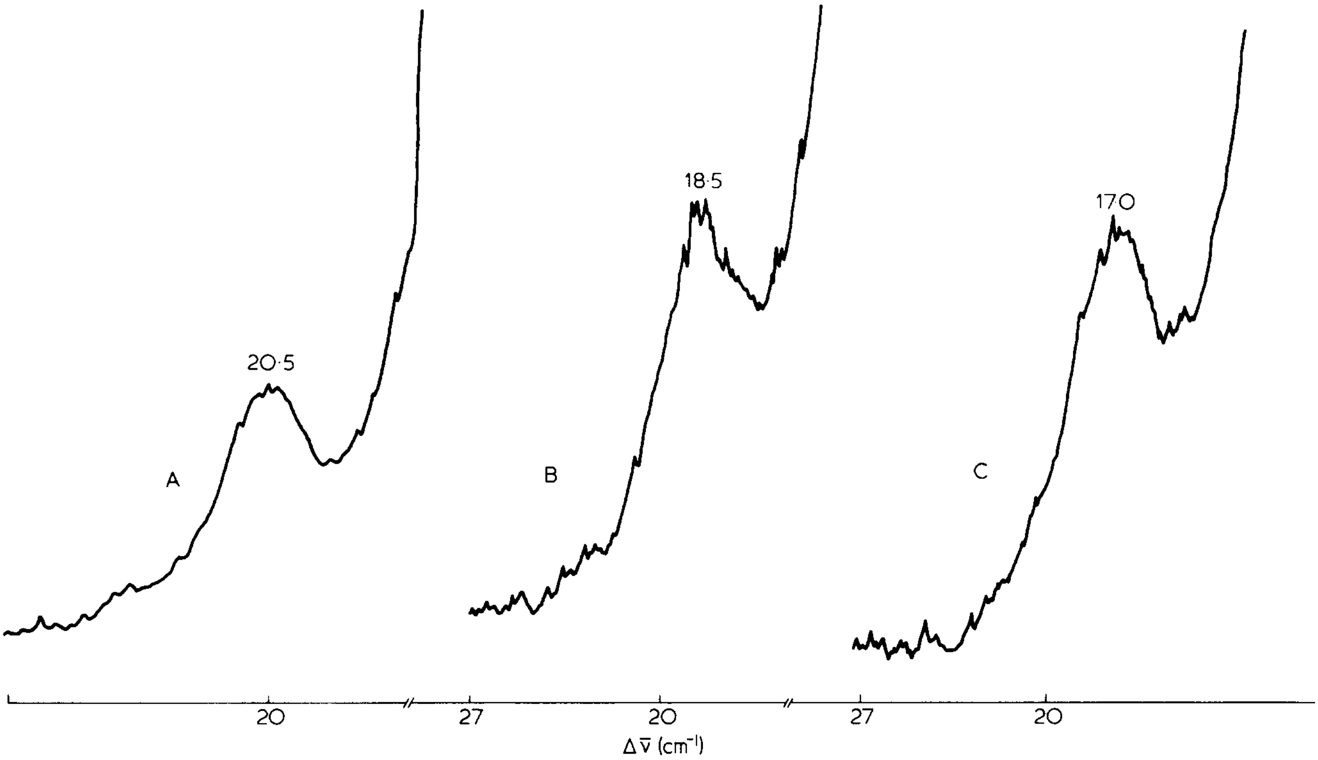

Figure 1 Some examples of the low frequency band due to the longitudinal accoustic mode. Samples of Rigidex 9 heated to 673 (A), 573 (B) and 473K (C) before quenching into liquid nitrogen

where $\langle r^2 (T)_0$ is the mean square end-to-end distance at temperature T.

We have investigated the effect of melt temperature on lamellar thickness over the range 433–673K. The results, shown in *Table 2*, confirm our hypothesis that the structure of the crystalline material produced from a glass is related to the temperature from which the glass was produced.

POLYETHYLENE CRYSTALLIZED UNDER RAPID CONDITIONS

In order to ascertain whether our observation is true only for material crystallized from the glass, or if it is a more general phenomenon, we repeated the experiments using different refrigerants. *Table 3* shows data comparing the effect of solid CO_2/alcohol(193K) and ice/water mixtures (273K) as quenching agents. Both refrigerants have temperatures in excess of T_g for polyethylene.

Clearly the same relationship is true here: the structure of the crystalline solid depends on its melt precursor, although no intermediate glassy phase had been produced.

One possible explanation for this relationship could be that the samples are increasingly decomposed with increasing melt temperature. However, several experiments carried out successively on the same sample showed complete repeatability. Furthermore, the results in *Table 2* are incompatible with a decomposition phenomenon.

Most crystallization theories for example those found in refs 1 and 13 predict that the lamellar thickness is a function of molecular weight and supercooling, i.e. $(T_m - T_c)$ where T_m is the equilibrium melting temperature and T_c is the temperature of crystallization. Supercooling, in turn, is a function of cooling rate and nucleation density. We have, therefore, investigated the effect of both of these variables on our rapid cooling experiments.

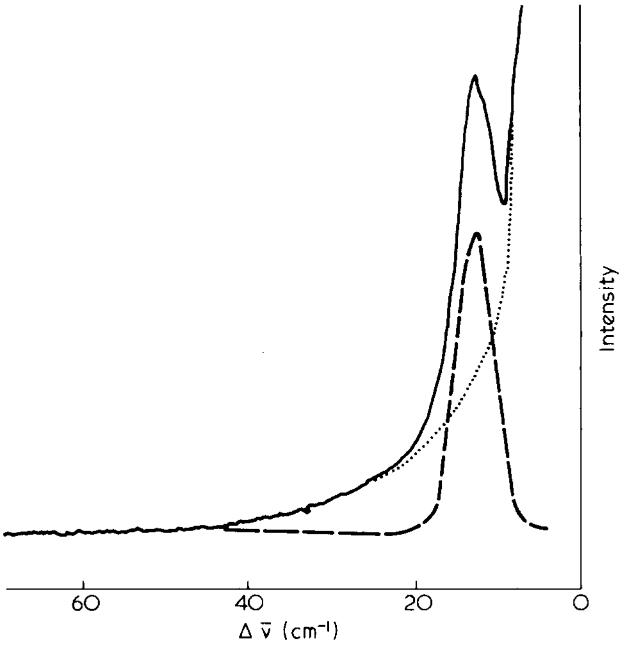

Figure 2 Deconvolution of the low frequency Raman spectrum

Effect of cooling rate

Rapid cooling rates are produced when the polyethylene melts are quenched into refrigerants such as solid CO_2/alcohol or ice/water. The former has a temperature of 193K and the latter 273K, thus if T_c is near 400K, the cooling rate of the samples in the two mixtures will differ by a factor of 2 at T_c (unless they are limited by thermal transfer). Despite this difference, the data in *Table 3* shows that for a particular melt temperature, the change in lamellar thickness produced by the two quenching agents is $\sim$5%. Thus, we conclude that

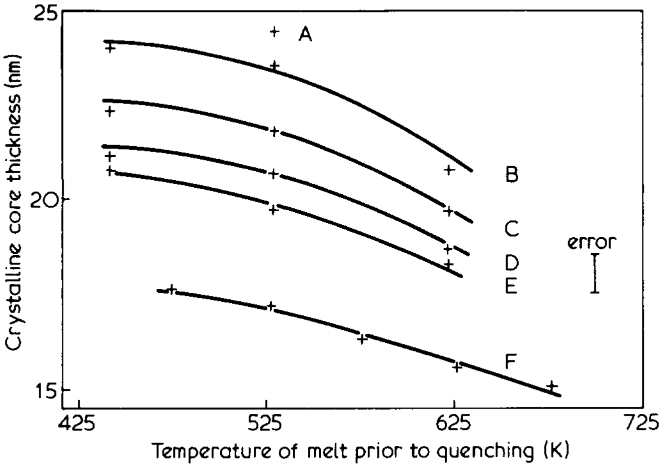

Figure 3 Effect of melt temperature on the lamellar thickness of samples of Rigidex 9 quenched into liquid nitrogen and at controlled cooling rates. A – 20K min^{-1}; B – 40; C – 80; D – 160; E – 320; F – quenched. The plotted lamellar thicknesses were calculated using equation 1, and the values of the LA mode frequencies corrected to the nearest 0.5 cm^{-1}

at very fast cooling rates, lamellar thickness is essentially unaffected by the cooling rate.

Controlled cooling experiments were carried out using the d.s.c. instrument as an oven. Samples were cooled from the melt temperature at controlled rates of 320, 160, 80 and 40 Kmin^{-1}. Even with these relatively modest cooling rates we still observe a dependence of the lamellar thickness on the prior melt temperature. The data are shown in *Figure 3*.

From these experiments on the effect of cooling rate two things are now clear:

(1) for a particular cooling rate, lamellar thickness is inversely proportional to the melt temperature;

(2) for a particular melt temperature, lamellar thickness is inversely proportional to the cooling rate; this relationship is only in evidence for relatively slow cooling rates.

Another explanation for this relationship could be that altering the melt temperature in some way alters the temperature at which the material crystallizes. A higher melt temperature causes crystallization to occur at lower temperatures, thus such samples will have a larger degree of supercooling giving rise to smaller lamellae. To investigate this possibility we cooled a sample as quickly as possible (40 Kmin^{-1}) in the d.s.c. detecting crystallization from the exotherm. It was observed that the d.s.c. traces of the sample heated to 600K and cooled, and then heated to 450K and cooled were essentially identical*, although the sample had quite different *LA* mode frequencies. This, it appears that the temperature of crystallization is not affected by the temperature of the melt.

Effect of nucleation density

The size of spherulites in melt crystallized material is a direct consequence of the number of nucleation sites in the sample at the time of crystallization. If the nucleation density is high, we observe small spherulites. Conversely, if it is low, we see larger ones. To investigate the effect of nucleation density on lamellar thickness, the following experiments were performed successively – on the same film of Rigidex 9 (~30 μm thick).

(i) A sample was heated to 473K and quenched. A film with small spherulites and a lamellar thickness of 17.5 nm was produced.

(ii) The same film was heated to 673K and quenched. This time the film had large spherulites and a lamellar thickness of 15.0 nm.

(iii) The sample was again heated to 473K and quenched. The spherulites were again of large size, but the sample had a lamellar thickness of 17.4 nm.

These experiments support the well established view that on heating the melt to high temperature, nuclei are irreversibly destroyed[14], but it also appears that the lamellar thicknesses formed under such quenching conditions are not governed by the nucleation density. Further support for this conclusion comes from the fact that similar effects have been observed when other grades of linear polyethylene, of widely differing origin (and hence inevitably different nucleation density), are quenched from the melt. *Table 2* contains the results from quenching experiments performed on Rigidex 50 and the high molecular weight sample. Comparison of the data leads to the conclusion that altering the $\bar{M}_n$ and $\bar{M}_n/\bar{M}_w$ does not alter the observation that the frequency of the *LA* mode is dependent on the melt temperature and that altering these properties does not alter the lamellar thickness produced from a particular melt temperature.

Another explanation for our observations is based on the model illustrated in *Figure 4*. According to this hypothesis, the temperature of the melt prior to quenching influences the ratio of the core thickness to that of the fold zone, i.e. $l_c/2l_f$. The Raman method is only sensitive to changes in l_c, and is relatively insensitive (at least in the case of polyethylene) to the value of l_f. With this model, our experimental conditions could be said to indicate a reduction in the value

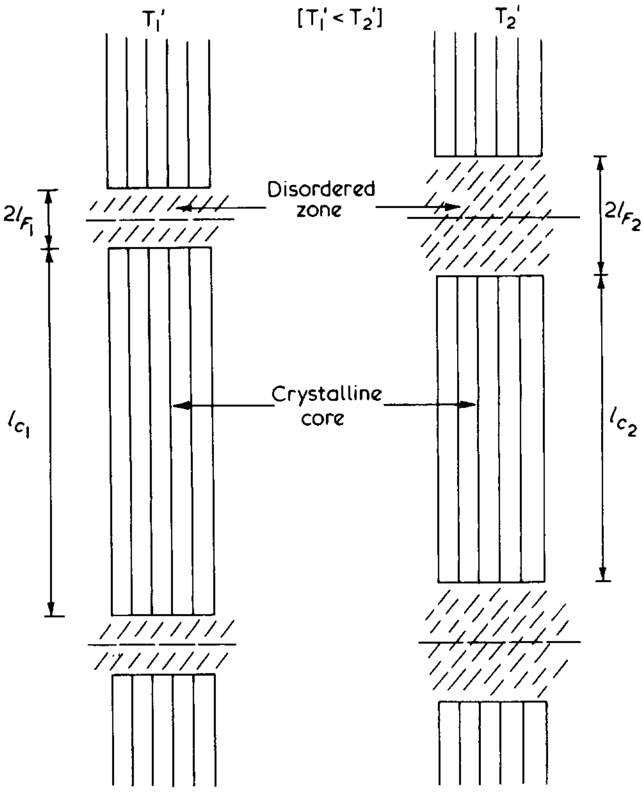

Figure 4 Illustration of the hypothesis that the melt temperature T' affects the ratio $l_c/2l_f$ but not the lamellar thickness $l_c + 2l_f$

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* Both the temperature at which crystallization was detected and the maximum temperature were within 1K for the two runs

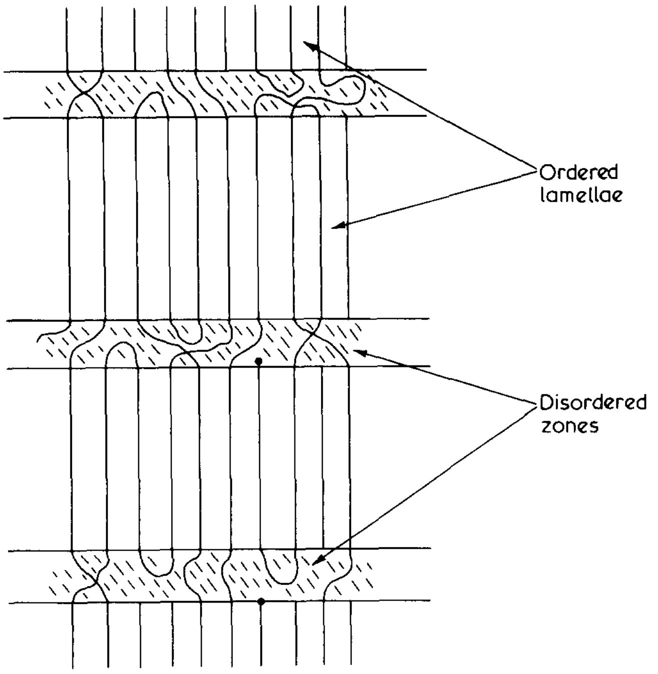

Figure 5 Schematic of the model involving molecules meandering through different lamellae

of l_f (concomitant with the increase in l_c), without changing $l_c + 2l_f$. If this is so, then the X-ray crystallinity will be proportional to l_c. For samples quenched into liquid nitrogen, from melt temperatures in the range 473–673K, the variation in l_c is about 12%. However, the X-ray crystallinities vary very little. Values of 0.68, 0.65 and 0.66 were obtained from samples quenched from 473, 573 and 673K respectively.

Thus it is clear that the crystallinity of the final sample is independent of the temperature of its melt precursor. Hence we conclude that these observations are inconsistent with the model illustrated in *Figure 4*.

DISCUSSION

From the experimental evidence cited above, we conclude that the structure of melt crystallized polyethylene is related to the temperature of its melt prior to cooling. As we have pointed out above, the radius of gyration of molten polyethylene falls with increasing temperature (although this has not yet been confirmed by neutron scattering experiments[15]). In our Note on this subject we suggested a direct link between this property of the melt and the lamellar thickness of the solid produced from it. This cannot be the case because molecular weight of the polymer does not alter its lamellar thickness when quenched from a particular melt temperature.

It is clear that we need to look for a more fundamental property of the melt. One such property is the CH_2–CH_2 *trans/gauche* ratio. This ratio will control the average link length in the melt and hence the overall convolution of the chains. It will also control the radius of gyration of a monodisperse polymer. The ratio of *trans* to *gauche* will fall with increasing temperature in a well understood way[17] and we suggest that it is this variable which influences the final structure.

We have suggested that the polymer chains in the solid lie in approximately the same positions in the solid as they did in the melt precursors, a proposal supported by recent neutron scattering data. We therefore favour a model close to the fringed micelle model for polyethylene cooled from the melt at other than very slow rates, and can see no reason for involving a chain folded structure. The model proposed by Flory in 1962 and largely ignored in recent textbooks would appear to us to be close to reality, i.e. we feel that the chains meander at random throughout a lamellar stack, folding back upon themselves or proceeding into adjacent lamellar cores in a completely random manner (*Figure 5*).

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