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The supercooling dependence of the initial fold length of polyethylene crystallized from the melt: unification of melt and solution crystallization

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Following the previous recognition [1], reached with the aid of real time low angle X-ray diffraction (using a synchrotron X-ray source) that in melt crystallized polyethylene the initial (primary) lamellar thickness is much smaller than hitherto envisaged, we have proceeded to construct the full relationship between primary fold length (l_g^*) and supercooling (ΔT) covering a wide range of crystallization temperature (T_c). The principal result of this work is the identification of supercooling as the sole factor which determines l_g^*. Comparison with crystallization from solution [2–4] has revealed that the l_g^* against ΔT curves are completely superposable thus removing the gap which has existed up to the present between melt and solution crystallization, bringing about a welcome unification of these two separate (at least as far as fold length was concerned) aspects of polymer crystallization. Further, we show that while ΔT determines l_g^*, subsequent thickening is determined by the absolute temperature. Isothermal thickening in particular proceeds first by a large discontinuous step followed by a continuous logarithmic increase with time. The importance of these findings and in particular the affirmation of the unique role of supercooling for chain folding and lamellar crystallization in general is emphasized.

1. Introduction

This fifth and last paper in the set [1–4] on polymer crystallization serves a dual purpose. First, it uses the new recognition concerning the value of the primary, unthickened fold length in melt crystallized polyethylene reported in the preceding paper [1] to establish the full, and hopefully this time definitive, relationship between the primary fold length and supercooling. Secondly, we shall draw upon the results of the three-part series on solution crystallization [2–4], and compare the fold length values there obtained with the corresponding values relating to melt crystallization just established. As will be seen this comparison encompasses a wide range of crystallization temperatures with considerable overlap between melt and solution crystallization regarding both supercooling and values of the absolute temperature at which the crystallization has been conducted. It will emerge that this comparison leads to a welcome unification of the two hitherto separate aspects of polymer crystallization, those from melts and solutions.

The background and motivation have already been recalled in the Introductions of the preceding papers. The essential points, for self contained reading are as follows: the principal entity of polymer crystallization is the lamella, which is most usually characterized by a single parameter, the lamella thickness, l which, as is familiar,

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corresponds to the fold length. It is very well established for crystallization from dilute solutions that l is a function of supercooling (ΔT) there being an inverse relation between l and ΔT. This dependence has led to the development of the kinetic theories of chain folding which are able quantitatively to predict both l, and the crystal growth rates. The predictions of these theories regarding l however cannot be fully tested because the lamellae themselves start thickening soon after they have formed while still at the crystallization temperature. This is the isothermal thickening phenomenon [5, 6] referred to repeatedly in the previous papers [1–4], where such thickening of older portions of the lamellae may occur concurrently with their continuing growth.

In a previous series of papers [7–9] we attempted to extrapolate to l_g* by measuring values of l as a function of time on systems where we were able to crystallize very fast by increasing the overall nucleation rate. In that work we measured lamellar thickness using Raman longitudinal accordian mode (LAM) spectroscopy, a technique which can only be used at, or below, room temperature. Consequently we looked at samples which had been partially crystallized and then quenched. We found two LAM modes corresponding to a small and a large lamellar thickness. The intensity of the peak corresponding to thinner lamellae decreased with its position remaining constant. The peak corresponding to the larger thickness grew in intensity and moved to lower wave number shifts (i.e. towards greater crystal thickness) at the same time. Accordingly we associated these peaks respectively with material which had not yet crystallized at the crystallization temperature but only crystallized on quenching (the thin lamellae) and with the material crystallized at the crystallization temperature and undergoing isothermal thickening (the thicker lamellae). We then extrapolated to the value of the thickness these thicker lamellae would have had at zero crystallization time.

This work suffered from two distinct drawbacks: first we were forced to look at quenched samples, and secondly we used a polyethylene with a broad molecular weight distribution. Recently we were able to overcome both these problems by using a sharp fraction and examining it by low angle X-ray scattering (LAXD) during crystallization. The latter was achieved using the high intensity available from the Synchotron Radiation Source (SRS) at Daresbury. As we have already reported [1] this work demonstrated that the interpretation in our previous work was incorrect. It has now emerged that the lamellae first form with a thickness which is much lower than the extrapolated values we reported previously [7–9], and then thicken suddenly to a large value (about twice the original) which subsequently increases further but this time continuously, logarithmically with time. Accordingly the correct interpretation of the two Raman peaks is that the one corresponding to thin lamellae is a superposition of both lamellae formed on quenching and the lamellae as formed initially (l_g*) before they have undergone the large discontinuous increase in thickness, the first stage of the isothermal thickening. The second peak is due to the lamellae which have already increased their thickness by this large initial jump and which are continuing to thicken logarithmically with time. Thus we are now able to assess the true initial lamellae thicknesses, l_g*, for a sharp fraction, the work we are to report in this paper. As already stated we now find that l_g* is much smaller than previously believed, and further and most significantly, that l_g* values of melt and solution crystallized material are substantially identical for identical undercoolings. Having recognized this through the single synchrotron X-ray experiment we had a chance to perform at one particular T_c, we could now resort to the initially used Raman technique, applicable only after the sample has been cooled to room temperature, to obtain the full l_g* against T_c (and ΔT) curve for melt crystallization, to be reported in what follows. The use of a sharp fraction is still essential as it enables full crystallization of all crystallizable material at T_c which eliminates (or at intermediate times reduces) the number of lamellae formed on cooling.

2. Experimental procedures

In all the melt crystallization studies reported here we used the sharp fraction of polyethylene from the National Bureau of Standards (NBS), Washington with $M_w = 32\,100$; $M_w/M_n = 1.14$, Samples were crystallized rapidly by increasing the overall nucleation rate using the enhanced self nucleation method described in detail elsewhere [8]. The polymer samples in the form of 100 μm thick discs were first melted at 160° C in a Mettler hot stage then cooled rapidly (at about 20° C min^{-1}) to about 70° C during which they crystallized. This procedure ensured identical samples for subsequent enhanced self nucleation. The discs were then heated quickly to 125° C and then more slowly (at 1° C min^{-1}) until all birefringence disappeared (typically at 134° C), then cooled rapidly (at about 30° C min^{-1}) to the desired crystallization temperature where they crystallized by the enhanced self nucleation process. The spherulites were seen to reappear gradually just as the reverse of melting and *not* by the normal radial growth [8]. Samples were held at the crystallization temperature for various lengths of times before removal from the hot stage and quenched in water. These quenched samples were then examined using Raman spectroscopy. We also used the differential scanning calorimeter (DSC) to perform directly comparable experiments, and measured the time taken for the samples to crystallize at each crystallization temperature.

3. Results

All the samples showed two Raman LAM peaks, one at low and one at high wave number shift ($\Delta\nu$). (See for example Fig. 2 of our previous paper [1]). We shall only be concerned here with the one at high $\Delta\nu$ corresponding to thin lamellae. As we stated in Section 1 this peak has two components [1], one from the lamellae crystallized at the crystallization temperature, T_c, and the other from lamellae crystallized on quenching. The peak due to quenched lamellae is quite broad and its intensity decreases with crystallization time. The peak due to lamellae crystallized isothermally at the chosen T_c is sharper and its intensity at first increases as more lamellae form and then decreases as they thicken. In all cases we may estimate from our DSC measurements how much material had crystallized at T_c and how much crystallized on cooling. We are then able to measure the position of the Raman LAM peak as a function of time and we find that at short times, when a substantial amount of material crystallizes on quenching, the peak is at a high wave number shift. As the crystallization time increases and the proportion of material which crystallized on quenching decreases so the peak at first moves to slightly lower wave number shifts, and then this position remains constant (this occurs once approximately 80% of the polymer has crystallized at T_c). The intensity of this peak decreases as the crystallization time increases. We have taken the value of the wave number shift of this peak to calculate $l_g{}^*$ values according to:

$$l_g{}^* = 314.9/\Delta\nu \,\text{nm} \qquad (1)$$

The results for $l_g{}^*$ against crystallization temperature are plotted in Fig. 1. The data are also presented in Table I, together with the crystallization time required before < 20% of the polymer will crystallize on quenching as assessed by DSC experiments.

4. Discussion

We have, we believe, succeeded in obtaining true $l_g{}^*$ values for polyethylene crystallized from the

TABLE I Details of the crystallization of the samples and values of initial fold lengths

Crystallization temperature (° C)	Crystallization method*	Time for 80% of crystallizable material to crystallize (min)	Initial fold length ($l_g{}^*$) nm
128	ESN	12	22.0
126.5	ESN	7	20.0
126	ESN	5	18.6
126	ESN	5	17.8
125	ESN	1	18.0
124	R	10	17.3
121	R	3	15.8
120	R	1	16.2
120	R	1	14.0
110	D	–	12.0
95	D	–	10.0
85	D	–	9.1

*ESN – Enhanced–self nucleation (see Chivers *et al.* [8] for details).
R – Normal radial growth of spherulites.
D – Droplets (see Barham *et al.* [9] for details).

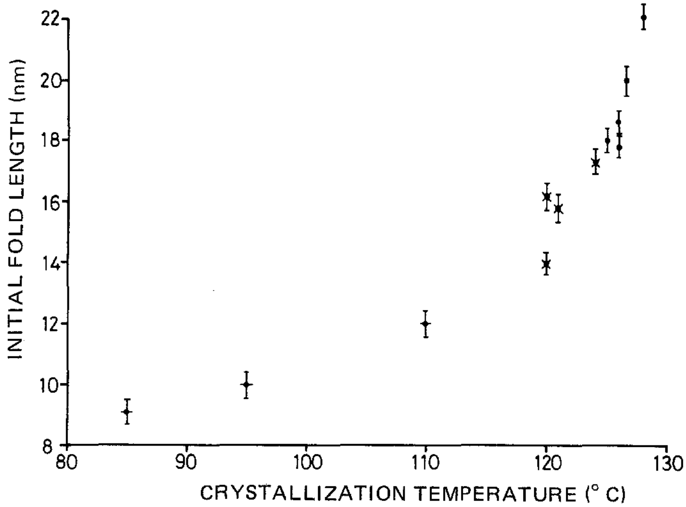

Figure 1 A graph of the initial fold length (l_g*) as a function of crystallization temperature for polyethylene fraction of $M_w = 32\,100$. Points marked † are from droplet experiments, those marked ‡ are from normally crystallized material, and the others from enhanced self nucleation experiments.

melt. The kinetic theories of Hoffman *et al.* [10] predict

$$l_g^* = \frac{2\sigma_e T_m^\circ}{\Delta H \Delta T} + \delta l \qquad (2)$$

where σ_e is the end surface free energy, ΔH the enthalpy of fusion, T_m° the equilibrium melting point and δl a term approximately constant at the relevant supercoolings. Accordingly a plot of l_g* against $1/\Delta T$ should be linear with slope $2\sigma_e T_m^\circ/\Delta H$ and intercept δl. We have plotted our data in this form in Fig. 2 taking $T_m^\circ = 144.7°$ C [11] for the NBS fraction with $M_w = 32\,100$. From this we find $2\sigma_e T_m^\circ/\Delta H = 3.01 \times 10^{-5}$ cm K and $\delta l =$ 2.81 nm.

We have recently reported [12] Raman spectroscopy data obtained on polyethylene fractions crystallized at very high supercoolings achieved by the droplet technique described previously [9]. The data from that work do not fit on the same l_g* against $1/\Delta T$ line as the presently obtained ones. Accordingly we have reexamined our Raman spectra to see whether there were two peaks even in those samples crystallized at temperatures below 110° C, the temperature previously identified (erroneously as it turns out) with the lower temperature limit for isothermal thickening. We found a second peak in those traces where we had scanned to high enough wave number shift; (in several experiments we had stopped the scan after seeing the first peak). These second peaks are of small intensity, but nonetheless quite clear. Thus we may now suggest that even in these samples the lamellae, once formed, thicken by a single large step. At these low temperatures we have shown previously [9] no further isothermal thickening is seen. These additional data are also

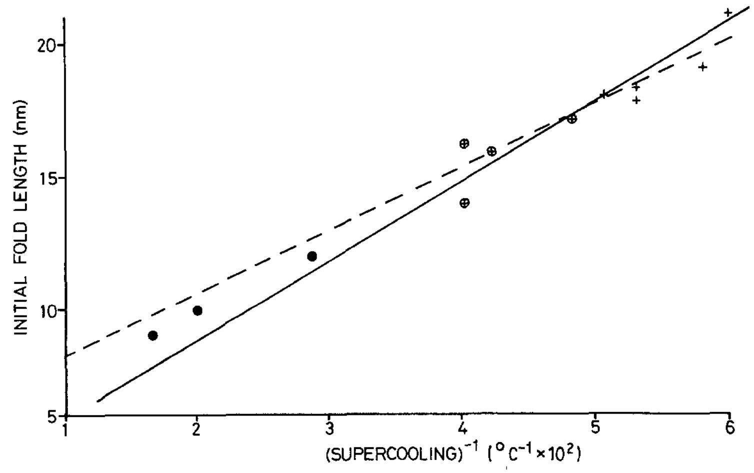

Figure 2 A graph of initial fold length (l_g*) against inverse supercooling (taking T_m° = 144.7° C for the $M_w = 32\,100$ fraction). The dashed line is a best fit to the points from normally crystallized material (⊕) and those from the enhanced "self" nucleation experiments (+). The solid line is a best fit when the results from droplet experiments (●) are also included.

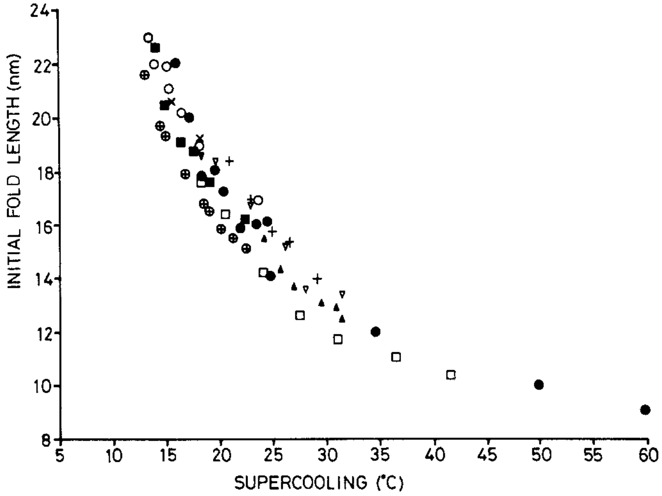

Figure 3 A graph of the initial fold length (l_g*) against supercooling for both melt crystallization (this work) and solution crystallization [4]. Solvents: □ – xylene, ■ – hexyl acetate, ⊕ – ethyl esters, ○ – dodecanol, ▽ – dodecane, ▲ – octane, X – tetradecanol, + – hexadecane, ● – melt crystallized.

included in Table I and in Fig. 2. If we take account of these points we find $2\sigma_e T_m{}^\circ/\Delta H = 2.4 \times 10^{-5}$ cm K and $\delta l = 5.87$ nm.

At this stage we may profitably compare our newly determined l_g* values and parameters derived therefrom with those obtained from solutions covering a wide range of solvents, crystallization temperatures and supercoolings obtained on crystals with widely differing morphologies as reported in the preceding papers [2–4]. Fig. 3 displays all the l_g* values measured as a function of ΔT. The data points are all seen to show the same trend with ΔT, in fact the data all lie closely on a single curve. Even the parameters of σ_e and δl, as from Equation 2, are very similar for melt and solution crystallization (compare Table I of reference [4] with the figures above).

We feel that the above findings are very significant, as they show that the fold length of polyethylene crystals is primarily determined by the supercooling, respective of whether they were crystallized from the melt or from solutions. The presence or absence of a solvent and the chemical nature of the latter, if of any consequence at all, are relegated to a secondary role. Further, since the morphology (lateral habits, sectorization) depend more on the absolute crystallization temperature rather than on the supercooling [2–3] we can deduce that the shape of the crystals and the presence or absence of curved growth faces do not significantly affect the actual initial lamellar thickness.

Finally some comments on the relevance for theories may be opportune. The unique supercooling dependence of l_g*, being firmly established, certainly excludes one recent scheme according to which crystals form with identical fold lengths to begin with and all variations of l with ΔT are due to subsequent isothermal thickening [13]. We see that in solution crystallization there is no isothermal thickening, while in melt crystallization, the basic relation between l and ΔT is upheld even after subtracting the effect of isothermal thickening. At this stage it may well appear that the traditional kinetic theories [10] are obeyed throughout. Nevertheless as stated in the preceding papers [1–4] it is difficult to see how the mechanism underlying the kinetic theories can apply in the T_c regime where the crystals grow with curved faces. Recent theoretical developments [14] based on surface roughening (i.e. nucleation free growth above a certain temperature, T_R) in close analogy with corresponding growth mechanisms in simple crystals [15, 16] have the potential to account for the development of curved crystal faces. Most surprisingly, recent computer simulations have revealed [17] that a relation, broadly of the form of Equation 2, also holds for this nucleation free growth mechanism. Thus, data as in Fig. 3 cannot in principle distinguish between these theories. We suggested in the previous paper on solution crystallization [4] that the two classes of theories may possibly both be valid but apply to different T_c requirements in terms of absolute temperature. If so, it would still be very surprising that the l_g* against T_c, or ΔT, curves should reveal no discontinuity when passing from one regime of crystal growth to another, particularly if the regimes are as different as implied by a transition from a nucleation controlled to a nucleation free growth mechanism.

If we detach ourselves from all preconceived notions it will be seen that one salient factor dominates the whole scene, namely the supercooling. It appears that the supercooling alone determines the crystal thickness, hence the fold length, by which the crystals grow and in this respect virtually nothing else has any influence at all. It seems that the chains "want" to fold with a particular fold length, (or without invoking any particular molecular model, crystal growth along the chain direction ceases beyond a certain length) such as is determined by the supercooling and nothing else. Such a salient fact, here so strikingly affirmed, must surely remain the solid factual foundation on which all our further thinking in this field must be based. We consider this fact as the most important outcome of the present programme.

5. Conclusion

We have shown that polyethylene, as crystallized from the melt, thickens isothermally in the course of growth over the full T_c range covered, down to 88° C, the lowest T_c value featuring here. We have obtained the initial $l_g{}^*$ value over the full T_c range in question and established relations between $l_g{}^*$ and ΔT. The $l_g{}^*$ values were found to be all much lower than claimed previously. We found that $l_g{}^*$ is uniquely determined by ΔT while isothermal thickening is primarily influenced by the absolute temperature in line with our original working hypothesis [7]. Comparing of $l_g{}^*$ values obtained here on melt crystallization with those obtained on crystallization from solution [4] revealed virtually complete correspondence in terms of ΔT, thus removing the hitherto existing gap regarding corresponding $l_g{}^*$ values, placing both types of crystallization on a unified basis. In final analysis the full set of papers [1–4] has reaffirmed the overriding role of supercooling which uniquely determines the lamellar thickness, and hence fold length by which crystals grow.

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