

A STUDY OF ISOTHERMAL LAMELLAR THICKENING IN POLYETHYLENE BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A systematic study of isothermal crystallization in polyethylene has been carried out using differential scanning calorimetry. The process of isothermal lamellar thickening has been investigated. The DSC curves for melting of samples crystallized under different conditions show two melting peaks, one at a low temperature and the other at a higher temperature. This phenomenon has been investigated in detail and it has been shown that the high-temperature peak is due to the melting of the isothermally crystallized fraction while the low-temperature peak is due to the melting of the remaining fraction which crystallizes on cooling to room temperature. The details of the latter fraction reveal the existence of molecular fractionation on crystallization from melt. The results connected with the high-temperature peak show that the process of lamellar thickening during isothermal crystallization involves the molecular fractionation and isothermal annealing simultaneously. It is shown that at a higher degree of supercooling, even the initial stage of crystallization is dominated by chain refolding.

INTRODUCTION

The crystallization of polyethylene under different conditions has been investigated by several groups of workers using different techniques. Bulk polyethylene crystallizes in the form of lamellae whose upper and lower surfaces consist principally of chain folds. The thickening of lamellae crystals during isothermal crystallization has also been followed by various investigators [1–4], but the mechanism responsible for this process is not fully understood. Hoffman and Weeks [1], on the basis of small-angle X-ray diffraction (SAXD) studies, attributed this thickening to the annealing of precipitated lamellar crystals similar to that observed above the crystallization temperature. On the other hand, Kawai et al. [2,3], who investigated this problem using differential scanning calorimetry (DSC), concluded that the lamellar thickening is a result of molecular fractionation induced by crystallization. According to this mechanism, in a polydisperse system on cooling the higher molecular-weight species precipitate earlier from the melt giving rise to thinner lamellae, while the lower molecular-weight species crystallize

more slowly at a later stage of crystallization and form thicker lamellae. The net result of these processes would be the thickening of the whole crystal. Recently, Dlugosz et al. [4] investigated this problem using low-frequency Raman spectroscopy (LFRS), SAXD and electron microscopy. The main aim of their study was to make a comparison between the various techniques in providing information about lamellar thickening. Their results, however, do not fully support either of the earlier-suggested mechanisms. According to these authors, the lamellar thickening is a two-step process, the first stage being dominated by the molecular fractionation and the second by annealing of the lamellar crystals formed during the first stage. To investigate this problem further, we have undertaken a detailed study of the lamellar thickening using DSC. The effect of crystallization conditions on the crystallization process has been investigated. It is shown that though the lamellar thickening is a two-step process, with a decreasing degree of supercooling the annealing process becomes increasingly dominant.

Further, the results demonstrate that the DSC, which is a relatively simple technique, is capable of providing as useful information about the crystallization process as can be obtained by any other, more sophisticated technique.

EXPERIMENTAL

Material

The linear polyethylene used in this work was Marlex 6002 with $M_n = 11\,300$ and $M_w/M_n = 12.4$. The sample density at room temperature was 0.963 g cm^{-3} .

Crystallization

The present investigations were carried out in a Perkin-Elmer differential scanning calorimeter (DSC-1B). The melting temperature, T_m , was determined from the location of the peak maximum. Indium ($T_m = 429\text{ K}$) was employed as the standard for calibration.

Isothermal crystallization of polyethylene from the melt at various temperatures was carried out in the sample-can of the DSC. For this purpose, in every case a 3–5-mg sample was first heated to 440 K and kept at this temperature for about 30 min to erase any previous morphological history. The sample was then rapidly cooled to the desired temperature for crystallization. To study the effect of crystallization time, the process was terminated after the desired period by cooling the sample rapidly to room temperature. The cooling rate adopted in all cases was 32 K min^{-1} .

In some cases step crystallization was also carried out. For this purpose the sample was first melted and then kept at 440 K for 30 min. The sample was then rapidly cooled to the preselected crystallization temperature (say, T_1). After isothermal crystallization at this temperature for a preselected time, the sample temperature was lowered rapidly to the new crystallization temperature (T_2). The crystallization was then continued at this temperature for some time before being terminated in the usual manner.

DSC curves for the melting of samples crystallized under different conditions were obtained at a heating rate of 4 K min^{-1} .

RESULTS AND DISCUSSION

Origin of double melting peaks

Some typical DSC curves, obtained for the melting of samples crystallized under different conditions, are shown in Fig. 1. A general feature of these curves is the appearance of two melting peaks; one at a low temperature, hence forth called peak I; the other at a higher temperature, henceforth called peak II. The onset time of this phenomenon is found to depend on the crystallization temperature. The lower the crystallization temperature or higher the degree of supercooling, the earlier the double peak appears. At higher crystallization temperatures, even at long enough times ($> 300 \text{ min}$) peak II is not seen. It is observed that for a given degree of supercooling the

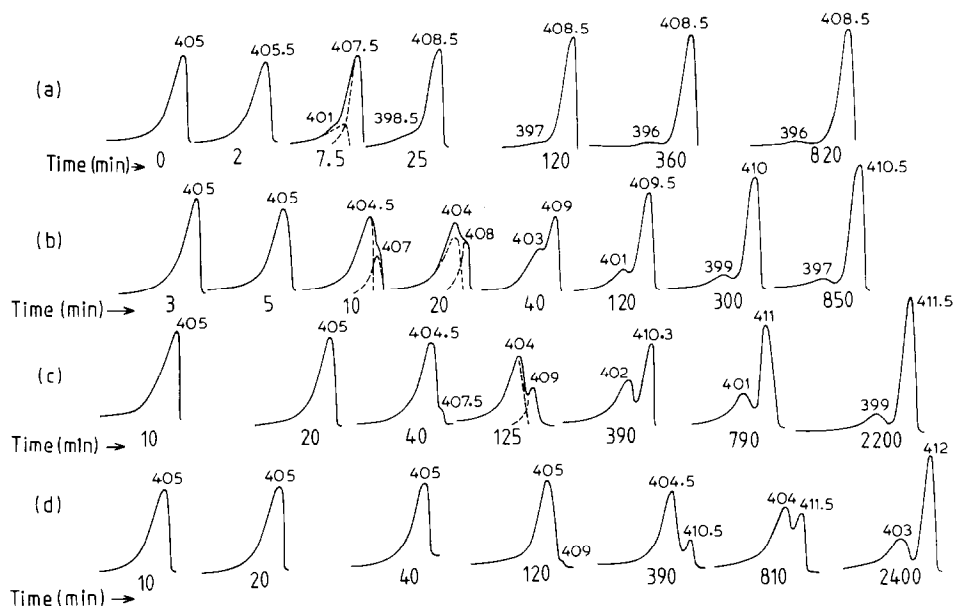


Fig. 1. Some typical DSC curves for melting of samples crystallized at (a) 395 K, (b) 398 K, (c) 400 K and (d) 401 K.

area under peak II increases at the expense of the area under peak I. From this observation it can be concluded that peak II corresponds to the melting of that fraction of the sample which crystallized isothermally, and peak I corresponds to the melting of the remaining fraction which crystallized subsequently as the sample was being cooled to room temperature. At longer crystallization times, a larger fraction of the sample is isothermally crystallized and, therefore, peak II becomes progressively more dominant while peak I undergoes a decrease in size.

Further support for the above conclusion is provided by the results of step crystallization shown in Fig. 2. This figure depicts the DSC curves for the melting of two samples which were crystallized isothermally in two steps as described earlier. In both cases, three melting peaks are seen. The highest-temperature peak corresponds to the melting of the fraction crystallized isothermally in the first step at a higher temperature, T_1 . The intermediate peak corresponds to the melting of the fraction crystallized at the lower temperature T_2 . The lowest temperature peak is due to the melting of the fraction crystallized during final cooling to room temperature. Dlugosz et al. [4] also arrived at a similar conclusion on the basis of LFRS data.

The effect of heating rate on the two peak temperatures for a sample crystallized at 398 K for 120 min is shown in Fig. 3. Peak II shows a greater degree of superheating as compared to peak I. This indicates that the isothermally crystallized fraction has longer lamellae [5] as compared to the fraction which crystallized during cooling. It may further be noted that the areas under the two peak were found to be independent of the heating rate, thus, ruling out a possibility of any of these peaks arising due to recrystallization during heating.

Molecular fractionation

The dependence of the two peak temperatures on crystallization time, for different degrees of supercooling, is shown in Fig. 4. Here, with increasing

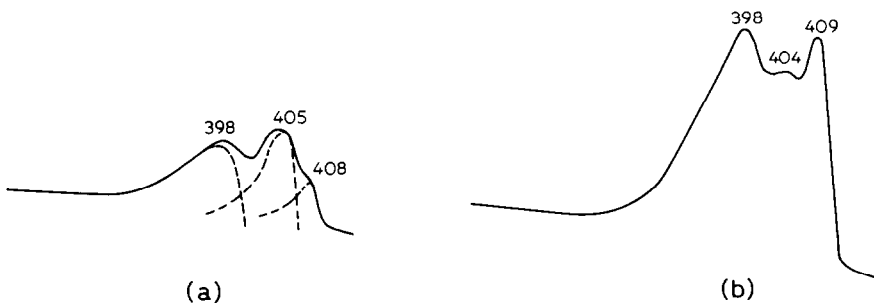


Fig. 2. DSC fusion curves of samples which were crystallized isothermally in two steps, $T_{c1} = 400$ K and $T_{c2} = 397$ K. The crystallization times used were: (a) $t_1 = 50$, $t_2 = 25$ min; (b) $t_1 = 200$, $t_2 = 20$ min.

time the peak I temperature is found to decrease, and that of peak II to increase. As discussed above, peak I corresponds to the melting of the fraction which remained uncrystallized during isothermal crystallization, but was crystallized during cooling. Therefore, the set of curves in the lower part

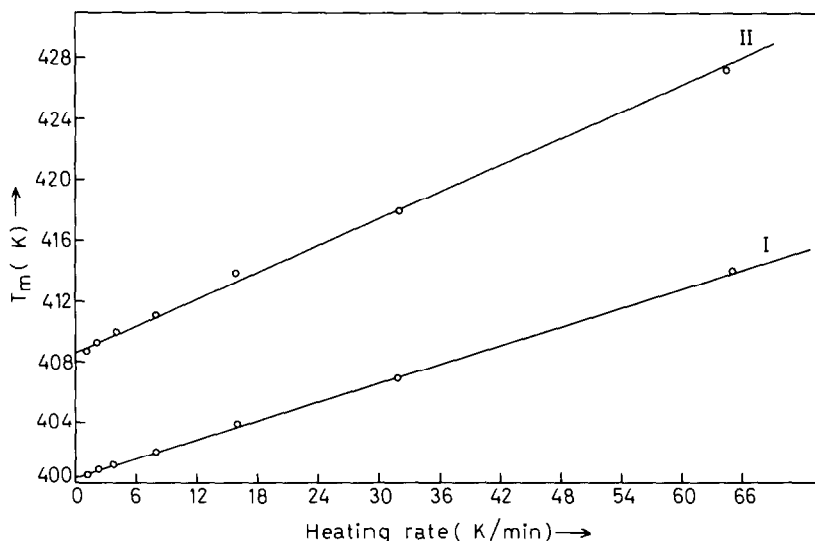


Fig. 3. The dependence of the melting temperature of the isothermally crystallized polyethylene samples on the heating rate. The curves I and II correspond to the melting peaks I and II, respectively.

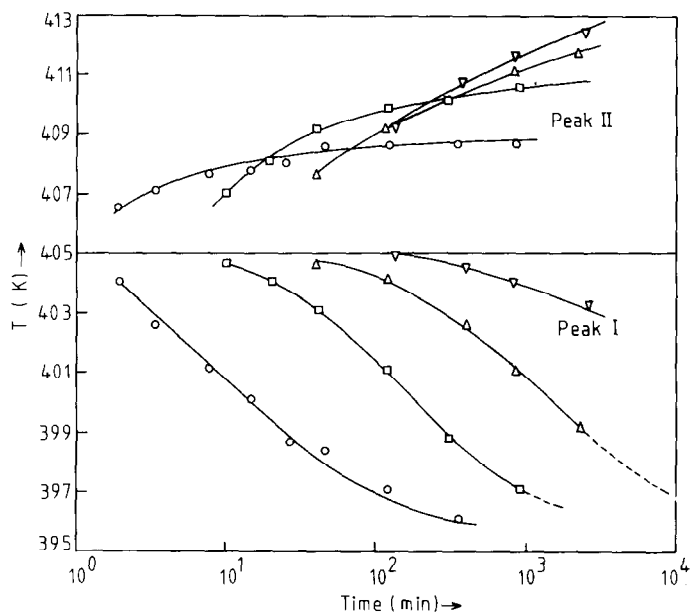


Fig. 4. A plot of melting temperature vs. time for Marlex 6002 samples crystallized at different temperatures: $T_c = 395$ (O); 398 (□); 400 (Δ); and 401 K (▽).

of Fig. 4 depict the characteristics of this fraction. Here it is observed that at any degree of supercooling, the melting temperature of this fraction decreases with increasing crystallization time.

This result can be understood in terms of the molecular fractionation on crystallization from the melt. Such a fractionation on crystallization from solution as well as from a melt has been reported in the literature [6–13]. It leads to a rejection of the lower molecular-weight molecules which may or may not crystallize subsequently. Accordingly, during isothermal crystallization from the melt, the average molecular weight of the uncrystallized fraction is expected to decrease with increasing time. As the melting temperature is dependent on the average molecular weight of a polymer sample, the melting temperature of this fraction on crystallization during cooling should decrease with increasing crystallization time. This is in agreement with the experimental findings. The persistence of peak I even at long crystallization times lends further support to the hypothesis of molecular fractionation. Mehta and Wunderlich [13] have shown that for a given crystallization temperature, material below a critical molecular weight does not crystallize. On this basis it is anticipated that even when the crystallization is complete, a small portion of the material would still remain uncrystallized; this fraction would crystallize on cooling. Thus, for a given crystallization temperature with increasing crystallization time the melting temperature of this fraction would tend to reach a limiting value as seen in Fig. 4. As the critical molecular weight increases with increasing crystallization temperature [13], the limiting value of the melting temperature of the uncrystallized fraction on crystallization is expected to increase. This is in agreement with our observations.

Isothermal lamellar thickening

Curves in the upper part of Fig. 4 depict the dependence of peak II temperature on crystallization time for different degrees of supercooling as obtained in the present experiment. It has been shown earlier that peak II corresponds to the melting of the isothermally crystallized fraction under any given crystallization conditions. Therefore, these curves also represent the melting temperature of the isothermally crystallized fraction. It is observed that for a given degree of supercooling, peak II or the melting temperature of the isothermally crystallized fraction increases with crystallization time, this change being first rapid and then gradual.

The melting temperature of a given polymer crystal depends on (a) the molecular weight of the polymer, (b) the lamellae thickness and (c) the degree of perfection. The molecular-weight dependence of the melting temperature of polyethylene has been investigated by several workers [14–16]. It has been observed that the molecular-weight dependence of the melting temperature is appreciable at low molecular weights but tends to saturate at

higher values. The dependence of melting temperature on lamellae thickness is rather stronger. The melting temperature of a crystal can be raised by annealing it at a temperature higher than the crystallization temperature. A definite correlation between the melting temperature and the lamellae thickness has been observed [17–19]. However, from thermodynamic considerations also, the melting temperature of a crystal of finite thickness l may be expressed as

$$T_m = T_m^0 \left[1 - \frac{2\sigma_e}{\Delta H_f} \cdot \frac{1}{l} \right] \quad (1)$$

where T_m^0 is the equilibrium melting temperature, σ_e is the free surface energy per unit area of the basal face and ΔH_f is the change in enthalpy per unit volume on fusion. In the derivation of relation (1) the surface energy contributions from the lateral faces have been assumed to be negligible. The observed results for polyethylene are very well represented by relation (1) [20]. Using the literature value for ΔH_f and eqn. (1), Illers and Hendus [21] have obtained for linear polyethylene the values $T_m^0 = (414.5 \pm 0.5)$ K and $\sigma_e = (79.5 \pm 2.5)$ erg cm⁻². These results compare well with the accepted values for these parameters, viz. $T_m^0 = 414.4$ K [22] and $\sigma_e = 70$ erg cm⁻² [23]. Taking the latter value of T_m^0 and σ_e and for heat fusion, $\Delta H_f = 70$ cal g⁻¹ [22], using eqn. (1) the melting temperature data shown in Fig. 4 were converted into the corresponding fold periods. The results of this computation are shown in Fig. 5. This figure now depicts the dependence of the lamellae thickness on the crystallization time for various degrees of super-

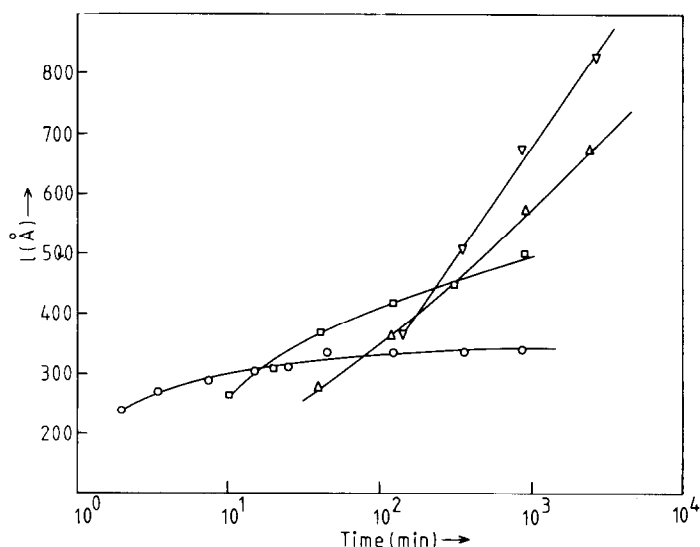


Fig. 5. The variation of fold length with crystallization time for Marlex 6002, samples crystallized at different temperatures; $T_c = 395$ (○); 398 (□); 400 (Δ); and 401 K (▽).

cooling. The trend of variation for any degree of supercooling is similar to that obtained by Dlugosz et al. [4] from LFRS measurements.

The results shown in Figs. 4 and 5 are suggestive of some thickening of the lamellae which occurs on storage at the crystallization temperature. At lower crystallization temperatures (395 and 398 K) in regard to lamellar thickening the curves can be divided into two regions. Initially, the thickening proceeds at a faster rate and then slows down, but remains operative at sufficiently long times. However, at higher crystallization temperatures (400 and 401 K) the distinction between the above-mentioned two regions tends to disappear. At these temperatures the curves rise more or less linearly with the logarithm of time from the point when first sign of any crystallinity is observed.

Observations of the thickening of lamellae at the crystallization temperature have been made previously by Hoffman and Weeks [1], Kawai [2] and his co-workers [3] and Dlugosz et al. [4]. We will now examine our results in the light of various theories of thickening proposed by these authors. As mentioned earlier, Hoffman and Weeks [1] explained the increase in X-ray long spacing by the annealing of lamellae after they have crystallized, whereas Kawai [2] suggested a mechanism involving molecular fractionation during crystallization.

If, as proposed by Kawai et al. [2,3], the lamellar thickness is controlled only by molecular fractionation, then the distribution of thickness should broaden continually in the direction of thicker lamellae. Such a process should result in the broadening of the melting peak for the isothermally crystallized fraction as the crystallization proceeds. On the contrary, however, the melting peak is sharpened with increasing crystallization time. This observation favors the existence of some kind of annealing process at longer times. It has been observed that at lower crystallization temperatures the initial rapid thickening is slowed down at a time when the crystallization is more or less complete. Thus, at times longer than these the lamellae continue to thicken without any further growth of crystallinity. This is suggestive of an annealing process, similar to that suggested by Hoffman and Weeks [1], being operative at these times. However, as discussed above, there is also definite evidence for the existence of some kind of molecular fractionation. The phenomenon of isothermal crystallization, therefore, appears to be rather complex. It is, perhaps, a consequence of the simultaneous operation of these two processes. The relative contribution of these is expected to be a function of crystallization time and the degree of supercooling.

The effect of crystallization temperature on the time dependence of the melting temperature or the lamellar thickness, shown in Figs. 4 and 5, respectively, can be explained in terms of time and temperature dependence of the two suggested mechanisms for a given degree of supercooling, as the crystallization proceeds, the rate of molecular fractionation decreases while the effect of annealing remains unchanged. On the other hand, on decreasing

the degree of supercooling, the effect of annealing increases and the rate of molecular fractionation decreases. This is because of the fact that with decreasing degree of supercooling, the crystallization rate decreases and, therefore, the crystals, once formed, have more time for annealing at that temperature before newer crystals are precipitated. Therefore, at lower crystallization temperatures, the initial stage of crystallization is dominated by the molecular fractionation coupled with isothermal thickening of the lamellae once they are formed. This results in a rapid rate of lamellar thickening. As the crystallization proceeds to completion, the contribution of molecular fractionation gradually decreases and the continued thickening is caused by more and more annealing of the crystals formed, thus leading to a decrease in the rate of thickening. At higher crystallization temperatures, the effect of molecular fractionation decreases and the thickening due to chain refolding takes over. This results in the straightening of the curves in Figs. 4 and 5 corresponding to higher crystallization temperatures.

It can, therefore, be concluded that lamellar thickening during isothermal crystallization from a melt involves the processes of molecular fractionation and annealing simultaneously. Their relative contributions are determined by the degree of supercooling and the crystallization time. At a given degree of supercooling, the molecular fractionation dominates to begin with and then gradually gives way to annealing. However, for a given time of crystallization the annealing process becomes more and more dominant with decreasing degree of supercooling.

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