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Novel Melting Phenomena in a Series of Isothermally Crystallized Polyethylene Single Crystals

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ABSTRACT

Polymer single crystals or lamellae are widely used in models for more complex systems such as fibers, films, or bulk polymer. Determination of important thermodynamic and physical properties for the crystals is often frustrated by their tendency to reorganize on heating. Partly as a consequence of this, the melting ranges for high molecular weight polymers are often quite broad. A novel technique has been developed which permits a more detailed examination of the melting/morphology relationships that exist in single crystals. This has led to the observation that high molecular weight polyethylene (PE) single crystals possess much narrower melting ranges than had been previously reported. It has been possible to determine distinct transformation temperatures for the {100} and {110} fold sectors that exist in some PE crystals. Melting point determinations have been made on a series of isothermally crystallized PE crystals using DTA. Narrow multiple peaked thermograms were obtained, and peak position and ratio could be related to morphological differences between the crystals.

INTRODUCTION

Polymer single crystals, or rather polymer lamellae, are widely used in developing models for fibers, films, and bulk polymer. To better understand the behavior of these commercially important classes of materials, it is necessary to study the properties of lamellae or single crystals. Measurement of the melting point, dissolution temperature, or heat of fusion of such crystals allows the deduction of important thermodynamic and physical properties [1]. However, these crystals tend to anneal [2], recrystallize [3], or superheat [4] during the heating cycle. This prevents accurate determination of the above parameters. Efforts have been made to allow for these reorganizational processes with only limited success. Most thermograms for high molecular weight polymers are characterized by their breadth relative to those for low molecular weight organic solids. Besides the reorganizational processes previously mentioned, this breadth is also attributed to a large distribution of crystallite sizes [5] or to degrees of perfection within the crystal.

A technique has been developed which demonstrates that broad thermograms can be resolved into a number of narrow melting peaks. Further, this technique permits the electron microscopic examination of single crystals whose thermal history has been recorded in the Differential Thermal Analyzer. This technique was applied to a series of polyethylene (PE) single crystals grown under isothermal crystallization conditions. Results of this study, which produced novel information regarding the melting process, are presented in this paper.

EXPERIMENTAL

Details of the crystallization procedure are given elsewhere [6]. However, it should be noted that crystals were grown from Marlex 6001, a high molecular weight linear PE. Crystallization was performed isothermally at a number of different temperatures. The crystals were all washed three times by a decantation process at their particular crystallization temperature (T_c). This washing reduced the concentration of impurities, primarily of low molecular weight PE, to less than one-thousandth of their original concentration.

After washing, the crystals were allowed to come to room temperature. Part of each batch was exchanged to acetone by repeated centrifugation and washing with acetone. Some of the acetone exchanged sample was allowed to air dry and was finally dried under vacuum for several days. A portion of the acetone suspension was also exchanged to silicone oil. This exchange was achieved by adding

oil to the suspension in acetone (or xylene) and then evaporating the original suspending medium. Complete evaporation of acetone or xylene was obtained by application of a high vacuum for several days. All exchanges, evaporations, etc., were carried out at room temperature.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) runs were made on both the dried down sample (solid) and the oil exchanged suspensions (exch. to oil). These runs were made on various sample weights at different heating rates and sensitivities. However, this work will be primarily concerned with DTA runs on "exch. to oil" samples run at $20^{\circ}\text{C}/\text{min}$. All DTA runs were carried out in 2 mm tubes using a DuPont 990 Thermal Analyzer and Cell Base with a standard DTA cell. All runs reported have been at least duplicated and often five or more scans were made.

RESULTS AND DISCUSSION

Sample sizes for DSC and DTA are typically on the order of 1 to 6 mg [1-5, 7, 8]. Thermograms obtained from this size sample of high molecular weight PE are usually broad, simple fusion curves, covering some 10 to 15°C [1]. Lower molecular weight samples give multiple peaks, generally interpreted as evidence of some reorganizational process [3]. Radiation-induced cross-linking has been used to inhibit reorganization and produces narrower fusion curves [2, 8]. However, irradiation does not simply cross-link the crystal surfaces [7], leading one to question the significance of melting temperatures so obtained.

A study was made of the effect of "solid" sample size on the thermogram. This led to a study of "exch. to oil" crystals and the effect of heating rate on their thermograms. This work has been covered in more detail elsewhere [6]; however, for completeness a summary is included here. Finally the effect of T_c on the thermogram was examined.

DTA thermograms were obtained on various weights of the "solid" sample for one crystallization temperature, namely 86°C . Two of these runs at $20^{\circ}\text{C}/\text{min}$ are shown in Fig. 1. At the higher weight, 2.76 mg, a broad simple fusion curve was obtained. As sample weight

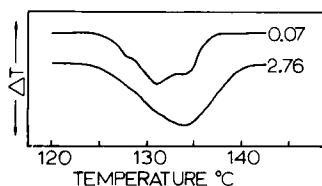


FIG. 1. DTA runs on "solid" sample at $20^{\circ}\text{C}/\text{min}$. Weight of sample given in milligrams.

decreased the thermogram became more complex and eventually at the lower weight, 0.07 mg, three peaks were discernable. These are contained within the spread of the broad peak from the larger sample.

After melting, these samples were recrystallized from the melt by cooling at a programmed rate. When thermograms were run on these melt-recrystallized materials, a single broad peak was obtained. The shape and position were essentially the same, regardless of sample weight. This observation suggests that sample weight differences shown in Fig. 1 may be due to poor thermal conductivity of the powdered sample. As the weight of a powder sample is increased, the distribution of thermal states becomes increasingly broader. The thermocouple detects the average of this distribution of states, resulting in a single broad peak at higher weights.

In an effort to check this idea, the "solid" sample was dispersed in silicone oil. This is a nonsolvent for the polymer and has the same order of magnitude thermal conductivity as solid polymer. Thermograms from these dispersions indicated that for a given weight of polymer the oil-dispersed samples had narrower multiple peaks than the "solid." This was true up to the highest sample weight used.

The narrowest multiple peaked thermograms were obtained when the crystals were dispersed in oil without ever drying them down, i.e., "exch. to oil" samples. A comparison between the thermograms of "solid" and "exch. to oil" samples for the same crystal preparation and with approximately the same weight of polymer is shown in Fig. 2. Note the narrowness of the "exch. to oil" peaks, approximately 1.5°C at half peak height for the largest peak in the thermogram. Peaks this narrow have not previously been reported for any polymer sample. It should also be noted from Fig. 3 that the positions of the peak maxima for the "exch. to oil" samples are independent of heating rate in the range 5 to $80^{\circ}\text{C}/\text{min}$. Peak position is unchanged but the thermogram width seems to increase as heating rate is increased.

The "exch. to oil" thermogram shown in Fig. 2 is apparently composed of three peaks; the two low temperature peaks are narrow, the high temperature peak is somewhat broader. These peaks will be

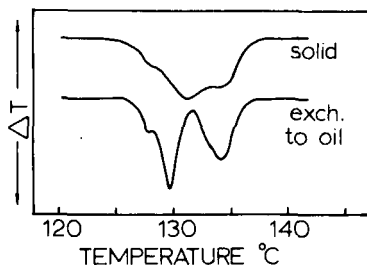


FIG. 2. DTA runs on "solid" and "exch. to oil" samples. Samples both have approximately 0.1 mg of polymer and were run at $20^{\circ}\text{C}/\text{min}$.

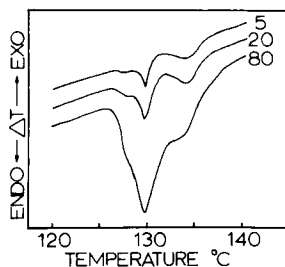


FIG. 3. DTA runs on "exch. to oil" samples of approximately 0.1 mg. Heating rate is given in $^{\circ}\text{C}/\text{min}$.

referred to as first, second, etc., in order of increasing temperature of their endotherm maximum. A sample was heated just to the maximum of the first peak, quenched, then reheated. The resulting thermogram is shown in Fig. 4(a). The first peak has completely disappeared, the second peak remains unchanged, and the third peak shows some slight change in shape.

With regard to the origin of the peaks, in light of previous work on annealing and recrystallization, it is suggested that the third peak represents the melting behavior of crystals which have already undergone some reorganization. Additional evidence will be presented later. The presence of a first and a second peak could be the result of impurities including a separate crystalline phase, or a phase transition including annealing and/or recrystallization. However, no rate dependence typical of phase transitions [9] was observed (Fig. 3). In addition, previous studies have found no evidence for separate crystalline phases [10]. The care taken to crystallize isothermally and wash the samples tends to rule out the presence of impurities, certainly in the quantities

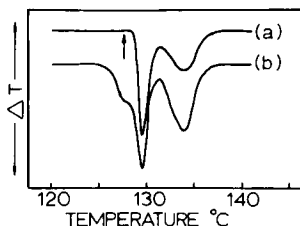


FIG. 4. (a) An "exch. to oil" sample was heated just to the point indicated by the arrow and quenched. On reheating the thermogram was obtained. The point indicated by the arrow corresponds to the first peak maximum. (b) For comparison, the thermogram of an untreated "exch. to oil" sample.

indicated by the peak size. The implication is therefore that isolated lamellae of PE crystallized at 86°C exhibit two independent melting transitions.

As widely known, PE crystals grown at about this temperature from xylene exist as truncated lozenges with $\{100\}$ and $\{110\}$ fold sectors [10]. It has been suggested that a definite difference in transformation temperature should exist for these two sectors [11]. Studies performed to date, with DSC have not revealed such a difference. It is suggested that the first and second peaks discussed above represent the transformation temperatures of the two sectors. Previous annealing studies and heat treatments have been carried out on lamellae sedimented on carbon grids [11-13]. In line with these experiments, crystals heated to the first peak maximum in the DTA should show evidence of preferential reorganization of one of the sectors, if the model is correct. An electron micrograph from a sample of those crystals which gave Fig. 4(a) on reheating is shown in Fig. 5. The following are observed on this and other micrographs: darkening of all or part of the $\{100\}$ sectors; the ends of the $\{100\}$ sectors are bowed toward the crystal center; and striations develop which are parallel to $\{010\}$ planes in $\{100\}$ sectors.

The above observations are taken as evidence for preferential melting and subsequent recrystallization of $\{100\}$ sectors. These observations were made only when crystals were heated to the first peak maximum. Crystals heating just 1.5° lower, to the onset of melting, show no such changes. Crystals were also heated to the second peak maximum, quenched, and examined under the electron microscope. Micrographs are not shown; however, the crystals appeared as disk-shaped objects with no structural detail being observed on their surfaces. This is taken as evidence that the $\{110\}$ sectors have now also melted and recrystallized on quenching. It is concluded that the first and second peaks as shown in Fig. 4(b) represent the melting of $\{100\}$ and $\{110\}$ sectors, respectively.

One should also note that the observation of two melting peaks for these crystals implies the existence of different surface energies for the two fold sectors. This is based on the assumption that the lamella thickness is the same for the two sectors. The existence of two surface energies suggests that there may exist different chemical reactivities for the two sectors. Different reactivities have not so far been reported. However, previous chemical studies have only been carried out on dried down crystals. These may have undergone some surface damage during the drying process.

DTA measurements have also been carried out on single crystals grown isothermally at a number of different temperatures. These measurements were made at various heating rates on "exch. to oil" samples. Figure 6 shows typical scans made at 10°C/min. The following are observed: the ratio of the first two peaks to the third peak gradually increases as T_c increases; where three peaks exist,

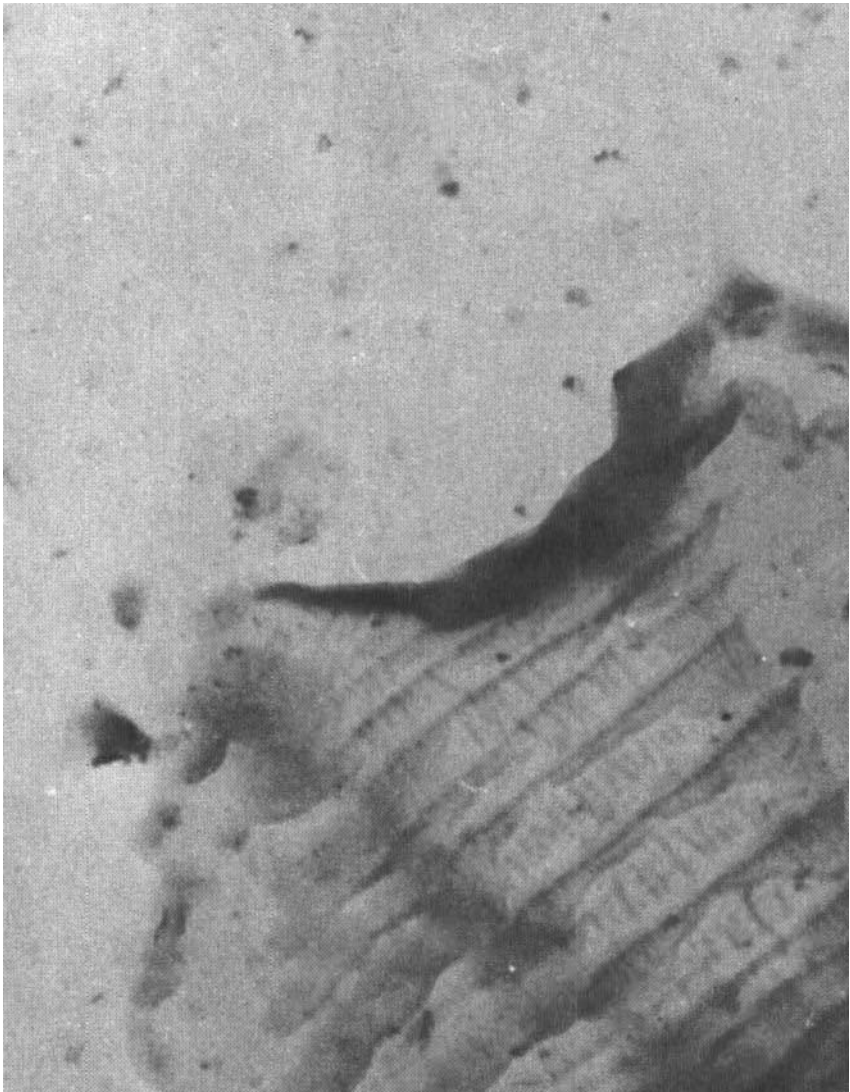


FIG. 5. An electron micrograph of a sample of crystals that gave Fig. 4(a) on reheating. The bowed end and $\{010\}$ striations in the $\{100\}$ sector are clearly visible.

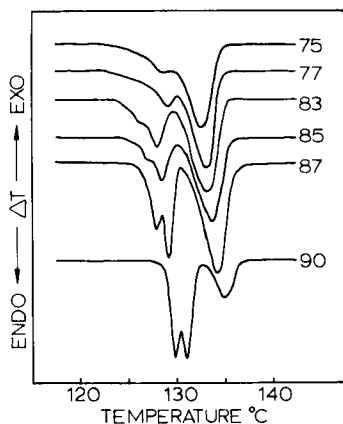


FIG. 6. A series of DTA curves obtained on "exch. to oil" samples. The isothermal crystallization temperature of the original crystals is given for each curve in °C. Sample weights were within the range 0.07 to 0.15 mg, and all runs were made at 10°C/min.

the ratio of the first peak to the second peak increases with increasing T_c ; and with the exception of the first two crystallization temperatures, all peak positions move to higher temperatures with increasing T_c .

Peak positions (T_m) from DTA runs at 20°C/min are plotted as a function of T_c in Fig. 7. Similar observations may be made for DTA scans at both rates. However, additional data can be derived from the plots made in Fig. 7.

For example, the curves for the first and second peaks appear to intersect, if extrapolated, at a T_c of approximately 96°C. Similarly, curves for the first and third peaks intersect at a T_c of 103°C and a T_m of 139.5°C, and curves for the second and third peaks intersect at a T_c of 110°C and a T_m of 141°C. Additional data and more sophisticated analysis of the thermograms are necessary before much significance can be placed on these particular points of intersection.

Data from 75 and 77°C crystals appear to be out of line with that derived from crystals grown at higher temperatures. However, two points should be remembered: 1) crystals grown at 75 and 77°C do not possess distinct {100} fold sectors, and 2) the lower the crystallization temperature, the more easily will crystals reorganize. In fact, the onset of melting of all the crystals falls on a straight line as

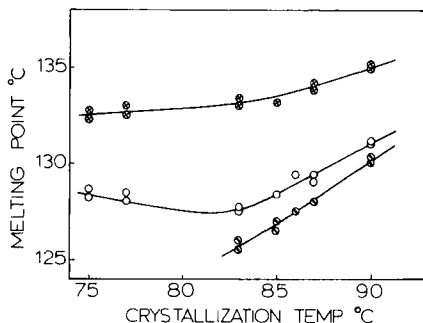


FIG. 7. The two or three melting points (peak maxima) were recorded for a series of isothermally crystallized PE samples. All DTA runs were made at $20^{\circ}\text{C}/\text{min}$. \odot , \circ , and \otimes represent first, second, and third melting peak respectively, in order of increasing temperature of peak maxima.

a function of T_c when run at $20^{\circ}\text{C}/\text{min}$. Changes observed in the ratio of the first and second peaks to the third and in the ratio of first to second are consistent with our knowledge of the morphological changes which take place as T_c increases. For example, as T_c increases, lamella thickness increases; there would be higher melting points for the crystals and correspondingly lower probability of reorganization during heating. Similarly, as T_c increases a larger fraction of the polymer exists in the $\{100\}$ fold sectors [14]. This would lead to the observed changes in ratio of first to second peaks.

CONCLUSIONS

1. A technique has been developed which demonstrates that high molecular weight PE, in single crystal form, possesses much narrower melting ranges than had previously been reported. This observation should aid in the elucidation of polymer crystal structure.
2. Using the above technique it has been possible to demonstrate that $\{100\}$ and $\{110\}$ fold sectors in truncated PE crystals possess different transformation temperatures. This leads to the suggestion that these sectors should possess different chemical reactivities.
3. The above observation was made on crystals grown at a single crystallization temperature. Data derived from a series of isothermally crystallized PE samples appear to support this observation. Work is being continued on this series of crystals: (a) to develop a

more sophisticated analysis of the thermograms, and (b) to examine the possibility of selective sector reactivity.

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