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Seeding of Supercooled Polyethylene with Extended Chain Crystals.

by

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ABSTRACT

Seeding of supercooled polyethylene melt and solution with extended chain single crystals did not markedly decrease the degree of supercooling necessary to initiate crystal growth. No extended chain growth was induced with these nuclei. An analysis of the first traces of crystal growth allowed some conclusion about nucleation and growth mechanism. In order to account for the here presented measurement a growing crystal must have a 10,000 to 30,000 Å thick surface layer which increases in perfection from the outside to the inside. A differential scanning calorimeter was used for most of the experiments.

INTRODUCTION

Linear flexible high polymers usually crystallize from melt and solution only after a supercooling of the order of 10 degrees has been reached. The resulting crystals are accordingly imperfect. The main imperfection is a platelet-like growth habit in which the molecular chains are arranged in a more or less sharply folded conformation.[1] On crystallization of polyethylene from solution these platelets are 100 to 150 Å thick and possess a melting point of about 120°, a temperature 20° below that of the melting point of equilibrium crystals.[2] Crystallization under normal conditions from the melt may increase this thickness by a factor 2-5 depending on crystallization temperature and time with a corresponding increase in melting point. Much thicker crystals, however, have up-to-date only been grown under high pressure conditions.[3] These crystals are close to equilibrium and contain fully or largely extended molecular chains[4] and gave a higher melting point[5] and dissolution temperature.[6] It is thus possible to mix ordinarily crystallized polyethylene with the extended chain crystals and on heating reach a temperature where the extended chain crystals alone remain unmolten or undissolved. The extended chain polyethylene crystals should accordingly be an ideal nucleating agent for crystal growth.

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The research presented in this paper was designed to analyze the effect of equilibrium crystal seeds on a chemically identical supercooled polyethylene melt and o-xylene solution of polyethylene.

Earlier work by Cormia, Price, and Turnbull[7] has shown that in the melt homogeneous nucleation of polyethylene is only possible below about 90°. Above this temperature, in particular at or above 120°, nucleation has to be heterogeneous. Work by Kargin and co-workers[8] on polymer melts has indicated that spherulites can be nucleated by a variety of agents, including glass and other unrelated surface structures. Willems[9] showed that oriented epitaxy can be achieved on nucleating polymer crystal growth from solution with single crystals of alkali halides. The extended chain crystals should on this basis be the most ideal nuclei. Two major questions to be answered in this paper are, is it possible to reduce significantly the supercooling necessary for crystal growth by seeding with extended chain crystals?, and is it possible to grow extended chain crystals from melt or solution by seeding with the proper nuclei? Both questions will be answered negatively. In addition, some detailed information on initial crystal growth has been obtained.

EXPERIMENTAL

A. Materials. Linear polyethylene polymerized with a Ziegler catalyst was used for this research. The number average and weight average molecular weight were 9800 and 130000 respectively. A molecular weight distribution by gel permeation chromatography of this material has been published in reference 5, (Polymer P_1).

B. Preparation of Seeds. The seed material was crystallized at 4350 atm. hydrostatic pressure at 227° for 20 hours and was then cooled at 1.6°/hr. to room temperature where the pressure was released (see reference 5, sample 33). The resulting extended chain single crystals had a bulk density of 0.997 at 25° and a sharp equilibrium maximum melting point of 138.7° on slow heating (see reference 5). At faster heating rates, such as commonly used in differential thermal analysis the crystals superheat before melting.[10]

For seeding, it was desirable to have as large a surface as possible. For this reason the bulk material was sliced on a Spencer "820" microtome using steel knife edges. An electron micrograph of a replica of the cut surface is shown in Fig. 1. It is clearly visible that the crystals of extended chain polyethylene are not distorted by this procedure, but are cleaved by brittle fracture parallel to the chain direction. The direction of the striation normal to the lamellar surface is the chain direction.[4] The striations are caused by a random crack propagation.[5] On heating the fracture surface the striations are smoothed out at a temperature between 110° and 120° as can be seen in Fig. 2. Above this temperature perfect crystal surfaces should be available for nucleation.

The single crystal lamellar thickness ranged up to 3μ for the sample in question. During the investigation it was noted that the slice-thickness could not be lowered below a critical value without influencing the melting behavior of the crystals. Figure 3 shows the melt beginning, peak, and melt end of slices of extended chain polyethylene as a function of slice thickness. The value for infinite thickness was determined on a chunk of material. The approximate weight for all measurements was 0.12 to 0.47 mg. The heating rate was 10.0°/min. A Perkin Elmer differential scanning calorimeter was used for these measurements (see below for more details). Above 6μ no effect can be noted. Annealing 4μ and 2μ slices at 136° recovered most of the melt range lowering. For the here presented experiments 8μ slices were used throughout.

C. Dilute Solution Seeding. 0.1 Weight percent polyethylene solution in o-xylene was thermostated in a silicon oil bath with a long term temperature constancy of ± 0.06°. About 0.5 to 1.5 mg. exactly weighed slices of seeds were lowered into the solution in 80 mesh copper gauze baskets. The baskets were withdrawn after washing in pure o-xylene of the same temperature and weighed periodically after drying in vacuum. Blank experiments indicated the error limit to be ± 0.04 mg. Unseeded crystallization was checked by determining the appearance times of crystals as a function of temperature. The results were identical to the already published data on polyethylene dissolved in toluene (Reference 11, Fig. 1). These times which ranged from 500 min. at 92° to 5 min. at 78°, formed the upper time limit for seeding experiments. The dissolution temperature of the extended chain material in o-xylene was determined to be 110.9 ± 0.5°, giving the upper temperature limit of experimentation.

D. Melt Seeding. A Perkin-Elmer (Norwalk, Conn.) differential scanning calorimeter[12] was used to measure the effect of extended chain single crystal seed material on chemically identical melted bulk polyethylene.

Basically the calorimeter consists of two small sample holders kept at constant temperature by supplying different electrical power to each sample holder. The differential power imput is recorded alongside time and temperature signals.

The sample is enclosed in 21.5 ± 0.2 mg. aluminum capsules before insertion into the sample holder. An empty aluminum capsule serves as reference. The sample and reference holders are gold pans over which thin aluminum covers are placed.

Preliminary calibration adjusted all controls, so that over the whole temperature range of 350° to 450°K, the power recording remained on scale. The most sensitive range of about 5 mcal./sec. full scale deflection was used for the power recording whenever possible (occasionally the quantity of material being melted was too great and a switch had to be made to half this sensitivity). The heating rate chosen was 5°/min. Nitrogen, flowing at a rate of 15 $cm.^3$/min. was used as the inert atmosphere in the calorimeter. The enviromental temperature was kept constant by a regulated air bath.

The temperature range was calibrated with zone refined chemicals. The absolute accuracy of temperature recording of the extrapolated start of melting of the reference materials is ± 0.5°, while the reproducibility of equal mass melting curves is about ± 0.2°. Different weights and geometry of sample produce temperature lags. In addition superheating of extended chain polymers[10] does shift the observed melt end temperatures upward. The amount of seed material used was 0.1 to 0.4 mg., and the weight of the polymer melt was from 2.0 to 9.5 mg.

The general procedure included heating the sample (high pressure crystallized seeds and folded chain crystallized polymer) in the calorimeter to 137°, which is above the melting temperature of the folded chain material, but below the melting temperature of extended chain single crystal seed material. After 5 minutes at 137°, the calorimeter was cooled at a rate of 80°/min., to the predetermined crystallization temperature. It was held at this temperature between 2 and 3660 minutes. Then the temperature was raised 5°/min. to 147 or 167° under specific heat measuring conditions.[13] To get an exact baseline, the sample, which was now completely molten, was cooled using 80°/min. rates to the crystallization temperature, and after thermal equilibration reheated using 5°/min. rates again to the molten state. No crystallization occurred in the quick cooling prior to obtaining a baseline as long as the temperature was kept above 125°, the temperature where first quick crystallization of non-seeded polymer occurs.

Three types of information were taken from the power-temperature recording made after crystallization at the chosen temperature.

1. The deviations from the specific heat baseline of the high melting extended chain material, and any lower melting crystals were obtained.
2. The total relative amounts of extended chain seed material and lower melting polymer were evaluated from planimeter tracings of the melting curve areas, which are proportional to the heat of fusion.
3. For 126.4^{o} and 128.3^{o} crystallization temperatures the melting curves were reduced to 1 mg. of crystallizable polymer. Different crystallization times were compared to judge the change in perfection of the crystallized polymer with time.

All experiments with seeds were compared with duplicate measurements without seeds.

RESULTS

A. Dilute Solution Seeding. 23 seeding experiments were made between 101.4^{o} and 95^{o}. 24 hours was chosen as the crystallization time. No weight increase of the seeds was detected within the experimental accuracy of ± 0.05 mg., which would be indicative of a 5 to 10% increase. A crystallization at 91^{o} finally led to crystal growth outside and on the basket containing the seeds. On rinsing and weighing, the sample weight had still not increased measurably.

B. Melt Seeding. The amount of polymer crystallized is plotted in Fig. 4 as a function of the crystallization temperature. Different curves refer to different crystallization times. Experiments at 20, 48, and 120 hours fall on the same curve indicating completion of the fast portion of crystallization and reorganization. No crystallization was detected above 131.2°. The smallest amount which could be detected was 0.04 mg. melting over a 5 degree temperature range or correspondingly less or more for broader or narrower melting ranges. A 5 to 10% increase in heat of fusion of the seeds could thus have been detected. The maxima of the melting curves of the different seeded and unseeded crystallization experiments are plotted in Fig. 5 as a function of crystallization temperature and grouped in different crystallization times. The seeds were always well separated with a higher melting peak of 141.1°, a temperature which shows clear effects of superheating.[10] The equilibrium melting point of this substance was measured by dilatometry[5] to be 138.7°.

Figure 6a, and b show the melting curves of seeded and unseeded polymer grown per milligram of original weight of molten polymer crystallized at 126.4°. The ordinate is largely magnified for the presented curves. The 2 and 5 min. curves in Fig. 6a, and b respectively are just above the limit of detection of the calorimeter.

From 30-60 min. crystallization time on, no difference can be detected for seeded and unseeded polymer, so that Fig. 7 represents melting curves of a selection of both, seeded and unseeded crystal growth after the indicated crystallization times. Figure 8 is a similar curve for crystallization at 128.3°.

DISCUSSION

One major point to be made of Fig. 4 and 5 is, that there is no evidence of extended chain crystal growth from the melt due to having the proper seeds present. In no case did the heat of fusion of the seeds increase. Any new material crystallized had a melting point considerably below that of the extended chain crystal seeds.

The second observation is that the maximum crystallization temperature for a given crystallization time is only shifted by about one degree to higher values due to seeds. Figure 4 indicates this small increase by the shaded area in the curves for different crystallization times. The highest temperature where any crystals could be grown onto the seeds for 48-120 hours crystallization time was 131.2°, still 7.5° below the maximum equilibrium melting point of 138.7° of the extended chain crystals. Slow primary nucleation is thus not the reason for supercooling of polymer melts which in turn leads to chain folded crystallization at sufficiently low temperatures. The small difference in degree of crystallization between seeded and unseeded samples disappears as soon as crystallization times are increased.

The nature of the first polymer crystallizing can be judged from Fig. 6a, and b. The crystallinity calculated from the heat of fusion of the samples whose melting curves are shown in Fig. 6 are given in Table 1. For seeded samples the seed weight is excluded (about 0.3 mg. or 3 to 5% of the total weight for the short time crystallizations). Quite clearly the first polymer crystallizing onto the extended chain seeds is less perfect and grows more rapidly than the first crystals found in the unseeded melt. Since the quantities involved are very small, little or no calorimeter lag is present on melting. Superheating for this type of crystals heated at 5°/min. will be no more than 0.5°[10], so that the peak and end of melting temperatures of Table 1 are expected to be close to the correct values.

Table 1

Crystallinity of Samples in Fig. 6.

Mode of Crystallization at 126.4°		T_b (°C)	T_p (°C)	T_e (°C)	Crystallinity (%)
seeded	2 min.	130.0	131.6	134.5	0.6
seeded	5 min.	130.0	132.5	136.0	1.8
seeded	10 min.	130.0	134.5	137.4	3.5
seeded	15 min.	128.6	134.5	137.8	5.6
unseeded	5 min.	132.4	135.0	137.4	0.4
unseeded	10 min.	130.9	134.4	137.4	1.0
unseeded	15 min.	130.9	134.7	137.4	2.2
unseeded	23 min.	130.4	134.9	137.8	4.3

The initial crystals growing onto the seeds seem to melt at 130-132°, while the initial unseeded crystals melt at 134-136°. In the seeded growth more perfect crystals are found later on, the amount melting up to 132° varies very little initially, while the crystals melting at 132 to 133° increase the most. At even higher temperatures a somewhat seperated second component melts which might be crystals growing independently of the seeds. In the unseeded case the reverse is true, the largest initial increase is in lower melting crystals. The maximum experimental melting point does not shift in the first 15 minutes. The available active surface for nucleation in the seeded experiments was about 0.1 cm.^{2}/mg. After 2 minutes a layer of 6000 Å would have to grow onto the surface to account for 0.6% crystallinity. Even if this number is somewhat too large because of possible additional independent nucleation, it shows that relatively large amounts of imperfect growth occurs on a perfect surface for appreciable depth.

The following crystallization picture can account for the above observation. A sufficiently supercooled molecule adds to the growing crystal surface to form a rather imperfect crystalline layer. Its structure is determined by the path of fastest growth. Overlapping with this first step is a continuous reorganization of this layer until a metastable state is reached. Additional layers are added normally long before the reorganization is completed, so that in the steady state a growing crystal has a surface layer with decreasing chemical potential from the outside to the inside. In principle this picture is in accord with the theoretical treatments of the literature, recently reviewed by Hoffmann.[14]

Figure 6a can now be interpreted as showing initially an only slowly varying active growth area, determined by the seed surface area. The 2 and 5 minute melting curves show how the perfection increases as thicker layers build up. After about 10 minutes the first larger amount of metastable crystal, melting between 134 to 137° is reached. Estimates would have to place the thickness of the reorganizing layer for the chosen conditions at about 10,000 to 30,000 Å. If there are no perfect crystals present to add onto, a suitable nucleus has to be developed. Since experiments on droplet crystallization[7] suggest a heterogeneous mechanism, either a special long life chain conformation in the melt or a foreign surface starts the growth. This type of nucleus has a different geometry from the extended chain seeds, usually assumed to be a small bundle of folded chains.[14] It will differ from the surface nuclei on the extended chain polymer seeded material since it does not have the benefit of a perfect substrate to grow on (a substrate which allows zero side surface free energy). This nucleus must correspondingly develope into a more perfect crystal initially, possibly with a larger fold length.[14] Figure 6b indicates this higher initial perfection. As the nucleus grows, more and more less perfect surface layer is developed, so that the melting curves are starting earlier at later times. After 30-60 minutes crystallization time at 126.4° all differences between the two modes of nucleation are obliterated.

Further evidence for this picture comes from the later crystallization stages shown in Fig. 7 (and 8). The low melting portion between 130 and 133° increases rapidly until it reaches an almost constant value at about 30 min. crystallization at 126.4°. As soon as the largest portion of crystallization is over and the growth faces become stationary, somewhere between 60 and 300 min., this portion decreases in absolute amount. Whatever is left may be contained in low molecular weight portions, interior defects and frozen tie molecules. Anderson[15] has discovered these separate low molecular weight crystals. Keith[16] has shown experimentally the existence of tie molecules. Our own measurements on specific heats[2] indicate that this is the portion of the melting curve where partially reversible "growth of defects" occurs. This is the region where the tie molecule equilibria recently calculated by Zachmann[17] and Fischer[18] seems to be located. The shift of the melt end to higher and higher temperatures in Fig. 7 and 8 can be attributed to instrumental lag on the increasing heats of fusion. A lesser amount of this may even be contained in the melting peak data of Fig. 5, which indicate that crystallization time in the initial period of crystal growth is more important for a higher temperature melting peak than crystallization temperature.

The solution data point to a similar picture, although, not quite as much detail could be obtained from the present set of data which only confirm the impossibility of seeding extended chain crystal growth from solution and the impossibility of increasing the maximum crystallization temperature by seeding. Earlier experiments on dendritic and single crystal growth habits[19], however, have indicated that two different primary nuclei must be active in this type of crystallization. Some nuclei give rise to geometrically perfect folded chain single crystals or dendrites. It seems that only a long life chain conformation can act as a nucleus in this case. Any foreign nucleus would have to lead to crystallographically unrelated portions of the final crystals grown from different sides of the nucleus. Such crystals have been found in form of hedgehog dendrites and single crystal clusters.[19]

Acknowledgements.

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Legends to Figures

Fig. 1. Electron micrograph of a replica of the surface of the microtome sliced polyethylene extended chain single crystal. Magnification 10,000 x

Fig. 2. Electron micrograph of replica of a surface similar to Fig. 1, but heated to 120° before replication

Fig. 3. Melting characteristic of microtome slices of extended chain polyethylene as function of the slice thickness. Open circles melt begin, filled circles melting peak, triangles melt end. All measurements at 10°/min. and subject to superheating.

Fig. 4. Total crystallization as a function of crystallization temperature. Drawn out curves represent from left to right 15 min, 60 min, 5 hours, and 20 to 120 hours crystallization time. Key to symbols.

15 min.	seeded ⧗	unseeded X
60 min.	seeded ■	unseeded □
5 hours	seeded ◒	unseeded ◐
20 hours	seeded ▲	unseeded △
48 hours	seeded ●	unseeded ○
120 hours	seeded ◑	

Legends to Figures

Fig. 5. Melting peak temperatures, T_p, of seeded and unseeded polyethylene melt. Triangles seed melt peaks. The curves from the bottom up represent 15 minutes, 60 minutes, 5 hours, and 20 to 120 hour crystallization times. Symbols identical to Fig. 4.

Fig. 6. Melting curves of crystals grown at 126.4° for the given times. a) seeded b) unseeded

Fig. 7. Melting curves of crystals grown at 126.4° for 23, 30, 60, 300, and 3660 min., respectively. The temperatures are uncorrected for superheating and instrument lag. Seeded and unseeded runs are indistinguishable within instrumental accuracy.

Fig. 8. Melting curves as in Fig. 7, at 128.3° 60 min, 303 min, and 1140 min.

Figure 1

Figure 2

Figure 3

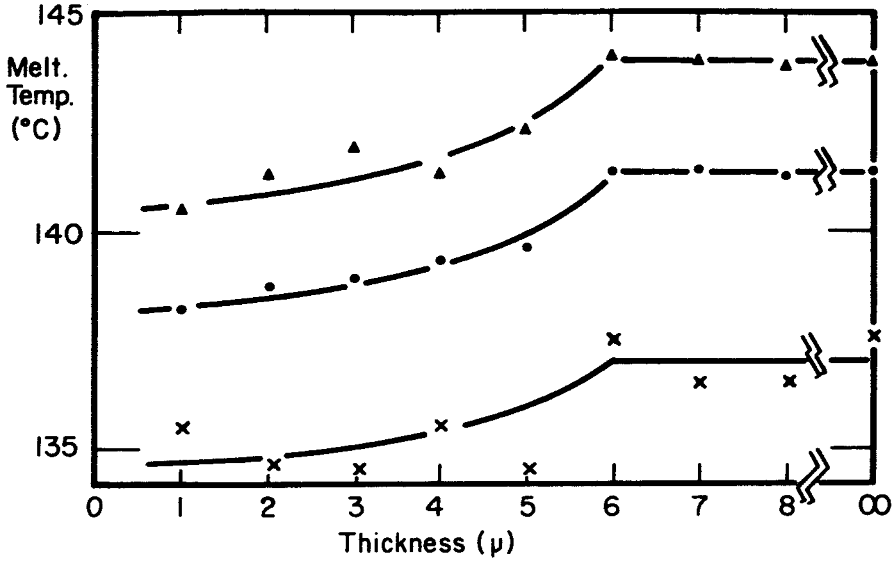

Figure 4

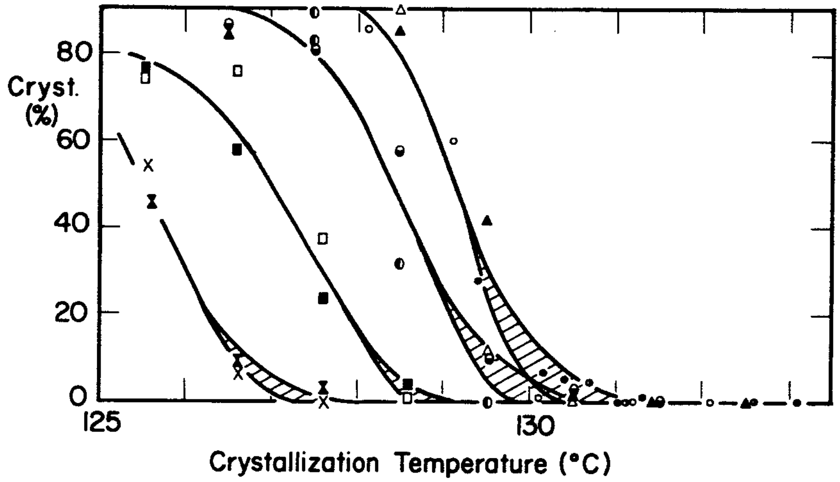

Figure 5

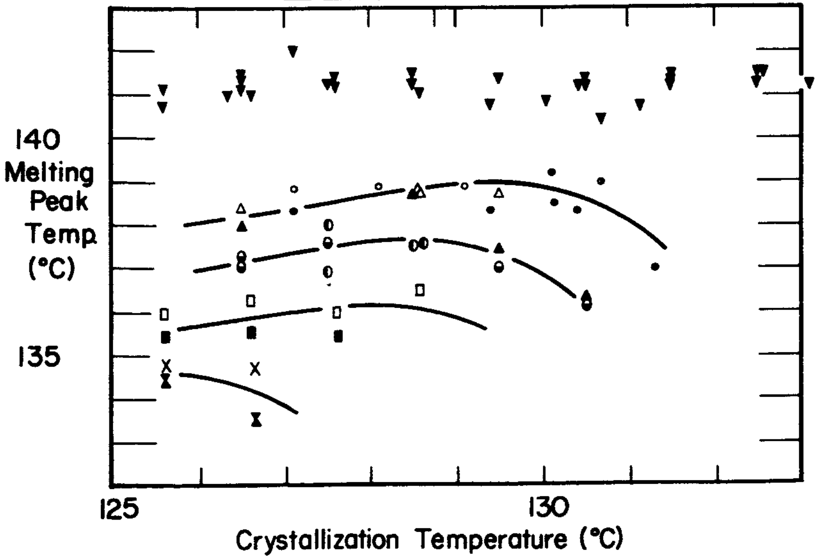

Figure 6a

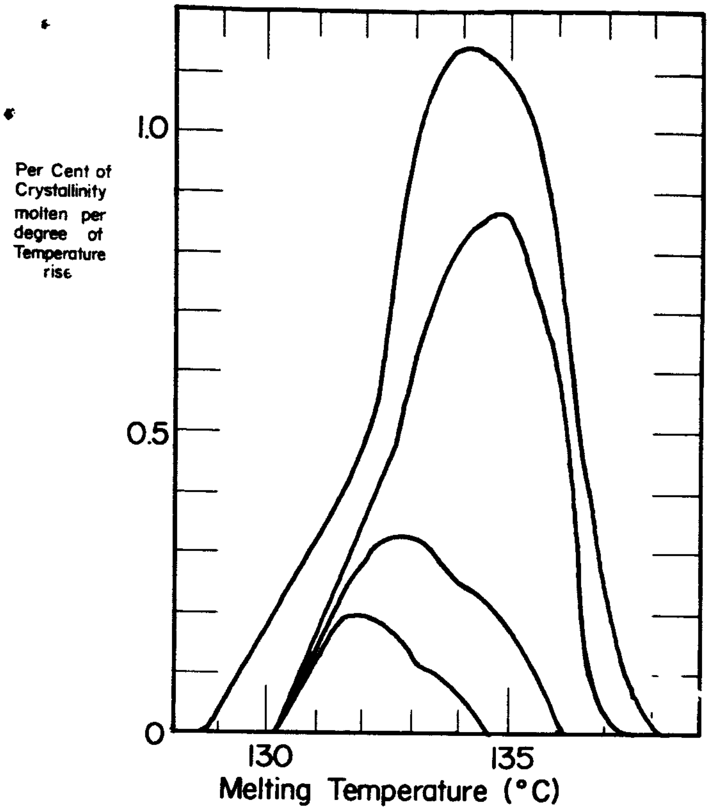

Figure 6b

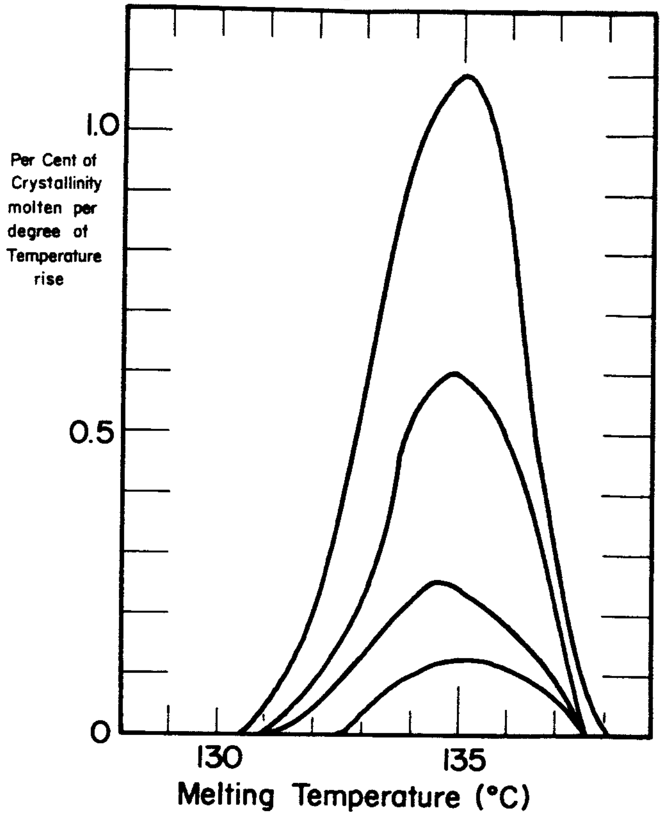

Figure 7

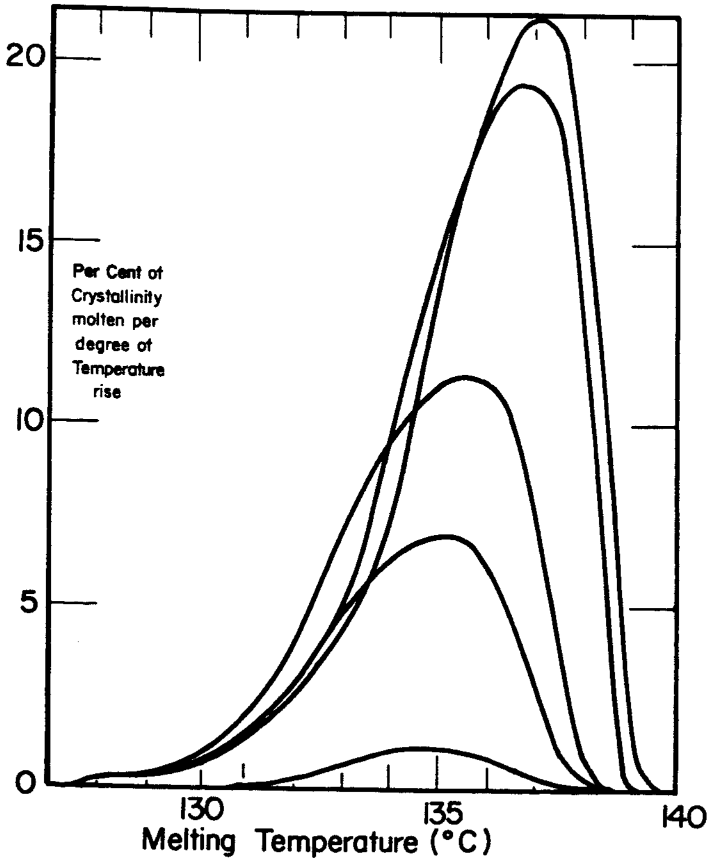

Figure 8