JOURNAL OF POLYMER SCIENCE: PART A-2 VOL. 7, 2091–2097 (1969)

Extended-Chain Crystals. V. Thermal Analysis and Electron Microscopy of the Melting Process in Polyethylene

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Synopsis

Differential thermal analysis and electron microscopy of partially molten, extended-chain polyethylene crystals, grown under elevated pressure, was performed. It could be shown that melting peaks on the low temperature side of the main melting peak are due to narrowly distributed, low molecular weight polymer segregated in extended-chain crystals. Superheating of crystals before melting increased with molecular weight and chain extension. The melting mechanism of extended chain crystals was shown to be a successive peeling off of chains which leaves the chain extension constant up to melting of the last crystal trace.

INTRODUCTION

Two effects have been reported previously on thermal analysis of extended-chain polyethylene. First, DTA traces show a number of small "prepeaks" before the main melting peak.[1,2] Second, extended-chain crystals of polyethylene were shown to superheat temporarily before the final melting for all but zero heating rates.[3] In this fifth paper of a series dealing with extended-chain crystals, the question of multiple prepeaks and superheating will be analyzed using information from thermal analysis experiments on extended chain crystals of polymer fractions. In addition, the melting mechanism will be discussed on the basis of electron micrographs of fracture surfaces of partially molten polymers.

EXPERIMENTAL

Materials

Materials used in this research were a linear polyethylene (M) with weight-average molecular weight 153,000 and weight- to number-average molecular weight ratio 18, and four fractions FR 1, FR 1P, FR 2, and FR 3A of the following weight average molecular weights and polydispersities: 2,550 (1.6); 78,300 (5.3); 24,100 (3.8); 101,000 (3.5). A more detailed analysis of these samples is given in the third paper of this series.[4]

All samples were crystallized at 4.8 kb at 220–225°C for 10–20 hr followed by annealing. Details are listed in the third paper of this series,[4] which deals with identical crystals.

Methods

Thermal analysis was carried out with a duPont Model 900 differential thermal analyzer and a Perkin-Elmer Model 1b differential scanning calorimeter. The differential thermal analyzer was calibrated to ±0.5°C; sample amounts were about 1 mg; the standard heating rate was 10°C/min. For superheating studies, techniques described previously were followed.[3] The differential scanning calorimeter was run at 5°C/min with 3–4 mg samples. Details of the heat of fusion technique were outlined previously.[5]

For morphology studies during melting only polyethylene M was used. Small pieces of the pressure-crystallized and annealed sample were sealed under vacuum in glass vials and heated beside the dilatometers in the equilibrium melting experiments described in paper four of this series. At preselected temperatures and times vials were withdrawn from the bath and quickly quenched in ice water. The sample pieces were then fractured at liquid nitrogen temperature, replicated, and studied with the electron microscope.

RESULTS

Figure 1 contains DSC tracings of type M whole polymer and three fractions. Fractions FR 1 and FR 1P when added in the proper proportions would reproduce the curve for the whole polymer. The small arrows mark the beginning of significant melting.

The main melting peak temperature as a function of heating rate is plotted in Figure 2. Also plotted in Figure 2 are data on pressure-crystallized high molecular weight polymethylene (PM) and on polyethylene M samples (curves III and IV) cooled slowly (0.6°C/min) at atmospheric pressure and rapidly quenched (450°C/min). These last three curves were reported earlier.[3]

Figure 3 shows the melting kinetics of pressure crystallized polyethylene M as followed by dilatometry (see paper four of this series). After reaching an equilibrium crystallinity of 46.7% at 137.5°C, the bath temperature was quickly raised to 138.3°C, the maximum melting point for this polymer. The decrease in crystallinity as a function of time at the melting temperature was then followed dilatometrically. After 100 hr 0.1% crystallinity was left. This was verified by calorimetry and electron microscopy (see Fig. 6) on quenched sample pieces removed from the dilatometry bath.

The change in morphology on partial melting arrested by ice water quenching is displayed in Figures 4–6. Figure 4*a* is typical of a well crystallized extended-chain fracture surface (98.1% crystallinity). Figure

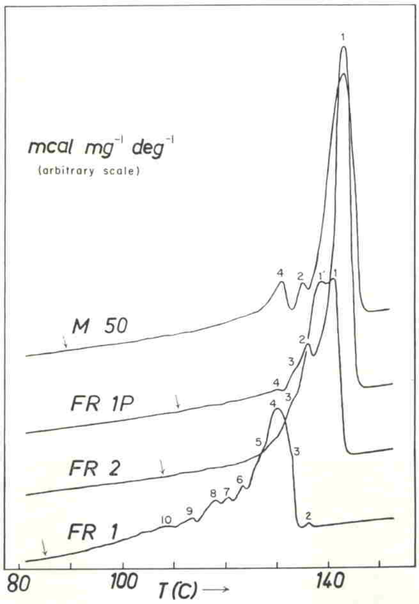

Fig. 1. Thermograms of polyethylene M and Fractions FR 1, FR 2 and FR 1P. Arrows indicate beginning of melting. Curves were taken on the differential scanning calorimeter.

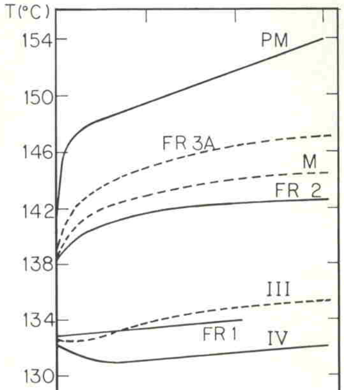

Fig. 2. DTA temperatures of the main melting peak as a functon of heating rate. Data for PM, III, and IV are taken from Hellmuth and Wunderlich.[3]

4b shows the fracture surface of a similar sample which was kept at 137.5°C until no further melting could be detected by dilatometry. At this temperature the crystallinity had decreased to 46.7%. The polymer melted at this temperature recrystallizes on quenching to poorly formed, folded-chain structures which give on fracture no recognizable crystals

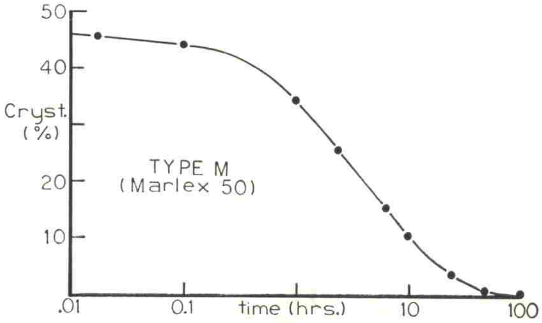

Fig. 3. Crystallinity decrease with time for extended chain crystals of polyethylene at the melting temperature 138.3°C. The sample had previously reached an equilibrium crystallinity of 46.7% at 137.5°C.

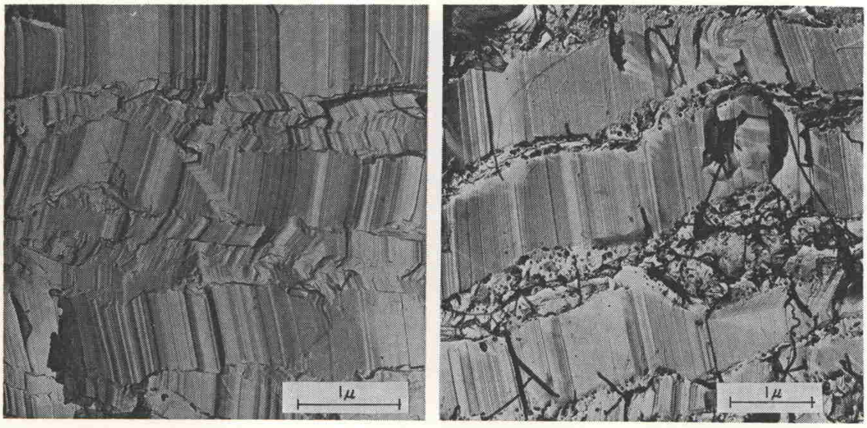

Fig. 4. Electron micrographs of fracture surfaces of polyethylene M: (a) as crystallized, (b) after heating to 137.5°C and quenching in ice water. Scale bar denotes 1μ.

because of their small size and deformation during fracture. It is clearly shown in Fig. 4*b* that the smaller crystals have melted first. Figure 5*a* shows an area illustrating intersection and branching of extended chain lamellae as described in detail elsewhere.[6] Figure 5*b* shows a similar area in a sample which was, equilibrated at 137.5°C and then heated for 10 hr at 138.3°C so that the crystallinity had decreased to 10.7% (see Fig. 3). To be noted are the missing small lamellae, as in Figure 4, and also the squared-off ends of lamellae which were rounded before heating (see Fig. 5*a*). Also, it can be noted that a large number of the kinks still remain under these conditions. Figure 6 illustrates the appearance of the last trace of crystal melting. The sample fracture surface was made after keeping the extended chain crystals 100 hr at 138.3°C (last point in the graph Fig. 3). The total crystallinity before quenching was at that time 0.1%. Differential thermal analysis of the quenched material indicated a small amount of high-melting extended-chain polymer in addition to the

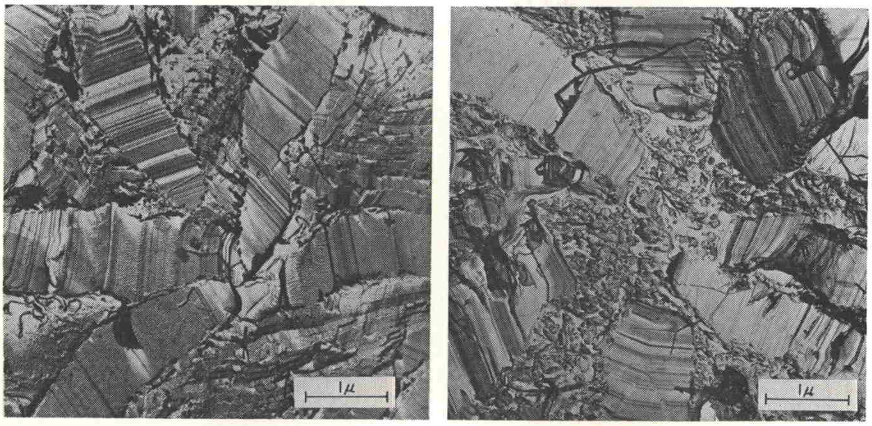

Fig. 5. Electron micrographs of fractures surfaces of polyethylene M: (*a*) as crystallized, (*b*) after heating to 138.3°C for 10 hr and quenching in ice water. Scale bar denotes 1 μ. (The crystal surfaces in (a) were decorated by "ripples" as described elsewhere.[6]

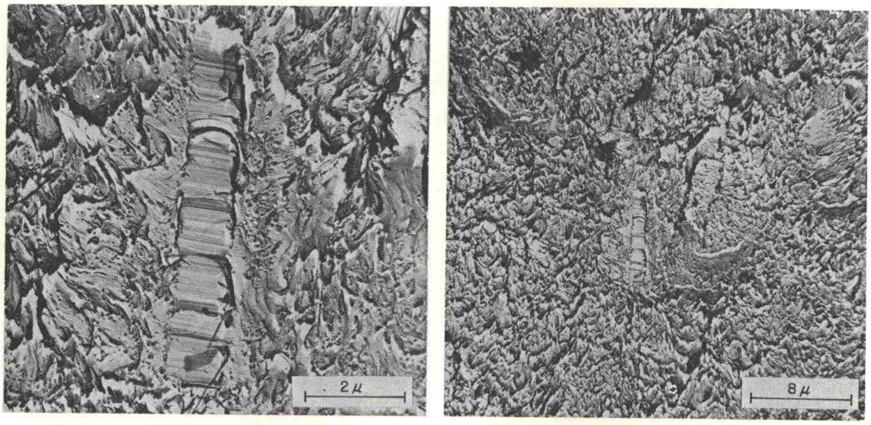

Fig. 6. Electron micrograph of the last trace of crystallinity: (*a*) scale bar denotes 2 μ, (*b*) scale bar denoter 8 μ.

poorly crystallized material produced on ice water quenching. The electron microscopy reveals occasional leftover extended-chain crystal fragments. Quite clearly, the residual lamellae still maintain their full extension and have squared-off ends. The lateral dimensions which were previously of the order of magnitude 100 μ have decreased to 10 μ and less.

DISCUSSION

The present experiments conclusively show that the prepeaks discovered in broad molecular weight distribution extended chain crystals are due to the low molecular weight portion of the polymer. It was found before that high molecular weight extended-chain crystals of polymethylene do not show prepeaks in the thermogram.[7] Removing most of the low molecular weight polymer from polyethylene M by separating out fraction FR 1, left fraction FR 1P. On crystallization under pressure, fraction FR 1P contains considerably less material melting in the prepeak temperature region, while fraction FR 1 is made up completely of material melting in the prepeak temperature region. In fact, many more melting peaks appear in fraction FR 1. In the set of melting curves of Figure 1, peaks are labeled from 1 to 10 in order of melting temperature. It will be noted that all samples show an almost perfect correspondence of peak temperatures. The interpretation by Kardos et al.[2] that peak 4 is caused by melting of folded chain crystals can only accidently be true for not too well crystallized polymer; the assignment of peaks 2 and 5 to rotational transitions is completely unwarranted.

By a resolution of the peak areas and comparison with the total heat of fusion, a reasonable agreement with the molecular weight distribution could be obtained for fraction FR 1, as was expected from the results of dilatometry in the foregoing paper of this series. Heating to temperatures between low temperature peaks followed by quenching was shown previously[1] to remove the separate low-temperature peaks; instead a broad single melting peak in the same region can be produced. We conclude from these results that on crystallization under elevated pressure, the low molecular weight portion of the polymer (up to molecular weight 10,000, or about 30% of polyethylene M) segregates preferentially into a limited number of mixed crystals, each including a narrow molecular weight distribution. On quicker crystallization, the molecular weight distributions become broader and overlap increasingly to obliterate the separate peaks. Even better crystallization conditions might produce sharper and more closely spaced melting peaks.

Figures 2 and 3 indicate the superheating of the samples on fast melting in comparison with previous work.[3] Only peak 1 in Figure 1, the peak which can be attributed to the high molecular weight mixed crystals, shows significant superheating. The superheating before melting depends on both molecular weight and lamellar thickness. A more detailed discussion of superheating of a variety of extended-chain polymers will be published shortly.[8] Of interest from the present data is the fact that folded-chain lamellae of higher molecular weight (curve III) and fully-extended-chain lamellae (curve FR 1) of low molecular weight and of similar lamellar thickness have similar superheating characteristics. Since the lateral lamellar size of these two samples is possibly also comparable, this might be taken as evidence that in folded chain lamellae, melting can start at every chain fold on the side surface of the crystal. The melting curve of Figure 3 was taken under conditions where only mixed crystals of high molecular weight and relatively large chain extension were present (0.5–3 μ). Figure 3 shows that for an accurate maximum melting point determination, the last steps must be taken extremely slowly. In the present case one week was necessary to reach complete melting at 138.3°C.

The electron micrographs which illustrate the progress of melting were taken at stages of melting indicated by Figure 3. Figure 4*b* corresponds to time zero, Figure 5*b* corresponds to the 10-hr point, while Figure 6 illustrates the last traces of crystals melting at 100 hr. In all pictures the residual extended chain crystals are distinct from the already melted material, which on quenching recrystallized poorly. The small lamellae melt first (Fig. 4), in accord with the view that the low molecular weight material is segregated into eutectic-like crystals of narrow molecular weight distribution and this causes the prepeaks visible in the thermograms. Figure 5 shows that the larger lamellae start melting at the less stable rounded tips and points of impingement or intersection formed during crystal growth.[6] As melting progresses, the lamellae become increasingly shorter in their lateral dimensions while keeping their thickness in the molecular chain direction. The "breaking" of lamellae discussed previously[9] may be due to the start of melting at intersection points and other imperfections in addition to, or instead of mechanical strain at the large lamellar surfaces as assumed before. Figure 6 shows melting of one of the last pieces of an extended-chain crystal. It is still a well formed crystal and not even one of the thickest ones found in this type of sample. The results are thus in full support of the view that melting of extended chain lamellae starts at the outer edges and proceeds layer after layer in directions perpendicular to the molecular chain direction only. Melting proceeds by the peeling off of the extended chains of the crystal, one at a time starting from the ends, rather than by the entire lamella becoming progressively smaller in the chain direction.

This work was supported by the Office of Naval Research, the National Science Foundation, and the National Aeronautics and Space Administration.

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Received March 20, 1969
Revised June 23, 1969