

Melting of Ultrahigh Molecular Weight Polyethylene

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Synopsis

On heating in DSC, samples of UHMWPE show a single, fairly sharp, melting endotherm which may be increased to a peak temperature of 147°C and 77% crystallinity by annealing at elevated temperatures. An irreversible conversion of nascent to folded crystals, between 134 and 142°C, was observed by heating nascent UHMWPE powder in the calorimeter. In the presence of *n*-hexatriacontane, the melting endotherm of UHMWPE was depressed and broadened and the conversion of nascent to melt-crystallized polyethylene facilitated on heating. A melt-crystallized mixture of ordinary linear polyethylene (HDPE) and UHMWPE was not resolved on remelting. After annealing this mixture for 12 h at 130°C, HDPE was fractionated and the melting of UHMWPE was sharpened. Crystals of UHMWPE, prepared from dilute solution in xylene, show a single sharp melting endotherm and high crystallinity, but the melting peak is reduced in temperature compared to nascent crystallized powder.

INTRODUCTION

Since the morphology of semicrystalline polymers is sensitive to thermo-mechanical history, calorimetric melting curves from such materials often exhibit a marked lack of uniformity unless controlled melting and recrystallization precede thermal analysis. In this way, we attempt to eliminate frozen-in structural variations in solid polymers. However, a close examination of the melting behavior of the "original" polymer may elucidate the origins of unique structures in polymers. Usually the specific morphology results from processing and aging. However, melting may also indicate the nature of the synthetic polymerization process. For example, nascent structures formed during the synthesis of polyethylene have been described.¹ Here, the unique structure of the polymer results from simultaneous polymerization, precipitation, and crystallization—a process which is determined by the nature of the catalyst.²⁻⁴ We have examined the melting of nascent polyethylene at various temperatures and annealing conditions and in the presence of paraffin and linear polyethylene in order to probe the characteristics of the nascent state.⁵⁻⁷ In addition, we have studied the calorimetric melting behavior of nascent polyethylene following dissolution in boiling xylene and precipitation from dilute solution.^{8,9}

EXPERIMENTAL

Materials

Samples of commercial grade ultrahigh molecular weight polyethylene (UHMWPE) were obtained from Hercules (Hercules 1900) and from Hoechst

(Hostalen GUR 412, 413, 415). The Hercules 1900 polymer was reported to contain no additives and to have a viscometric molecular weight of 4×10^6 . It was produced using a Ziegler-Natta catalyst in a slurry process with a hydrocarbon diluent.¹⁰ Similarly, GUR 412 has a viscometric molecular weight about 4×10^6 , but contains a corrosion inhibitor. The GUR 413 has a slightly higher molecular weight (4.5×10^6) and the GUR 415 has a viscometric molecular weight about 6×10^6 . UHMWPE samples were obtained in the form of a fine white powder which had been recovered directly from the heterogeneous polymerization process. The paraffin sample was *n*-hexatriacontane from Aldrich Chemical Co. and the linear polyethylene was obtained from Dow Chemical Co. (HDPE). HDPE had been pelletized by the manufacturer, thus imposing a thermal history on the polymer due to processing. "Baker-analyzed" reagent xylene, obtained from J. T. Baker Chemical Co., was used without further purification and antioxidant, 2,6-di-*t*-butyl-*p*-cresol was 99 + %, Gold Label, from Aldrich Chemical Co.

Solution Crystallization

Solutions of 0.05 and 0.1% Hercules UHMWPE were prepared by heating the polymer containing 2 wt% (based on the polymer) antioxidant, 2,6-di-*t*-butyl-*p*-cresol, in boiling xylene for 24 h. Solutions were cooled slowly to room temperature and the clouds of precipitated polymer filtered and dried.

Calorimetry

Melting and recrystallization were studied in a differential scanning calorimeter (Perkin-Elmer DSC-4) calibrated with an Indium standard.

RESULTS AND DISCUSSION

On heating in DSC at $10^\circ\text{C}/\text{min}$, all samples of UHMWPE showed a single, fairly sharp, melting endotherm. The melting temperature at the peak and the calculated crystallinity¹¹ are tabulated in Table I. Prolonged annealing at specific temperatures lead to increases in peak temperature and crystallinity. For example, following annealing at 134°C for 12 h, values of peak temperature and crystallinity are given in the table. Apparently, the fraction of high melting nascent polyethylene may be increased by annealing. Perhaps, this occurs by epitaxial crystallization of disordered material onto the extended chain crystals of the nascent polymer.¹²

TABLE I
Melting Behavior of UHMWPE

Material	T_m ($^\circ\text{C}$)	Crystallinity (%)	After annealing	
			T_m ($^\circ\text{C}$)	Crystallinity (%)
Hercules	145	74.6	147	77.2
GUR 412	143	59.9	145	71.3
GUR 413	143	66.6	146	70.1
GUR 415	143	57.6	146	66.6

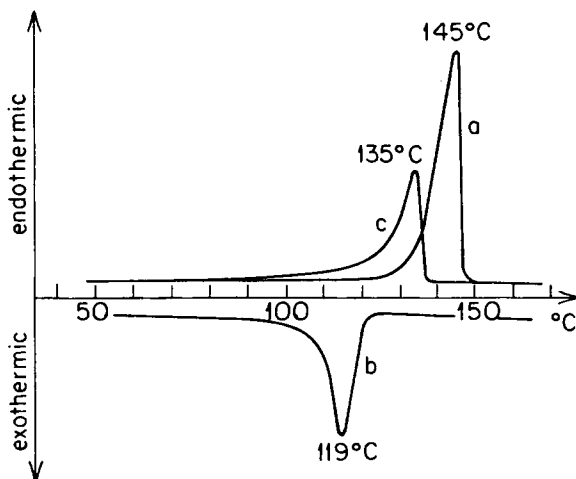


Fig. 1. Melting (a), recrystallization (b), and remelting (c) of UHMWPE (Hercules 1900) in DSC.

The effect of heating and cooling rates on the melting and recrystallization of UHMWPE was studied. For the Hercules polymer, at a heating rate of $10^{\circ}\text{C}/\text{min}$, the single sharp peak at 145°C shown on heating to 170°C , was followed by a crystallization exotherm at 119°C on cooling at $10^{\circ}\text{C}/\text{min}$ back to 25°C (Fig. 1). Subsequently, a second melting at a heating rate of $10^{\circ}\text{C}/\text{min}$ yields a single broad melting endotherm at 135°C and a crystallinity of 46.6%. We assign the initial endotherm to the melting of nascent crystals and the subsequent melting endotherm at 135°C to melt-crystallized or folded polyethylene crystals. Varying the heating rate from 1 to $120^{\circ}\text{C}/\text{min}$ increased the apparent melting point (at the peak) of nascent polyethylene from 142 to 167°C . Similarly, after a repeated melting, the peak melting temperature of the melt crystallized polymer increased from 132 to 154°C . We do not attach significance to the increases in melting peak with increasing heating rates. However, we point out that the superheating of the nascent crystals was just slightly greater than for folded crystals of polyethylene. Analogously, by increasing the cooling rate from 1 to $100^{\circ}\text{C}/\text{min}$ following the initial melting, the apparent supercooling is increased as the crystallization temperature is reduced from 119 to 81°C . Following reheating at $10^{\circ}\text{C}/\text{min}$, all samples melted at about 130°C , suggesting that the change in cooling rate was insufficient to markedly change the crystallinity of the cooled polyethylene melt.

The irreversible conversion of nascent to folded crystals could be observed by heating the nascent polyethylene at selected temperatures and times before melting in the calorimeter (at $10^{\circ}\text{C}/\text{min}$).^{6,7} For example, for Hercules UHMWPE, heating above 134 and up to 142°C for 15 min produced a continual conversion from nascent to melt-crystallized polyethylene. Under these conditions, the conversion was most rapid from 139 to 141°C , corresponding to the onset of the melting endotherm for nascent crystallized polyethylene. Similarly, heating at 140 or 140.5°C for 1–60 min yielded increasing amounts of folded crystals. Following annealing at 131 – 132°C , for 30 min, the melt-crystallized UHMWPE (generated by melting and recrystallization of nascent crystals) exhibits multiple melting peaks on subsequent

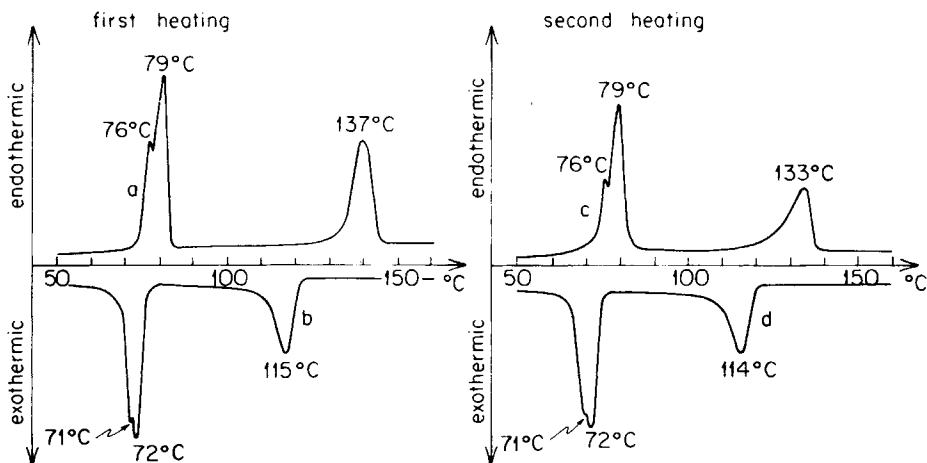


Fig. 2. Melting (a), recrystallization (b), and repeat (c and d) of a mixture of 5.0 mg *n*-hexatriacontane and 5.0 mg UHMWPE (Hercules 1900) in DSC.

remelting. Polyethylenes typically undergo molecular weight and "linearity" fractionation during annealing and thinner, less perfect, lamellae melt prior to large crystals.¹³⁻¹⁶

The effect of *n*-hexatriacontane paraffin on the thermal behavior of UHMWPE was examined. Following heating from 25°C, pure *n*-hexatriacontane shows a sharp melting peak at 79°C, with a smaller impurity peak at 76°C. On cooling at 10°C/min, corresponding recrystallization exotherms occur at 72 and 71°C. On heating an equiweight mixture of *n*-hexatriacontane with UHMWPE at 10°C/min, melting of the paraffin still occurs at 79°C, but the melting peak is broadened (Fig. 2). The melting of nascent UHMWPE is evidenced by a broadened endotherm at 137°C (reduced from 145°C in pure UHMWPE). Apparently, the paraffin extracts material from the polyethylene, thereby changing the melting pattern of paraffin. Moreover, the melting point of nascent polyethylene was depressed by the presence of molten paraffin. Indeed, following crystallization and remelting, the melting point of melt crystallized polyethylene was also depressed (by about 2°C) by the paraffin. Similarly, on annealing the nascent polyethylene, the presence of molten paraffin facilitates the conversion (melting) of nascent to melt crystallized polyethylene. Heating for only 1 min at 134°C was adequate to melt about half the nascent polyethylene in the presence of 50 wt% *n*-hexatriacontane (Fig. 3). In addition, annealing in the presence of molten paraffin increases the melting temperature and sharpens the nascent peak. Perfection of some of the nascent polymer on annealing is apparently simultaneous with the melting of some nascent polyethylene crystals. With increasing weight fraction of paraffin, the melting peak attributed to nascent polyethylene is increasingly depressed. The molten paraffin readily plasticizes UHMWPE, increasing the free volume and facilitating chain motion, enabling melting at lower temperatures and a more rapid conversion from nascent to melt crystallized state.

In addition to the effect of paraffin, we have examined the melting behavior of mixtures of ordinary linear polyethylene and UHMWPE. On heating at 10°C/min, pure linear polyethylene (HDPE) showed a melting endotherm

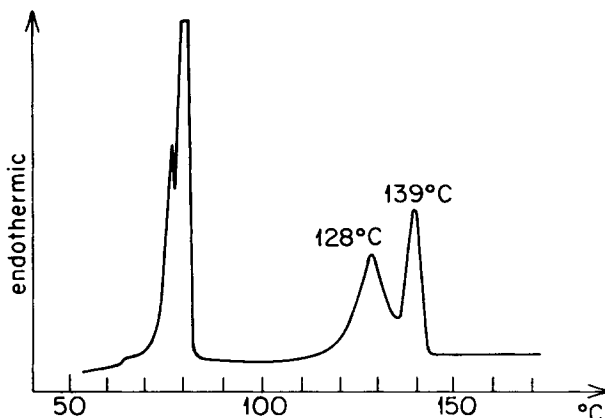


Fig. 3. Melting of a mixture of 5.0 mg *n*-hexatriacontane and 5.0 mg UHMWPE (Hercules 1900) after annealing at 134°C for 1 min.

peaking at 133°C, with not much change on remelting following crystallization. Following annealing between 125 and 130°C, multiple melting peaks result showing extensive fractionation.¹³ An equiweight mixture of HDPE and UHMWPE on heating at 10°C/min showed two clearly resolved melting peaks at 132 and 145°C, apparently unchanged from the pure materials (Fig. 4). Following melting and crystallization, a single peak at 135°C results on remelting, as melt-crystallized HDPE and UHMWPE were not resolved. On annealing the mixture of HDPE and UHMWPE before melting, the melting endotherm for HDPE was broadened while the melting of nascent UHMWPE crystals was sharpened. Perhaps, the molten HDPE extracts less perfect components from UHMWPE. Following 12 h annealing at 130°C, the HDPE endotherm separates into two peaks as fractionation occurs (Fig. 5).

Dried mats of crystals prepared from dilute solution show a single sharp melting endotherm in DSC and the same crystallinity as nascent crystallized powder. However, the peak melting temperature was reduced from 145 to

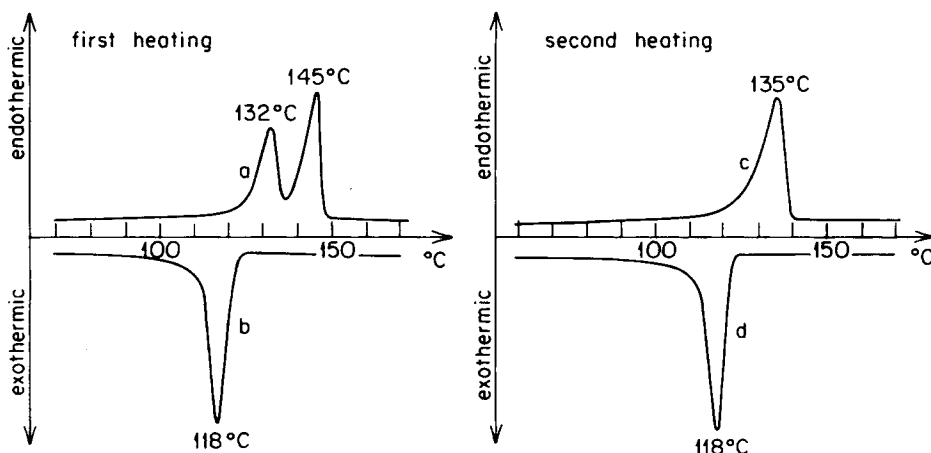


Fig. 4. Melting (a), recrystallization (b), and repeat (c and d) of a mixture of 5.0 mg HDPE and 5.0 mg UHMWPE (Hercules 1900).

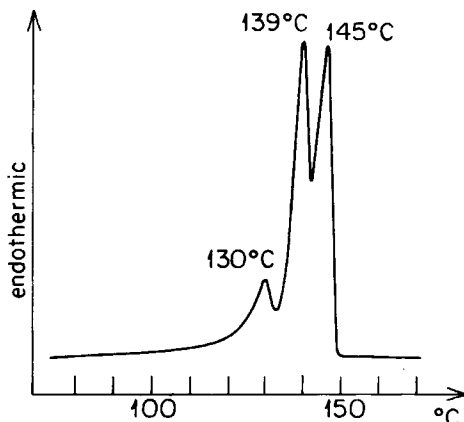


Fig. 5. Melting of a mixture of 5.0 mg HDPE and 5.0 mg UHMWPE (Hercules 1900) after annealing at 130°C for 12 h.

142°C. A melting point of 142°C for mats of crystals of UHMWPE prepared from dilute solution has been observed by us repeatedly. Electron microscopy to confirm the lamellar character of such crystals will be pursued. Although the nascent, extended chain, packing in UHMWPE is lost on dissolution, crystallization from dilute solution allows the formation of crystals of increased perfection. Since these are likely composed of folded polymer chains, the melting point was somewhat depressed.

CONCLUSIONS

As-received powder, or nascent crystallized UHMWPE, shows a higher melting temperature and crystallinity than after crystallization from the melt. Both the melting point and crystallinity can be increased by high temperature annealing. With increasing heating rate from 1 to 120°C/min, the apparent melting peak increased from 142 to 167°C, while, for the corresponding melt-crystallized polymer, the melting peak increased from 135 to 154°C. Thus, the superheating of UHMWPE slightly exceeded that of HDPE. An irreversible conversion of nascent to melt crystallized UHMWPE occurred between 134 and 142°C and was a monotonic function of time. In the presence of *n*-hexatriacontane, the melting point of nascent UHMWPE was depressed and conversion to melt-crystallized UHMWPE was facilitated. Mixtures of HDPE and UHMWPE appear to melt independently, but crystallize together to yield a single crystallization exotherm and, subsequently, a single melting endotherm. Annealing melt-crystallized mixtures of HDPE and UHMWPE produces multiple melting peaks because of fractionation. Precipitation on cooling dilute solutions yields crystals of UHMWPE of increased perfection. The morphology of UHMWPE crystals may be controlled by crystallization under specific conditions.

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