

Melting of Drawn Polyethylene Films

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Synopsis

If drawn, crosslinked, high molecular weight polyethylene films are restrained during melting, two endothermic peaks may be noted on a scanning calorimeter. In x-ray diffraction experiments, the appearance of a single new peak accompanies the disappearance of the orthorhombic pattern. The new peak is thought to be due to hexagonal chain packing above the melting temperature. The results are interpreted in terms of a small amount of fibrillar crystals in the drawn films.

INTRODUCTION

Various experiments can be performed in studying the fusion behavior of drawn, crystalline polymer films. In the usual case, the film is unrestrained while heated at a constant rate. Peterlin and Meinel^{1,2} found, for highly drawn, linear polyethylene samples, a small (approximately 2–3°C) increase in the melting temperature T_m over that for the undrawn material. They attributed the elevation in T_m to thicker crystallites in the drawn films. In studying multiple melting endotherms of nylon 66 films, Bell and co-workers^{3–5} found that stretching the films converted a kinetically favored morphologic crystalline form (Bell's form I) to the thermodynamically favored form II.^{3,4} Similar results were obtained with poly(ethyleneterephthalate).⁵ Results from various experiments led Bell to favor the interpretation of the two endotherms in terms of fusion of chain-folded and fibrillar crystals.

Restraining the films to prevent retraction during the melting process leads to different results. Simov et al.⁶ melted poly(ethyleneterephthalate) fibers under stress in a dilatometer. With increasing stress, the melting temperature first went through a maximum, then a minimum. Clough⁷ reported on the melting under restraint of crosslinked polyethylene films that had been crystallized from the oriented network. Two endotherms were observed, the smaller, higher-temperature one being attributed to the fusion of fibrillar crystals as proposed by Keller and co-workers.^{8,9}

The present paper discusses the melting of drawn films of crosslinked polyethylene which were restrained during the fusion process. Preliminary results have been reported.¹⁰ As in the case of stress-crystallized films,⁷ a second endothermic peak is observed. This now is, however, much larger than that found for the stress-crystallized films. In addition, x-ray dif-

fraction patterns were recorded¹⁰ at temperatures above the range where the endotherms are located. These x-ray results are discussed in terms of conversion of a small amount of fibrillar crystallites in the drawn films from orthorhombic to hexagonal chain packing during the fusion process.

EXPERIMENTAL

Sample Preparation

Experiments were conducted primarily on a high molecular weight linear polyethylene sample, AC-1220, obtained from the Allied Chemical Company ($M_v = 1.5\text{--}2 \times 10^6$). Films compression molded to approximately 0.01 in. were irradiated to dosages of 1 to 6 Mrad on a van de Graaff generator above the crystallite melting temperature. Details of the preparation process and characterization of the resulting network have been presented.⁷ Table I gives the estimated molecular weight between crosslinks, M_c , for the networks.

TABLE I
Polyethylene Network Characterization

Dose, Mrad		Estimated \bar{M}_c
	AC-1220	
1		11,000
1.5		8,700
6		6,100
	Marlex 6002	
10		4,500
20 ^a		4,400

^a Irradiated at room temperature.

A small number of experiments were performed on Marlex 6002 linear polyethylene ($\bar{M}_w = 165,000$, Phillips Petroleum Company) irradiated to 20 Mrad at room temperature. The higher dosage was required in order to cause network formation in this lower molecular weight sample. \bar{M}_c was estimated to be 4400. This value is approximately equal to that for the 10-Mrad sample irradiated above the crystallite melting temperature previously described.⁷

The crosslinked films were drawn with a hand-operated device, from an initial length of 1 in. at an approximate rate of 2 in./min. Drawing at elevated temperatures was accomplished by placing the stretching device in a silicone oil bath at stretching temperatures T_s of 100° and 120°C. A mild neck formed and propagated during the drawing operation.

Scanning Calorimetry

After removal from the bath, small strips of the film were clamped in DSC pans (Perkin Elmer differential scanning calorimeter Model DSC - 1B) using 0.25-in. internal retainer rings to hold the ends of the film against the

pan edges, thus preventing retraction.⁷ Runs on restrained unstretched films were compared with free unstretched films to verify that the clamping arrangement did not produce anomalous results. In some cases, one or two extra rings had to be added to assure film restraint during fusion. A heating rate of 10°C/min was employed. The instrument was calibrated by the fusion of indium, and the temperature was corrected 2°C for instrument lag.

X-Ray Diffraction

Wide-angle x-ray diffraction measurements were made on drawn films in the temperature range 135° to 177°C. A Warhus camera was used with Ni-filtered Cu radiation and was evacuated during the experiments. The films were restrained by replacing the heater sample holder with a pair of clamping rings. A controller held the temperature to within $\pm 0.5^\circ\text{C}$ of the set temperature. The heater was calibrated by the fusion of Fisher TherMetric Standard adipic acid ($T_m = 151.4^\circ\text{C}$). A typical heating schedule is shown in Table II.

TABLE II
X-Ray Diffraction, Typical Heating Schedule, and Results^a

Temperature, °C	Exposure time, hr	Results ^b
134	4	Or only
140	16	Or only
143.5	5	Or only
145.5	16	Or only
148	24	Or + weak A
150.5	24	weak Or + A
153.5	^c	A only

^a 1-Mrad irradiated AC-1220, $\alpha = l/l_0 = 5$, $T_s = 100^\circ\text{C}$.

^b Or = Orthorhombic (110) and (200) peaks; A = new peak.

^c Sample broke and retracted during exposure; diffraction pattern obtained from period prior to break.

A limited number of small-angle x-ray diffraction photographs were also made with the Warhus camera at temperatures above 150°C.

RESULTS

Figure 1 shows representative DSC results for the fusion of drawn 1-Mrad-irradiated films held at various fixed elongations $\alpha = l/l_0$. As the sample weight was only approximately known, the peak sizes are not accurately normalized for equal sample size. The unoriented films were annealed in the oil bath for 2 min to duplicate the thermal treatment afforded the drawn samples. For the drawn films, considerable melting occurred in the temperature range 135°–150°C. At the lower elongations, this was observed as a broad tail to the principal peak occurring at about 130°C.

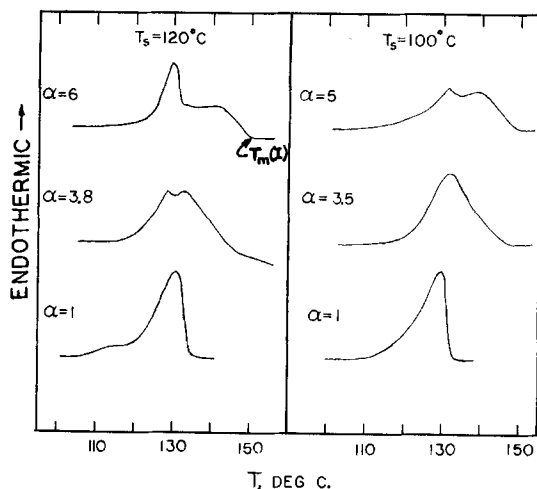


Fig. 1. DSC fusion endotherms for restrained films of 1-Mrad-irradiated AC-1220 linear polyethylene, drawn to $\alpha = 1/l_0$ at T_s .

As the elongation increased, an additional peak emerged from the tail. The temperature corresponding to this peak increased with increasing elongation, its tail extending to a final melting temperature $T_m(I)$ of 148° – 150°C .

In some instances following fusion, the baseline assumed a lower position than prior to melting (Fig. 1, $\alpha = 6$), and sometimes a marked difference in slope was noted (Fig. 1, $\alpha = 3.8$). These effects are presently unaccounted for, but may reflect small difference in sample contact with the pan bottom before and after melting.

In comparing these fusion results with those from the same polyethylene which had been crystallized under stress,⁷ one notes that both cases have two melting peaks with final melting occurring at about 150°C but that the higher temperature peak is much larger in the present case.

In x-ray diffraction experiments, the final orthorhombic diffraction peaks disappeared at about 150°C as the drawn samples were heated while being maintained at fixed elongation. A small amount of the orthorhombic crystals was transformed into another crystal form in this temperature region. A single x-ray peak with a spacing of 4.3 – 4.4 \AA replaced the orthorhombic pattern (see reference 10 and Table II). The orthorhombic peaks returned and the new peak disappeared when the sample was again cooled to some crystallization temperature below T_m (Fig. 2). The new peak has been observed up to temperatures of 177°C , the upper limit of the experiments. No additional endotherms were noted with the DSC up to temperatures of 200°C .

The sample, if not restrained, retracted during fusion, giving rise to an irregular DSC endothermic response terminating just above the melting temperature of the unoriented samples. The additional x-ray peak was not observed if the sample was not held at fixed elongation.

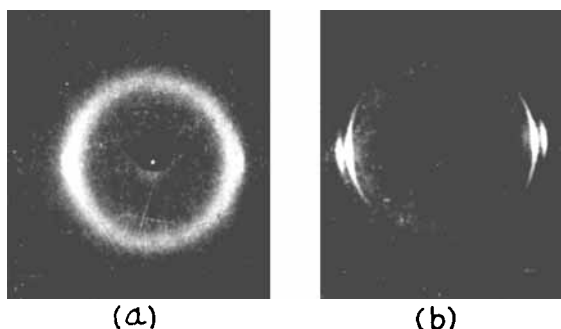


Fig. 2. X-Ray diffraction from restrained films of 1-Mrad-irradiated AC-1220 linear polyethylene, drawn to $\alpha = 3.5$ at $T_s = 120^\circ\text{C}$: (a) 2-hr exposure at $T = 163^\circ\text{C}$; (b) 1-hr exposure after cooling sample a to 118°C .

Small-angle x-ray diffraction photos of drawn films ($\alpha = 5$, $T_s = 100^\circ\text{C}$) taken at 152°C or higher showed weak equatorial scattering.

The final melting temperature $T_m(I)$ decreased with increasing irradiation dose, as for the stress-crystallized case (Table III, Fig. 3c). For this high molecular weight sample, the heating rate was rapid enough such that the melting experiments could be run on clamped, uncrosslinked samples without detectable film retraction occurring. The decrease in the final melting temperature between the 0- and 6-Mrad samples, about 7°C , is larger for the drawn films than for the unoriented samples, about 3°C . (The data in the final column of Table III are for two samples with identical thermal histories.)

TABLE III
Melting Temperature at Various Irradiation Doses

Sample	Irradiation dose, Mrad	$T_m(I)$, ^a $^\circ\text{C}$	T_m , ^b $^\circ\text{C}$
AC-1220	0	149-150	134.9
AC-1220	1	147-148	—
AC-1220	1.5	146	—
AC-1220	6	142	131.8
Marlex 6002	20 ^c	139-140	—

^a $\alpha = 5-5.5$, $T_s = 120^\circ\text{C}$.

^b $\alpha = 1$, $T_x = 120.6^\circ\text{C}$.

^c Irradiated at 30°C .

Experiments were also run on the lower molecular weight Marlex sample. Figure 3 compares the endotherm resulting from a sample stretched at 120°C to $\alpha = 5.5$ with an unstretched sample. The absence of any melting occurring above 140°C recalls similar results from the stress-crystallized experiments⁷ for this more highly crosslinked sample and is in line with the decreasing value of $T_m(I)$ with increasing irradiation dose (Table III).

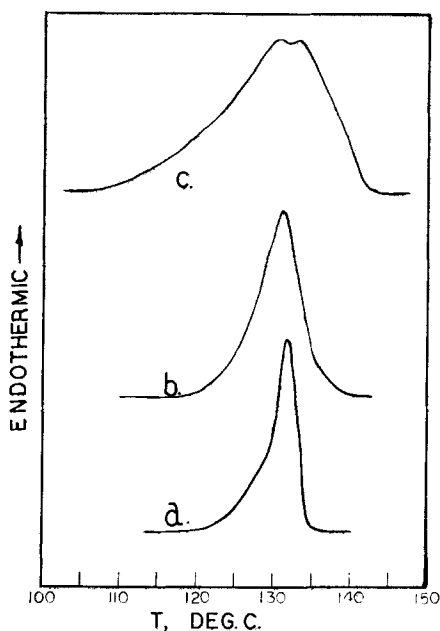


Fig. 3. DSC fusion endotherms for restrained drawn films of linear polyethylene: (a) Marlex 6002, 20 Mrad, $\alpha = 1$; (b) Marlex 6002, 20 Mrad, $\alpha = 5.5$, $T_s = 120^\circ\text{C}$; (c) AC-1220, 6 Mrad, $\alpha = 5$, $T_s = 120^\circ\text{C}$.

DISCUSSION

The most notable feature of the endotherms for the drawn films is the presence of the higher-temperature melting peaks. The temperature range for this portion of the endotherm is the same as that for the stress-crystallized samples.⁷ The magnitude of the peak, however, is much greater, accounting for 50% or more of the total area under the endotherm for some films. (In the stress-crystallized case, the higher temperature peak (I) was about 10% or less of the total area.) The detection of x-ray diffraction from the orthorhombic crystals at temperatures up to 150°C indicates that the endothermic peak is caused by fusion of the crystallites and not by the thermal response to chain retraction, for example, or other factors.

Observation of the x-ray peak ($d = 4.3 \text{ \AA}$) at temperatures well above 150°C indicates that a small amount of the orthorhombic chain packing is transformed into another, assumed hexagonal, form. From this it was concluded¹⁰ that a small amount of the orthorhombic crystals existed as fibrils (with length along the c -axis greater than that of lamellar crystals), these being formed during the drawing process. These crystals will be designated form I, as in the stress-crystallized case. The existence of such crystals in drawn films had earlier been suggested by Keller and Machin.⁸ For drawn films, only a portion of the large higher-melting DSC peak is due to the transformation of form I crystals to the new chain packing.

The superheating detected from the higher-melting crystals in fiber prepared from stirred solutions^{11,12} necessitates consideration of this phenomenon in the present case. Mandelkern¹¹ observed superheating of 2°C at heating rates as low as 0.5°C/day. If the crystal perfection in the drawn films approached that in the stirred solution crystals, x-ray diffraction might be detected in the 16-hr exposure at temperatures a few degrees above the actual crystal-melting temperature. However, it appears that superheating is not important in the present case. First, for the $\alpha = 5$ film, the DSC melting temperature at 10°C/min, 150°C, is not higher than that determined by the slow heating schedule used in the diffraction experiments. The presence of superheatable material would lead to higher apparent melting temperatures at the higher heating rate.

A further difference in the two cases is noted. The high-melting temperatures (above 135°C) are not observed in the unrestrained drawn films. The melting temperature elevation is due to the stressed final noncrystalline state, not to high crystal perfection. It is unlikely that drawing the crystal films would lead to chain-extended crystals of high perfection.¹³ The crosslinks themselves would also be one source of imperfection.

The two peaks in the endotherms resulting from the fusion of unrestrained nylon 66 and isotactic polystyrene were interpreted by Bell and Dumbleton⁵ as due to lamellar and fibrillar crystallites. In addition, their results support the view that the fibrillar crystallites are comprised of partially extended chains. A similar model was proposed⁷ to explain the two peaks observed on melting restrained stress-crystallized polyethylene. In the present case, the lower-temperature peak is similarly attributed to the fusion of lamellar crystallites, resulting from recrystallization of relaxed chains on fibrillar nuclei and from the annealing of deformed blocks pulled from the original crystal structure.^{14,15,16}

The large higher-temperature DSC peak must reflect crystal melting in addition to the transformation of the small amount of type I crystallites to hexagonal packing. The main contribution to this peak is believed to be due to fusion of crystals (under stress) comprising a mixture of folded chains and tie chains between crystallites. An increase in area under the higher-temperature end of this peak (145°–150°C) with increased elongation suggests a larger amount of fibrillar crystallites.

The rapid depression of $T_m(I)$ with increasing irradiation dose as compared to unoriented films might be interpreted in terms of the partially extended chain crystallites. As the irradiation dose varies from 1 to 6 Mrad, the estimated average chain length between crosslinks decreases from 1150 to 640 Å. The increasing dose thus causes increasing limitations on the length of extended chains incorporated into crystallites. One might thus expect a more rapid decrease in T_m than for the lamellar crystals where crosslinks increase crystal imperfection but affect lamella thickness to a lesser extent.

The observation of endotherms with two peaks is unique to the very high molecular weight sample. The increased degree of crosslinking in the

Marlex sample was necessary to prevent flow during fusion. This, in turn, as seen for AC-1220, decreases $T_m(I)$ to such an extent that peak separation becomes increasingly difficult. Thus, the conclusions reached regarding fibrillar crystals do not necessarily apply to uncrosslinked samples of moderate molecular weight.

Experimental work performed at U.S. Army Materials and Mechanics Research Center, Watertown, Massachusetts.

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Received February 25, 1971

Revised May 6, 1971