Polymere

Differential Thermal Analysis of Pressure Crystallized Polyethylene

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Introduction

Crystallization of linear polyethylene (Marlex 6050) at elevated pressure results in a considerable change in its morphology (1). Electron microscopy, DTA and density measurement of samples crystallized under pressures up to 5000 atmospheres have been reported previously (1,2). In this paper similar pressure-crystallization studies on medium density polyethylene (MPE) (2.6-CH₃ groups per 1000 carbon atoms) and a high molecular weight polymethylene (PM) are reported in addition to more complete DTA results for pressure-crystallized linear polyethylene (LPE) (Marlex 6050-1.4 CH₃ groups per 1000 carbon atoms). The microscopy and density results for the Marlex 6050 samples obtained in this work are similar to those described in the literature although the details of the crystallization process are different.

Experimental

Crystallization Conditions

A high-pressure dilatometer, described in another publication (3), was used to obtain pressures up to 5000 atmospheres. The apparatus was calibrated at all temperature and pressure conditions by observation of the polymorphic transitions of silver iodide and ammonium iodide. Temperature control to within ±1 °C up to 250 °C was obtained by placing the dilatometer in a modified circulating-air oven.

The crystallization procedure was as follows: After loading the bomb with polymer, the dilatometer was assembled and the sample compressed at room temperature for one hour at 100 atmospheres. The pressure was then raised to the desired value, and the oven temperature was raised to the desired level. The volume change during melting was monitored to assure complete melting. After one-half hour at 10 °C above the melting temperature, the temperature was lowered at a rate of 3 °C per minute and the sample crystallized. Upon cooling to room temperature the pressure was released.

The polymethylene sample was not prepared using the above procedure. In this case the sample was heated to 227 °C at atmospheric pressure, after which the pressure was applied. After 20 hours at 227 °C the sample was slowly cooled to room temperature followed by release of the pressure. This is the same method employed for the preparation of the samples described in reference (4).

Density

The density was measured at 23 °C with a titration-floatation technique using isopropanol and water as the miscible non-solvents. The densities and density crystallinities obtained by using the values of $V_a$ and $V_c$ employed by Chiang and Flory (5) are listed in table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallization pressure, atm.</th>
<th>Density at 23 °C</th>
<th>Crystallinity Based on Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium-density</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polyethylene</td>
<td>1</td>
<td>0.9313</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>2500</td>
<td>0.9376</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.9395</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9737</td>
<td>82</td>
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<td>Marlex 6050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polyethylene</td>
<td>1</td>
<td>0.9092</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.9318</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>0.9893</td>
<td>92</td>
</tr>
<tr>
<td>Polymethylene</td>
<td>4760</td>
<td>0.9951</td>
<td>96</td>
</tr>
</tbody>
</table>

1) density at 25 °C.

Electron Microscopy

Platinum-carbon replicas of fracture surfaces obtained at liquid nitrogen temperatures were prepared. The fracture surfaces of the Marlex 6050 samples were essentially identical to those described previously (1). An apparent decrease in the number of kink bands is attributed to the differences in the method of crystallization. Micrographs of MPE crystallized at 5000 atm. and PM crystallized at 4760 atm. are shown in fig. 1 and 2, respectively. Details of these and the other micrographs are discussed later.
**Differential Thermal Analysis (DTA)**

The DTA scans were obtained using the DuPont 900 Differential Thermal Analyzer. Heating rates of 1, 5, and 10 °C/min. were used to determine the effect of rate on the temperatures of the various peaks observed. Following melting in the microcells, the samples were heated to 50 °C above the melting point, held for 1/2 hour and allowed to recrystallize by cooling at 5 °C/min. In several instances, however, the samples were heated only 2-3 °C above the melting point and immediately cooled at 5 °C/min. All of the samples were subsequently melted a second time at the same rate used for the first melting.

Typical curves are shown in fig. 3–5 for a heating rate of 1 °C/min on the DuPont analyzer; the temperatures of the peak positions are listed in table 2. The dashed curves in fig. 3–5 represent the second melting. The use of a small sample size obviates the necessity of using an extrapolated melting point in the terms described by Poland and Wunderlich (6). However, an extrapolation as a function of heating rate is still indicated.

**Discussion**

**Electron Microscopy**

The fracture surfaces of the MPE sample crystallized at 1, 2500 and 3000 atm. resembled those previously described for LPE crystallized at 1 atm. (1,7); they had an irregular, fibrillar appearance suggesting that failure occurred by drawing rather than fracture. If extended-chain lamellae are present (as indicated by DTA) they are apparently too small and too randomly distributed to be observed.

When MPE was crystallized at 5000 atm., however, extended-chain lamellae as shown in fig. 1 were observed. In comparison with LPE crystallized at 5000 atm. (1) the extended-chain lamellae were considerably smaller in both lateral size and thickness. The observed thickness varied between 0.1 and 0.5 microns. In addition a considerable quantity of irregular fibrillar material, usually attributed to “fracture” of folded chain lamellae interconnected by tie molecules (7) was present. The striation spacing (200–400 Å) was somewhat larger than observed on the 4760 atm. PM and previous (1) or present 5000 atm. LPE samples (200–300 Å).

The fracture surface of the 4760 atm. PM sample is indistinguishable from the 5000 atm. LPE sample except for the presence of thicker extended-chain lamellae. The maximum thickness observed on the PM sample was 5 μ as compared with 3 μ on the LPE sample. If fractionation occurs by molecular weight (8) a greater thickness is expected since the PM has a considerably higher molecular weight (4) than the Marlex 6050 LPE sample.

![Fig. 1. Electron micrograph of fracture surface of medium-density polyethylene crystallized at 5,000 atm. showing extended-chain lamellae. The scale bar represents 0.5 μ](image1)

![Fig. 2. Electron micrograph of fracture surface of polymethylene crystallized at 4,760 atm. showing striated, extended-chain lamellae. The scale bar represents 1 μ](image2)

**Differential Thermal Analysis**

There are 4 major features of the DTA data that need interpreting in addition to the density and electron microscope results:

1. The number and temperature of the endothermic peaks;
2. the effect of heating rate on the endothermic peaks;
3. The relative melting and crystallization temperatures of folded and extended-chain lamellae and
4. the “memory” effect evidenced by the second melting. Each of these features is discussed below.