

Dilatometric Study of the Melting Point of Three High-Pressure Crystallized Samples of Marlex Polyethylene

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Synopsis

The melting points of three polyethylenes differing in molecular weight distribution from 47,000 to 147,000 were determined as $141^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ by dilatometric techniques. Sample preparation procedures were developed to ensure uniform thermal history prior to measuring length as a function of temperature in a precision dilatometer. The specific volume data were reproducible within 0.02%, reflecting the careful annealing procedure used and the extended time allowed for equilibrium to be attained.

INTRODUCTION

The object of this work was to determine the equilibrium melting point of linear polyethylene and compare the value to the predicted value of $141^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Three polymers, differing only in molecular weight distribution, were studied and sample preparation procedures were developed to ensure uniform thermal history in the samples. A precision dilatometer was built for this investigation.¹

EXPERIMENTAL

The dilatometer, to be described in detail elsewhere in this journal,² had a constant temperature bath that could be controlled to $\pm 0.01^{\circ}\text{C}$. The sample was constrained to a constant diameter of 0.2553 in. so that only its length changed significantly with temperature. All samples were approximately 2 in. long and the dilatometer was sensitive to changes of 0.00005 in. in sample length. Temperature and change in sample length were continuously monitored on a strip-chart recorder.

Three different types of Marlex high density polyethylene were used in the investigation: Marlex 6001, molecular weight 147,000; Marlex 6002, molecular weight 131,800; and Marlex 5095, molecular weight 47,100.

The polymers, supplied as $1/8$ in. granules, had to be molded into cylinders that conformed accurately to the sample chamber. This was done by first extruding the polymer through the sample chamber and allowing the poly-

mer to solidify in the chamber. The extruded sample had an axial density gradient and was slightly tapered so it required further preparation.

The extruded sample was cut to approximately 2.1 in. in length and inserted in the sample chamber. The base of the sample chamber was then sealed and placed in the constant temperature bath. An oil dam was threaded to the sample chamber to prevent the heat transfer fluid from contacting the sample and a piston was brought into contact with the sample. The piston excluded air from the sample chamber during annealing. The constant temperature bath was then heated to 190°C and held for 1 hr to eliminate all traces of residual structural order that might have been present in the melt. The pressure on the sample was then increased to 550 atm. It was found that samples cooled under this pressure had the exact dimension of the sample chamber and were free of voids. Samples cooled under a lesser pressure did not conform to the sample chamber dimensions, while samples cooled under higher pressure had a larger diameter than the sample chamber after being removed from the chamber.

The sample was held at 550 atm and 190°C for an additional hour and then the device was cooled at a constant rate of approximately 0.5 °C per minute to approximately 30°C. During cooling, the pressure was constantly maintained in spite of shrinkage of the polymer. On reaching 30°C, the pressure on the sample was slowly released. The sample chamber assembly was then removed from the bath and the sample recovered. The sample dimensions were determined with precision micrometers to ± 0.00005 in. The sample was then weighed to ± 0.0001 g and its specific volume and density calculated. The sample was then ready for testing.

The sample was replaced in the sample chamber and the assembly repositioned in the constant temperature bath. The piston was brought in contact with the sample and, to ensure proper seating of the sample, the pressure was slowly increased to 550 atm and slowly released to 1 atm absolute pressure. A linear variable differential transformer (LVDT) attached to the piston was used to determine when complete relaxation of the sample occurred. If the LVDT output and bath temperature were constant over a 1-hr period, equilibrium was assumed and the measured sample length and density were used as initial points. The bath temperature was then increased to the next step. When the temperature and LVDT output were constant for a 1-hr period, equilibrium was assumed and the change in sample length recorded. Equilibrium required from 18 to 36 hr as evidenced by a constant LVDT output, the longer times occurring in the melting range of the polymer.

RESULTS AND DISCUSSION

Table I shows the data for the three polymers investigated. The data are plotted in Figure 1 as expansivity versus temperature. The highest molecular weight polymer, Marlex 6001, has the steepest initial slope. The initial slopes decrease with decreasing molecular weight. Above 120°C the

TABLE I
Specific Volume of Marlex Polyethylenes as a
Function of Temperature at 1 Atmosphere

Marlex 5095		Marlex 6001		Marlex 6002	
Temperature, °C	Sp. vol., cc/g	Temperature, °C	Sp. vol., cc/g	Temperature, °C	Sp. vol., cc/g
20.00	1.0511	25.00	1.0359	25.00	1.0360
51.70	1.0615	50.00	1.0418	60.00	1.0467
79.40	1.0785	75.00	1.0523	100.00	1.0680
107.20	1.1038	100.00	1.0678	120.00	1.0873
121.10	1.1212	120.00	1.0832	130.00	1.1069
132.20	1.1503	130.00	1.0992	135.00	1.1248
137.80	1.1786	135.00	1.1160	137.50	1.1486
140.50	1.2072	137.50	1.1440	139.00	1.1792
142.20	1.2399	139.00	1.1780	141.00	1.2296
143.30	1.2473	141.00	1.2218	143.00	1.2304
146.10	1.2622	143.00	1.2234	150.00	1.2361
151.70	1.2664	150.00	1.2606		
176.70	1.2844	160.00	1.2379		

curves become flat and coincide. The curves show discontinuities between 18% and 20% expansivity. The discontinuities for the three polyethylenes studied occurred at $141^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. This compares well with the melting point predicted by extrapolating melting point data for normal paraffins.

The annealing procedure is necessary to ensure a sample uniform in dimension and thermal history. Most important is the fact that the data

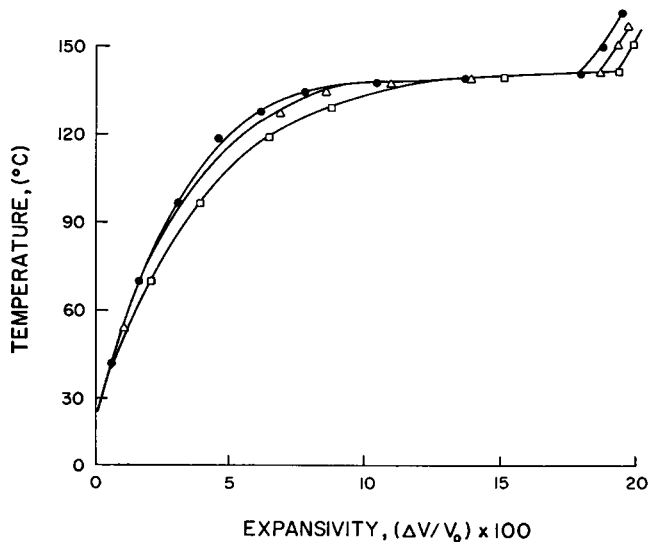


Fig. 1. Expansivities of Marlex polyethylenes: ○) Marlex 6001; △) Marlex 6002; □) Marlex 5095; V_0 = specific volume at 25°C and 1 atm.

were equilibrium data. The rate of change of specific volume at constant temperature was less than 2×10^{-7} cm³/g per min when the data point was recorded. This rate of change corresponds to a change in sample length of 0.00001 in. in a 1-hr period.

The specific volume data were very reproducible. The original samples were rerun and new samples were made and expansivities determined and the results compared to the original data. In all cases the data were within 0.02% of the initially determined values.

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References

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