

of approximately 2°C per minute. The beginning of solidification is indicated at point (D) in Figure 2 and continues to point (F). The baseline is gradually re-established in the region labeled (G). It is of interest to note the evidence of supercooling before crystallization in the region prior to point (E). In this nonequilibrium process, point (E) is taken as the crystallization temperature.

Bundy<sup>10</sup> has shown that the effect of external pressure for the used thermocouples (Chromel-Alumel) is negligible up to 10 kb.

The overall precision of our temperature measurements is  $\pm 0.7^\circ\text{C}$ . The temperature calibration was carried out by measuring  $T_A$  for five pure compounds as melting standards. The indium and tin used were Fisher Certified Reagents. According to the supplier's analysis, the purity of the indium was 99.99%, while that of the tin was 99.96%. The organic compounds used: adipic acid, benzoic acid, and naphthalene, were high purity samples (Fisher Certified TherMetric Standards). The calibration data between 80 and 230°C were averaged to a net thermocouple correction of  $-0.2^\circ\text{C}$ .

### Materials

The polyethylene was characterized by gel-permeation chromatography through the courtesy of J. C. Moore of the Dow Chemical Co. The polymer was a sample of Marlex 6009 from the Phillips Petroleum Company. Additives were 0.022% Ionel (2,6-di-tert-butyl-4-methyl-phenol) and 0.033% DLTDP (*N,N*-dilauryl thiodipropionate). The polymer was identical to polymer A used in earlier high-pressure crystallizations.<sup>11</sup> Because of improvement in GPC technique, the molecular weight data reported here are thought to be somewhat more accurate than those reported earlier.<sup>11</sup> We find  $M_n = 8530$ ,  $M_w = 153000$ .

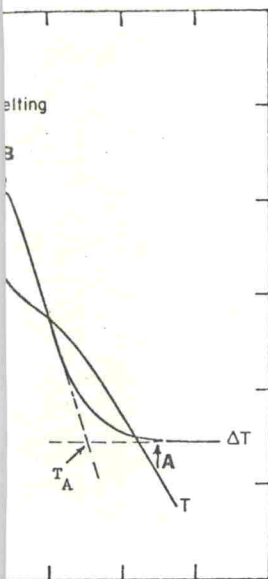
The ethylene-butene-1 copolymer is a laboratory sample containing 1.8 mole-% butene-1 which was provided by the Research Department of the Hercules Corporation. The comonomers were polymerized in a low-pressure reaction under conditions favorable to random copolymerization. The material was identical to sample B-2 in previous crystallization and melting experiments.<sup>12,13</sup> The molecular weight data were obtained by gel-permeation chromatography by B. A. Denenberg of Waters Associates.  $M_n = 9100$ ,  $M_w = 120,000$ . Both polymers were used as received.

## EXPERIMENTAL DETAILS AND RESULTS

### PDTA of Folded-Chain Polyethylene

Polyethylene crystallized by cooling from the melt was used as the starting material for the first series of experiments. In all of the runs of this series the sample was crystallized in the cell by cooling from the melt at atmospheric pressure at about 2°C/min before each melting experiment. This procedure assured that the starting material of each run initially had the same folded-chain morphology regardless of the pressure at which the

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T trace. The breadth of  
fusion, mass, and thermal  
depends upon the heating  
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in the case of a polymer.  
all amount of sharp melt-  
DTA cell,  $T_A$  is the tem-  
surface of the cylindrical  
ctor in polymer DTA is  
materials. In calorimetric  
e has exhibited a tempera-  
crystalline portion fused.<sup>7</sup>  
occur far below the range  
ed-chain polyethylene of  
se to the temperature at  
as been absorbed.<sup>9</sup> This  
adding the thermocouple  
ne  $\Delta T$  trace to the baseline  
characteristic.<sup>9</sup> Point (C)  
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be followed in the PDTA  
ch results in a cooling rate