

## Differential Thermal Analysis of Polyethylene under High Pressure\*

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### Synopsis

The design of a differential thermal analysis apparatus for use at elevated pressure is described. Experiments on melting and crystallization of folded-chain crystals of polyethylene and poly(ethylene-butene-1) copolymer, and melting of extended-chain polyethylene crystals have been conducted at pressures up to 4200 bars. The precision in transition temperature measurement was  $\pm 1^\circ\text{C}$ . The Clausius-Clapeyron equation predicts the melting point increase with pressure at atmospheric pressure to be  $32.0^\circ\text{C}/\text{kb}$ . The melting point depression due to copolymerization remained constant over the complete pressure range analyzed on the poly(ethylene-butene-1) used in this study. Crystallization of polyethylene is retarded at elevated pressures, and a 50% larger degree of supercooling is necessary at 5000 bars to give a crystallization rate equal to that observed at atmospheric pressure. The difference in melting point between folded-chain and extended-chain polyethylene increases from  $8.4^\circ\text{C}$  at 1 bar to  $25.6^\circ\text{C}$  at 3000 bars.

### INTRODUCTION

Crystallization of polyethylene from the melt under hydrostatic pressure above 3600 bars has led to largely extended-chain crystals.<sup>1,2</sup> These crystals are in a condition which is close to equilibrium, in contrast to the folded-chain crystals as usually grown at atmospheric pressure.<sup>3</sup> Since thermal analysis is one of the most direct methods of study of crystallization and melting, differential thermal analysis (DTA) has been adapted to the pressure range of interest. In this paper a high-pressure DTA apparatus (PDTA) capable of measuring at up to 4500 bars pressure will be described. Melting data for folded-chain crystals of polyethylene and poly(ethylene-butene-1) copolymer and extended-chain crystals of polyethylene at various pressures have been obtained. Crystallization of the homopolymer and the copolymer upon cooling at a constant rate has been measured at various pressures.

\* This paper was presented in part at the 1966 IUPAC meeting in Tokyo and Kyoto.

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## HIGH-PRESSURE DIFFERENTIAL THERMAL ANALYSIS

## PDTA Cell Design

DTA has been performed in pressure equipment of various geometries by other researchers<sup>4,5</sup> but generally some concession had to be made for the sake of attaining high pressures. The present apparatus was designed to provide optimum geometry and thermal characteristics for DTA in a cell which can be easily pressurized and manipulated. A cylindrical geometry with thick walls provides for symmetrical placement of sample and reference substances and a uniform temperature gradient. Uniform pressure at the surface of sample and reference is assured through the use of nitrogen gas as the pressure-transmitting medium. The apparatus has been used up to 3700 bars and 200°C. By proper design of all components of the system it should be possible to reach 6500 bars and 500°C with this type of high pressure DTA cell.

As shown in Figure 1, the cell is a cylinder 6.25 in. in length, 2 in. in outside diameter, with an 0.1875-in. bore. The bore is closed at both ends by identical plugs which form "cone-in-cone" high-pressure seals. Seals of this type function by forcing a plug with a taper of 58 or 59° into a seat tapered at 60°. The interface is a narrow annulus which carries the entire sealing force on a small area. The two plugs of this cell are drilled axially for the insertion of Chromel-Alumel thermocouples which are encased in a stainless steel sheath of 0.0625 inch outside diameter. The gap between the thermocouple sheath and the bore of the closure is sealed by brazing with a silver alloy. The junction of the thermocouple is electrically insulated from the sheath by a packing of finely powdered magnesium oxide. Four wires emerge from each junction so that the temperature  $T$  and temperature difference  $\Delta T$  circuits originate at the same point in the thermocouple. (The cell was fabricated by Pressure Products Industries of Hatboro, Pennsylvania, who also assisted in its design.)

The tip of one thermocouple is surrounded by a reference substance which does not suffer any thermal transitions in the range of temperature under investigation. A tightly wound cylinder of asbestos paper is suitable as a

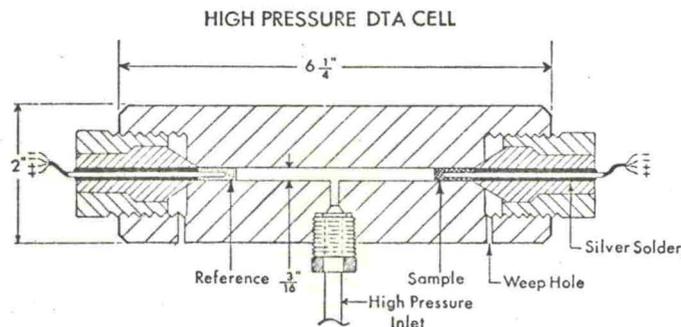


Fig. 1. PDTA cell.

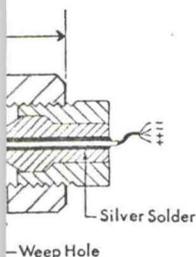
## TEMPERATURE ANALYSIS

of various geometries by had to be made for the apparatus was designed to meet the requirements for DTA in a cell.

A cylindrical geometry of sample and referent. Uniform pressure throughout the use of nitrogen apparatus has been used of all components of the cell at 500°C with this type of

25 in. in length, 2 in. in diameter. The cell is closed at both ends by high-pressure seals. Seals of type 58 or 59° into a seat which carries the entire weight of the cell. The seals are drilled axially and are encased in a metal jacket. The gap between the seal and the jacket is sealed by brazing. The thermocouple is electrically insulated by a layer of magnesium oxide. The temperature  $T$  and temperature point in the thermocouple is measured. (Products Industries of design.)

reference substance which is used for the measurement of temperature under pressure. The apparatus is suitable as a



reference. The polymer specimen under investigation must be in the shape of a cylinder to make good thermal contact with the walls of the cell. For the experiments on melting and crystallization of folded-chain polymers under pressure, samples were formed to the proper dimensions in a small stainless steel hand mold. A hole is drilled axially to within 0.125 in. of one end to accept the sheathed thermocouple. Specimens of extended-chain polyethylene were machined to size and drilled to accept the thermocouple. For calibration a dummy specimen was machined from polytetrafluoroethylene. Where the tip of the thermocouple would fit in the usual polymer plug, a cavity of 0.0625 in. diameter and 0.0625 in. length was left in the dummy for insertion of a few milligrams of the calibrant. By this means the sample geometry is preserved for all runs.

The body of the PDTA cell was machined from a high temperature alloy, René 41, which contains 55% Ni, 19% Cr, 11% Co, and 10% Mo. The cell is heated by three strip heaters, each rated for 200 W at 115 V ac. The heating rate is controlled by supplying a chosen voltage to the heaters from a variable autotransformer. The normal heating rate chosen was 4°C/min. To assure good thermal contact, the heaters are bolted to a three-section jacket of pure aluminum which is firmly clamped to the outside of the PDTA cell.

Nitrogen gas under pressure is supplied to the PDTA cell from a 200-cm<sup>3</sup> pressure reservoir. Since the volume of the reservoir is 125 times the volume of the cell, there is no measurable change in pressure as a result of heating the cell during a run. The nitrogen in the reservoir is compressed over oil by means of a high-pressure intensifier in an apparatus described previously.<sup>6</sup> The piston of the intensifier can be manually stroked as many times as necessary to reach the desired pressure. To measure the pressure in the cell, a 6900-bar Bourdon tube gauge (Heise Bourdon Tube Company) is connected directly to the high pressure side of the system. This gauge proved highly reliable in operation and could easily be read to 7 bars. During the course of the present experiments, the gauge was rechecked by the manufacturer by using a dead-weight tester which had been calibrated by The National Bureau of Standards. Up to 5800 bars no measurable deviation was found from the original calibration.

The electronic circuitry of the PDTA apparatus represents a standard DTA measuring circuit.

## Analysis of Data and Calibrations

Three points on the  $\Delta T$  trace were identified: the first deviation from the baseline (A), the peak (B), and the return to baseline (C). For a sharply melting substance, A is the melting point. Figure 2 is a direct copy of the melting and crystallization sections of a PDTA trace made on folded-chain polyethylene at a pressure of 2250 bars. The reproducibility of  $T_A$  was usually  $\pm 1^\circ\text{C}$ . The peak in the  $\Delta T$  trace usually comes at the end of the melting plateau. The peak temperature  $T_B$  differs from  $T_A$  only

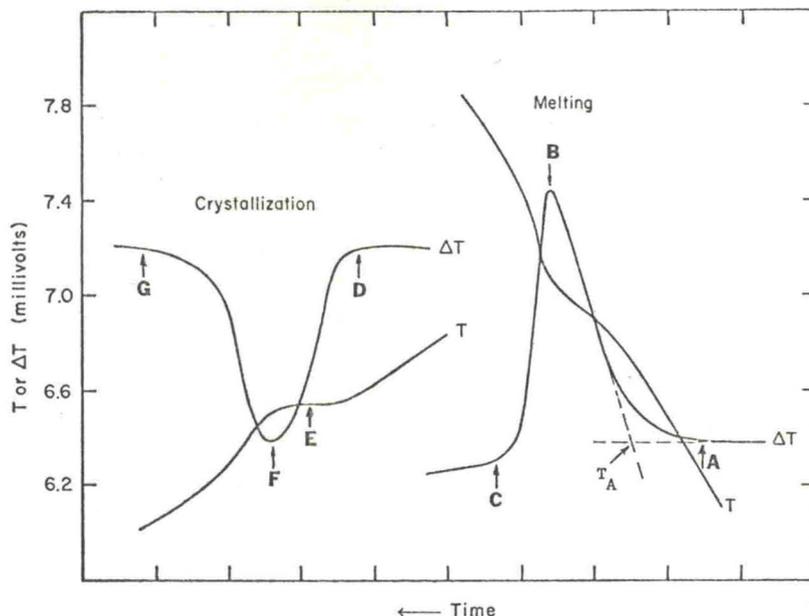
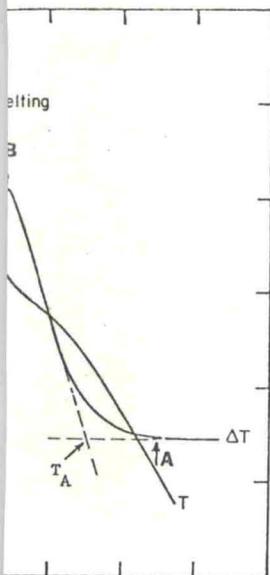


Fig. 2. PDTA traces of melting and crystallization under pressure.

because the temperature of the cell has been rising during fusion as indicated by the positive slope of the plateau in the  $T$  trace. The breadth of the plateau,  $T_B - T_A$ , varies with the heat of fusion, mass, and thermal diffusivity of the substance which is melting and depends upon the heating rate, the temperature gradient across the sample, and any heat leakage along the thermocouple.

The melting process is somewhat complicated in the case of a polymer. The polymer sample chosen is larger than the small amount of sharp melting material used for calibration. Thus in the PDTA cell,  $T_A$  is the temperature at which melting begins on the outer surface of the cylindrical polymer specimen. A second complicating factor in polymer DTA is inherent in the melting behavior of polymeric materials. In calorimetric experiments, even slowly crystallized polyethylene has exhibited a temperature range of about  $15^\circ\text{C}$  in which 90% of the crystalline portion fused.<sup>7</sup> Some evidence suggests that slight melting may occur far below the range in which major melting is observed.<sup>8</sup> For folded-chain polyethylene of high crystallinity,  $T_B$  has been shown to be close to the temperature at which all of the heat of fusion of the sample has been absorbed.<sup>9</sup> This observed peak temperature must be corrected by adding the thermocouple calibration constant. From the peak, return of the  $\Delta T$  trace to the baseline is not instantaneous but exhibits an exponential characteristic.<sup>9</sup> Point (C) in Figure 2 indicates the return to steady-state conditions.

Crystallization of the fully melted polymer can be followed in the PDTA cell by merely turning off the heater current which results in a cooling rate



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of approximately  $2^\circ\text{C}$  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  $230^\circ\text{C}$  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  $2^\circ\text{C}/\text{min}$  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

experiment was conducted. The starting material had a density of 0.9674 g/cm<sup>3</sup>, a melting peak temperature at atmospheric pressure of 134.0°C, and was spherulitic in appearance when examined with the polarizing microscope. Spherulites ranged from 20 to 50  $\mu$  in diameter and showed typical maltese cross extinction patterns with negative birefringence.

The results listed in Table I were obtained in PDTA runs on several

TABLE I  
Melting and Crystallization of Folded-Chain Polyethylene under Pressure

Trace	<i>P</i> , bars	Melting temperature <i>T<sub>m</sub></i> , °C	Crystallization temperature <i>T<sub>c</sub></i> , °C
Avg	1	134.0	124.3
55	200	138.4	127.6
59	607	145.8	134.4
83	774	151.1	138.0
29	1000	157.0	139.9
57	1210	156.0	143.9
41	1750	166.0	153.4
42	1900	—	155.2
43	1985	—	156.7
32	2000	169.7	156.8
38	2260	—	160.8
38	2270	174.3	—
60	2610	—	166.2
60	2630	179.4	—
35	2880	—	169.4
35	2920	184.2	—
36	2940	—	170.3
48	3157	186.5	—
48	3174	—	170.8
63	3530	—	178.1
63	3690	195.4	—

samples of this polymer. The same sample was used for several runs. In each instance, the points represent the corrected peak-temperatures.

The heating rate was 4°C/min. The melting temperature at atmospheric pressure, 134.0°C is the average of nine determinations and has a standard deviation for a single measurement of  $\pm 0.7^\circ\text{C}$ . All other points represent individual measurements.

The crystallization temperature represents the plateau which occurs upon cooling of the sample from the melt at constant pressure. In any such procedure the observed crystallization temperature will depend upon the cooling rate. In the present experiments the cooling rate was approximately 2°C/min.

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PDTA runs on several

ethylene under Pressure

Trace	Crystallization temperature $T_x$ , °C
	124.3
	127.6
	134.4
	138.0
	139.9
	143.9
	153.4
	155.2
	156.7
	156.8
	160.8
	—
	166.2
	—
	169.4
	—
	170.3
	—
	170.8
	178.1
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### PDTA of Ethylene-Butene Copolymer

As in the homopolymer case, the sample was always crystallized at atmospheric pressure before each of the runs listed in Table II. It can be seen that the copolymer melting and crystallization temperatures lie below those of the homopolymer.

TABLE II  
Melting and Crystallization of Ethylene-Butene Copolymer under Pressure

Trace	$P$ , bars	Melting temperature $T_m$ , °C	Crystallization temperature $T_x$ , °C
Avg	1	128.3	119.8
77	303	134.1	124.0
67	718	142.4	132.6
73	1180	150.3	139.4
71	2040	164.8	153.0
75	2920	178.1	165.6

### PDTA of Extended-Chain Polyethylene

It was not possible to produce extended-chain crystals in the PDTA cell because fixed temperatures could not be maintained at high pressure with the control system designed for DTA. Occasional leaks in the pressurization system (not in the PDTA cell) made it difficult to hold pressures above 3000 bars for long periods of time. Therefore a sample of extended-chain polyethylene crystallized at 214°C and 5030 bars in a preparative apparatus,<sup>14</sup> was used for the third series of PDTA runs. The sample had a density of 0.9906 g/cm<sup>3</sup>. Spherulites of 65  $\mu$  diameter were present in sections examined in the polarizing microscope. Replicas of the fracture surface showed numerous extended-chain lamellae of 5000 Å thickness. A fresh piece of this material was used in each PDTA run. The results are listed in Table III.

TABLE III  
Melting of Extended Chain Polyethylene under Pressure

Trace	$P$ , bars	Melting temperature $T_m$ , °C
109	1	142.4
117	211	149.8
118	498	157.3
116	807	165.0
113	2370	197.3
112	2920	209.8
119	4130	229.0

## DISCUSSION

## Effect of Pressure on Melting

A number of melting experiments on a variety of polyethylene samples under pressure can be found in the literature. In most cases it is only possible to distinguish whether branched or linear polyethylene was measured, little further characterization is usually presented. Along with chemical information, the thermal history, density, morphology, and heating rate are necessary to discuss melting. Without this information, it is difficult to compare the results of various workers, since under the common name polyethylene they may actually be measuring quite different substances. In particular, on slow heating folded-chain crystals will reorganize to more perfect crystals and yield false data. Heating rates used in this research were shown to be sufficiently fast to convert metastable folded-chain crystals to metastable melt with a minimum of reorganization.<sup>24</sup> Complications from superheating for more perfect extended-chain crystals will be discussed below.

The results of all available investigations on linear polyethylene are included in Table IV. It was necessary to take graphical points from many of the papers, since numerical data were not tabulated. The graphical or numerical character of the data is indicated by "g" or "n," respectively, in column 1. The melting temperature versus pressure data for each reference were fitted to the same quadratic form:  $T_m = A + BP + CP^2$ . Examination of Table IV shows that the slope ( $B$ ) and curvature ( $C$ ) of the melting curves differs among the several sets of data. Experimental difficulties as well as difference in samples accounts for the wide spread. Apart from our measurements, only Baltenas and Igonin used differential thermal analysis; all other values were arrived at by slow volume measurements. In all the studies quoted, the melting curve of polyethylene decreases in slope with increasing pressure; on a  $T_m$  versus  $P$  graph the curves bend toward the  $P$  axis. Such behavior is typical of both polymers and nonpolymeric materials and is coupled to the observed decrease in compressibility with pressure.

It is difficult to evaluate the slope of the melting curve near atmospheric pressure because the curve rises steeply in this region. One procedure is to compute the slope by differentiating the least-squares expression and evaluating  $dT_m/dP$  at 1 bar. The results are shown in column 7 of Table IV. This may underestimate the steeper slope at low pressures. A better method is to calculate the slope from the point measured at atmospheric pressure and the point at the next highest measured pressure. Slopes calculated from our measurements by the latter method are listed in Column 8 of Table IV together with the published values of the slopes of other workers. In column 7 we list the slopes calculated by the least squares method.

To calculate  $dT_m/dP$  at 1 bar for equilibrium melting, it is only necessary to know the values entering the Clausius-Clapeyron expression. In the

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TABLE IV  
Least Squares Analysis of Melting Data  $T_m = A + BP + CP^2$

Sample or researcher, reference and format	A	B × 10 <sup>2</sup>	C × 10 <sup>6</sup>	T <sub>m</sub> , °C		dT <sub>m</sub> /dP (least squares)	dT <sub>m</sub> /dP
				At 2 kb	At 5 kb		
Extended chain, this paper (n)	143.7	2.673	-1.475	191.3	240.4	26.7	35.2
Folded-chain, this paper (n)	134.9	1.963	-0.9576	170.6	209.4	19.6	22.1
Folded-chain copolymer, this paper (n)	128.3	1.994	-0.9908	164.2	203.2	19.9	—
Baer and Kardos <sup>15</sup> (g)	136.8	3.328	-3.708	188.6	210.5	33.3	39
Baltenas and Igonin <sup>16</sup> (n)	133.3	2.765	-1.598	182.2	231.5	27.6	—
Hellweg <sup>6</sup> et al. <sup>17</sup> (g)	132.5	3.372	-4.028	183.8	200.4	33.7	—
Karasz and Jones <sup>18</sup> (g)	135.8	3.141	-1.935	190.9	244.4	31.4	28.0
Matsuoka <sup>19</sup> (g)	137.1	2.988	-2.210	188.1	231.3	29.9	—
Osugi and Hara <sup>20</sup> (g)	147.1	1.615	-0.2672	178.3	221.2	16.2	25

limit of a hypothetically perfect crystal these quantities are the equilibrium melting temperature  $T_m^\circ = 414.6^\circ\text{K}$ , the volume change on fusion  $\Delta V_f^\circ = 0.224 \text{ cm}^3/\text{g}$ , and the heat of fusion  $\Delta H_f^\circ = 69.2 \text{ cal/g}$ .  $T_m^\circ$  has been estimated from the dilatometric melting points of a highly crystalline extended chain polymethylene of high molecular weight.<sup>11</sup> The value of  $V_s^\circ$ , the specific volume of perfect solid polyethylene, has been calculated from x-ray measurements of the unit subcell<sup>21</sup> extrapolated in temperature up to the melting point,<sup>22</sup> and  $V_l^\circ$  has been estimated by extrapolating the volume of molten polyethylene to the melting point. The value of  $\Delta H_f^\circ$  has been calculated by extrapolating measured values to 100% crystallinity.<sup>23</sup> Using these values in the Clausius-Clapeyron relation results in:

$$dT_m/dP = 32.0^\circ\text{C}/\text{kb}$$

This value is only in reasonable agreement with the directly measured value  $35.2^\circ\text{C}/\text{kb}$  by PDTA on extended-chain crystals, an indication that the metastable folded-chain crystals are too far from equilibrium to be described by the Clausius-Clapeyron equation.

The melting point depression of the copolymer compared to the homopolymer remains constant over the whole pressure range at about  $6.4^\circ\text{C}$ . The same analysis as was carried out previously under atmospheric melting conditions seems to apply.<sup>13</sup>

#### Effect of Pressure on Crystallization

The data headed "crystallization" in Tables I and II were recorded during cooling of the molten polymers under pressure in the PDTA cell. The samples solidified in this manner were subsequently remelted at atmospheric pressure in the PDTA apparatus. Since their remelting temperatures were in no case higher than that of the folded-chain starting material, we conclude that under pressure in the cell they did not crystallize into the extended chain form.

The crystallization temperatures were fitted to a quadratic equation by a least-squares procedure. The coefficients are given in Table V.

TABLE V

	A	B × 10 <sup>2</sup>	C × 10 <sup>6</sup>	T <sub>c</sub> , °C	
				at 2 kb	At 5 kb
Homopolymer	123.9	1.797	-0.7982	156.6	193.8
Copolymer	119.4	1.794	-0.7312	152.4	190.8

In both polymers the degree of supercooling necessary for crystallization increases by 50% in going from atmospheric pressure to 5000 bar. The conclusion from this experiment is that under identical supercooling (expressed in °C below the melting point) crystallization under elevated pressure is retarded.

### Comparison of the Melting Curves of Extended-Chain and Folded-Chain Crystals

ities are the equilibrium change on fusion  $\Delta V_f^\circ = 2$  cal/g.  $T_m^\circ$  has been a highly crystalline ex-  
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a quadratic equation by a n in Table V.

	$T_z, ^\circ\text{C}$	
	at 2 kb	At 5 kb
32	156.6	193.8
2	152.4	190.8

ssary for crystallization in- re to 5000 bar. The con- cal supercooling (expressed nder elevated pressure is re-

The higher melting temperature of extended-chain polyethylene at 1 bar has been studied previously.<sup>1,11,24,25</sup> The data presented in Table III and Figure 3 are the first measurements to show that this behavior persists at elevated pressures. From the PDTA experiments it is clear that under pressure, extended chain crystals remain stable at temperatures above the melting range of folded-chain crystals.

From Figure 3 it can be seen that the difference in melting temperatures between extended and folded-chain polyethylene increases upon going to higher pressures. At 1 bar the difference is 8.4°C, while at 3000 bars the difference in melting temperatures is 25.6°C. One part of the increase in melting point at atmospheric pressure is accounted for by greater perfection of the extended-chain crystals, as measured by the density increase from 0.9674 to 0.9906 g/cm<sup>3</sup> and the increase in lamellar thickness from the usually found 100–200 Å to 5000 Å. Superheating is another feature of extended-chain polymer crystals.<sup>24</sup> All of the extended-chain crystals of linear high polymers which have been analyzed to date (polyethylene,<sup>24</sup> polyoxymethylene,<sup>26</sup> polytetrafluoroethylene,<sup>27</sup> polycaprolactam,<sup>28</sup> and selenium<sup>29</sup>) show a very slow velocity of melting. Even at a heating rate of 4°C/min, it is possible to conduct heat faster into the crystal than melting can proceed. As a result, the interior of the crystal superheats temporarily and shows a higher melting temperature. Extended-chain polyethylene crystals similar to those analyzed here showed a melting temperature of 138.7°C in slow dilatometric experiments.<sup>11</sup> From the magnitude of the divergence of the melting points of folded- and extended-chain crystals it

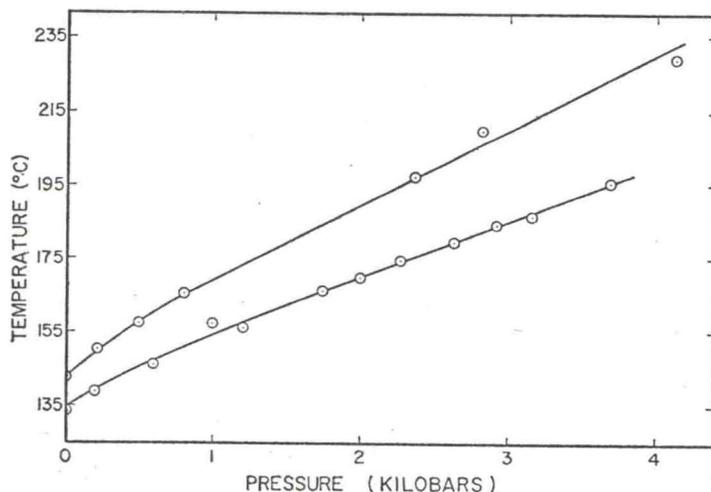


Fig. 3. Melting curves of extended-chain and folded chain polyethylene: (upper) extended-chain polyethylene; (lower) folded-chain polyethylene.

seems reasonable to assume that parallel with the decrease in crystallization rate demonstrated above, the melting rate decreases with increasing pressure. The PDTA apparatus is unfortunately not suited to a study of superheating because its large mass limits the heating rate. Presently it is thus not possible to decide whether the divergence in melting points is purely kinetic in origin or not.

This work was supported by the Office of Naval Research.

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Received July 29, 1968

Revised August 30, 1968