

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° has been estimated from the dilatometric melting points of a highly crystalline extended chain polymethylene of high molecular weight.¹¹ The value of V_s° , the specific volume of perfect solid polyethylene, has been calculated from x-ray measurements of the unit subcell²¹ extrapolated in temperature up to the melting point,²² and V_l° has been estimated by extrapolating the volume of molten polyethylene to the melting point. The value of ΔH_f° has been calculated by extrapolating measured values to 100% crystallinity.²³ 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°C . The same analysis as was carried out previously under atmospheric melting conditions seems to apply.¹³

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 ²	C × 10 ⁶	T _z , °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.