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

The higher melting temperature of extended-chain polyethylene at 1 bar has been studied previously.[1,11,24,25] 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/cm³ 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.[24] All of the extended-chain crystals of linear high polymers which have been analyzed to date (polyethylene,[24] polyoxymethylene,[26] polytetrafluoroethylene,[27] polycaprolactam,[28] and selenium[29]) 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.[11] From the magnitude of the divergence of the melting points of folded- and extended-chain crystals it

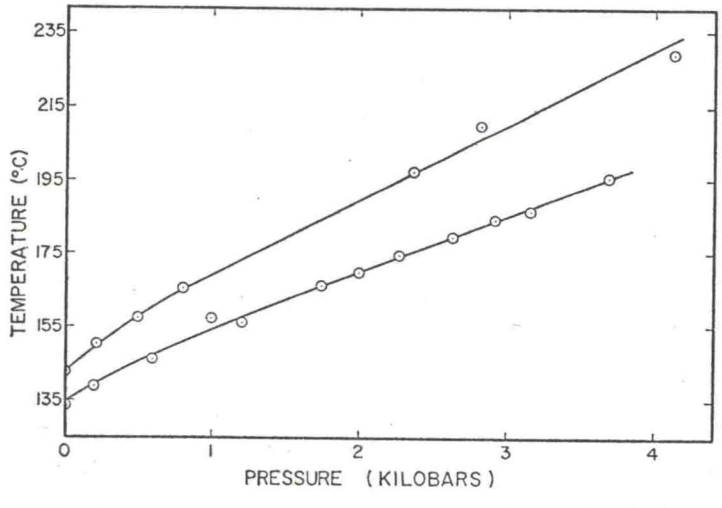

Fig. 3. Melting curves of extended-chain and folded chain polyethylene: (upper) extended-chain polyethylene; (lower) folded-chain polyethylene.