

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

THEODORE DAVIDSON† and BERNHARD WUNDERLICH,  
*Department of Chemistry, Rensselaer Polytechnic Institute, Troy,  
New York 12181*

### 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.

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† Present address: Department of Materials Science and Chemical Engineering, Northwestern University, Evanston, Illinois 60201.