

Morphology of Polyethylene Crystallized from the Melt Under Pressure

PHILLIP H. GEIL,* *Camille Dreyfus Laboratory, Durham, North Carolina*,
FRANKLIN R. ANDERSON, *Chemstrand Research Center, Durham,*
North Carolina, and BERNHARD WUNDERLICH,† and TAMIO
ARAKAWA, *Department of Chemistry, Cornell University, Ithaca, New York*

Synopsis

The morphology of linear polyethylene crystallized under pressures up to 5300 atm. has been investigated. Electron micrographs of fracture surfaces obtained from these samples show that the majority of the polymer, at the highest pressures, crystallizes in the form of extended chain lamellae which can be as thick as 3μ . Electron diffraction patterns show that the molecules are normal to the lamellae. At lower pressures part of the polymer crystallizes in the form of folded chain lamellae, the proportion increasing with decreasing pressure. Well defined kink bands can be observed in the thicker extended chain lamellae. It is suggested that either molecular weight fractionation or an end-to-end alignment of the molecules and subsequent folding takes place during the growth of the extended chain lamellae.

INTRODUCTION

Linear polyethylene crystallized under pressure may have a density approaching the theoretical perfect crystal density and a melting point close to the limiting value for large, perfect crystals.^{1,2} The morphology of such a sample is thus of considerable interest. In this paper we present a report of the investigation of the internal morphology of linear polyethylene crystallized under pressures up to 5300 atm. and with densities as high as 0.994 g./cc. Further details concerning the properties of these and other similar samples are described in a paper in preparation.²

Wunderlich^{1,3} has previously discussed the growth of polyethylene single crystals from dilute solution under elevated pressure. The crystals in general resemble those obtained at atmospheric pressure at similar supercoolings (the melting point and therefore the crystallization temperature increases with pressure). At constant supercooling the thickness or fold period increases only slightly with pressure.

Anderson has pointed out^{4,5} that at least three morphologically distinct lamellar structures can be observed in linear polyethylene crystallized from the melt at atmospheric pressure. These he has labeled types I, II, and

* Present address: Case Institute of Technology, Cleveland, Ohio.

† Present address: Rensselaer Polytechnic Institute, Troy, New York.

III lamellae. Type I consists of broad, folded chain lamellae resembling those found in single crystals grown from solution. The smaller of the two small-angle x-ray diffraction long periods from melt crystallized polyethylene is essentially equal to their thickness.⁵⁻⁷ Type I lamellae are found in both whole polymers and in fractionated samples. Whereas in fractionated polymer they can be observed on both exterior and fracture surfaces, in whole polymer they are usually visible only on exterior surfaces. When whole polymer is fractured, microdrawing apparently takes place in regions occupied by type I lamellae. The resulting "fracture" surfaces are covered with broken fibrils. This microdrawing is believed to be due to the presence of tie molecules connecting neighboring lamellae.^{5,7} Type II lamellae consist of narrow or ribbon-like layers whose thickness is essentially equal to that of type I. They have been found only in higher molecular weight, fractionated samples and were not found in the samples discussed in this paper. Therefore, type II lamellae will be of no further concern to us here.

As observed on fracture surfaces, type III lamellae have an appearance similar to the bands observed to essentially occupy the entire volume of highly crystalline polytetrafluoroethylene.^{7,8} Anderson has suggested⁵ that they are probably similar to paraffin crystals, consisting of fully extended chains. Type III lamellae are found in whole polymer and in the lower molecular weight fractions. Each individual crystal is of about the same thickness over its lateral extent, but the crystals in a given sample may vary considerably in thickness. By varying the temperature of crystallization the relative proportion and thickness of types I and III lamellae can be varied for a given sample. With increasing temperature the fold period of type I, the maximum thickness of type III and the relative proportion of material crystallizing in type III increases. Although, with fractionated polymer, type III lamellae were found only in fractions with molecular weights below 12,000, Anderson suggested⁵ that by waiting for longer periods of time at still higher temperatures it should be possible to obtain type III lamellae from polymer of much higher molecular weight.

EXPERIMENTAL

Table I lists many of the properties of the samples used for this investigation. Samples of a linear polyethylene (Marlex 50) were enclosed in brass bellows and heated to the crystallization temperature at atmospheric pressure. The chosen pressure was then applied in 1-2 min. by using a pressurestat previously described.⁹ The pressure and temperature were kept constant for the time listed, after which the temperature was reduced at a rate of 4°C./hr. to about 50°C., at which time the pressure was released and the sample removed. (For a full description of the sample preparation techniques, see Wunderlich.^{2,3}) The atmospheric pressure samples (A and B, Table I) were prepared by quenching the sample quickly from the molten state to the crystallization temperature.