

Lamellar Structure and Organization in Polyethylene Gels Crystallized from Supercritical Solution in Propane

Continuous networks of lamellar crystals contained within mechanically self-supporting cylindrical plugs of high porosity have been obtained by crystallizing polyethylene from supercritical propane solutions. Under the proper conditions, these structures show well-developed lamellar morphologies that reveal details of the interlamellar junctions as well as the interlamellar organization. Since the solvent, which is a compressible supercritical gas during the course of polymer crystallization, assures a random distribution of crystallites during nucleation and crystal growth and since it can be removed by a controlled depressurization of the system without disruption of the resulting mechanically stable network, it is possible to "freeze" and view the polymer crystals, undisturbed by the changes brought about by solvent removal. The process described is a supercritical fluid to crystal phase transition accompanied by gelation, in distinction to such a transition from the liquid phase.¹

We reported on the phase equilibria of linear polyethylene with supercritical propane recently.² A characteristic parameter that defines one of the stability limits of a supercritical propane solution of linear polyethylene is a critical end point that lies at the intersection of the 3-phase line that connects the triple point of the polymer with the gas-liquid critical locus. For a high molecular weight fraction of linear polyethylene, that point lies at about 118 °C and 640 bar.

We prepared samples from solutions of linear polyethylene that had been crystallized by cooling from the supercritical regime at 125–130 °C while maintaining approximately constant pressure. Cylindrical (porous) polyethylene plugs in the density range of about 0.03–0.20 g cm⁻³ were obtained in this manner from polyethylene solutions as dilute as 5–7% w/w. Above this limit the available space in the containing vessel is completely filled by the crystalline polymer, with the density of the resulting plug dependent on the concentration of the initial solution.

Samples for examination in the scanning electron microscope (SEM) were removed by gentle fracture from the plugs. Some samples were treated with a 4% solution of osmium tetroxide for over 1 h, which did not affect the structure but which, in initial experiments, appeared to enhance the contrast. Additional experiments did not verify the enhancement. Pulsed coating with gold in a sputter coater was used to reduce specimen heating. Examination was performed with a Hitachi S-800 field emission SEM at 2–3 kv.

In the range of concentration studied, the SEM revealed lamellar stacks exhibiting branching, interpenetration, and splaying of the lamellae. In some samples, the lamellar stacks assumed a rough spherical symmetry and, in others, a more random stack morphology. The supermolecular organization was dependent on the polymer concentration, molecular weight, and cooling rate of the supercritical solution.

Figure 1 is a micrograph of the structure obtained from a rather concentrated solution (23.7%), cooled to 100 °C at the relatively rapid rate of about 0.5 °C/min. The micrograph shows the somewhat random organization of the lamellar stack. Figure 2 shows the lamellae, or lamellar composites, in more detail.

If a solution is crystallized more slowly under near-isothermal conditions at 115 °C, a more organized morphology results (Figure 3). This somewhat spherical

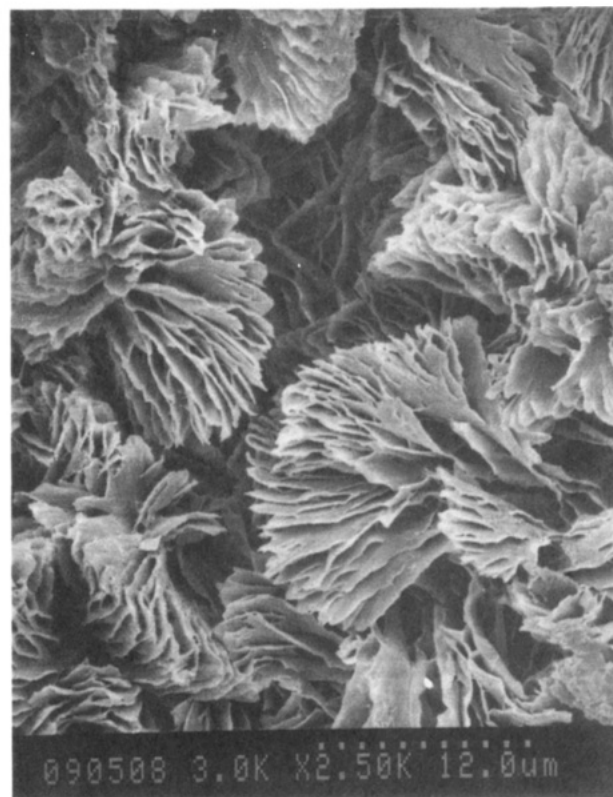


Figure 1. SEM micrograph of sample S-3, HDPE 1 (a commercial high density polyethylene with $M_n = 7300$ and $M_w = 43000$) (rapid cooling).

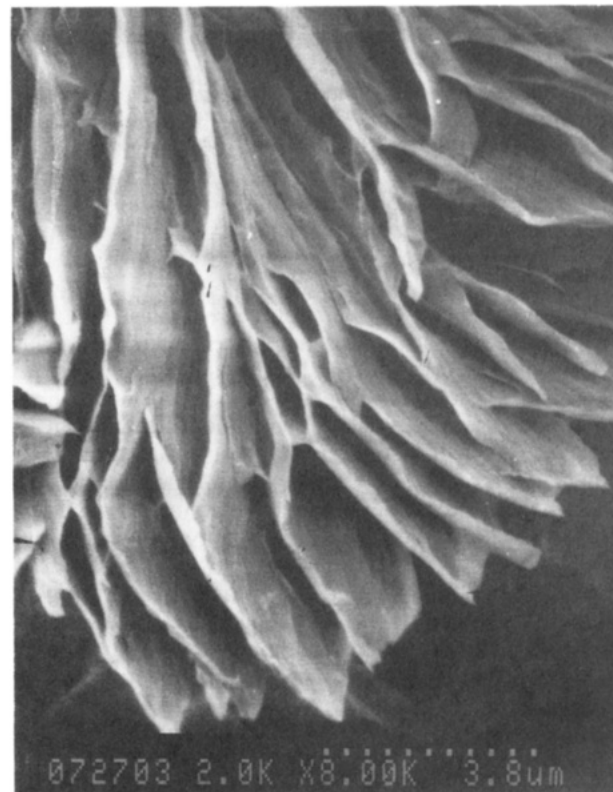


Figure 2. SEM micrograph of sample S-3, HDPE 1.

superstructure has the appearance of a collection of lamellar stacks, which do not appear to have grown from a common center. The ends of many small branched lamellae are arranged in almost parallel sequences. The interconnection or branching of the lamellae frequently

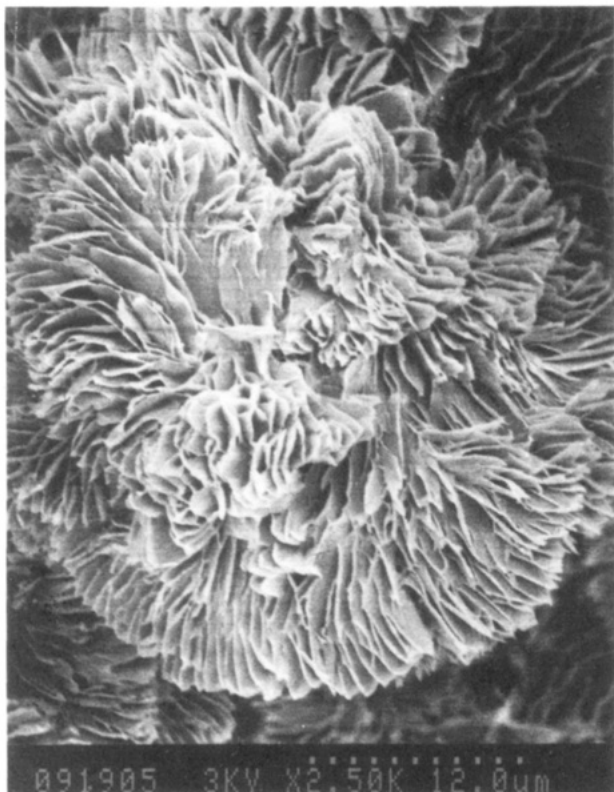


Figure 3. SEM micrograph of sample S-36, HDPE 1 (crystallized isothermally at 115 °C).

occurs at small angles. The resulting overall surface appearance is that of complex coiling. The lamellae exhibit a higher frequency of branching compared to the more rapidly cooled sample.

A micrograph of a sample prepared from a more concentrated solution (~35%), which, because of excessive viscosity, could not be distributed uniformly throughout the cell volume prior to crystallization, shows more randomly arranged platelets on the surface of a dense region (Figure 4). Crystallization may have taken place from the swollen liquid rather than the supercritical phase in this case.³

The morphology of these polyethylene structures is similar, in many ways, to that obtained under various conditions by crystallizing dilute solutions in liquid solvents, as shown by Woodward and other authors.⁴ Crystalline structures in the form of porous plugs can also be prepared from supercritical propane solutions of branched polyethylene (LDPE), from isotactic polypropylene, and, undoubtedly, from other supercritical solutions of crystalline polymers such as poly(4-methylpentene-1) and also crystalline copolymers. This method provides a new and convenient way of examining the morphology of polymers that can be crystallized over a broad concentration range from solutions whose viscosities can be made one or more orders of magnitude less than

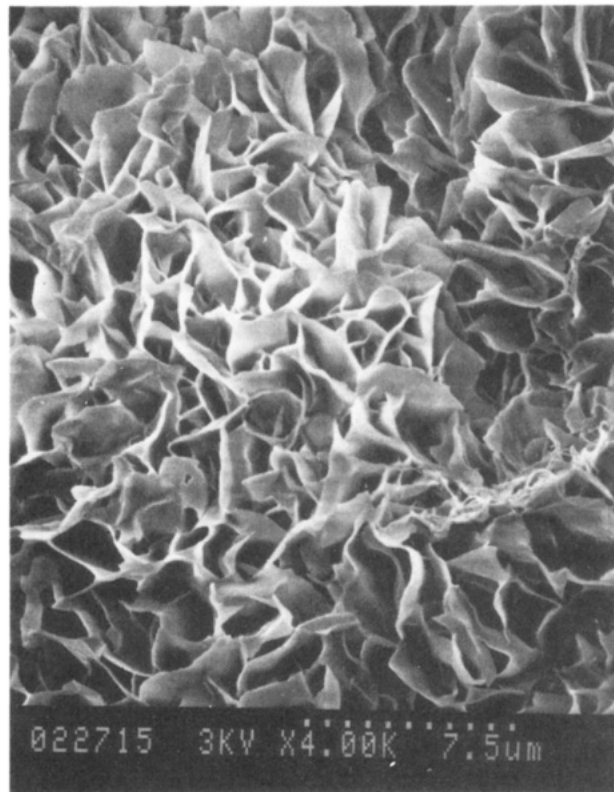


Figure 4. SEM micrograph of sample S-9, NBS 1475 (NIST standard reference linear polyethylene with $M_n = 18\,310$ and $M_w = 53\,070$; crystallized from a more concentrated solution).

those characteristic of liquid polymer solutions of comparable concentrations. In this way, the collapse of loose structures upon evaporation of a liquid solvent can be avoided.

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References and Notes

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