

NOTES

*Transcrystalline Orientation in Polymers*

The transcrystalline morphology frequently observed in semicrystalline polymers is generally located in the surface region of the bulk polymer. This type of crystalline character develops as an elongated spherulitic structure that results in a columnar, uniaxial orientation normal to the polymer surface. Many investigators have reported on the temperature dependence of transcrystalline orientation in polymers.<sup>1-7</sup> With rare exceptions, the depth generally does not exceed several thousandths of an inch before terminating against equiaxed spherulitic structures which are characteristic of the bulk polymer morphology.

This work deals particularly with the preparation of a thick transcrystalline region. Preliminary studies with compression-molded films of high-density polyethylene (unmodified Marlex 5003, Phillips Petroleum Co.) indicated that at least two processing variables exhibited a controlling influence on the resultant crystalline character. These were the magnitude of the temperature gradient across the polymer film thickness and the imposition of a stress during crystallization. The utilization of these factors with reasonable control provided the means for preparing transcrystalline high-density polyethylene films.

The temperature differential maintained across the specimen thickness during crystallization was considered to be the prime factor in orienting the spherulitic development,

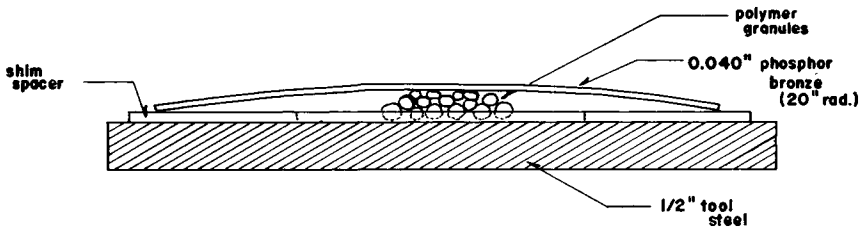


Fig. 1.

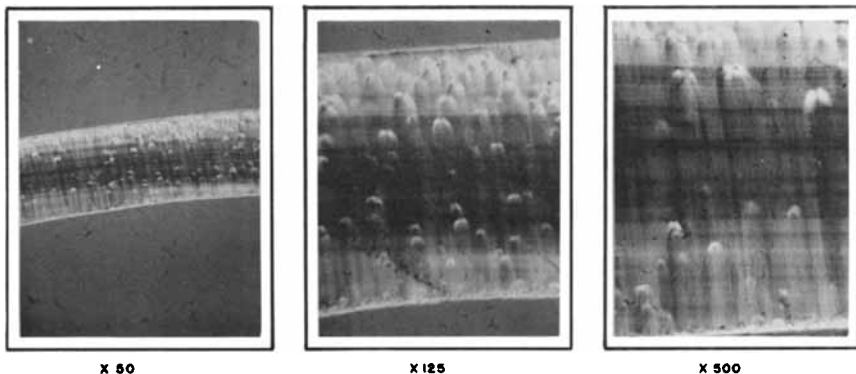


Fig. 2.  
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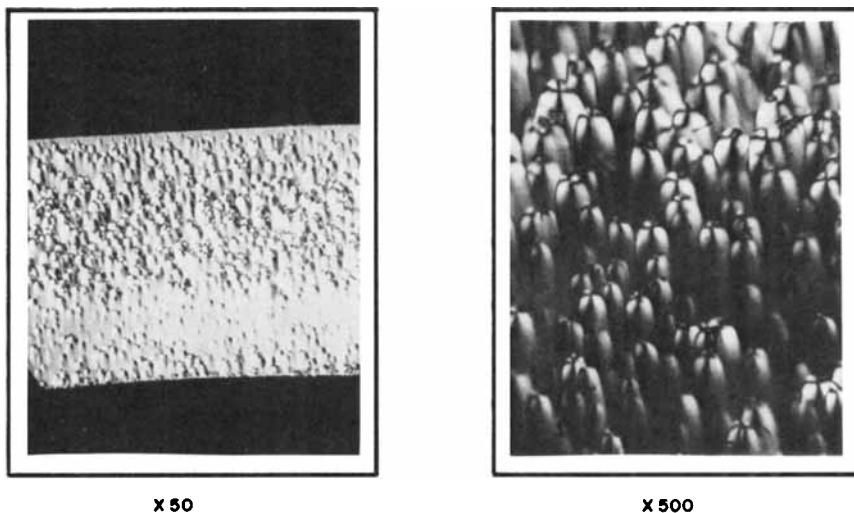


Fig. 3.

presumably after nucleation had initiated. This was accomplished by removing the hot mold assembly from the press and quenching from one side to give directional crystallization to the polymer melt.

Films were compression molded at 350°F. A 10-min residence time was used to insure thermal equilibrium in the polymer melt. In order to evaluate the effect of the magnitude of the temperature gradient on the spherulitic development, different quenching processes were used. They were cooling in the press, air, cold tap water, a Dry Ice/alcohol mix, and liquid nitrogen. The most satisfactory transcrystalline films were obtained by quenching from one side with cold tap water. The spherulites developed into a fibrillar, columnar mode and exhibited prominent extinction rings. With the Dry Ice/alcohol mix used for quenching, the columnar mode was retained but the extinction rings were no longer observed and the fibrillar texture appeared to be more pronounced, somewhat resembling a haystack. Cooling with liquid nitrogen resulted in a textureless microcrystalline polymer phase. Crystallization in the press and in air produced films containing both columnar and equiaxed spherulites.

Crystallization while in the presence of an applied stress was found to be beneficial for preparing thicker transcrystalline films and also enhanced the length of the columnar spherulites. Without the external stress, transcrystalline films more than 0.020 in. thick were very difficult to prepare.

The imposition of a stress on the polymer melt was done by preparing specimens in a mold assembly as shown in Figure 1. A shim spacer of the desired thickness was placed on a 1/2-in.-thick bottom plate of tool steel. The polymer material was positioned inside the shim cavity and then covered with the concave side of a bent 0.040-in.-thick phosphor bronze top plate. The phosphor bronze plate had a preset curvature approximately 20 in. in radius. When the hot melt pressing was removed from the molding press, the elasticity of the phosphor bronze generated a stress on the polymer melt. Subsequent quenching was done by removing the assembly from the press and placing the phosphor bronze side into the path of the coolant. The heavier steel plate prevented premature cooling from the opposite side.

Microtomed cross sections of the films were prepared and the crystal structure studied with a Reichert Zetopan polarizing microscope. Photomicrographs of the cross sections of films 0.010, 0.020, and 0.080 in. thick are shown in Figures 2, 3, and 4, respectively. It should be noted that the crystalline alignment is both unidirectional and

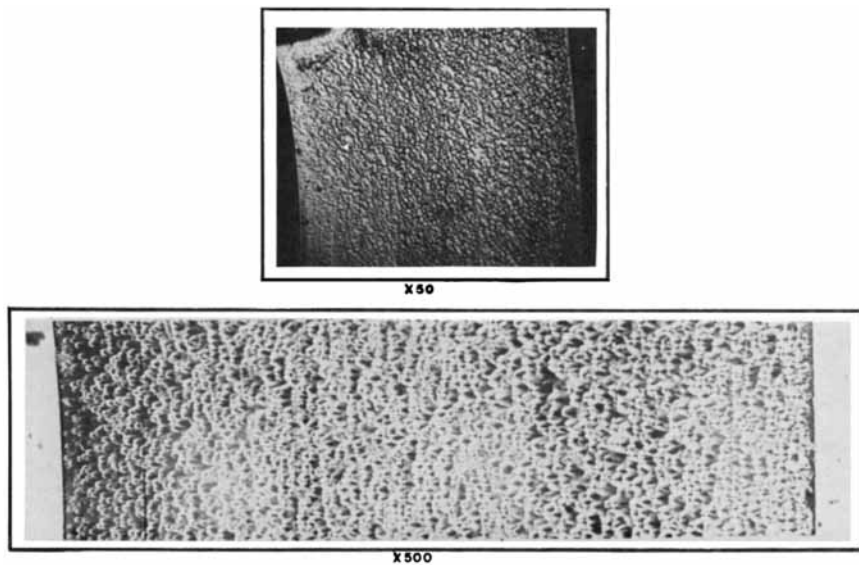


Fig. 4.

uniaxially oriented normal to the polymer surface. Apparently, nucleation originated on the quenched side of the film and growth propagated away from it during cooling.

#### References

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