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### Folded Chain Lamellar Crystal Self-Decoration of Extended Chain Crystals of a Random Terpolymer Main Chain Liquid Crystal Polymer

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## FOLDED CHAIN LAMELLAR CRYSTAL SELF- DECORATION OF EXTENDED CHAIN CRYSTALS OF A RANDOM TERPOLYMER MAIN CHAIN LIQUID CRYSTAL POLYMER

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### ABSTRACT

Surface melting of extended chain crystals of a flexible segment containing liquid crystal polymer followed by quenching is shown to result in the epitaxial crystallization thereon of folded chain lamellae, i.e. self decoration. It is proposed that the initial extended chain lamellae form by chain folding in the mesomorphic state followed by rapid chain extension by the "chain sliding mechanism", the same mechanism that has been in the literature for the proposed similar crystallization of polyethylene under anabarcic conditions.

### INTRODUCTION

We have previously demonstrated that main chain thermotropic liquid crystal polymers (LCPs) containing flexible segments can crystallize from the nematic state (in thin films) and from solution as folded chain lamellae for both a random terpolymer of an aliphatic segment, oxybenzoate and dioxyphenyl (ABP- $n^*$ , refs. 1,2) and an

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<sup>\*</sup>  $n$  represents the number of CH<sub>2</sub>s in the aliphatic segment.

aliphatic aromatic azomethine polyether (AZMEP-10, ref. 3). The folded chain crystals have been observed for aliphatic segment lengths as short as four carbon atoms. Folded chain lamellae were also observed on the surfaces of thick samples of ABP-n crystallized from the nematic state in a magnetic field (ABP-5, ref. 4) or by compression molding (ABP-7, refs. 5,6). On the other hand the interior of these latter bulk crystallized samples, as well as the interior of extruded pellets and fibers, consisted of, apparently, extended chain lamellae; they were 200-1800Å thick, with the average chain length of the polymer used for their preparation being of the same size. It was suggested [5,6] that these extended chain lamellae form by a mechanism similar to that for pressure crystallized, extended chain lamellae of linear polyethylene (LPE); i.e. chain folding in the mesomorphic state followed by chain extension [7].

Wunderlich and Melillo have described a technique for "decorating" linear polyethylene (LPE) and poly tetrafluoroethylene (PTFE) extended chain crystals with folded chain lamellae [8]. A cut surface of the sample is rapidly heated above  $T_m$  and cooled, the molecules on the surface recrystallizing epitaxially on the extended chain crystals as folded chain lamellae. We describe similar results here for an injection molded sample of the ABP-7 LCP. The interpretation is the same, i.e., the folded structure formed upon initial crystallization, which occurs epitaxially on the residual extended chain crystals, is frozen in.

## EXPERIMENTAL

The polymerization and chemical characterization of the GBP-7 polymer has been described [9]. A sample of molecular weight  $\bar{M}_n = 13,500$ ,  $\bar{M}_w = 29,000$  (polystyrene equivalent by BPC) was injection molded as a 6 inch long, 1/8 inch thick, 0.5 inch gauge width, end gated sample. For the micrographs shown here the sample was fractured in the transverse direction in tension or cut in the same direction with a saw. The cut surface was touched for a few seconds to the surface of a hot plate at ca. 160°C. ABP-7 has a  $T_{k-m}$  transition at 142°C and a  $T_{m-n}$  transition at 170°C. The nature of the intermediate mesomorphic state has not yet been determined;  $hk0$  electron diffraction patterns, with multiple orders of reflection, remain essentially unchanged through the  $T_{k-m}$  transition [2]. Both the fractured and cut samples, with and without heat treatment, were etched for a short time, ca. 1 minute, in a 0.5%  $KMnO_4$ , 85%  $H_3PO_4$  solution [10] before standard Pt-C-polyacrylic acid replication. Observation was in a JEOL-100C transmission electron microscope.

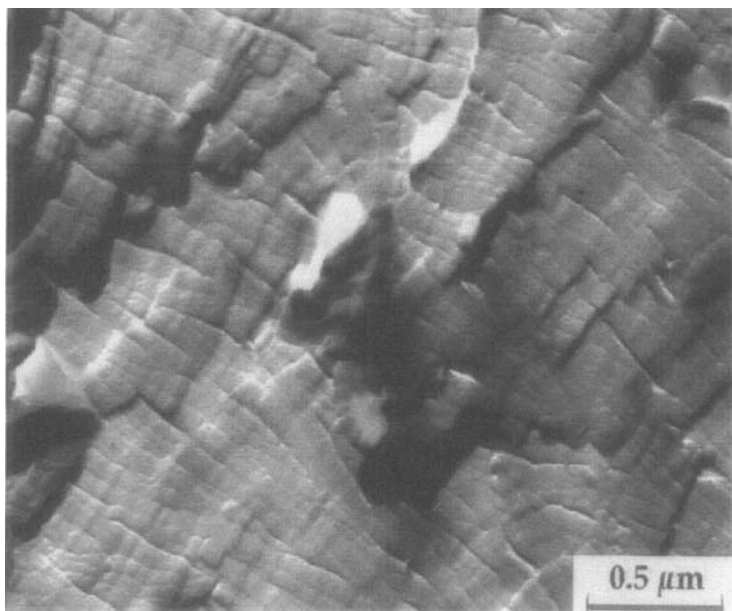


Fig. 1. Fracture surface (0.5%  $\text{KMnO}_4$  etched) of an injection molded ABP-7 sample. Arrows indicate tapered ends of extended chain lamellae.

## RESULTS

Figure 1 is a replica of the fracture surface from near the middle of the cross-section. A substantial amount of polymer remains attached to the replica. In between the residual polymer extended chain lamellae can be seen. They are similar in appearance to those observed on fracture surfaces of the magnetic [1] and compression molded [5] samples and extended chain LPE [11] and PTFE [12]. Whereas the extended chain lamellae in all of the latter samples were of considerable lateral width and were tapered on the ends, the lamellae here are considerably smaller. The taper of the ends are clearly evident in the figure (arrows).

Figure 2 shows the decorated etched surface. As in the case of the decorated LPE and PTFE[8], thin lamellae are observed on the underlying extended chain lamellae. The tapering of the ends is again

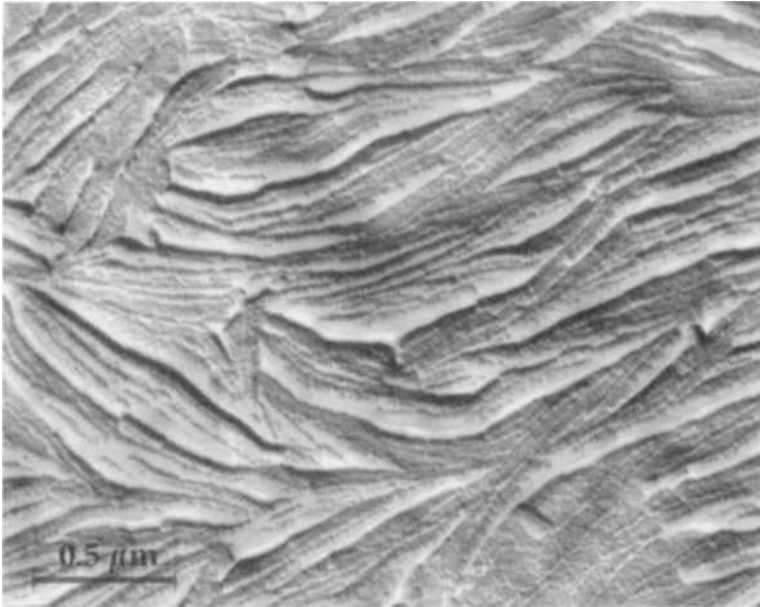


Fig. 2. Self decorated (etched) surface of a sample similar to that in Fig. 1.

clearly evident. This tapering of the ends is attributed to stopping of the transformation from folded chain lamellae in the initial crystallization in, in LPE, the disordered hexagonal (i.e. condis or liquid crystalline) state [13] or here in the mesomorphic state. The observation of thin lamellae (Fig. IV-67; [12]) and striations on the "bands" (Fig. IV-66, [12]) of PTFE crystallized with a free surface, which, when fractured, yield the normal micrographs of extended chain lamellae, we also suggest are related to the free surface observations of ABP 5 and 7 described above.

#### DISCUSSION AND SUMMARY

The similarity in appearance of the ABP-7, LPE and PTFE extended chain lamellae, both before and after decoration, suggests a similar mechanism of crystallization, i.e. crystallization in the mesomorphic state as folded chain lamellae followed by chain extension and subsequent three-dimensional crystallization. In LPE we have

proposed that the extended chain crystallization is accompanied by molecular weight fractionation [11]. The variation in maximum thickness of the molded and magnetic field crystallized samples, as well as of these injection molded samples suggests a similar effect here as well. This micrograph is from the middle of the cross-section of the injection molded bar. Related micrographs from longitudinal sections and as a function of distance from the surface are described in another paper [5]. The observations described here, in combination with the solution and thin film crystallization studies [1,2], indicate flexible segment LCPs crystallize in the same manner as other flexible backbone polymers.

It is noted crystallization of the ABP-7 polymer as either folded chain or extended chain crystals, even though being a random configuration terpolymer, cannot be explained in terms of the non-periodic lattice (npl) model\* [14]. It would appear, however, to be compatible with the paracrystalline lattice (pcl) model of Biswas and Blackwell [15].

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