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SOLUTION GROWN FOLDED CHAIN CRYSTALS OF A RANDOM TERPOLYMER THERMOTROPIC LIQUID CRYSTAL POLYMER

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ABSTRACT

Large, lamellar single crystals have been grown from a xylene solution of a random configuration, flexible segment containing terpolymer that has a "rigid" enough backbone to form liquid crystalline "melts". The lamellar thickness is less than 150Å with M_n corresponding to a chain length of ca. 800Å. Since electron diffraction indicates the chain axes are normal to the lamellae, chain folding of the type observed in single crystals of flexible backbone polymers, such as polyethylene, is required.

INTRODUCTION

Recently we have reported on the growth of folded chain lamellar single crystals from the liquid crystalline state in thin films of both irregular (1,2) and regular (3) liquid crystal (lc) polymers. These polymers have all had flexible (aliphatic) segments. In this report we describe our initial observations of solution grown lamellar single crystals of one of the previous polymers, a random (C_7 - a seven

carbon flexible segment) terpolymer of azelaoate $\left(\overset{\text{O}}{\parallel} \text{C} - (\text{CH}_2)_7 \overset{\text{O}}{\parallel} \text{C} \right)$, oxybenzoate $\left(\overset{\text{O}}{\parallel} \text{C} - \text{C}_6\text{H}_4 - \text{O} \right)$ and dioxyphenyl $\left(\text{O} - \text{C}_6\text{H}_4 - \text{O} \right)$ of nearly equal mole ratio (2,4). It is shown that large, folded chain single

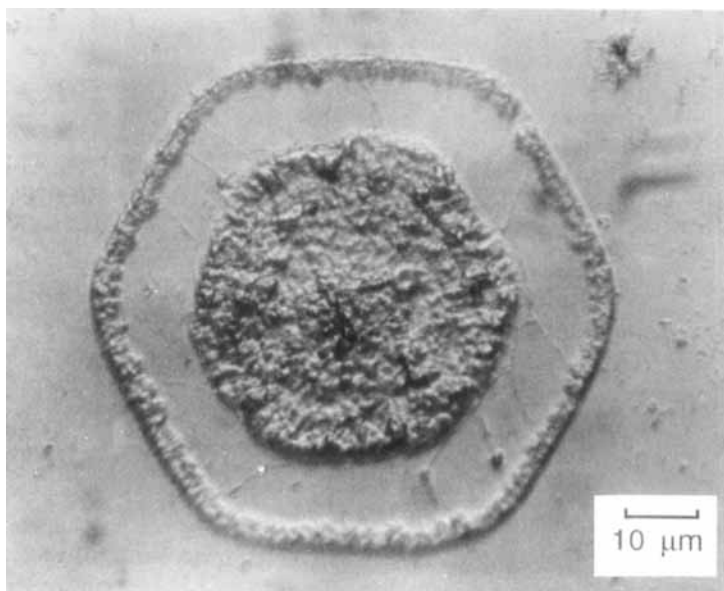


Figure 1. Optical micrograph (oblique reflected light) of the solution crystallized C₇ (seven carbon flexible segment) terpolymer single crystal.

crystals, similar to those described for flexible backbone polymers (e.g., ref. 5) can also be grown from these more "rigid backbone" polymers.

MATERIALS AND METHODS

The inherent viscosity of the polymer used, supplied by Dr. John Carter of The Goodyear Tire and Rubber Company, as measured in tetrachloroethane/phenol (60/40) solution was 0.77. The GPC (polystyrene equivalent) values of M_n and M_w are 13,500 and 29,000 respectively (4). DSC indicates transitions at ca. 135, 145 and 165°C, the latter to a presumed nematic state (6). The 145°C transition has the largest ΔH value.

The polymer was crystallized at 100°C, followed by cooling to room temperature. Samples were deposited on glass slides and the

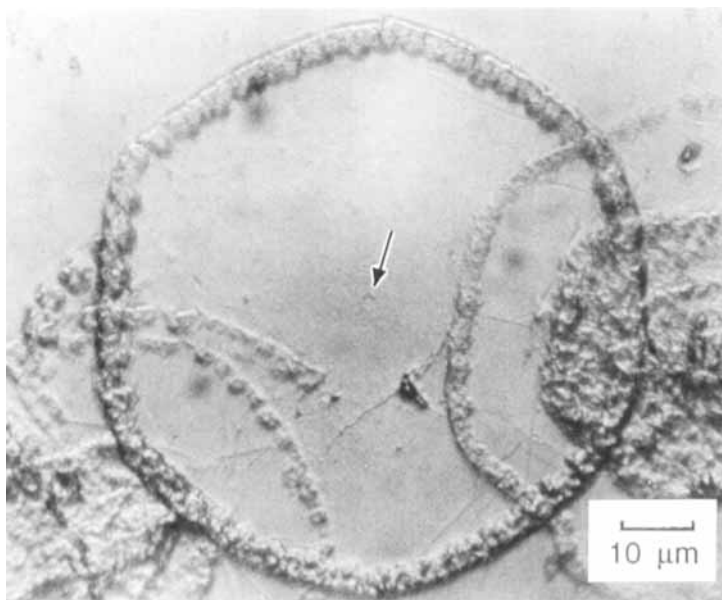


Figure 2. Optical micrograph, as in Figure 1, of a predominantly single layer single crystal. The small hole (arrow) in the center is attributed to the loss of the primary nucleus.

solvent evaporated. The samples were then observed by optical microscopy in oblique, reflected light (Reichert Zetopan) or, following shadowing by Pt-C, in a JEOL 100C transmission electron microscope (TEM).

RESULTS AND DISCUSSION

Figures 1 and 2 are representative optical micrographs of the solution grown crystals. The crystals are as large laterally as any non-dendritic solution grown lamellar polymer crystals that we know of; they are so large that they are inconvenient for TEM, being larger than the grid squares on 200 mesh grids. The rims on the crystals and the central overgrowth in Figure 1 consist of irregular lamellae (see

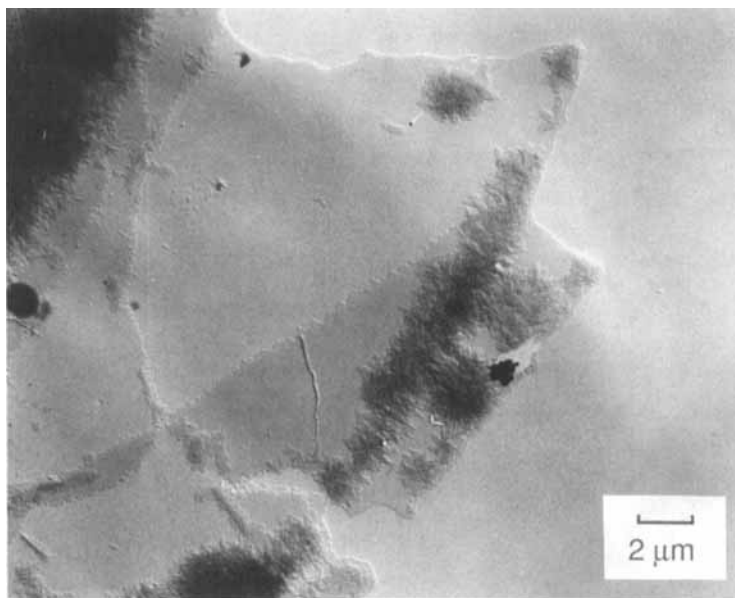


Figure 3. Transmission electron micrograph of a portion of the C₇ (seven carbon flexible segment) terpolymer single crystal.

Figure 3) that apparently grew during solvent evaporation; they seem to be only on the upper surface of the crystals. As in Figure 2, many of the essentially single later crystals have a small hole in the center, as if the nucleus has been removed. The reason for this hole and the apparent presence of the central overgrowths on only one side of the crystal is being sought. Tentatively it is suggested that the primary nucleus may be considerably thicker than the lamellae (as in poly-3,3-bis(chloromethyl)-oxacyclobutene (7,8)) and, in a sense, is pushed out of the crystals that have the hole when they are deposited on the slide; those in which it is retained develop the central overgrowth.

From the width of the shadowed lamellar edges in the TEM micrograph shown in Figure 3, the thickness of the lamellae at the edge of the crystals is less than 150Å. With the M_n value corresponding to an extended chain length of 800Å, chain folding of

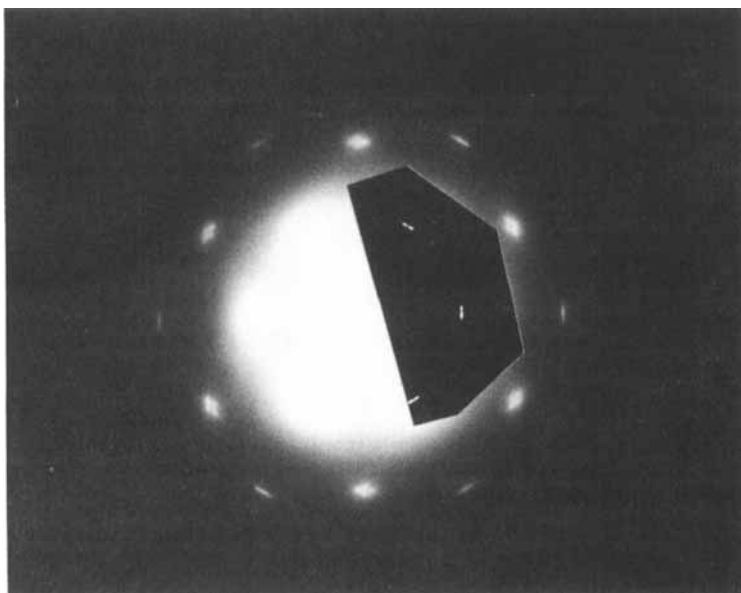


Figure 4. Electron diffraction pattern of the C₇ (seven carbon flexible segment) terpolymer solution grown crystals.

the type observed in flexible chain polymers, such as polyethylene, is clearly indicated. However, since these chains have an irregular configuration with the flexible segments having an average separation of ca. 23.5 Å, clearly a regular, adjacent reentry is not possible.

When the random terpolymer is melt crystallized from the "nematic" state an orthorhombic unit cell occurs (2). Electron diffraction from the solution grown crystals (Figure 4), in agreement with their shape, indicates a hexagonal unit cell. The hexagonal diffraction pattern is similar to that observed in the orthorhombic crystals after they have been heated to 210°C, i.e. above the highest lc-lc transition.

The above results extend our previous suggestions that the morphology of flexible segment containing "liquid crystalline"

polymers in the crystalline state, permitted that the flexible segment is long enough, is the same as that of polymers with a "totally" flexible backbone, e.g., polyethylene. Thus we conclude that chain folding is the "preferred" mode of crystallization for all polymers if the chain is flexible enough to permit it. The availability of crystals such as these will (and is) permitting detailed studies of the mechanisms of the various c-lc and lc-lc transitions, the "crystal" structure in the presumed lc state, and the effects of crystallization temperature, annealing and deformation, etc.

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