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Annealing Effects in Solution Grown Single Crystals of a Random Terpolymer Liquid Crystal Polymer

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ANNEALING EFFECTS IN SOLUTION GROWN SINGLE CRYSTALS OF A RANDOM TERPOLYMER LIQUID CRYSTAL POLYMER

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ABSTRACT

Single crystals of the terpolymer undergo lamellar thickening when annealed below a presumed crystal-liquid crystal transition temperature, similar to flexible backbone polymers such as polyethylene below their melting point. Annealing in the nematic state results in rosettes of lamellae which are suggested to be present as such in that state.

INTRODUCTION

A characteristic feature of folded chain single crystals of flexible backbone polymers, such as polyethylene, is the increase in thickness that occurs when annealed between the α relaxation temperature and the melting point (eg, ref 1). Recently we have reported the growth of folded chain single crystals of a random terpolymer, backbone flexible segment containing, thermotropic liquid crystal polymer from dilute xylene solutions [2].

Similar folded chain lamellar crystals of this and related polymers of various flexible segment lengths have been grown from the nematic

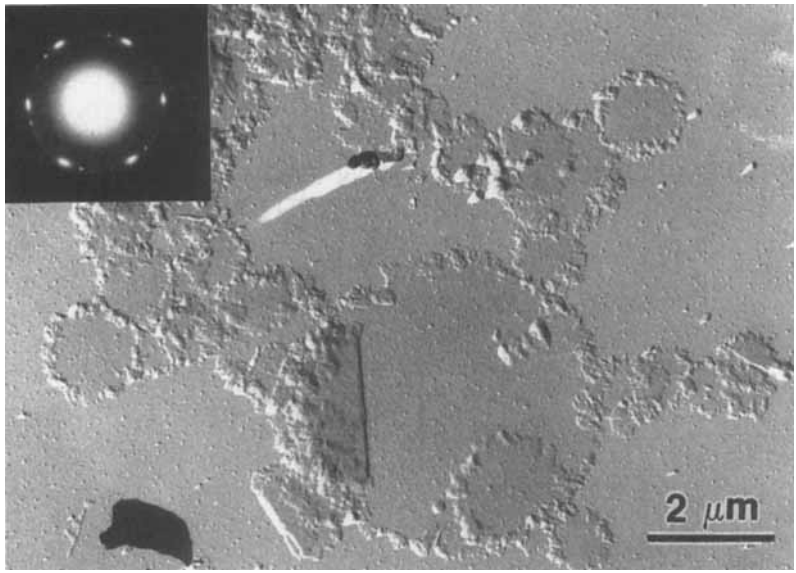


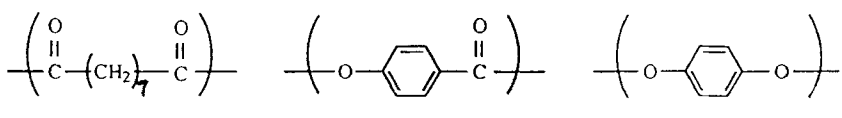
Figure 1. Single crystals and electron diffraction pattern (inset) of the C_7 terpolymer grown from an 0.002 wt.% xylene solution.

state in quiescent and sheared thin films [3,4] and on the surfaces of bulk samples crystallized from the nematic state [5] and in the presence of a magnetic field [3]. We report here the effect of annealing the solution grown crystals both below and above temperatures at which it has been proposed that these polymers undergo a crystal-liquid crystal transition (T_{c-lc}) and a higher temperature, liquid crystal-liquid crystal transition to a nematic state [6,7].

MATERIALS AND METHODS

The polymer used for this study was a random (C_7 - seven carbon flexible segment) near equimolar terpolymer of azelaoate (A), oxybenzoate (B) and dioxyphenyl (C) with an average chain length of

A B C



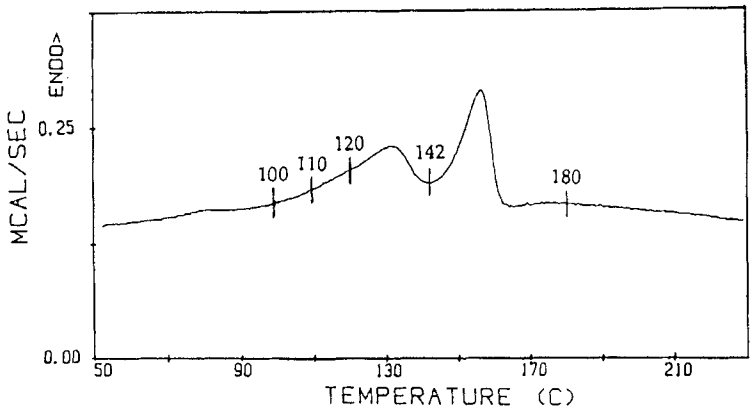


Figure 2. D.S.C. scan (20°C/min heating rate) of single crystals of the C_7 terpolymer crystallized by slow cooling of an 0.05 wt.% xylene solution. The hatch marks represent the annealing temperature utilized for the results described here.

ca. 800A. It was supplied by Dr. John Carter of the Goodyear Tire and Rubber Co. The single crystals were grown from a dilute solution (0.002 wt%) in xylene at 50°C followed by rapid cooling of the solution. The crystals, approximately 100A thick, consisted primarily of single layers with a highly irregular growth face (Fig. 1). They were much smaller then those produced by slow cooling [1]. Electron diffraction patterns (insert in Fig. 1) consisted only of 6 spots in a hexagonal array, indicative of less order than in the slow cooled samples for which multiple orders were observed. These crystals were used for the annealing experiments due to their lack of the overgrowths observed at the centers and edges of the larger, slow cooled crystals.

The crystals were deposited on carbon coated glass slides, floated on water and picked up on 200 mesh electron microscope grids. They were either shadowed with Pt-C on the slides before floating, as for Fig. 1, or annealed in sealed volatile DSC pans in a Perkin Elmer DSC-4 before shadowing, then examined in a JEOL-100C electron microscope. DSC scans (Fig. 2) of dried crystals (prepared by slow cooling as in ref. 1) show a $T_{c-\ell c}$ at 132°C and $T_{\ell c-\ell c}$ at 155°C. Bulk C_7 terpolymer samples

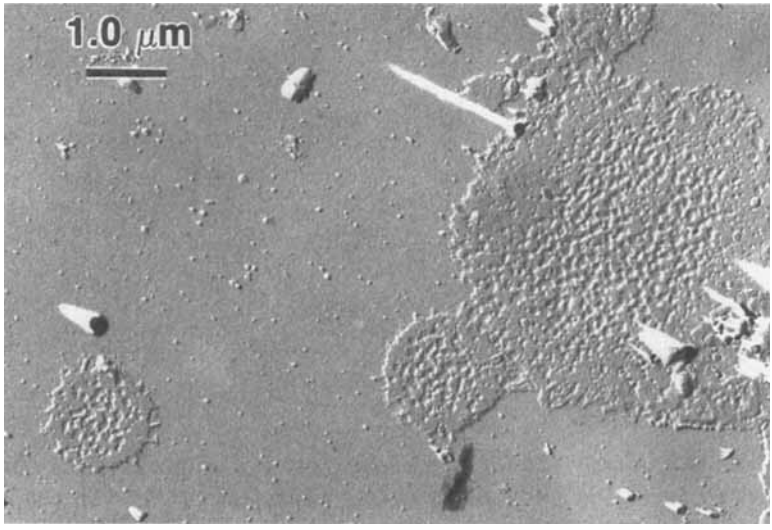


Figure 3. Crystals similar to those in Fig. 1 annealed 24 hours at 100°C.

have these transitions at 147 and ca 170°C, respectively, with the $T_{\ell c\text{-}\ell c}$ transition being much less clearly defined, in a heating scan, than here [5,7].

RESULTS AND DISCUSSION

Figure 3 shows the results of annealing the 0.002 wt% C_7 terpolymer crystals at 100°C for 24 hours. The edges of the crystals have smoothed to some extent, any overgrowths have disappeared (both of which occur also for annealing at 100 and 110°C for 1-2 hours), holes have developed and the crystal has thickened to ca 200A; i.e. the results are similar to those described for annealed polyethylene single crystals [1,8]. Similar results for the C_7 terpolymers were obtained for annealing times at 120°C as short as 10 minutes [5].

Electron diffraction patterns of the 120°C, 10 min. annealed crystals are still a hexagonal array of 6 spots indicating a retention of the folded chain, single crystal structure despite the significant rearrangement; this again is similar to the results for polyethylene [1]. Patterns were not taken of the 24 hour, 100°C annealed samples.

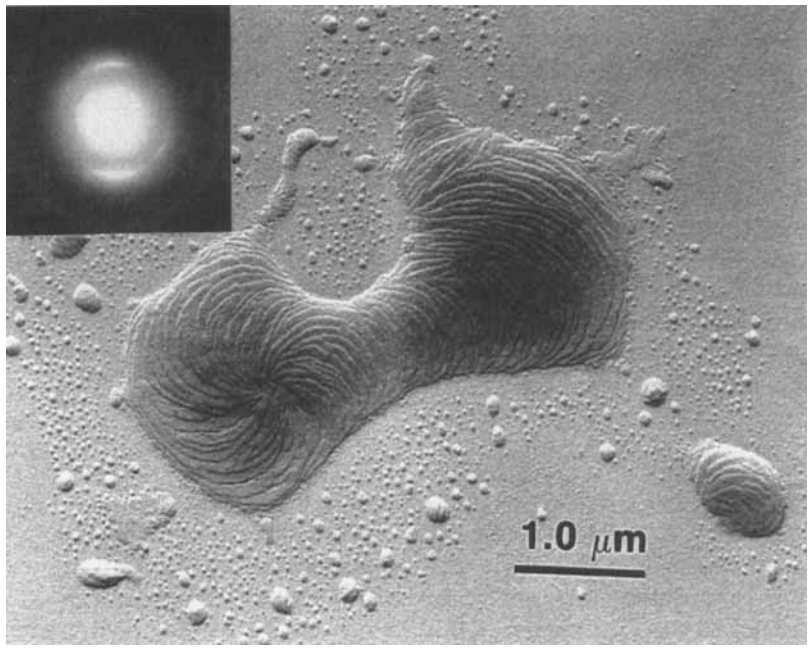


Figure 4. Crystals similar to those in Fig. 1 annealed 10 minutes at 180°C.

Annealing between $T_{c\text{-}\ell c}$ and $T_{\ell c\text{-}\ell c}$ results in even further surface roughening and rearrangement, but a retention of the hexagonal single crystal pattern after cooling [5]; i.e. as shown by electron diffraction at elevated temperatures for the lamellae crystallized from the nematic state, the $T_{c\text{-}\ell c}$ transition does not result in a change in lateral packing of the molecular segments [4].

Figure 4 shows the results of annealing at 180°C for 10 minutes, i.e. above $T_{\ell c\text{-}\ell c}$ and therefore presumably in the nematic state. The lateral dimensions of the crystals have shrunken (the original dimensions of this overlapping set of crystals is indicated by the outer boundary of the "bumps" on the substrate) the overlapping crystals have merged and a rosette of ca 100 A thick overlapping lamellae have developed from a common center. It is noted that this is not a screw dislocation, but

rather a set of tilted lamellae (electron diffraction patterns from the edges of such a rosette consist of only 2 arcs, suggesting the molecular axes lie on a cone about the rosette center [5]) all developing, apparently simultaneously from the common center.

We know of no explanation for the development of this rosette type of morphology by normal crystal growth mechanisms. Extending our previous suggestions of chain folding in the nematic state of these polymers [2-5], it is suggested the rosettes of lamellae are present in essentially this form at the annealing temperature, i.e. in the presumed nematic state. Further details of the morphology of the solution grown crystals, for C_6 and C_7 terpolymers, as well as of the effect of annealing will be described in a subsequent paper [9].

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