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Chain folding in single crystals and sheared ("fiber") samples of a liquid crystal polymer

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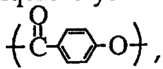
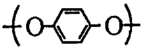
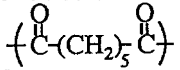
Summary

Lamellar single crystals, ca. 100Å thick and with predominantly reentrant chain folding have been grown from the quiescent and sheared liquid crystalline state of a liquid crystalline random configuration terpolymer containing C_7 flexible segment.

Introduction

In a previous report (1) we have described the growth of lamellar single crystals of a liquid crystal terpolymer (2) composed of ca. equal mole ratios of oxybenzoate , dioxyphenyl  and pimeloate  $-\!\!\left(\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right)\!\!-$ (a C_5 flexible spacer). In this note we report on the structure of similar crystals with a C_7 spacer (based on azelaoate (3)) and also on the lamellar structure formed in sheared samples of this polymer sheared in the liquid crystalline state, resulting in a "fiber" texture. Subsequent deformation of the "fiber" sample results in easy shear between the lamellae, suggesting the presence of few or no tie molecules and tending to confirm our earlier suggestions (1) of the prevalence of adjacent reentry folding in crystals of this type of liquid crystal.

Experimental

The polymer was supplied by Dr. John Carter, Goodyear. The inherent viscosity in tetrachloroethane/phenol (60/40) is 0.77. The molecular weights as measured by GPC (polystyrene equivalent) are $M_n = 13{,}500$ and $M_w = 29{,}000$ (3), i.e. the molecules have a number average chain length of over 800Å. As in the previous report (1), small amounts of the polymer were spread (spontaneously) on glycerine at 210°C. This is above the highest liquid crystal-liquid crystal (lc-lc) transition temperature (~ 165°C, (4)) with the polymer presumably being in the nematic state (4). DSC suggests other transitions at ca. 135 and 145°C with that at 145°C having the largest ΔH value. The film was picked up on a glass slide, washed several times on a water surface and picked up on a carbon coated electron microscope (EM) grid. After shadowing with Pt-C, if desired, they were examined in either a JEOL 100C or Philips 400 electron microscope. A Philips hot stage was used to obtain electron diffraction patterns at elevated temperature.

The "fiber" samples were prepared by shearing small portions of the material between glass slides on a hot plate at ca. 200°C, followed by cooling to room temperature, floating on water, shadowing with Pt-C if desired, and picking up on EM grids. Further deformation of these samples was obtained by picking the film up off the water surface on a Mylar film and stretching the film in a hand stretcher as done previously for polyethylene single crystals (5).

Results and Discussion

Figures 1 and 2 show a typical electron micrograph and diffraction pattern of the C_7 terpolymer. The crystals, as for the C_5 polymer, consist of lamellae ca. 80-100Å thick. They grow on top of a basal lamellar film, originally in contact with the glycerine, which is of apparently uniform thickness (ca. 220Å as measured at the edge of holes in the film). In contrast to the C_5 ter-polymer, the film here is granular. Use of reprecipitated polymer, after filtering hot from chloroform in an attempt to remove potential cross-linked material, did not significantly reduce the granularity.

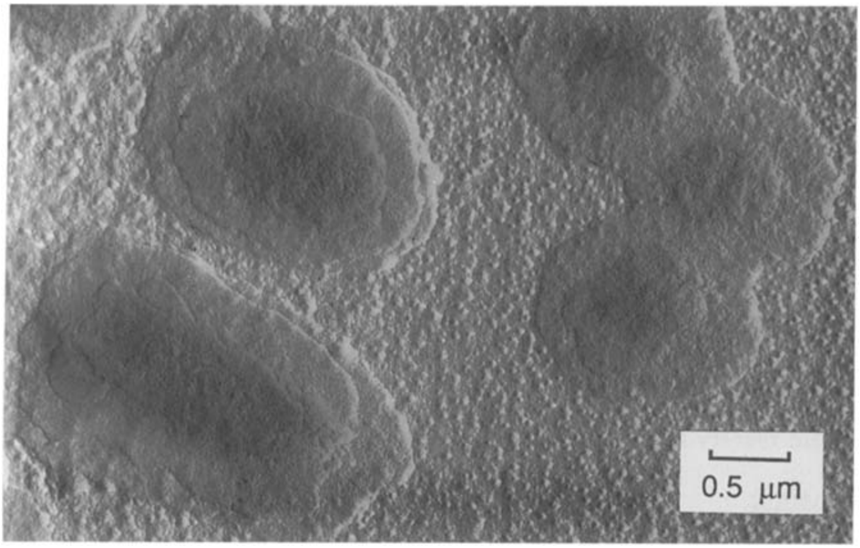


Fig. 1. Single crystals of the C_7 terpolymer crystallized by cooling from above 200°C on a glycerin substrate. A continuous, granular basal film forms the substrate on which the crystals grow.

The electron diffraction patterns at room temperature (Fig. 2a) are similar to those of multi-lamellar crystalline regions of the C_5 terpolymer (1). They can be indexed as resulting from the superposition of three orthorhombic unit cells ($a = 8.3$Å, $b = 5.0$Å) rotated by ± 60 and 0°. However the larger 2θ reflection (presumably 200) is very weak compared to the inner reflections and cannot be seen on the reproduction. In the C_5 polymer the 110 and 200 reflections are of near equal intensity. It is thus possible that only portions of a "crystal" are orthorhombic with the spacing given, with the remainder being orthorhombic with $a = \sqrt{3}b$; the observation of the twelve 210 reflections is the result of the superposed orthorhombic patterns; they would not be seen for a hexagonal structure. As pointed out previously (1) the presence of the 210 reflections suggest

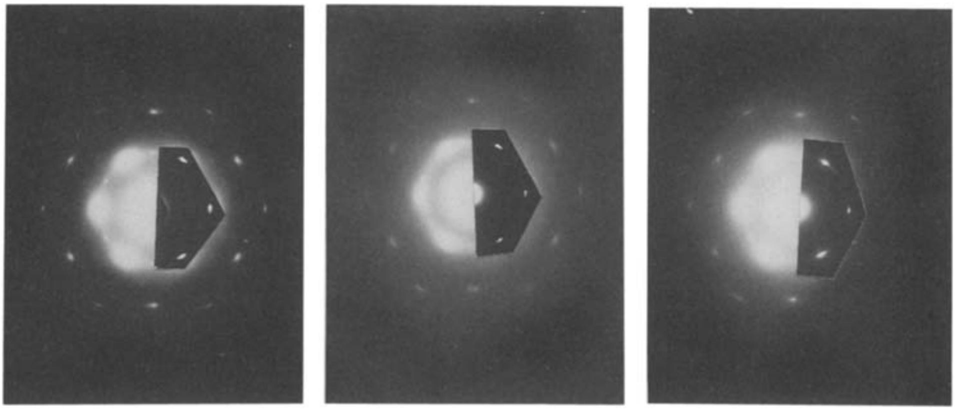


Fig. 2. Electron diffraction patterns at: a) room temperature, b) 153°C and c) after cooling back to room temperature from a maximum temperature of 210°C.

the planes of the phenyl rings do not alternate by ± 30° or 60° to the a axis along the molecular axis as in polyhydroxybenzoic acid (6,7), but rather that the planes have a common orientation, resulting in a herringbone structure in projection onto the a* b* plane (see Fig. 4, ref. 1 or Fig. 8, ref. 7); a statistical distribution also would not seem appropriate since the electron density in projection would again cause 210 to be forbidden.

Upon heating up to 155°C there is no significant change in the form of the diffraction pattern (Fig. 2b), suggesting there is only axial translation of the molecules; phenyl and carbonyl group 180° flips (7,8) would not affect the pattern. Double diffraction is seen in this pattern (see, e.g., the 310 reflections) due to the superposition of two crystals slightly rotated. Above the highest lc-lc transition the pattern has the form of a single diffuse ring, as would be consistent with a nematic or smectic structure in molecular axis projection. In the C_5 terpolymer a single set of sharp hexagonal reflections are occasionally seen superimposed on the diffuse ring (9); their possible presence in the C_7 polymer at these temperatures is still being examined. Cooling of the C_7 polymer from above the lc-lc transition results in reformation of single crystals (Fig. 2c). The 210 reflections, however, are missing suggesting a more irregular packing of the phenyl rings and the pattern appears to be hexagonal. In thicker regions of the film, stacks of the 80-100Å thick lamallae develop (Fig. 3). These still give use to single crystal diffraction patterns, the higher orders in patterns such as in Fig. 2 being most readily observable in these thick films.

An electron micrograph and diffraction pattern of the sheared ("fiber") sample are shown in Figs. 4 and 5. Although the thickness of the lamellae in the "fiber" samples, which are oriented essentially normal to the shear direction, is difficult to measure due to their tilt, they clearly are also on the order of 100Å. Dark field micrographs also suggest a similar thickness. (We note this is considerably thinner than the several hundred angstrom thick lamellae reported previously, for instance, by Woods and Thomas (10), Hudson et al. (11) and

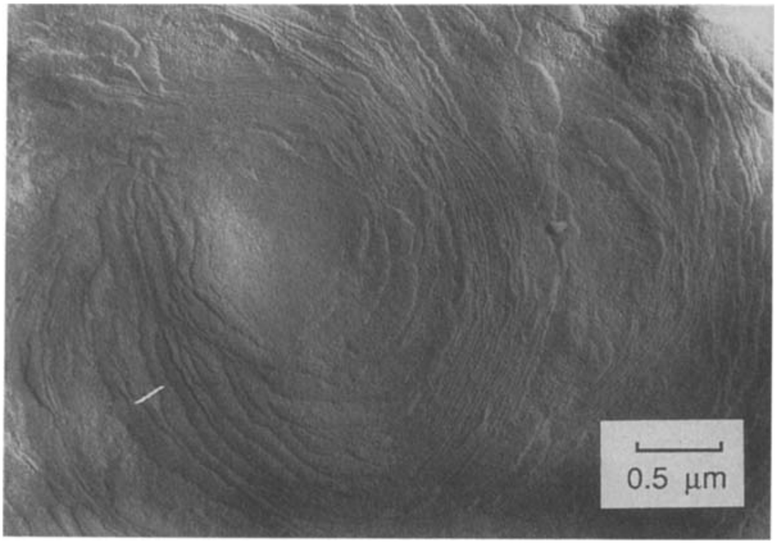


Fig. 3. Pt-C shadowed relatively thick portion of a spontaneously spread film of the C7 terpolymer.

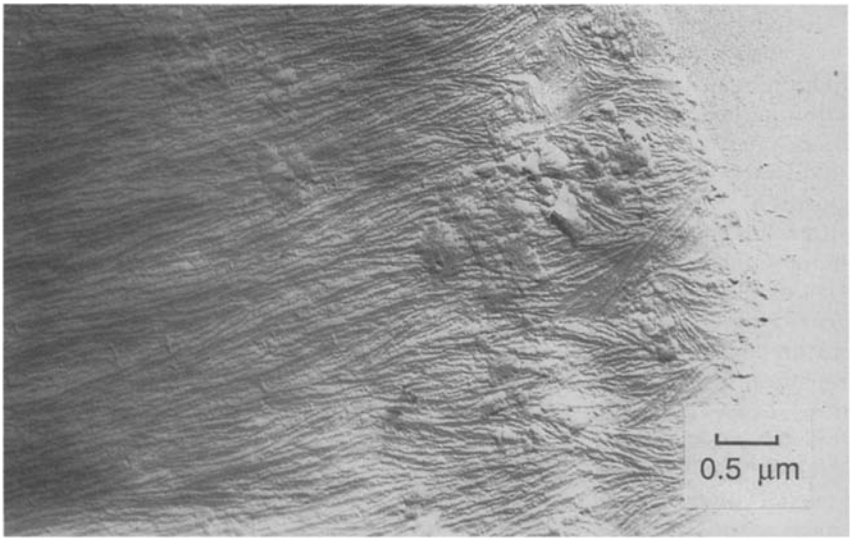


Fig. 4. Shadowed thin film of the C7 terpolymer that had been sheared between two glass slides at ca. 200°C and then cooled rapidly.

Mazelet and Kleman (12) for flexible segment containing liquid crystal polymers for which the molecular weight was not given and for which they concluded that there was no definite evidence for folding (10,11) or that an extended conformation was most likely (12)).

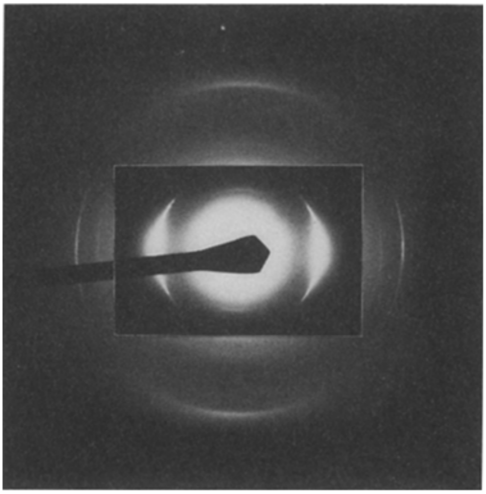


Fig. 5. Electron diffraction pattern at room temperature of material similar to that in Fig. 4. Fiber axis is vertical.

The electron diffraction pattern (Fig. 5) shows relatively poor orientation (these samples were not annealed; annealing below the c-lc transition often improves the orientation (13)). The equatorial reflection spacings (d = 4.33, 2.48, and 2.16Å,) agree with the 110, 310 and 220 reflections of the single crystal patterns. A weak 200 is again visible just inside the 110 arc. The meridional reflections are aperiodic (d = 5.85 , 3.35 and 2.14Å) as would be expected for a terpolymer with a random configuration (14). An additional weak reflection can be seen between the 3.35 and 2.94Å lines, as well as two further out.

It is not possible on the basis of micrographs such as Fig. 4 to determine the relative numbers of molecules folding back into a lamella and those extending into the next lamella (i.e. tie molecules). This is of obvious concern relative to the potential mechanical properties of oriented samples of these liquid crystal polymers as well as for its implications on the crystallization and folding processes themselves. As shown in Fig. 6, for the drawn, sheared ("fiber") sample, shear between the lamellae occurs easily, suggesting few or no tie molecules, i.e. almost complete reentry.

In summary, this is further evidence of the prevalence of significant degrees of chain folding during crystallization of liquid crystal polymers from the, often presumed, more or less extended chain liquid crystalline state. With single crystal lamellae as thin as 35Å having been grown by the process used here (15), it is clear that chain folding of the type associated with flexible chain polymers such as polyethylene also occurs for liquid crystal polymers with flexible segment in their backbone. Current research is directed at the effect of segment length on the development of folds. As in our previous papers we suggest that the results, particularly the thinness of the lamellae (16), suggests a preponderance of adjacent reentry in the single crystals crystallized from the liquid crystal state and also suggests that significant degrees of chain folding, in the form seen in, e.g., polyethylene single crystals, occurs in these polymers in the liquid crystal state.

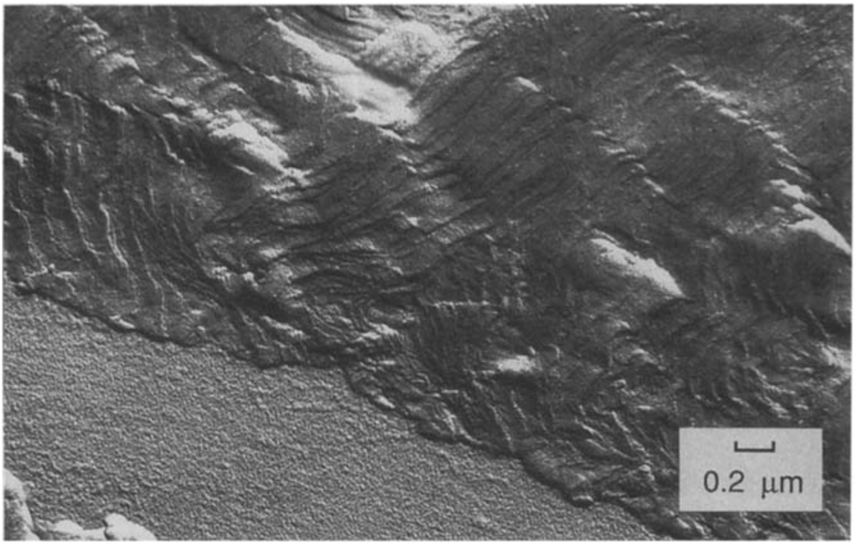


Fig. 6. Electron micrograph of a sample of the C7 terpolymer oriented as for Fig. 4 and then drawn 50% on a Mylar substrate in the same direction as that of the initial orientation.

Acknowledgement

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