Morphology of a thermotropic random terpolymer liquid crystal polymer crystallized in the bulk: compression mouldings, extrudates and fibres*

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The morphology of extruded pellets, compression and injection moulded articles, and melt spun fibres of a random liquid crystal terpolymer has been investigated. Etching and self-decoration techniques have been used, which reveal a lamellar morphology in bulk samples. The lamellae, ranging from 50 to 1800 Å in thickness depending on the preparation technique, are oriented perpendicular to the fibre or extrusion direction in melt spun fibres and extruded pellets. Extruded pellets are analogous to a composite material with 0.2–1.8 μm diameter 'fibres' of the liquid crystal being embedded in a less oriented matrix; greater alignment of the lamellae is observed in the 'fibres'. The thickness of the lamellae observed in melt spun fibres ranged from 500 to 800 Å. Thinner lamellae (50–130 Å) are observed on the surface of compression moulded specimens with thicker (200–1800 Å), presumably extended chain lamellae in the interior. The thickness and degree of alignment, or order, of the lamellae is dependent on the cooling rate. Selected area electron diffraction confirms that the chain axes are perpendicular to the lamellae.

(Keywords: morphology; liquid crystal polymer; electron diffraction)

INTRODUCTION

In previous papers[1–6] we have described the morphology of a family of thermotropic random terpolymer liquid crystal polyesters crystallized from the nematic state in quiescent and sheared thin films and from solution. In all cases a folded chain lamellar morphology was described, contrary to expectations for crystallization, for instance, from nematically aligned, extended chain polymers, with or without flexible segments in their backbones; kinetic based polymer crystallization theory would predict extended chain nuclei and growth. In the first of our papers[1] we reported that one of the polymers in the family (C_5, see below) crystallized from the nematic state in the presence of a magnetic field as extended chain lamellae in the interior of bulk samples, but as thin (possibly folded chain) lamellae on the free surfaces of the same sample. In this paper we describe related observations of the morphology of another polymer of this family (C_7) crystallized under conditions of commercial interest, i.e. as compression and injection mouldings, extrudates and melt spun fibres, utilizing fracture, etching and self-decoration techniques to reveal internal structure as well as replicas for the compression moulding free surface. To date, the largest commercial market for liquid crystal polymers (LCPs) has been in the form of solution spun (i.e. lyotropic LCPs) fibres. Although the chemical architecture of many of the available LCPs suggests desirable commercial properties (see, for example, ref. 7) only limited commercial applications have been made to date of thermotropic LCPs. This is in large part due to the morphology of the objects, as produced in practical, low cost moulding operations. Thus, for instance, although intricate and/or thin walled parts can be moulded from LCPs, owing to their low melt viscosity in the LC state, the molecular alignment of the chains that results in the low viscosity also results in anisotropic parts, often with a skin–core structure[8–12]. The result is an anisotropy of properties that is thickness dependent[13,14]. Most of the above-cited papers, as well as others in this area, have utilized wholly aromatic, 'rigid-rod' LCPs; we utilize here a semiflexible LCP containing an aliphatic segment.

EXPERIMENTAL

Although the prior research was on the C_4–C_7 terpolymers, the results described here are limited to the C_7 terpolymer, which was the only sample available in sufficient quantity to permit bulk sample preparation. As described in ref. 5, the C_7 terpolymer is a nearly equimolar 'random' terpolymer of azelaic acid, hydroxybenzoic acid and hydroquinone, yielding the following chemical units

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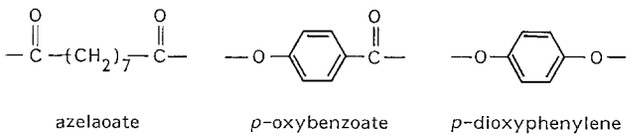
in the backbone:



azelaoate *p*-oxybenzoate *p*-dioxyphenylene

The C_7 polymer used here had $\bar{M}_n = 13\,500$, $\bar{M}_w = 29\,000$ (in terms of the polystyrene equivalent) and an inherent viscosity of 0.77 dl g^{-1} in 40/60 tetrachloroethane/phenol solution at 30.00 ± 0.02°C. D.s.c. indicates a T_{k-m} of 142°C and a T_{m-m} of about 170°C, with a biphasic (mixed isotropic–nematic) region beginning at about 260°C (ref. 15).

Pellets of the as-polymerized resin were prepared by extruding the polymer at 280°C from a Parr Reactor 4551, through a 7.9 mm die into a water bath and finally through a 50.8 mm Killion Pelletizer. Scanning electron microscope (SEM) samples of the pellets were prepared by fracturing the pellets with a razor blade, at liquid nitrogen temperatures, parallel and perpendicular to the extrusion direction; these will be referred to as longitudinal and cross-section samples, respectively. Some of the fractured pellets were then etched in, for example, a 1 wt% potassium permanganate in 85% *o*-phosphoric acid solution in an ultrasonic bath for 2–15 min. The etched samples were washed first with running water for 10 min, then with hydrogen peroxide (H_2O_2) in an ultrasonic bath for 15 min and finally with distilled water in the ultrasonic bath for 15 min. The procedure closely follows that suggested by Rybnikar[16]. This etching procedure has been used extensively in our laboratory and has been found to be quite useful for semicrystalline polymers[17]. More recently, this technique has been applied to LCPs and, using similar etchants, has proved effective for both rigid-rod and semiflexible systems[18,19]. Etching of the C_7 polymer was much more rapid than for polyethylene. The as-fractured and etched pellets were gold sputter coated prior to investigation in a Hitachi S570 SEM.

Compression moulded specimens (50.8 mm × 12.7 mm × 3.2 mm) of the C_7 LCP were prepared in a standard Carver laboratory hot press. A moulding temperature of 210°C, i.e. in the liquid crystalline (nematic) state, and pressures of ~ 10 000 psi (68.95 MPa) were used. Following moulding, the pressure was released and the material allowed to remain at the moulding temperature for 20 min with the platens just touching the mould. The sample was then either slow cooled, by turning off the platens and allowing the mould to cool to room temperature, or water quenched by submerging the mould in cold water.

Both the moulded surface and cross-section of the moulded samples were studied; the cross-section samples were fractured by hand at ambient temperature. Some of the samples were etched in a 1 wt% potassium permanganate in 85% *o*-phosphoric acid solution, as described previously. SEM samples were gold sputter coated prior to investigation. Pt/C replicas of the surfaces were prepared for transmission electron microscope (TEM) investigation; the desired surface was Pt/C shadowed in a vacuum evaporator and drops of an aqueous polyacrylic acid (PAA) solution were deposited on the coated surfaces. Once dry, the PAA, along with the Pt replica, was stripped from the surface and the PAA removed by floating on water. The replicas were then picked up on copper grids and examined in a Jeol 100C TEM operated at 100 kV.

Table 1 Mechanical properties of C_7 terpolymer and A900

Test	C_7 LCP	A900[a]
Heat distortion (°C) (ASTM D648)	74	168
Flex modulus (psi)[b] (ASTM D790)	1.1×10^5	1.2×10^6
Tensile at break (psi)[b] (ASTM D638)	1.8×10^3	2.3×10^4
Elongation (%)	2	2

[a] A900 is a commercial, wholly aromatic LCP from Hoechst-Celanese; data from J. Tweedie, Goodyear Research
[b] 1 psi = 6.895×10^3 Pa

Material crystallized as a free surface, i.e. not in contact with a mould, was also investigated. Free surface samples were prepared by stripping the aluminium foil from one side of the mould, thereby exposing the polymer in the mould to air, at 210°C, and allowing the materials to cool slowly in the mould. The material that stuck to the aluminium foil, and therefore was not slow cooled but air quenched, was also investigated.

Injection moulded tensile bars ~3.2 mm × 12.7 mm × 152.4 mm) were also fractured or cut transverse and longitudinally, and examined as-fractured, etched and self-decorated. The self-decoration was accomplished by briefly touching a cut (razor blade cut at room temperature) surface to a hot plate at around 160°C, followed by replication. As indicated by the subsequent micrographs of both as-fractured and etched samples, substantial amounts of polymer adhere to the replica. Various properties of the injection moulded bars were measured (by J. Tweedie, Goodyear Research) in comparison with similar mouldings of the wholly aromatic liquid crystal polymer Vectra A900 produced by Hoechst-Celanese; they are tabulated in *Table 1*.

Lastly, melt spun fibres of the C_7 LCP were prepared by spinning through a 0.38 mm spinneret at 200°C. Longitudinal sections of the fibres were obtained by embedding the fibres in epoxy and ultramicrotoming. Both the surface and embedded sections were etched as described previously, gold sputter coated and examined in a Hitachi S570 SEM. Cross-sections were also obtained, but the images, etched and as-sectioned, were uninterpretable.

RESULTS AND DISCUSSION

As-received pellets

SEM micrographs of the longitudinal and cross-sectional as-fractured surfaces of a C_7 LCP pellet are shown in *Figures 1* and *2*, respectively; the extrusion direction is approximately horizontal in *Figure 1* and perpendicular to the page in *Figure 2*. It is interesting to note that the fracture behaviour of the pellets is qualitatively analogous to fibre reinforced materials, even though only a single polymer is present. While fracturing these samples by hand it was noticed that fracturing in the extrusion direction (longitudinal samples) required much less force than cross-sectional fracturing. Additionally, while the longitudinal fracture was 'clean', the cross-sectional fracture did not proceed 'straight through' the sample, but rather took a jagged, angular course, at times running parallel to the extrudate direction. This behaviour

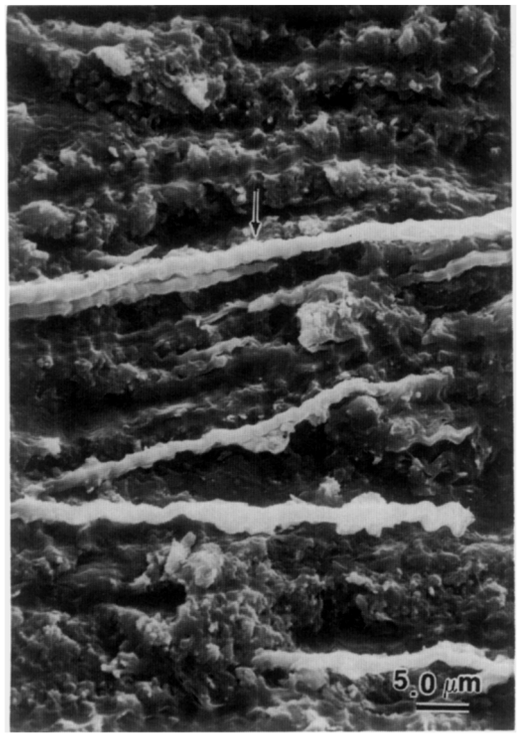


Figure 1 SEM micrograph of a longitudinal fracture surface (no etching) from an as-received extruded pellet of the C_7 terpolymer. The extrusion direction is approximately vertical; the arrow denotes 'fibres' of the polymer, which formed during processing

is similar to that observed for fibre reinforced materials with our longitudinal fracture corresponding to fracture along, or parallel to, the fibre direction and our cross-sectional fracture corresponding to fracture across, or perpendicular to the fibre direction. *Figures 1* and *2* demonstrate that, in addition to the fracture behaviour, the appearance of the fracture surfaces is also comparable to fibre reinforced materials. The arrows in *Figure 1* and *2* denote 'fibres' of the LCP within the extruded sample; the diameter of the fibres ranged from 0.2 to 1.8 μm.

An etched, longitudinal fracture surface of an as-received pellet is shown in *Figures 3a* and *b* (*Figure 3b* is a higher magnification micrograph of the area shown in *Figure 3a*). It is apparent from *Figure 3b* that the 'fibres' etch in a different manner from the rest of the sample; however, both exhibit a lamellar texture with the lamellae oriented on edge, roughly perpendicular to the extrusion direction. A greater degree of order is observed in the 'fibres'; the orientation of the lamellae is more uniform in the fibres than in the remainder of the specimen, where a more disordered orientation of the lamellae is displayed. Also, single lamellae are seen to extend from the fibres to 'non-fibrous' regions, as denoted by the arrows in *Figure 3b*. It is not known whether the observed differences between the 'fibrillar' and 'non-fibrillar' structures are due to a difference in conformation or a difference in chemical structure.

It is interesting to note that etching (even for relatively short times, such as 2 min) results in a 'deep' etch, especially between the 'lamellae'. It is expected that the etchant primarily attacks the aliphatic spacer, although similar etchants have proved effective in aromatic systems lacking aliphatic units[20]; it is possible that the inter-lamellar regions have a higher concentration of aliphatic spacers (as would be the case if the lamellae are chain folded) or chain ends. Clearly, however, more material is being removed than would correspond to a fold surface, regular or irregular.

The resolution of the SEM used in this study was not sufficient to obtain higher magnification micrographs necessary to determine the lamellar thickness; additionally the orientation of the lamellar edges seen in *Figure 3a* and *b* makes it difficult to accurately measure their thickness. With these precautionary notes in mind, the measured thickness of the lamellae ranged from ~500 to 1300 Å; the extended chain length of the C_7 LCP was ~800 Å. Additionally, the chain axis direction cannot be determined from SEM studies; however, it is expected to be parallel to the extrusion direction based on the TEM studies described in the next section.

Figures 4a and *b* (*Figure 4b* is a higher magnification micrograph of the area shown in *Figure 4a*) are SEM micrographs of the outer surface of an as-received pellet that has been etched. The 'fibres' seem to be more prevalent on the pellet surface as compared to those seen on the interior, longitudinal fracture surfaces; in addition, they are much 'wavier' than those observed in the interior of the pellet. However, unlike the pellet longitudinal fracture surface, etching of the 'fibres' seen on the surface does not reveal a distinct lamellar structure; faint striations perpendicular to the 'fibres' can be seen on the original micrograph, but may correspond to cracks in the gold coating. It is likely that the differences observed between the inner and surface regions are the result of a skin–core effect, which is suggested by the increased percentage of fibrillar, or aligned, material observed on the surface as compared to the inner regions.

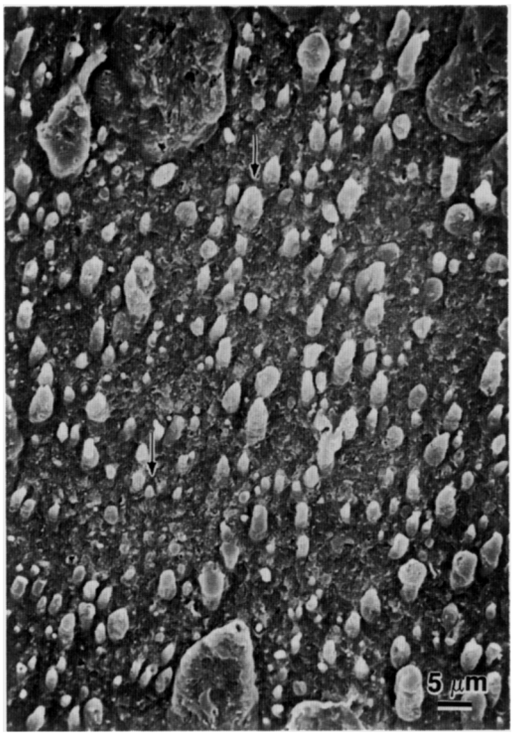


Figure 2 SEM micrograph of a cross-sectional fracture surface (no etching) from an as-received extruded pellet of the C_7 terpolymer. The extrusion direction is normal to the page; the arrows denote two of the many 'fibres' of the polymer, which formed during processing

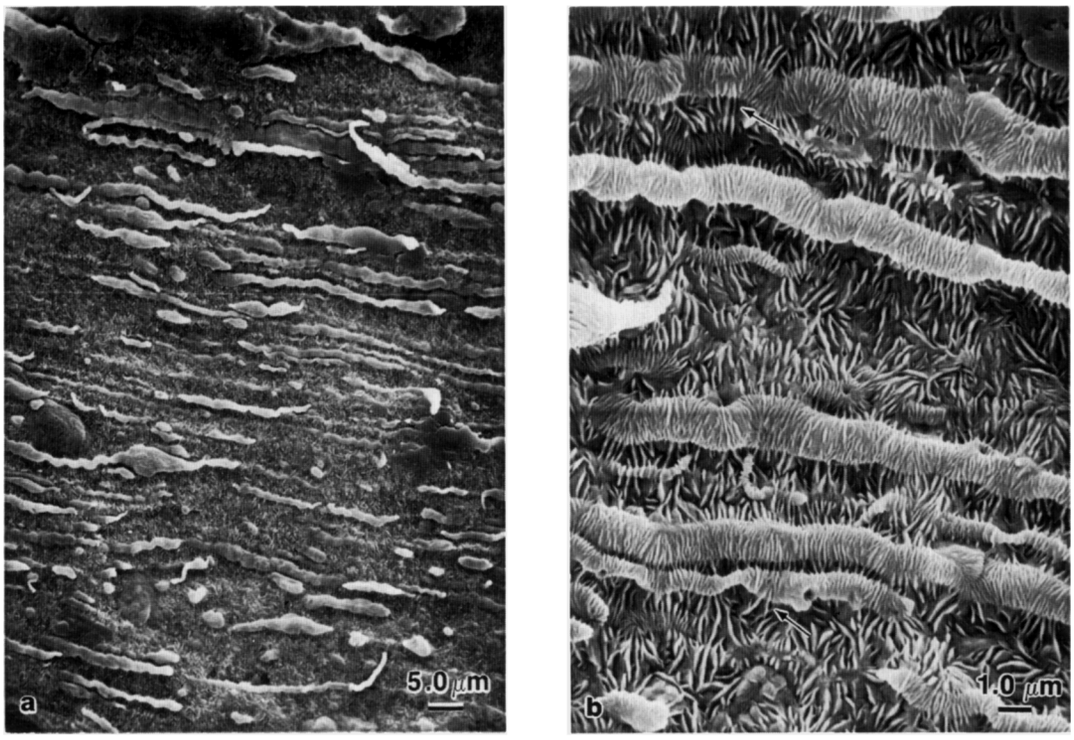


Figure 3 (a) SEM micrograph of an etched longitudinal fracture surface from an as-received extruded pellet of the C_7 terpolymer, and (b) higher magnification micrograph of the area shown in (a). The arrows in (b) denote single lamellae which extend from the fibres to 'non-fibrous' regions. The extrusion direction is approximately horizontal in both (a) and (b)

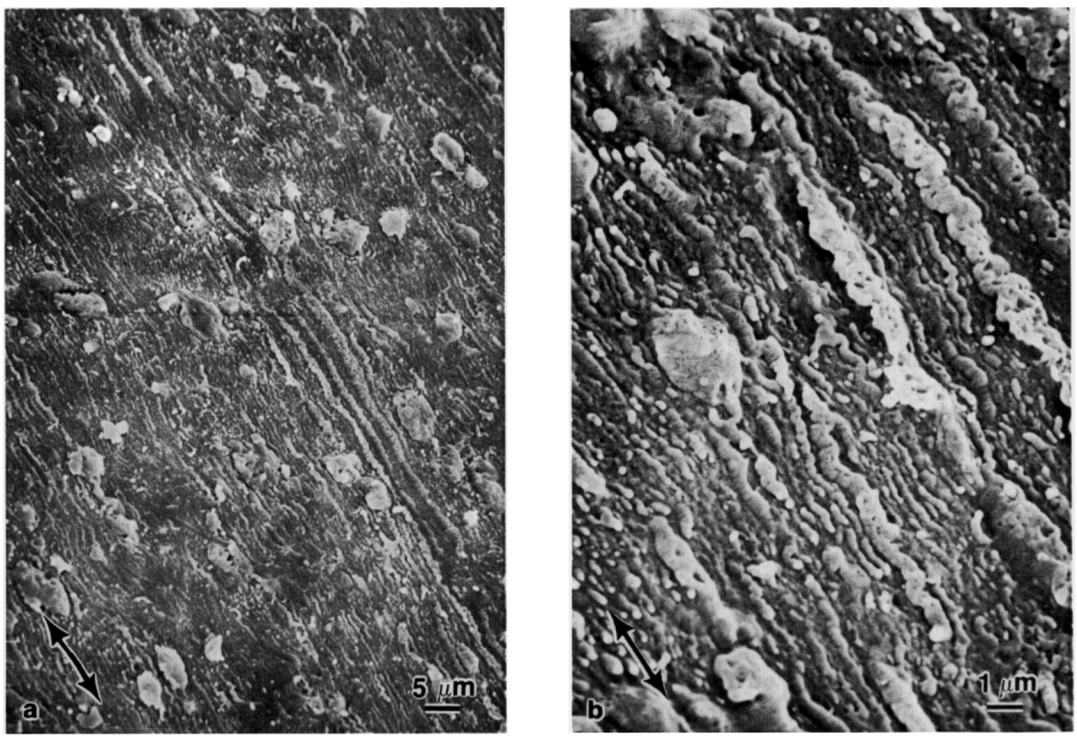


Figure 4 (a) SEM micrograph of an etched outer surface of an as-received extruded pellet of the C_7 terpolymer, and (b) higher magnification micrograph of the area shown in (a). The arrows denote the approximate extrusion direction

Compression moulded samples

A cross-sectional fracture surface (no etching) of a compression moulded specimen is shown in *Figure 5*; the sample was slow cooled. The fracture surface is suggestive of lamellae from which some long fibrils have been pulled out. Etching, however, clearly reveals lamellar texture. *Figures 6a* and *b* are SEM micrographs of an etched cross-section of the fracture surface of a slow cooled, compression moulded sample. Although a lamellar texture is again observed, the orientation of the lamellae varies, with a nearly common orientation persisting over large areas. The average thickness of the residual lamellae

is approximately 650 Å; the average spacing is about twice this value. Etching also appears uniform throughout the sample, i.e. the fibrous structures observed in the pellets are absent in compression moulded samples. The apparent lamellae in the as-fractured sample are normal to the lamellae observed after etching; the former correspond to the more or less wavy features extending, for example, from the upper left to the middle right in *Figure 6a*.

Figure 5 SEM micrograph of a cross-sectional fracture surface (no etching) from a compression moulded, slow cooled sample of the C_7 terpolymer

TEM replicas of etched cross-sections of slow cooled, compression moulded samples aided in establishing the chain direction of the molecules in relation to the lamellae and provided a more accurate measure of the lamellar thickness; two examples of very lightly etched samples are given in *Figures 7a* and *b*. Determination of the chain axis direction is possible because various amounts of polymer adhered to the replica when it was stripped from the sample surface, and consequently selected area electron diffraction patterns of the polymer could be obtained. One such diffraction pattern, corrected for image rotation, and corresponding bright field image is presented in *Figure 7b*; the black areas are polymer that adhered to the replica. The chain axis direction, determined from the diffraction pattern and denoted by an arrow in *Figure 7b*, is approximately perpendicular to the lamellae. The thickness of the lamellae varies greatly in these samples, ranging from 360 to 1800 Å, but seems to be relatively constant in a given lamella except at the edges, which are tapered. *Figures 7a* and *b* are similar to those of the extended chain (magnetically aligned) specimen shown in ref. 1.

The morphology of water quenched, compression moulded samples differs to a degree from the slow cooled, compression moulded samples. An SEM micrograph of an etched cross-section is shown in *Figure 8*. TEM micrographs of a replica of an etched cross-section of a compression moulded, water quenched specimen are shown in *Figures 9a* and *b*. The higher magnification micrographs (*Figure 9a* and *b*) reveal a common lamellar orientation persisting over short distances, while lower magnification micrographs (*Figure 8*) show that the overall lamellar orientation of water quenched samples is more disordered than seen in slow cooled samples. Note that the area shown in *Figure 9b* was apparently

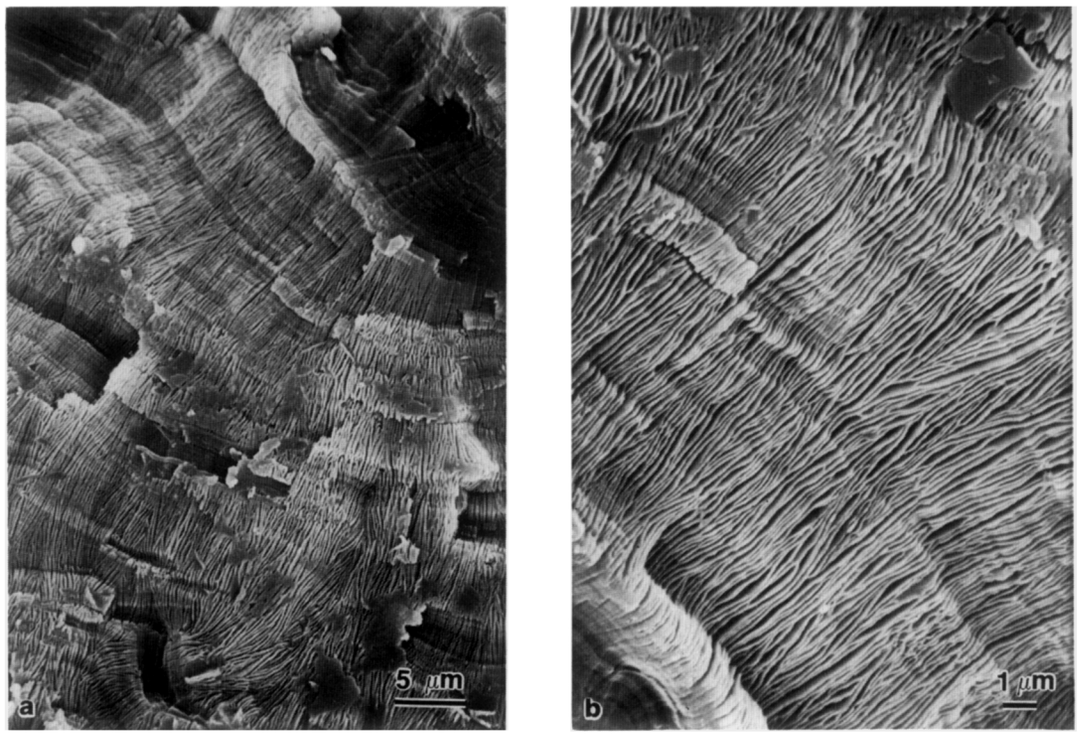


Figure 6 (a) SEM micrograph of an etched cross-sectional fracture surface from a compression moulded, slow cooled sample of the C_7 terpolymer, and (b) higher magnification micrograph of the area shown in (a)

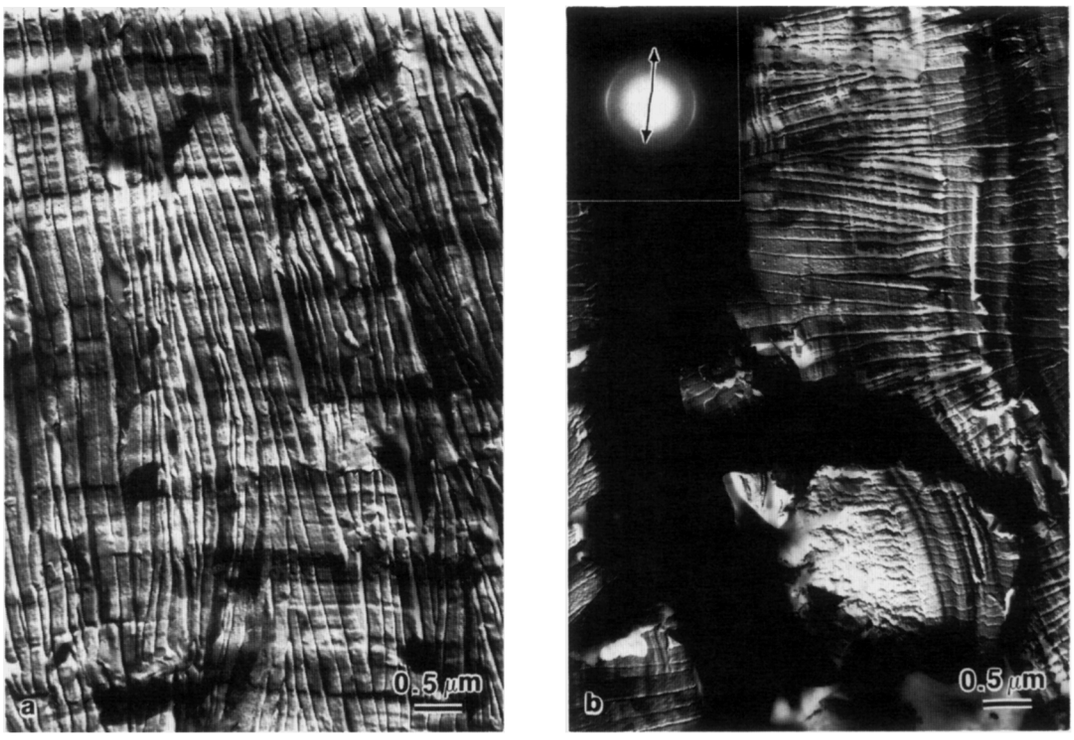


Figure 7 (a) TEM micrograph of a replica from an etched cross-sectional fracture surface of a compression moulded, slow cooled sample of the C_7 liquid crystal polymer; (b) same as (a), including the corresponding selected area electron diffraction pattern; the orientation of the image with respect to the diffraction pattern has been corrected for image rotation. The large black regions are polymer which stuck to the replica and gave rise to the diffraction pattern. The arrow denotes the approximate molecular axis direction

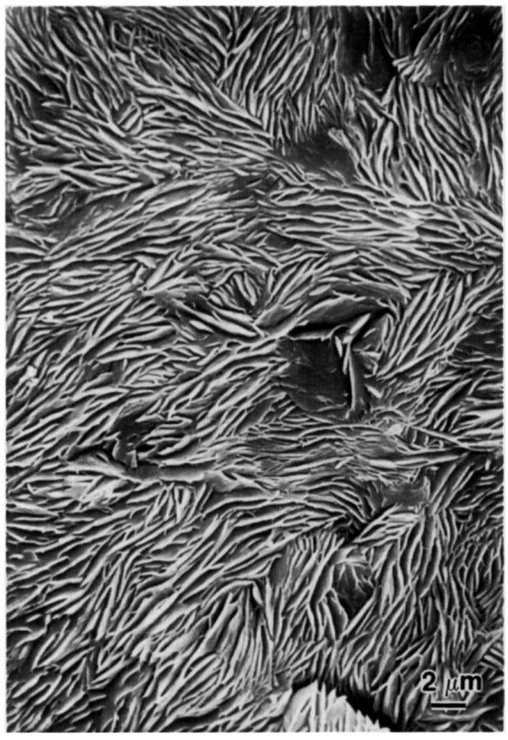


Figure 8 SEM micrograph of an etched cross-sectional fracture surface from a compression moulded, water quenched sample of the C_7 terpolymer

not etched as severely as the area shown in *Figure 9a*; also, both were more deeply etched than the areas shown for the etched, slow cooled samples (*Figures 7a* and *b*). *Figure 9a* reveals that the lamellae themselves are textured; unfortunately the severity of the etching prevents further characterization of the texture. A wide range of lamellar thicknesses is again seen, ranging from 200 to 700 Å; i.e. they seem thinner than in the slow cooled sample and also thinner than the number average chain length.

Figure 10 is an SEM micrograph of an etched, 'compression moulded' free surface which was exposed to air during cooling (i.e. the material that stuck to the aluminium foil peeled from the hot mould surface, as described in the experimental section, was cooled rapidly in air). The lamellae are clearly more closely spaced than on the interior of the sample (*Figure 8*) and seem to be organized in sections of spherulites. *Figures 11* and *12* are TEM micrographs of replicas of a similar 'air quenched' free surface, unetched and etched, respectively. A lamellar surface, similar in appearance to the free surface of the magnetically aligned sample (Figure 9 in ref. 21), is observed on the unetched free surface shown in *Figure 11*. These lamellae appear to be much thinner than those seen in cross-sectional images of compression moulded samples shown in *Figures 7a* and *b*. The orientation of the etched lamellae seen on the 'air quenched' free surfaces appears less uniform than those observed on etched, interior, cross-sectional surfaces of either the slow cooled or water quenched samples.

Thin lamellae were not observed on the unetched free surface of the material that remained in the mould (following removal of the aluminium foil and slow cooling to room temperature); this surface was essentially featureless. The etched free surface of this sample, however, did display thin lamellae. This is shown in the TEM replica in *Figure 13*; the thickness of the lamellae, determined from the length of the Pt/C shadow shown in *Figure 13*, is 50–130 Å, with some uncertainty owing to lack of knowledge of the actual shadow angle.

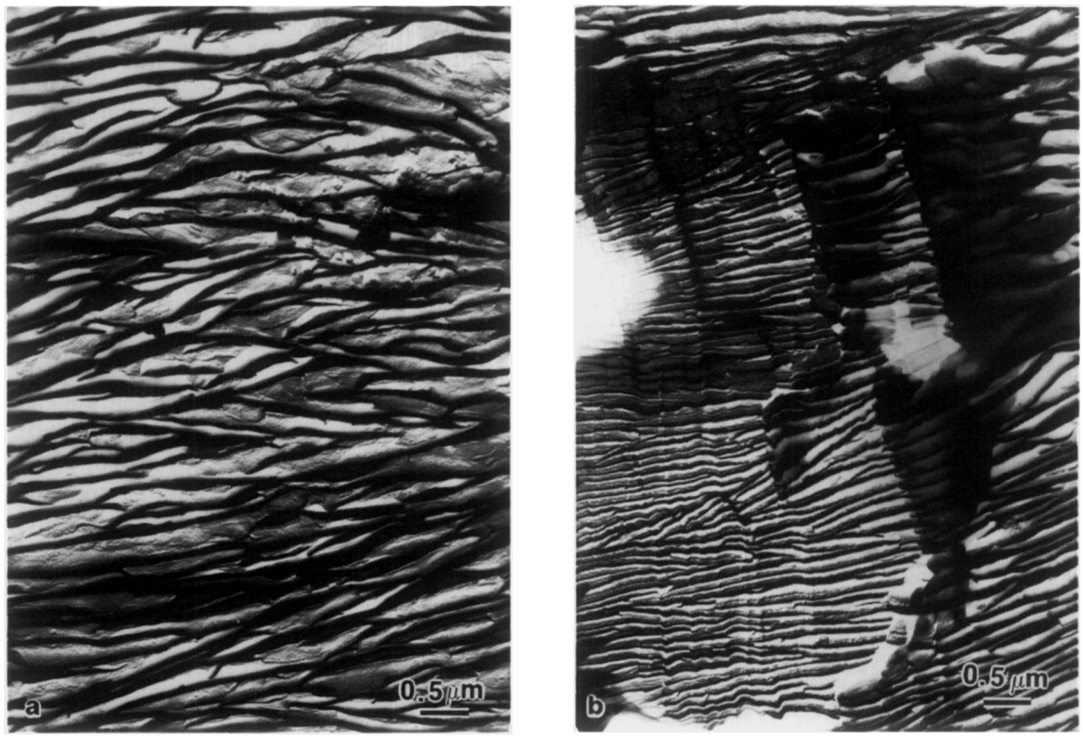


Figure 9 (a) and (b) TEM micrographs of a replica from an etched cross-sectional fracture surface of a compression moulded, water quenched sample of the C_7 terpolymer

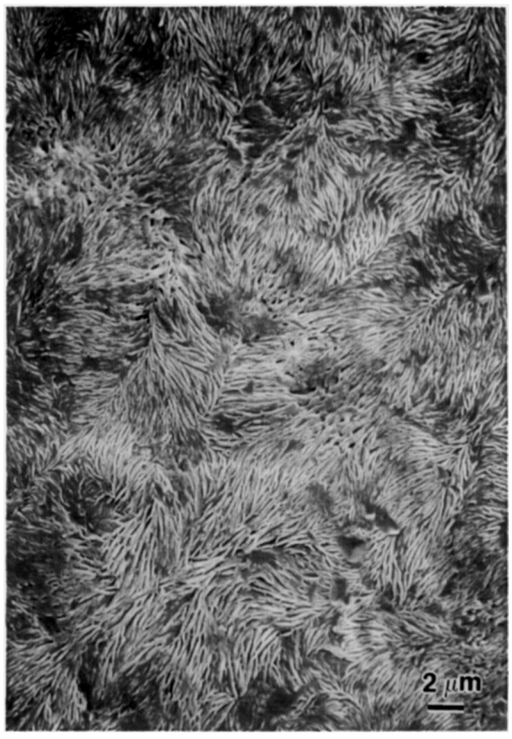


Figure 10 SEM micrograph of an etched, air quenched, 'compression moulded' free surface of the C_7 terpolymer

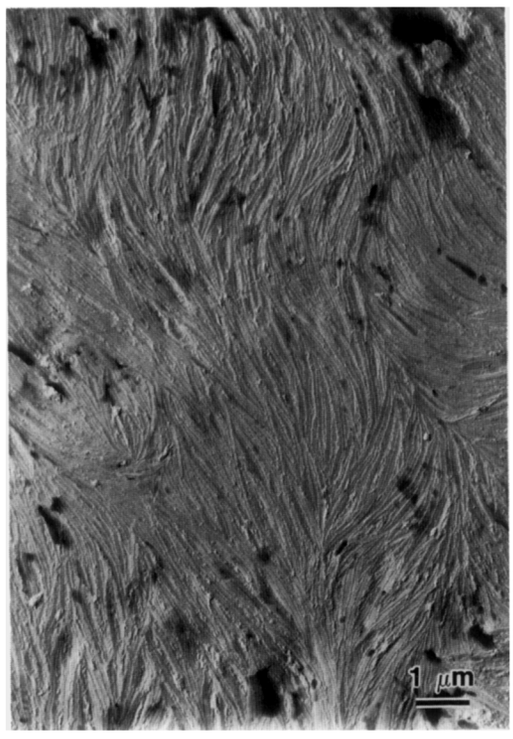


Figure 11 TEM micrograph of a replica from an unetched, air quenched, 'compression moulded' free surface of the C_7 terpolymer

The average thickness of the interior lamellae observed in etched, slow cooled, compression moulded samples, relative to the chain direction determined from selected area electron diffraction, suggests that they consist of extended chains; the same cannot be said for water quenched samples. Both, however, display a variety of lamellar thicknesses, with the water quenched samples generally being thinner than the number average extended chain length of 800 Å. Although the conformation of the molecules cannot be determined with certainty, it appears that the quenched samples consist of chain extended, not extended chain, lamellae, i.e. they too are folded, but with only one to two folds per molecules. Surface regions allowed to crystallize as a free surface, on the other hand,

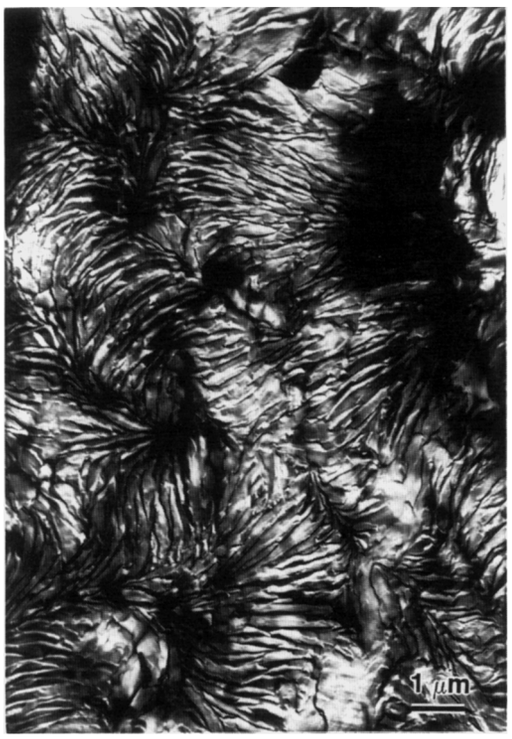


Figure 12 TEM micrograph of a replica from an etched, air quenched, 'compression moulded' free surface of the C_7 terpolymer

Figure 13 TEM micrograph of a replica from an etched, slow cooled, 'compression moulded' free surface of the C_7 terpolymer

displayed thin (50–130 Å) lamellae upon etching. In light of these initial observations, it would be interesting to determine if the lamellae observed in the slow cooled, compression moulded samples are indeed extended chain lamellae, and also if they formed from initially folded chain structures, as these results suggest.

Injection moulded samples

Figure 14 is a TEM micrograph of a lightly etched transverse fracture surface of an injection moulded tensile bar. The appearance is similar to that of the compression moulded samples. Because of the extreme amount of material adhering to the surface, it was not possible to obtain micrographs of longitudinal (parallel to the flow direction) fracture surfaces or to examine potential skin–core effects. For this purpose self-decorated samples were examined. Micrographs from regions near the surface and in the interior of a cross-section are shown in *Figures 15a* and *b*, with the interior of a longitudinal section in *Figure 15c*. The most obvious feature on these surfaces, we suggest, represent the lamellae within the sample, with the surface texture on these thick lamellae being due to thin lamellae formed by the rapid heating and subsequent cooling of the polymer on the surface; epitaxial crystallization of folded chain lamellae has occurred. Wunderlich and Melillo[22] used this technique to self-decorate fracture surfaces of extended chain (pressure crystallized) polyethylene, interpreting their results as above.

Comparison of *Figures 15a* and *b* suggests a skin–core effect; the thick lamellae near the surface are both thinner than in the interior and are oriented normal to the surface (this sample was taken from near the gate; unfortunately there is insufficient polymer available at this time to prepare additional injection moulded objects for further characterization). The right side of this micrograph represents the mould surface, the replica having 'gone around' the corner; the interior thick lamellae are seen to be continuous with those on the surface. In the interior, the thick lamellae are more randomly oriented, in agreement with the fracture surface micrograph (*Figure 14*). In addition, in a few locations, the thin lamellae are nearly parallel to the fracture surface. On the longitudinal surface the thick lamellae are seen to form a chevron-type

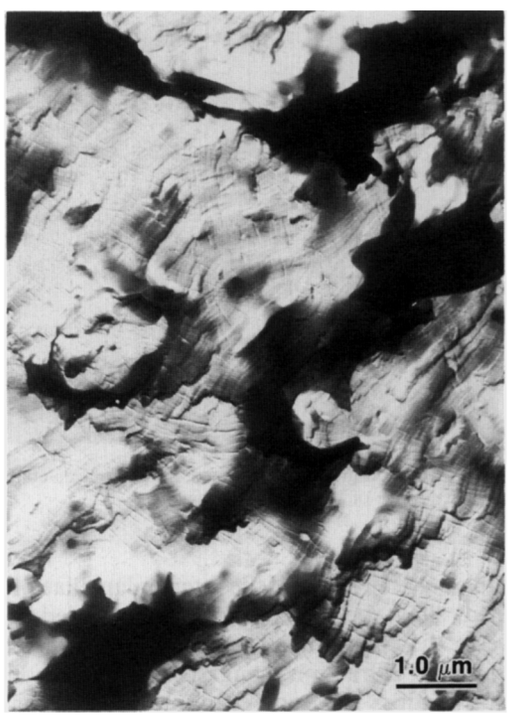


Figure 14 Transverse fracture surface of a C_7 terpolymer injection moulded bar

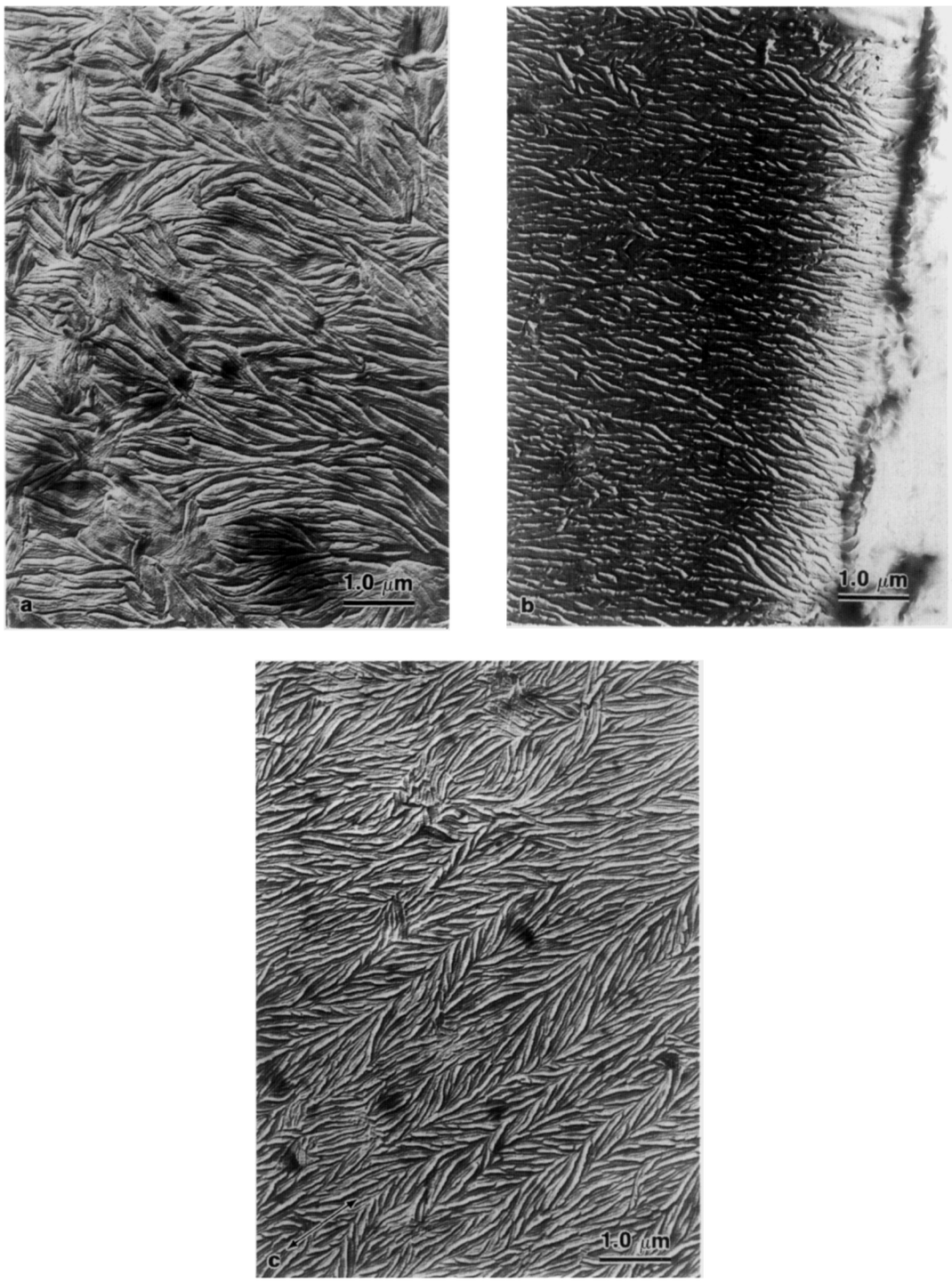


Figure 15 Self-decorated surfaces of a C_7 terpolymer injection moulded bar. (a), (b) transverse surfaces, with (b) at the edge of the bar. (c) Longitudinal surface; the arrow indicates the direction of the axis of the bar

pattern, the axis of the chevron being parallel to the axis of the tensile bar; the location of this replica relative to the surface of the bar is not known. Also not known is how to correlate the arrangement of the lamellae on the two types of sections; i.e. almost no regions are seen in which the thick lamellae are parallel to the transverse surface, except for a few regions in *Figure 15a*. A further note of caution in interpreting these micrographs results from their being razor cut surfaces; deformation accompanies the cutting and may influence the observed structure. On the other hand, the difference in appearance of the three micrographs suggests that the deformed material melted and is not affecting the observations.

Table 1 compares the heat distortion temperature, flexural modulus, tensile strength and elongation with those of Vectra A900. As would be expected from the low T_{k-m}, the heat distortion temperature is lower; this can be an advantage in processing. On the other hand, the poorer ultimate properties, as well as the ease of fracture—all of which we attribute to the observed morphology—suggest that it would not be suitable for moulded objects.

Figure 16 SEM micrograph of an etched, outer surface of a melt spun fibre of the C_7 terpolymer. The fibre axis is approximately horizontal

Drawn fibres

Fibres spun from the C_7 terpolymer also displayed disappointing mechanical properties compared to commercially available LCPs. Examination of their morphology shows the reasons behind their poor mechanical properties. *Figure 16* is an SEM micrograph of the etched outer surface of a drawn fibre. While the unetched fibre surface is essentially featureless, etching once again reveals a lamellar texture, with the lamellae perpendicular to the fibre axis (note that a substantial portion of the surface is unetched). An interior longitudinal view of the fibres is shown in *Figure 17*. The fibre shown was microtomed using a glass knife and etched; the approximate centre of the fibre is shown in *Figure 17*. The structures parallel to the fibre direction in *Figure 17*, such as seen in the upper left corner, are thought to be knife marks, i.e. artifacts of the microtoming process. The thickness of the lamellae, in both the surface and interior regions, ranges from 500 to 800 Å. Comparison of *Figure 16* and *17* shows that there is little difference between the etched outer and interior surfaces. No evidence of a skin–core effect is observed.

SUMMARY

As is well known for 'rigid-rod' LCPs[8–12], the morphology of the bulk flexible segment containing LCP, as studied here, is also dependent on the processing technique. A greater range of textures, however, has been observed. Extruded pellets exhibit a 'fibrillar' composite morphology in which 0.2–1.8 mm 'fibres' of the terpolymer are observed parallel to the extrusion direction. Etching techniques revealed a lamellar texture, with the lamellae, ranging from 500 to 1300 Å in thickness, oriented approximately perpendicular to the extrusion direction. The 'fibres' etched in a different manner from the remainder of the pellet; in addition a greater degree of lamellar alignment was observed in the fibrillar structures. Differences were also noted between the interior and surface regions of the extruded pellets. The liquid crystalline 'fibres' were more prevalent on the pellet surface than in the interior, although the surface region did not display a distinct lamellar texture upon etching.

Compression moulded samples possessed a similar lamellar structure. The orientation of the lamellae varied throughout the sample; however, a common lamellar orientation persisted over large areas in slow cooled samples, presumably related to the liquid crystal domains in the liquid crystal state. The molecular orientation in the domains may be related to that in the pellets from which the sample was moulded, and to the flow during compression. Selected area electron diffraction confirmed that the molecular axes are perpendicular to the lamellae. The thickness of the interior lamellae observed in slow cooled samples ranged from 360 to 1800 Å with an average value of ~650 Å. Water quenched specimens displayed a more disordered lamellar texture; the lamellar thickness ranged from 200 to 700 Å. Etched surfaces of material that was allowed to crystallize as a free surface and slowly cooled, revealed quite thin lamellae, 50–130 Å thick. The extended chain length (~800 Å) indicated that the interior lamellae of the compression moulded, slow cooled samples are indeed extended chains; on the other hand chain folding presumably exists in the surface regions. The similarity in appearance between this material and pressure crystallized, extended chain polyethylene suggests that the chains initially folded during crystallization and then extended, possibly through the same mechanism of sliding diffusion postulated by Hikosaka[23,24] for the growth of extended chain crystals of polyethylene during crystallization from the disordered

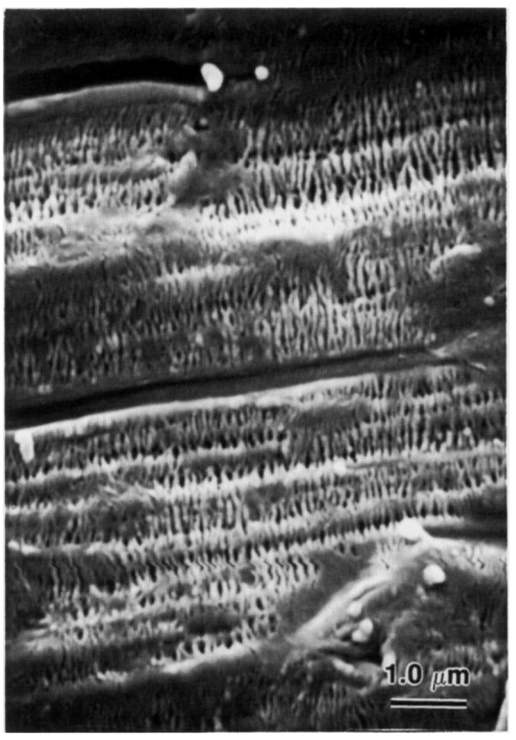


Figure 17 SEM micrograph of an etched, longitudinal surface (i.e. the approximate centre of the fibre, revealed by microtoming) of a melt spun fibre of the C_7 terpolymer. The fibre axis is approximately horizontal

hexagonal or nematic state under pressure. Variations in the uniform thickness of the lamellae, from lamella to lamella, suggests fractionation by molecular weight during processing. The basic morphology of injection moulded samples is similar to that of the compression moulded samples, i.e. extended chain or, at least, chain extended lamellae. The results of the self-decoration are in agreement with the suggestions above of folding followed by extension.

Lastly, melt spun fibres have been found to consist of well formed lamellae, highly oriented in the direction perpendicular to the fibre axis. Virtually no differences were observed between the outer and interior regions: both consisted of highly oriented lamellae 500–800 Å thick. No evidence of a skin–core effect was observed.

The presence of extended chain, or at least chain extended, lamellae in the interior of all of the bulk samples is obviously detrimental to the properties. Failure is likely both at the surfaces of the lamellae (although etching might have destroyed tie molecules, there is no evidence for their existence) and between the molecules, just as in pressure crystallized polyethylene. A processing process is required that will at least randomize the positions of the chain ends, even if the anisotropic orientation is maintained (or desired, as in fibres).

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