# Morphological observations of nascent poly(*p*-oxybenzoate)

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Observations have been made on as-polymerized, non-stirred, 'solution' polymerized poly(*p*-oxybenzoate). A uniformity of thickness of the resulting lamellae, for given polymerization conditions, indicates a nucleus determined thickness, with oligomer addition primarily on the lateral faces. Bilayered lamellae are the predominant form in many of the preparations, regardless of the phase I/phase II crystal modification ratio. Lack of cohesion at the interface of the layers suggests a parallel packing of the chains in these lamellae, with opposite chain direction in the two layers. A domain structure is observed in many of the lamellae and is presumed to be related to propagation of defects in phenyl ring and molecular direction on close packed planes in the two crystal forms. The presence of fibrils connecting fractured lamellae indicates some form of surface connection of neighbouring 'extended chain' molecules in a layer, similar to the folding of flexible molecules in lamellar crystals of, for example, polyethylene.

**(Keywords: morphology; polymerization; polyethylene)**

## INTRODUCTION

Recently we described a technique to grow, by polymerization between glass slides, single crystals of poly(*p*-oxybenzoate) (PpOBA)† of suitable orientation and thinness for electron diffraction (ED)[1,2]. These crystals were either grown by polymerization in a Therminol 66‡ solution or from the monomer melt. In this paper we describe scanning electron microscopy (SEM) observations of the PpOBA material that formed in the bulk solutions surrounding the slides, observations which have both raised significant questions concerning currently proposed polymerization mechanisms in the literature and provided some answers.

PpOBA and related copolymer 'rigid rod' liquid crystal polymers (LCPs) can be polymerized by condensation polymerization in a high temperature monomer solvent. Two related mechanisms of polymerization are generally accepted, depending on the concentration[3]. In both cases the initial steps involve the formation of short chain oligomers which crystallize out of solution at a degree of polymerization (DP) of 10 or less to form paraffin-like, i.e. extended chain, lamellar crystals by lateral aggregation. In dilute solutions further chain growth was suggested to occur by simultaneous crystallization and polymerization of oligomers on the two 'end' surfaces (i.e. the top and bottom, containing the ends of the molecules), both of which remain active yielding lamellar crystals whose thickness is the same as the polymer molecular length. With more concentrated solutions 'multilayered' lamellar (or 'slab-like') crystals grow from solution, the oligomers adding more or less end to end within a lamella before joining by polymerization. Although the authors describe horizontal lines within individual lamellae presumed to correspond to the oligomer end groups, this would seem to require no variation in length of the precipitating oligomers. If the polymerization–precipitation temperature is below the crystal–liquid crystal transition ($T_{c\text{-}lc}$) it was suggested that further polymerization (chain growth) does not occur, the ends being unable to approach each other when 'locked' in the crystal lattice. If axial translation is possible (i.e. above $T_{c\text{-}lc}$) polymerization may proceed, the end result again being lamellae in which the chain length equals the lamella thickness.

Although the monomers and polymers are polar, i.e. have a direction to their backbone, there is as yet no evidence as to whether the chains are parallel, antiparallel or randomly directed in the resulting crystals. In addition, although chain folding has been suggested to occur in the as-polymerized lamellae[3–5], there has neither been evidence nor a plausible mechanism presented for it. It would seem to require end-linking of neighbouring chains, a feature which would require both an antiparallel packing of neighbouring chains and a more than expected flexibility and mobility, even if the link is made by the addition of a hairpin-shaped oligomer rather than reaction between two neighbouring chain ends.

Recently Taesler *et al.*[6] have extended the above mechanism to incorporate a proposal for the growth of whiskers of PpOBA, these structures being formed during polymerization in dilute solutions. They suggest that in the case of sufficiently dilute solutions, end-linking of the oligomers occurs during precipitation on the chain end surfaces as above, whereas oligomers on the lateral surfaces, which presumably have not reacted, may

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[†] Also described as poly(hydroxybenzoic acid) or poly(acetoxybenzoic acid) depending on the monomer used

[‡] Trademark of Monsanto Co. for a heat transfer fluid containing bi- and triphenyls

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actually redissolve as the concentration of monomer in the solution is depleted by the polymerization.

Two orthorhombic crystal structures have been described for the as-polymerized PpOBA[5]; phase I has unit cell parameters $a=7.52$ Å, $b=5.70$ Å, $c=12.49$ Å while phase II, based on our single crystal ED results[1], has $a=11.06$ Å, $b=3.78$ Å, with $c$ being reported[5] as 12.6 Å.

## EXPERIMENTAL

*Para*-acetoxybenzoic acid was obtained from Aldrich Chemical Co. Solutions of the monomer, usually 1/5 by wt/vol, in Therminol 66 were prepared at temperatures of *c.* 250°C. Several drops of the liquid were placed between glass microscope slides which were usually stacked six high, clipped together and then immersed in the residual solution in an Ehrlenmeyer flask and heated, in a heating mantle, to the desired temperature.

The flasks were not stirred. In general, for the samples described here, the reaction was allowed to proceed until acetic acid evolution ceased. Following polymerization of the PpOBA and removal of the slides for use for ED and transmission electron microscopy (TEM), the material polymerized in the bulk solution was filtered, washed with acetone in a Soxhlet extractor overnight to remove residual monomer, and dried for SEM observation, d.s.c. and X-ray analysis. It is noted that the crystal–liquid crystal transitions of the materials grown in the bulk solution and between the slides, on first heating as well as cooling and second heating scans, in a given preparation were remarkably close (0.2°C) despite the difference in thickness of the lamellae for the two samples (3–500 Å for the material grown between slides *versus c.* 0.5 $\mu$m for the bulk material)[1]. X-ray scans of the powders were run, in reflection, on a Scintag PAD-X $\theta$-$\theta$ diffractometer.

## RESULTS AND DISCUSSION

*Table 1* lists the conditions of polymerization of the various samples described below along with their $T_{\text{c-lc}}$ (on a first heating scan, as shown in *Figure 1*). The DP is not known. Using the data of Economy *et al.*[7] relating $T_{\text{c-lc}}$ to DP suggests all of the samples have a DP above 90. $T_{\text{c-lc}}$ is seen to generally increase with increasing polymerization time and temperature, suggesting, as expected, an increase in molecular weight.

Also listed in the table is the ratio of the intensities (peak height above background) of the $110_{\text{I}}$ and $200_{\text{II}}$ reflections as an indication of the relative amount of phase I and phase II crystals in the samples. The amount of amorphous scatter in all of the samples was essentially zero. For the value listed, the $110_{\text{I}}$ peak height has been divided by two due to its multiplicity; $200_{\text{I}}$ could not be used due to overlap with another reflection. Our results appear to agree with the data of Lieser (samples 1–4, Tables I and II in ref. 5), the relative amount of phase II increasing with increasing molecular weight.

*Figure 2* shows an SEM photo of sample 1. Although a domain structure similar to that shown here was seen on other samples as well, it was most clearly seen on this sample. Various angles close to 60° and 90° are seen between the striations on the 'end' surfaces. The 0.8 $\mu$m thick lamellae appear to be made up of small plates of similar thickness (*c.* 600 Å) and varying width oriented normal to the lamellae (or slab-like crystals as termed in the papers by Lieser *et al.*[3] and Economy *et al.*[4], for instance). It is not known whether this observed morphology develops during acetone washing, by removal of intervening low molecular weight material, or develops in this form during polymerization. In either case it is clear that the polymerization within a lamella is not homogeneous. As shown by the TEM and ED studies described below, we suggest the domains

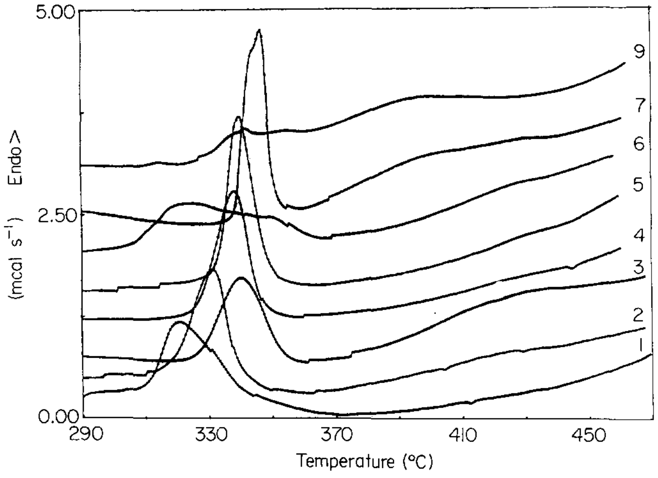

**Figure 1** D.s.c. scans for many of the samples described below. The first heating scans are shown. Curves are labelled with sample number. Insufficient whisker sample (sample 8) was available to measure

**Table 1** Polymerization conditions for bulk solution-polymerized samples

| Sample no. | Conc.[a] (wt/vol) | Polymerization temperature, $T_p$ (°C) | Polymerization time, $t_p$ (h) | $T_{\text{c-lc}}$ (°C) | Length, $l$ ($\mu$m) | $I_{110_{\text{I}}}/2I_{200_{\text{II}}}$[b] |
|---|---|---|---|---|---|---|
| 1 | 1/5 | 295 | 1.5 | 320 | 0.8 | 1.8 |
| 2 | 1/5 | 300 | 1.5 | 328 | 0.8 | 2.4 |
| 3 | 1/5 | 290–300 | 7 | 340 | 0.8 | 2.4 |
| 4 | 1/5 | 300 | 10 | 336 | 1.3 | 1.7 |
| 5 | 1/5 | 300–350 | 5 | 340 | 0.3–1 | 1.9 |
| 6 | 1/25 | 300 | 2 | 325 | 3 | 2.7 |
| 7 | 1/100 | 350 | 7 | 346 | 1.6 | 1.0 |
| 8 | 1/70 (mineral oil) | 330 | 6 | – | – | – |
| 9 | 1/70 (paraffin) | 330 | 6 | 342 | 0.1 and 3 | 5 |

[a] In Therminol 66 unless noted
[b] Ratio is related to relative amount of phase I and phase II in the samples

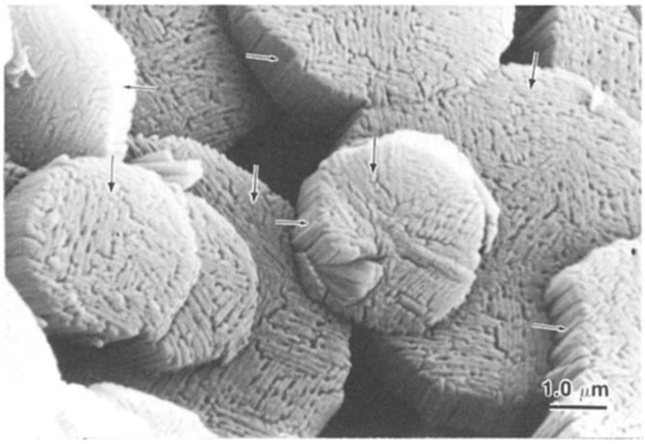

**Figure 2** SEM photo of sample 1 ($T_p = 295°C$, $t_p = 1.5$ h in 1/5 Therminol 66). The large arrows indicate 'end' surfaces, the small arrows lateral (growth) surfaces of the lamellae

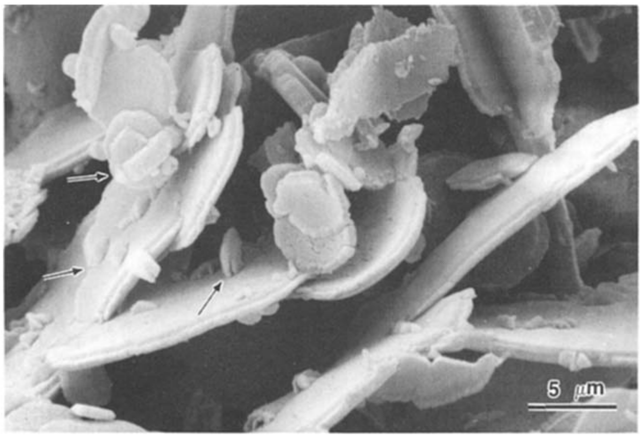

**Figure 3** Sample 2 as polymerized ($T_p = 300°C$, $t_p = 1.5$ h, 1/5 Therminol 66). Arrows indicate lamellar overgrowths at 90° to the end surfaces

correspond to differences in lattice orientation, i.e. the lamellae are not single crystals, but do have correlated lattice orientations and may consist of both phase I and II.

*Figures 3* and *4* are of sample 2, a sample polymerized for the same time, but at a temperature 5°C higher than sample 1. Although of approximately the same total thickness (0.8 μm), they are considerably wider. In particular, however, most of them are clearly bilayered whereas there was no visible evidence for bilayering in sample 1. Only a few of the crystals near the centre of *Figure 3* may be monolayer lamellae. It is noted that in this sample, in contrast to those in *Figures 6*, *12* and *13* below, the lateral size of the two bilayers in a single lamella differ, permitting their clear observation. In many cases, however, the two layers are of the same width, with only a line on the lateral growth faces showing the presence of bilayers.

The lateral surfaces or edges of the lamellae in sample 1 are straight; in sample 2, however, they are tapered (shown most clearly by the large arrows at the upper left and right of *Figure 4*). At the upper right of *Figure 4* there is some evidence of plates at the edge of the crystal; the surface texture does not show a domain structure although porosity is present.

Interestingly, the thickness of these lamellae, as well as that of nearly all of the lamellae in the preparation (and also those in other isothermal preparations) is nearly the same regardless of the lateral dimensions. This, we suggest, implies that the thickness of the lamellae is determined by the thickness (or length in the molecular axis direction) of the nucleus, oligomers only adding on to the lateral sides of the nucleus and lamellae, but not to the end surfaces. When addition on the end surfaces occurs, it appears to often occur with the molecular axes of the new lamellae lying on the surface, possibly through some form of epitaxy. The resulting lamellae grow at 90° angles to the 'end' surface of the original lamella (arrows on *Figure 3*).

Of particular interest relative to the mechanisms of polymerization is the effect of the ultrasonic treatment used in an attempt to disperse the lamellae. As shown in *Figure 4*, not only do the fracture surfaces reveal that the lamellae are of essentially uniform thickness across their cross section but, in addition, there is no cohesion to the bilayers over most of their interface. With the molecules being polarized, we suggest the bilayers form by the oriented, oppositely directed crystallization of the initial oligomers, with subsequent oligomer crystallization preserving that opposing orientation; thus end-linking cannot occur across the interface. As shown by the smaller arrow in *Figure 4* there is some evidence that at the edge of the crystal the interface has become coherent; here randomly oriented or antiparallel oligomer crystallization may have occurred.

Unfortunately, it is not known whether these lamellae are phase I or II crystals (or contain domains of each). The X-ray scan for this sample suggested there was about 2.5 times as many phase I crystals as phase II; there is no corresponding morphological variation.

*Figure 5* is from another region of the same powder as in *Figure 3*. A domain structure is visible on the surface of some of these crystals. Only a few of them show clear evidence (line on the lateral surface, larger headed arrows) of being bilayered. There are thin layers on the surfaces of some of the lamellae (small arrows). These layers, we suggest, are the result of the infrequent addition of a single layer of oligomer which is spreading across the end surface. In addition, there are lamellae which are thinner than the majority of those present. These appear to be lamellae growing on the surface of larger lamellae, thus restricting the volume of solution available to the lateral edge; it is not known if they are also bilayers.

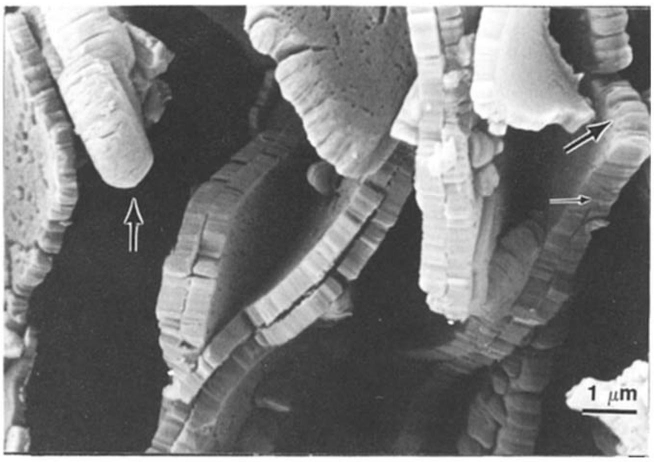

**Figure 4** Ultrasonically dispersed sample 2. The lack of bilayer cohesion in the interior of the lamellae is evident. The large arrows indicate tapered lateral edges. Further lateral growth beyond the small arrow appears to be as a monolayer

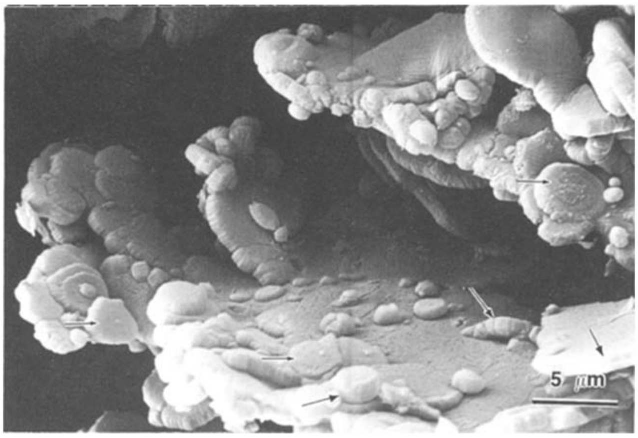

**Figure 5** Another region of sample 2. The arrows indicate thin layers spreading over the end surfaces of the lamellae, possibly due to oligomer crystallization. A domain structure on the end surface, consisting of parallel striations, is present on the lamellae at the top right

**Figure 6** Sample 3 ($T_p = 290$–$300$°C, $t_p = 7$ h, 1/5 Therminol 66). The arrows indicate evidence of a bilayered lamellar structure on fracture faces, with the large-headed arrows indicating the position of the beginning of a gradual thinning of the lamellae near the outer edge

The uniformity in thickness raises a significant question relative to the previously proposed[3,6] mechanisms of polymerization; on the basis of that mechanism one would expect the thickness of the centre of the lamella, which has existed for a longer time, to be thicker. The tapering at the edges suggests that oligomer (and monomer) addition occurs primarily at the edge of the crystal, up to some maximum thickness, and then stops, i.e. that growth is not occurring on the end surfaces.

Two samples were prepared under temperature conditions as samples 1 and 2, but with longer polymerization times (samples 3 and 4; 290–300°C, 7 h and 300°C, 10 h respectively). Fracture faces of the lamellae *c.* 0.8 µm thick in sample 3 (*Figure 6*) again reveal the presence of bilayers (arrows); there is no appearance of a lack of cohesion. The lamellae are approximately the same thickness as in samples 1 and 2. This sample is the only sample that showed a gradual decrease in thickness on the outer edge of the lamellae, possibly due to the variation in temperature during polymerization, as well as a tapered lateral face within *c.* 1000 Å of the edge. The gradual decrease in thickness is best seen on the fracture faces indicated by the large headed arrows. The portion of this sample polymerized between slides is shown in *Figure 21*.

Polymerization for a longer time than for sample 2, but at the same temperature, resulted in lamellae with a smaller diameter, but increased thickness (sample 4, *Figure 7*). Some of the 1.3 µm thick lamellae are still bilayers. All have slightly tapered lateral surfaces, giving rise to a 'rounded' lateral surface, and porous end surfaces; the 'platelets' making up these lamellae appear to be more rod-like than planar and no domain structure is obvious. These lamellae were not dispersed and thus we do not know the cohesion at the bilayer interface; the rods appear to be coherent across the interface.

During polymerization of sample 5 the temperature fluctuated; possibly as a result, a multitude of morphologies were observed (*Figures 8–15*). *Figures 8* and *9* show a region consisting of an apparent mixture of *c.* 0.6 µm thick platelets and whiskers or ribbons of similar dimensions in two directions. Two of the aggregates are shown at higher magnification in *Figure 7*. There is a suggestion in these aggregates that the centre consists of one or more lamellae with the ribbons growing out from both the lateral edges and the end (molecular) surfaces. This effect can be seen even more clearly in *Figure 10*, with ribbons growing out from two ends of the lamella, at a shallow angle to its end surface (near the centre of the lamella) and normal to this surface. The ribbons growing normal to the surface, we assume, were

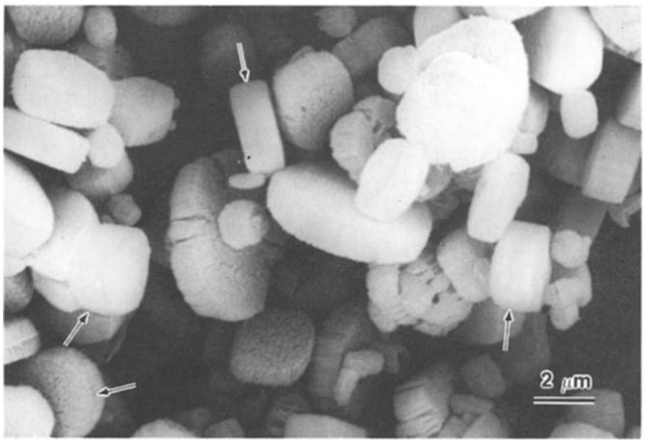

**Figure 7** Sample 4 ($T_p = 300$°C, $t_p = 10$ h, 1/5 Therminol 66). Arrows indicate traces of the bilayer interfaces. The lamellar thickness is the same regardless of the disc's lateral dimensions. A porous end surface, with the lamellae being composed of rods, is evident

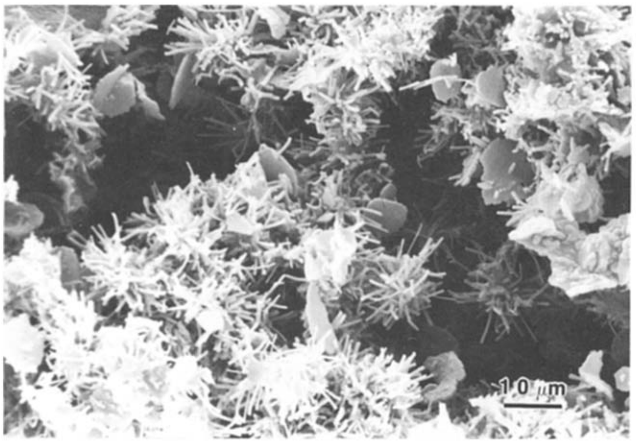

**Figure 8** Low magnification view of a portion of sample 5 ($T_p = 300$–$350$°C, $t_p = 5$ h, 1/5 Therminol 66). Lamellae and ribbons are present

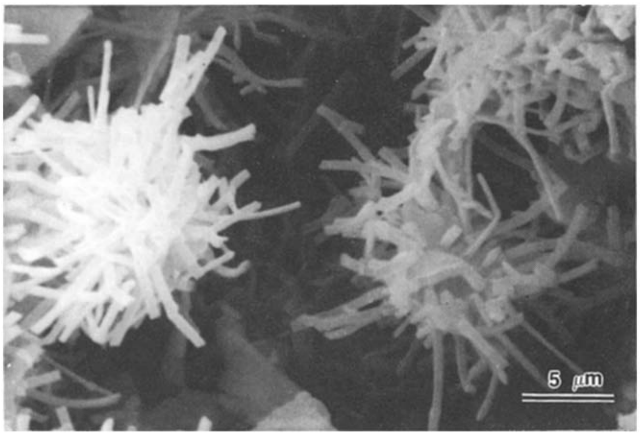

**Figure 9** Higher magnification of a region of sample 5 similar to that in *Figure 8*

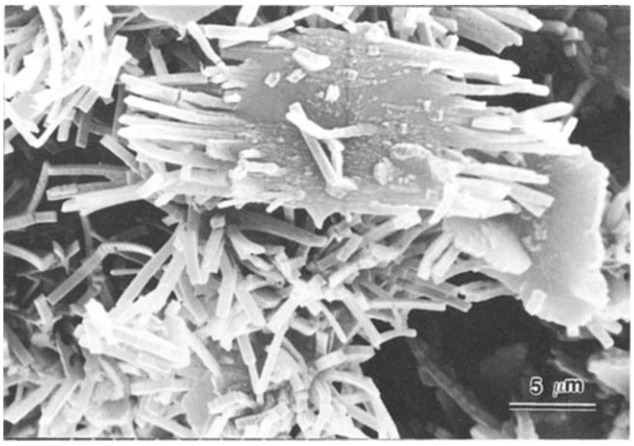

**Figure 10** Isolated lamella from sample 5. Ribbons are seen to be growing from two ends of the lamella as well as from its surface

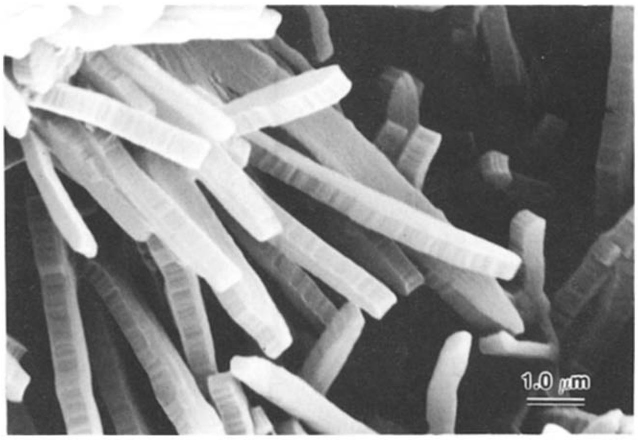

**Figure 11** Higher magnification of lamella shown in *Figure 10*. The ribbons appear to be monolayers, with a smooth end surface and striations on the lateral faces. They are uniform in thickness

broken during handling resulting in only short stubs remaining. Smaller overgrowths can be seen forming rows on the lamella surface. The ribbons or 'fingers' are shown at higher magnification in *Figure 11*. They are seen to be uniform in thickness in the chain axis direction (striation direction), but to vary slightly in width; the end surface is relatively smooth. The structure shown in *Figure 10* is highly reminiscent of the phase II crystals grown between slides in sample 2[1], even though those lamellae and ribbons were an order of magnitude thinner. It is not known, however, whether these crystals are also phase II. None of these lamellae or ribbons appear to be bilayers.

Most regions of the same powder (*Figure 12*, from the same SEM stubs as *Figures 8–11*) had spherical aggregates of either thin ($\sim 0.3\,\mu$m, left and lower) or thick ($\sim 1\,\mu$m, centre and upper right) lamellae. Within each aggregate the lamellae are again of near uniform thickness, suggesting a nucleus determined thickness. More or less single lamellae are present at the right hand side of the photo. The thick lamellae, shown at higher magnification in *Figure 13*, are again bilayers, but with a non-planar interface.

The wide diversity of types of morphologies localized in regions in the powder, we suggest, is related to the fluctuating temperature during polymerization. In combination with the observations of a uniform thickness in individual lamellae, regardless of their morphological organization, we suggest the different types of structure reflect differing conditions at their time of nucleation (i.e. temperature and concentration). We also suggest that lateral growth of the individual lamellae (and their aggregates when present) is rapid but that longitudinal growth, along the molecular axes, is essentially non-existent. Monomer addition, for example, might occur at temperatures high enough for simultaneous polymerization, but oligomer addition, if it occurs, is primarily in the form of the oligomer axes lying on the

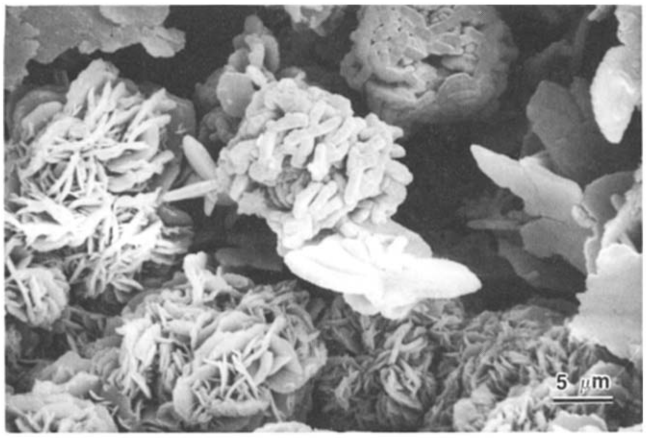

**Figure 12** Another region of sample 5. Spherical aggregates of thick or thin lamellae are present

**Figure 13** Higher magnification of a 'thick' lamella aggregate as in *Figure 12*. The bilayer interface is irregular

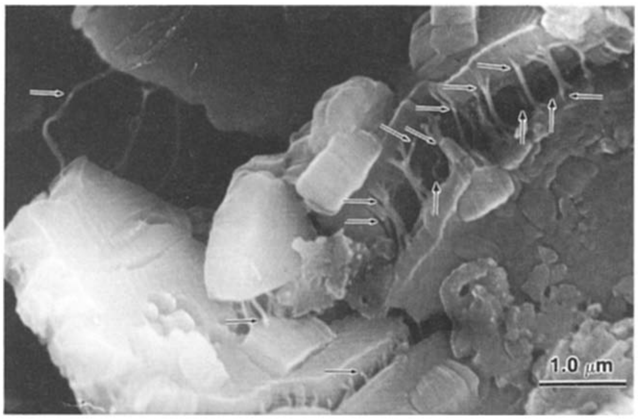

**Figure 14** Ultrasonically dispersed sample 5. The small-headed arrows indicate 'bright spots' on the fibres that appear to correspond to the original surface of the lamellae. The large-headed arrows indicate another set of fibres connecting an underlying lamella. A domain structure is evident on the end surface of the lamella at the left

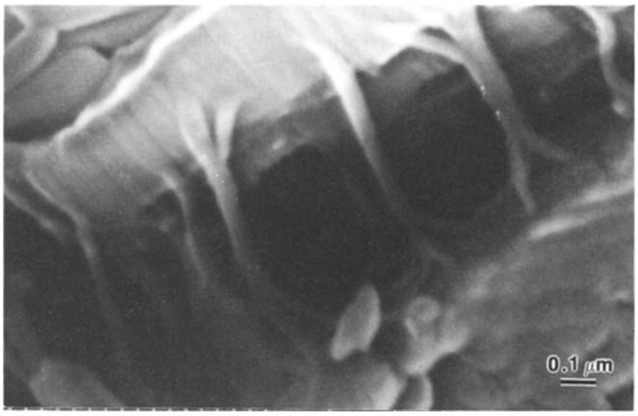

**Figure 15** Higher magnification view of a portion of *Figure 14*

end surface giving rise to the growth of new lamellae at 90° angles to the old. Only occasionally (as in sample 2, *Figure 5*) is there addition of oligomers on the end surfaces with a common axis to those of the underlying lamellae. When this occurs it permits lateral addition of additional oligomers to this 'secondary nucleus' and a spreading of a thin layer across the end surface.

The rapid lateral growth is consistent with the observation of regions of similar morphological structure in the powder, differing from region to region. These regions may well correspond to the varying conditions of polymerization, a given type of morphology being nucleated and 'rapidly' grown at some particular temperature and concentration and then settling out of solution; these samples were not stirred during polymerization, permitting the structures successively nucleated and grown to layer out in the precipitated powder. The non-stirring also permitted observation of all of the as-polymerized materials in a non-damaged state.

A portion of sample 5, consisting primarily of *c.* 0.5 μm thick lamellae, was treated ultrasonically in ethyl alcohol for 50 min at room temperature in an attempt to disperse the powder as well as to seek evidence for bilayering. A domain texture is present on the surface (*Figure 14*), again oriented at *c.* 60 and 90° angles, but of even more interest was the observation of fibres connecting opposite fracture faces of individual lamellae. As shown in *Figures 14* and *15*, these fibres appeared to be stripped off the fracture face, being related to the striations on the fracture face, and are longer than the thickness of the lamellae. Although possibly not obvious in the reproductions, bright 'spots' are seen on the fibres at points (small arrows) that appear to correspond to the original 'end' surface of the lamellae. In addition, there is another set of fibres (larger headed, vertical arrows) below the most obvious ones on the right side of *Figure 14*, which appear to connect a second underlying lamella.

Clearly there is some form of connection of the ends of neighbouring molecules or clusters of molecules on the end surfaces of the lamellae. Whether these connections are in the direction of the striations giving rise to the domain texture or at other directions is not yet known. Although it is tempting to propose the presence of folds on the surface, either of individual molecules or the clusters, we know of no other evidence for their existence. We also recognize, despite several suggestions for their existence in the literature[3–5] without any evidence, that tight molecular folds would be difficult, if not impossible, to form during crystallization of pre-existing molecules due to the stiffness of the backbones, and they are unlikely to form during polymerization. For the latter to occur would require both a hairpin conformation for an adding oligomer (where we have already suggested end-surface oligomer addition is unlikely) and antiparallel directions for the two molecules being connected. The only possibility that seems even feasible is a suggestion of Miller[8] that if ring oligomers are present in the solution, these could break and add to the end surfaces to form the 'folds'. Even this suggestion, however, requires the unlikely end-surface addition to antiparallel chains. On the other hand, the presence of such connections on the surface would clearly prevent any further end-surface oligomer addition and thus contribute to the uniformity in thickness.

When polymerization was carried out from a more dilute solution (sample 6, *Figure 16*) for relatively short times, thick (*c.* 3 μm) relatively small-diameter aggregates of rod-like particles formed. These have an end-surface texture as well as coarse lateral-surface striations. Although in most cases the rods are parallel within an aggregate, occasionally they are seen to grow out at slight angles (arrows) to the majority of the rods. In other cases the rods appear to be platelet-like, i.e. anisotropic in their lateral dimensions. It is possible that these structures are

**Figure 16** Sample 6 ($T_p = 300°C$, $t_p = 2$ h, 1/25 Therminol 66). The 'lamellae' are more or less cylinders composed of rods or ribbons. Shallow-angle branching of the rods is seen in some regions (arrows)

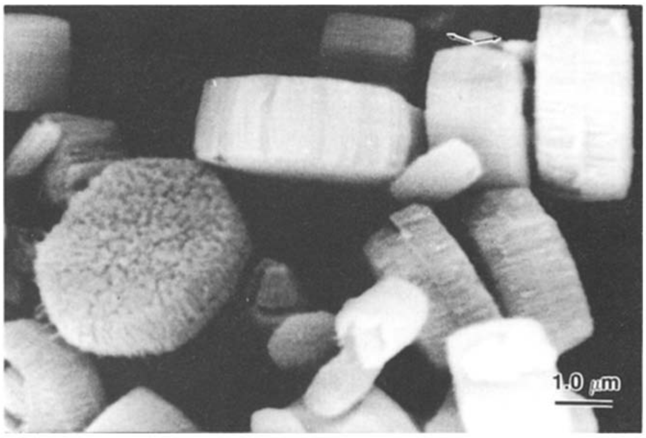

**Figure 17** Sample 7 ($T_p=350°C$, $t_p=7$ h, 1/100 Therminol 66). Bilayered, disc-like lamellae of various diameters are seen, similar to those in *Figure 7* (sample 4), although from a much more dilute solution. Arrows at upper right indicate taper of the lateral faces

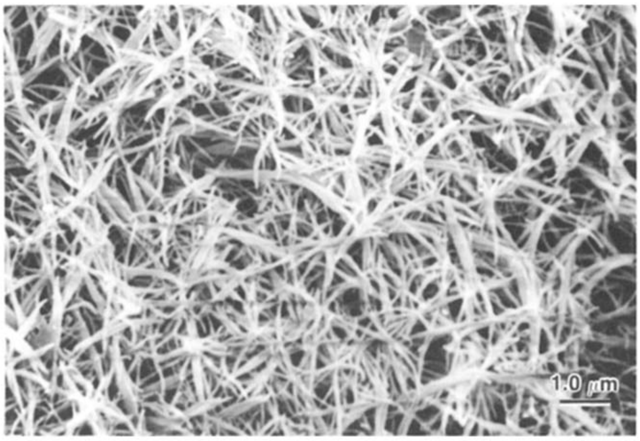

**Figure 18** PpOBA whiskers in sample 8 ($T_p=330°C$, $t_p=6$ h, 1/70 mineral oil)

intermediate between the whiskers grown in very dilute solution (Taesler *et al.*[6]) and the lamellae. The nucleus of the aggregate we suggest, as above, was a 'rod' with length equal to the thickness of these small-diameter lamellae. Lateral growth has occurred, to a limited extent, apparently by the 'addition' of further rods, each of which is relatively coherent and acetone resistant, due to end-linking at random locations along the rod's length, but with relatively little rod to rod interaction. Further end growth has been arrested both by the low concentration and, possibly, short time of polymerization.

Unexpectedly, however, polymerizing from an even more dilute Therminol 66 solution (1/100), at a higher temperature (350°C) led to disc-like, bilayered lamellae (sample 7, *Figure 17*). Relatively small-diameter cylinders are also present. These lamellae, regardless of their diameter, are all *c.* 1.6 µm thick. They have slightly tapered lateral faces (arrows) with a clear centre line and a porous surface. They appear to be composed of rod-like particles, with no domain structure being evident. It is not clear whether the rods extend across the bilayer interface. The lamellar thickness of both of these dilute solution samples, sample 6 being about three times as thick as from the 1/5 solutions, suggests an inverse effect of concentration on lamellar thickness, possibly similar to that proposed by Taesler *et al.*[6].

Using a 1/70 mineral oil (liquid paraffin) solution, as used by Yamashita *et al.*[9], we also obtained whiskers (sample 8, *Figure 18*). Since our mineral oil solution also was not stirred, the lack of full whiskers in the 1/100 Therminol 66 solution-polymerized sample cannot be attributed to a lack of stirring; rather than concentration alone it may be related to the solvent used or, as shown by Kricheldorf *et al.*[10], it may be that a small amount of impurity is poisoning the whisker growth in sample 7. The fact that sample 8 did yield whiskers suggests that the impurities are not present in the monomer, but may have developed due to the polymerization temperature or solvent used.

These whiskers are phase I, ED patterns as a function of temperature showing a transformation at *c.* 330°C to a pattern consisting of several orders of equatorial reflections, a 2 1 1 reflection and the meridional reflections[11], in agreement with the X-ray results of Yoon *et al.*[12] and Coulter *et al.*[13], for instance, and the ED results of Li *et al.*[14,15] for pOBA/mOBA 95/5 copolymer sheared films.

Confirmation that concentration alone is not the total answer to the formation of whiskers, but that the choice of solvent also plays a role, is shown by *Figures 19* and *20* (sample 9). Although most of the material in this sample, polymerized in ordinary paraffin wax, consisted of small-diameter more or less cylindrical aggregates of rod-like particles, as in *Figures 16* and *17* (arrows in *Figures 19* and *20*), extremely large, thin and a few thick lamellae were observed. The thin lamellae are 600–1200 Å thick; whether or not they are bilayers is not clear. The thick lamellae seem to have a relatively coherent surface film that was absent or washed away (with the acetone) over much of the crystal, and a highly porous interior. We have no explanation at present for the relatively isolated growth of these large platelets; clearly this solvent is worthy of further consideration.

The individual isolated crystals grown from solution between slides appear to be single domains, although with a granular texture possibly related to the rods seen in the bulk solution-polymerized material. *Figure 21a* is a dark field micrograph of thin film crystals from sample 3, with the corresponding bright field micrograph in *Figure 21b*. These crystals are similar to those of sample 2 described previously (Figure 1, ref. 1) except for their somewhat shorter 'fingers'. As in the case of the bulk solution-polymerized samples, it is not known if the rough surface and granular texture is a result of the removal of intervening low-molecular-weight material by the

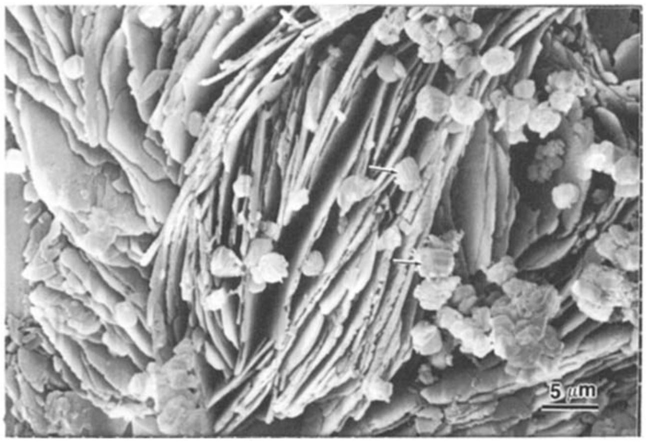

**Figure 19** Sample 9 ($T_p=330°C$, $t_p=6$ h, 1/70 paraffin). Thin lamellae and cylindircal aggregates of rod-like particles (arrows) are present

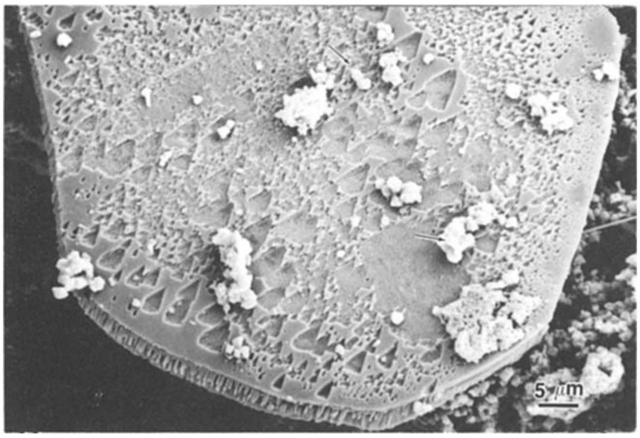

**Figure 20** A large, thick PpOBA lamella from sample 9. The 'debris' on the surface are the cylindrical particles in *Figure 19*. In regions where the coherent end-surface film is absent (possibly etched with acetone) a porous interior is revealed which is also evident on the lateral face

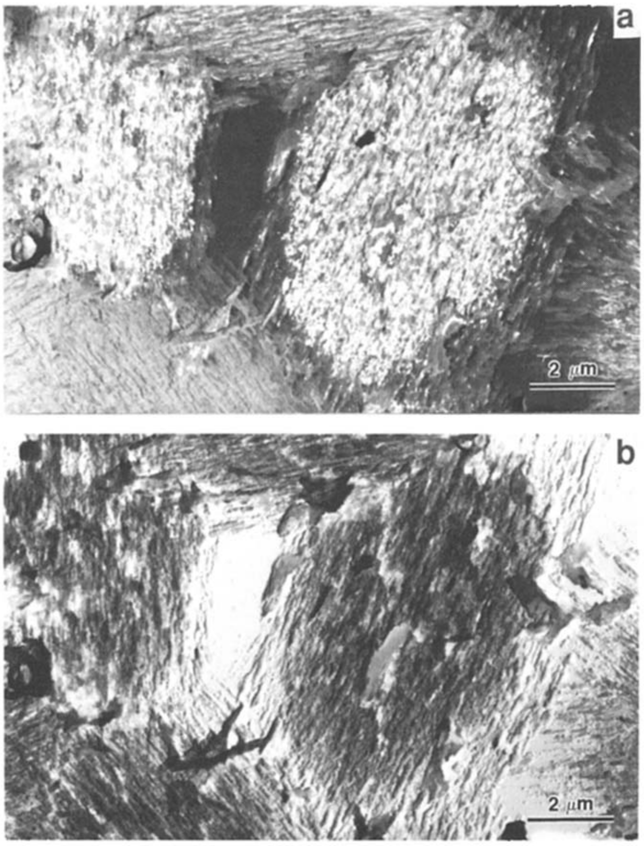

**Figure 21** (a) Dark and (b) bright field TEM micrographs of the thin-film (phase II) solution-polymerized crystals in sample 3

acetone wash or if the growth occurs in this fashion. In both types of sample, the presence of a common lattice orientation over large selected areas suggests that the rods are not independent entities, but must somehow be related to an inhomogeneous end-linking process in already crystallized oligomers or, possibly, lateral shrinkage of the lattice during polymerization.

The inhomogeneous polymerization in the solution-polymerized material differs markedly from the situation in melt polymerization. *Figures 22a* and *b* are bright and dark field micrographs of (different) thin film melt-polymerized PpOBA crystals (180°C, 71 and 24 h, respectively), also washed with acetone after polymerization (see ref. 16 for further details). The crystal in *Figure 22a* consists of lamellae *c.* 80 Å thick; the elongated laths correspond to phase II with the broader lamellae possibly corresponding to phase I. In this crystal the *a* axes of phase II are at 0 and ±60°, $a_{\mathrm{II}}$ being parallel to the 'cracks' in the crystals. In the dark field micrograph (using $200_{\mathrm{II}}$), the perfection of the lattice, as shown by the Moire lines, extends for large distances. As shown by the diffraction patterns in *Figure 23*, in other melt-polymerized crystals, branching of phase II occurs at angles of 63–64° or 75° to the main phase II growth direction, and at ±19° (*a* axis direction) to the phase I *b* axis. These angles are presumably related to the angles between various close-packed planes in the crystals, the branchings corresponding to the propagation of defects in phenyl ring orientation and/or chain direction.

## CONCLUSIONS

It is recognized that this has not been a comprehensive study of the effect of polymerization time, temperature and concentration on the morphology and polymerization mechanisms of PpOBA; such a project is now in progress. Even at this stage, however, it is clear that it is advantageous for morphological observations not to stir the polymerizing solution. Based on the various micrographs and data above we can draw the following conclusions:

1. Many, but not all, of the lamellae polymerized at various temperatures in Therminol 66 develop as bilayers. The relative number suggests that they consist of phase I and phase II; on the other hand bilayers

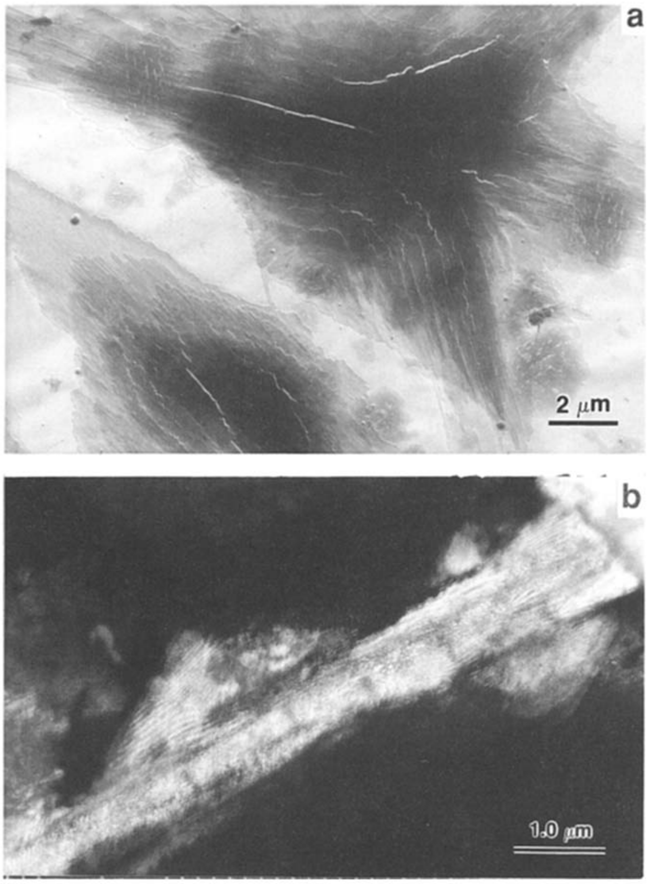

**Figure 22** (a) Bright and (b) dark field TEM micrographs of thin-film melt-polymerized PpOBA ($T_p = 180°C$, $t_p = 24$ h (a) and 71 h (b)

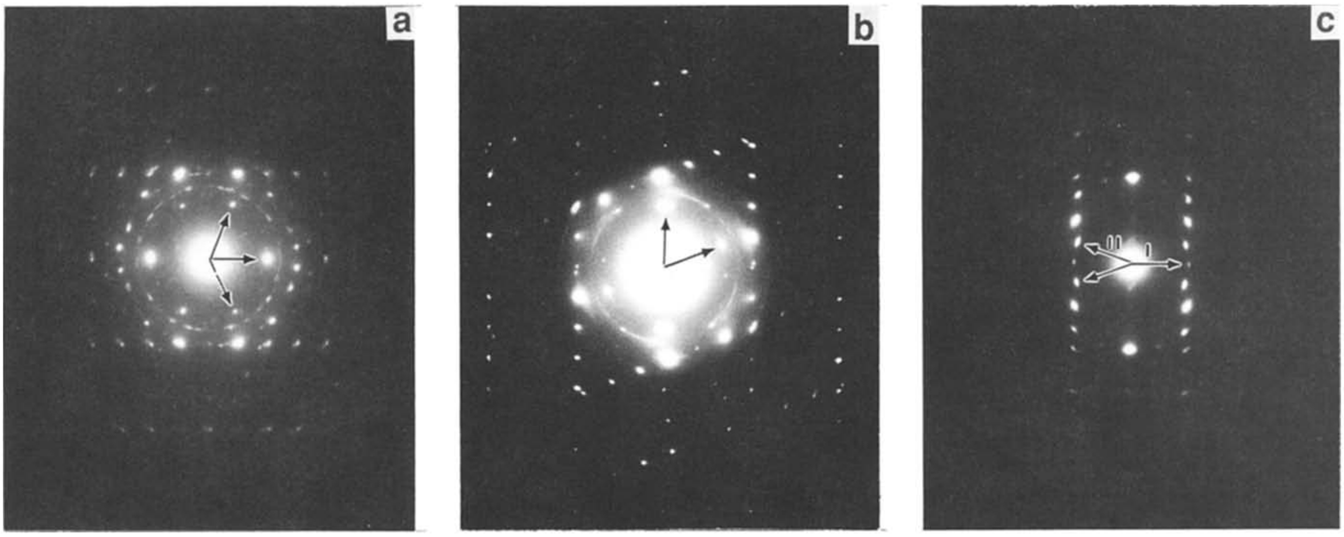

**Figure 23** Electron diffraction patterns (selected areas 7 μm in diameter) of thin-film melt-polymerized PpOBA with various domain textures. (a) Three phase II patterns at 0 and ±63°; (b) two phase II patterns at 0 and 73°C; (c) a phase I pattern and two phase II patterns at ±19° (angle between $a_{II}$ and $b_I$)

have been clearly observed for thin film melt-polymerized PpOBA phase II crystals but, at the time of writing, bilayers for phase I crystals have not yet been clearly observed[16]. In as much as the presence of the bilayers with, in some cases, a lack of cohesion at the interface, suggests a parallel packing of the chains in each layer in opposite direction in the layers, clarification of the relationship of the phases to the presence of bilayers should help clarify the molecular orientation in the two crystal phases.

2. As suggested in the literature[3,4] $T_{c\text{-}1c}$ appears to increase with increasing time and temperature of polymerization; this has been suggested to be due to an increase in molecular weight due to end-linking of oligomers in the lamellae. No clear correlation of the ratios of phase I to phase II or lamellar thickness with polymerization conditions was observed for this limited set of samples.
3. The morphological observations suggest that the thickness of the lamellae is determined primarily by the thickness (length) of the nucleus, with oligomer addition primarily on the lateral faces of the lamellae. There are suggestions that individual lamellae grow rapidly to their final dimensions and then settle out of solution in these unstirred samples.
4. In a sample in which the lamellae were fractured while being ultrasonically dispersed, fibres were stripped off the fracture faces which were longer than the thickness of the lamellae. The fibres suggest the presence of connections of neighbouring molecules, or clusters thereof, at the surfaces of the lamellae, i.e. some form of folds.
5. In many of the samples, a domain structure is observed on the end surfaces; it is proposed that it is related to various, lattice-related orientations of the phase I and II crystal forms.
6. The presence of rods and/or platelets oriented normal to the end surfaces of the lamellae and of the same length as the lamella thickness, suggests inhomogeneous end-linking of the oligomers in the crystals. Melt polymerization, on the other hand, results in uniform, essentially perfect lamellae (see ref. 16 for more details).
7. In agreement with Yamashita *et al.*[9] and Taesler *et al.*[6], polymerization in dilute solution Therminol 66 and mineral oil generally results in thicker, small-diameter lamellae, with whiskers being the extreme. However, in dilute paraffin both small-diameter thick lamellae (cylinders) and large lateral dimension, thin and thick lamellae formed.

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## REFERENCES

1 Liu, J. and Geil, P. H. *J. Macromol. Sci.* (*Phys.*) 1992, **B31**, 163
2 Liu, J., Rybnikar, F. and Geil, P. H. *J. Macromol. Sci.* (*Phys.*) in press
3 Lieser, G., Schwarz, G. and Kricheldorf, H. K. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1599
4 Economy, J., Storm, R. S., Matkovich, V. I., Cottis, S. G. and Nowak, B. E. *J. Polym. Sci., Polym. Chem. Edn* 1976, **14**, 2207
5 Lieser, G. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1611
6 Taesler, L., Petermann, J., Kricheldorf, H. K. and Schwarz, G. *Macromol. Chem.* 1991, **192**, 2255
7 Economy, J., Volksen, W., Viney, C., Geiss, R., Siemens, R. and Karis, T. *Macromolecules* 1988, **21**, 2777
8 Miller, R. Midland, MI, personal communication, 1992
9 Yamashita, Y., Kato, Y., Endo, S. and Kimura, K. *Makromol. Chem., Rapid Commun.* 1988, **9**, 687
10 Kricheldorf, H. R., Ruhser, F., Schwarz, G. and Adebahr, T. *Makromol. Chem.* 1991, **192**, 2371
11 Liu, J., Rybnikar, R. and Geil, P. H. paper presented at American Chemical Society meeting, San Francisco, CA, April 1992
12 Yoon, D. Y., Masciocchi, N., Depero, L. E., Viney, C. and Parrish, W. *Macromolecules* 1990, **23**, 1793
13 Coulter, P. D., Hanna, S. and Windle, A. H. *Liq. Cryst.* 1989, **5**, 1603
14 Li, L. S., Lieser, G., Eichin, R. R. and Fischer, E. W. *Makromol. Chem., Rapid Commun.* 1987, **8**, 159
15 Li, L. S. *Makromol. Chem., Rapid Commun.* 1989, **10**, 481
16 Rybnikar, F., Liu, J. and Geil, P. H. *Makromol. Chem.* submitted