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Lamellar macrocrystals of nascent liquid crystal polymers

A. Lucero, F. Rybnikar, T.-C. Long, J. Liu and P. H. Geil*
Materials Research Laboratory and Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

and B. Wall and J. L. Koenig
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA
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Large (up to 0.5 mm) single crystals of two liquid crystalline polymers, poly(*p*-oxybenzoate) (PpOBA) and the presumably random copolymer poly(*m*-oxybenzoate/2,6-oxynaphthoate) (1/1) [P(mOBA/ONA)], have been grown by the confined thin film melt polymerization technique at 180–200°C. These large, thick 'macro' crystals, as well as single disclination domains, form in regions in which the 'monomer melt' spans the gap between the confining surfaces; when the 'melt' only wets one of the surfaces thin, small crystals and single disclination domains are formed, as reported previously. When reheated to the polymerization temperature the copolymer disclination domains appear to revert to the liquid crystal state. The macrocrystals transform at the higher, 275°C d.s.c. measured T_{k-m} of the copolymer. All of these structures, however, are composed of *ca.* 100 Å thick lamellae for the growth conditions used. *FT*i.r. microscopy confirms the copolymer nature of the P(mOBA/ONA) samples. Copyright © 1997 Elsevier Science Ltd.

(Keywords: poly(*p*-oxybenzoate); poly(*m*-oxybenzoate/2,6-oxynaphthoate); liquid crystal polymers; lamellae; single crystals)

INTRODUCTION

We have previously described the growth, morphology and crystal structure of a number of nascent (as-polymerized) condensation polymers prepared by our confined thin film melt polymerization technique (CTFMP). Of particular concern here are prior reports on poly(*p*-oxybenzoate) (PpOBA)[1,2], poly(2,6-oxynaphthoate) (PONA)†[3] and the 1/1 copolymer poly(*m*-oxybenzoate/2,6-oxynaphthoate) [P(mOBA/ONA)][4]. In all cases lamellar single disclination domains and single crystals were described. The lamellae were *ca.* 100 Å thick regardless of the polymerization temperature and polymerization time for temperatures below the melting point of at least one of the monomers (e.g. for PpOBA from 130 to 180°C, with the monomer melting point being 196°C).

For most of the CTFMP samples the monomer was cast on a glass surface in a thin layer from dilute acetone solution, the sample was then covered with another glass and heated at the desired temperature. As shown in detail in refs 1 and 4, as the constrained monomer is heated it sublimes, then recrystallizes on both interior surfaces and subsequently 'melts', all at a temperature below the d.s.c. determined melting point of the monomer. For the samples described in the previous reports the liquid formed on both surfaces, wetting it to various degrees, but did not span the gap between the surfaces. For the samples shown in ref. 1 it appeared the lamellar disclination domains formed preferentially on the upper surface, and the lamellar crystals on the lower surface. Furthermore, there is generally a variation in morphology across any given surface (see, e.g. ref. 4). For the samples described here a similar preparation technique was used, the only difference being that thicker monomer films were cast, often on both surfaces, and after 'melting' the sample was compressed such that, in the regions of interest, the liquid spanned the gap between the surfaces. The growth of related macrostructures from random 1/1/1 terpolymers of *p*-acetoxybenzoic acid (pABA), hydroquinone, and various aliphatic diacids[5] will be described in a subsequent paper.

We know of no related work on the morphology of nascent, bulk melt, polymerized liquid crystal polymers except for two micrographs in our paper on CTFMP poly(4,4-oxybibenzoate)[6]. This material consisted of large blocks of 'fibrous' material that split readily both parallel and perpendicular to the fibre axis. Electron diffraction (ED) showed the fibres were actually single crystal whiskers, but not known is whether the whiskers in a block have a common lattice orientation; i.e. whether the block is a single crystal.

EXPERIMENTAL

The monomers pABA ($T_m = 196°C$) and mABA ($T_m = 135°C$) were used as furnished by TCI America. 6-acetoxy-2-naphthoic acid ($T_m = 226°C$) was prepared by acetylation of 6-hydroxy-2-naphthoic acid[3], a gift

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* To whom correspondence should be sent

† Although usually labelled poly(2,6-oxynaphthoate) the monomer is 6-acetoxy-2-naphthoic acid. In the following we will use the poly(2,6-oxynaphthoate), (PONA) terminology

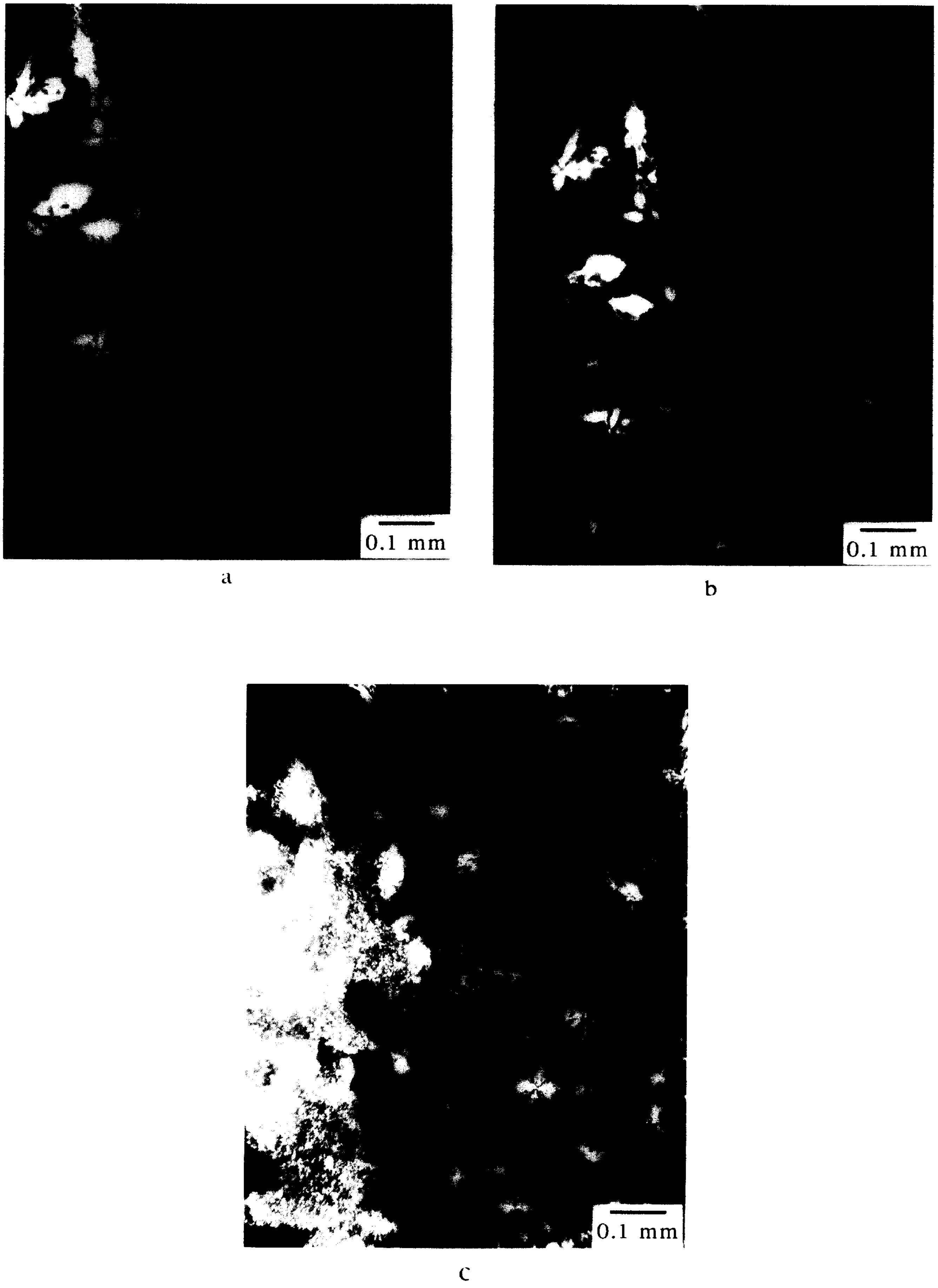


Figure 1 Optical micrographs (a) 4 h, (b) 5 h and (c) 22 h of PpOBA taken between crossed polars during polymerization at 185°C. The two small arrows on the left indicate the same macrocrystals at the successive times (after reaching the polymerization temperature); the small arrow at lower right indicates a spherulite-like structure. The large, white arrow in (c) indicates a barrel structure, shown better in *Figure 2*

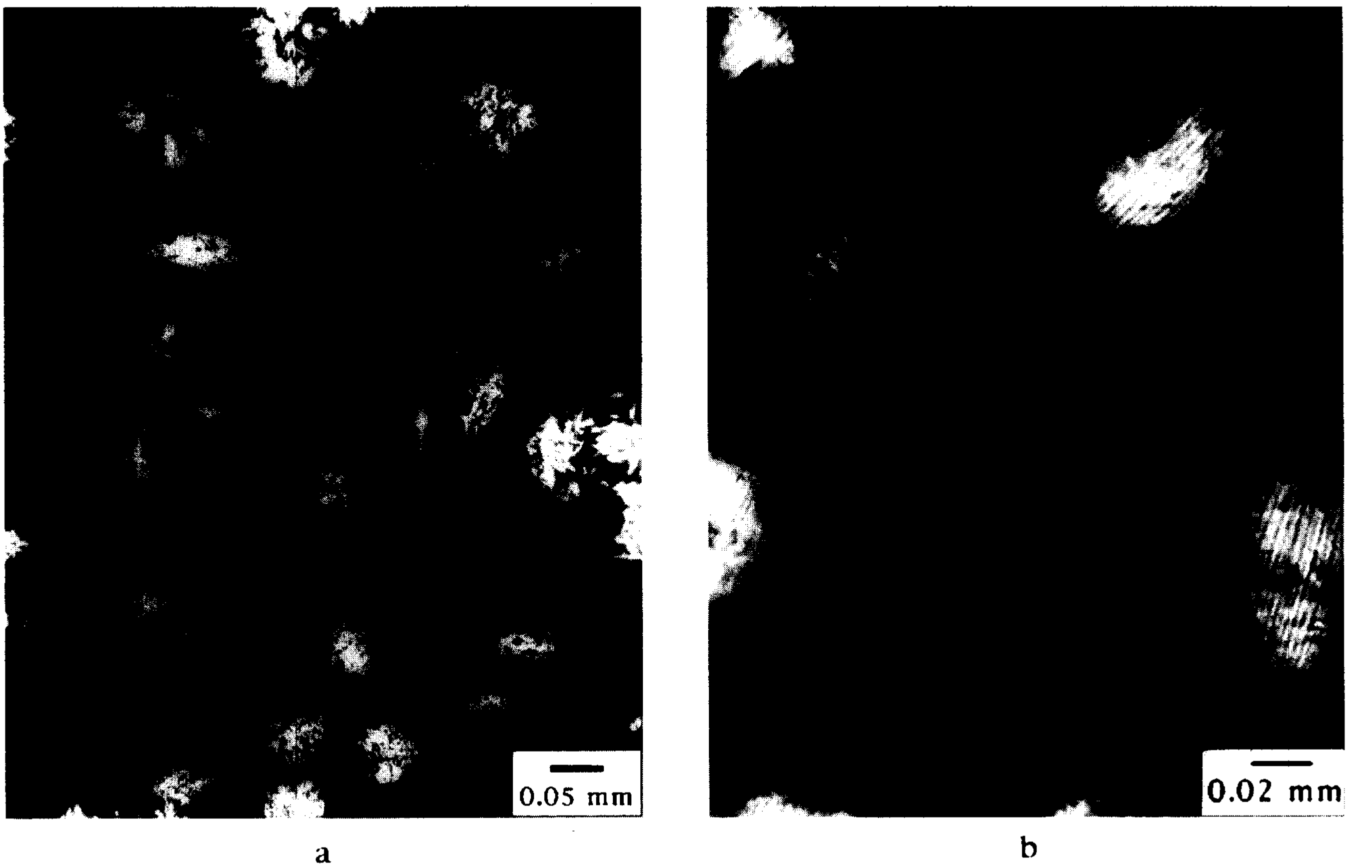


Figure 2 (a) Optical micrograph (180°C, 4 h) from a different area of the sample in *Figure 1*. Small arrows indicate individual macrocrystals, large, white arrows the barrels. (b) Higher magnification micrograph, between crossed polars, of the barrels after polymerization for 20 h at 180°C

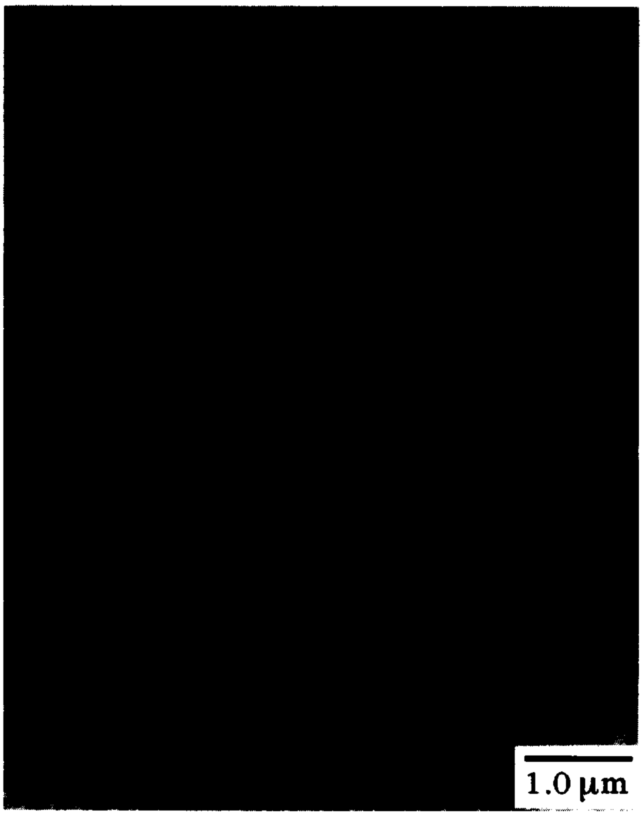


Figure 3 Reflected light (steep oblique) micrograph of a PpOBA sample polymerized 24 h at 180°C

from Hoechst-Celanese. The monomers were dissolved in acetone at a concentration on the order of 1% and cast on glass cover slips with, in many cases, several layers used. Two cover slips were then placed face to face and either wrapped in Al foil and heated on a thermostatted hot plate or observed on an optical microscope (Reichert Zetopan) fitted with a Kofler hot stage. In many cases the cover slips were pushed together after melting to ensure gap spanning films were produced across portions of the sample. Following polymerization, samples were prepared for observation under a reflected light microscope and a transmission electron microscope (TEM) by separating the slides and washing with acetone to remove any residual monomer. TEM samples were prepared by shadowing with Pt/C, coating with C and either stripping the replica with polyacrylic acid or floating on HF to remove the glass.

*FT*i.r. (using KBr pellets) and d.s.c. samples were prepared by scraping the material from the cover slips (crystals, disclination domains and any other matrix material, see subsequent micrographs) using a razor blade. Samples were run on a Mattson Galaxy 3000, 32 scans at 4 cm^{-1} resolution and a Perkin Elmer DSC IV, respectively. For *FT*i.r. microscopy the glass was removed with HF and the washed sample picked up on a CaF_2 disc; observations were made in transmission using a Spectra-Tech Irμs microscope

RESULTS AND DISCUSSION

*Poly (*p*-oxybenzoate)*

Figure 1 shows several optical micrographs taken using crossed polars during the polymerization of PpOBA at

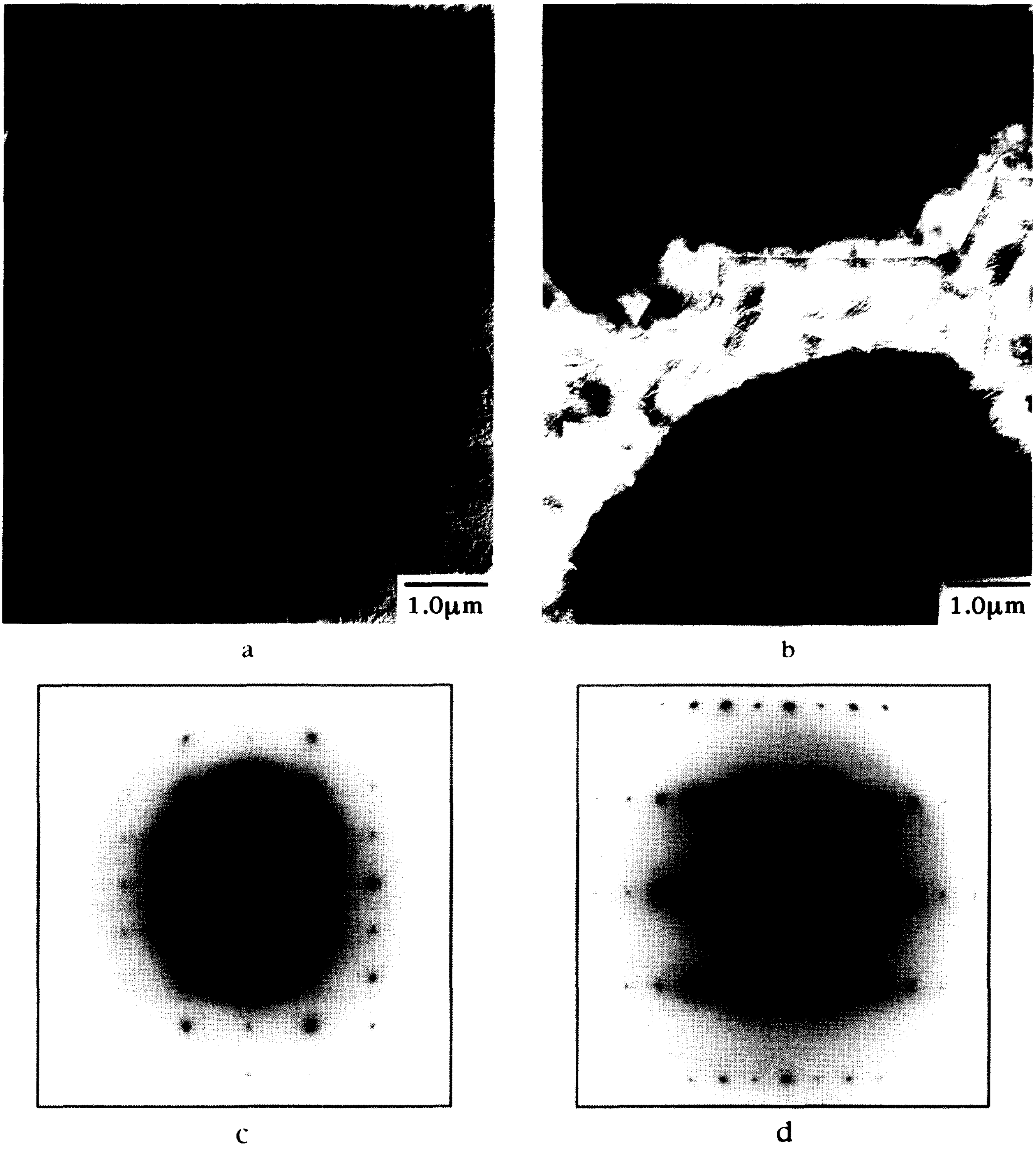


Figure 4 Electron micrographs of (a) a portion of a macrocrystal and (b) a barrel and a portion of a macrocrystal [0 0 1] phase I (c) and II (d) ED patterns from a portions of PpOBA macrocrystals polymerized 24 h at 180°C

180°C; the small arrows indicate identical structures in successive micrographs. These micrographs were taken subsequent to the sublimation, recrystallization and 'melting', all of which processes were similar to those shown in Fig. 1 of ref. 1. The coherent material at the left side of the micrographs corresponds to the edge of the monomer film. It also appears to be made up of the diamond shaped structures (macrocrystals) which here are intergrowing. In addition to the macrocrystals, spherulitic-like structures (lower right arrow) and square to rectangular structures (barrels, large, white arrows in *Figure 1c* and *Figure 2*) were seen, the barrels becoming visible between crossed polars late in the polymerization process.

Figure 2a shows another area of the same sample, the small arrows indicating relatively well formed macrocrystals and the large, white arrows indicating the barrels. While the barrels have relatively low and uniform birefringence, except at their ends, the macrocrystals and the rest of the material are finely mottled. All of the mottled material is believed related to the macrocrystals. Close examination of this sample at 2 h, by observation in non-polarized light, revealed that the barrels developed coincidentally with the macrocrystals;

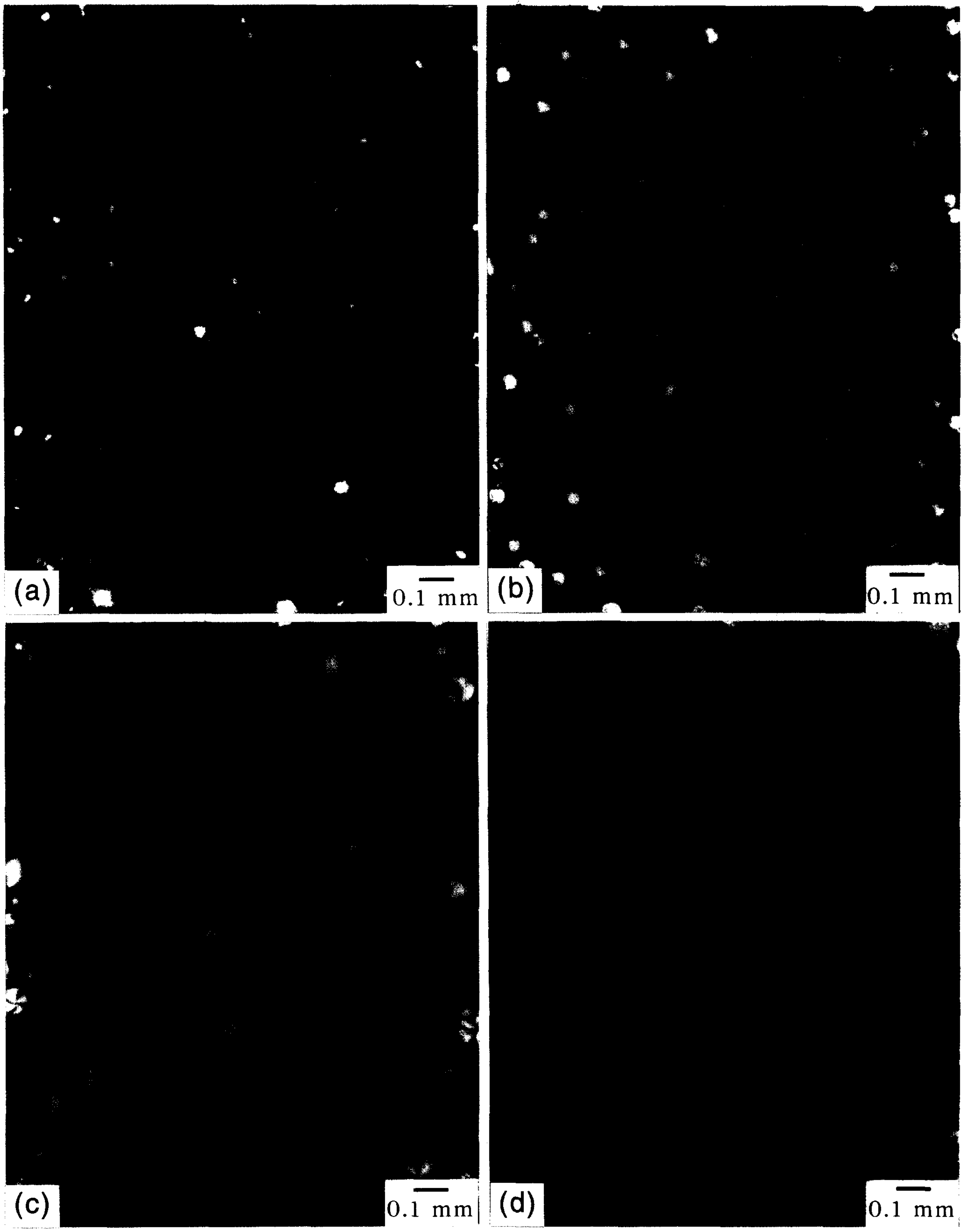


Figure 5 Optical micrographs (crossed polars) of P(mOBA/ONA) during polymerization at 185°C for (a) 6 h, (b) 11 h, and (c) 22 h. The arrows indicate identical macrocrystals in successive micrographs. (d) shows the result after crystallization during cooling to room temperature after 23 h at 180°C. The single disclination domains in (d) looked the same as those in (c), the domains in this sample remaining in the liquid crystalline state at 180°C for this time of polymerization

the birefringence, however, was so low they were barely visible. *Figure 2b* is an optical micrograph of the barrels (different sample) at higher magnification, taken at room temperature while still between the cover slips. The birefringence is now relatively uniform, decreasing at all edges, and they are rounded on their short edges. The numerous dark lines parallel to the long axes of the macrocrystals and 'rectangular' structures, cracks as

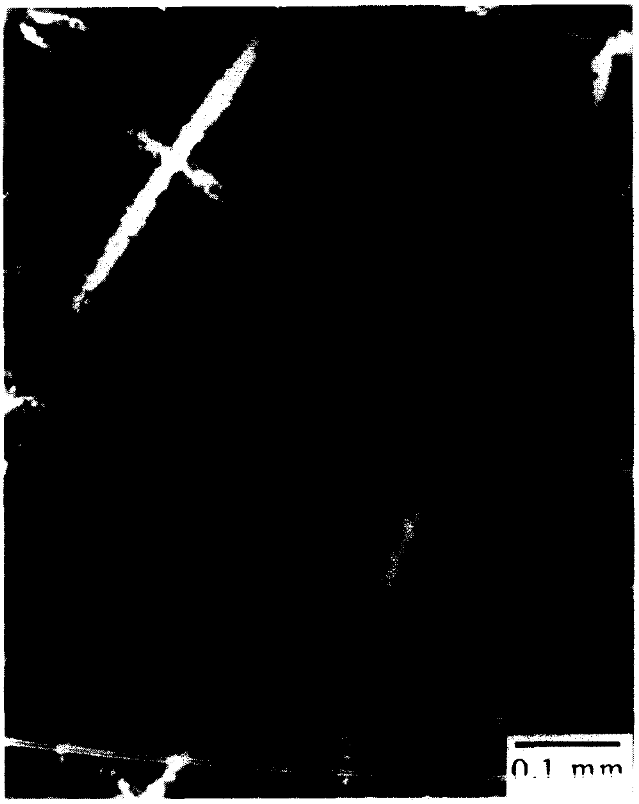


Figure 6 Optical micrograph (crossed polars) of a P(mOBA/ONA sample polymerized at 197°C for 23 h

observed in TEM micrographs, are the origin of the term 'barrel' as applied to the rectangular structures.

One would expect the primary difference in index of refraction to be between $n_\perp$ and $n_\parallel$, relative to the molecular axis. If so, one would then not expect to see birefringence with the illumination parallel to the molecular axis, as ED shows is the case for the macrocrystals. Simulation of the unit cells of PpOBA for both Phases I and II, based on our ED patterns and the Cerius^2 molecular simulation software [7, 8] indicate the carbonyl groups, which should make a significant contribution to $n_\perp$, have a preferred orientation nearly parallel to the phenyl rings in both phases. The largest component is parallel to **b** in Phase I and **a** in Phase II, the phenyl rings lying at 28° to **b** in I and 25° to **a** in II. This, we suggest, gives rise to the birefringence observed for the macrocrystals.

When observed in reflected light using a split sample, after washing, the macrocrystals have a smooth surface, re-entrant facets on their edges and are embedded in a rough surfaced matrix (*Figure 3*). The latter material is the molten material surrounding the structures in *Figure 1* and *Figure 2a* following, presumably, solidification during cooling. We suggest the smooth surface of the macrocrystals, at this magnification, represents a fracture surface while the rough matrix surface is a free surface from residual melt which no longer spanned the gap at least at the time of solidification. The re-entrant lateral faces contribute to the irregularity of the structures observed between crossed polars.

Electron micrographs of (a) a portion of a macrocrystal and (b) a barrel (the long axis, parallel to the lines in most of the barrels, is the short axis here) and an edge of a macrocrystal are shown in *Figure 4*. The rough surface of the matrix shows no sign of being a fracture surface. In *Figure 4a* the surface of the macrocrystal is seen to consist of lamellae; shadow length measurements indicate an *ca.* 100 Å lamellar thickness. The shadows show the surface of the macrocrystal, as observed, is below that of the matrix. In *Figure 4b* Moiré patterns are seen to cover most of the area of the macrocrystal, indicating a nearly common lattice orientation of the superposed lamellae, with fracture occurring between the lamellae. ED patterns (*Figure 4c*) from such areas give rise to both phase I and II $hk0$ single crystal patterns; i.e. the diamonds are large PpOBA macrocrystals as labelled above. As in the thin crystals[1] the long cracks are parallel to the phase I **a**-axis.

The morphology of the barrel in *Figure 4b* is less clear. While the rounded edges are relatively smooth, the straight edges are rougher. In this micrograph there is no evidence of a lamellar structure, the shadowing suggesting a fine scale granular surface with ridges 'parallel' to the rounded edges. We suggest this barrel grew with a free surface even though the neighbouring macrocrystals have a fracture surface. In some cases voids form in the gap spanning film due, presumably, to the generation of acetic acid during polymerization which has not diffused out of the film, with the macrocrystals and barrels continuing to grow on the surface on which they originally nucleated. ED patterns were again [0 0 1] single-crystal-like, with the cracks, corresponding to the lines in *Figure 2b* giving rise to the 'barrel' appearance and again lying parallel to the phase I **a**-axis.

D.s.c. and *FT*i.r. scans from this type of material were shown in ref. 1, i.e. 'thick' material was used for the samples. The d.s.c. scan, from a sample polymerized 5 h at 180°C, showed T_{k-m} peaks at 290 and 320°C, the latter probably due to material that underwent further polymerization by end linking during heating and then undergoing the T_{k-m} transition at the normal temperature. An additional, T_{m-m} peak at 390°C is attributed to the same, now high molecular weight material. The 290°C peak suggests a relatively low DP, consistent with the lamellae being extended chain crystals. A lamellar thickness of 100 Å corresponds to a DP of 16. The *FT*i.r. scans showed residual carboxyl and acetoxy bands, as well as a large ester band in the 1650–1800 cm^{-1} region, again consistent with the low molecular weight.

*Poly(*m*-oxybenzoate/2,6-oxynaphthoate)*

Optical micrographs (crossed polars) of the same area of a 1/1 mixture of the two monomers as it was held at 185°C for increasing times are shown in *Figure 5*, with *Figure 5d* being the same area after 23 h at 185°C followed by cooling to room temperature. In *Figures 5a–c* both single, 4-brush disclination domains and diamond-shaped macrocrystals are observed, the arrows indicating the same macrocrystals in successive micrographs. As observed some of the disclination domains are brilliantly and uniformly coloured in addition to having the 4-brush pattern. The domains here were red in *Figure 5b* and blue in *Figure 5c*, with others being yellow, green and orange, usually being of a similar colour in a given region but differing from region to region and with time in a given sample.

In *Figure 5d* the disclination domains have crystallized, being in the liquid crystal state at the 185°C polymerization temperature, even though T_{k-m} of the

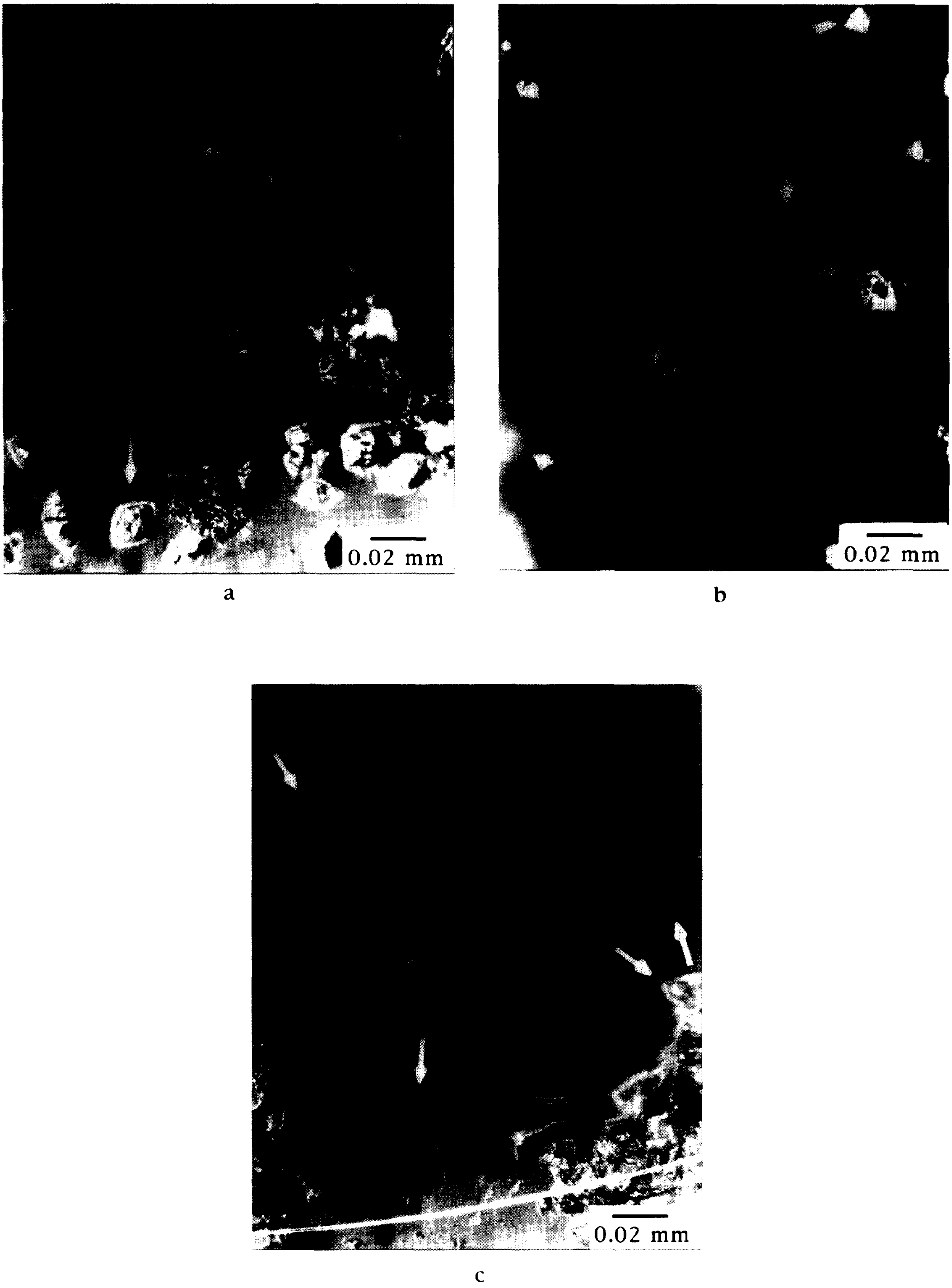
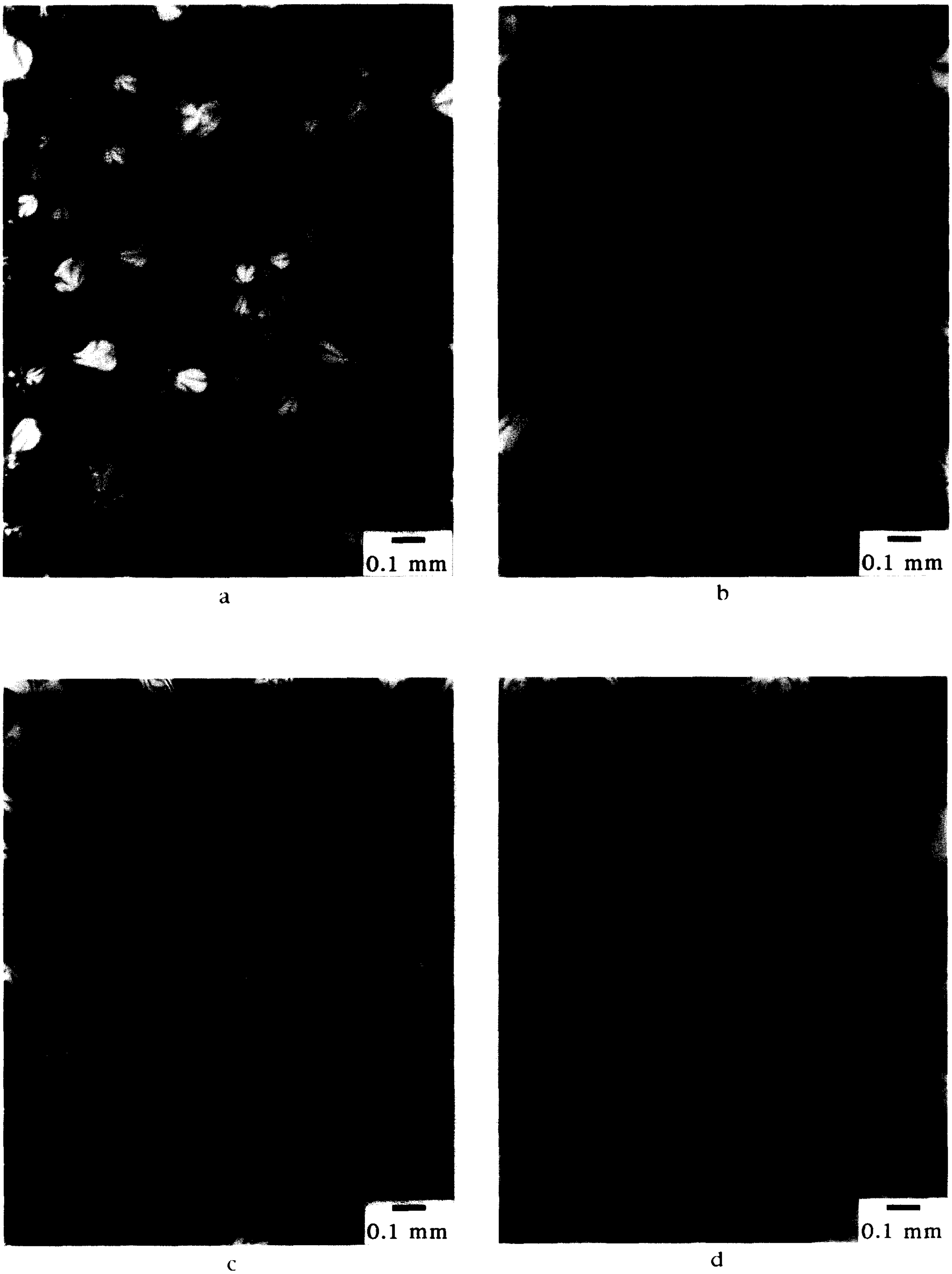


Figure 7 Reflected light micrographs (a) and (c) of P(mOBA/ONA) following splitting and washing of the sample. The large, white arrows indicate macrocrystals, the small arrows microcrystals. The sample in (b) is the same area as in (a), taken using crossed polars, the bright regions being macrocrystals both isolated and embedded in the matrix material. The large arrows in (c) indicate macrocrystals protruding from the matrix material



a

b

c

d

Figure 8 Optical micrographs for polymerization times of (a) 1 h, (b) 2 h (c) 3 h and (d) 5 h of a region of the sample in *Figure 5* in which the film did not span the gap [except for the small circle near the bottom of (b) and (c)]. Arrows indicate identical domains in successive micrographs. Crystallization has occurred at the 185°C in the larger domains in (d), resulting in the mottling of the edges and the development of a ring structure

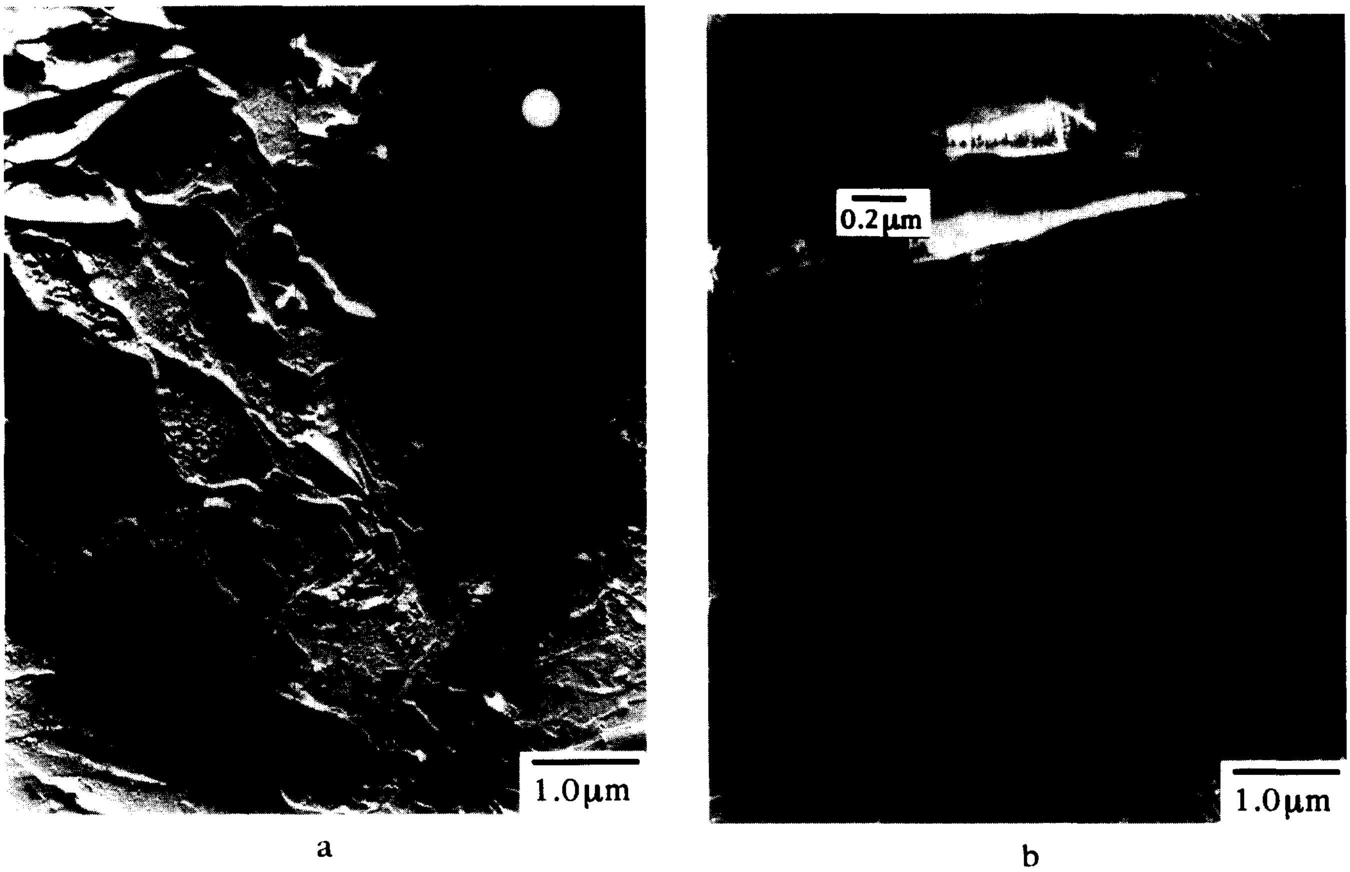


Figure 9 Replicas of the fracture surfaces of presumably (a) a macrocrystal and (b) a disclination domain. The arrows in (b) indicate regions in which the lamellae are normal to the fracture surface; a higher magnification of the region near the upper arrow is inset at the proper orientation. The ED pattern inset in (a) is from lamellae attached to the replica

resulting polymer is 270°C. The macrocrystals, on the other hand, do not change in appearance upon cooling and have a relatively low birefringence, attributed to the same effect as for PpOBA. As shown in *Figure 6*, from a region containing particularly large macrocrystals (polymerized 4.5 h at 197°C with the micrograph taken at 197°C), they are dark when the long or short axis is lined up with the polarizer. If held long enough at the polymerization temperature the disclination domains crystallize, i.e. become mottled when thick or develop an irregular, concentric ring structure when thin (see *Figures 8* and *10* below and ref. 4).

In some samples, as in the case of PpOBA, voids develop in the gap spanning film as polymerization continues. As shown in *Figure 7*, macrocrystals (large arrows) can be seen both isolated in the void area (*Figure 7a*) as well as extending out from the aggregates (*Figure 7c*). In addition, just barely visible in reflected light in the void areas, are the small, thin, nearly square 'single surface' crystals (small arrow) described in ref. 4. The aggregates are believed to be composed of mixtures of the macrocrystals (the birefringent regions in *Figure 7b*) and the disclination domains.

In portions of a gap spanning sample in which the film does not initially span the gap but wets both surfaces independently, large disclination domains were observed. *Figure 8* shows a representative area from the same sample as in *Figure 5*. As growth proceeds, contact between two domains results in 'instantaneous' rearrangement of the brushes. The two single disclination domains merge to form a new single disclination domain when the domains are small. An example, shown in *Figures 8a* and *b*, is the change in the region near the middle of the micrograph with further polymerization. Many of the larger domains in *Figures 8b–d*, however, have several disclination axes, pinning at the edges being prevalent. The apparent overlap of some domains in the figures, without merger, is due to their presence on both surfaces with a void in between. The circular region near the bottom of *Figures 8b* and *c* is a region in which the molten film did span the gap, disclination domains growing in the 'column'. In *Figure 8d* there has been a general decrease in the birefringence of the thicker domains and mottling of their appearance. This we attribute to their crystallizing at the polymerization temperature, presumably as the chain length has increased. In *Figure 8c*, crystallization has just started around the edges of the large domain at the top. The appearance of the crystallized domains is retained as they are cooled to room temperature and the mottling is seen, at higher magnification, to be the result of the ring structure shown in *Figure 10* below.

It has not been possible to obtain electron micrographs of the free surface of an isolated P(mOBA/ONA) macrocrystal. *Figure 9a* is believed to be from a fracture surface of a macrocrystal in a region that did span the gap; lamellae are seen predominantly, but not totally (left side) parallel to the surface. The inset ED pattern is from lamellae extracted with the replica; it is identical to that obtained from the thin, single substrate crystals[4].

In ref. 4, morphology of the single surface single disclination domains was left undefined. As shown in *Figure 10* a coarse surface ring structure is seen, with unshadowed samples having irregular, concentric dark

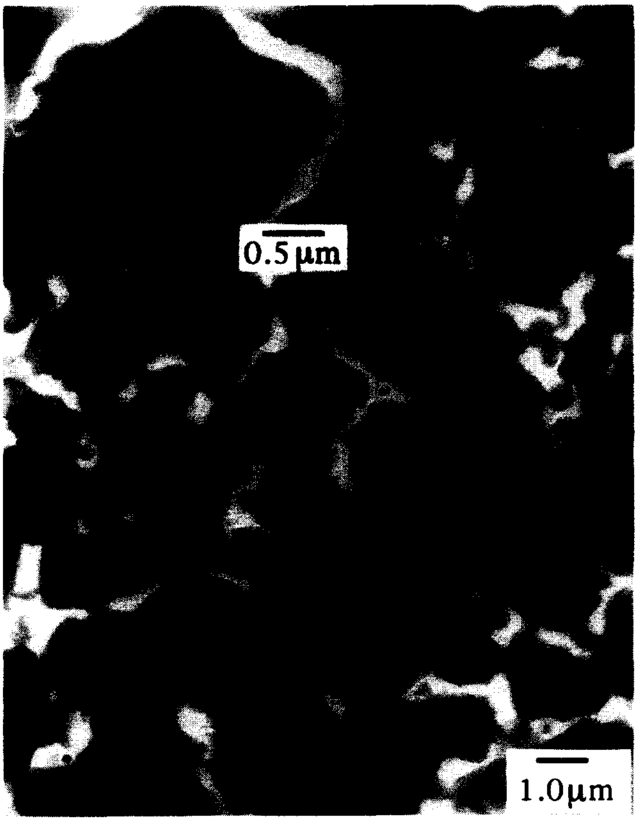


Figure 10 Electron micrograph of a shadowed thin film of P(mOBA/ONA) polymerized at 180°C, 17 h. The inset shows a single disclination domain at higher magnification

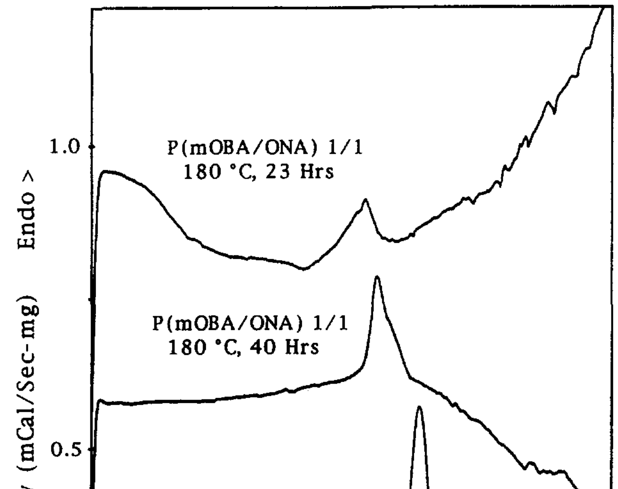


Figure 11 D.s.c. scans of P(mOBA/ONA) and PONA homopolymer polymerized as shown (from ref. 4)

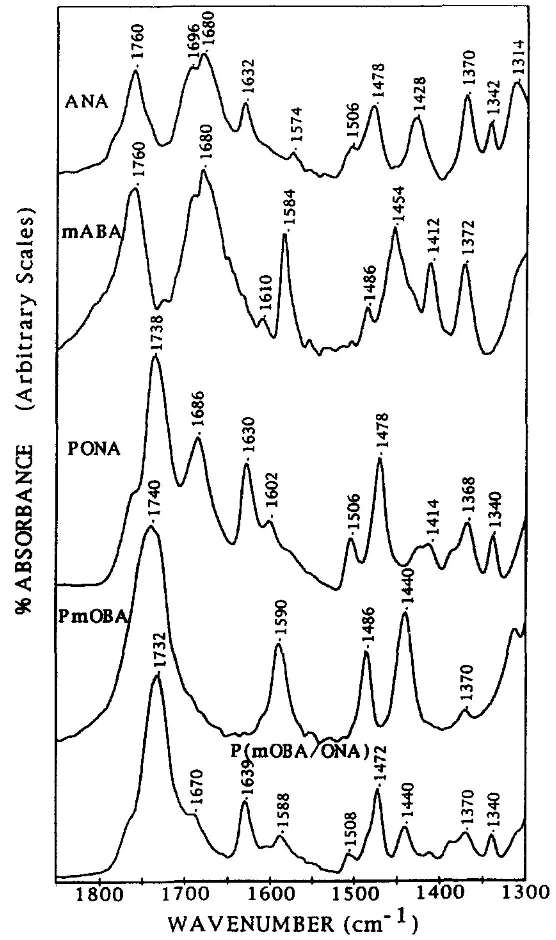


Figure 12 *FT*i.r. scan of monomer, homopolymer and copolymer (from ref. 4)

lines that appear associated with the surface rings, but the contrast, which is not affected by the beam, far exceeds that expected for the slight variations in thickness. There is some suggestion, as at the centre of the inset, that lamellae are involved, but we still have no explanation for the contrast. On the other hand, as shown in *Figure 9b*, lamellae do appear to be present in the disclination domains in the gap spanning films, after crystallization, the 100 Å thick lamellae being observed both on edge (inset) and parallel (lower left and right) to the fracture surface .

Of obvious concern, particularly since this is presumably a random copolymer and mABA has a T_m (135°C) well below the polymerization temperature, is whether the samples are really copolymers, the relative composition (if they are) and the molecular weight (i.e. the chain length). D.s.c. and *FT*i.r. scans of thick CTFMP samples scraped from the glass, shown in *Figures 11* and *12*, are reproduced from ref. 4. They represent a mixture of the P(mOBA/ONA) materials shown in *Figures 5* and *8*; i.e. they are not just macrocrystals. The d.s.c. scan suggests a T_{k-m} of 270–280°C, depending on the degree of polymerization, as compared to a 325°C T_{k-m} for CTFMP polymerized poly(2,6-oxynaphthoate) (PONA)[4]. *FT*i.r. reveals reasonable, but not large, molecular weight as indicated by the large decrease in absorption of the 1680, 1696 cm^{-1} carboxyl and 1760 cm^{-1} acetoxy bands, accompanied by the development of the 1732–1740 cm^{-1} ester band. The presence of mOBA and ONA residues in the copolymer

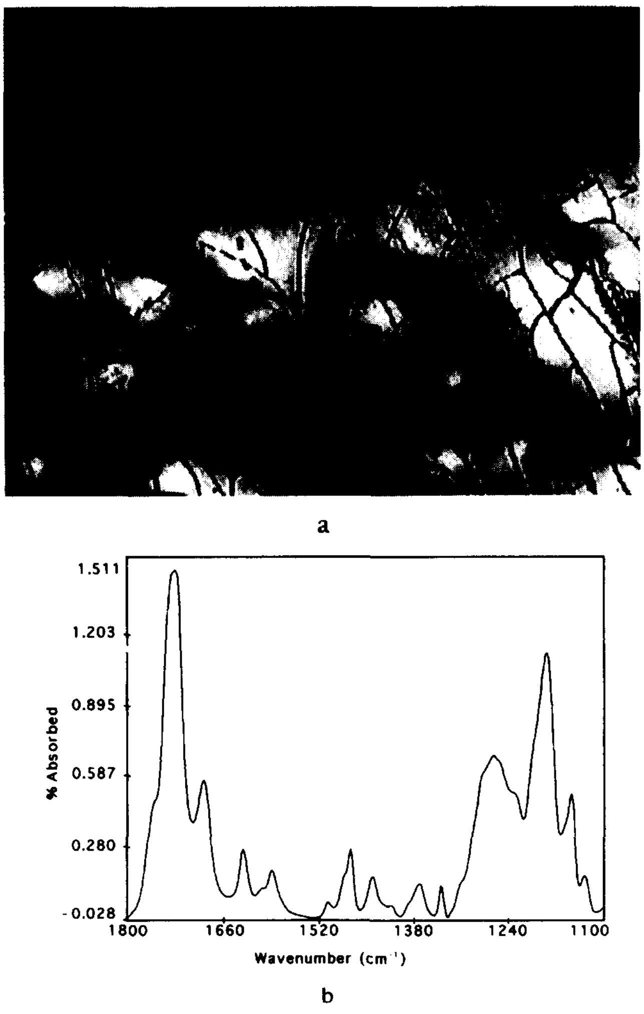


Figure 13 Optical micrograph and *FT*i.r. scan of P(mOBA/ONA) macrocrystals. The selected area for the *FT*i.r. scan is indicated on the optical micrograph

can be identified by the 1588, 1440 cm^{-1} and 1639, 1472 cm^{-1} bands, respectively. Although we have not identified a common internal thickness band, the relative intensities of the latter peaks, in comparison with that of the ester band, clearly suggest the mABA/ONA ratio is less than 1/1 although both residues are present.

In an attempt to determine the composition of the macrocrystals an *FT*i.r. microscope was used. The region chosen for *Figure 13* contains two relatively thin macrocrystals, barely visible, in addition to matrix material. The scan is similar to that in *Figure 12* except for a somewhat larger absorption due to residual carboxyl groups that may be due to the presence of lower molecular weight matrix material surrounding the macrocrystals. The mOBA/ONA ratio is larger than in *Figure 12*; again we clearly have copolymer in the region observed but cannot differentiate between macrocrystal and matrix. Selected areas throughout this sample gave similar scans; a region with disclination domains had only one carboxyl peak and a *ca.* 1/3 mOBA/ONA peak intensity ratio while a region similar to that in *Figure 5* showed only a small carboxyl peak and a mOBA/ONA peak ratio greater than 0.5.

Upon reheating a sample such as that in *Figure 5d*, still between the cover slips, flow of the matrix, which melts, can occur at the original polymerization temperature (*Figure 14b*). With slight further heating the disclination domains change appearance, the centers losing their mottling and a suggestion of a 4-sector ring birefringence pattern developing (*Figure 14c*); by 240°C they have almost disappeared (*Figure 14d*). In *Figure 14e* a 4-brush pattern can again be seen at the centres of the disclination domains, but they appear to be very small. The macrocrystals, on the other hand, seem to gradually decrease in birefringence with increasing temperature (*Figures 14c–e*), with their centres becoming mottled in *Figures 14d* and *e*. At *ca.* 270°C the macrocrystal birefringence nearly disappears but, surprisingly, at 275°C it returns, uniformly across the macrocrystal (*Figure 14f*). The macrocrystals finally melt at 280°C, in agreement with the d.s.c. results.

The apparent difference in thermal behaviour of the disclination domains and the macrocrystals, as well as their mechanism of formation, is not yet understood. Clearly the disclinations are growing (polymerization occurring) in the liquid crystal state. However, as in PpOBA[1] and many of our other CTFMP polymers, the polymerization temperature is nearly 100°C below the T_{k-m} measured on the resulting material and, as shown above, the disclination domains begin to show significant changes in structure when heated back to just above the polymerization temperature. We suggest the crystals that formed in the domains when cooled to room temperature melt and the domains return to the liquid crystalline state even though the subsequently measured T_{k-m} is 100°C higher. There is no indication of a transition in the d.s.c. scans of the washed material at the polymerization temperature although, as noted in ref. 9, the 'melt' does have a transition (endothermic peak) at the polymerization temperature while the original T_m peak of the monomer is no longer present.

Compression of the film at these temperatures (i.e. 185–250°C), while on the hot stage, results in flow and disruption of the disclination while the crystals, on the other hand, retain their rigidity.

Contrary to the disclination domains, the macrocrystals presumably grow, by polymerization, in the crystalline state with molecules (monomers and/or oligomers) adding on both laterally and on the lamellar surfaces. For reasons not yet known, as for single surface film crystals and disclination domains, chain growth along the back-bone, i.e. the lamellar thickness, is restricted to *ca.* 100 Å, with end linking not occurring across the lamellar interface. End linking would prevent the easy fracture that is observed. Of concern relative to the growth process of the crystals, however, is our earlier observation[1] that the single surface PpOBA Phase I and Phase II single crystals have a similar shape. This we attributed to the crystals growing in the liquid crystal state (metrically hexagonal for the high temperature forms of both phases[2] and then transforming to one or the other of the two phases during cooling or as the chains became long enough. Both phases have an orthorhombic unit cell, with nearly superimposable point lattices (i.e. $a_{\rm I} \approx 2b_{\rm II}$, $a_{\rm II} \approx 2b_{\rm I}$) and, considering the results here as well, we now suggest they polymerize-crystallize simultaneously in one or the other forms. This would help explain why at a polymerization temperature of 130°C the two types of crystals do differ in appearance and stability within a solvent[1]. It is noted, however, the PpOBA disclination domains, grown simultaneously at, e.g. 180°C and clearly in the liquid crystal state, also consist of *ca.* 100 Å thick lamellae that can be either

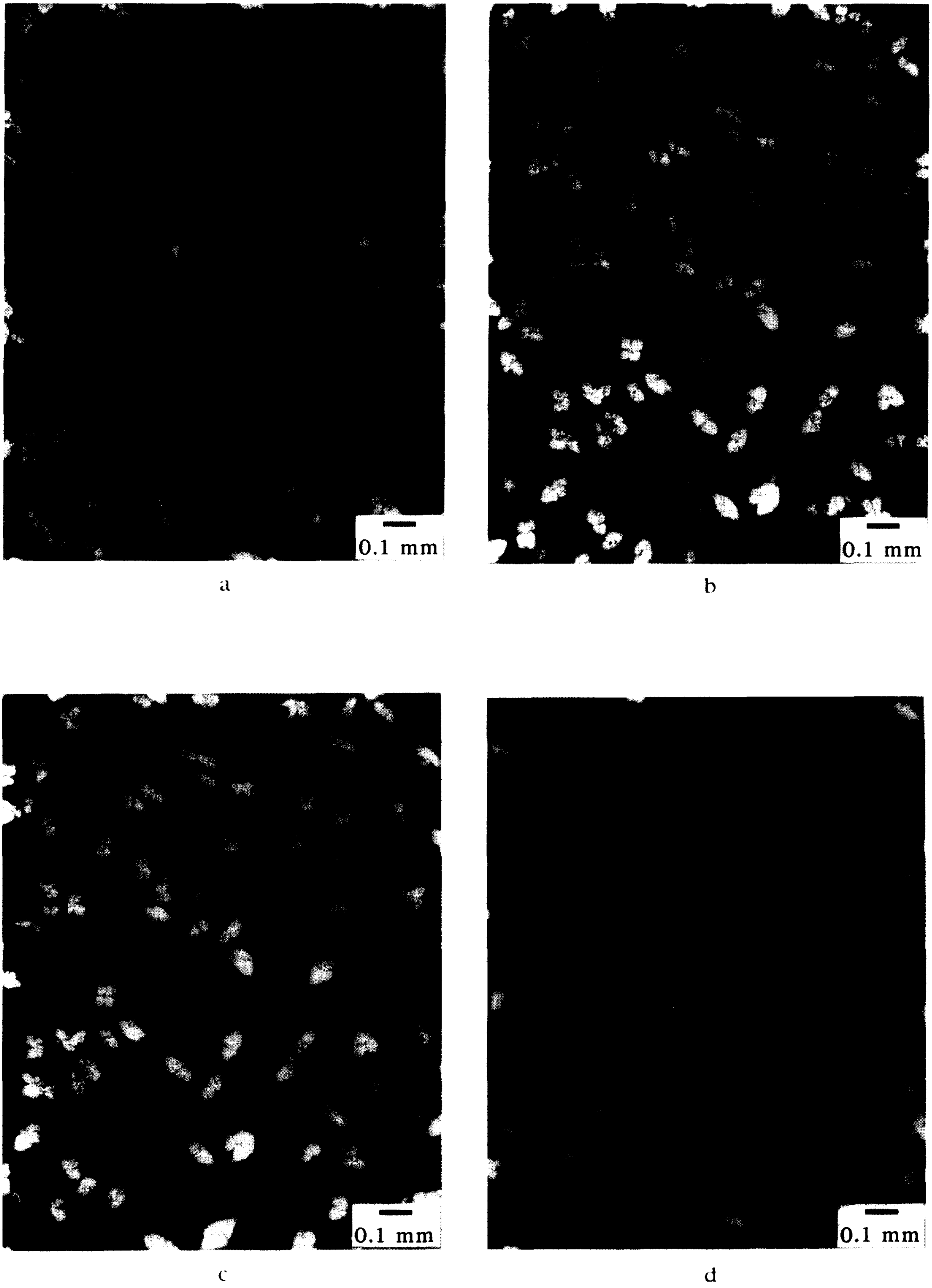
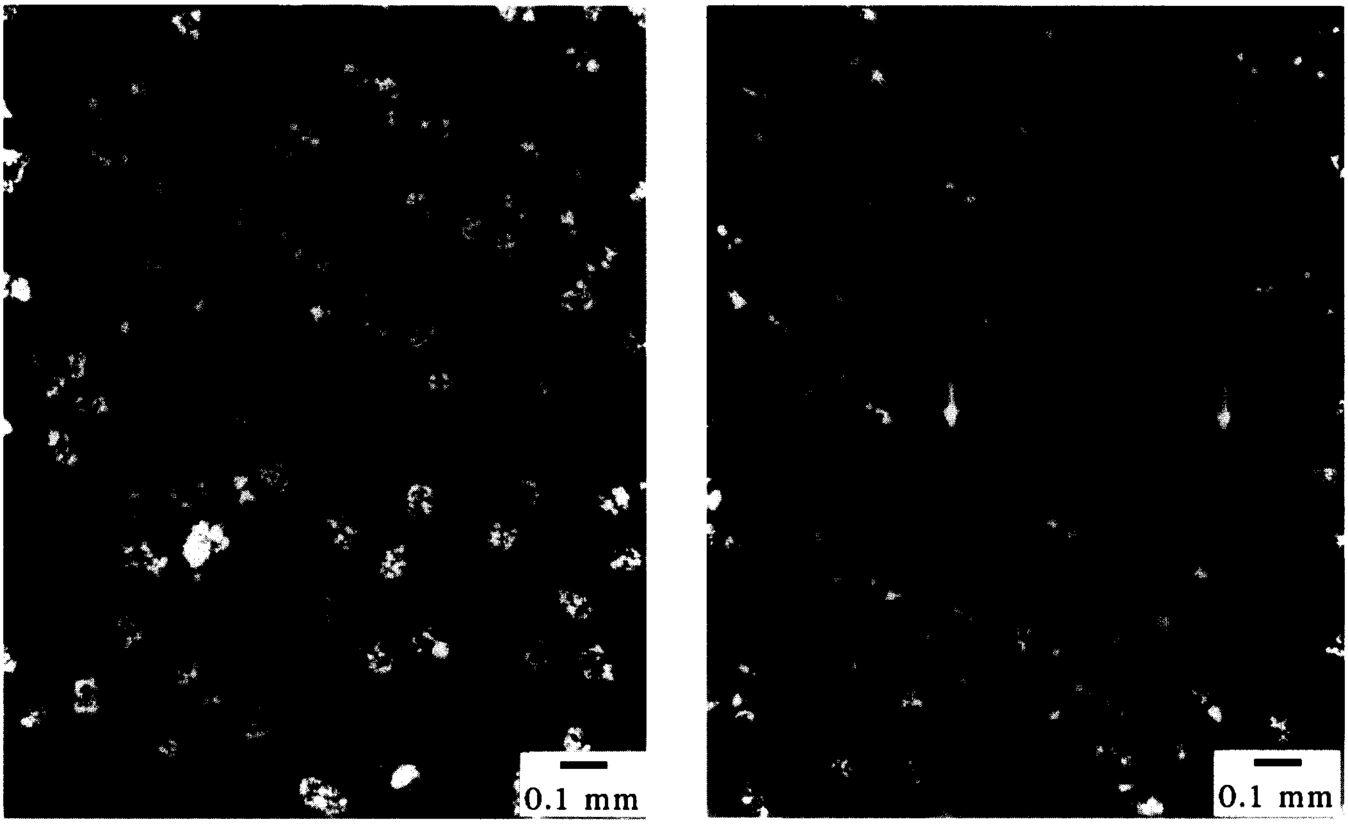


Figure 14 Optical micrographs of the copolymer sample in *Figure 5d* as it was reheated (a) 25°C, (b) 180°C, (c) 191°C, (d) 240°C, (e) 265°C and 275°C. Identical structures on successive micrographs are indicated by arrows with one area shown in (a) and (f) and a different area in (b)–(e)



e

f

Figure 14 Continued

Phase I or II; these phases must form during cooling for short polymerization times or, for sufficient time, as the chain length becomes long enough. We are thus left with no explanation as yet for either the prevalence of lamellae of 100 Å thickness nor the reason for the simultaneous development of crystalline macrocrystals (and microcrystals) and liquid crystalline disclination domains.

CONCLUSIONS

Macrocrystals of both homo- and co-polymer polyesters, as large as 0.5 mm in lateral dimensions and composed of lamellae on the order of 100 Å thickness were grown during simultaneous polymerization-crystallization by the CTFMP technique. Their growth is aided, but not restricted, to regions in which the 'monomer' melt spans the gap between the confining surfaces. The single disclination domains formed simultaneously, with polymerization and crystal growth in the liquid crystalline state, are also composed of *ca.* 100 Å thick lamellae after crystallization. When reheated to the polymerization temperature the disclination domains appear to revert to the liquid crystalline state, while the macrocrystals remain crystalline, the latter melting when the d.s.c. measured T_{k-m} is reached. No explanation for this difference in behaviour is known as yet.

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