

CRYSTAL STRUCTURE AND MORPHOLOGY OF NASCENT SAMPLES OF SYMMETRIC AROMATIC POLYESTERS II. POLY(*p*-PHENYLENE 2,6-NAPHTHALATE)*

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Abstract Confined thin film melt polymerization (CTFMP) of naphthalene chloride/hydroquinone (NC/HQ, 1/1, molar) mixtures at polymerization temperatures (T_p) below *ca.* 300 °C resulted in relatively thick, elongated crystals. Polymerization of NC/HQ above 300 °C between glass yielded well-formed lamellar crystals *ca.* 100 Å thick. Phase I and II [001] ED patterns were obtained for all T_p , the relative amount of phase I increasing with T_p . Polymerization of naphthalene dicarboxylic acid/hydroquinone diacetate 1/1 mixtures at high T_p also yielded lamellar crystals that “curled up” off of the substrate. When the high temperature CTFMP polymerization was conducted between mica, aggregates of lamellae on-edge developed but epitaxial growth did not occur. Epitaxial growth of lamellae between mica could be obtained, however, by confined thin film solution polymerization, with both of the latter samples yielding apparently related ED patterns from a different unit cell than phase I or II. Fiber patterns, obtained from sheared samples, indicated considerably greater crystal disorder than in the nascent crystals. Refinement of the phase I unit cell parameters, based on the [001] and [011] ED patterns, with modeling based on Cerius², suggests a monoclinic phase I unit cell with $a = 7.76$, $b = 5.71$, $c = 14.99$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 99.7^\circ$, $\rho = 1.47$ g/cm³, space group P12₁/a1.

Keywords Poly(*p*-phenylene 2,6-naphthalate, Crystal structure, Morphology, Confined thin film melt polymerization

INTRODUCTION

In the previous paper^[1] we described the morphology and crystal structure of nascent poly(*p*-phenylene terephthalate) (PPT), the symmetrical version of the liquid crystal polymer poly(*p*-oxybenzoate) (PpOBA), prepared by confined thin film melt polymerization (CTFMP)^[2] and solution (CTFSP) polymerization. The crystal structure was determined by comparing electron diffraction (ED) patterns with simulations using Cerius² (Molecular Simulation, Inc.). In similar, earlier studies, utilizing ED patterns from CTFMP single crystal lamellae and single crystal whiskers prepared by solution polymerization, we described the phase I crystal structures of PpOBA^[3] and poly(2,6-oxynaphthoate) (PONA)^[4]. In addition the morphology of single crystals, disclination domains and superlattices of the, presumably, random copolymers poly(pOBA/ONA) (3/1, 1/1 and 1/3 mole ratios), prepared by CTFMP, have been described^[5]. Although [001] and fiber (sheared) ED patterns were obtained from both CTFMP and CTFSP samples of the copolymers, no attempt was made to determine their crystal structure; many of the [001] patterns resembled the phase I and II patterns of the homopolymers, with a variety of monoclinic [001] patterns also being seen for the CTFSP samples. In all of these polymers the

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molecules have a direction to their backbone, with parallel chain packing being proposed for the phase I PpOBA and PONA crystal structures. Lack of good phase II ED patterns containing *hkl* reflections for both homopolymers has prevented an as-reliable determination of their structures.

In this paper we describe our observations of the results of applying the CTFMP process to the polymerization of the non-directional, alternating co-polymer, poly(*p*-phenylene 2,6-naphthalate) (PPN). This polymer is the symmetric version of the alternating 1/1 copolymer P(*p*OBA/ONA). Preparations of poly(2,6-naphthalene terephthalate), with oppositely directed ester groups, and poly(2,6-naphthalene 2,6-naphthalate), the symmetric version of PONA, are in progress. We know no reports in the literature of the crystal structure or properties of PPN

Of particular interest relative to the random poly(*p*OBA/ONA) copolymers has been the origin of the aperiodic, meridional (apm) reflections observed by both X-ray diffraction from drawn, bulk melt polymerized samples (e.g., Refs. [6–8]) and electron diffraction from sheared thin films of solution and CTFMP polymerized polymer^[5]. All of the sheared (ED) samples, on the meridian, had only a composition independent reflection with a *ca.* 2.1 Å spacing and another, apparent 002 reflection that varied with composition. The latter was *ca.* 6.8 Å in 3/1, 7.4 Å in 1/1 and 8.0 Å in 1/3 ratio copolymers, also varying by several tenths of an Angstrom with thermal history.

X-ray diffraction from “melt” drawn fibers of bulk polymerized co-polymer showed several orders of meridional reflections, again with a constant 2.1 Å reflection (corresponding to 006 for PpOBA and 008 for PONA) and 2–3 additional reflections which are neither orders of the innermost, apparent 002 reflection or related to the 2.1 Å reflection. (see, e.g., Ref. [9]). For the 50/50 monomer ratio, corresponding to the composition of our copolymer PPN, the spacings were 7.49, 2.95 and 2.09 Å. These apm reflections have been interpreted by Windle and coworkers in terms of aggregation of identical, non-repeating sequences to form “crystals” with a non-periodic lattice (npl)^[6] whereas Blackwell and coworkers have attributed the origin of the patterns to a paracrystalline lattice (pcl)^[7] “in which short, non-identical sequences form layers with their centers approximately on a common plane perpendicular to the chain axis”^[10]. In addition to the apm reflections, quadrant reflections were seen on the “first layer line”; for the 30/70 copolymer they were at *d* = 3.3 Å, indexed as 211, with the layer line spacing along the meridian corresponding to 14.9 Å while the innermost meridional reflection was at 7.89 Å. The first layer line spacing for the 211 reflection was said to be “approximately half that for the first meridional”^[7]. The “211” reflection was also seen at *d* ≈ 3.3 Å for the range of compositions examined by Blackwell and coauthors (e.g., Ref. [7, 11]), with the layer line spacing corresponding to the “pseudo-dimer” repeat distance; i.e., the average composition dependent dimer length^[7]. Wilson *et al.*^[12] indicate that on heavily exposed films the third and fifth layer lines, presumably with fractional spacings of the first, can be seen, without meridional reflections; not stated, however, is whether this is for the as-drawn fibers or for the annealed samples as discussed below in which a number of first layer line reflections are observed. Also not stated is whether this is for all the compositions they examined, which have either 2 or 3 apm reflections at 2θ angles less than that of the 2.1 Å reflection, or only some.

Equatorial ED reflections were observed for all CTFMP as-drawn or sheared co-polymer samples^[5]. For a 1/1 sample sheared at 210°C they were at 4.7 and 3.5 Å. Blackwell and coworkers report, on the basis of X-ray diffraction, 4.6, 2.6 and 2.3 Å for as-drawn random copolymers of a range of compositions from 25/75 to 75/25 copolymers (the 2.3 Å reflection is described as extremely weak and diffuse in Ref. [11], but all are listed as strong in Ref. [10]); these plus the 3.1 Å (in 75/25, Ref. [13]) or 3.3 Å^[7, 10, 11] quadrant reflection on approximately the 1st apm layer line were ascribed to the 110/200, 020/310, 220/400 and 211 reflections of an orthorhombic (pseudo-hexagonal (PH)) packing of the “crystalline” segments, similar to that for the high temperature (phase III) form of PpOBA (see Ref. [14]).

Both Windle and co-workers and Blackwell and co-workers report that annealing the drawn fibers results in a change in lateral packing of this structure, but little or no change in the apm reflections^[12, 13]. Blackwell *et al.* describe a new unit cell for the 75/25 copolymer, after annealing at 275°C, 30 days, with strong equatorial reflections at 4.57 (110), 3.83 (200), 3.13 (210) and 2.33 Å (310), and first layer line reflections at 5.21 (011),

4.29 (111) and 3.04 Å (211) which they attribute to a second orthorhombic polymorph with $a = 7.6$ and $b = 5.7$ Å^[13]. Reflections from the original PH structure were superimposed. The annealed form was related to the orthorhombic form I typically found for PpOBA at room temperature (see, *e.g.*, Refs. [3] and [14]). Windle *et al.* described annealing results for fibers of a wide range of composition^[12]; for samples rich in pOBA they report an orthorhombic cell (O') similar to that described by Blackwell *et al.* whereas for 1/1 and 1/3 samples a different orthorhombic cell (O'') with $a = 8.3$, $b = 5.4$ Å was reported. In the X-ray diffraction patterns the difference between the two cells is primarily the difference in spacing between 110 and 200, this being much larger in the O' cell than in O''. Not stated, however, is whether the first layer line spacings were observed for O''; 111 and 211, but not 011, were reported for the O' patterns. Unfortunately, neither group of authors report the z coordinates of the first layer line reflections. Also of interest relative to the following is their indication^[12] of the observation of a small amount of diffraction from a crystal structure resembling phase II of PpOBA, in low molecular weight copolymer rich in pOBA, and an apparent splitting of off-meridian layer line O' spacings when annealed near the melting point. It is noted the "melting point" in the above descriptions is actually the T_{k-m} transition; *i.e.* from crystal to liquid crystal.

Of concern below will also be comparison of the observed ED patterns with those from PpOBA and PONA, the ED patterns usually being sharper and more readily interpreted than x-ray fiber patterns since both single crystal and "fiber" type patterns can be obtained. In particular, we have described single crystal [001] patterns of phase I and II of both polymers, patterns from epitaxially crystallized phase I PpOBA and PONA and phase II PpOBA (lamellae normal to the substrate, permitting obtaining single crystal patterns from one or a few hkl zones containing the molecular axis), and phase I (PpOBA and PONA) and phase II (PpOBA) patterns from whiskers (similar to the epitaxial samples except only a single zone). ED patterns from sheared (fiber-type) samples were also reported. These patterns have been used for determinations of the phase I crystal structures of both homopolymers. In addition, single crystal phase I (POBA and PONA) and phase II (POBA), as well as phase I whisker (POBA and PONA) patterns, were obtained as a function of temperature^[3, 4, 14, 15].

EXPERIMENTAL

2,6-Naphthalenedicarboxylic acid (NDCA, TCI America, Inc., decomposition before melting), 2,6-naphthaloyl chloride (NC, prepared from NDCA as described in Ref. [16]) or dimethyl 2,6-naphthalene dicarboxylate (DMNDC, Aldrich, $T_m = 190$ – 193 °C) and hydroquinone (HQ, Aldrich, $T_m = 172$ – 175 °C) or hydroquinone diacetate (HQDA, Aldrich, $T_m = 121$ – 123 °C) were used. The CTFMP was carried out as previously described^[2]. 1% acetone solutions of the mixed monomers in *ca.* 1/1 mole ratio were cast on glass cover slips or mica, covered with the same substrate and heated on a thermostatted hot plate or hot stage of an optical microscope to temperatures (T_p) between 100 and 350 °C. Polymerization times (t_p) varied with the T_p and are described relative to individual figures below. For the CTFSP samples shown here polymerization was carried out in 1% Therminol 66* (T66), Marlotherm S** (MTS) and mineral oil (MO) solutions between either glass cover slips or mica sheets.

Our standard transmission electron microscope (TEM) sample preparation techniques (*e.g.*, Ref. [2] or [17]) were used, with Au coating rather than Pt/C shadowing being used for in-situ calibration of ED spacings when desired. Samples were removed from the substrates using dilute HF. TEM and ED were done on various microscopes; JEOL 100C, Philips 400, 420, and CM12, and a Tesla BM 500.

Details of the measurement of spacings on the ED patterns and simulation of the unit cell are the same as described for PPT in the previous paper^[1]. Spacings were measured by eye with a lens on films and by profile scans (NIH Image) on both original and background subtracted scans.

* Trademark of Solutia, Inc. for a heat transfer fluid

** Trademark of Huls America, Inc. (Creanova Inc.) for a heat transfer fluid.

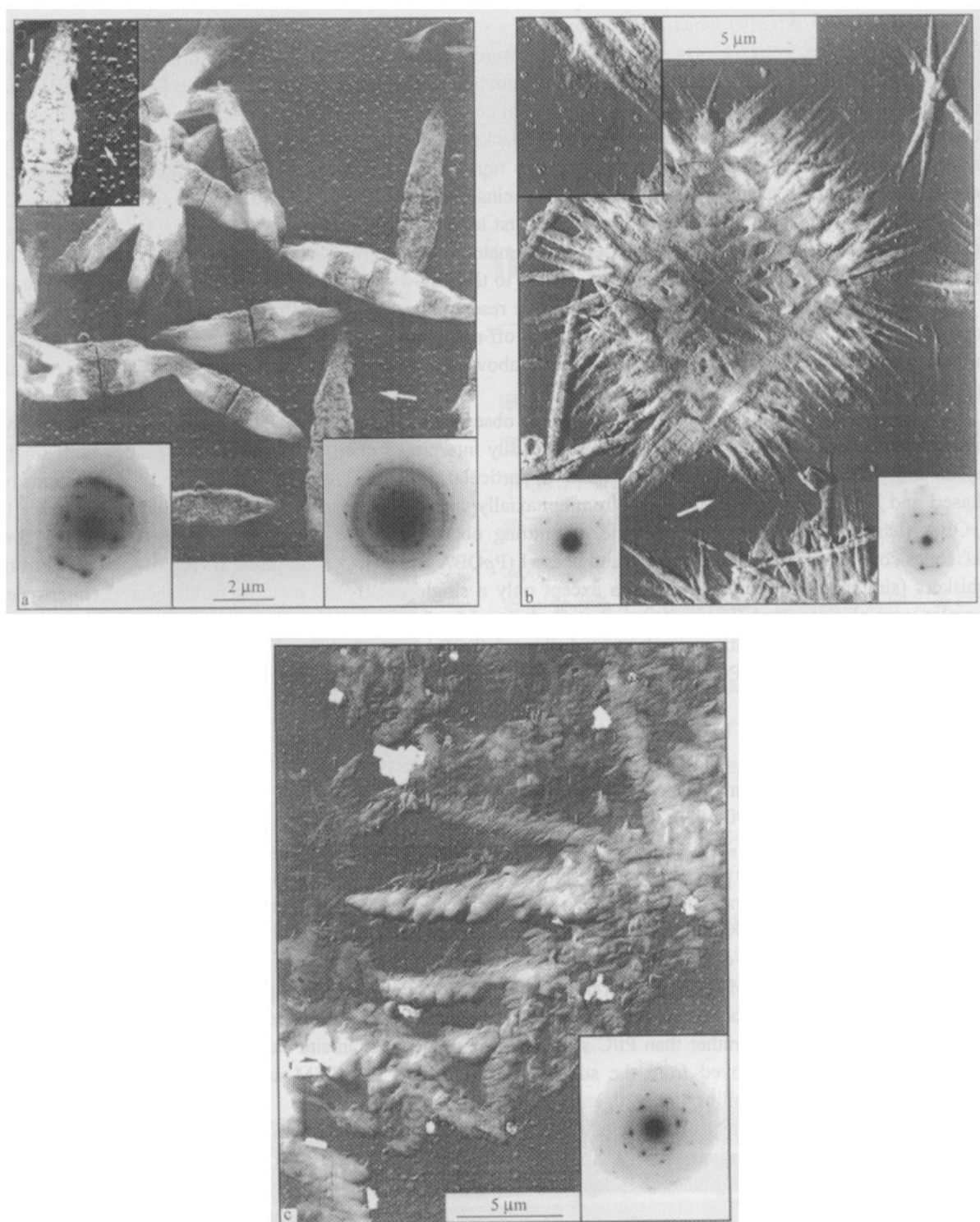


Fig. 1 NC/HQ samples polymerized between glass at (a) 200°C, 14 h; (b) 220°C, 14 h and (c) 240°C, 3 h
For inserts see text

RESULTS AND DISCUSSION

Morphological Observations

NC/HQ samples were prepared on glass at T_p between 170 and 240°C. At 200°C thick, pointed, elongated crystals were observed (Fig. 1a), the majority giving rise to phase II type ED patterns with phase I patterns occasionally being seen (insets with phase II on the right, both patterns having a weak pattern of the other phase superimposed). Similar structures were seen at 170 and 180°C T_p . Frequently individual thin lamellae, *ca.* 80 Å thick, could be seen at the edges of the thick crystals (arrow, also inset). Although these crystals roughly resemble the thick crystals of PET grown at 225°C, which were composed of lamellae at an angle to the substrate^[18], there is no suggestion of lamellae within the thick PPN crystals.

The basic elongated crystal morphology is retained at $T_p = 220^\circ\text{C}$, but many of the crystals are organized into cross-hatched structures (Fig. 1b). Most of this sample gave rise to single, phase II ED patterns (as in the lower right insert in Fig. 1(b); with the inner-most reflection assigned to 200), b^* is parallel to the long axis of the elongated crystals. Phase I patterns were seen infrequently (inset, lower left) but, when seen, the reflections were sharper than those of phase II. The insert at upper left, of the region indicated by the arrow, consists of a thin, leaf-shaped lamella; these lamellae gave rise to the phase I patterns, with a^* parallel to the long axis.

At $T_p = 240^\circ\text{C}$ (Fig. 1c) the morphology has a resemblance to that at the lower T_p but appears even more irregular and with the appearance of helical twisting of the elongated crystals. Only phase I patterns were obtained. In all of the samples polymerized at these relatively low T_p the substrate is covered with small, more or less, circular ridges and/or flat particles. These presumably are residues from the polymerization process, the ridges possibly being left when reaction by-products were dissolved following shadowing.

Somewhat surprisingly, NC/HQ PPN samples polymerized between mica, at high T_p , between 340 and 370°C, and short t_p were totally composed of well-formed lamellae. At 340°C/3 h, (Fig. 2a), 350°C/1 h and 370°C/1 h (Fig. 2b) the *ca.* 100 Å thick lamellae were more or less parallel to the substrate. In addition, however, small mounds of nearly perpendicular lamellae were observed, as in the insert in Fig. 2(b). The periodicity of these lamellae was 250–300 Å. For longer polymerization times at the higher temperatures, *e.g.* at 360°C/3 h and 370°C/3 h, splaying or round clusters of, presumably, nearly perpendicular lamellae were the predominant form (Figs. 2c and d). As shown by the inserts in Fig. 2(c), the lamellar nature of the clusters can be easily seen in regions in which they are tilted. The inserts in Fig. 2(d) are enlargements of an individual, small cluster and the edge of one of the large ones. In both inserts striations, again with an approximate 250–300 Å spacing, are seen; these are parallel, extend the entire diameter of each cluster and, presumably, correspond to lamellae on-edge. Similar, nearly featureless, round clusters were also observed in the 360°C/3 h sample and for a sample with $T_p = 380^\circ\text{C}$, $t_p = 3$ h. Epitaxy does not seem to play a role in their formation; the striations in neighboring clusters are at various angles to each other. As shown in Fig. 2(b), even at $T_p = 370^\circ\text{C}$, $t_p = 1$ h some of the smaller domains had a perpendicular orientation for the lamellae, as shown by the arrows in the insert, with the visible edges being smooth rather than granular as in the 370°C/3 h sample.

The lamellae parallel to the substrate all gave rise to phase I ED patterns, as shown in the insert to Fig. 2(a). The structures consisting of perpendicular lamellae gave rise to ED patterns appearing to contain hkl reflections (inset ED pattern in Fig. 2c); as discussed in reference to Fig. 9(a), where the pattern is shown at larger size, they are apparently from a monoclinic cell that is neither phase I or II. In these samples the c axis is normal to the lamellae, in the plane of the substrate. The zig-zag or parallel indentions on the surface of the 370°C T_p , 3 h t_p samples (Fig. 2d), present on all of the larger clusters at this T_p , may be related to differential thermal shrinkage of the polymer and substrate, as proposed for cracks observed in the CTFMP lamellae in PPT [1]; the parallel indentations are approximately normal to the lamellae.

PPN samples also were prepared by CTFMP between glass from DMNDC/HQDA (Fig. 3a, $T_p = 340^\circ\text{C}$, $t_p = 15$ h) and NDCA/HQDA (Fig. 3b, $T_p = 300^\circ\text{C}$, $t_p = 17$ h, Au coated for ED calibration) and by CTFSP from NDCA/HQDA in MTS (Fig. 3c, 1 % concentration, $T_p = 380^\circ\text{C}$, $t_p = 3$ h). All gave samples giving rise to single crystal ED patterns, but both CTFMP samples gave non-orthogonal patterns (inserts in Figs. 3a and b) while the

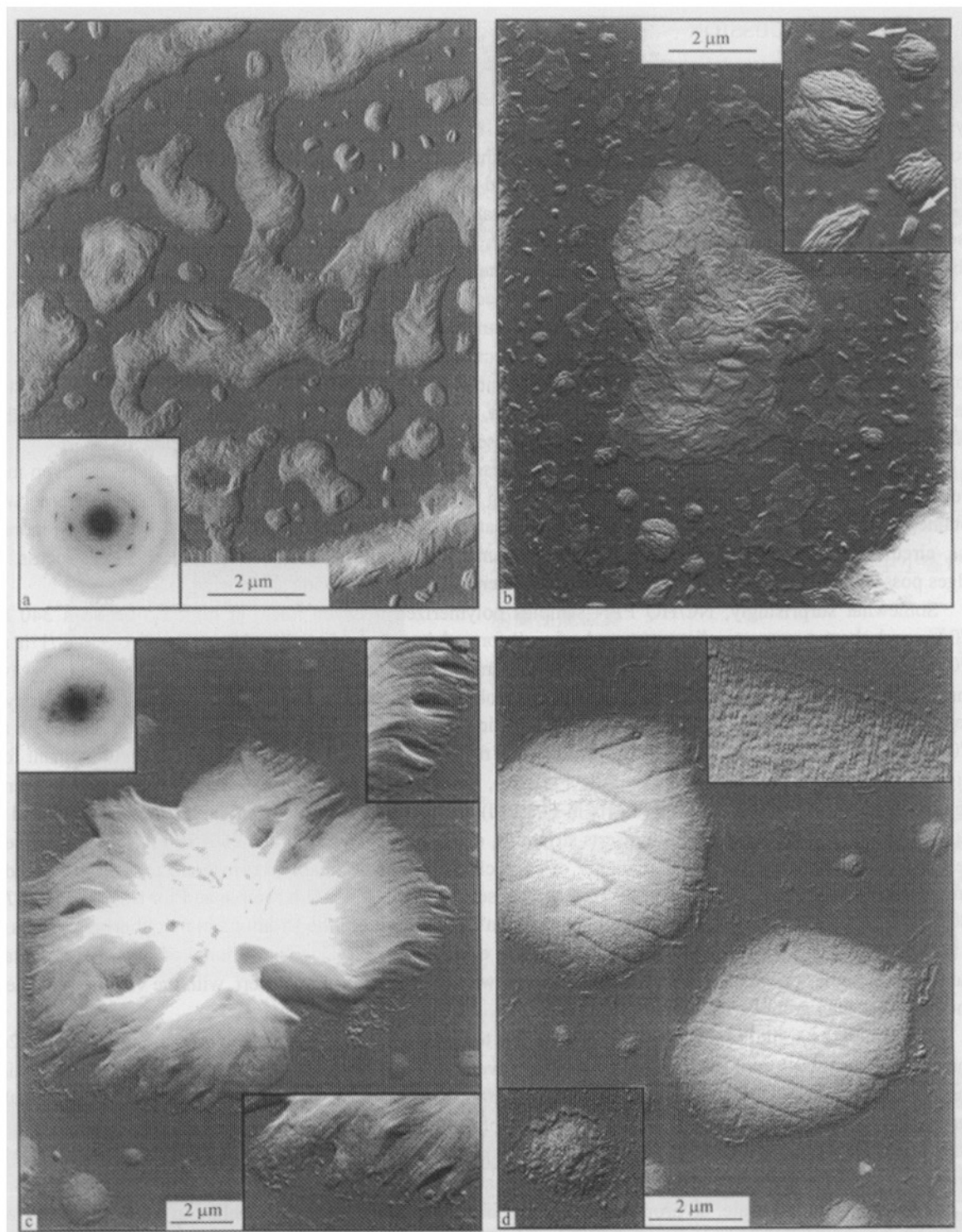


Fig. 2 NC/HQ samples polymerized between mica at (a) 340°C, 3 h; (b) 370°C, 1 h; (c) 360°C, 3 h and (d) 370°C, 3 h. For inserts see text

CTFSP sample gave phase I ED patterns (inserts in Fig. 3c). The DMNDC/HQDA CTFMP sample, which consisted of films and “chunks” of material of poorly defined morphology, also gave rise, less frequently, to

phase I patterns. The reflections in the non-orthogonal patterns were more diffuse and arced than in the phase I patterns and were often twinned. In Fig. 3(a), the films of polymer are curling up off the substrate, a feature seen in some, but not all, areas. The inset pattern, from the “enhanced” area of the micrograph, is at the correct

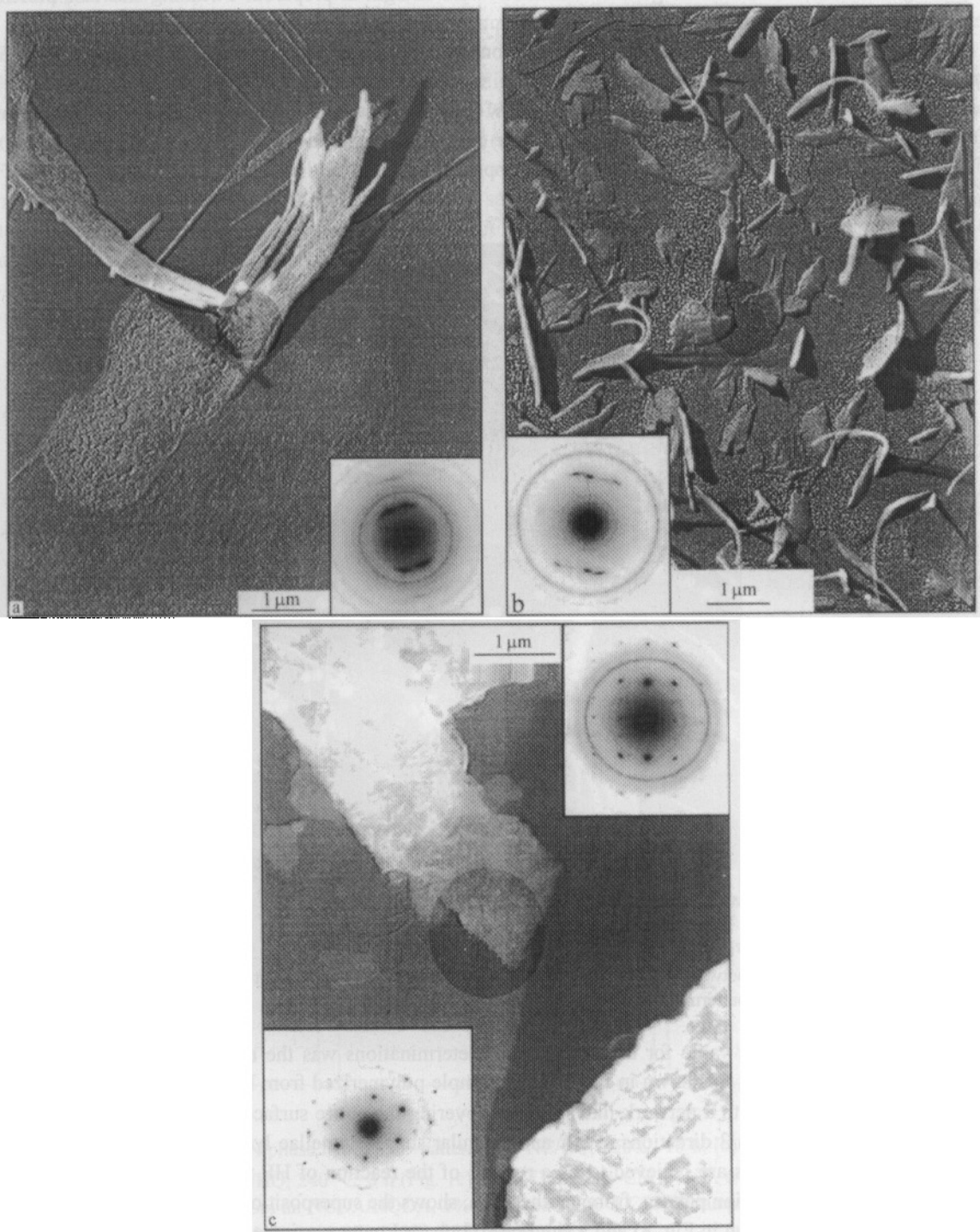


Fig. 3 CTFMP samples of (a) DMNDC/HQDA, 340°C, 15 h and (b) NDCA/HQDA, 300°C, 17 h and (c) a CTFSP sample, 1% NDCA/HQDA concentration in MTS, 380°C, 3 h. For inserts see text

orientation; there is no obvious relationship with the shape of the film. The NDCA/HQDA CTFMP sample (Fig. 3b) consisted of thick platelets lying either on the substrate or at a substantial angle, often with one or more curved, whisker-like appendages; this sample was Au-decorated for ED calibration. As indicated by the shadows, the curling is a result of beam damage; the “whiskers” were straight as prepared. Twinning was also present in the ED patterns, which were similar to those for the sample in Fig. 3(a), but was less prevalent.

The solution polymerized sample (Fig. 3c) also consisted of thick platelets, similar to those of PPT^[1]. They apparently fractured while in suspension, with some suggestion that they consisted of thinner lamellae. The alternating intensity of the adjacent reflections on the $h10$ and $h20$ row lines in the inset [001] ED pattern (lower left, see also Fig. 5b) suggests the possibility of double diffraction from these platelets; however this pattern was from the end of the crystal extending down from the upper left (circle) and is relatively thin. Other regions of this sample yielded $[0\bar{1}1]$ patterns, also inset.

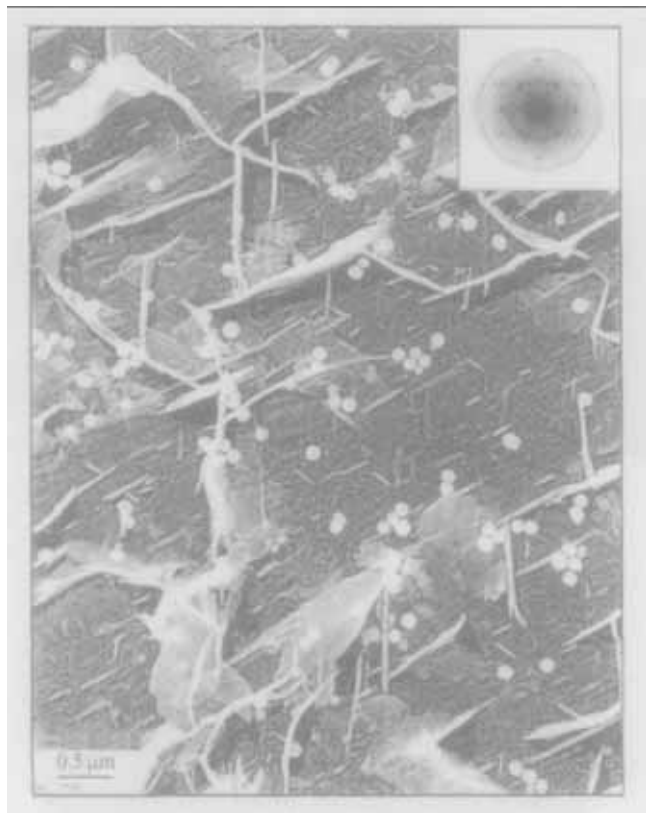


Fig. 4 NA/HADA sample polymerized at 250–330°C for 52 h between mica as a 1% solution in Therminol 66. The inset ED pattern is from a different area of the sample.

Of potential significant value for crystal structure determinations was the result of CTFSP between mica using a dilute (1%) solution. As shown in Fig. 4, for a sample polymerized from NA and HQDA, at 250–330°C, for 52 h in T66, in addition to a network-like structure covering the entire surface, relatively thick (300–600 Å) on-edge lamellae oriented in 3 directions at 60° and irregular shaped lamellae lying on the surface can be seen. The small spherical particles are believed to be a residue of the reaction of HF with the substrate; they are not shadowed. The inset diffraction pattern, from another area, shows the superposition of 3 [100] ED patterns at 60° (assuming the indexing shown in Fig. 8) and a single [001] phase I pattern oriented such that $\langle 200 \rangle^*$ in the [001] pattern is parallel to $\langle 002 \rangle^*$ of one of the [100] patterns. This pattern and another from a region showing a single orientation are shown enlarged in Fig. 8 below. The common orientation of $\langle 200 \rangle^*$ and $\langle 002 \rangle^*$ suggests the

growth direction of the on-edge lamella on the surface is b , with the epitaxial lamellae “falling over” to yield the crystals giving the $[001]$ patterns. This is in agreement with the epitaxial patterns being $[100]$, b and c lying in the plane of the substrate. Epitaxial samples were also obtained by CTFSP between mica at, *e.g.*, 350°C , using MTS and MO as solvents

“Good” ED patterns representative of the various phase I $[001]$ found are shown in Figs. 5(a)–(d), with other zones in Figs. 5(e) and 5(f). In Fig. 5(a), from a NC/HQ, $250^{\circ}\text{C}/16\text{ h}$ sample there is an alternation of intensity along the $hn0$ row lines for $n = 0$ –2, while in Fig. 5(b), from the MTS $380^{\circ}\text{C}/3\text{ h}$ solution polymerized material as in Fig. 3(c), the same alternation on these row lines is seen to higher orders, but is reduced or absent on the outer row lines with $n = 3$ and 4. The alternation (and general form) is reminiscent of the patterns of PPT in Figs. 4(a) and (b), Ref. [1], as well as the phase I patterns of PpOBA and PONA. While there is the possibility of multiple scattering, the pattern in Fig. 5(a) is from a sample consisting of only a few lamellae and the similar pattern inset in Fig. 3(c) is from a thin sample as well; it is this type of pattern we used for comparison with the simulated patterns based on the modeled crystal structure.

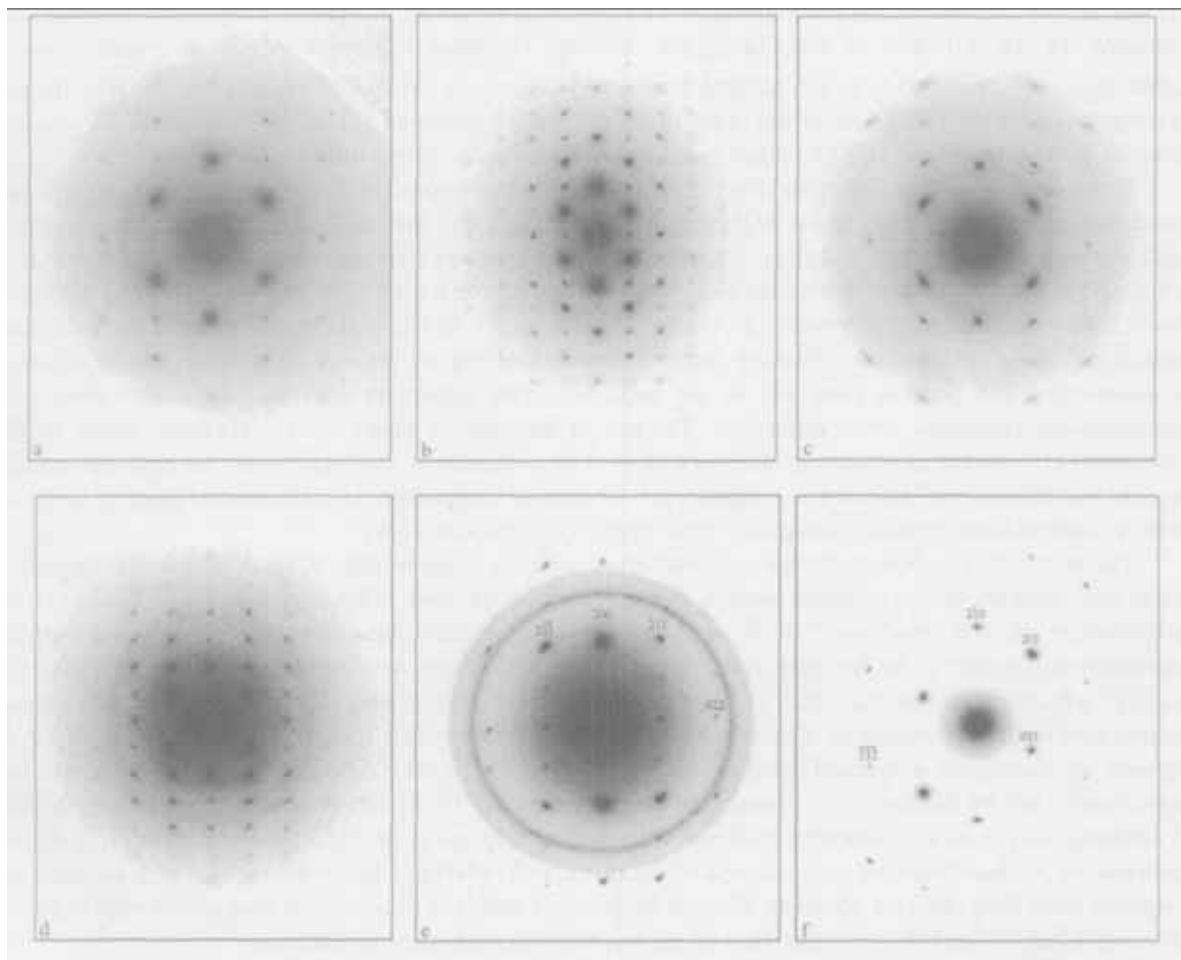


Fig. 5 “Representative” PPN phase I $[001]$ ED patterns: (a) NC/HQ, 250°C , 16 h; (b) 1% NDCA/HQDA in MTS, 380°C , 3 h (Fig. 3c); (c) NC/HQ, 240°C , 3 h (Fig. 1c); (d) NC/HQ in 1-CN, 245°C , 6 h. Phase I $[0\bar{1}1]$ and $[1\bar{2}2]$ patterns are shown in (e), from an NCDA/HQDA, 1% MTS, 380°C , 3 h CTFSP sample, (Fig. 3c) and (f), from an NC/HQ sample polymerized between mica, 160°C , 72 h, respectively.

In Fig. 5(c), from the NC/HQ 240°C/3 h sample in Fig. 1(c), $\{410\}$ and $\{320\}$ are enhanced, $\{210\}$ are nearly as strong as $\{200\}$ and the alternation of intensity on the $h10$ and $h20$ row lines is absent; the pattern is similar to that inset in Fig. 2(b) and Fig. 4(f) for PPT [1]. For PPT the changes in intensity were attributed to a 10° tilt about b , bringing in the $\{32\bar{1}\}$, $\bar{3}41$, $\{41\bar{1}\}$ and $\bar{6}02$ reflections. A similar tilt about b is likely here if growth of the molecules occurs with the ends attached to the substrate (as shown below, $\beta = 99.7^\circ$). The pattern in Fig. 5(d) is from a sample polymerized in 1-CN at 245°C for 6 h; these samples were used to prepare the sheared samples whose ED patterns are in the next figure. The pattern resembles those of PPT in Fig. 4(e)^[1], with $\{210\}$ enhanced relative to $\{200\}$, the alternation effect greatly reduced and an asymmetric distribution of intensities in the quadrants. As printed, with a upwards and $-b$ to the right, 110 and $\bar{1}\bar{1}0$ are stronger than $\bar{1}10$ and $1\bar{1}0$ while 410 , $\bar{4}\bar{1}0$ and 320 , $\bar{3}\bar{2}0$ are weaker than the corresponding reflections in the neighboring quadrants and 420 , $\bar{4}\bar{2}0$, 310 , $\bar{3}\bar{1}0$ and 220 , $\bar{2}\bar{2}0$ are strengthened. This was attributed there, and here, to a small tilt about one of the diagonals; representative simulations for the tilts in Figs. 5(c) and (d) are given in Ref. [1] with similar simulated patterns being obtained for PPN. The variations in intensity from pattern to pattern are indicative of the difficulty of determining the "correct" reflection intensities to use in crystal structure determinations. Phase I $[0\bar{1}1]$ $[1\bar{2}2]$ patterns are shown in Figs. 5(e) and (f). The spacings in Fig. 5(a), (b) and (e) were used for the refinement of the unit cell parameters; as discussed below, the unit cell of the on-edge lamellae in the CTFMP and CTFSP sample on mica are believed to be from a different unit cell.

Representative phase I patterns from sheared samples are shown in Figs. 6(a)–(d). All patterns are composed, in the lower half, of a scan of the negative, and in the upper half of a background subtracted (rolling 2 ball) pattern prepared using NIH Image. These samples were prepared from material solution polymerized in 1-CN at 245°C for 6 h and then sheared by hand with a razor blade on a glass slide on a hot plate at temperatures above the polymerization temperature, *e.g.*, *ca.* 310°C. Also shown, in Fig. 7, are profile scans of the meridional reflections, using background subtracted patterns, from a number of patterns of different initial exposure (corresponding ED patterns from Fig. 6 are indicated). The uppermost scan has the pattern from gold superimposed, permitting direct calibration. The rest of the patterns shown were "calibrated" based on the innermost (110) equatorial reflection, taken as 4.58 Å (4.58 s on patterns; the listed values are believed accurate to only one decimal, the second being appropriate for internal comparison on an individual pattern) based on both the sheared sample pattern with gold and the single crystal patterns above.

The pattern in Fig. 6(a) is assumed representative, with the apparent 002, 003, 005 and 007 strong. (It is noted that, contrary to the epitaxial samples in Fig. 8 below, 007 here is stronger than 002.) With 011 (the reflection on the first layer line, 5.61 Å), 110 and 200 being present, there is no apparent alignment of the molecules with respect to the substrate; cylindrical symmetry is assumed. Also visible are apparent 013, 016, 116 and 017 reflections. On the other hand the third "equatorial" reflection appears split (see Fig. 6c), but to a lesser degree than would correspond to it being a first layer line reflection. This reflection, with a spacing of 3.2 Å, appears to correspond in general position and appearance, to the 211 reflection reported by Windle and coworkers^[12] and by Blackwell and coworkers^[13] in as-drawn ($d = 3.3$ Å) and in annealed copolymer ($d = 3.04$ Å) although 011 is at a considerably different spacing than they report for the annealed sample (5.21 Å). As indicated by the superimposed scale, several of the meridional reflections (in particular 002, 003 and 005) are displaced from their expected positions. Also, as shown more clearly in the corresponding profile scan in Fig. 7, 005 is split and 002 and 003 have shoulders on the low and high angle sides, respectively.

Another example of the splitting of reflections and their displacement from expected layer line positions is shown in the more intense sheared sample pattern shown in Fig. 6(b); the corresponding profile scan is the second from the bottom in Fig. 7. All of the meridional reflections inside 008 (enlarged in the insets), except 004, are split, with the weaker reflection being at larger angles than 003, 005, and 006, inside 002 and on both sides of 007. Except for the extra reflection outside 005, the splitting appears to have the same $\Delta\theta$. If attributed to the superposition of a small angle spacing, as discussed relative to a similar observation for PPT [1], that spacing here is *ca.* 1/3 the layer line spacing, *i.e.*, *ca.* 60 Å, corresponding to *ca.* 3.5 "dimer" repeat periods. With the

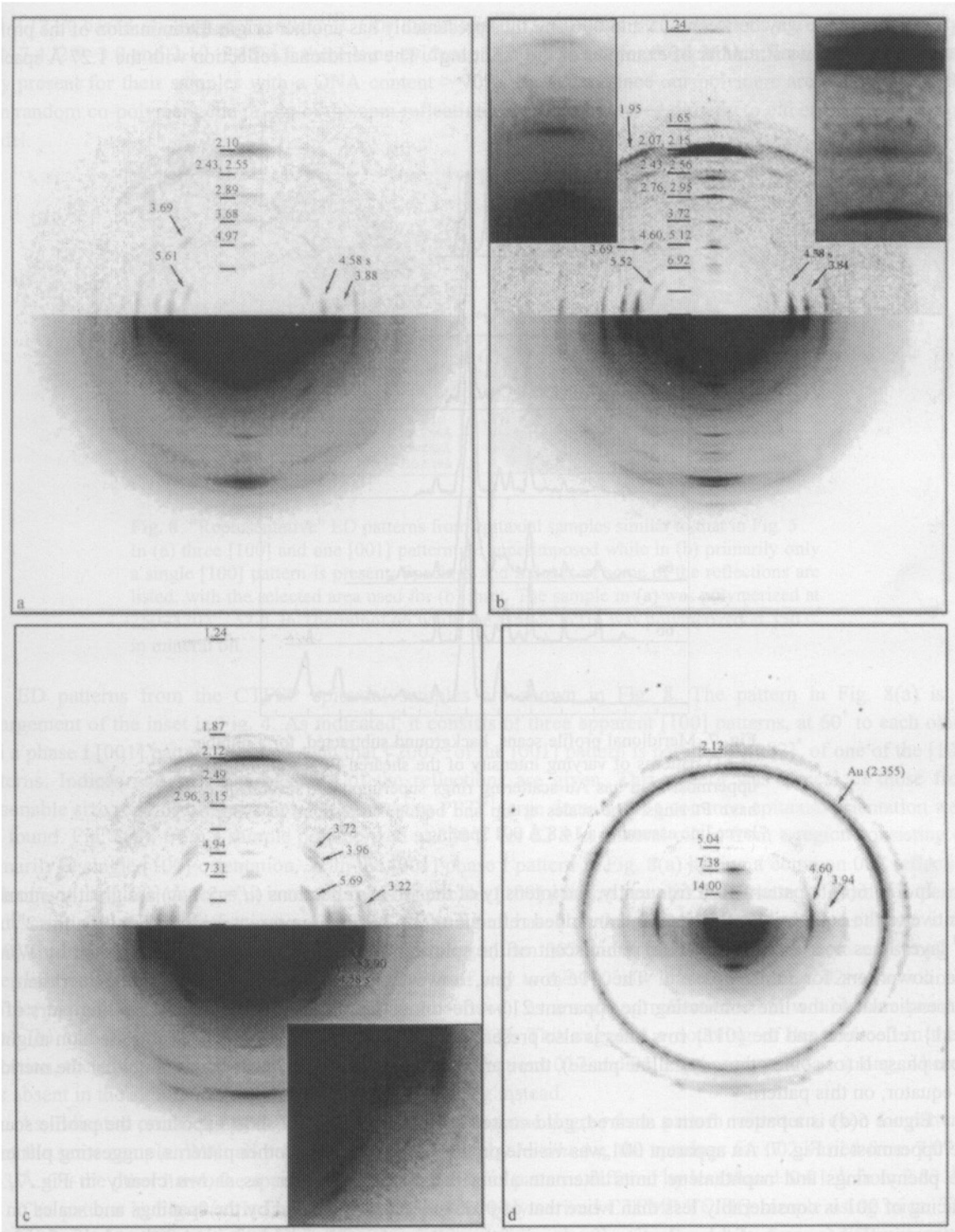


Fig. 6 “Representative fibers” ED patterns from sheared 1-CN polymerized (245°C, 6 h) samples of PPN
For inserts see text

initial sample being low molecular weight, the splitting may thus be due to segregation in layers without significant end-linking during the high temperature shear. The “extra reflection” outside 005, on the other hand,

appears nearly half-way between 005 and 006 and thus presumably has another origin. Examination of the profile scans in Fig. 7 shows a number of examples of the “splitting”. The meridional reflection with the 1.27 Å spacing is 0012.

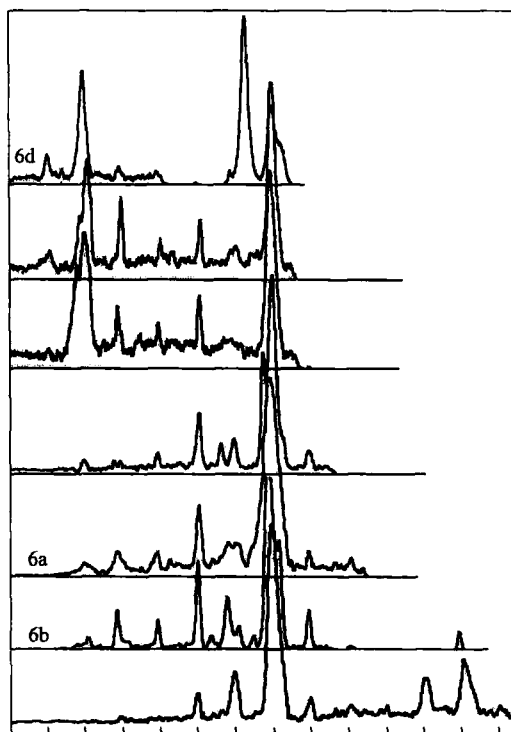


Fig. 7 Meridional profile scans, background subtracted, for a number of ED patterns of varying intensity of the sheared PPN samples. The uppermost scan has Au scattering rings superimposed; several others have Pt rings. The scales at top and bottom correspond to expected layer-line assuming a 14.8 Å 001 spacing.

In Fig. 6(c), a pattern seen frequently, the intensity of the “011” reflections ($d = 5.7$ Å) are greatly enhanced relative to the equatorial reflections and an added reflection ($d = 3.96$ Å) is present midway between the 2nd and 3rd layer lines near the 01 ℓ row line, reminiscent of the splitting of off-meridian layer lines reported by Windle and coworkers for O’ samples^[12]. The 01 ℓ row line, however, appears tilted relative to the meridian, but perpendicular to the line connecting the apparent 211 reflections; this tilt of both the line connecting pairs of the {211} reflections and the {01 ℓ } row lines is also present in Figs. 6a and b. Although the extra reflection might be from phase II (or some other crystalline phase), there are no other “extraneous” reflections, on either the meridian or equator, on this pattern.

Figure 6(d) is a pattern from a sheared, gold coated sample, taken with a short exposure; the profile scan is the uppermost in Fig. 7. An apparent 001 was visible on this and a number of other patterns, suggesting planes of the phenyl rings and naphthalene units alternate along the c -axis. However, as shown clearly in Fig. 7, the spacing of 001 is considerably less than twice that of 002. Indeed, as indicated by the spacings and scales on the patterns in Fig. 6, many of the reflections in many of the patterns are not orders of either 001 or half of 002; *i.e.* they are apm reflections. Based on the separation of 110 and 200 these patterns might be compared to those from the O’ cell defined by Windle, *et al.*^[12]; however, they did not observe O’, the PH phase transforming to O’ on annealing a 1/1 copolymer. Blackwell and coworkers have reported meridional spacings for a 50/50 copolymer (7.49, 2.95 and 2.09 Å by diffractometer, 7.43, 2.84 and 2.02 Å on a film, with predictions of 7.41, 4.26, 2.98

and 2.12 Å based on their pcl model)^[13]. Our meridional 002, 005 and 007 reflections agree reasonably well (7.2–7.4, 2.9–3.0 and 2.10–2.15 Å); there is no evidence in our patterns for the 4.26 Å reflection which also was only present for their samples with a ONA content > 70%. However, since our polymers are alternating rather than random co-polymers, the origin of the apm reflections cannot be ascribed directly to either the npl or the pcl model.

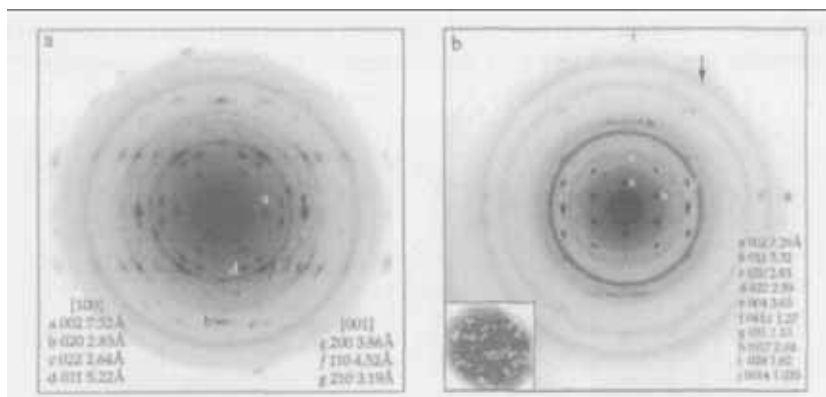


Fig. 8 “Representative” ED patterns from epitaxial samples similar to that in Fig. 5. In (a) three [100] and one [001] pattern are superimposed while in (b) primarily only a single [100] pattern is present. Spacings and indexes of some of the reflections are listed, with the selected area used for (b) inset. The sample in (a) was polymerized at 250–320°C, 52 h, in Therminol 66 while the sample in (b) was polymerized at 350°C in mineral oil.

ED patterns from the CTFSP epitaxial samples are shown in Fig. 8. The pattern in Fig. 8(a) is an enlargement of the inset in Fig. 4. As indicated, it consists of three apparent [100] patterns, at 60° to each other, and a phase I [001] pattern oriented such that $\langle 200 \rangle^*$ of the [001] pattern is parallel to $[002]^*$ of one of the [100] patterns. Indices and spacings of some of the reflections are given. This pattern was typical of those from reasonable size regions of the sample; in contrast to PPT^[11] large domains of a common epitaxial orientation were not found. Fig. 8(b), from a sample polymerized at 350°C for 22 h in mineral oil, is from a region consisting of, primarily, a single [100] orientation. With the [001] phase I pattern in Fig. 8(a) having a common 002 reflection with one of the [100] patterns, it is tempting to assume the [100] patterns are also from phase I. In order to permit its description the [100] reflections are labeled on the figure based on that assumption. However, as shown in the [100] simulation below (Fig. 12), 007 should be stronger than 002 and it is absent. Instead there are strong 7th layer line reflections on a row line at a distance *ca.* half way to the 010 row line. In addition a 021/2 ℓ row line is visible, particularly on the right side of the pattern (arrow), as are strong reflections that would correspond to 01/27 (h) and 041/21 (f) labeling the reflection at *b* as 020. This suggests a doubling of the unit cell in the *b* direction, the row line then being 05 ℓ and the strong reflections 017 and 91. Furthermore 028 is strong, whereas it is absent in the simulation and 0.2.11 is relatively strong instead.

As indicated on the figures, 002 (and 004) varied to some degree from pattern to pattern, even for patterns from the same sample. With all patterns being calibrated by *in-situ* Au, the spacings for 002 varied from 7.07 to 7.33 Å. On the other hand, the spacings for 020 on the same patterns differed by less than ± 0.01 Å from 2.83 Å.

The pattern in Fig. 9(a) is from a high temperature polymerized CTFMP TC/HQ sample using mica. This pattern, in which 002 ($d = 7.27$ Å) is the only visible meridional reflection, is clearly from a different crystal structure than either the CTFMP single crystal or the sheared samples, resembling, to an extent, the patterns from the epitaxial samples. In particular 002 is on the meridian with the 7th layer line reflections split. On the other hand there are many more reflections on the equator and first layer line. As printed the 2.86 (presumably the 020 in Fig 8b), 4.31 and 5.27 Å (presumably the 011 reflection) reflections are on rows at a slight angle to the

equator. It is noted the patterns shown were calibrated based on the 2.27 Å Pt ring, which is more diffuse than the ring from Au. The spacings of the two strong, inner equatorial reflections are 4.9 and 4.3 Å, based on a gold calibrated pattern, compared to 4.58 and 3.83 Å for the two innermost equatorial reflections in phase I. With the PH phase for P(pOBA/ONA) of various composition having equatorial reflections at *ca.* 4.6, 2.6 and 2.3 Å^[7, 10, 11], and an annealed 75/25 copolymer having intense reflections at 4.57, 3.83, 3.13 and 2.69 Å (Ref. [13], presumably the O' of Ref. [12]), these patterns from samples polymerized between mica must be from a different crystal structure than phase I or any of those described by Windle and coworkers^[12] or Blackwell and coworkers^[13].

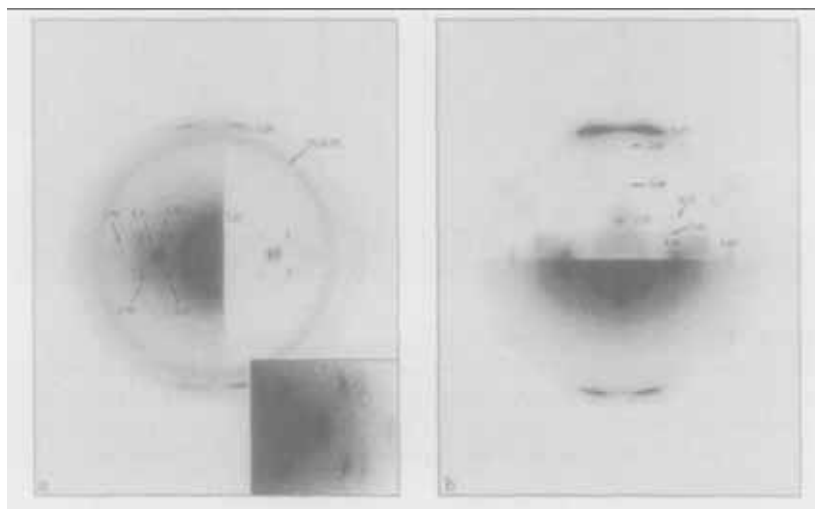


Fig. 9 ED patterns from high temperature (NC/HQ, 360 °C, 3 h) CTFMP samples polymerized between mica. The pattern in (b) suggests it is from a single zone, differing from that in Fig. 8(b), with 002, 004 and 006 being visible on the negative.

An apparently related pattern, from a different mica sample, is shown in Fig. 9(b). Here only the [310], [020] reflection (and [040]) are on the equator, suggesting a common orientation for the *a* and *b* axes in all of the lamellae in the round cluster. On this pattern 004 and 006, as well as 002, could be seen on the meridian, at *ca.* 3.7 and 2.45 Å. The 004 and 006 reflections are too weak to locate well enough to determine if they are apm reflections; we do not believe they are. Although we have not attempted to determine the crystal structure of this modification, in part due to the apparent variation in the 002 spacing, the lack of an [001] pattern and the apparent large unit cell size, it clearly is not orthorhombic.

A phase II pattern (200 = 5.88, 110 = 3.45 Å), seen frequently from the lower *T_p* CTFMP NC/HQ PPN samples, is shown in Fig. 10(a). In many of these patterns (not visible here), a low intensity phase I pattern is superimposed with a common orientation. The *hk0* spacings of this phase II are close to those of phase II of PpOBA (*a* = 11.15, *b* = 3.80 Å^[3]) and PONA (*a* = 11.6, *b* = 3.8 Å^[15]). A single, non-orthogonal, pattern, here from DMNDC/HQDA, is shown in Fig. 10(b), with the more often observed twinned pattern in Fig. 10(c). Spacings are listed on the patterns. The spacings of the reflections in Figs. 10(b) and (c) do not agree with either phase I or the pattern observed for the samples polymerized between mica. Thus, there are apparently at least four crystal structures possible for PPN at room temperature.

PPN Phase I Crystal Structure

Refinement of the ED spacings^[19] using the [001] and $[0\bar{1}1]$ patterns in Figs. 5 and 6 leads to a unit cell (Fig. 11) with *a* = 7.76, *b* = 5.71, *c* = 14.99 Å, $\alpha = \gamma = 90^\circ$, $\beta = 99.7^\circ$, $\rho = 1.47$ g/cm³. Corresponding spacings are 110 = 4.58, 200 = 3.82, 020 = 2.85 and 002 = 7.39 Å. The *hk0* reflections, as expected, are in good agreement with the spacings obtained from the [001] patterns as well as the equatorial reflections on the sheared sample patterns. 002 is also in reasonable agreement with the spacings observed on the sheared sample patterns when 002 is not split

(e.g., Fig. 6d) and with the “center of gravity” of the split patterns; however it clearly does not correspond to the values of 001 when the latter was observable.

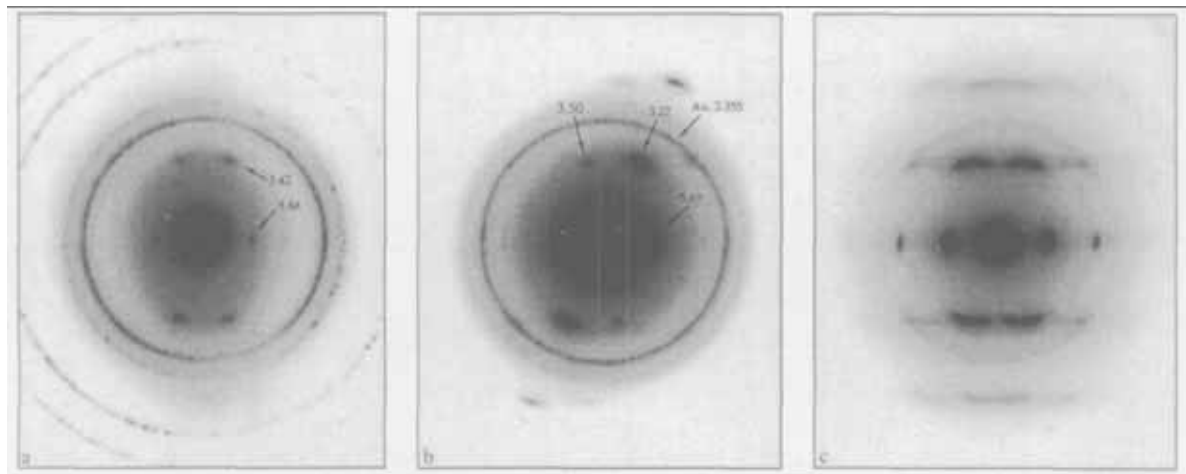


Fig. 10 (a) Phase II PPN [001] pattern from a NC/HQ, 220°C, 14 h CTFMP sample polymerized between glass. (b) and (c) Patterns from CTFMP DMNDC/HQDA samples polymerized between glass 340°C, 15 h.

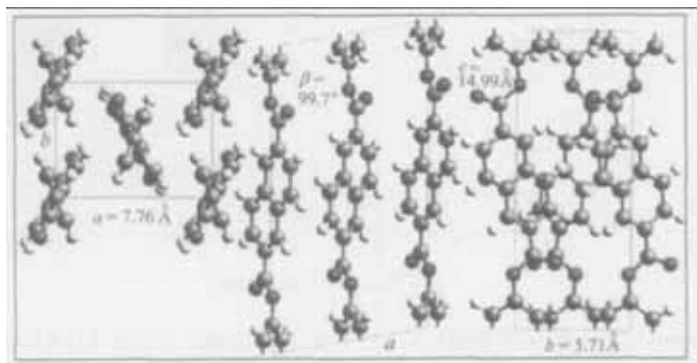


Fig. 11 Proposed PPN unit cell

With nearly identical appearing [001] ED patterns for PPT (Fig. 4a, Ref. [1]) and PPN (Fig. 5a), including the alternation of intensity along the orthogonal row lines, the projection of PPT and PPN crystal structures along c are essentially the same in the simulated unit cell (Fig. 11). The space group, $P2_1/a$, is also the same. As for PPT, the chains were rigidly rotated 6° symmetrically about their axes, following minimization, to obtain better agreement with the [001] patterns. The resulting simulated intensity distribution for [001] (Fig. 12) is essentially identical to that for PPT, with similar good agreement with the observed patterns. Again the simulated pattern, as for PPT, has a poorer agreement with the non-alternating ED pattern, in Fig. 5(d), than with the alternating pattern. The simulation is also in reasonable agreement with the intensity distribution in the $[0\bar{1}1]$ pattern in Fig. 5(e) except for the lack of $1\bar{1}1$ in the simulation. Comparison of the simulated phase I [100] pattern with that obtained from the epitaxial CTFSP sample (Fig. 8b) indicates some large differences in measured and predicted intensities for some of the reflections, particularly those at larger scattering angles. In particular, 007 is predicted to be 1.8 times the intensity of 002 and is essentially absent and the 024:022:020 ratios are predicted to be 2.1:1.1:0.3 and are clearly in the opposite direction. There is, in addition, the suggestion of a doubling of the unit cell in the b -axis direction, with the 01/27 and 041/21 strong reflections and the $011/2\ell$ row line. It was these

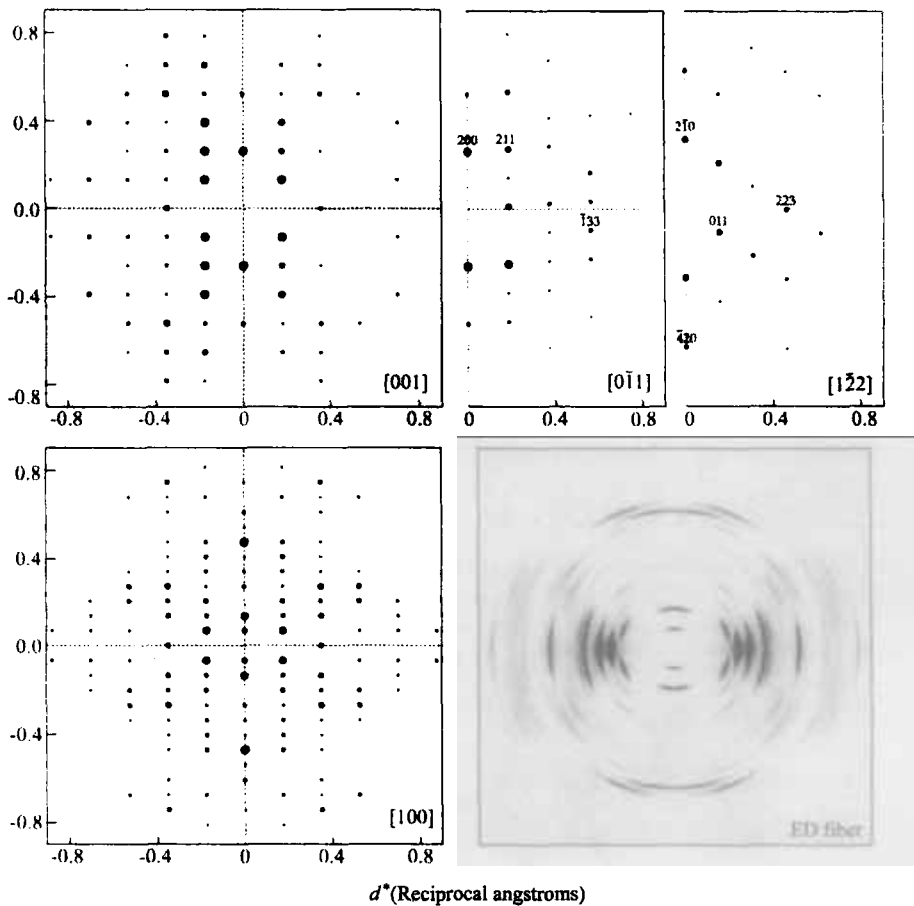


Fig. 12 Simulated phase I a) [001], b) $[0\bar{1}1]$ c) $[1\bar{2}2]$ and d) fiber ED patterns based on modeling with Cerius². Two intensities are shown for [001], the right side being at a lower intensity to show the relative intensities of the inner reflections. The fiber pattern was simulated with crystal sizes of $a = 100$, $b = 200$, $c = 500$ Å and an orientation breadth of 7°.

discrepancies that lead to the conclusion the mica samples had a unit cell different than phase I. In the simulated fiber pattern 007 and 011 are strong, in apparent agreement with the sheared “fiber” patterns in Figs. 6(a)–(c). Also visible in the “fiber” patterns, as in the simulation, are 013, 015, 016 and 017, but 012 was absent in all of the observed patterns although present in the simulation. Thus even though, as noted above, in the ED fiber patterns the 01 ℓ row line appears to be at an angle with $\langle 001 \rangle$ and 011 has a spacing of 5.5–5.6 Å, rather than the predicted 5.33 Å, tentatively we suggest the fiber patterns are from phase I crystals.

CONCLUSIONS

As in the case of PPT^[1], the PPN results also represent some of the problems in determining crystal structures using electron diffraction, the biggest problem in this case being obtaining reliable data for other than $hk0$ reflections. The use of sheared samples is suspect, the patterns always being more diffuse, with fewer reflections, and arced relative to those from CTFMP samples. The introduction of disorder is obvious. For PPN, as for PPT^[1], polymorphism is also present, “phase II” patterns being obtained from both, as well as non-orthogonal patterns from apparently additional unit cells. Furthermore the samples polymerized between mica, which would be expected to yield good patterns containing 00 ℓ reflections, did, but the unit cell differs from that giving rise to the [001] patterns from the CTFMP lamellae grown between glass.

Using the spacings on the patterns from the CTFMP glass samples for refinement of the phase I unit cell, the cell for PPN is similar to that for PPT, with a longer c axis; both have a $P12_1/a1$ space group with $a = 7.76$, $b = 5.71$, $c = 14.99$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 99.7^\circ$ for PPN as compared to $a = 7.89$, $b = 5.49$, $c = 12.65$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 100.33^\circ$ for PPT. However, we suggest the unit cell described here should be considered as only a first approximation, with further non-[001] zones being needed as well as clarification of the relationship, if any, between the structures of the CTFMP-glass and mica and CTFSP-mica samples.

Both the glass and mica substrate CTFMP samples, when polymerized at high T_p , gave rise to well formed lamellae, on the order of 100 Å thick for all conditions examined. Contrary to when similar polymerization conditions were used for PpOBA and PONA, there was no evidence of epitaxial polymerization/crystallization on mica for the CTFMP samples. However the lamellae were all normal to the substrate, arranged in sheafs or circular aggregates, whereas for PPT they were parallel to the substrate. On the other hand, as for PPT^[1], the CTFSP samples between mica were clearly epitaxial, with c lying in the plane of the substrate.

Of additional remaining concern is the origin of both the apm and "split" reflections. With PPN being a regular, alternating copolymer, the npl model would not seem to apply as an explanation of the apm reflections. However, it is possible that end group alignment, in the nascent crystals, with different end groups could lead to a register plane alignment, as proposed in the pcl model^[7]. Further attempts to obtain single crystal patterns from additional zones for both the phase I and the epitaxial samples, as well as samples of PNT (polynaphthalene terephthalate), the same chemical composition as PPN but with the ester group directions reversed, are in progress. Of particular interest will be examination of the apm and split reflections as a function of thermal history and molecular weight as well as determination of the crystal structure of the modification in the CTFMP and CTFSP samples polymerized on mica. As for PPT, the results and discussions above represent both the value of using electron diffraction, and some of its problems, for crystal structure determination of polymers.

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