

CRYSTAL STRUCTURE AND MORPHOLOGY OF NASCENT SAMPLES OF SYMMETRIC AROMATIC POLYESTERS I. POLY(*p*-PHENYLENE TEREPHTHALATE)*

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Abstract The morphology and crystal structure of poly(*p*-phenylene terephthalate) (PPT), prepared by confined thin film melt (CTFMP) and solution (CTFSP) and bulk solution polymerization, were characterized by transmission electron microscopy, electron diffraction and molecular modeling. The unit cell is monoclinic (P2₁/a space group) with parameters $a = 7.89$, $b = 5.49$, $c = 12.65$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 100.33^\circ$, density = 1.48 g/cm³, the a , b and β values differing slightly from those reported previously in the literature. A degree of variation in relative intensities of $hk0$ reflections in, apparently, untitled [001] ED patterns was observed from a given sample, suggesting some variation in molecular packing. ED evidence was found for a second phase, with [001] appearing the same as for phase II of the related poly(*p*-oxybenzoate) (PpOBA) polymer. CTFMP crystals polymerized above 220°C (up to 370°C) and CTFSP crystals polymerized at 300°C consisted of lamellae 100–200 Å thick.

Keywords Poly(*p*-phenylene terephthalate), Electron diffraction, Crystal structure, Confined thin film melt polymerization, Epitaxy, Morphology

INTRODUCTION

Our presentation at PP 2002 gave examples of the advantages of using electron diffraction and our technique of confined thin film polymerization^[1, 2] for the characterization of condensation polymer crystal structures. With the resulting crystals generally consisting of extended chain lamellae *ca.* 100 Å thick, yielding [001] ED patterns with $hk0$ spacings, kinematic diffraction can be assumed. Methods for obtaining zones containing hkl reflections were described, with examples drawn from published papers on poly(*p*-oxybenzoate) (PpOBA)^[3], poly(2,6-oxynaphthoate) (PONA)^[4], poly(3-bromo-4-oxybiphenylene-4'-carbonyl)^[5], polyterephthalic anhydride^[6] and polyethylene terephthalate^[7]. In addition, we summarized recent results on the non-directional, alternating copolymers, poly(*p*-phenylene terephthalate) (PPT) and poly(*p*-phenylene 2,6-naphthalate) (PPN). These results are the basis for this and a following paper^[8]. The crystal structures of these polymers, and poly(2,6-naphthalene terephthalate) (PNT) and poly(2,6-naphthalene 2,6-naphthalate) (PNN) which are currently being examined, are of interest because of their relationship to the related directional PpOBA, PONA and the 1/1 copolymer P(pOBA/ONA).

The phase I crystal structures of PpOBA^[3] and PONA^[4] were characterized utilizing electron diffraction (ED) patterns from CTFMP single crystal lamellae and single crystal whiskers prepared by solution

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polymerization. Lack of good phase II ED patterns containing hkl reflections for both homopolymers has prevented as-reliable determination of the phase II structures. In addition, the morphology of single crystals, disclination domains and superlattices of the, presumably, random copolymers poly(*p*OBA/ONA) (3/1, 1/1 and 1/3 mole ratios), prepared by CTFMP, have been described^[9]. Although [001] and fiber (sheared) ED patterns were obtained from both CTFMP and CTFSP (solution) samples of the co-polymers, 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 molecules have a direction to their backbone, with parallel chain packing being proposed for the phase I *Pp*OBA and PONA crystal structures^[3, 4].

The crystal structure of PPT has been described in the literature^[10], being determined from a combination of computer modeling and powder X-ray diffraction. In addition it is a demonstration in the molecular modeling program Cerius²^[11]. In the former the cell is described as monoclinic, space group $P2_1/a$ with unit cell parameters of $a = 7.98$, $b = 5.33$, $c = 12.65$ Å, $\beta = 98.98^\circ$. In order to obtain a 110/200 X-ray diffraction intensity ratio close to that observed, they assigned crystal sizes, in the version of Cerius² utilized, of 260 Å along a , 100 Å along c and 10,000 Å along b , with temperature factors of 0.8, 0.5 and 0, and lattice strains of 0.4, 0.2 and 0 along a , b and c , respectively. Due to the use of an early Cerius² type program, they did not minimize bond lengths, bond angles and torsion angles for the molecules in the cell. The demonstration, on the other hand, uses a P_1 superlattice (to permit the rotation) in which the molecules at the corner of the cell are rotated about c by 12° while the one in the center is not. This results in an asymmetric predicted electron diffraction [001] pattern, which is not discussed, agreement being sought for X-ray powder patterns only. Crystal sizes, temperature factors and lattice strains of 300, 10000 and 100 Å; 0.32, 0.32 and 0.05; and 0.6, 0.2 and 0.05 were assumed for the 3 lattice directions, a , b and c . The rotation, in particular, was done to bring the predicted 110/200 X-ray diffraction intensity ratio close to that obtained experimentally. The cell in Ref. [10] is the same as that described considerably earlier by the same authors in a paper devoted to the high temperature crystal structures of PPT and *Pp*OBA^[12]; although PPT is intractable, infusible and insoluble^[10], they interpret their high temperature X-ray diffraction data as indicating it goes through a gradual, second order phase change in the temperature range from 370 to 470°C that involves 180° rotations of the phenyl rings and a tendency towards hexagonal packing.

A theoretical *ab initio* conformational calculation for 4-hydroxyphenyl terephthalate (actually the acid), as a model for PPT was reported by Saebø *et al.*^[13] This was followed by a report^[14] on a comparison of "high quality" *ab initio* and molecular mechanics calculations of the conformation. In neither paper did they compare their results to the conformation described in Refs. [10] and [12]. They concluded the phenylene ring and terephthalate unit in each PPT repeat unit lie at an angle of 66° in the model compound, a value close to the 67° reported by Hanna *et al.* in Ref. [10], but that conformations with dihedral angles of $90 \pm 30^\circ$ have almost the same energy. The terephthalate unit, including the ester group and, in this case, the terminal carboxylic acid group, was said to be planar.

At about the same time Janischen *et al.*^[15] suggested that the PPT molecule has a 2_1 helical conformation in the unit cell, the successive chemical repeat units being twisted by 180° about C—O. Apparently, the carbonyl groups on a given terephthalate residue faced in the same direction, whereas in the cell for *Pp*OBA they face in opposite directions^[3]. A $P\bar{1}$ unit cell "containing two antiparallel chains" for this non-directional molecule was suggested, with $a = 7.85$, $b = 5.48$, $c = 25.38$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 98.62^\circ$. Comparison of a predicted X-ray diffraction pattern was made with an experimental powder pattern with claimed good agreement. A diagram of the proposed unit cell was not given. Unfortunately, the table of atomic coordinates published did not indicate the suggested twist, nor did a corrected table sent to us by one of the authors. In addition, we have been unable to generate a model unit cell using the Cerius² program^[11], as described below, with their parameters and a 2_1 helical conformation that yields a simulated [001] pattern in agreement with that observed.

Kimura *et al.*^[16] have described the morphology of bulk dilute solution polymerized PPT in liquid paraffin. In contrast to *Pp*OBA which, for similar polymerization conditions, polymerized in the form of single crystal whiskers, the PPT consisted of aggregates of thin plate-like crystals. The [001] ED diffraction shown is similar to

that we show in Fig. 4(a) below, although their schematic of the diffraction pattern has an asymmetric distribution of intensity that is not apparent in the original ED pattern shown. They report an a axis spacing of 7.87 and b axis spacing of 5.55 Å (actually $a^* = 0.127$ and $b^* = 0.180$ Å⁻¹ since only an [001] pattern is shown).

EXPERIMENTAL

Terephthaloyl chloride (TC, Aldrich Chemical Co., $T_m = 79$ – 81°C) or terephthalic acid (Aldrich, $T_m > 300^\circ\text{C}$) and hydroquinone (HQ, Aldrich, $T_m = 172$ – 175°C) or hydroquinone diacetate (HQDA, Aldrich, $T_m = 121$ – 123°C) were used as monomers, as supplied. The CTFMP was carried out as previously described^[1], 1% acetone solutions of the mixed monomers (TC + HQ or HQDA) in *ca.* 1/1 mole ratio being cast on glass cover slips or mica, covered with the same substrate and heated on a thermostatted hot plate or hot stage of a optical microscope to temperatures (T_p) between 100 and 350°C . For $T_p > 220^\circ\text{C}$ the polymerization was carried out in a nitrogen atmosphere for most of the figures shown here; however, similar crystals were found for polymerization in air. CTFMP polymerization times (t_p) varied with the T_p and are described relative to individual figures below. CTFSP samples were prepared, between mica, in Marlotherm S^{*} using a 1% solution of TA and HQDA at 300°C for 24 h. In order to prepare sufficient material for X-ray diffraction and DSC measurements, a TC/HQ sample was polymerized in the bulk for both 5 h at $T_p = 150^\circ\text{C}$ and 24 h at 240°C . PPT was also “bulk” polymerized in Therminol 66^{**} (*ca.* 1 % solution, at 300°C) and 1-chloronaphthalene (1-CN, *ca.* 1% solution at 235°C , the boiling point).

Our standard transmission electron microscope (TEM) sample preparation techniques (*e.g.*, Ref. [1] 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 CM 12 and a Tesla BM 500.

For determination of unit cell parameters and comparison with the Cerius² modeling results, the ED patterns were scanned with a Relisys 9624 scanner and Adobe Photoshop/Art Scan software (gray scale, photo grade, $\gamma = 1$) at a resolution of 1500 dpi for accuracy; the spacings were measured with NIH Image software. A least squares refinement program was used for determination of the cell parameters^[18]. The molecular simulation program Cerius² (4.5) with the Drieding force field was used, as previously described^[3, 4], to simulate the molecular conformation and packing in the unit cell and the resultant diffraction patterns. Following minimization of the single chain conformation using the Minimizer module, the chain conformation developed was rebuilt in the crystal using the Crystal Builder module and the selected space group symmetry.

The intramolecular interactions utilized (valence terms) include bond stretching, angle bending, torsional and inversion terms. The intermolecular interactions include van der Waals and Coulombic terms. For our periodic system the Ewald summation method was used in the minimizing calculations. Van der Waals interactions between atoms separated by three bonds were excluded from the energy term. Other parameters were usually chosen as the default options except in those cases in which settings were recommended in the manual for polymer-type periodic systems. A minimized chemical repeat unit of a single molecule was used to build the unit cell. The bond lengths, bond angles and torsion angles were minimized without restraint to obtain the minimum packing energy. For the simulated electron and X-ray diffraction patterns a global isotropic temperature factor of $B_{\text{iso}} = 5 \text{ Å}^2$ was used. A crystal thickness of 50 Å was used for the ED pattern displays, compensating somewhat for the variable substrate (and resulting sample) tilt by increasing the number of orders of reflections displayed. As suggested by the program a slight, symmetric rotation (4° about the c axis) of the resulting molecular positions was done to improve the agreement with the observed patterns.

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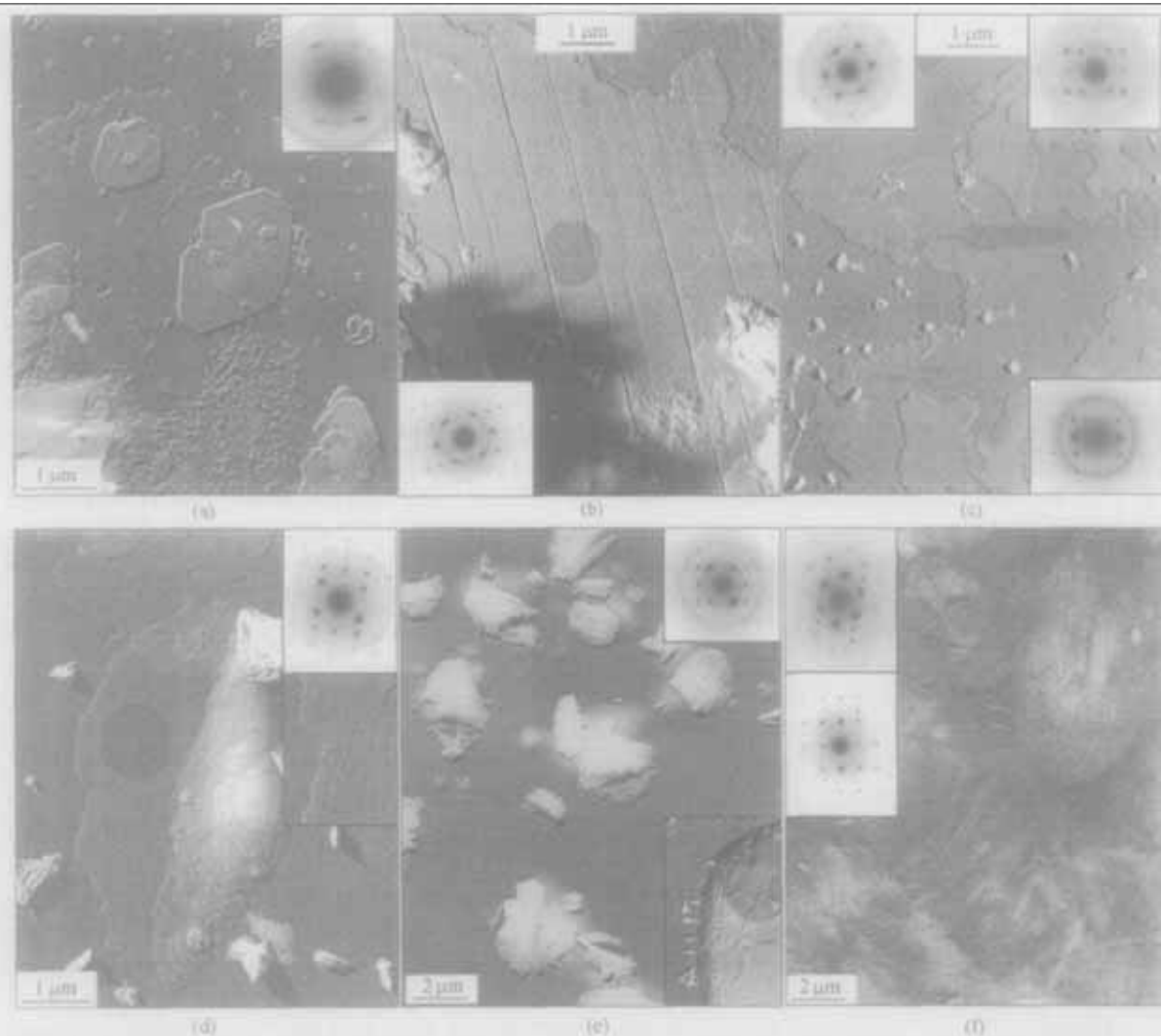


Fig. 1 TEM micrographs of CTFMP samples of TC/HQ polymerized at: (a) 160 °C, 6.5 h between mica; the inset ED pattern is from a sample of acetone cast TC; (b) 250 °C, 8 h, between mica; a properly oriented [001] ED pattern from the highlighted area is inset; (c) 270 °C, 6 h, between mica in an N₂ atmosphere. The ED pattern inset at upper left is properly oriented relative to the crystal at lower left; the other two inset patterns are from another grid square; (d) 270 °C, 6 h, between glass; the inset [001] ED pattern, properly oriented, is from the highlighted area; (e) 310 °C, 6h, between mica in an N₂ atmosphere, the properly oriented [001] ED pattern is from the highlighted area in the inset micrograph; (f) 340 °C, 1 h, between mica in an N₂ atmosphere. The ED patterns are from other areas of the sample

RESULTS AND DISCUSSION

Morphology Observations

The TC/HQ samples of PPT were polymerized between glass and mica at T_p between 100 and 350 °C (polymerization on mica resulted in epitaxial polymerization/crystallization for PONA^[17] and PpOBA^[19–21]). All of these samples had a basic lamellar structure, with lamellae on the order of 100 Å thick regardless of the T_p and t_p . Representative micrographs and ED patterns (in most cases from the samples shown, as insets) are shown for the TC/HQ and TC/HQDA samples in Figs. 1 and 2, respectively. For $T_p = 100$ °C, $t_p = 3$ h (not shown) the samples appeared to consist of single, *ca.* 50 Å thick lamellae or several lamellae in a stack, most of which were

punctured full of holes. We suggest this is due to low molecular weight material being extracted with the acetone used to wash the samples before replication, the thickness corresponding to only four chemical repeat units. Large areas gave rise to single crystal ED patterns, sometimes [001] (see below) and sometimes slightly tilted about b .

At 160°C ($t_p = 6.5$ h, on mica) the lamellae were ca. 100 Å thick. (Fig. 1a) Some regions of the polymer lamellae were also full of holes (lower center), to the extent that only small sections of the lamella remain, but the majority (middle and left) was of uniform thickness. The relatively thick plate-like crystals, composed of thin lamellae, are attributed to the oligomer or residual monomer recrystallized from the acetone. ED was not obtained from these crystals. The inset pattern is from TC monomer cast from acetone and differs considerably from the PPT patterns below.

At T_p of 220°C and above, on glass and mica, irregular boundary, single crystal lamellae, 100–200 Å thick, were obtained (Figs. 1b–e). Cracks, such as in Fig. 1(b) (TC/HQ, 250°C, 8 h, between mica, under N_2 , lamellar thickness ca. 200 Å), we have previously attributed to differential shrinkage of the crystal and substrate during cooling from T_p . However, a thin step can be seen running nearly parallel to the edge of the cracks, with curved “surface cracks” of apparently the same depth in the thicker regions between the lamella cracks. This step could be due to variations in chain length or a result of material precipitating on the surface following washing. Accepting the former suggests the cracks develop during polymerization due to shrinkage as a result of the loss of the condensation byproduct (HCl). The inset [001] ED pattern is from a 1 µm diameter selected area indicated approximately by the highlighted area. The general form of the [001] ED pattern in Fig. 1(b) and inset in the other parts of this figure resembles the phase I [001] pattern of PpOBA and PONA (e.g., Ref.[3, 4]). In the ED pattern inset in Fig. 1(b) 200 is slightly more intense than 110 and considerably more intense than 210. These relationships were found to vary from pattern to pattern. The pattern indicates the molecular axes are normal to the lamellae, with the a -axis ($\langle 200 \rangle$) normal to the cracks; this is the same direction as observed for PpOBA (Fig. 1a, Ref. [22]).

Similar crystals were also observed (Fig. 1c) for $T_p = 270^\circ\text{C}$, $t_p = 6$ h, between mica, with a N_2 atmosphere. The [001] ED pattern inset at the upper left is properly oriented relative to the crystal at lower left, the growth faces appear to be [110]. In contrast to the pattern inset in Fig. 1(b), 310 is more intense than 210. In the [001] pattern inset at upper right, from another area of this sample, 210 are the strongest reflections, with 200 being weaker than 110. The variation in intensity distributions in [001] patterns is shown more clearly in Fig. 4 below. The pattern at lower right, from the same grid square as that at upper right, is a $[0\bar{1}1]$ zone pattern indicating a tilt of c in the $\langle 010 \rangle$ direction of ca. 20° . Although there are no obvious cracks in the crystals shown, cracks similar to those in Fig. 1(b) were present in other crystals in the same preparation and the multi-lamellar regions in this picture had narrowly spaced (thin) cracks visible in the negative.

The thin steps on the single lamella portion of the crystal in Fig. 1(d) (shown at higher magnification in the inset) are parallel to the a -axis in the properly oriented, inset [001] ED pattern. This sample was also polymerized from HQ/TC, at 270°C, 6 h, but between glass without N_2 . Similar steps were seen for poly(ethylene terephthalate)(PET)^[7] where they were attributed to the competition of the molecular axes attempting to be normal to the substrate and the triclinic unit cell with $\gamma = 106^\circ$. PPT, however, has a monoclinic unit cell with $\gamma = 90^\circ$ and $\beta = 100^\circ$; a similar stepping off the substrate of molecules normal to the substrate should induce slip edges parallel to $\langle 010 \rangle$. Thus the origin of these surface steps is unknown. In the ED pattern 200 is weaker than 110 and has about the same or slightly weaker intensity than 210. Whereas the reflections on the $h10$ and $h20$ row lines alternate in intensity in the insets in Figs. 1(b) and (c) (upper left), the intensity here and in the upper right inset in Fig. 1(c) is relatively uniform on $h20$. The small, thick crystals resemble crystals of the monomer HQ and again may be a residue from the rinsing. The lamellae in these two micrographs were ca. 140 and 110 Å thick, respectively.

At 310°C (6 h, on mica, under N_2) the polymerization appears to have occurred within droplets (Fig. 1e). As shown by the inset, the crystals are still lamellar, ca. 130 Å thick, with thinner lamellae on the top of the stack. The ED pattern is from the approximate area indicated in the inset. In none of the samples polymerized by

CTFMP on mica was there any indication of epitaxial orientation; the molecular axes were essentially normal to the substrate. Regions consisting of several crystals also showed no evidence for homeotropic epitaxy^[17], the parallel cracks in the crystals lying at apparently any angle.

Crystals were obtained at T_p as high as 340°C (Fig. 1f, TC/HQ, 340°C/1 h, on mica under N_2). They again consist of stacks of lamellae with irregular edges, similar to the inset in Fig. 1(e). The inset ED patterns are from other areas of the same sample, the lower pattern being $[0\bar{1}1]$. The contrast is due to relative variations in the thickness of the mounds. Since the polymer has no measurable first order transition temperature, T_m or T_{k-m} , and is said to undergo a gradual second order transition above 370°C^[12] the presumption is that the crystals form during the polymerization rather than during cooling, possibly being in a liquid crystal oligomeric state in the initial stages of polymerization and crystallizing as the chain becomes long enough. Windle and coworkers^[10, 12] do not give a degree of polymerization for their samples; Saebø *et al.* indicate they had prepared samples by polymerization of HQ and TC in methyl chloride and pyridine solution with 4–7 repeat units (HQ–TC or HQ and TC not stated) that had “polymeric” physical properties^[14]. Assuming the former, 7 repeat units correspond to a 90 Å chain length, shorter than the thickness of all the lamellae described above.

Crystals prepared from HQDA and TA, in 1% Therminol 66 solution at 300°C for 16 h, were generally less well defined in terms of their morphology (Fig. 2a). They appear to consist of relatively thick plates with the suggestion, in some micrographs (based on Moiré patterns and thinner lamellae), that the plates were stacks of lamellae. They generally appear broken and irregular, as here. The ED pattern shown, properly oriented relative to the highlighted selected area used, has an asymmetric distribution of intensity that was also seen for some of the CTFMP samples polymerized at various temperature. For instance, the apparent 410, 320 and 520 are stronger than the corresponding reflections in the $\bar{h}k0$ and $hk\bar{0}$ quadrants, while 110, 220 and 310 are weaker. This asymmetry is attributed to sample tilt, a similar simulated pattern being produced for a tilt of 10° about an axis at 45° to $\langle 010 \rangle$. In the $hk0$ quadrant all of the reflections except 110 and 200 are actually $hk\bar{1}$ reflections,

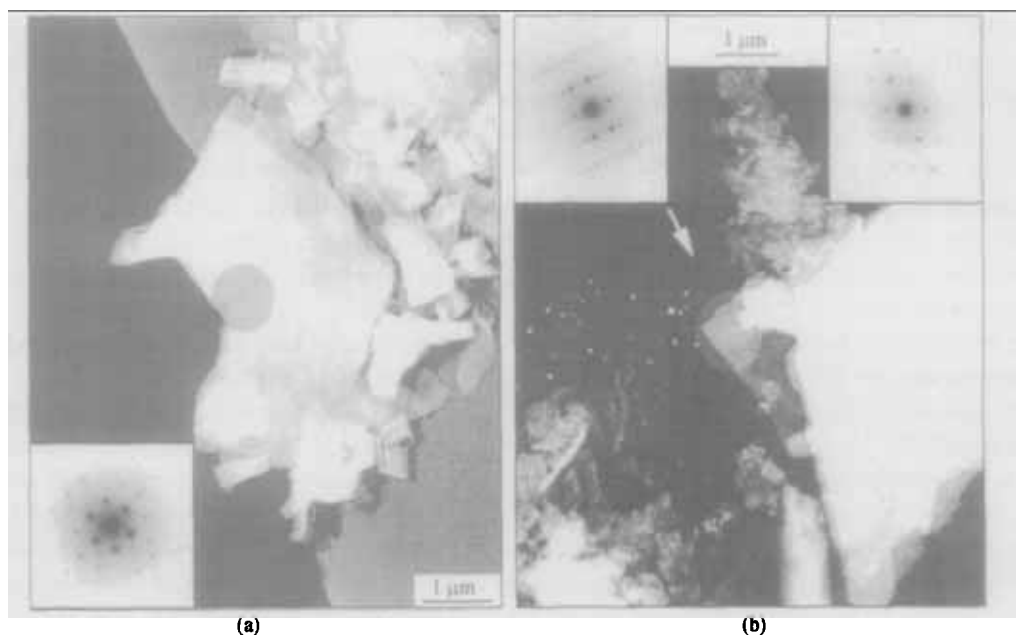


Fig. 2 (a) Crystals prepared from HQDA and TA in bulk 1% Therminol 66 solution at 300°C for 16 h. The inset $[001]$ ED pattern is from the highlighted area. (b) CTFMP crystals prepared from HQDA/TC at 160°C, 72 h, between mica. The insert ED pattern at the upper left, properly oriented, is from the highlighted area; that at upper right is from an area of the sample consisting of irregular crystals as in the region between the two patterns

while in the $\bar{h}k0$ and $h\bar{k}0$ quadrants the reflections with 2θ greater than that of $\bar{3}10$ are $\bar{h}k2$ and $h\bar{k}1$, respectively (see Fig. 9c below).

HQDA/TC polymerized by CTFMP between mica ($T_p = 160^\circ\text{C}$, $t_p = 72$ h) gave two types of crystals, (Fig. 2b) angular crystals composed of lamellae similar to those in Fig. 2(a) and even less regular crystals. The ED patterns from the irregular crystals (upper right inset, from a different region of the sample) may correspond to the $[12\bar{2}]$ zone of phase I (see simulations in Fig. 9 below); interestingly, it has nearly the same form as the $[001]$ pattern of PET^[7] and $[011]$ pattern, α phase of poly(butylene terephthalate) (PBT)^[23]. “Normal” $[001]$ ED patterns, similar to those inset in Fig. 1, were also obtained from this sample with no obvious difference in the corresponding morphology. Further examination would be needed to determine if the irregular crystals are actually PPT. On the other hand, the angular, lamellar crystals in this sample gave rise to phase II ED patterns (in terms of the nomenclature for PpOBA^[3]) as shown by the upper left inset. These crystals are believed to be PPT, probably of low molecular weight because of the low T_p . Phase II patterns were not obtained for the TC/HQ CTFMP samples. Preparation of other samples, by CTFMP, were attempted using HQDA and TA or dimethyl terephthalate but were, in general, unsuccessful in terms of producing samples giving ED patterns; micrographs were not taken.

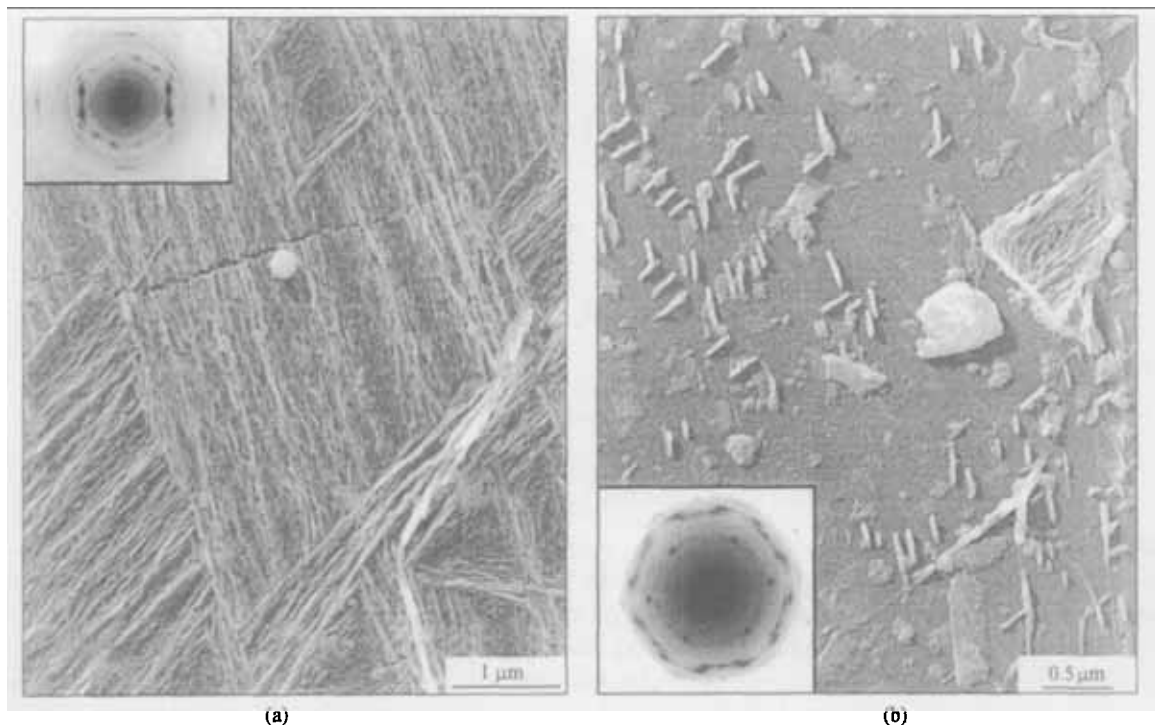


Fig. 3 CTFSP epitaxially oriented crystals prepared between mica from a 1% solution of TA and HQDA in Marlotherm S at 300°C for 24 h. The 2 micrographs are from different regions of the same sample.

The on-edge lamellae gave rise to $[120]$ ED patterns (insets, enlarged in Figs. 7c and d), while the lamellae lying on the surface give rise to $[001]$ patterns (inset in Fig. 3b)

On the other hand, TA and HQDA, polymerized by CTFSP between mica in Marlotherm S (Figs. 3a and b) resulted in epitaxial crystallization of 3 sets of on-edge lamellae oriented at 60° to each other. In some regions the apparent lamellae, *ca.* 200 Å thick, were closely packed in relatively large domains of common orientation (Fig. 3a), yielding $[120]$ ED patterns (inset, from a different area), whereas in other regions of the same sample relatively thick (*ca.* 400 Å), isolated on-edge lamellae and irregular, parallel lamellae were found (Fig. 3b). The

inset pattern, from a different area, consists of three [120] patterns and one [001] pattern, with the $\langle 100 \rangle^*$ of the [001] pattern parallel to $\langle 001 \rangle^*$ of one of the [120] patterns (see Fig. 7d below).

An FTIR scan of bulk polymerized PPT (HQ/TC, 150°C/5 h, acetone extracted prior to characterization), used for the X-ray scan shown in Fig. 11 below, is shown in Fig. 4. That only a relatively low molecular weight was attained is shown by the retention of the 1725 and 1693 cm^{-1} bands, also present in the TC monomer; ester bond formation is shown by the development of the 1737 cm^{-1} band as a shoulder on the 1725 band and disappearance of the 1760 and 855 aryl acid chloride bands. The 1500 and 1409 bands in PPT are attributed to the phenyl rings. The small peak at 1790 cm^{-1} is attributed to a small amount of poly(terephthalic anhydride)^[6]. With a chemical repeat period (the same as the physical repeat) of 12.63 Å, a 100 Å thick extended chain crystal consists of molecules with eight repeat units (HQ + TC).

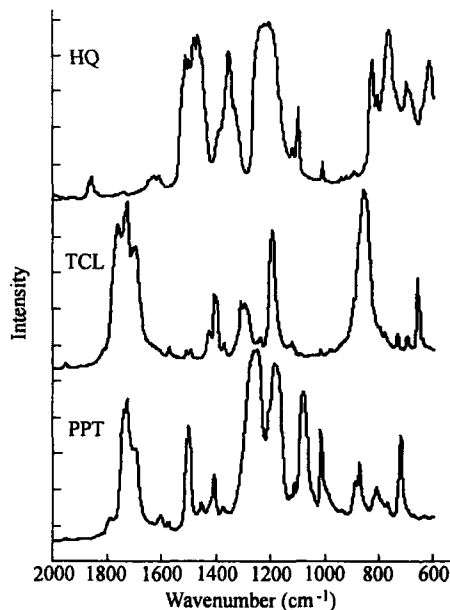


Fig. 4 FTIR scans of the two monomers (HQ and TC) and of a bulk polymerized sample (HQ/TC, 150°C, 5 h).

Electron Diffraction Results

As indicated above, the intensity distributions in the [001] ED patterns varied considerably from pattern to pattern, even from crystals on the same TEM grid. An example of a “good” [001] pattern (numerous reflections and presumably non-tilted) is shown in Fig. 5(a), with some of the observed variations in Figs. 5(b)–(e). Additional zones, obtained by tilting the beam or by the tilted orientation of the crystal on the substrate, and a phase II pattern are shown in Fig. 6. Patterns corresponding to sheared samples (“fiber” ED patterns) and the epitaxially oriented CTFSP sample are shown in Fig. 7.

In Fig. 5(a) the phase I type pattern has a symmetrical distribution of intensity in the 4 quadrants of the pattern, with an alternating decrease of intensity from 200, 110, 020 and 130 along the $h00$, $h10$, $h20$ and $h30$ row lines. 200 is approximately the same intensity as 110, with 210 considerably weaker. In Fig. 5(b), for which the crystal was apparently slightly tilted ($< 1^\circ$) about the b^* axis, the alternation of intensity is seen to extend even further in the reciprocal lattice and also occurs along the orthogonal row lines. The pattern in Fig. 5(b) was taken from solution polymerized crystals as in Fig. 2(a), and, because of the crystal thickness, multiple scattering is possible. For instance, the 200 reflection could serve as a main beam for the increased intensity in the 310, 310 and 400 reflections. However, the pattern in Fig. 5(a) was obtained from a 270°C/6 h CTFMP single thickness lamella, similar to that shown in Fig. 1(c) (see upper left inset pattern), for which multiple scattering is unlikely.

It is, thus, this type of pattern that was used for comparison with the simulated ED patterns obtained from Cerius².

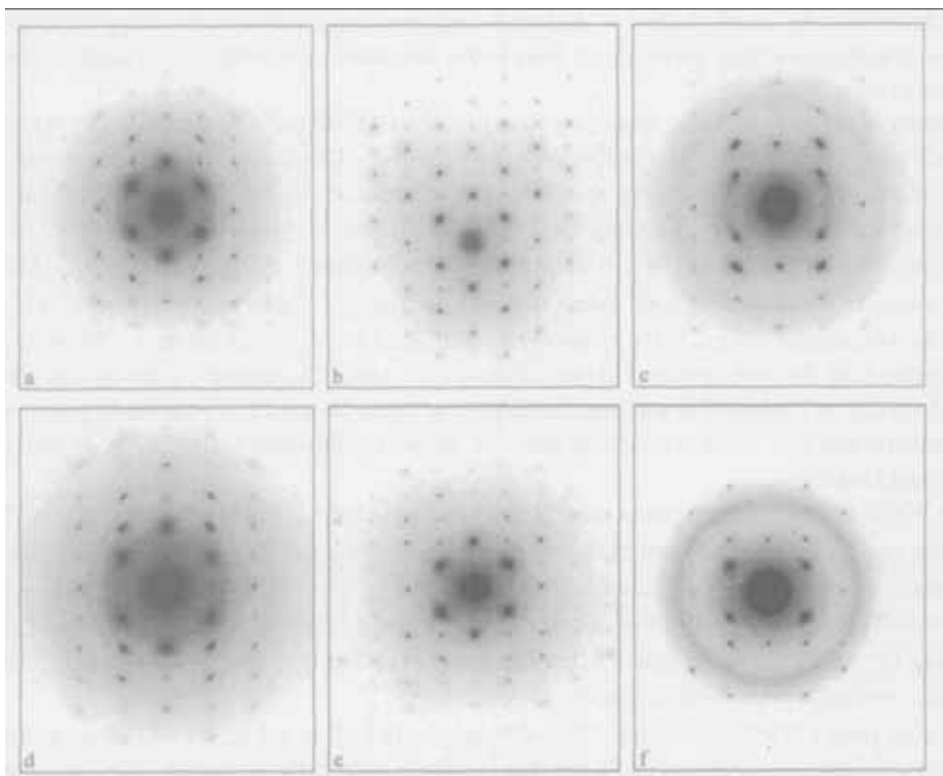


Fig. 5 ED patterns related to [001] from: (a) the sample in Fig. 1(d); (b) the sample in Fig. 2(a); (c) the sample in Fig. 1c; (d) a CTFMP sample polymerized at 370 °C, 1 h, between mica, under N₂; (e) same pattern as inset in Fig. 2(a); (f) a CTFMP sample polymerized at 230 °C, 14 h, between glass

Figure 5(c) is from the same sample as in Fig. 5(a) (see upper right insets in Figs. 1c and d); not only is there no alternation of intensity along the row lines, but 210 is the strongest reflection. In Fig. 5(d) (370 °C, 1 h, between mica) the alternation of intensity along the orthogonal row lines is nearly absent but 210 is weaker than 200 and 110. We suggest these variations are not the result of tilt of the crystal. A slight tilting about *a* or *b* would enhance the intensity of 2 neighboring quadrants, as in Fig. 5(b). Tilting 10° about, *e.g.* a 30 or 45° diagonal in the [001] zone, measured from the *b* axis, so as to bring in first layer line reflections, leads to an asymmetric pattern; the intensity of the apparent 210 and $\bar{2}\bar{1}0$ (actually 211 and $\bar{2}\bar{1}\bar{1}$) are enhanced, as in Fig. 5(c), but the actual $2\bar{1}0$ and $\bar{2}10$ are weakened. In addition $4\bar{1}\bar{1}$ and $\bar{4}1\bar{1}$ (apparent 410 and $\bar{4}\bar{1}0$) become strong while $4\bar{1}1$ and $\bar{4}11$ are weaker (see simulation in Fig. 9b). To enhance the apparent {210} in all four quadrants would require superposition of patterns from tilt about diagonals in neighboring quadrants, which is unlikely, and furthermore the apparent {410} are not enhanced. We also found no tilt yielding patterns with a lack of alternation of intensity along *h*20. We thus conclude these are “correct” variations in intensity distribution in [001].

In Fig. 5(e) (from the crystal shown in Fig. 2a) there is a tendency toward an asymmetric distribution of intensity, given reflections in the *hk*0 and $\bar{h}\bar{k}0$ quadrants having opposite intensity ratios relative to their neighboring reflections than those in the $\bar{h}k0$ and *h* $\bar{k}0$ quadrants. For instance, $\bar{1}10$ and $1\bar{1}0$ are weaker than 110 and $\bar{1}\bar{1}0$. However, 410, $\bar{4}\bar{1}0$ and 320, $\bar{3}\bar{2}0$ are weaker than the corresponding reflections in the

neighboring quadrants and 310 , $\bar{3}\bar{1}0$ and 220 , $\bar{2}\bar{2}0$ are strengthened. A distribution of tilts about one diagonal, similar to the simulation in Fig. 9(b), could lead to this type of pattern. It is noted that the simulation shown is for a 20 Å thick crystal, the small thickness, and thus long reciprocal lattice rods, being required to have the superposition of reflections from several layer lines in the simulation; a variation in tilt angle for thicker crystals would lead to a similar result.

The pattern in Fig. 5(f) was also frequently found for the CTFMP samples (here for a (230°C/14 h sample). In it there is a nearly symmetrical distribution of intensity, but the alternation along the row lines is absent, and 200 is about the same intensity, or weaker, than 210, both of which are weaker than 110. The apparent {410} and {320} are also particularly strong in all quadrants while {310} and {220} are nearly absent. A 10° tilt about b , bringing in the $\{32\bar{1}\}$, $\bar{3}41$, $\{41\bar{1}\}$ and $\bar{6}02$ reflections, will enhance the apparent {320}, {410} and {600} reflections, but nearly eliminates {200} (see simulation in Fig. 9c). Furthermore 110 and $\bar{1}\bar{1}0$, although not apparent in the simulation, are *ca.* 133% as intense as $\bar{1}10$ and $1\bar{1}0$. A 10° tilt about b is likely if growth of the molecules occurs with the ends attached to the substrate ($\beta = 100^\circ$). In summary, although the patterns in Figs. 5(b), (e) and (f) can be explained to a reasonable degree in terms of sample tilt, the variations in Figs. 5(a), (c) and (d) apparently can not; we thus conclude that PPT shows considerable variability in its [001] patterns and thus in its lateral packing.

Figures 6(a)–(e) shows patterns from other phase I zones, with the zones listed on the figures. The indices of the reflections can be determined from the corresponding simulations in Fig. 9. Figures 6(a) and b ($[1\bar{1}1]$ and $[1\bar{1}3]$) are from the bulk solution polymerized material as in Fig. 2(a) (TC/HQDA, 1% in Therminol 66, 300°C/16h). Figure 6(a) presumably suffers from considerable multiple scattering, the central row line extending at *ca.* 30° (including $10\bar{1}$ and $\bar{1}01$) being absent in the simulation (Fig. 9d). $30\bar{1}$ in Fig. 6(b) (absent in the simulation, Fig. 9e) is also attributed to multiple scattering.

Figure 6(c), from a CTFMP, TC/HQ, 270°C/6 h sample ($[0\bar{1}1]$, as in Fig. 1(c), ED inset at lower right) has a “more correct” intensity distribution and is the type of pattern used in the refinement. Similar patterns were also found in other CTFMP samples, as indicated by the inset in Fig. 1(f). Figure 6(d), from the bulk polymerized TC/HQ sample used for the FTIR and X-ray measurements ($[021]$, TC/HQ, 150°C/5 h) is relatively weak and was not observed for the CTFMP samples. Figure 6(e), from a TC/HQDA, 160°C/72 h sample as in Fig. 2(b), has an appearance much like the [001] patterns from PET^[7] and [011] from PBT^[23]. The spacings, however, in this $[12\bar{2}]$ pattern differ slightly from those for PET and considerably from those for PBT, the three inner most spacings being 3.19, 3.55 and 5.09 Å for the PPT pattern shown, 3.26, 3.59 and 5.18 Å for PET [001] and 3.52, 3.84 and 5.51 Å for PBT [011]. Comparison of these patterns with the corresponding simulated zones in Fig. 9 (below) aid in confirming the correctness of the modeled crystal structure; numerical comparison of intensities, however, is not appropriate since the direction of the beam relative to the reciprocal lattice was by chance rather than predetermined tilt.

A phase II pattern is shown in Fig. 6(f), from the same TC/HQDA sample as in Figs. 2(b) and 6(e). Assuming the pattern is from an orthorhombic unit cell, a and b are 11.54 and 3.52 Å, respectively, as compared to 11.15 and 3.80 Å for PpOBA phase II. The phase II patterns came from the lamellar appearing material in Fig. 2(b) whereas the $[12\bar{2}]$ came from the more granular appearing material.

A simple “fiber” pattern obtained by shearing a 1-CN prepared sample at 350°C is shown in Fig. 7(a). As prepared (at 235°C) presumably only short chain oligomers are obtained, permitting the shear at elevated temperatures; at the shearing temperature it is presumed further polymerization by end-linking occurs. Figure 7(a) consists of the superposition of $[110]$ and (weakly) $[100]$ zones; simulations of these two zones are shown in Fig. 10 below based on the unit cell described in the next section. In the actual pattern, 002 and 006 from the two zones are merged, yielding the arcs, with the 110 arc indicating a variation in chain alignment along the draw direction. The main quadrant reflections are 011, 013, 015, 016 and 022.

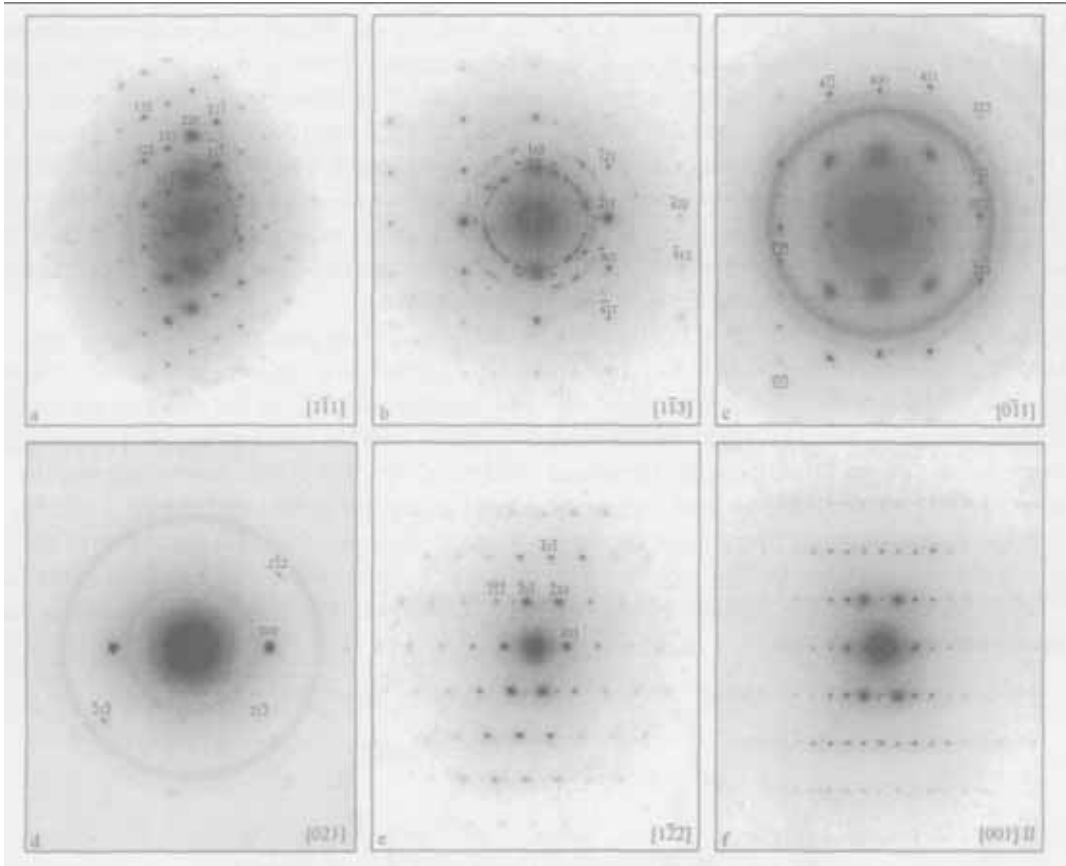


Fig. 6 ED patterns from other phase I zones and phase II. (a) and (b) $[1\bar{1}1]$ and $[1\bar{1}3]$, respectively, from the bulk solution polymerized material as in Fig. 2(a); (c) $[0\bar{1}1]$, same as the pattern inset in Fig. 1(c); (d) $[021]$ from a bulk melt polymerized HQ/TC sample ($150^{\circ}\text{C}/5\text{ h}$), morphology unknown; (e) $[12\bar{2}]$, same as the pattern inset at upper right in Fig. 2(b); (f) presumably $[001]$, phase II, same as the pattern inset at upper left in Fig. 2(b).

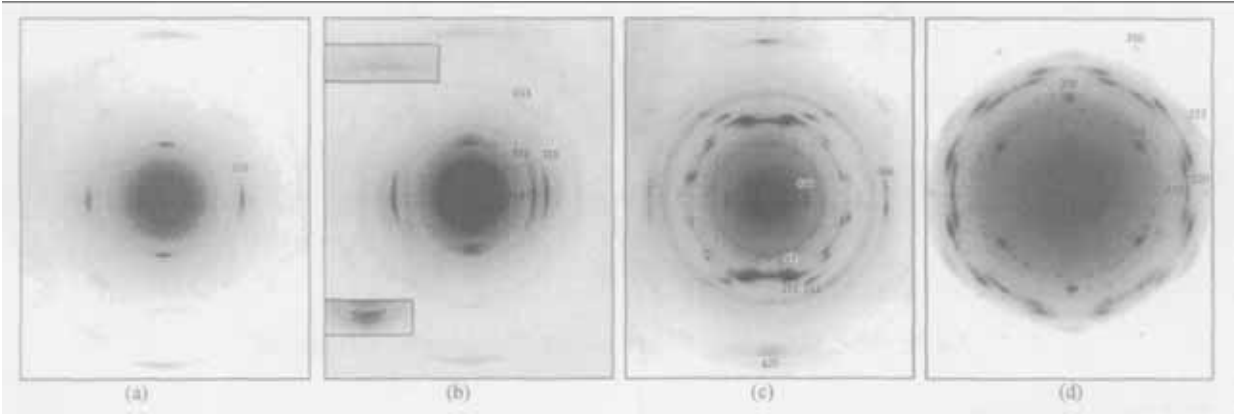
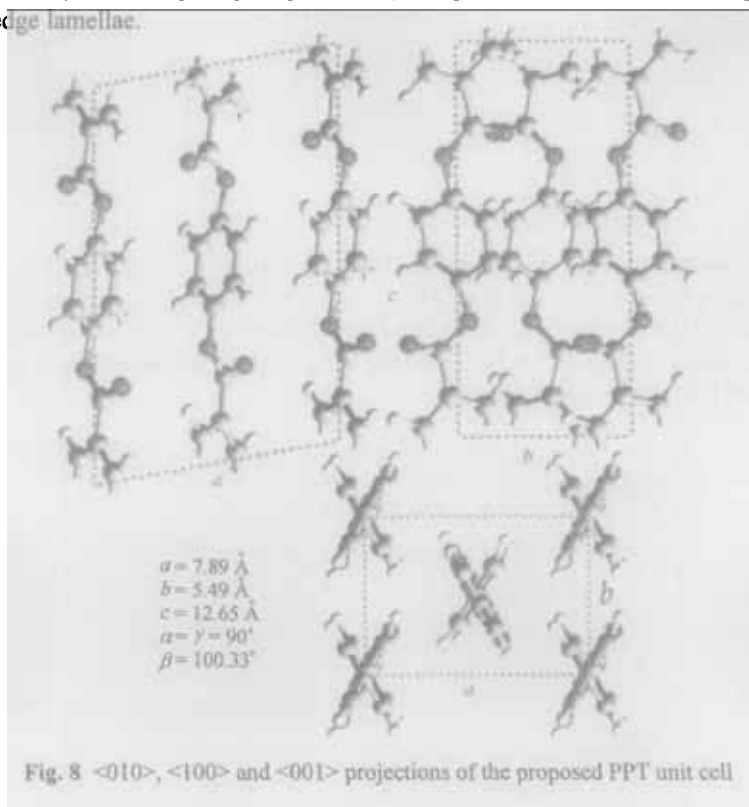


Fig. 7 (a), (b) “Fiber” ED patterns obtained from a solution polymerized sample (TC/HQ, 235°C in 1-CN) subsequently sheared at 350°C . 001 can be seen on the negative for (a). Splitting of the meridional reflections are shown in the insets of (b). (c) $[120]$ pattern from predominantly a single domain of the epitaxially oriented sample in Fig. 3(a). (d) Superposition of three $[120]$ patterns at 60° and an $[001]$ pattern, from an area similar to that in Fig. 3(b).

A more complex “fiber” pattern is shown in Fig. 7(b). Both 002 and 006 are split; as shown enlarged in the insets, there are 4 reflections for 002 and at least 3 for 006, the innermost reflection for both sets being narrowly split. $\Delta\theta$ for the more widely split reflections is ca. the same. The middle reflection of the widely split reflections 002 reflections corresponds to the “correct” spacing. Similar splitting has been observed for sheared PpOBA where there was no suggestion as to its cause^[1]. We suggest here, and for PPN where a similar splitting was seen^[8], that it may be due to a small angle periodicity due to alignment of chain ends in planes normal to the shear direction; the spacing corresponds to 150–200 Å. In addition, the inner equatorial reflection on the right side has a spacing similar to that expected for 010, but 010 should be forbidden in the proposed unit cell; we have no explanation for its presence unless it is due to residual monomer.

Figures 7(c) and (d) are from the CTFSP sample, with Fig. 7(c) being predominantly from a single domain of epitaxially polymerized material, as in Fig. 3(a), while Fig. 7(d) is from a region as in Fig. 3(b), in which both lamellae on edge (here with three orientations at 60°) and lamellae lying flat on the substrate are present. The latter pattern consists of three [120] patterns and one [001] pattern, with the *b*-axis in the [001] pattern parallel to the equator of one of the [100] patterns. Meridional reflections were not visible in this pattern. The relative orientation of [001] and the [120] patterns suggest the lamella giving rise to the [001] pattern grew with *b* and *c* parallel to the mica surface and then collapsed onto the substrate. However, the [120] patterns from the lamellae on edge suggest *b* is at an angle to the substrate. This differs from the case for PPN; as shown in the following paper^[8], epitaxial CTFSP yields samples giving rise to [100] patterns, with *b* and *c* lying in the plane of the substrate for the on-edge lamellae.



PPT Crystal Structure

Refinement of the unit cell parameters, initially done using the spacings from the [001] and $[1\bar{1}1]$ patterns, resulted in values of $a = 7.89$, $b = 5.49$, $c = 12.65 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 100.33^\circ$, unit cell volume = 539.07 Å³; while *c* is the same, *a*, *b* and β differ slightly from the values given by Hanna *et al.*^[10] The space group is $P2_1/a$, the same as they proposed and the molecular packing (Fig. 8) is also very similar. The spacings from the

[120] patterns, obtained later from the CTFSP epitaxy samples, agreed well with those resulting from the initial refinement.

Simulated ED patterns are shown in Figs. 9(a)–(i) for comparison with those in Figs. 5 and 6. The observed alternating intensity on the row lines in the [001] zone of Fig. 5(a) is seen to be well reproduced in the simulation in Fig. 9(a). The observed patterns for the other zones are also all in reasonable agreement. Discrepancies include the $\bar{1}01\text{--}10\bar{1}$ row line in $[1\bar{1}1]$, $30\bar{1}$ in $[1\bar{1}3]$, and 311 in $[0\bar{1}1]$, all of which are missing in the simulations, and 011 stronger than 022 in $[12\bar{2}]$; all of these “discrepancies” could be the result of multiple scattering.

Clearly, however, the simulated [001] pattern does not agree well with the patterns shown in Figs. 5(c) and (d). The reason for the variation in these patterns is not known. Possibilities include end group effects from the low molecular weight, multiple and/or dynamic diffraction effects from thick crystals and chemical defects introduced during polymerization. A simulated [001] ED pattern corresponding to the unit cell in the Cerius² demo^[11] is shown at lower right in Fig. 9(i). Because of the rotation of only the central molecules, done to give agreement with the experimental X-ray pattern (below), the pattern is highly asymmetric and does not correspond to any of the observed patterns.

Figure 10 shows simulations of the $[1\bar{1}0]$ and $[100]$ zones, for comparison with the “fiber” patterns in Figs. 7(a) and (b), and of the $[120]$ and $[1\bar{2}0]$ zone for comparison with the patterns from the CTFSP epitaxy samples in Figs. 7(c) and (d). Agreement in both cases is good except for the unexplained apparent 010 reflection on the right side of the equator in Fig. 7(b). Note the simulation in Fig. 10(b) is rotated 90° relative to the pattern in Fig. 7(c).

A comparison of simulated and observed X-ray diffraction scans in are shown in Fig. 11. The sample used for the X-ray scan was bulk melt polymerized at $T_p = 150$, $t_p = 5$ h and acetone extracted before measurement, the pattern from the 24 h, 240°C sample was similar, except for having a broad “amorphous” peak at *ca.* 10–14° 2θ . Good agreement between the observed and simulated scans is seen except for the near absence of the 38° peak in the observed scan; this peak was also much lower in intensity in the observed scan reported by Jehnichen *et al.*, than in their calculated scan^[15]. The simulated scan was calculated assuming a global temperature factor of $B_{\text{iso}} = 5 \text{ \AA}^2$ and crystal dimensions of 100, 150 and 200 Å in the *a*, *b* and *c* directions respectively. Also shown inset on Fig. 11 are the experimental and simulated scans from the Cerius² demo; the former appears to be the same as the experimental scan in Ref. [10]. The 12° rotation of the central molecule was done to reduce the intensity of 200 relative to 110. Slight differences in spacings of the 110 and 200 peaks between the two experimental scans correspond to the differences in unit cell dimensions obtained.

CONCLUSIONS

The results above and in the subsequent paper on PPN represent some of both the advantages and the problems in determining crystal structures using electron diffraction. Although we were able to prepare single crystals of PPT by both CTFMP and solution polymerization, the relative intensities of the apparent [001] ED patterns varied considerably from pattern to pattern even for patterns from single lamellae (Figs. 1b–d). Solution polymerized PPT, while giving similar ED patterns to the CTFMP samples, were relatively thick (appearing to be composed of thin lamellae), with no evidence of whisker formation. Some of the ED patterns, as in Figs. 5(a) and (b) and 6(a), suggest significant multiple scattering. Although the pattern in Fig. 6(a) can only be explained in terms of multiple scattering, the [001] pattern in Fig. 5(a) was from a sample one lamella thick, making multiple scattering unlikely. Other patterns, apparently also related to phase I [001], were obtained. In some cases (Figs. 5e and f) reflections from the higher order layer line are suggested to have contributed due to sample tilt. On the other hand, the origin of the non-alternating pattern in Figs. 5(c) and (d) and the variation in the 210/110 intensity ratio in Fig. 5(c) from that in Figs. 5(a), (b) and (d) are unknown. Multiple scattering (or dynamic scattering effects) are not believed to contribute since the pattern in Fig. 5(c) was obtained from a single lamella (as in Fig. 1d). The patterns in Figs. 5(c) and (d) are suggested to represent “true” differences in molecular packing, possibly due to differences in molecular weight (end group contributions) or constraints due to adherence to the substrate.

Polymorphism is also present, “phase II” patterns being obtained from some PPT samples.

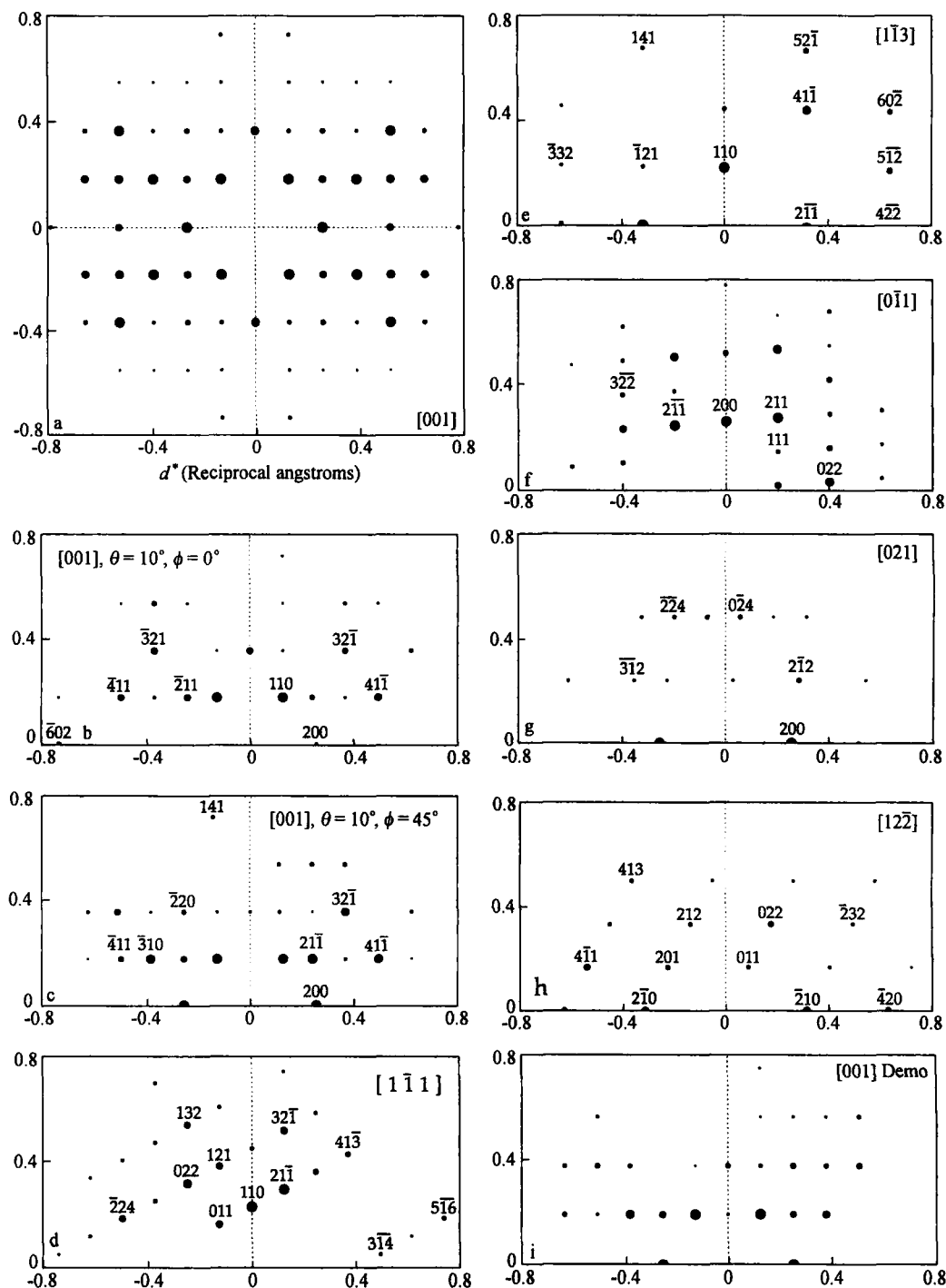


Fig. 9 Simulations of ED patterns related to the observed patterns in Figs. 5 and 6. The indices for the various patterns are indicated on the Figure. Figs. 9(b) and (c) correspond to “[001]” patterns with the beam tilted 10° about b and a diagonal at 45° to the b -axis. The pattern in i) corresponds to the proposed unit cell in the Cerius² demonstration. Note some of the simulations are rotated 90° relative to the corresponding ED pattern

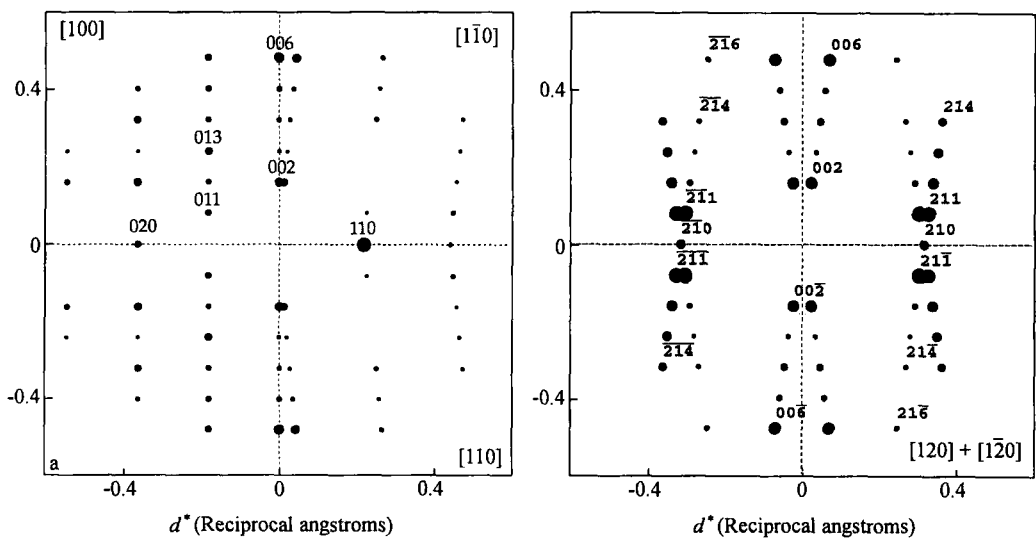


Fig. 10 Simulations of ED patterns related to the observed patterns in Fig. 7
(a) [110], [1 $\bar{1}$ 0] and [100]; (b) [120] and [1 $\bar{2}$ 0]

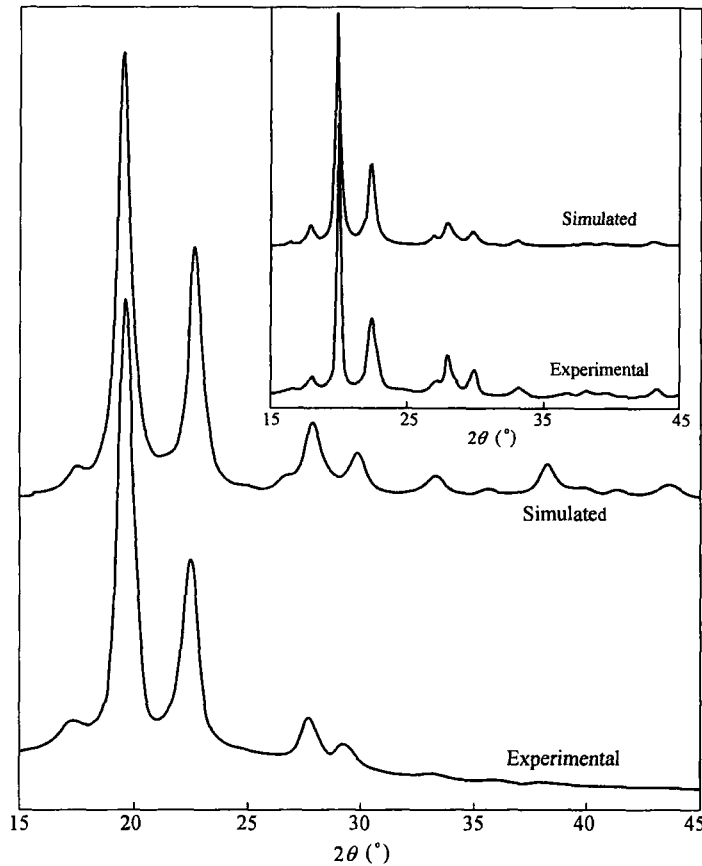


Fig. 11 Observed (bulk melt polymerized, HQ/TC, 150°C/5 h) and simulated X-ray diffraction scans
The inset patterns are from the Cerius² demonstration, the observed pattern being the same as in Ref. [10].

Only the CTFMP samples polymerized from HQ and TC, at $T_p \geq 220^\circ\text{C}$, gave rise to well formed lamellae, on the order of 100–200 Å thick for all conditions examined. At lower temperatures (thinner) lamellae also formed but holes developed in them when washed with room temperature acetone; they thus are suggested to consist of low molecular weight oligomers, possibly even shorter than corresponding to the lamellar thickness. Contrary to when similar polymerization conditions were used for PpOBA and PONA, there was no evidence of epitaxial polymerization/crystallization when mica was used as the substrate for melt polymerization, the lamellae were all parallel to the substrate and apparently randomly arranged.

On the other hand, the CTFSP samples from TC and HQDA with mica as a substrate were highly oriented in an epitaxial fashion, with $\langle 210 \rangle^*$ and c lying on the substrate. The lamellae, in this case, were normal to the substrate and again about 100 Å thick.

The unit cell parameters and packing obtained for PPT differed to a degree from those reported by Hanna *et al.*^[10] based on powder X-ray diffraction and similar modeling. Both have a $P2_1/a$ space group. Our values, with values from Ref. [9] in parentheses, are $a = 7.89$ (7.98), $b = 5.49$ (5.33), $c = 12.65$ (12.65) Å, $\alpha = \gamma = 90^\circ$, $\beta = 100.33^\circ$ (98.98°), unit cell volume = 539.07 Å³ (density = 1.48 g/cm³). Our spacings agree with values we obtained from X-ray diffraction patterns from bulk polymerized PPT, with that pattern also differing from the X-ray pattern obtained by Hanna *et al.* The inadequacy of the demonstration program for PPT included with the Cerius² molecular modeling software was demonstrated.

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