

# Morphology of polypivalolactone: A polymer with a direction

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*(Received 13 June 1983)*

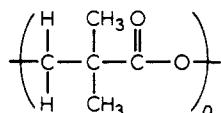
The morphology of polypivalolactone crystallized from the melt in the  $\alpha$  and  $\gamma$  crystal forms is described. In both forms large, rather perfect lamellae form; the crystal structures require antiparallel chain packing in the lamellae in both forms and a predominantly adjacent re-entry chain folding is suggested.

(Keywords: polypivalolactone; morphology; regular folding; electron diffraction; spherulites)

## INTRODUCTION

Polypivalolactone (PPVL) promises to be a highly useful material for polymer morphology research. As shown in several previous papers, it crystallizes readily, to a high degree, in the form of large spherulites composed of the  $\alpha$  phase when cooled slowly from the melt (e.g. refs. 1–3). Two additional crystal forms have been identified, a  $\beta$  phase induced by stretching  $\alpha$  PPVL<sup>4</sup> and a  $\gamma$  phase formed coincidentally with the  $\alpha$  phase to varying degrees, the amount increasing with increasing cooling rate<sup>2,3</sup>.

Of particular interest with respect to current controversies over the degree of regular, adjacent re-entry folding in melt-crystallized polymers (see a number of papers and discussion comments in ref. 5) is the chemical structure of PPVL.



The polymer has a direction to its backbone and thus one can distinguish between crystal structures in which adjacent chains are parallel, antiparallel or statistically random in direction. In all published X-ray diffraction  $\alpha$  crystal structure studies there has been qualitative agreement with a  $T_2G_2$  conformation, resulting in an antiparallel 2/1 helix structure, as proposed by Carazzolo<sup>6</sup>. The structure is thus compatible with the formation of adjacent re-entry folds. In the  $\beta$  phase the fibre repeat of 4.76 Å suggests a planar zigzag structure<sup>4</sup>; Clark<sup>7</sup> indicates that the chain directions are statistically random

in the  $\beta$  crystal structure and thus during deformation there must be a destruction of the adjacent re-entry folding if it is present in the original samples. The  $\gamma$  phase has not been as well characterized by X-ray diffraction, always being formed together with the  $\alpha$  form. Prud'homme and Marchessault reported<sup>3</sup> the characteristic  $d$  spacing of  $\gamma$  PPVL using an unoriented X-ray pattern and, based on unpublished conformational calculations, suggested it had a 3/1 helix conformation. Using single crystal-like electron diffraction patterns, similar to those described below, we have been able to determine the  $\gamma$ -form crystalline structure<sup>8</sup>. It is orthorhombic ( $a=8.23$  Å,  $b=11.27$  Å,  $c$ =fibre axis=6.04 Å) with the space group  $P2_12_12_1$ . The  $c$  axis spacing is essentially the same as for the  $\alpha$  unit cell; the  $\gamma$  form is also a 2/1 helix. As in the  $\alpha$  unit cell, there are two segments per unit cell, in an antiparallel chain packing. The melting points of the  $\alpha$  and  $\gamma$  phases are 230°–240°C and 210°–220°C respectively, depending on crystallization and annealing conditions, permitting determination of the relative amount of  $\alpha$  and  $\gamma$  phases by d.s.c. measurements<sup>2,3</sup>.

Substantial degrees of  $\gamma$  crystallization can be obtained by quenching molten films into dry ice-methanol (supercooling of  $\sim 250^\circ\text{C}$ ), quenching rates which exceed those used for the polyethylene samples used for the neutron diffraction results which have been interpreted as showing the absence of essentially all adjacent re-entry folding (e.g., in ref. 9, the samples were quenched into ice-water with  $T_m=140^\circ\text{C}$ ). The tabletop quench used for this work closely approximates the rate used for polyethylene. Since a statistically random chain direction is an at least metastable crystal form (the  $\beta$  form), it seems reasonable to expect that if rapid crystallization of PPVL resulted in a random non-adjacent re-entry type of folding, if folding occurs at all, the resulting sample should be predominantly in the  $\beta$  phase, or at least in a

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† It is noted that in the original paper by Oosterhof<sup>1</sup> the  $\beta$  and  $\gamma$  nomenclature was reversed from that now in common use.

phase with a statistically random chain direction. A lamellar morphology involving chain folding in a unit cell with antiparallel chain packing,  $\alpha$  and  $\gamma$ , requires that a given chain either re-enter in the adjacent lattice position or at odd integer positions, i.e. 1, 3, 5, 7, etc., lattice positions. Although crystallization in an antiparallel unit cell does not require adjacent re-entry chain folding, for the morphology of the PPVL samples examined here it seems the only reasonable explanation. In this paper we report the results of our initial examination of the morphology of PPVL crystallized in the  $\alpha$  and  $\gamma$  form. The effect of crystallization of PPVL from the glass is discussed in another paper<sup>10</sup> and research is in progress on the effect of quenching rate and temperature from which quenched on the resulting morphology and crystal structure.

## EXPERIMENTAL

The PPVL was supplied by Tennessee Eastman Co. Samples for optical microscopy and X-ray diffraction were prepared by melting a small amount of PPVL (0.1–0.2 g) on a glass slide on a hot plate at 260°C. In order to obtain samples rich in  $\gamma$  phase, the polymer was spread to form a uniform film ~0.05 mm thick and then quenched to room temperature by removing the slide from the hot plate and placing it on the tabletop. Samples consisting almost entirely of  $\alpha$  phase were prepared in a similar fashion except that the slide was left on the hot plate as it cooled to room temperature. For  $\gamma$  phase X-ray patterns, portions of the quenched film rich in  $\gamma$  phase were selected using the optical microscope.

Two stage replicas for electron microscopy of the

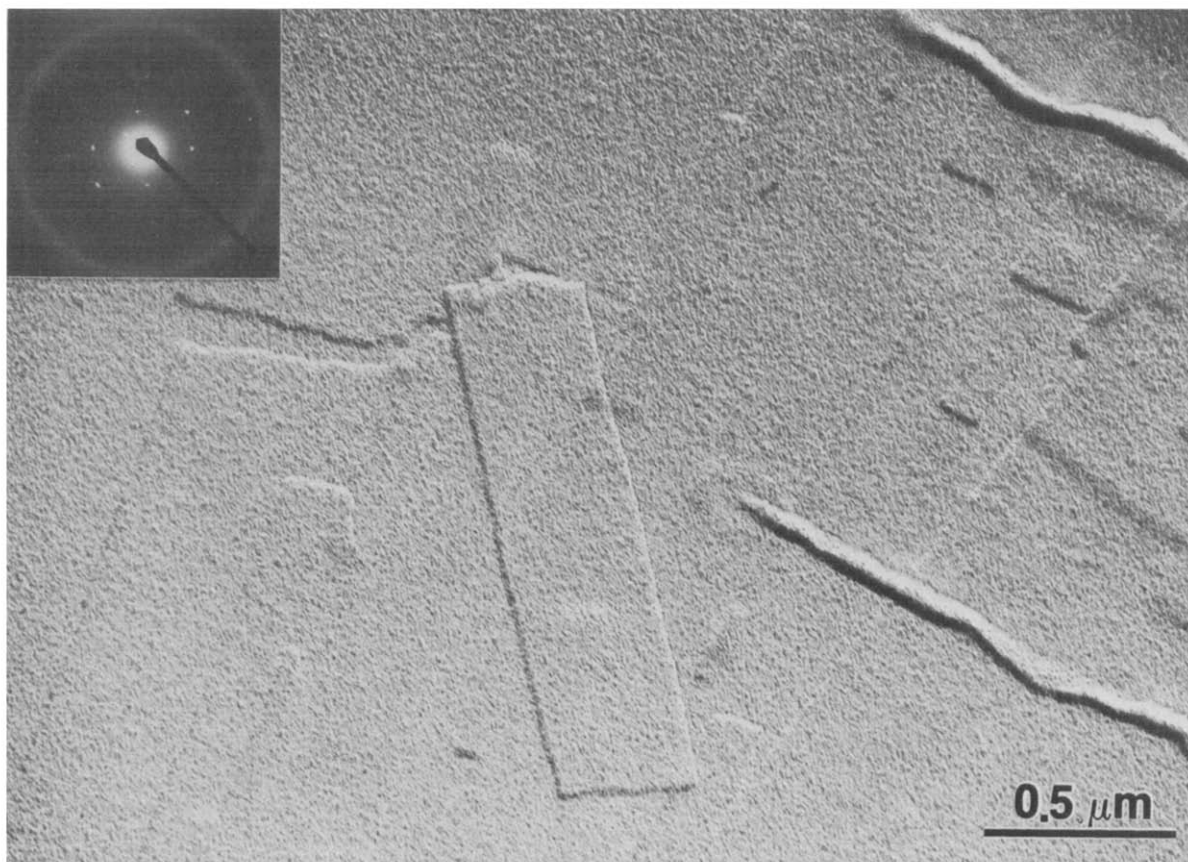
0.05 mm thick samples above were prepared using polyacrylic acid as a primary replica, shadowing them with Pt-C at 30° or 45°, backing with carbon, followed by dissolution of the polyacrylic acid by floating on distilled water.

Thin films for electron microscopy and diffraction were prepared by dissolving the PPVL in trifluoroacetic acid at 60°C to form a 0.03% concentration solution. Immediately after preparation, a few drops of the warm solution were cast on carbon-coated mica on a hot plate set at 260°C, allowed to remain for 3 min as the solvent evaporated and then either allowed to cool slowly on the hot plate (turned off) for 20 min before removal (slow cooled) or removed immediately (quenched). A JEOL 100 B electron microscope was used for microscopy and diffraction; diffraction patterns were taken in the microbeam mode using an approximately 1200 Å diameter beam at suitably low intensity.

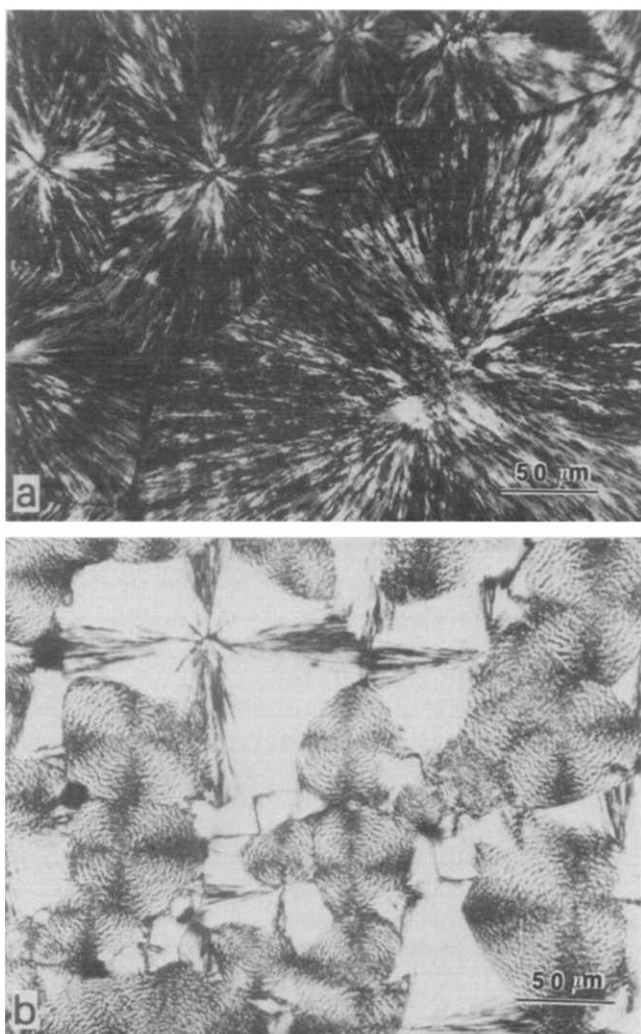
## RESULTS

Lamellar single crystals of PPVL can be grown from nitrobenzene. As shown in *Figure 1*, they are lath-like, about 70 Å thick. The orientation of fibres formed when they fracture suggests chain folding parallel to the long axis. Electron diffraction patterns (insert) indicate they have the  $\alpha$  unit cell.

Optical micrographs between crossed polaroids of the slow-cooled and quenched films are shown in *Figures 2a* and *b*. The bright spherulites in *Figure 2b* were shown by X-ray diffraction to be composed of  $\alpha$ -form crystals while the dark ones are composed of  $\gamma$ -form crystals. A



**Figure 1** Portions of single crystals of PPVL precipitated from nitrobenzene. A representative ( $\alpha$ ) electron diffraction pattern is shown in the insert



**Figure 2** Optical micrographs, between crossed polaroids, of PPVL slowly cooled (a) and quenched (b) from the melt. (b) is printed to enhance the irregular ring structure of the  $\gamma$ -form spherulites

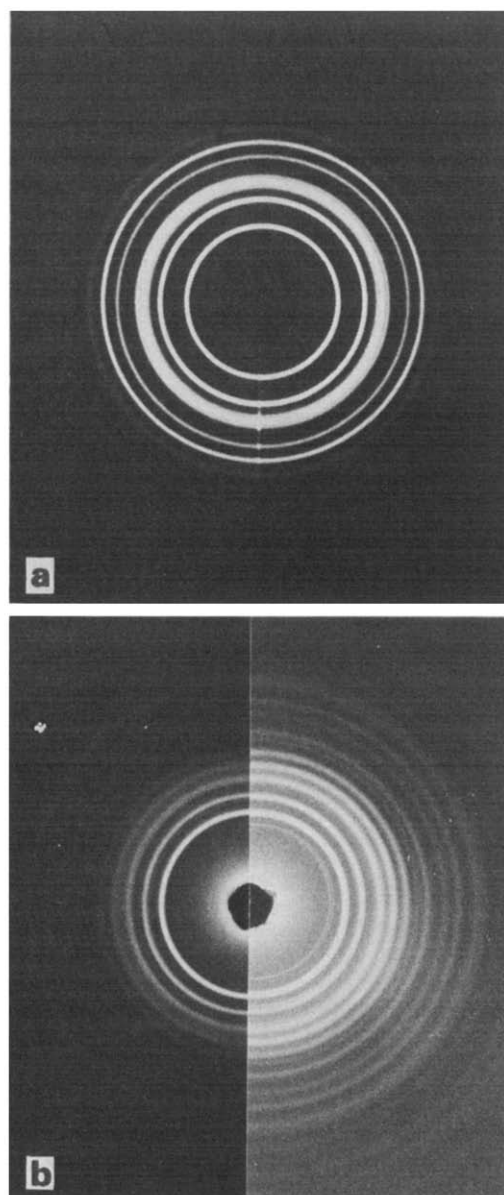
small amount of  $\gamma$  form is seen in the slow-cooled film and a considerably higher amount is present in the quenched film. The  $\gamma$ -form spherulites have an irregular ring structure. The ring spacing appears to be independent of the cooling conditions, although this is in need of further examination.

X-ray patterns from the two phases,  $\alpha$  and  $\gamma$ , are shown in Figures 3a and b respectively. The spacings agree with those reported previously. One notes in Figure 3b a low-intensity eccentric ring with a spacing of 7.75 Å just inside the first strong (110 $\gamma$ ) reflection. It is due to a small amount of  $\alpha$  form, being the 100 reflection of the  $\alpha$  phase.

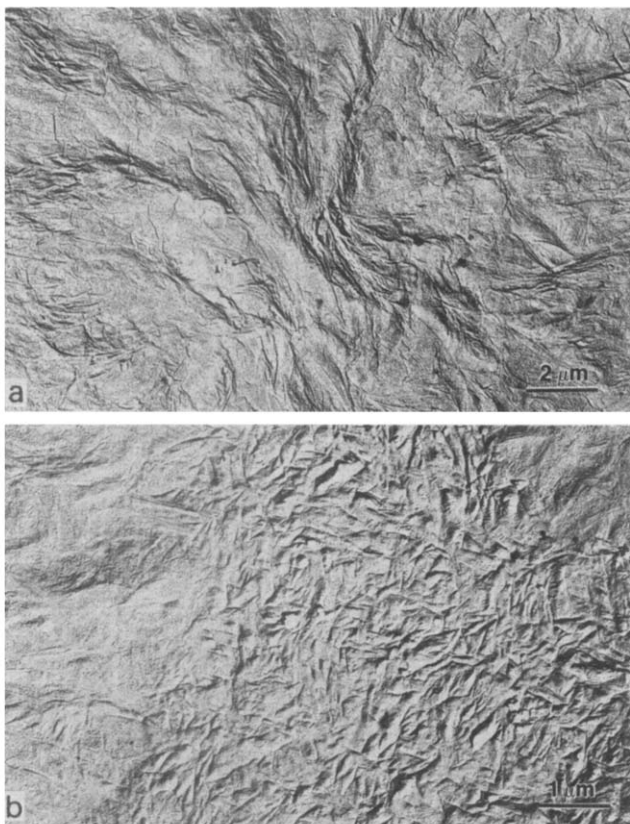
Electron micrographs of replicas of portions of the two types of spherulites are shown in Figures 4a and b. The  $\alpha$  form is seen to have a smoother surface than the  $\gamma$ . Although lamellar, in neither case is the morphology of the crystals clearly seen. In particular there is no evidence of the ring structure (e.g. twisting lamellae as in polyethylene) in the  $\gamma$ -form spherulites. It is suggested that at least some of the lack of distinction is due to low molecular weight materials covering the surface.

Electron micrographs of the shadowed, slow-cooled thin films are shown in Figure 5 with corresponding electron diffraction (microbeam) patterns of both slow-

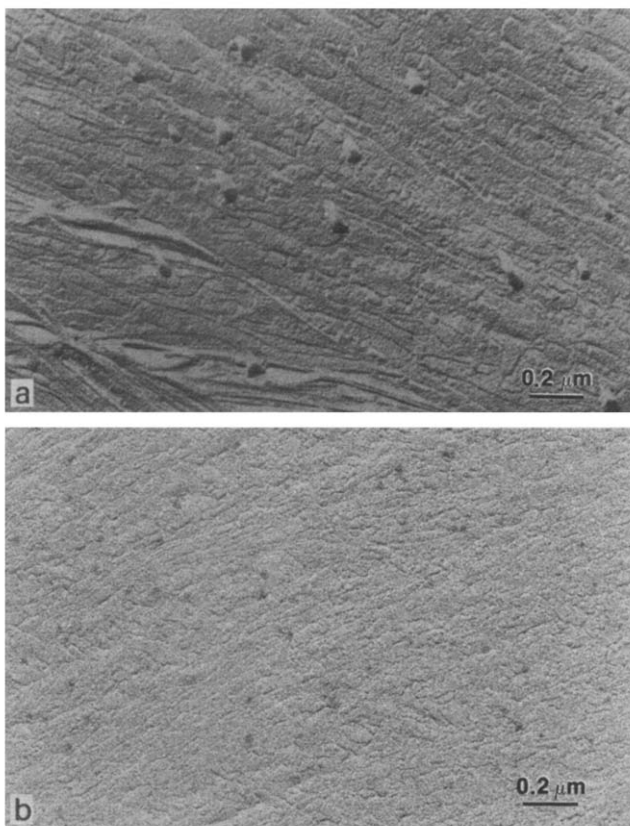
cooled and quenched ( $\gamma$ ) samples in Figure 6. Both the  $\alpha$  and  $\gamma$  crystals in the slow-cooled samples are seen to be lamellar, the  $\gamma$  crystals being 120–180 Å thick. From the slow-cooled samples single-crystal diffraction patterns were obtained, with as many as 10 orders of reflections being visible. These are the samples and patterns used for the crystal structure determination<sup>8</sup>. In patterns from quenched samples the spots are seen to be broadened into arcs indicating a distribution of orientations. In the slow-cooled samples, all of the crystals in the region illuminated by the beam have a common orientation. One notes in the  $\gamma$  electron diffraction pattern the presence of 100 and 030 reflections, although of very low intensity. A weak 101 can also be observed on the original diffraction pattern but is disguised in the primary beam in the reproductions. 100, 010 and 030 are forbidden in the P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group. Reflections 100 and 010 are never observed in X-ray patterns while 100 and 030 are clearly absent in electron diffraction patterns of single crystals tilted out of the  $hk0$  diffracting



**Figure 3** X-ray diffraction patterns of films having preeminently  $\alpha$  (a) and  $\gamma$  (b) crystal structure. The eccentric inner ring on the long-exposure right half of (b) is from a small  $\alpha$  spherulite at one edge of the irradiated area



**Figure 4** Replicas of the surface of 'thick' films of PPVL crystallized slowly from the melt. (a) Central portion of an  $\alpha$  spherulite. (b) Portions of  $\alpha$  (left and top right) and  $\gamma$  (centre-right) spherulites



**Figure 5** Shadowed thin films of PPVL crystallized slowly from the melt. Portions of (a)  $\alpha$ -form and (b)  $\gamma$ -form spherulites

position, respectively, around the  $a$  and  $b$  axes (Figure 6d). These facts, together with the satisfactory agreement reached<sup>8</sup> refining the  $\gamma$  structure in space group  $P2_12_12_1$ , suggest that the observation of 100, 010 and 030 is due to double diffraction effects. Between the first two strong  $\gamma$  reflections ( $d=6.65 \text{ \AA}$  and  $d=5.64 \text{ \AA}$ ) it is possible to detect in the original of X-ray patterns a very low-intensity ring with a  $d$  of approximately  $6.1 \text{ \AA}$ . This reflection cannot be seen on reproductions of the pattern and can be only indexed as 001  $\gamma$ . It could be due either to double diffraction effects or to disorder in the  $c$  axis direction (either mutual displacement of neighbouring chains and/or a few parallel chains). The latter is suggested by the observation that annealing in the  $150^\circ\text{--}200^\circ\text{C}$  temperature range results in an increase in intensity of  $hk1$  reflections and a decrease or disappearance of the 001 reflection.

#### DISCUSSION

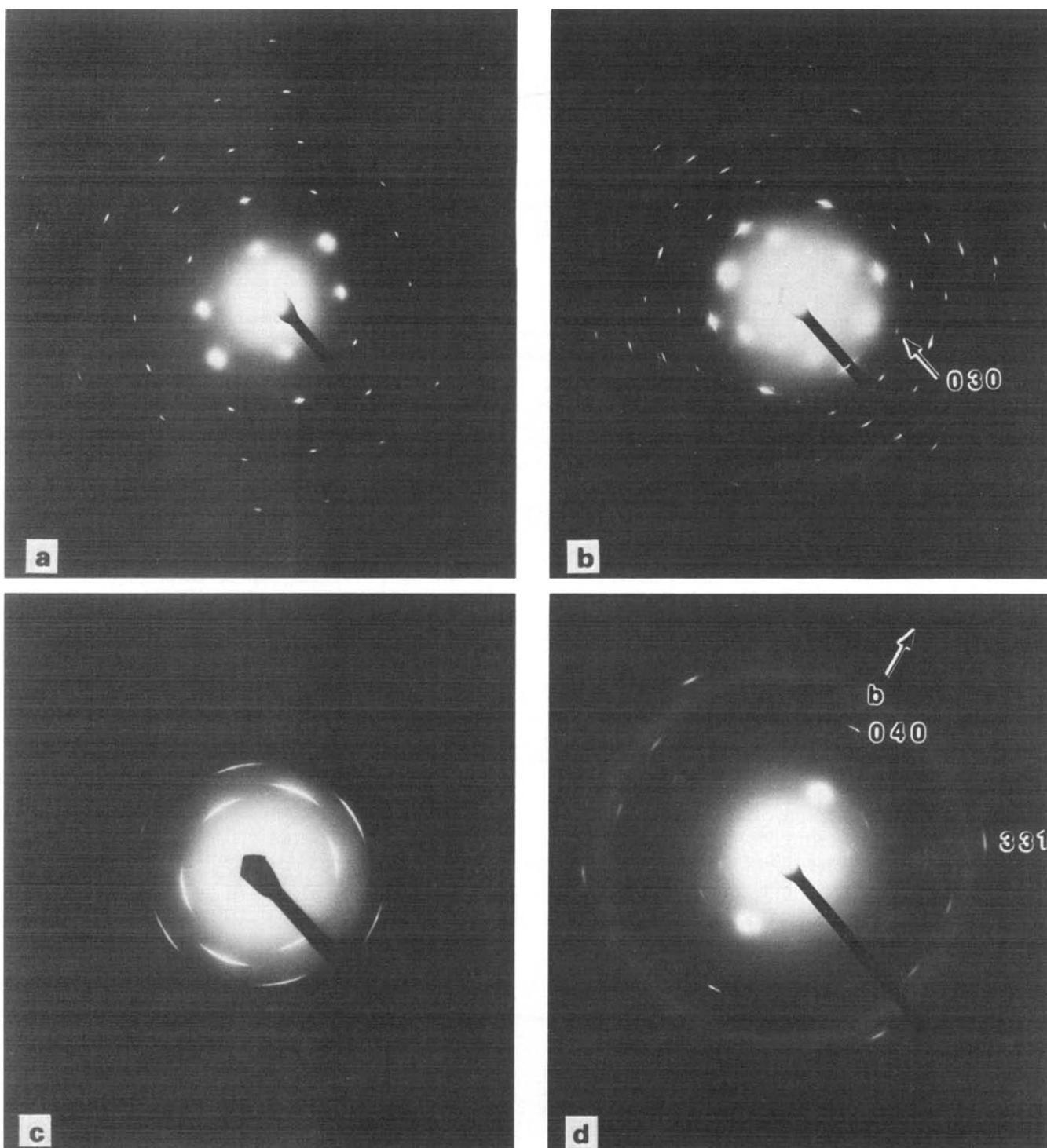
As indicated above,  $\gamma$ -form crystals of PPVL, as crystallized from the melt either by slow or rapid cooling, are large crystals. In the slow-cooled films, superimposed crystals have a common orientation, resulting in the single crystal-like electron diffraction patterns. Even in quenched films, there is only a small degree of rotational disorder in superimposed lamellae in areas of the size of the beam, i.e.  $\sim 12000 \text{ \AA}$  diameter. The double diffraction reflections in the  $\gamma$  electron diffraction patterns are consistent with the large size and thickness of the crystals.

Consider now the question of regular adjacent re-entry folding as compared to an irregular folding. The single crystals are only  $70 \text{ \AA}$  thick; the molecules have a diameter of at least  $5 \text{ \AA}$ . Since the unit cell requires an antiparallel chain packing, if non-adjacent re-entry occurs there would have to be an amorphous surface layer  $10\text{--}15 \text{ \AA}$  thick on each surface in which the molecules cross over each other. This is inconsistent with the high degree of crystallinity of this polymer, indicating that adjacent re-entry must be the predominant mode of crystallization for the single crystals.

The same argument cannot be applied as readily to the melt-crystallized samples. The lamellae are considerably thicker, of the order of  $120\text{--}180 \text{ \AA}$ . A  $15 \text{ \AA}$  amorphous surface layer of overlapping molecules would result in a crystallinity of 75 to 85%, only slightly lower than that measured. On the other hand, the fact that the quenched samples crystallize as  $\gamma$ , with antiparallel chain packing, rather than with some form of statistical packing as in the  $\beta$  form, suggests that even in the quenched samples the majority of the chains fold in an adjacent re-entry mode. The presence of a very weak 001 reflection in the  $\gamma$ -form X-ray diffraction patterns of fast-cooled samples suggests slight perturbations of the two-fold helical symmetry, perturbations which decrease on annealing. However, in both the  $\alpha$  and  $\gamma$  crystal forms we suggest that an adjacent re-entry chain folding is the preferred mode, with varying degrees of disorder in the packing introduced by the rate of crystal growth, a disorder which apparently can be reduced by motion within the crystal during annealing.

#### ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation Polymer Program through Grants DMR



**Figure 6** Electron diffraction patterns from portions of (a) slow-cooled  $\alpha$  spherulite, (b) slow-cooled  $\gamma$  spherulite and (c) a quenched  $\gamma$  spherulite. The pattern in (d) is from a slow-cooled  $\gamma$  spherulite tilted about the  $b$  axis

78-18804, 79-23324 and 81-08300. One of us (T.K.) was also supported by the Japanese Society for the Preservation of Science. A portion of the research described above was carried out at Case Western Reserve University with the remainder at the University of Illinois. The use of the University of Illinois Materials Research Laboratory and Center for Electron Microscopy is acknowledged.

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