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Chain Tilt in α-Poly(vinylidene fluoride)

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Whether or not chain-folded crystals exhibit chain tilt (alignment of molecular stems oblique to lamellar normals) influences the structure of fold surfaces, particularly when folding is likely to be irregular as in crystallization of polymer of medium or high molecular weight from the melt. It also has significant bearing upon current interpretations of banding in spherulites,[1] and in this note we wish to clarify the status of α-poly(vinylidene fluoride) (α-PVF$_2$) in this regard.

Although occurrence of chain tilt is virtually assured in lamellar crystals of triclinic or monoclinic symmetry, its presence or absence in crystals of orthorhombic symmetry is believed to depend upon whether or not such tilt is needed to create adequate space for accommodation of relatively bulky folds in disordered fold surfaces. The best known example is polyethylene, in which chain tilt (commonly about 35°) appears to be mandated by unusually large disparity (~16.5%) between densities of crystalline and melt phases.[2] This is a compelling inference since (unfolded) paraffin molecules can crystallize in the same orthorhombic structure without chain tilt, and this also appears to be the case with oligomers that undergo limited folding.[3] Similarly, γ-PVF$_2$ with a comparable disparity in densities (~13.5%) and structure close to orthorhombic (monoclinic with $\beta = 93°$) is also known to exhibit a chain tilt (about 28.5°);[4] yet, on the other hand, poly(3-hydroxybutyrate), which is orthorhombic but with density differing from that of melt by only 7%, is said to crystallize without chain tilt.[5] In these terms, it would indeed be surprising if orthorhombic crystals of α-PVF$_2$, whose density differs from that of crystalline γ-PVF$_2$ by less than 1%, did not exhibit a chain tilt, at least when polymer of reasonably high molecular weight is crystallized from the melt.

Spherulites of α-PVF$_2$ crystallized in such circumstances are comprised of lamellae elongated along radially oriented **b** axes;[6] under suitable conditions flat-on segments of these lamellae can be seen in relative isolation as they protrude from spherulites grown in thin films. An example is shown in Figure 1, in which polymer of molecular weight $M_w = 525\,000$ and $M_n = 348\,000$ (Kureha KF-1100) has been crystallized isothermally at 168 °C. Selected-area diffraction from the area indicated using a beam of 100 keV electrons at normal incidence reveals only 020 reflections consistent with growth along a **b** axis, but an *hk*0 pattern is obtained by tilting the specimen about this axis (*in one direction only*) by 25°. PVF$_2$ is highly sensitive to radiation damage (at least 3 times more so than polyethylene[7]) and the exposures were necessarily very short to allow consecutive patterns to be recorded at successive tilts of 0°, +25°, and −25°; nevertheless, weak 100 reflections are clearly discernible in the *hk*0 pattern confirming unambiguously that the crystal is of polymer in the α-form. Chain tilts close to this magnitude were found consistently with such crystals, whose fold surfaces can thus be indexed nominally as (102). Identification of the α-phase is reinforced by significant contrast between morphology such as seen in Figure 1 and that typical of γ-phase crystals. One of these, found in the same specimen, is shown in Figure 2. Such crystals are characterized by copious overgrowths displaying both {110} and (020) facets, a habit in which overlayers show prominent facets *normal* to the growth direction (**b** axis) of basal layers in spherulites.[6,8] In Figure 2 this direction faces between 10 and 11 o'clock.

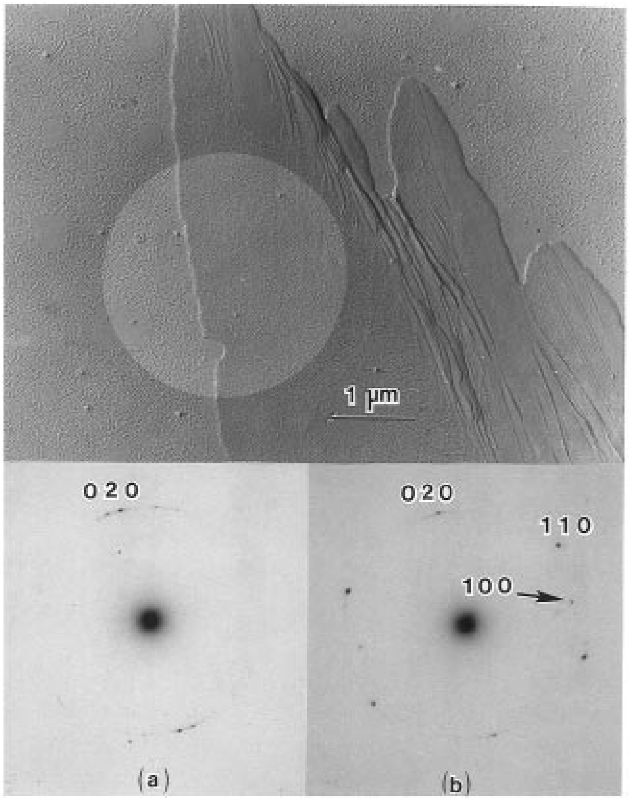

Figure 1. Lamellae of α-PVF$_2$ extending from a spherulite: electron diffraction patterns from the selected area shown were recorded (a) at normal incidence and (b) with the specimen tilted by 25° clockwise about the growth direction.

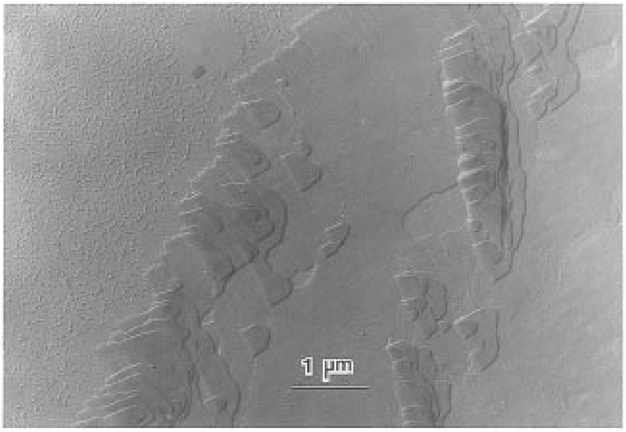

Figure 2. Lamellae of γ-PVF$_2$ from another region of the specimen in Figure 1 showing characteristic overgrowths.

It is evident that chain ends, whether located within lamellae or excluded from them as cilia, would tend to reduce congestion in disordered fold surfaces and thus

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weaken a requirement for chain tilt that is ascribable to such congestion. A moderating influence of this kind, varying inversely with molecular weight, might well obviate such a requirement in polymer of low molecular weight, or even in polymer of moderate molecular weight but large polydispersity. However, conditions under which a transition from occurrence to absence of chain tilt is likely to occur are difficult to predict quantitatively. From the above observations it appears that in α-PVF$_2$ they are intermediate between those under which our studies of banded spherulites have been conducted[6,9] and those under which Briber and Khoury[10] have, from dilute (0.5%) blends in poly(ethyl acrylate), grown crystals without chain tilt in polymer of relatively low molecular weight ($M_n = 47\,000$) but substantial polydispersity (2.7). α-PVF$_2$ crystals grown from dilute solution in more conventional solvents (using polymers of unspecified molecular weight or polydispersity) have also been reported to be without chain tilt;[8,11] in these cases, however, there is ambiguity in that features on fold surfaces (particularly in ref 11) suggest collapse of initially ridged structures possibly involving chain tilt. (The manner in which such a collapse, occurring by shear as ridged crystals are dried down before electron microscopy, can give false indications of as-grown morphology is well documented in the case of polyethylene.[2,12]) In any event, these observations have little relevance to correlation between chain tilt and banding in spherulites of α-PVF$_2$ grown from the melt;[9] we emphasize that in the latter circumstances we have found chain tilts of ~25° about **b** axes, fold surfaces being nominally (102).

References and Notes

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