# Direct evidence for chain orientation in poly(acetylene)

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Two conflicting structural models (platelet and fibril) have been proposed in the literature for pristine *cis*-poly(acetylene). The respective models have separate, distinct implications for the chemical, physical and electrical properties of the material, in particular, the *cis–trans* isomerization, doping and conduction mechanisms. Luttinger-type *cis*-poly(acetylene) was prepared and studied in the transmission electron microscope (TEM) by low-dose conventional imaging, in dark-field mode and by electron diffraction. Thin 'films' of the material were shown to consist of fibrillar nets, having fibrils of diameter 5–25 nm. Combined electron diffraction and dark-field observations in the TEM indicated the structural arrangement within the fibrils as that having polymer molecular chains aligned parallel to fibril axes.

**Keywords** *cis*-Poly(acetylene); structure of poly(acetylene); Luttinger poly(acetylene); transmission electron microscope; electron diffraction; orientation

## INTRODUCTION

Although the electrical properties of poly(acetylene) have been investigated for over two decades[1,2], the discovery of a technique to synthesize 'films' of the material[3] and the use of electron donors and acceptors to 'dope' it to metallic conductivity has produced intense interest in the polymer in the last five years. A prerequisite for any investigation of the conduction mechanism of this material is a complete understanding of its chemical nature, crystal structure and overall morphology. It is by now well established that, as synthesized by the Shirakawa[3] and Luttinger[4] methods, the poly(acetylene) 'films' produced actually consist of a mat of fibrils 20–50 nm in diameter. The structure of these fibrils, however, is still a matter of controversy. This controversy is confused by the fact that poly(acetylene) exists as one of two structural isomers, *cis* or *trans*. The *trans* isomer is the more thermally stable and, although the *cis* form is produced at low temperatures (−78°C), isomerization to the *trans* form takes place as the temperature is raised.

It is possible to predict the chain repeat unit from bond lengths and orders, but the packing of chains can only be derived from electron and X-ray diffraction experiments. The first such experiments were carried out by Baughmann[5–7]. In this work, experimental results determined by X-ray powder diffraction were compared with packing calculations for the *cis* polymer. Direct interpretation of experimental results was made difficult by the relatively small number of diffraction lines and the overlapping of intensities from powder samples. Consequently their derived space group and cell parameters must be viewed only as a first approximation. In fact, their space group assignment is the same as that of poly(ethylene). (Note that, contrary to normal practice, Baughmann assigned $b$ to the chain axis. Using $c$ as the chain axis, the space group becomes *Pnam*). Once corrected to standard notation they obtained values for the cell parameters of $a = 7.61$ Å, $b = 4.39$ Å and $c = 4.47$ Å.

The next work to appear was a study of the nascent morphology of poly(acetylene) by Karasz *et al.*[8] The preparation of films was carried out at room temperature and hence these had a significant *trans* content (40% by i.r.[9]; 15% by n.m.r.[10]), although the overall morphology was probably not significantly affected. They found that even when poly(acetylene) was polymerized directly onto electron microscope grids and observed immediately, the characteristic fibrillar net was still present. The fibrils ranged in diameter from 5 to 40 nm with the majority being about 20 nm in diameter. Their conclusion was that the rigidity of the polymer chain caused poly(acetylene) to crystallize immediately into these fibrils once formed.

A conflicting view has been presented by Lieser *et al.*[11–13], which forms the basis of the present controversy over the structure and morphology of poly(acetylene). Using polymer produced by the Shirakawa[3] and Luttinger[4] methods, Lieser and co-workers derived an entirely different picture of poly(acetylene). Their observations in the transmission electron microscope (TEM) led them to suggest that the observed fibrils were agglomerations of lamellae about 10 nm in thickness and between 10 and 200 nm in diameter. Furthermore in all X-ray diffraction experiments and in some electron diffraction patterns they observed a 001 reflection. This is a forbidden reflection in the *Pnam* space group, so this assignment is also questioned. Their final piece of evidence is that, although the 001 reflection is observed in some electron diffraction patterns, it is absent from most. Thus, they suggest, the lamellae are deposited preferentially in a uniaxial orientation onto a substrate with the polymer chain axis perpendicular to the lamellar surface and the fibril axis. This is in direct contradiction to the previously reported results and, more importantly, it is difficult to interpret the electrical properties on the basis of this model.

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This challenge to the accepted structure provoked further study at the University of Massachusetts, culminating in a series of papers by Karasz and co-workers on the structure of the *cis* polymer[14], the *trans* polymer[15] and the possibility of polymorphism, previously suggested by Wegner[13]. They employed direct polymerization onto TEM grids, with repeated washings and dryings to produce some highly aligned regions of fibrils. A small aperture was used to select only these areas, to form electron diffraction fibre patterns. These enabled identification of the *c*-axis (the direction of the polymer chain) as parallel to the fibril axis, and by separation of the diffraction rings into arcs some assignment of the *h, k, l* values was possible. Additional supporting evidence can be found in a paper by Fincher *et al.*[16] They studied the X-ray diffraction pattern of poly(acetylene) which had been simultaneously stretched and isomerized to the *trans* form. They firmly support the alignment of polymer chains and fibril axis, although they question the *Pnam* space group assignment.

As part of a wider study of electroactive polymers, we have examined *cis*-poly(acetylene) produced by the Luttinger method, to attempt to resolve the controversy over its structure.

## EXPERIMENTAL

### *Preparation of poly(acetylene) films*[4]

Several microscope slides were thoroughly cleaned. All subsequent operations were carried out in a nitrogen-filled glovebox. A solution of 0.02 g of sodium borohydride in 5 ml diglyme was prepared. Then 50 ml of a $10^{-3}$ M solution of hexaquocobalt(II) nitrate in ethanol and 50 ml diethyl ether were placed in a wide-necked bottle. The slides and the two solutions were cooled to $-78°C$. A deep-red colour, characteristic of the formation of the catalyst, developed upon mixing together the two solutions. A slide was dipped into the catalyst solution, quickly shaken to remove excess liquid and inserted into a glass tube through which a slow stream of purified acetylene was passed. Extremely thin purple-red, transparent films were formed after a few seconds exposure.

### *Transmission electron microscopy (TEM)*

The thin films of poly(acetylene) were floated off the glass slides onto distilled water and portions were scooped onto 3 mm diameter carbon-coated or unsupported TEM specimen grids. These were loaded into the prechamber of a Jeol 100 C TEM and dried down quickly, in vacuum, at room temperature. The time from sample preparation till electron microscope examination was kept to less than an hour, to preserve the *cis* character of the thin polymer layer, avoiding the slow, room-temperature isomerization to the *trans* form[17].

TEM study of poly(acetylene) is hampered by electron-beam-induced damage to the polymer structure. In the present work, several steps were taken to obtain meaningful information before irreversible loss to the damage process. Very low beam doses were employed, less than $10^{-1}$ C cm$^{-2}$ in the conventional and dark-field imaging modes and less than $10^{-2}$ C cm$^{-2}$ for electron diffraction. Kodak 'Industrex C' X-ray film was also used, having a high speed and detection efficiency, thus enabling efficient collection of image information during low-dose exposures. TEM images were recorded at × 20 000 magnification and image rotation and electron diffraction periodicities were calculated from lens current calibration curves. Stereo images were recorded for 0° and 5° specimen tilts.

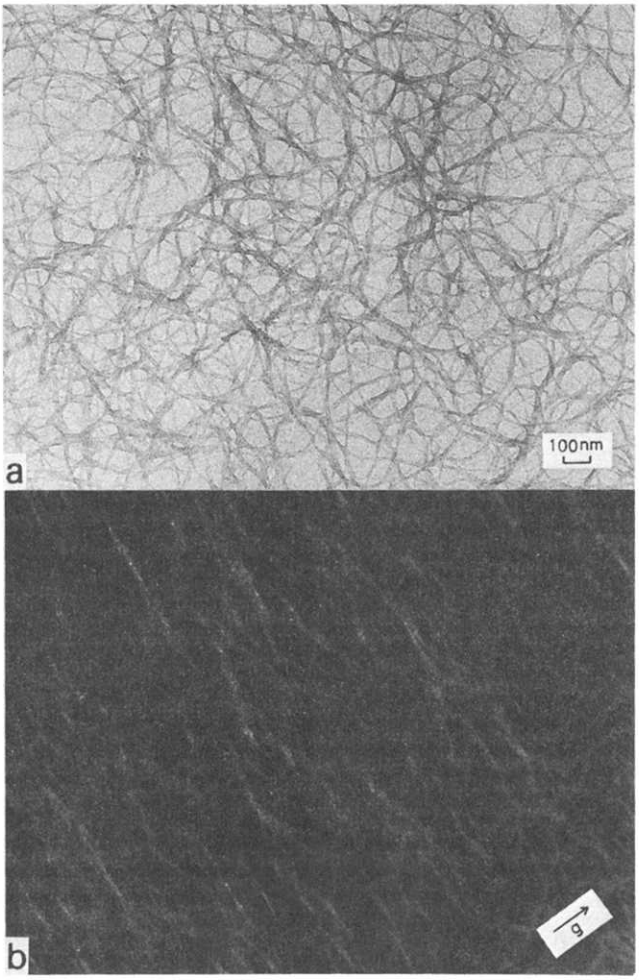

*Figure 1* (a) Conventional TEM image of fibrous poly(acetylene). (b) Corresponding dark-field TEM image for chosen vector *g*

## RESULTS AND DISCUSSION

The thin 'films' of poly(acetylene) were in fact shown to consist of random fibrous networks as in *Figure 1a.* Fibre widths ranged from 5 to 25 nm and tilting experiments in the TEM indicated similar variation in fibre depth, so a mean fibre diameter of around 15 nm can be quoted. Stereo images also revealed that the fibrils were often highly curved and intertwined, with some straight portions of up to 5000 nm in length. Some variation in film characteristics between individual preparations was noted, but these morphological differences were related to fibre thickening with increased time of reaction.

Electron diffraction polycrystalline ring patterns characteristic of *cis*-polymer were obtained (*Figure 2*); the smallest area analysed was that bounded by a 750 nm diameter effective aperture. Occasionally, some arcing was present in the ring patterns, attributed to physical stretch-aligning of the polymer near the specimen grid bars. *Table 1* shows the measured periodicities and their assigned Miller indices, in accordance with an orthorhombic unit cell, with assumed space group[5–7] *Pnam*, having cell dimensions $a = 7.58$ Å, $b = 4.34$ Å and $c = 4.47$ Å.

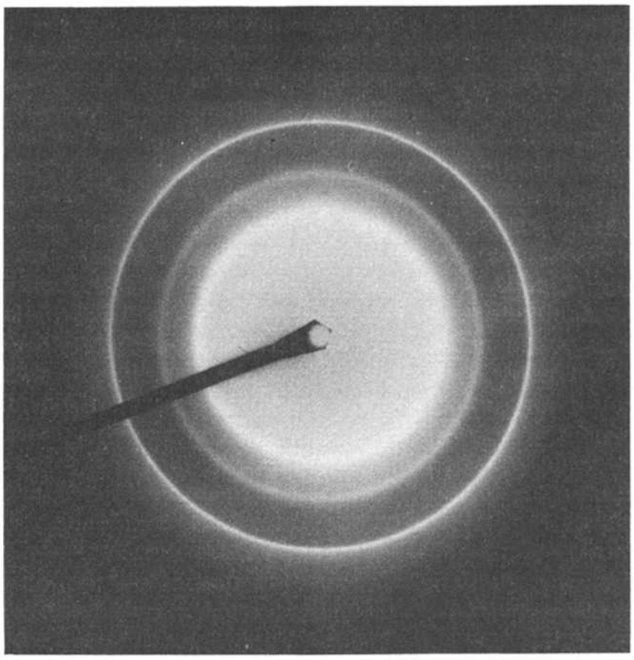

*Figure 2* Electron diffraction microcrystalline ring pattern from poly(acetylene) fibres

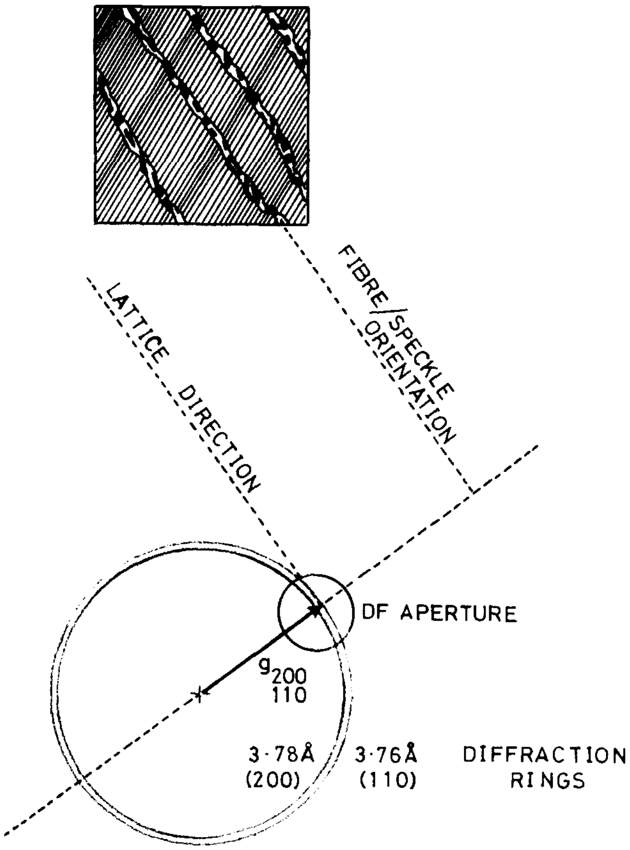

*Figure 3* Construction for the dark-field observation of *Figure 1b*

The relationship between the unit cell (that is, the crystal structure), the direction of the polymer chains and the fibre axis was examined, using the tilted dark-field TEM mode[18] to form images from electrons scattered by crystalline regions of the specimen. A conventional bright-field image of an area of the specimen (*Figure 1a*) showed the randomly oriented poly(acetylene) fibres. The dark-field aperture was centred on a small arc of the 3.78 Å (200) and 3.76 Å (110) reflections and the corresponding dark-field image was recorded (*Figure 1b*). The characteristic dark-field 'speckle' was apparent in some of the fibres, specifically those in the particular orientation defined by the chosen dark-field condition. The idealized construction (*Figure 3*) shows the selected dark-field vector, the observed orientation of the dark-field speckle and the fibre direction giving rise to the latter. Under these conditions the selected (*h*00) and (*hk*0) lattice planes lie normal to the dark-field vector by reciprocity and therefore parallel to the fibre axis. The *c*-axis is then the molecular axis *and* the fibre axis, oriented as shown in *Figure 4*. *Figure 5* shows combined (200) and (110) dark-field images for the two orthogonal vectors indicated. Again, strong reflections are present only for fibres which lie perpendicular to the chosen vectors, confirming the coincidence of polymer chain and fibre axis.

*Table 1*

| Experimentally observed<br>*d* (Å) | Calculated | |
|---|---|---|
| | *d* (Å) | *hkl* |
| (3.68–3.90) | 3.78 | 200 |
| 3.79 | 3.76 | 110 |
| (2.81–2.88) | 2.89 | 201 |
| 2.84 | 2.88 | 111 |
| | 2.85 | 210 |
| (2.15–2.18) | 2.18 | 310 |
| 2.17 | 2.16 | 020 |
| 1.89 | | |
| 1.72 | | |
| 1.64 | | |
| 1.19 | | |
| 1.08 | | |

Such dark-field orientation effects would not be observed for a randomly oriented sample and would be different in nature for fibres with polymer molecular chains aligned perpendicular to fibril axes.

The observation of preferred orientation revealed in dark field is sufficient to challenge the platelet model, as no individual platelet would confer a particular orientation on its neighbours. It is useful to re-examine the experimental evidence for the platelet model[11–13]. 'Platelet' has been interpreted from the TEM-observed morphology. However, our studies have shown that fibre thickening with increasing reaction time causes a loss in resolution of morphological detail and a 'platy' appearance can result. Secondly, electron diffraction periodicities have been indexed as (*hk*0) reflections, suggesting observation of platelets, down the *c*-axis. We have carried out model calculations which show that by slight variation of the unit cell parameters (which have not been accurately assigned in any case) it is possible to *fit* (*hk*0) assignments to the observed reflections. The electron diffraction evidence, taken on its own, is therefore poor. The only additional evidence for platelet morphology was the observation of 4.47 (assigned (001)) reflections in room-temperature X-ray Debye photographs and in electron diffraction patterns from polymer cooled to below −70°C[11,12]. This was interpreted as basal plane

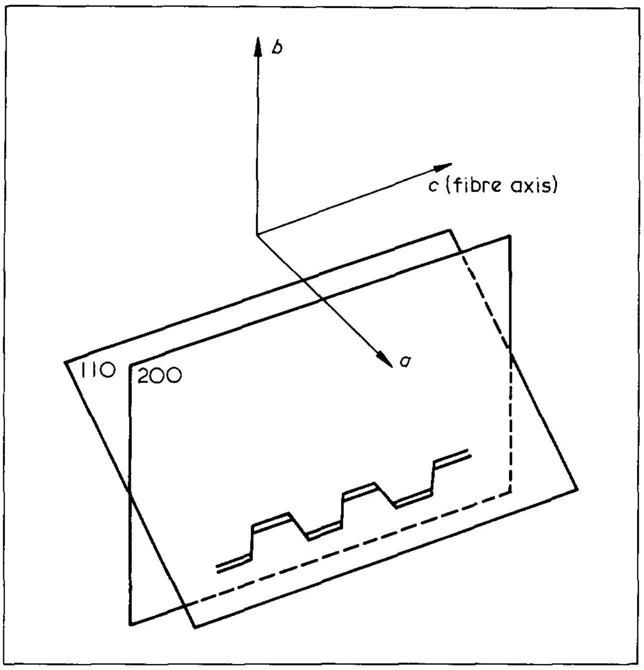

*Figure 4* Molecular *versus* fibre orientation in poly(acetylene).

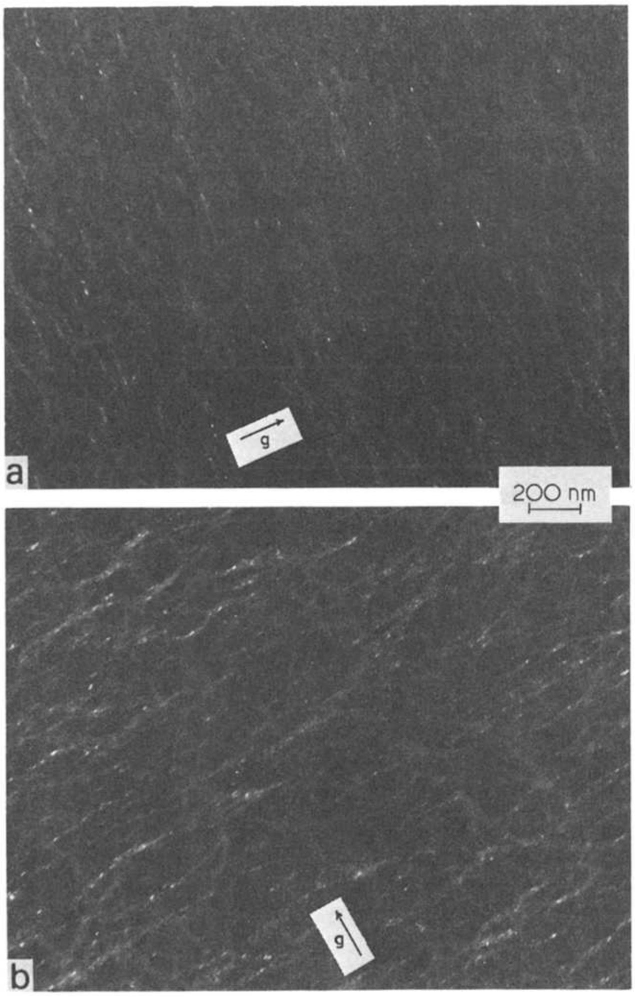

*Figure 5* (a) and (b) Dark-field images for orthogonal *g* vectors as indicated

diffraction from side-on platelets and led to questions of space group assignment, as (001) should be absent for orthorhombic *Pnam*. We have not yet attempted low-temperature electron diffraction, but this reflection was not observed in X-ray Debye photographs of our Luttinger poly(acetylene). In conclusion, we obtained *no* evidence for platelet structure or for the existence of polymorphism. It must be noted, however, that in this work we produced reasonably consistent samples via a single preparative route. Future studies will include other preparations of the *cis*-form, e.g. using the Shirakawa method[3].

## CONCLUSIONS

Thin-'film' preparations of Luttinger-type *cis*-poly(acetylene) have been examined by conventional imaging, in dark-field mode and by electron diffraction in the transmission electron microscope. Minimal exposure techniques were employed to record meaningful information prior to structural disruption under electron irradiation. The thin 'films' were shown to consist of fibrillar mats. Individual fibrils had diameters of between 5 and 25 nm and stereo images revealed extensive curving and intertwining of fibrils. Combined electron diffraction and dark-field observations in the TEM indicated the structural arrangement within the fibrils as that having *polymer molecular chains aligned parallel to fibril axes*. The alternative geometry, with polymer molecular chains perpendicular to fibril axis, was not observed although this result is not necessary to challenge the platelet model. No preferred growth direction would exist between platelets on such a model.

We have used consistent preparations of Luttinger-type material in this work and thus cannot rule out the possibility of polymorphism due to differences in preparative routes. However, it is important to note that the platelet model of Lieser and Wegner *et al.*[11,12] was partly based on observations of similarly prepared Luttinger-type *cis* polymer.

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