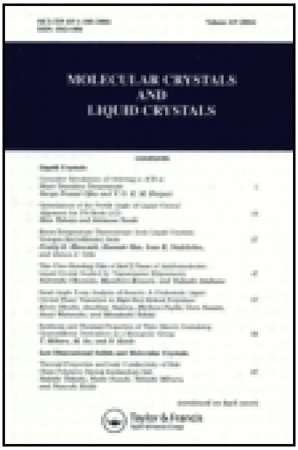

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Aspects of Stress Induced Crystallinity in Durham Polyacetylene

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ASPECTS OF STRESS INDUCED CRYSTALLINITY IN DURHAM POLYACETYLENE

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Abstract: Production of polyacetylene fibres is described together with details of doping and resultant conductivity behaviour.

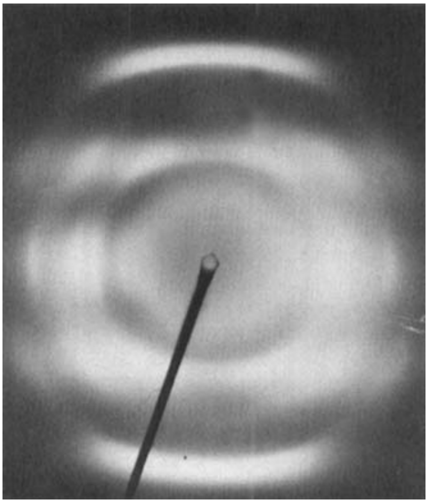
INTRODUCTION

Conducting polymers have been the subject of intense study since Shirakawa et al. [1] reported the production of 'films' of polyacetylene. This represented a major breakthrough in processing, as polyacetylene produced prior to that time was in powder form only. Subsequently many attempts were made to find ways of further manipulating the polymer produced, notably via the cis gel phase [2], dissolution of the arsenic pentafluoride doped material in arsenic trifluoride [3], graft copolymerisation [4] , but also by various other techniques [5,6] .

The possibility of true polymer processibility, however, became apparent from the work of Edwards and Feast [7] on a two stage route to polyacetylene. Their work involved the use of a soluble intermediate or precursor polymer which could subsequently be thermally transformed into polyacetylene. Polyacetylene produced via this so called 'Durham' route has somewhat different properties [8] from polyacetylene prepared by direct polymerisation of acetylene onto a catalyst, ie Shirakawa, Luttinger [9]. Films of Durham polyacetylene are fully dense showing none of the fibrillar nature of the polyacetylenes produced by direct polymerisation such as Shirakawa and Luttinger polymers. The morphology of polyacetylene prepared by the Durham route is not limited to simple dense films. By the use of conventional polymer processing techniques the precursor polymer can be manipulated to allow production of polyacetylene in a variety of forms. Work by White et al. [10] , Leiser et al. [11] and Leising [12] has already demonstrated the production of induced crystallinity in the Durham material, this latest work aims to show the logical extension of these techniques to enhance the variety of available morphologies and to demonstrate some of the structure/property relationships in the Durham material.

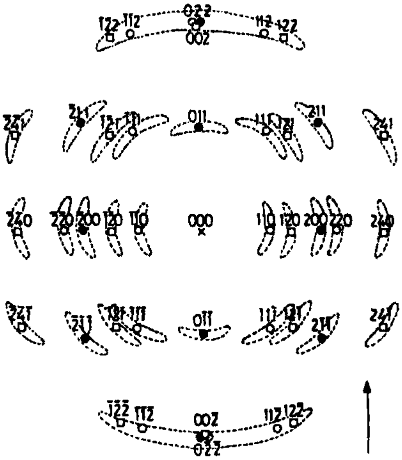
TRANSMISSION ELECTRON MICROSCOPY

Precursor polymer solution was pipetted onto TEM specimen grids (3mm dia, 400 mesh copper). The solvent was pumped off in a controlled atmosphere prechamber and the specimen was inserted into the vacuum of the microscope (~1×10^{-4} Torr). Selected Area Electron Diffraction (SAED) patterns, recorded at room temperature, showed that the dried-down precursor polymer was amorphous. The specimen was then heated, taking 10 minutes to reach 100 deg C and this temperature was maintained for a further 5.5 hours. SAED patterns recorded after increasing time intervals, showed that the precursor polymer had been transformed to a crystalline material (fig 1.).



SAED: after 5.5 hr at 100 °C

fig.1



Diffraction scheme. Arrow indicates stress / alignment direction.
[□$\langle 2\bar{1}0\rangle$; O$\langle 1\bar{1}0\rangle$; ●$\langle 0\bar{1}1\rangle$]

fig.2

The diffraction pattern indicated partial alignment directed from edge to centre of the grid squares. This alignment was attributed to the proposed crystallisation under stress due to film sagging. Post-experimental examination in the scanning electron microscope supported this hypothesis . Interplanar d-spacings and angles measured from the experimentally obtained electron diffraction patterns showed good agreement with the published data for trans-polyacetylene, in monoclinic crystal system, with unit cell parameters :

a = 4.24 A   b = 7.32 A   c = 2.46 A   B = 91.5 deg [13]

A schematic diffraction pattern (fig 2.) has been calculated for partial c-axis alignment of trans-polyacetylene. Polymer molecular chains were only weakly aligned from the grid bar to grid centre. Several torsional crystal orientations have arisen within this alignment constraint and consequently several different zone axes have been simultaneously observed ($\langle 2\bar{1}0\rangle$, $\langle 1\bar{1}0\rangle$ and $\langle 0\bar{1}1\rangle$ zones have been included). Reflections have been arced to account for the weak c-axis alignment (±20 deg) and broadened to account for the poor crystallinity of the polymer and further degradation under electron irradiation.

Film morphology was mostly continuous but some holes and tears developed during heating and fibrous morphology was observed in these highly stressed regions.

PRODUCTION OF FIBRES BY GEL DRAWING

To extend the scope of induced crystallinity from the microscopic level, work has been done on the production of orientation in macroscopic samples. Utilising the gel phase in Durham polyacetylene precursor polymer standard routes to fibre formation can be adopted, such as those reported by Lemstra and Smith [14], and by Pennings [15].

Concentrated solutions of Durham precursor polymer were placed into stoppered capilliary vessels inside an argon atmoshere glove box. The solutions were kept at room temperature for 24 hours to allow the gel phase to form. The gels produced were removed from the capilliaries, clamped at both ends and extended under constant load. After allowing a few minutes for the gels to collapse by solvent evaporation, fibres of the precursor polymer were formed. These fibres were then transformed for 5 hours at 80 deg C under dynamic vacuum to produce Durham polyacetylene fibres. By this very simple technique fibres with draw ratios of 10 are easily made. X-ray diffraction was used to assess the degree of alignment achieved .

D.C. conductivity was measured along the orientation direction using a four in-line contact geometry, and for undoped films was about 10 reciprocal ohm cm. at room temperature. The temperature dependence above 200 K is fitted by a simple activated law, with activation energy 0.45 eV.

Arsenic pentafluoride doping was carried out using standard techniques, and a value for the conductivity of one reciprocal ohm cm. was obtained after exposure to 30 mbar for several days; weight-uptake measurements indicated a dopant concentration of one molar percent. The values of conductivity and the doping behaviour are similar to the results obtained by us on unoriented films.

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