

Microstructural study of as-polymerized and isomerized fibrils of *trans*-polyacetylene

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Two kinds of *trans*-polyacetylenes (PA) were prepared for electron microscopy. For sample A, *cis*-PA was isomerized into *trans*-PA by annealing at 150°C. For sample B, acetylene was polymerized directly to the *trans* form at 80°C. Electron diffraction showed that the lattice parameters were larger for sample A than those of sample B, especially the *b*-axis. The expansion resulted from inclusion of remnant *cis* units as defects in the *trans* crystal. A lattice image of sample A revealed that crystallites had a fairly broad orientation distribution within the fibril, which was induced by chain extension by the transformation from *cis* to *trans* forms. The crystallite dimension along the polymer chain direction was smaller than that in the lateral direction. Based on this structural information, an intrafibrillar hopping mechanism was proposed for the electrical conduction of the iodine doped PA.

(Keywords: polyacetylenes; electron diffraction; lattice imaging; electrical conduction)

INTRODUCTION

Acetylene polymerizes into infusible and insoluble polyacetylene (PA) fibrils in which the PA polymer chains take either the *cis* or *trans* forms depending on polymerization temperature^{1,2}. Crystal structural models have been proposed both for *cis* and *trans* forms from X-ray and electron diffraction³⁻⁵. Electron microscope images in the dark-field mode showed uniaxially oriented crystallites in the fibrils prepared by Meyer's method⁶ and by the epitaxial polymerization method⁷. Upon doping with iodine, the chain becomes all *trans* to give an 'organic metal'⁸. However, the conductivity (σ) of iodine doped PA does not exceed 10³ S/cm even with partially oriented PA fibrils⁹. From the straight line behaviour for $\ln \sigma$ versus $T^{-1/4}$ (T =temperature), Chiang *et al.* suggested that the conduction was controlled by interfibrillar hopping¹⁰. Defects among the crystallites within individual fibrils also seem to have a serious role in conduction. This report concerns the fine structure of the fibrils and its reorganization during *cis-trans* transformation.

EXPERIMENTAL

Acetylene was polymerized epitaxially on terphenyl single crystals, which had been dipped in a toluene solution of Ti(OBu)₄/4AlEt₃ catalyst⁵. The substrate terphenyl crystals were then dissolved in toluene. The detached thin PA films were transferred onto copper grids for electron microscopy, and observed using a Hitachi HU-11B electron microscope. For determination of lattice spacing (*d*-spacing), aluminium evaporated onto the specimens on grids was used as an internal standard for electron diffraction.

Two kinds of samples were prepared. For sample A, *cis* PA was synthesized at -78°C and subsequently

isomerized into stable *trans* PA by heat treatment at 150°C for 30 min. For sample B, acetylene was polymerized at 80°C to give *trans*-rich fibrils. As previously reported⁵, the terphenyl crystal orients the fibrils predominantly into two special directions for both -78°C and 80°C polymerization temperatures. The angle between the two directions is consistent with that between (110) and (1 $\bar{1}$ 0) of the terphenyl single crystal. Figure 1 shows an electron micrograph of sample A. The fibril pattern did not change during the *cis-trans* isomerization by heat treatment.

For lattice imaging, the PA film was transferred onto a gold-coated holey support film ('microgrid') which had been mounted on the copper grid. The specimen thus prepared was coated with a thin layer of evaporated carbon to suppress electron charge-up, and observed with a 200 kV electron microscope, JEOL JEM-200CS. Total end-point dose, namely the electron dose needed for complete destruction of crystallinity, was measured to be about 0.3 C/cm² (200 kV, at 20°C) for the *trans* PA crystal. Considering this value and the sensitivity of the recording film, direct magnification was selected as 10⁵ for the lattice imaging of PA. In this way, total dose for taking one micrograph was estimated as 0.07 C/cm² on the specimen, which corresponded to one fourth of the total end-point dose for the *trans* PA crystal. Negatives of the electron microscope image showing lattice fringes were transformed optically into a diffraction pattern using an optical diffractometer.

RESULTS AND DISCUSSION

Figure 2 shows the electron diffraction patterns of samples A and B. Two sets of electron diffraction patterns, corresponding to the fibril orientation shown in Figure 1, are observed rotated about 70 degrees to each

other. The diffraction spots from sample A are fairly broad, which suggests inclusion of crystalline defects formed during isomerization in the solid state. On the contrary, diffraction spots from sample B are much sharper such that (020) reflections are separated from (011) reflections. Table 1 shows the lattice parameters. In general, the values are larger for the PA prepared through *cis* to *trans* isomerization than those of the pristine *trans* PA, especially the *b*-axis. Shirakawa has reported a relationship between the *trans/cis* ratio and the polymerization temperature². According to his data, the pristine *cis* PA, a precursor of sample A, and sample B can be estimated to be originally composed of 6 and 69% of



Figure 1 Electron micrograph of polyacetylene polymerized epitaxially on the substrate crystal of terphenyl at -78°C

trans units, respectively. Consequently, most *trans* units in sample A were produced during the heat treatment. As the isomerization occurred in the solid state, it is probable that there remained *cis* configurations in the fibrils. These act as defects in the *trans* crystal; hence, the *d*-spacing expanded. In order to observe more directly these distorted crystallites, a lattice image is useful.

Figure 3 is an electron micrograph of PA fibrils after isomerization (sample A), where many lattice fringes are observed. Direct measurement of their *d*-spacing on the micrograph and also the optical transforms of the negatives (inset in Figure 3) suggest that these fringes correspond either to (020), (200) or (110). A domain where the lattice fringe is coherently observed corresponds to one crystallite. Thus the crystallite dimension along the polymer chain direction was estimated to be 5 nm on the average, and was smaller than that in the lateral direction, i.e. the PA polymer chain was not completely in the *trans* zigzag form throughout the fine fibrils. It should be noted here that the crystallites had a fairly broad orientation distribution within the fibril. As the repeat distance of *trans* form is larger than that of *cis* form, the transformation necessitates a chain shift, e.g. for the isomerization of a crystallite of 50 *cis* CH units into the *trans* form, the crystallite lengthens by one *cis* repeat unit. Such an extension might induce disorientation of the crystallites within fibrils. As previously reported⁴, bulky iodine atoms penetrate into the PA lattice to form the doped PA^+I^- texture. It is probable that doping introduces additional defects into the consecutive *trans* units, but there is little chance that the regularly ordered PA^+I^- structure can be generated from the originally

Table 1 Unit cell parameters of *trans*-polyacetylene

	Polymerized at 80°C (sample B)	Polymerized at -78°C subsequently heat treated at 150°C (sample A)
<i>a</i>	0.732	0.739
<i>b</i>	0.400	0.418
<i>c</i>	0.242	0.246
density (g/cm^3)	1.22	1.11

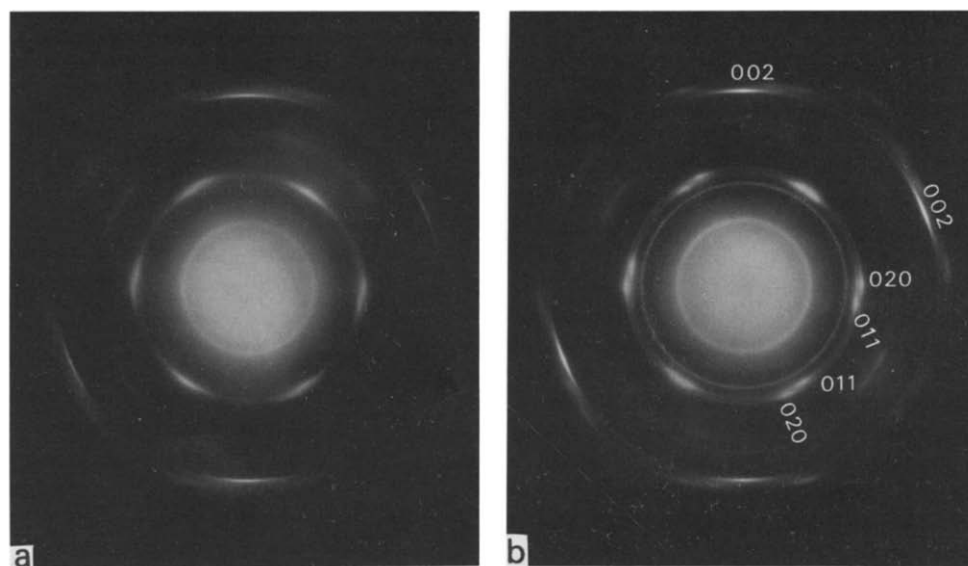


Figure 2 Electron diffractions of polyacetylenes: (a) polymerized at -78°C and heat treated at 150°C for 30 min; (b) polymerized at 80°C

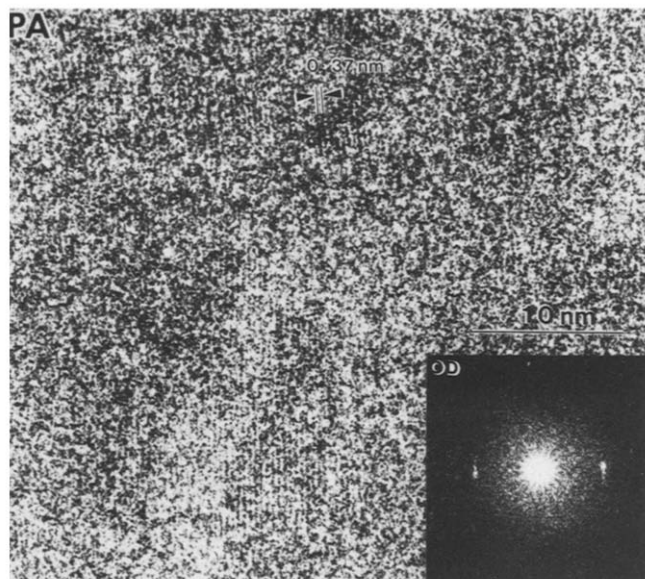


Figure 3 Lattice image of polyacetylene polymerized epitaxially on a terphenyl crystal and subsequently heat treated at 150°C for 30 min

disordered regions during doping. Hence, doping should make the ordered domains smaller. In this case, even if the PA^+I^- complex has much better conductivity within

the ordered domains, peripheral disordered regions still remain as insulators. Thus, macroscopic conduction seems to be controlled by the hopping mechanism even within the individual fibres, as well as the previously reported interfibrillar hopping.

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