The evolution of polyacetylene morphology upon doping

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Knowledge of the evolution of the fibrillar morphology of polyacetylene with doping is critical for an understanding of the chemistry of the doping process, the mechanisms for charge transport in the polymer and the insulator-metal transition. Earlier scanning electron microscopic (*SEM*) studies reported conflicting results of either swelling of the fibrils or a gross morphological change. In order to resolve these differences, *SEM* experiments were carried out to compare the changes in apparent morphology due to the use of various coatings and coating methods used to reduce charging effects, the effects of tearing on the cross sectional morphology and the effects of contrast in imaging the samples. Results definitively show that the fibrillar morphology is retained upon doping.

Keywords Polyacetylene; morphology; iodine-doping; scanning electron microscopy

INTRODUCTION

Although acetylene was first polymerized[1] as a grey powder in 1958, it was the preparation of polyacetylene films[2] which enabled detailed physical studies to be carried out. Polyacetylene has attracted much interest recently due to its ability to undergo reactions with oxidizing or reducing agents[3]. These reactions result in up to twelve orders of magnitude increase in conductivity and formation of the metallic state[4,5].

Early transmission electron microscopy and scanning electron microscopy (*SEM*) established that the nascent morphology of polyacetylene films synthesized using the Shirakawa technique is fibrillar[2]. Films generally have fibrils of 200 to 500 Å diameter with the detailed morphology of the fibrils and the crystallinity of the films having been found to be preparation dependent[6]. The morphology has a central role in both the doping and compensation of this system. The presence of fibrils is important for the rapid electrochemical doping and for potential battery applications[7]. Other morphologies have been suggested to result from polymerization under other conditions[8].

Knowledge of the dynamic evolution of the morphology with doping is critical for an understanding of the chemistry of the doping process, the mechanisms for charge transport in the polymer and the insulator-metal transition[4,5]. It was recently reported[9,10] that doping of this system results in the formation of platelets followed, at high doping levels, by a macroscopic morphological change to a uniform distribution of various size highly conducting regions. These data were purported to support a metallic island percolation model for the insulator–metal transition[11]. Contradictory observations of only a swelling of the individual fibrils, upon doping with iodine, have also been reported[12,13]. These latter results supported the view of the transition as a bulk phenomena in iodine doped polyacetylene despite some inhomogenieties in doping[4,14]. In order to resolve these experimental differences, we have carried out *SEM* experiments which compare the changes in apparent surface and cross section morphology due to the use of various coatings and coating methods to reduce charging effects, the effects of tearing on the cross sectional morphology and the effects of contrast in imaging the sample. The results show that the morphology of polacetylene is fibrillar and does not change significantly with doping.

EXPERIMENTAL

All *SEM* micrographs presented here were obtained using a JEOL JXA-35 scanning electron microscope. The JEOL SEM is capable of up to 50 Å image resolution in the scanning electron mode. The beam currents were kept sufficiently low to preclude sample damage ($\sim 10^{-11}$ A) with the maximum temperature increase estimated to be less than 1 K assuming a stationary beam[15] and a thermal conductivity[16] of 0.5 W/cm-K for the polyacetylene sample. For the micrographs shown in the figures, the digits

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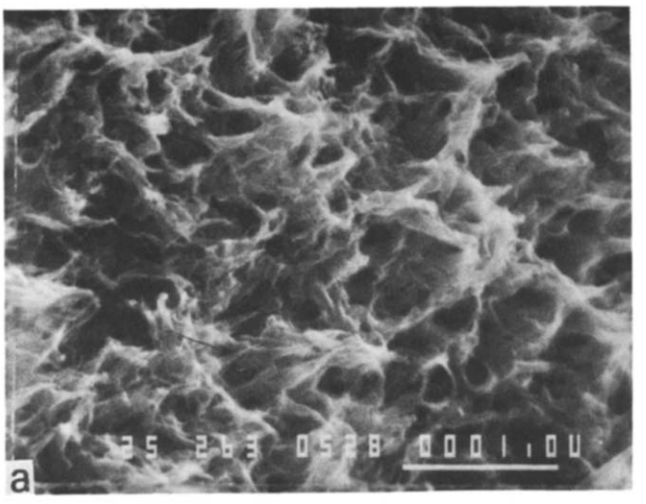


Figure 1a Cross-section of uncoated $(CHI_{0.08})_x$ film prepared at USTL

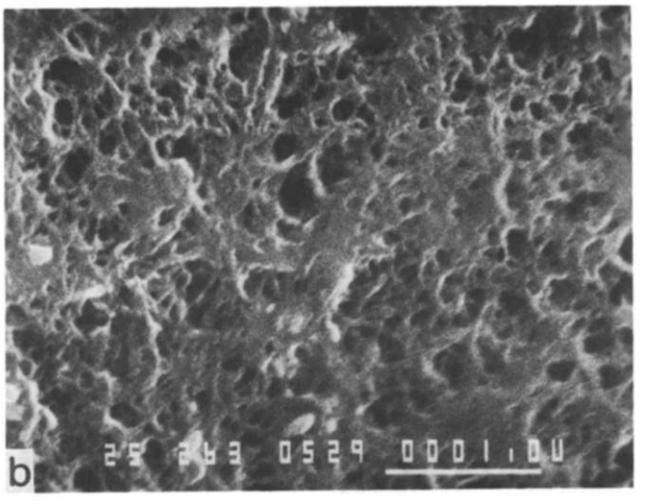


Figure 1b Surface of film shown in *Figure 1a*

give the conditions at the time the micrograph was taken. The first two digits on the left give the accelerating voltage in kilovolts. The next three digits give the magnification (e.g., $263 = 26 \times 10^3$). The following four digits are the micrograph number and the remaining digits indicate the length of the white bar in microns. Similar but more limited results were obtained using a Philips 500 SEM at the University of Pennsylvania.

Conductive coatings were applied using evaporation, sputtering and plasma magnetron sputtering systems. While the first two are conventional techniques and lack facilities for cooling the sample, the latter minimizes effects of high temperatures during coating operations. The average temperature increase for the magnetron system is approximately 1°C/100 Å of coating[17].

The polyacetylene samples were prepared at Universite des Sciences et Techniques du Languedoc (USTL) and at the University of Pennsylvania using the Shirakawa technique. Doping was carried out by exposing the polyacetylene to iodine vapour in an evacuated chamber. In order to study the morphology of the inside of the film, samples were fractured while submerged in liquid nitrogen to expose the cross-sections.

RESULTS AND DISCUSSION

Effects of conductive coatings and coating techniques

Materials such as polyacetylene are preferably overcoated prior to imaging in a *SEM*. Uncoated samples undergo charging during exposure to an electron beam and the accumulated charge may deflect the beam resulting in blurred images. Overcoating the surface with a metallic layer can reduce the charging effect, however, the coating may affect the observed morphology. The selection of coating and deposition technique are critical choices in sample preparation[18,19]. *Figures 1–4* exemplify the variations in apparent morphology observed for various coating techniques.

Figure 1a shows the cross section of an uncoated, iodine doped polyacetylene film prepared at USTL. The composition of the film is $(CHI_{0.08})_x$ as determined by weight uptake. The surface of the same film is shown in *Figure 1b*. It is readily apparent that the morphology is fibrillar in nature. Further doping of a polyacetylene sample from the same synthesis to $(CHI_{0.15})_x$ has no significant effect on the morphology of the film as shown by *Figures 2a* and *b*. These Figures show the cross section and surface respectively; the former is blurred due to sample charging.

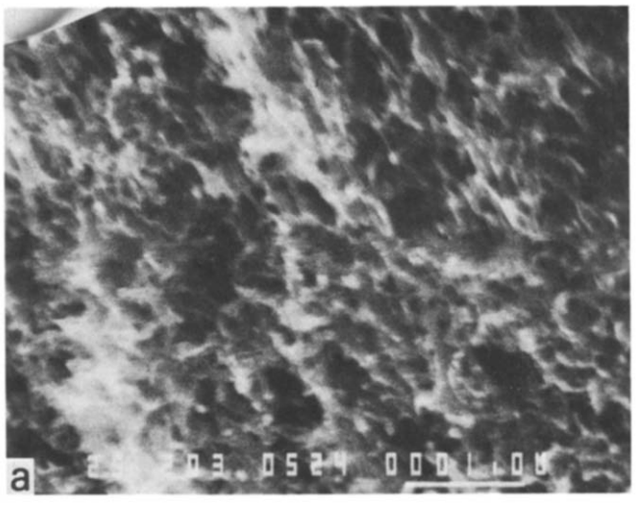


Figure 2a Cross-section of uncoated $(CHI_{0.15})_x$ film prepared at USTL

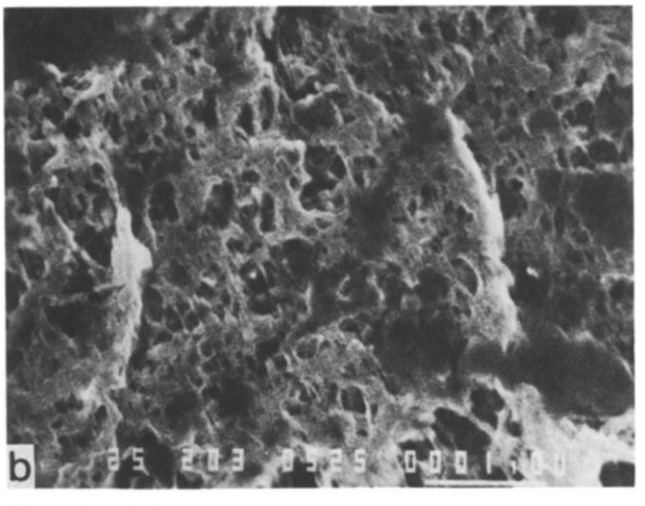


Figure 2b Surface of film shown in *Figure 2a*

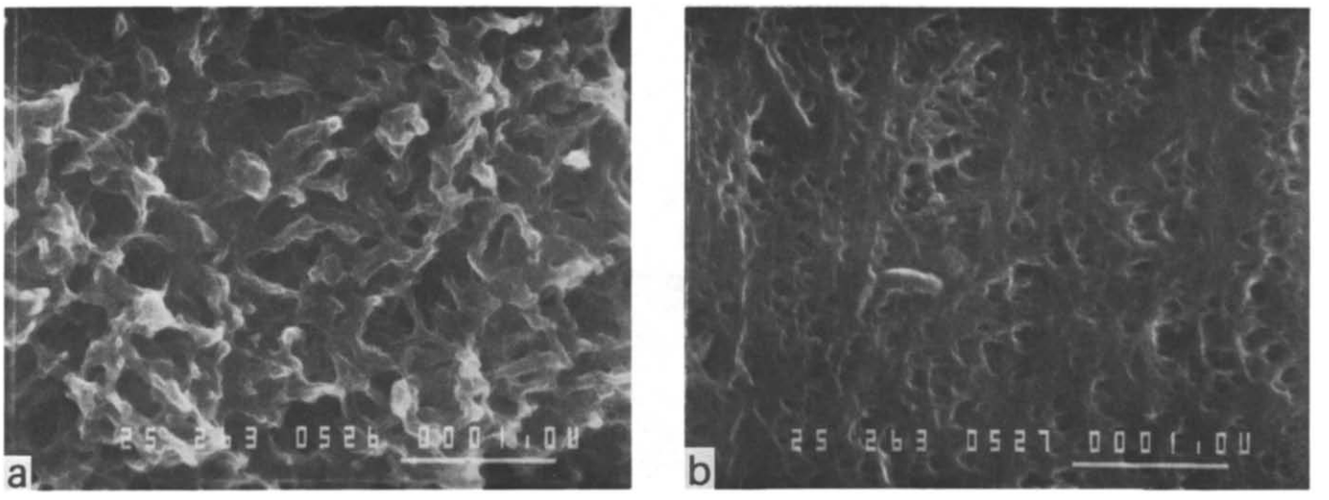


Figure 3 Cross-section (a) and surface (b) of $(CHI_{0.08})_x$ film coated with ~80 Å Au-Pd (60:40) alloy using a plasma magnetron sputtering system

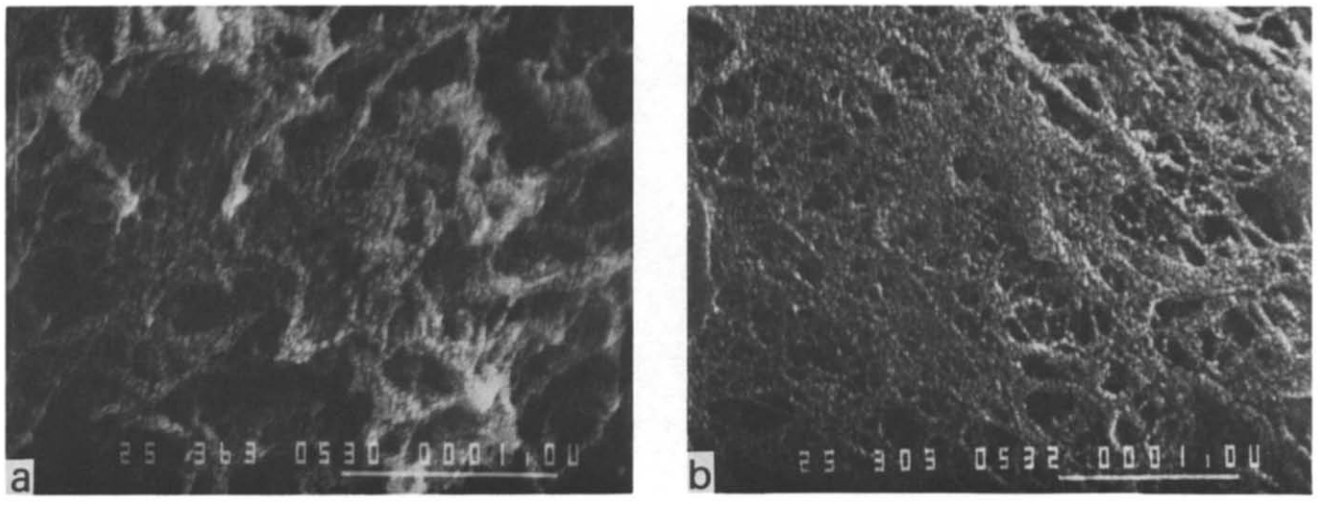


Figure 4 Cross-section (a) and surface (b) of film shown in *Figure 1* coated with ~80 Å evaporated gold

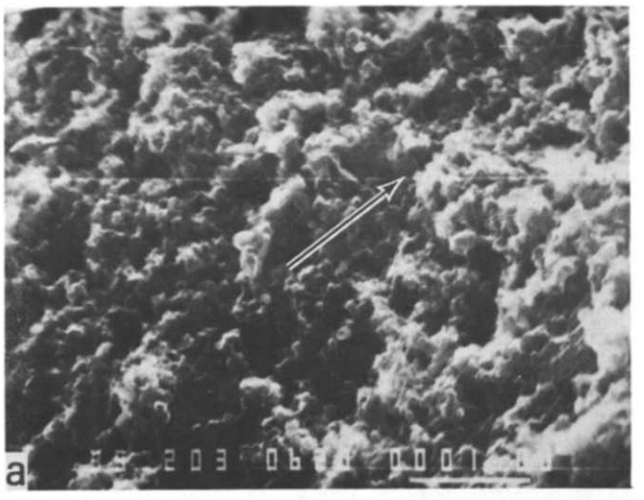
The same pieces of polyacetylene film displayed in *Figures 1a* and *1b*, coated with 80 Å of Au–Pd (60:40) alloy using a plasma magnetron sputtering system, are shown in Figure 3. The cross-section of the $(CHI_{0.08})_x$ sample is seen in *Figure 3a* and the surface in *Figure 3b*. This coating technique has not significantly altered the fibrillar morphology of the doped polyacetylene film. A similar result is obtained for the coated analogs of the more highly doped sample.

A portion of each of these films was also coated with ~80 Å of five nines gold in a conventional evaporation chamber. The cross-section of the $(CHI_{0.08})_x$ sample thusly prepared is shown in *Figure 4a* and the surface in *Figure 4b*. Both micrographs show a masking of the true sample morphology by beads of gold, giving a 'string-of-pearls' effect. However, the fibrillar nature of the film is still discernible. In more tightly packed films such as the $(CHI_{0.15})_x$ sample the coating may totally obscure the true morphology. The cross-section of this piece, *Figure 5*, shows another variation of artifact that occurs with samples having a highly structured topology. In this case there is an apparent 'blooming' of the sample resulting from the agglomeration of gold particles. Similar effects are also seen on other surfaces, for example, gold evaporated on Electrodag. This Figure also shows charging effects due to the discontinuous nature of the coating.

Use of a conventional sputtering technique to apply the gold coating results in other anomalies as shown in *Figures 6–8*. *Figure 6a* shows the surface of undoped *cis*-polyacetylene prepared at the University of Pennsylvania and coated via conventional gold sputtering. Due to shadowing, little, if any, gold is present on this portion of the surface. The slightly distorted fibrils are clearly visible. Note again the area of sample charging indicated by the arrow. Other, more heavily coated, portions of the surface of this sample reveal bright white spots superimposed on a smooth background (*Figure 6b*). These artifacts are also seen in micrographs of the cross section and surface of *trans*-polyacetylene coated by this method.

Sputtering gold onto iodine doped pieces of this film produces the same spurious results. The cross sections of $(CHI_{0.11})_x$ (*Figure 7*) and $(CHI_{0.2})_x$ (*Figure 8*) again display the same bright spot artifacts superimposed on the true fibrillar morphology of the film. Hence neither

Figure 5 Cross-section of film shown in *Figure 2* coated with ~80 Å evaporated gold



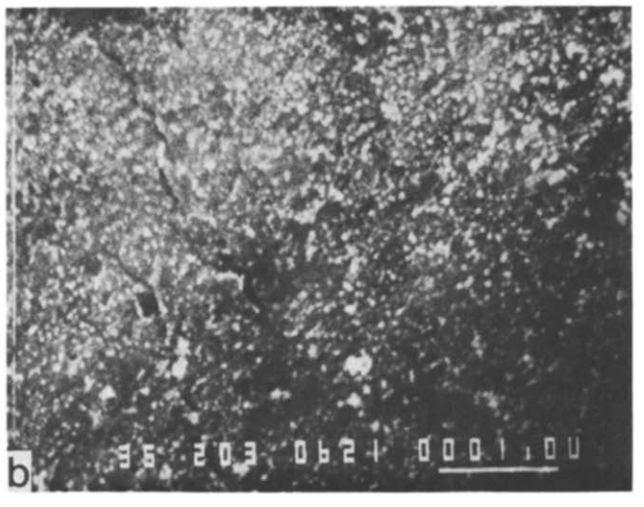


Figure 6 (a) surface of *cis*-polyacetylene prepared at the University of Pennsylvania lightly coated (≪100 Å) with sputtered gold, (b) more heavily coated (~100 Å) portion of the same piece of film

conventionally sputtered nor evaporated gold is suitable for *SEM* studies of polyacetylene unless the nature of the possible artifacts is taken into consideration.

Effects of tearing on the cross-sectional morphology

Polyacetylene synthesized in the presence of a Ziegler catalysts (Shirakawa technique) may be obtained in either the *cis* or the thermodynamically more stable *trans* isomer. The *cis* isomer is plastic while the *trans* moiety is comparatively brittle[20]. In addition, it has been shown[21] that the *trans* content increases with doping, again resulting in increased brittleness of the samples. The effect of this change in mechanical properties may result in images such as those shown in *Figures 9–11*.

Figure 9 shows the cross-section of a pristine polyacetylene film synthesized at the University of Pennsylvania and coated with 80 Å of evaporated gold. The effect of the coating is again apparent (see above). However, of more interest here are the white cone-like protrusions. Close examination of the micrographs reveals that these protrusions are bundles of individual fibrils which have been drawn together. The fact that they are raised above the surface enhances the efficiency of secondary electron collection and gives them their bright white appearance. A second preparation of polyacetylene, synthesized at

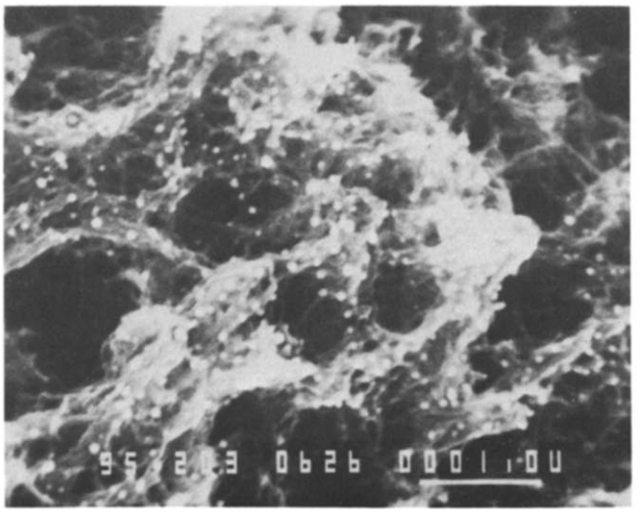


Figure 7 Cross-section of $(CHI_{0.11})_x$ film coated with ~100 Å sputtered gold

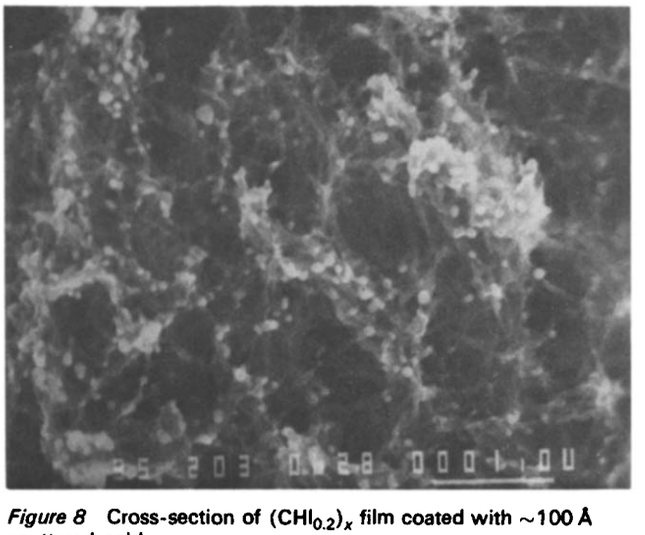


Figure 8 Cross-section of $(CHI_{0.2})_x$ film coated with ~100 Å sputtered gold

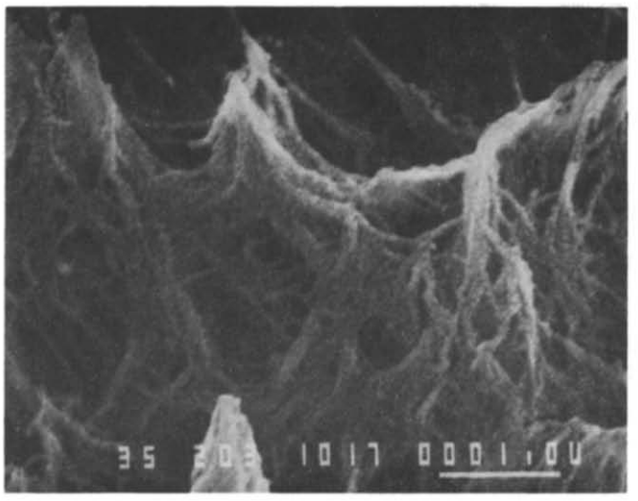


Figure 9 Cross-section of pristine polyacetylene film prepared at the University of Pennsylvania showing the effects of tearing; ~80 Å evaporated gold coating

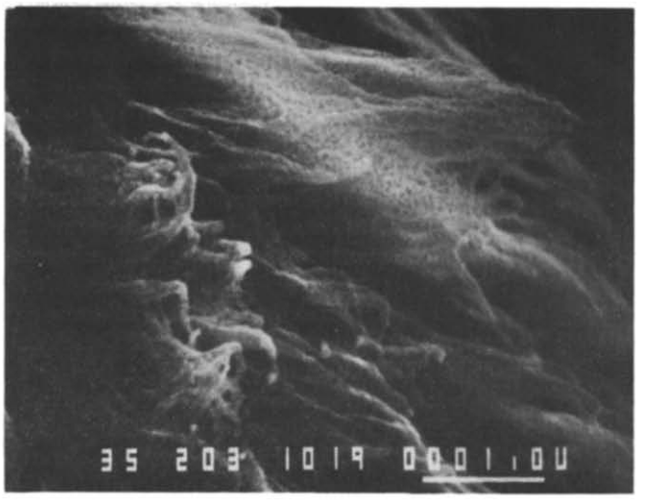


Figure 10 Cross-section of pristine polyacetylene film prepared at USTL showing the effects of tearing; ~80 Å evaporated gold coating

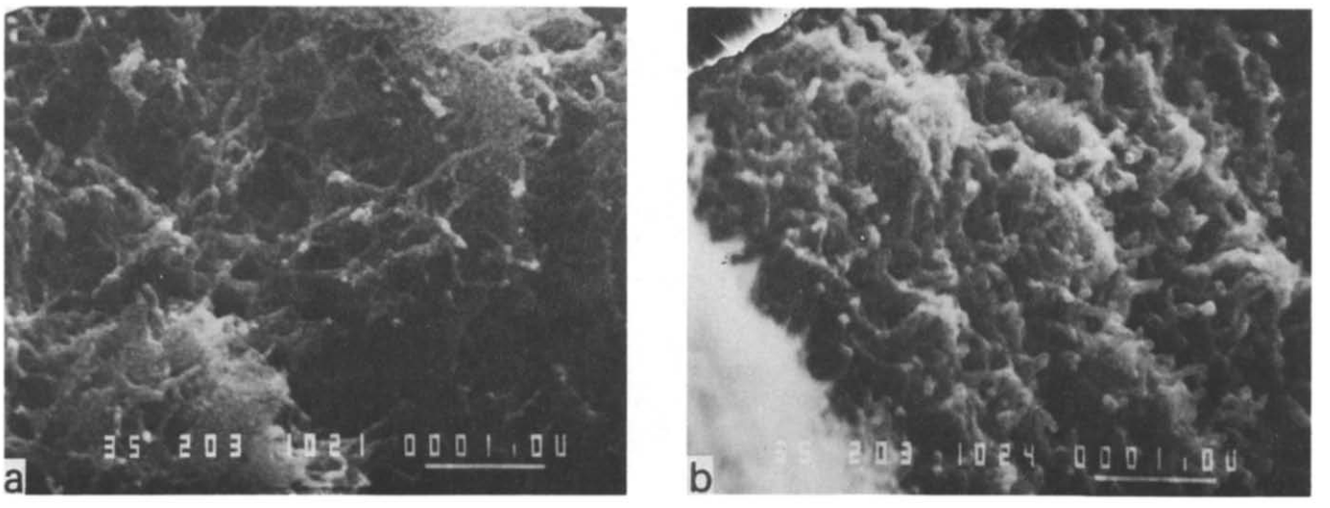


Figure 11 $(CHI_{0.21})_x$ with ~80 Å evaporated gold coating prepared (a) at the University of Pennsylvania and (b) at USTL

USTL, is displayed in *Figure 10*. The inherent fibrous nature of the sample is clearly visible. Again the individual fibres have been drawn together into bundles.

A piece of each of these films was doped with iodine to give $(CHI_{0.21})_x$ and then coated with evaporated gold. *Figure 11a* shows the cross-section of the doped University of Pennsylvania film which reveals a network of fibrils with several bright white areas. These areas are presumably broken fibrils that are being viewed end-on. This conclusion is substantiated by *Figure 11b*, the cross section of the iodine doped film synthesized at USTL. In this figure the individual fibrils are clearly visible with diameters between 300 and 500 Å.

Effect of contrast in imaging

When samples such as those discussed here are imaged under high contrast conditions much information normally contained in the grey scales is lost. This highlights certain bright features, such as the cones seen in *Figure 9*, making it extremely difficult to observe the actual morphology of the film. An illustration of this is shown in *Figure 12*, a high contrast analogue of *Figure 7*.

CONCLUSION

SEM experiments have been carried out to resolve the conflicting interpretations appearing in the literature concerning the effects of iodine doping on polyacetylene morphology. Artifacts caused by sample tearing, image contrast and coating deposition have been categorized. Contrary to previous reports[9,10], our work conclusively demonstrates that there is no significant modification of the morphology with iodine content. Particularly, the 'white-globules' previously assumed to be highly conducting regions, and therefore suggestive of a percolation model of the insulator–metal transition, are shown to be artifacts. We conclude that the fibrillar structure of the nascent polyacetylene film is maintained with iodine doping although there may be fibrillar swelling.

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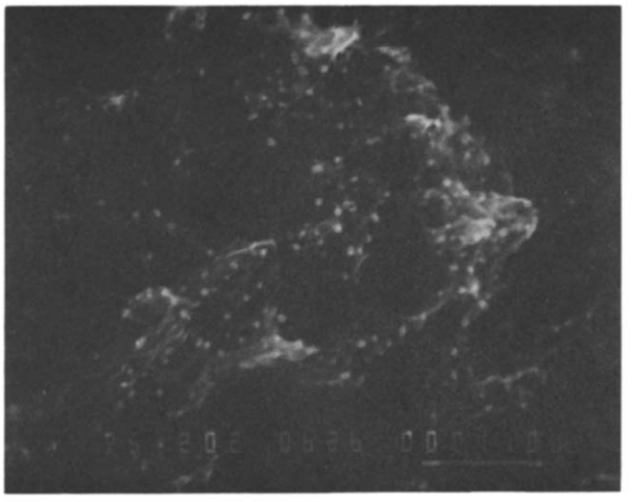

Figure 12 High contrast analogue of *Figure 7* exemplifying the effect of contrast on the apparent sample morphology

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