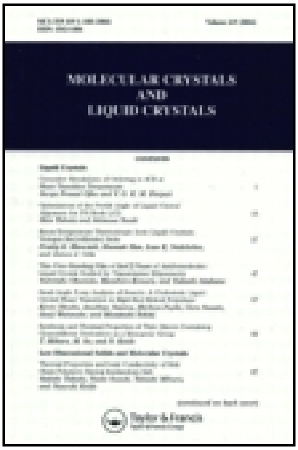

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MORPHOLOGY AND DOPANT DISTRIBUTION IN POLYACETYLENE

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We report the results of scanning electron microscopic studies of the morphology and dopant distribution in polyacetylene, $(CH)_x$. A variety of fibrillar and rod-like morphologies were observed for trans-$(CH)_x$ and $(CH)_x$ doped with iodine and AsF_5. Results show that iodine and arsenic distributions are uniform across the surface of the films to a resolution of 5000 A, with no significant difference in the concentration observed on the dull and shiny sides of the film. Hence any inhomogenieties in the dopant distribution must be on a finer scale. The fibrillar morphology was observed through the bulk of a film even after doping with iodine. Swelling of the fibrils is seen upon doping, with larger effects observed in the AsF_5 doped samples.

INTRODUCTION

Although acetylene was first polymerized[1] in 1958, it was the preparation of polyacetylene films[2] which enabled detailed physical studies to be carried out. Early scanning electron micrographs (SEM) and transmission electron micrographs (TEM) demonstrated[2,3] that these polymers had a fibrillar morphology with fibrils generally having diameters of 200-300 A. Upon doping with donors and acceptors the conductivity of polyacetylene, $(CH)_x$, increases by up to twelve orders of magnitude, resulting in the formation of the metallic state.[4,5]

The fibrillar morphology may play an important role in the doping mechanism, the insulator-metal transition and the temperature dependent conductivity in the metallic state. On the basis of some magnetic[6] and transport[7] studies it was proposed that small metal islands were formed upon doping.[6] However, other magnetic[8,9] and transport[10] studies show that though the dopant distri-

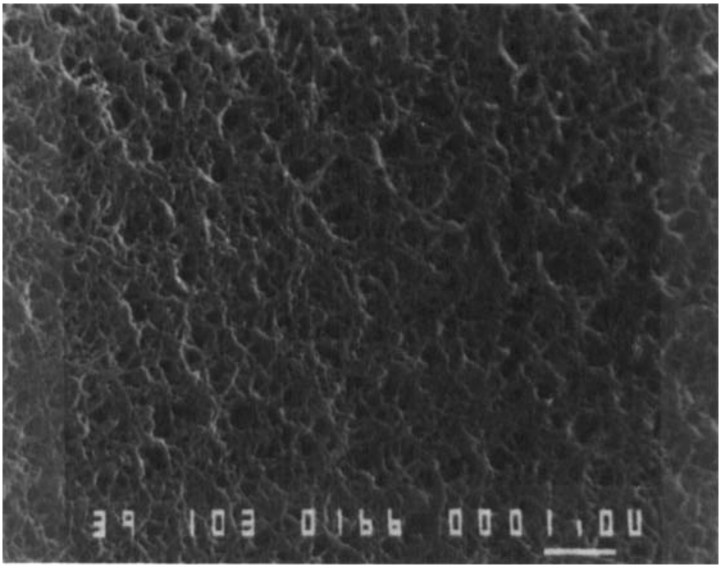

FIGURE 1. SEM micrograph dull side of *trans*-(polyacetylene). The key to the numbers on this and subsequent micrographs is the first two digits on the left give the accelerating voltage in kilovolts, the next three digits give the magnification (e.g., 363 $\equiv 36\text{x}10^3$), the following four digits are the micrograph number, finally, the last five digits give the length of the white bar scale in microns.

bution may be nonuniform, it is not segregated into metallic islands. In the latter case, it is suggested that the doping occurs through the soliton mechanism.[11,12] A preliminary SEM study suggested that the dopant distribution is not uniform (utilizing energy dispersive X-ray analysis, EDXA) on the scale of 5000 Å.[13] Another preliminary study suggested changes in $(CH)_x$ morphology upon doping.[14]

RESULTS AND DISCUSSION

We have carried out an extensive SEM study of $(CH)_x$ and the effects of doping by iodine and AsF_5. The results show the presence of the fibrillar morphology in $(CH)_x$. Generally the dull side was observed to be composed of fibrils ranging from 200 Å to 500 Å diameter for different sample preparations. The shiny sides of the films are matted, with the appearance of rigid rods of larger diameter than those fibrils on the dull side.

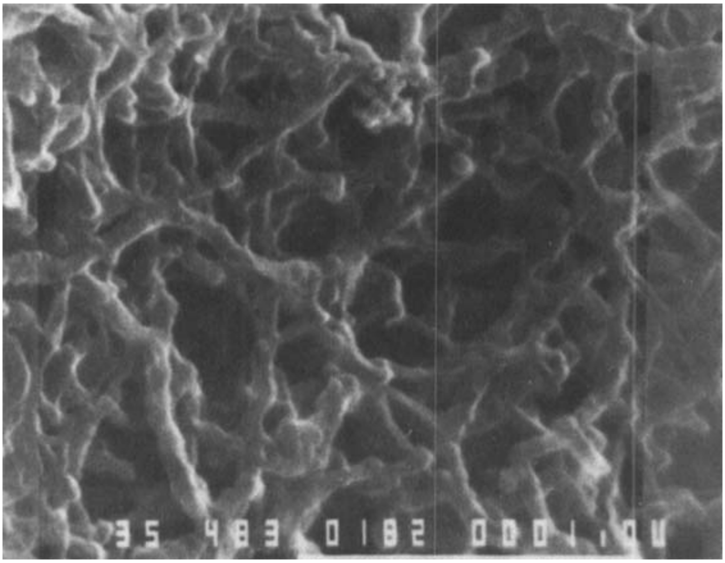

FIGURE 2. Dull side of $[CHI_{0.002}]_x$

Figure 1 is a "typical" example of the rough side of a trans-$(CH)_x$ film. In some cases the smooth side was so dense that it appeared solid.[15] Occasionally small amounts of nonfibrous material were observed on the shiny surface of the film.[15]

Doping with iodine causes an increase in fibril diameter up to a factor of two at high doping levels (greater than fifteen percent iodine) with small change, if any, at low levels. This is consistent with the proposal of intercalation of the dopant species between the polyacetylene chains.[16] Figure 2 is an example of the dull side of trans-$(CHI_{0.002})_x$. In this particularly clear micrograph, the fibrils appear twisted as in rope. No sign of small metallic particle regions is observed.

A sample of $(CHI_{0.008})_x$ was broken while held under liquid nitrogen. Figure 3 displays the SEM micrograph of the broken edge at ten thousand magnification. There is no obvious sign of significant change in the fibrillar structure throughout the bulk of the film.

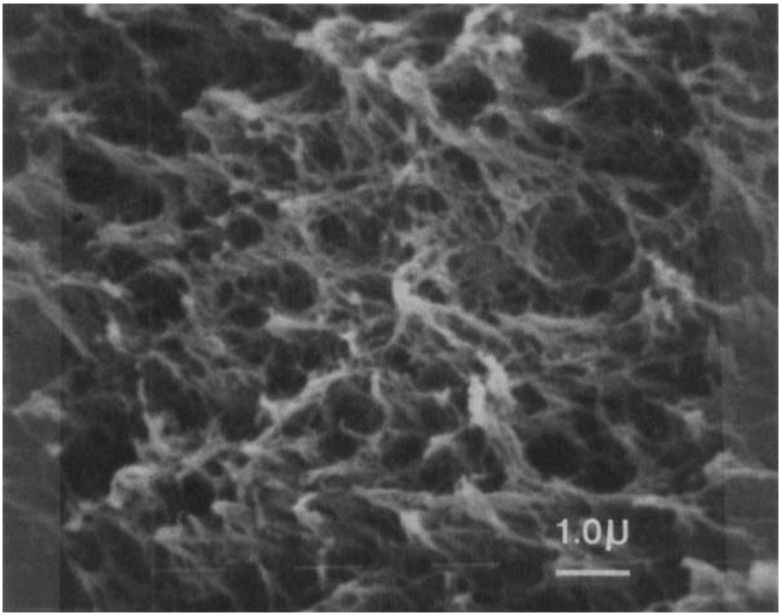

FIGURE 3. Broken edge of $[CHI_{0.008}]_x$ at 10,000 magnification. The white bar is one micron long.

EDXA studies showed no long-range variation of iodine or AsF_5 distribution (greater than 5000 Å) along the polymer surfaces. Also no significant difference was detected in dopant content between the dull and shiny sides. Figure 4 is an example of a typical EDXA result. This particular micrograph is for the dull side of $(CHI_{0.26})_x$. The center line in the scan is the beam path. The bottom line is the baseline for the signal. The top rapidly varying line is the signal (the amplitude variations are typical of system noise).

A dramatic swelling of the fibrils occurs upon AsF_5 doping.[15] An example of this is seen in Figure 5 for $[CH(AsF_5)_{0.039}]_x$. This may be due to the subsequent conversion of AsF_5 to AsF_6 and the simultaneous evolution of AsF_3 gas.[17,18] The diameter increases from 200 Å for undoped trans-CH_x to 400 Å at one percent doping, to 750 Å and 1000 Å for 3.9 percent and 6 percent doping with AsF_5 respectively. A low magnification view of the shiny side of $[CH(AsF_5)_{0.06}]_x$, which had been

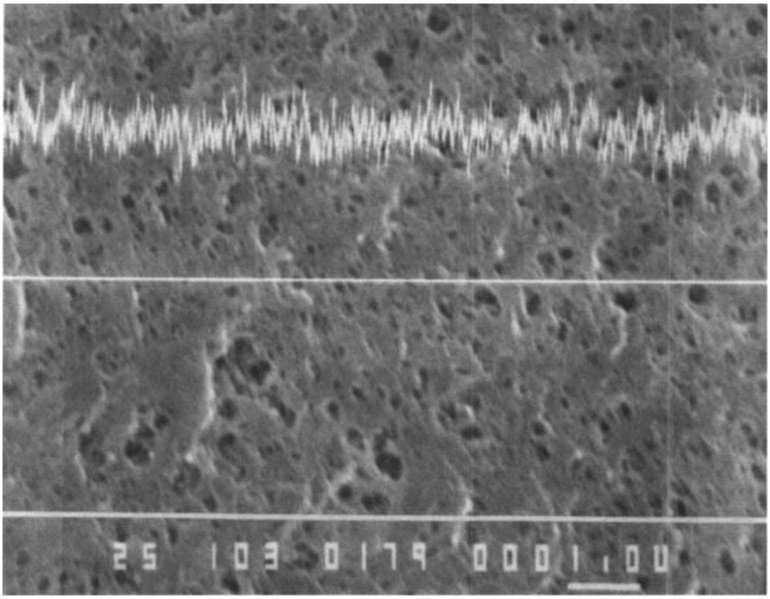

FIGURE 4. EDXA of dull side of $[CHI_{0.26}]_x$. See text for discussion.

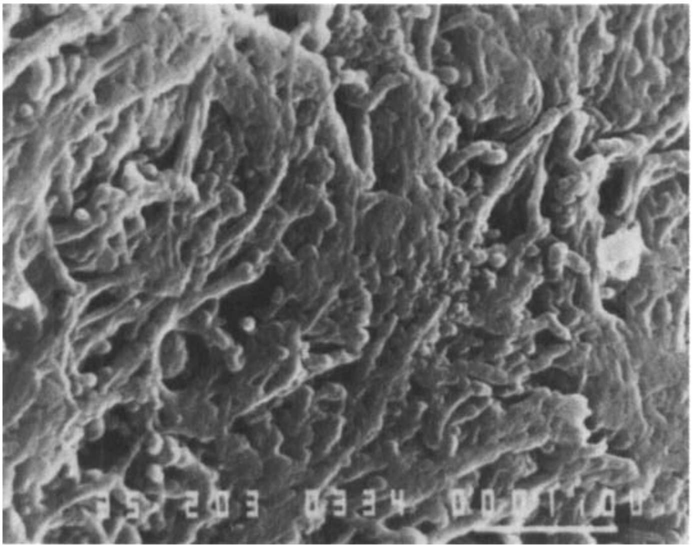

FIGURE 5. Dull side of $[\mathrm{CH}(\mathrm{AsF}_5)_{0.039}]_x$.

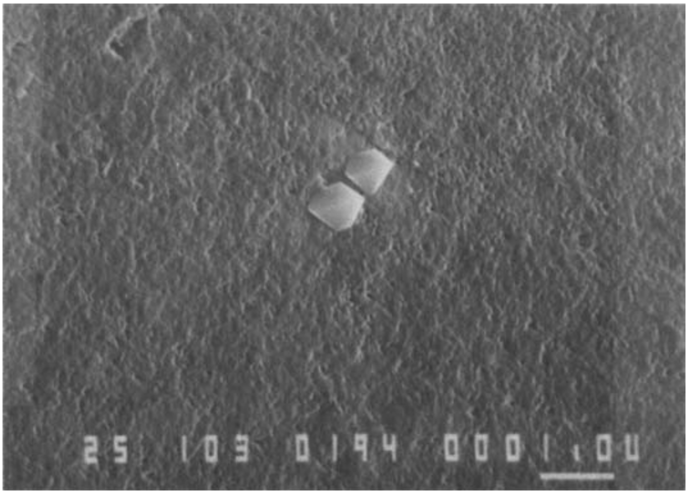

FIGURE 6. Smooth side of $[\mathrm{CH}(\mathrm{AsF}_5)_{0.06}]_x$.

exposed to ambient air for 15 minutes, Figure 6, reveals the presence of a degradation product, probably As_2O_3. This reinforces the importance of avoiding air exposure of AsF_5 doped films. EDXA and back-scattered electron images failed to reveal[15] any arsenic segregation on a scale of 5000 A.

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