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# MECHANICAL AND ELECTRICAL PROPERTIES OF HIGHLY ORIENTED RIBBONS OF POLYACETYLENE

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Abstract Films of polyacetylene have been prepared which can be converted into highly oriented ribbons (HOPA) with high tensile strength (up to 150 MPa). Iodine-doped HOPA shows an electrical conductivity one order of magnitude higher than that of unstretched films.



## INTRODUCTION

Several attempts were made to obtain oriented polyacetylene (PA) either by direct polymerization[1-3] or by mechanical deformation of the polymeric material.[4-6] In particular, extensibility has been reported for Shirakawa-type material but high orientation has not been observed by x-ray diffraction.[7] Very recently, highly oriented all-trans PA has been obtained from a precursor (synthesized by ring-opening polymerization[8]) by applying appropriate stress and temperature.[9,10]

We report here the preparation and properties of large ribbons of highly oriented cis-rich PA.

## RESULTS AND DISCUSSION

The material is synthesized at low temperature (typically -35°C) by solvent-free technique, using a catalyst based on mixed aromatic/aliphatic alkoxy-titanium derivative and $AlEt_3$.[11] A 30-50 $\mu m$ thick cis-rich (ca. 85%) dark-greenish film is obtained with metallic lustre, its overall density being approximately 0.9 $g/cm^3$. The film can be stretched in air by an Instron machine to give highly oriented ribbons, typically 15 cm long and 1 cm wide (HOPA).

Stress-strain curves show tensile strength in the range 85--150 MPa and ultimate extension ratio in the range 5-8 with a pronounced yield point at $L/L_0 < 1.1$ (Figure 1a). The stress--strain behaviour could indicate that some cross-links are remo-

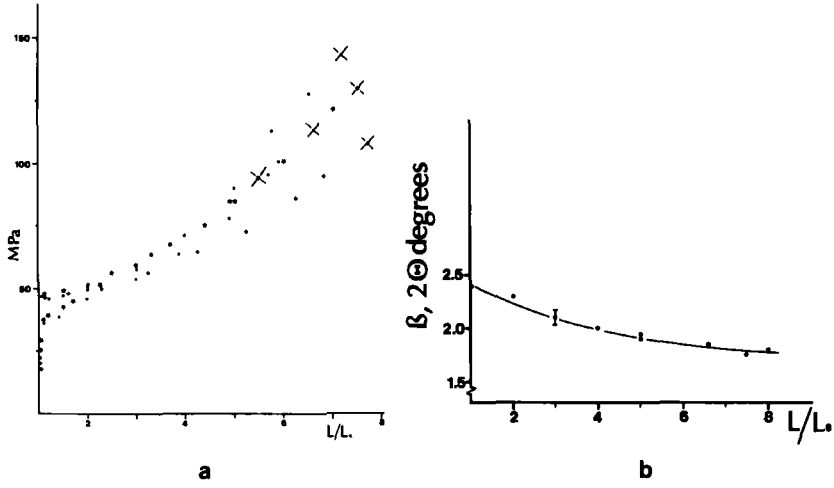


FIGURE 1 a) Stress-strain curves of cis-rich film: clamps distance = 20 mm; ( ☆ , ● ) $\dot{\epsilon}$ = 1 $Min^{-1}$; ( ★ ) $\dot{\epsilon}$ = 10 $Min^{-1}$; ( **o** , **+** ) $\dot{\epsilon}$ = 25 $Min^{-1}$; ( ✕ ) indicates the point of fracture.
b) Half-width of (110)-(200) multiplet in the x-ray pattern as a function of draw ratio.

ved during the drawing process. This would account for the improvement of the crystalline organization as suggested by the line-narrowing in the x-ray pattern (Figure 1b).

X-ray diffraction pattern of HOPA shows an high preferred orientation of the crystallites with the chain axis parallel to the stretching direction (Figure 2a). The degree of orientation (defined as the mean square cosine of the angular deviation of the chain axis from the draw direction[12]) is strictly related to the extension ratio (Figure 2b). Accordingly, SEM micrograph shows fibrillar morphology with the fibrils perfectly aligned along the stretching direction (Figure 3a).

HOPA as well as the unstretched film can be easily doped by Iodine in gas phase; Iodine concentration as high as $[CHI_{0.33}]_x$ has been obtained. Oriented specimens constantly display a conductivity one order of magnitude higher than that of unoriented ones, a maximum conductivity of 2200 $\Omega^{-1}cm^{-1}$ having been achieved for HOPA (Figure 3b).

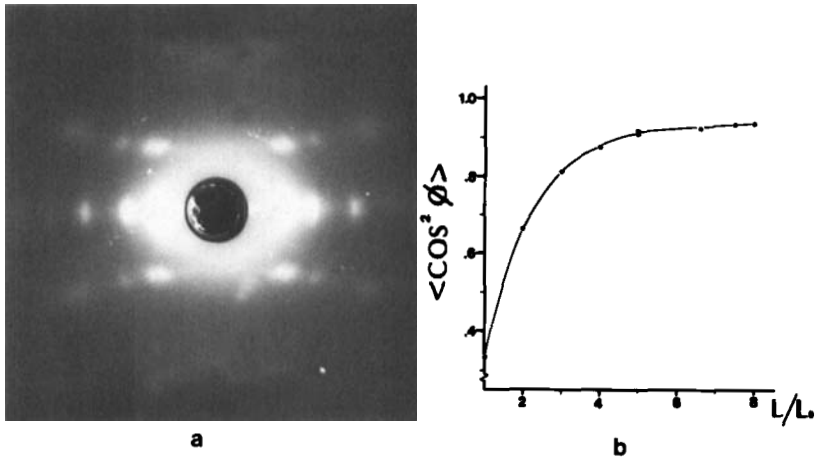


FIGURE 2 a) Wide-angle x-ray diffraction photograph of cis-rich HOPA, $CuK_{\overline{\alpha}}$ , draw direction vertical.
b) Mean square cosine of the angular deviation of the chain axis from the draw direction.

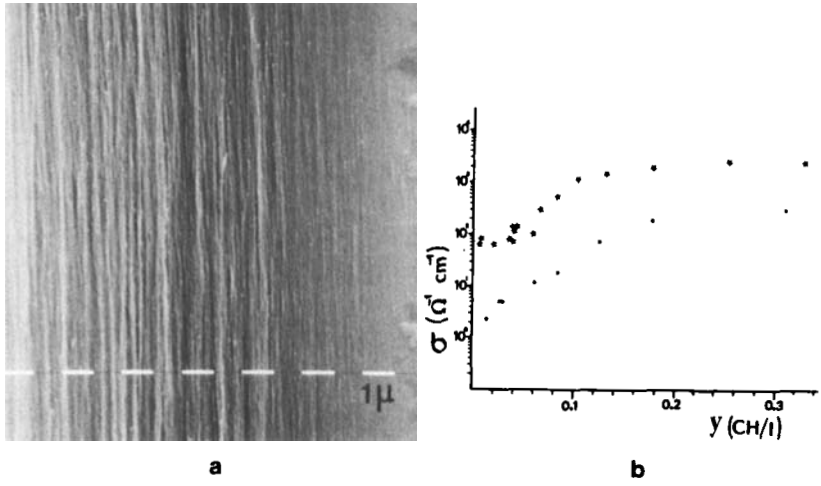


FIGURE 3 a) Scanning electron microscope picture of a longitudinal section of HOPA. Draw direction vertical.
b) Room temperature electrical conductivity of HOPA ( $\sigma_{\parallel}$ , ☆ ) and unstretched material ( ● ), as a function of Iodine content.

Significantly different behaviours are observed, in terms of both kinetics and saturation level, when working with other dopant species. As an example, $AsF_5$ leads to saturation level corresponding to $[CH(AsF_6)_{0.05}]_x$ with a conductivity of 800 $\Omega^{-1}cm^{-1}$.

## CONCLUSIONS

Film of PA have been synthesized which can be uniaxially stretched to obtain highly oriented large ribbons.

The materials display high ultimate extension ratio (5-8) and tensile strength (up to 150 MPa).

Morphology of HOPA is built up of highly oriented crystallites of PA arranged within fibrils perfectly aligned along the stretching direction. This accounts for the pronounced anisotropic behaviour of the material.

Iodine-doped HOPA shows an electrical conductivity along the stretching direction one order of magnitude higher than that typical of unstretched materials.

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