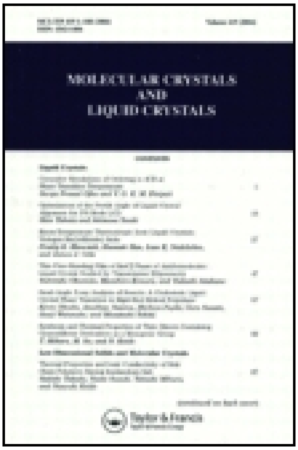

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# Connection Between Purity and Morphology of Polyacetylene

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# CONNECTION BETWEEN PURITY AND MORPHOLOGY OF POLYACETYLENE

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Abstract Rutherford Backscattering Spectroscopy, which has been used for the analysis of residual impurities in polyacetylene films polymerized with a Ziegler Natta catalyst, revealed Al and Ti traces concentrated near one surface of the film. The presence of oxygen indicated a partial sample oxidation. The inhomogeneity of the impurities distribution was interpreted by the formation of a high density layer in the initial stage of the polymerization, which acts as a barrier for the penetration of washing solvents.

## INTRODUCTION

The properties of polyacetylene films are strongly dependent on the presence of doping impurities. It has in particular been shown that the conductivity could be varied over more than ten orders of magnitude by doping with donors or acceptors. However polyacetylene is known to exhibit a great sensitivity to undesirable doping, in particular by the oxygen of the air. The determination of intrinsic polyacetylene properties requires then an accurate control of polymerization conditions in order to avoid undesirable impurities. In parallel to this study some recent papers[1,2] have shown that the morphology of polyacetylene films was strongly dependent on the polymerization conditions. Our aim was to study more in details the apparent relation between morphology and purity of polyacetylene.

## POLYMERIZATION PROCEDURE

Polyacetylene films have been synthetized by the CRM Group by the usual Shirakawa method[3,4]. Ziegler Natta type catalyst was used by a solution of $Ti(C_4H_9O)_4$ and $Al(C_2H_5)_3$ in toluene, with the ratio $Al/Ti = 4$. The production of a film required several successive operations performed in an inert atmosphere, or in high vacuum:

- preparation of the catalytic solution
- introduction of purified acetylene in the reaction vessel lowered to liquid nitrogen temperature
- growth of the film at the surface of the liquid catalyst
- purification of the film washed several times with toluene and dried under vacuum

After removal from the reactor, the side of the film which has been in contact with the catalyst solution appears dull grey, whereas the upper surface is bright and silvery colored, what is exactly the opposite of the behavior observed when a film is synthetized on the walls of a reactor[5]. This dissymetry in the aspect of the two opposite surfaces should be attributed to a difference of the film morphology. In particular the dull surface becomes brighter when the film is rubbed, which is probably due to the flattening of the fibrils merging from the surface.

Main parameters controlling the polymerization have been summarized in table 1. Traces analysis have been done by flame spectroscopy. However this technique is macroscopic and gives only a mean value of impurity concentration. Rutherford Backscattering Spectroscopy has been used in order to determine the profile of impurities concentration in the vicinity of the two surfaces.

TABLE I Polymerization conditions

| Monomer pressure | Pol. time | Density | Impurities content: RBS | | | |
|---|---|---|---|---|---|---|
| | | | Ti/C | Al/C | Ti/C | Al/C |
| 80cm Hg | 30' | 0.5g/cm$^3$ | 0.7 | 1.7 | 0.06 | 0.6 % |
| | | | bright | | dull side | |

## DETERMINATION BY RBS OF IMPURITIES DEPTH DISTRIBUTION

The surface of the analysed sample is struck by an incident beam of 2 MeV $\alpha$ particles. A solid state detector collects the particles backscattered at an angle of 160°. Using the classical laws of elastic collisions it is possible to show that the energy of a particle backscattered at the surface is: $E_5 = k^2_A E_1$ where $k_A$ is a simple function of incident particle and target atom masses. It is then possible to calculate for each element of the periodical table the energy at which it should be observed by RBS if the target is assumed to be infinitely thin. For a thick sample the probability of scattering at the surface is small and most particles loose a part of their incident energy in the sample, are scattered at depth x and loose a part of their energy before merging from the target at an energy $E_4$ (Fig 1). The difference of energy between 2 particles backscattered at the surface and at depth x by an element A, is proportional to x according to: $E = E_5 - E_4 = (S)_A . x$ where:

$$(S)_A = k^2_A \left(\frac{dE}{dx}\right)_{E_1} + \frac{1}{|\cos\theta|} \left(\frac{dE}{dx}\right)_{E_3}$$

It is then possible to deduce from a RBS spectrum the distribution of heavy elements in a light matrix.[6]

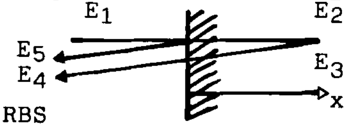


FIGURE 1
Principle of RBS

The two spectra performed on each side of a $(CH)_x$ film (Fig 2 and 3) show that most common impurities are Al, Ti and oxygen. We observe that the impurity concentrations, which have been reported in table 1, are larger on the bright face than on the dull face. The impurities may have two origins:

- remaining traces of the catalyst which have not been eliminated after purification of the film. The ratio of impurities concentrations on the two opposite sides is 2.8 for Al and 11.7 for Ti and decreases inside the film. A very paradoxical feature is that the purest face is the dull side which is in contact of the catalyst layer at the end of the polymerization.

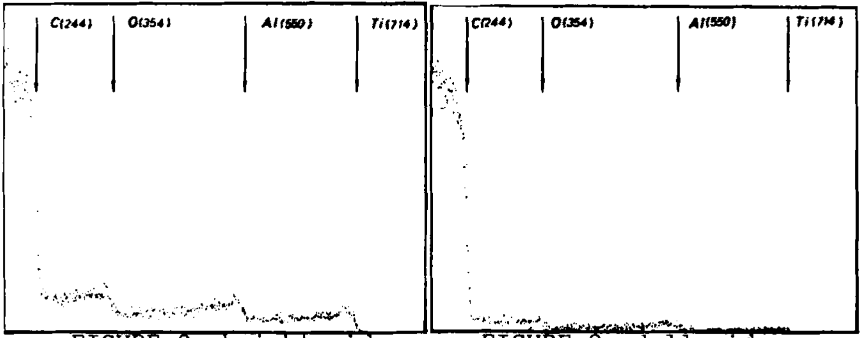
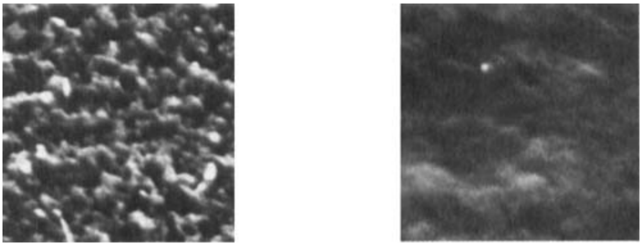


FIGURE 2: bright side FIGURE 3: dull side
Energy spectrum of backscattered particles

- a partial oxidation of the film since the ratio between atomic concentrations of oxygen and Ti is about 10 on the bright side and 20 on the dull side, whereas the stoechiometry from the catalyst is only 4.

## DISCUSSION AND CONCLUSION

Scanning electron micrographs performed on the two film sides (Fig 4 and 5) show an important difference of morphology, the dull surface clearly exhibiting cavities at a magnification of 2400 whereas the bright surface appears more compact. These observations are coherent with the work of Aldissi who recently reported[1] the existence of a compact surface on the monomer side and a lower density surface on the catalyst side in films polymerized on the layer of a catayst solution.



Scanning electron micrograph of $(CH)_x$

FIGURE 4: dull surface FIGURE 5: bright surface

Aldissi demonstrated using deuterated acetylene in the initial stage of polymerization, that the upper side is in fact the surface on which polymerization had been initiated. RBS has shown that it was also the less pure surface. It is then possible to suppose that the compact morphology forms a barrier which prevents the solvent diffusion when the film is purified, so that impurities from the catalyst will be retained preferentially at the dense surface.

In conclusion, it was possible to establish a connection between the compacity of the film morphology and the anomalous impurity concentrations revealed by RBS. It will be important to study the influence of the quite large spread of possible morphologies on $(CH)_x$ macroscopical properties.

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