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FUNDAMENTAL OPTICAL CONSTANTS OF CIS POLYACETYLENE

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Abstract: The optical reflectivity of thick films (20-30 μm) of fibrous polyacetylene (PA), highly oriented by mechanical stretching has been measured using polarized light. A Kramers-Kronig analysis of the data has been used to determine the optical constants for polarization parallel and perpendicular to the chain axis.

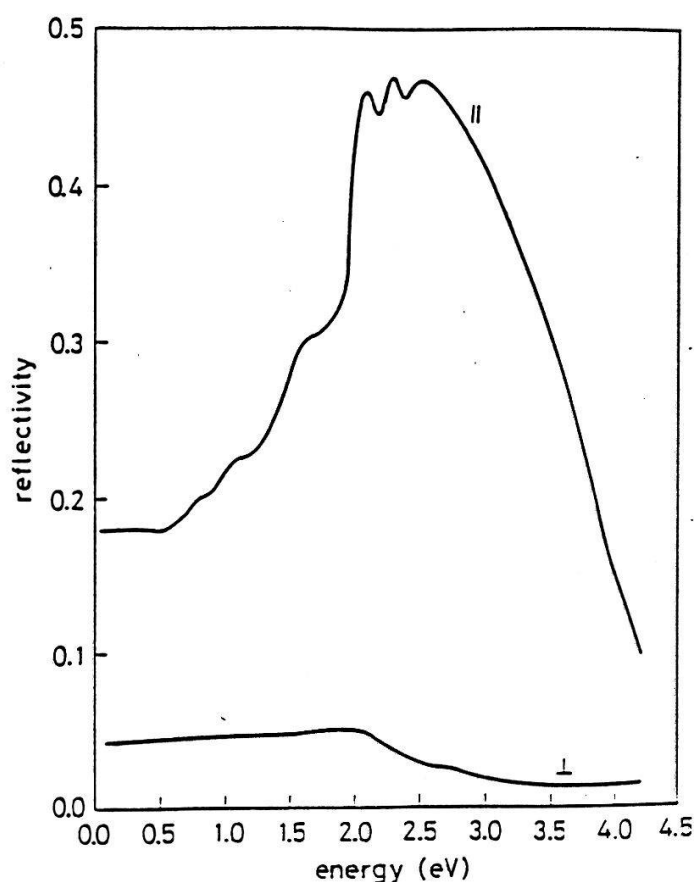
INTRODUCTION: The evaluation of the anisotropy of the optical properties of PA is in principle quite important for a better understanding of the optical transitions and of the mechanism of photogeneration of the carriers in a three dimensional polymer lattice using polarized light(1-2). So far an accurate investigation of the optical properties of fully oriented PA has been carried out only on Durham-PA(3). We have felt that, in consideration of its different morphology, the measure of the optical constants of the stretch-oriented Shirakawa PA could yield an additional insight on the nature of the interband transition of this prototype semiconducting polymer.

EXPERIMENTAL: Highly oriented (draw ratio 7) Shirakawa PA films were a gift by Enichem Research Labs.(4). The as synthesized film exhibits a fibrillar morphology and X-ray measurements carried out on this sample indicate a degree of cristallinity of 97% with a misalignment angle of 10 degrees. The reflectivity of the samples were measured in the energy range between 0.062 and 4.2 eV with polarized light parallel and perpendicular to the stretching axis(Fig.1). The complex refractive index $\tilde{n}(\omega)$ and the dielectric function $\tilde{\epsilon}(\omega)$ was obtained using KK trasformation on the reflectivity data.

DISCUSSION: In order to detect the effects of the interchain interactions on the optical response of PA we have worked out a tight binding model extended to include the

effect of the interchain coupling on the electronic energies and on the transition moments. Some caution should however be exerted in comparing the calculated and experimental anisotropies. In fact a contribution to the perpendicular absorption and reflectivity comes from the small (but not negligible) sample misalignment. The theoretical values of the optical constants should therefore be averaged on the possible orientations of the chain with respect to the stretching direction. This calculation(5) implies that sample misalignment accounts for almost entirely the absorption anisotropy and masks small but not vanishing interchain contribution to the perpendicular response.

Fig.1
Optical reflectivity measured with light parallel and normal to the stretching direction.



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