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# Molecular Crystals and Liquid Crystals

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## Anisotropic Optical and Transport Properties of Trans-(Ch)<sub>x</sub>

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ANISOTROPIC OPTICAL AND TRANSPORT PROPERTIES OF TRANS-(CH) $_{\rm x}$ 

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Abstract We have produced fully oriented highly crystalline trans-(CH), films, which exhibit dramatic polarization effects for light polarized parallel or perpendicular to the oriented (CH), chains. The polarization behavior in the vicinity of the bandgap and of the characteristic IR-modes, including those which are introduced as a result of doping with AsF5 is presented. DC-conductivity measurements allow to deduce the conductivity anisotropy of  $\sigma_{\parallel}/\sigma_{\perp} \sim 100$  for undoped and I2-doped trans-(CH), at 300 K.

#### 1. OPTICAL PROPERTIES IN THE VISIBLE RANGE

Fully oriented highly crystalline films of trans-(CH) $_{\rm X}$  have been prepared as described earlier  $^{\rm l}$ . Polarized optical transmission and reflection measurements in the visible range show extremly anisotropic behavior. In Fig.1 (a) the data for undoped samples are presented. We obtained -log(T) values greater than 3 for a film thickness of only a few 100 nm for polarization parallel to the chains and an anisotropy ratio  $T_{\rm L}/T_{\rm L}$  greater than 400. The maximum of the optical density is located at 2.1 eV for both polarization directions. However, if the reflectance is properly taken into account, the absorption maximum for parallel polarization will be shifted to approximately 1.5 eV, whereas the peak for

E $\perp$ c remains at 2.1 eV which implies an anisotropic band structure. The anisotropy of the refractive index  $n_{\parallel}/n_{\perp}$  of about 5 can be estimated from interference features around 1.3 eV in the reflectance spectrum.

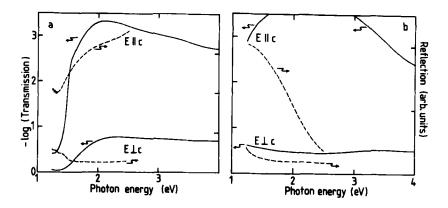


Fig.1 Transmission and reflection spectra of undoped (a) and  ${\sf AsF}_5{\sf -doped}$  (b) trans-(CH)  $_X$  for parallel and perpendicular polarization.

Transmission and reflection data of samples doped with  $\mathrm{AsF}_5$  are plotted in Fig.1(b). The steep absorption edge of the undoped samples disappears for both polarization directions in agreement with measurements on Shirakawatype (CH)\_X doped to metallic regime. The reflectance curves show a completely different shape compared to the undoped case for parallel polarization, whereas for perpendicular polarization the reflectance is relatively small and did not change remarkably with doping.

#### 2. INFRARED PROPERTIES

Similarly pronounced polarization effects are observed in the infrared region. In Fig.2(a) which is obtained from an undoped sample, one can see that the C-H out of plane vibration ( $1010\,\mathrm{cm}^{-1}$ ) completely disappears for E

parallel to the stretching direction, whereas the C-H stretching vibration at 30llcm<sup>-1</sup> is stronger for this polarization. The structural model commonly assumed requires a completely perpendicular polarization for both vibrations. Our results can only be explained by one of the following two assumptions: either the chain axis and the stretching direction are not parallel or the angle between the C-H bond and the chain axis differs from 90

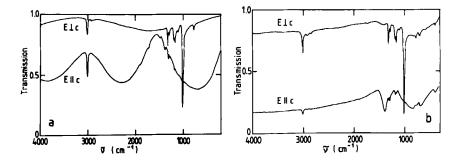


Fig.2 Infrared transmission spectra of undoped (a) and  ${\sf ASF}_5$  doped (b) trans-(CH) $_{\sf X}$  for E parallel and E perpendicular to the c-axis

degree, possibly because of the dimerization of the carbon backbone. Since the first assumption is highly unlikely considering the electron and X-ray diffraction evidence  $^2$  our data support the second assumption. From the Fabry-Perot resonance periods one can deduce the refractive indices for both directions in this spectral region having values of  $n_{\parallel}$  = 2.66 and  $n_{\perp}$  = 1.33. In Fig.2 (b) the infrared spectra are shown for a sample doped with 1.4 mol percent AsF5. There is little influence on the spectrum for perpendicular polarization, whereas for E parallel c the overall transmisison is strongly decreased and the well known doping induced bands 1380 cm $^{-1}$  and around 900 cm $^{-1}$  develop. The additional absorption

bands above and below  $1000~{\rm cm}^{-1}$  are caused by a residual amount of hexafluoroxylene which was not completely removed during the conversion.

### 3. TRANSPORT PROPERTIES

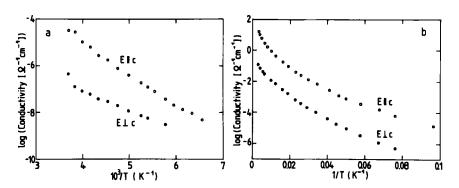


Fig.3 Temperature dependence of the dc-conductivity for undoped trans-(CH) $_{\rm X}$  (a) and for (CHI $_{0.09}$ ) $_{\rm X}$  (b)

Measurements of the temperature dependence of the conductivity and its anisotropy shown in Fig.3 reveal an anisotropy ratio of  $\sigma_{\parallel}/\sigma_{\perp} \sim 100$  both for an undoped sample (a) and for a sample reacted in solution with 9 mole % iodine. Whereas this ratio remains approximately constant down to 10 K for the iodine-doped sample, the anisotropy ratio decreases with decreasing temperature in the pure material. Different activation energies seem to be involved for the direction parallel and perpendicular to the chains.

#### REFERENCES

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