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OPTICAL PROPERTIES OF UNDOPED AND DOPED POLYACETYLENE FILMS

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We have measured the optical properties of undoped and iodine doped polyacetylene for photon energies from 0.05 to 3 eV. The electronic gap is essentially unchanged and there is no free-carrier absorption observable upon doping, even above the insulator-metal transition. We conclude that the longrange Coulomb interaction is the main origin of the electronic gap.

Polyacetylene, $(CH)_x$, has recently become of interest because it can be doped to a state of metallic conductivity **[1]**. In a previous publication we have reported on a systematic investigation of the mechanism of iodine doping in unoriented films **[2]**. In this paper we present a study of the optical properties of unoriented and shear polymerized $(CH)_x$ of various iodine concentrations in the visible and infrared spectral range.

Unoriented (CH)_X films have been prepared on quartz or silicon substrates at room temperature using a method similar to the one described by Ito et al. [3]. The films consist of grains of up to $5 \cdot 10^{-5}$ cm diameter. Oriented films have been polymerized under shear flow conditions [4]. They consist of parallel fibers in the plane of the film and have a length of the order of 10^{-2} cm and a nearly rectangular cross section of dimensions 1 to $2 \cdot 10^{-5}$ cm x 2 to $6 \cdot 10^{-6}$ cm. It was shown by electron diffraction that the chain axis is tilted against the normal to the film plane under an angle of about 30°[4,5]. All films were annealed for 3 hours at 160°C in order to convert them to $\frac{\text{trans}}{\text{cH}}$. Three samples of similar thickness were simultaneously doped by iodine vapour in the same system: one for optical measurements, one for measurements of the d.c. conductivity and one deposited on a quartz oscillator in order to measure the weight increase which is directly related to the iodine concentration. In a systematic series of measurements the iodine content in such a triplet of samples was stepwise increased. Transmission and reflection of films of the order of one thousand m R thickness were measured between 0.4 and 2.5 μ m. The data were evaluated in terms of the absorption coefficient K and the optical constants (n, k) using the formulas for multiple reflection and transmission. In the infrared region between 2.5 µm and 250 µm K was determined from transmission spectra and a reflectivity which was assumed to be wavelength independent and calculated from the known long-wavelength refractive index.

Fig. 1 shows the imaginary part of the dielectric function, $\xi_2 = 2 \text{ nk}$, of unoriented $(CH)_{\chi}$ for various iodine concentrations. Undoped $(CH)_{\chi}$ shows a fundamental band gap of about 1.35 eV. With increasing iodine content a band in ξ_2 is built up in the region of 0.5 to 1.5 eV. Concurrently, the strength of the intrinsic band centering at 2 eV is decreasing. The main point to note is, however, that even at the highest concentration of 7% the fundamental gap is still observable. Fig. 2 shows the optical conductivity $\vec{O} = c \cdot \boldsymbol{\varepsilon}_0 \cdot \mathbf{n} \cdot \mathbf{K}$ of iodine doped $(CH)_{\chi}$



Fig. (1) Imaginary part of dielectric function, \mathcal{E}_2 , or unoriented (CH)_x at various iodine concentrations vs. photon energy

E = 0.005 eV. Fig. 3 shows K vs. E for a sample of shear flow polymerized (CH)_x for linearly polarized light. Generally speaking, there are no strong polarization effects and the behaviour is not dras-



Fig. (2) Optical and d.c. conductivity, σ , of iodine doped (CH)_x vs. photon energy: Note change of abscissa scale at 0.5 eV!

over a wide energy range. Samples of different thickness from the same batch were used for the two energy ranges below and above 0.5 eV, respectively. Their iodine content was different but at or close to saturation in d.c. conductivity in both samples. Due to uncertainty in the thickness of both samples and the less accurate determination of K in the low-energy region, the low-energy curve had to be vertically shifted by a factor of 4 in order to fit the high-energy part at 0.5 eV. We observe an intrinsic region above 1.35 eV, a strong maximum at 0.5 eV and a continuous decrease from 0.5 eV to 0.005 eV. Superimposed on this slope, there are two doping-induced bands at 0.11 and 0.17 eV, which have been attributed to a vibration of a charged domain wall relative to the impurity and a molecular C-C vibration within the domain wall made infrared active by the doping, respectively [6]. At the lower end of our measuring range, E = 0.005 eV, σ has fallen to 60 (Ω cm)⁻¹ which is about one order of magnitude higher than the d.c. value of 5 $(\Omega \text{ cm})^{-1}$. The main conclusion from Fig. 2 is that we do not observe free-carrier absorption down to

> tically different from that of unoriented material, also not for E < 0.5 eV [2]. We note that there is more tailing of the absorption edge of undoped $(CH)_X$ in the oriented form. Also, K₁₁ is higher than K₁ at the absorption edge. This effect can also be viewed as an edge shift by 0.2 to 0.3 eV to lower energies for K_{II} as compared to K_{\perp} . The curve marked "doped" represents a fully iodinated sample with d.c. values of $\sigma_{II} = 90 (\underline{\Omega} \text{ cm})^{-1}$ and $\sigma_{\underline{L}} = 40 (\underline{\Omega} \text{ cm})^{-1}$. We obtained the same optical results for another sample with σ_{u} = $300 (\Omega \text{ cm})^{-1}$.

The optical anisotropy for shear flow polymerized (CH)_X is much smaller than for material oriented by stretching before and

during isomerization to trans-(CH), [7]. We feel that the explanation for this strong difference lies in the morphology. In most of the previous work on (CH),



Fig. (3) Absorption coefficient, K, of undoped and doped, shear-flow polymerized (CH)_x vs. photon energy a) E II fiber axis, b) E I fiber axis

it has been explicitly or implicitly assumed that the polymer chain axis is parallel to the long axis of the fibrils which are often described as being much longer in one dimension than in the other two. In our shear polymerized (CH), the fibers have an extremely long ratio of length to width but the chain axis forms an angle of 30° with the normal to the film plane. Since no preferred orientation of the chain axis with respect to the fiber axis has been observed [5], the observed weak overall optical anisotropy for rotation of E in the film plane is in agreement with the expectations. As an explanation of the anisotropy in the absorption edge we do not want to exclude a slightly preferred orientation of the chain axis relative to the fiber axis although it is not apparent from the electron diffraction work at this point.

Common to iodine doped unoriented and shear flow polymerized $(CH)_x$ are the strong broad absorption band at 0.5 eV and the absence of observable free-carrier effects even at iodine concentrations above the insulator-metal transition. It can be seen in Fig. 3 or in ref. [2] that the 0.5 eV band is comparable with the intrinsic absorption although it is of extrinsic

origin. Such a high oscillator strength seems only possible for strongly localized states. We therefore attribute this band to optical transitions from the valence band to iodine-induced localized levels in the gap and/or from such levels to the conduction band. There may be a weak free-carrier absorption covered by this strong absorption band extending to very low energies. The continuing decrease of σ to E = 0.05 eV in Fig. 2, however, shows that the free-carrier absorption, if it exists at all, is certainly not metallic-like [7]. Common to unoriented and shear flow polymerized $(CH)_X$ is further the persistence of the band gap upon full iodine doping, see Figs. 1 and 3. This result has to be reconciled with any viable model on the origin of the gap. The interpretation has to be made in terms of a bulk, homogeneously doped material for two reasons: (i) we know from the increase in iodine concentration as a function of time at constant vapour that the iodine diffuses into the bulk of pressure, the (CH)_x grains[2]; (ii) the X-ray Debye-Scherrer lines observable in undoped $(CH)_{X}$ disappear upon complete iodination indicating that the crystallinity of $(CH)_{y}$ is destroyed in the bulk.

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On the ideal polyacetylene chain the $2p_z$ valence electrons would form a halffilled π -band and the system would thus be metallic. Two mechanisms have been invoked to explain the existence of a band gap in undoped $(CH)_x$: (i) a chargedensity wave instability arising from the electron-phonon interaction (Peierls gap) [8,9]; (ii) a spin-density wave instability due to on-site Coulomb repulsion (Hubbard gap) [10]. The period of these modulations would be commensurate with the lattice in the undoped case. Low doping removes $\,\pi$ -electrons locally from the valence band leading to charged discommensurations [9]. At higher doping the period becomes incommensurate with the lattice. Based on mean-field theory for the one-dimensional electron gas [11] and appropriate coupling constants we find that in the incommensurate case both the Peierls and the Hubbard gap should be reduced by more than a factor of 10 relative to the value for the half-filled band. Numerical calculations by Kotani [12] show that the decrease of the gap should already become observable for a dopant level of the order of 1%. Our optical measurements show clearly that the gap is not shifted upon doping, not even for complete iodination where the electrical properties indicate a "metallic" state. We conclude therefore that the main origin for the gap is neither the electron-phonon nor the on-site Coulomb interaction. We suggest that instead it is mainly caused by the long-range part of the Coulomb interaction since this term would produce essentially the same gap in the doped and undoped case.

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