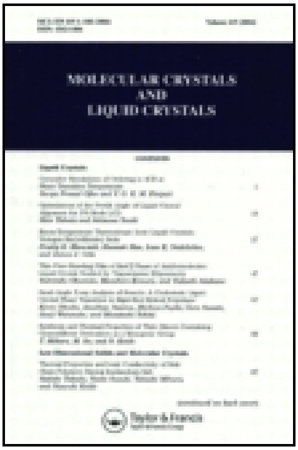

Molecular Crystals and Liquid Crystals

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ELECTRICAL AND OPTICAL PROPERTIES OF ORIENTED $(CH)_x$

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We have measured the optical and electrical properties of both graphoepitaxially grown and shear-flow polymerized polyacetylene films. The former show a pronounced optical anisotropy whereas the latter do not. This result is correlated with the orientation of the chain axes relative to the fibre axis, which is preferentially parallel in graphoepitaxially grown films. The electrical anisotropy was found to be rather weak. Optical measurements on doped $(CH)_x$ indicate that both the characteristic IR modes at 0.11 eV and 0.17 eV and the mid-gap absorption around 0.5 eV, which have been attributed to solitonic defects, persist up to the metallic level. This result shows that both the IR modes and the mid-gap absorption are not necessarily signatures for solitonic defects. Furthermore we conclude that the impurity potential is more effective than hitherto assumed.

INTRODUCTION

Though considerable efforts have been made to clarify the nature of the electrical transport in polyacetylene there is still an ongoing controversy on this subject[1]. The particular interest in this question stems from the doping induced semiconductor-metal transition which is accompanied by unusual magnetic and optical properties[2]. The interpretation of the observed phenomena can be given in terms of an idealized one-dimensional chain involving the concept of solitons which represent bond alternation defects extended over several CH units[3]. It has been shown theoretically[4] that charged solitons are created upon injection of carriers either by charge transfer from the dopant to the chain or by photoexciting carriers directly. Obviously the concept of a soliton is only meaningful as long as they are spatially separated. Due to their finite size of about 15 CH groups it is expected that the solitons as individual entities should no longer exist in the metallic regime.

On the other hand it is known that polyacetylene consists of a tangle of fibrils, that it is highly crosslinked and thus far from the idealized model substance. Thus the question arises whether a theory based on a one-dimensional chain reflects the experimental observations correctly. Indeed, this has been questioned and a model has been proposed which assumes that polyacetylene becomes strongly inhomogeneous upon doping, even more, that $(CH)_x$ can be best described as a composite material consisting of (dopant-induced) metallic and of insulating regions already at low doping levels[5].

In order to contribute to the solution of these questions we have extended our previous measurements[6] on unoriented $(CH)_x$ doped with iodine in two ways: firstly, we have performed experiments on oriented samples, secondly, we have also used SbF_5 as a dopant since various authors have proposed that I_2 penetrates $(CH)_x$ inhomogeneously in contrast to other dopants[7,8]. Among the experimental observations which have been quoted to support the soliton idea are the doping induced absorption band at approximately 0.5-0.7 eV (4000 cm^{-1} - 6000 cm^{-1}) and the absorption peaks in the infrared at 0.17 eV (1400 cm^{-1}) and 0.11 eV (900 cm^{-1}). These are independent of the dopant used and therefore necessarily related to the $(CH)_x$ itself. Since systematic optical absorption measurements up to the metallic regime are missing we emphasize in this paper the optical experiments, though also electrical data will be presented.

EXPERIMENTAL PROCEDURE AND CHARACTERIZATION OF THE $(CH)_x$ BY CONDUCTIVITY MEASUREMENTS

Oriented samples have been prepared by graphoepitaxy[9] and under shear flow conditions[10]. All films were transferred from the wall of a glass cylinder on which they were prepared either on to quartz or silicon substrates. The samples were annealed for 10 to 15 minutes at 180°C in order to convert them to trans $(CH)_x$.

Four samples of similar thickness (500 Å to 2000 Å) were simultaneously doped in the same system: two samples for the optical measurements in the visible and infrared, one for measurements of the dc-conductivity and one on a quartz oscillator to measure the weight increase by doping. The dopant concentration was increased by increasing the vapour pressure. In each case the weight as well as the dc-conductivity were measured as a function of time upon increasing the vapour pressure stepwise. Only after both had become independent of time final measurements were taken. In the case of I_2 the iodine concentration y could then be correlated with the iodine vapour pressure p (Torr) by $y = 0.28 \sqrt{p}$. In contrast to I_2 the doping with SbF_5 was less reproducible. We found that doping proceeds only properly in the presence of traces of water but we were not able to optimize the partial pressure of the water vapour. Therefore the doping source was switched off after having achieved a certain electrical conductivity. The excess of SbF_5 was pumped off until the current through the sample as well as the weight were independent of time. The conductivity increase as a function of dopant concentration was found to be markedly different for I_2 and SbF_5 doped samples. This is illustrated in Fig. 1, where the rather gradual increase of σ with iodine concentration is shown in comparison with the abrupt rise of σ in the range $0.05 < y < 0.1$ for SbF_5.

The absorption coefficient K in the infrared and in the visible was determined from transmission spectra and a reflectivity which was assumed to be wavelength independent and calculated from the known long wavelength refractive index. We have used thickness values as determined with the scanning electron microscope. The resulting numbers are about a factor of 2 to 3 smaller than those derived by Fincher et al.[11]. If, however, the thickness is scaled according to the ratio of apparent to bulk density, then our results are in sufficient agreement with the data of Ref. 11. The electrical conductivity was in most cases determined by two probe measurements except in a few cases where four probes were used to check the results.

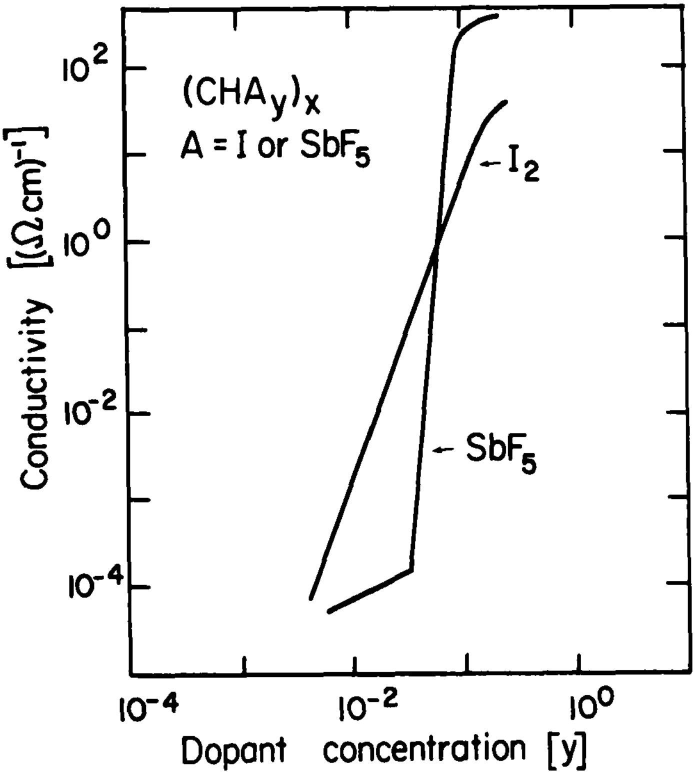

FIGURE 1 Electrical conductivity as a function of dopant concentration for the dopants indicated in the figure.

RESULTS WITH GRAPHOEPITAXIALLY GROWN FILMS

The optical absorption is found to be quite anisotropic for cis-rich and trans samples prepared under graphoepitaxial conditions. The absorption coefficients $K_{\parallel}$ and $K_{\perp}$ differ by a constant factor of about 4 between 0.5 eV and 3 eV, as shown in Fig. 2 for trans $(CH)_x$.

The observed similar shapes for $K_{\parallel}$ and $K_{\perp}$ below 3 eV indicate that the absorption process is the same for both directions. Attributing it to transitions within the π-bands of $(CH)_x$ chains and assuming that $K_{\perp}$ is negligibly small for an ideal structure, the observed optical anisotropy yields a measure for the degree of misalignment of the chains. It turns out to be larger than the misalignment of

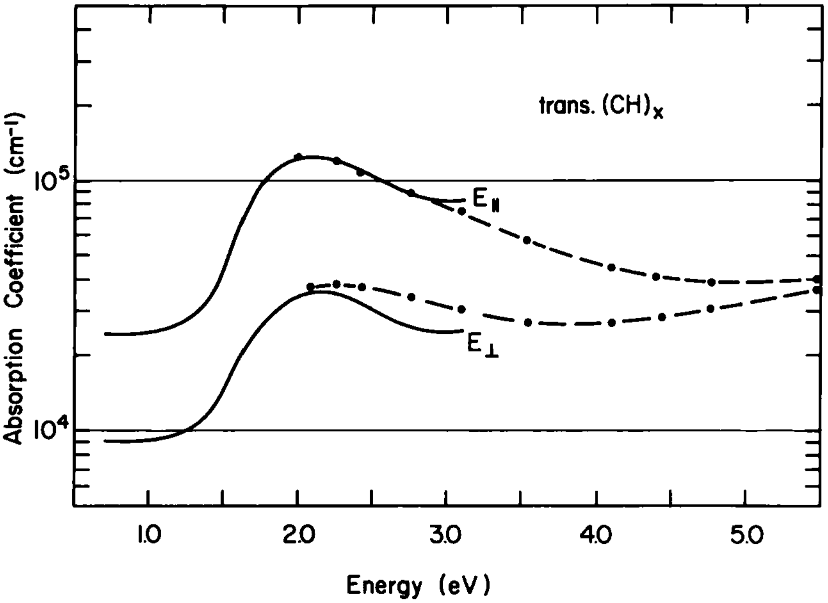

FIGURE 2 Absorption coefficient as a function of energy for light polarized parallel and perpendicular to the fibre axis.

the fibrils estimated from electron micrographs (compare Fig. 8 of Ref. 9). We believe that this difference is due to misorientations of the chain axes in the amorphous regions of the fibres, in qualitative agreement with decoration experiments[9]. At energies above 3 eV the optical anisotropy decreases and it is practically absent at 5.5 eV. This may be caused by the growing absorption involving σ -bands.

The electrical anisotropy $\sigma_\parallel / \sigma_\perp$ of undoped samples was at best 8, and it decreased with increasing iodine concentration to a value of about 3 (Fig. 3). Any anisotropy found by electrical dc-measurements is at least in part caused by the packing of the fibres in the film, and therefore does not allow to draw conclusions on the anisotropic carrier transport in $(CH)_x$.

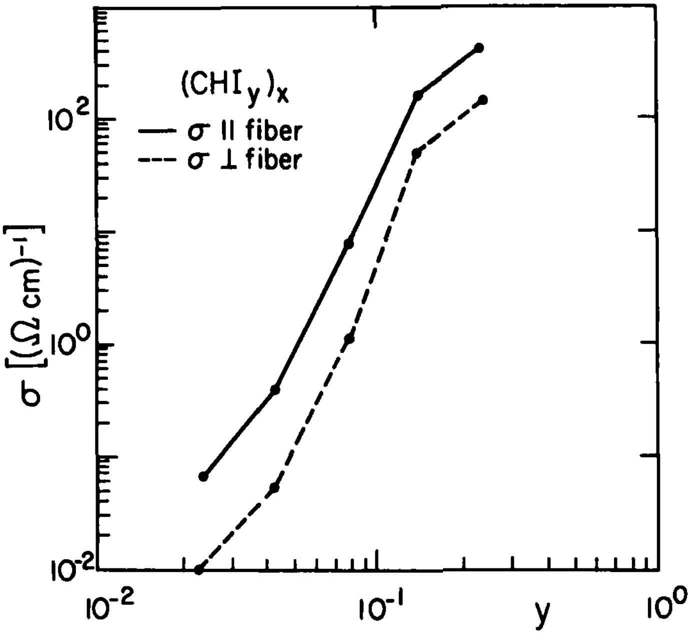

FIGURE 3 Electrical conductivity of a graphoepitaxially grown film measured parallel and perpendicular to the fibre axis.

OPTICAL MEASUREMENTS ON SHEAR-FLOW POLYMERIZED $(CH)_x$

Fig. 4 shows the absorption coefficient of shear-flow polymerized[9] undoped and SbF_5 doped $(CH)_x$. In these samples the chain axis is not preferentially oriented and therefore the optical absorption is only weakly anisotropic, as reported previously[12]. The undoped material shows the fundamental gap at ~ 1.35 eV. With increasing SbF_5 concentration up to $y \approx 0.06$ no significant change in absorption is observed, in particular no absorption band builds up between 0.5 and 1 eV as is usually found if $(CH)_x$ is doped with I_2 [6] or AsF_5 [13]. The slight increase in dopant concentration from $y \approx 0.06$ to $y \approx 0.09$ changes the absorption completely: the band gap of $(CH)_x$ disappears and the absorption in this energy range is reminescent of Drude behaviour. This abrupt transition observed in the optical absorption upon doping with SbF_5 and also apparent in the rapid change of electrical conductivity for the same concentration range (Fig. 1) is in contrast to I_2 doping where both the optical and

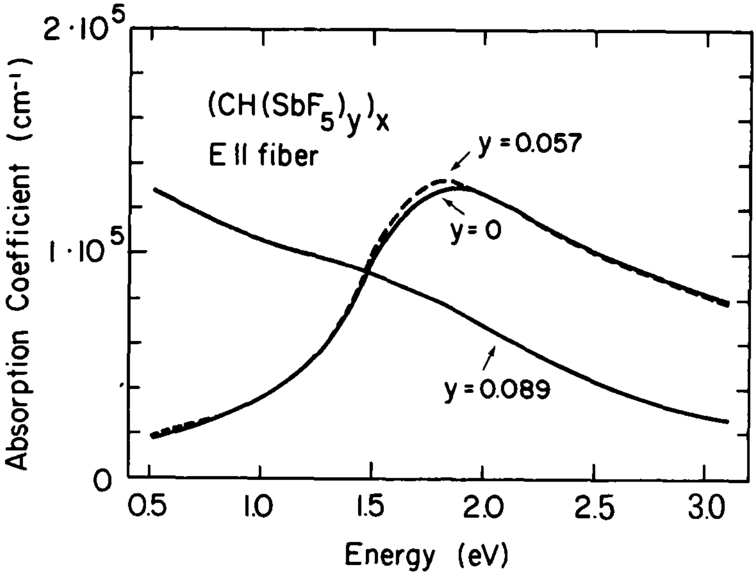

FIGURE 4 Absorption coefficient of a shear-flow polymerized film for various doping levels

electrical properties change quite gradually as a function of concentration. It appears that the acceptance of SbF_5 did not have any effect below $y = 0.05$; thus we have to assume that no reaction took place between SbF_5 and $(CH)_x$ and that SbF_5 was absorbed as a neutral entity below $y \approx 0.05$ for as yet unknown reasons.

Extension of these measurements to longer wavelengths are shown in Fig. 5a and b for SbF_5 and I_2 doping, respectively. For both dopants IR peaks appear at 0.11 eV and 0.17 eV, but again they show up abruptly for SbF_5 at a concentration of $y \approx 0.09$ whereas for iodine these peaks are visible even at the lowest concentration. It should be noted that there is some structure in these peaks, in particular in the case of SbF_5 doping. For both dopants the peaks persist up to the highest concentrations. This is also seen in Fig. 6 where the integrated peak absorption (as indicated in the inset) is plotted as a function of concentration: the absorption saturates at about the same value for both dopants. In the case of iodine inhomogeneous doping which has been proposed to explain electron energy loss spectra[7] and magnetic suscepti-

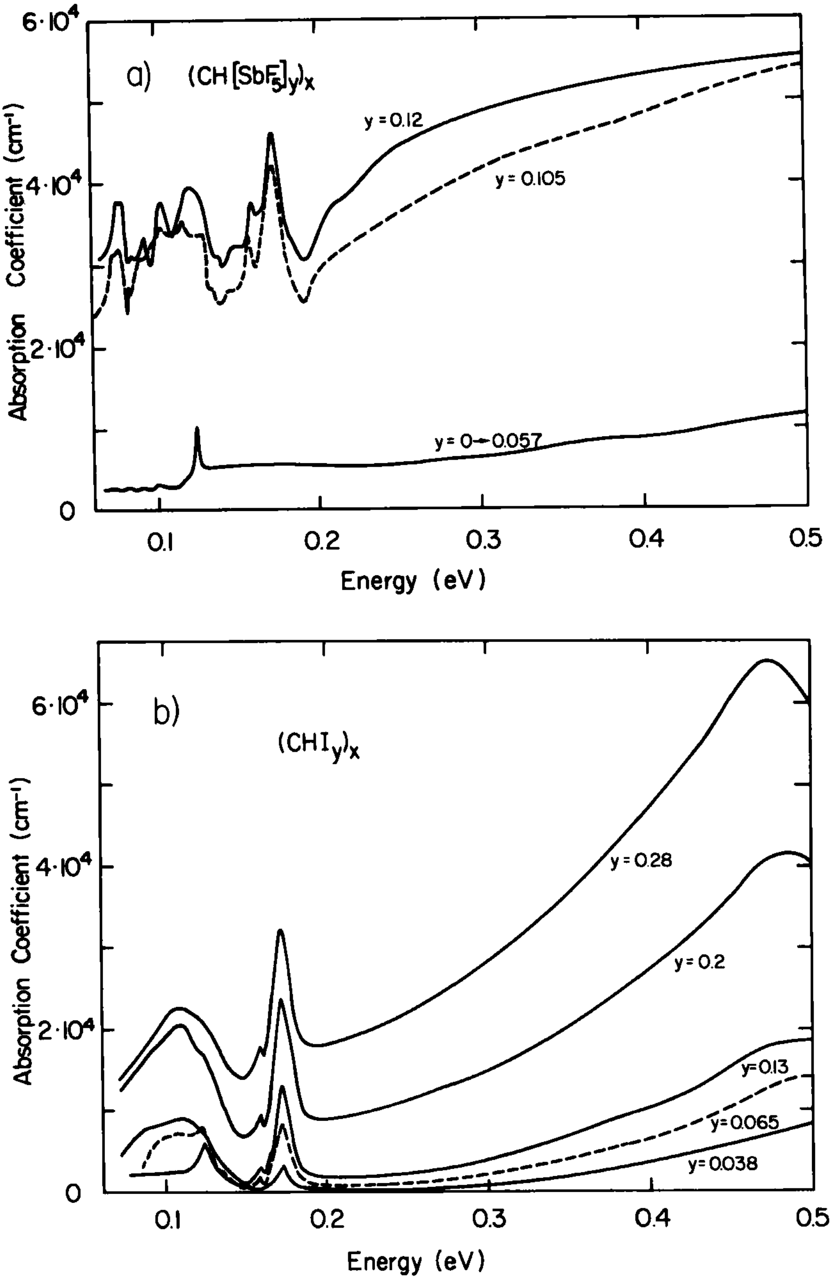

FIGURE 5 Absorption coefficient of $(CH)_x$ films in the infrared: a) SbF_5 doped samples, b) I_2 doped samples

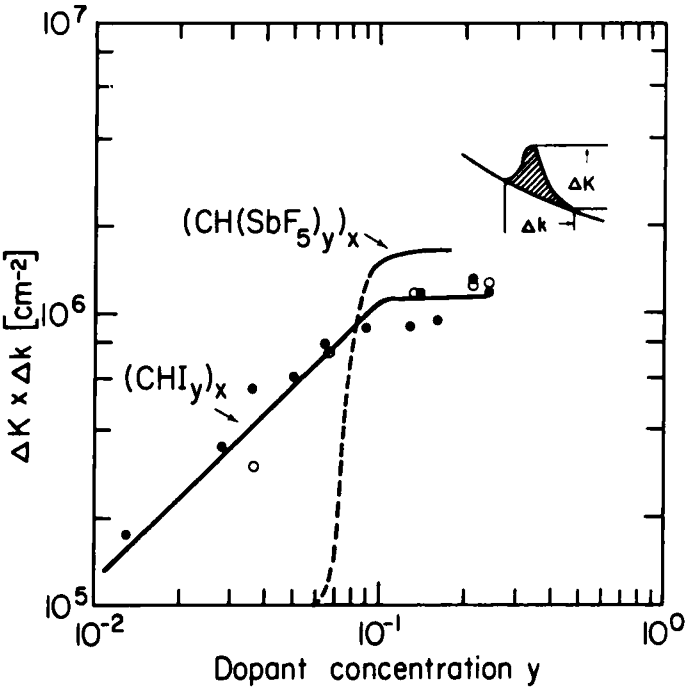

FIGURE 6 Integrated peak intensity of the IR peak at 0.17 eV (1400 cm^{-1}) for SbF_5 and I_2 doped $(CH)_x$. In the case of SbF_5 doped samples reproducible data have been only obtained below y = 0.06 (where no peak has been observed) and above y = 0.087.

bility data[8] might also be responsible for the persistence of the IR absorption (in correlation with the persistence of the optical gap). In the SbF_5 doped samples, however, the fact that the optical gap disappears completely while the IR peaks persist cannot be explained by inhomogeneity. An interpretation of the IR peaks should therefore also explain their existence in the highly conducting state (see also below).

Figs. 5a and b show that the absorption constant increases with energy between 0.1 and 0.45 eV, even at the highest dopant level, leading to a maximum around 0.5 eV. This maximum is quite pronounced for I_2 doping and broad for SbF_5 doping (see also Fig. 4). This spectral shape gives clear evidence for a non-Drude behaviour below 0.5 eV even if it seems consistent with a Drude behaviour at higher energies.

ON THE EVIDENCE FOR SOLITONS IN THE OPTICAL ABSORPTION SPECTRA

An important question in connection with the interpretation of experiments on doped $(CH)_x$ is whether charged solitons are created in $(CH)_x$ upon doping. Besides magnetic experiments[14] both the optical absorption near mid-gap and the appearance of two IR peaks are in agreement with theoretical expectations and have therefore been taken as evidence for charged solitons[13,15]. Since these solitons are intrinsic defects of the bond alternation pattern, which is usually believed to be the origin of the electronic gap, they are intimately related to the existence of the gap. Thus the fact that, in the highly conducting state of I_2 doped $(CH)_x$, both the mid-gap absorption and the IR peaks remain visible could be associated with the persistence of the electronic gap (possibly as a consequence of inhomogeneous doping). However these same features are observed in the optical absorption spectrum of SbF_5 doped samples at a dopant level where the optical gap has completely disappeared. Therefore they cannot be explained exclusively as a consequence of solitonic defects.

Neglecting disorder, heavily doped $(CH)_x$ is expected to exhibit an incommensurate Peierls distortion with a strongly reduced electronic gap (by a factor of about 10 relative to that of undoped $(CH)_x$) such that quantum fluctuations become relevant. It is tempting to associate the observed maximum in the absorption spectrum of heavily doped $(CH)_x$ (in particular with SbF_5) with such a "fluctuating Peierls gap". However, on the one hand, its energy of about 0.5 eV is larger than anticipated , on the other hand, this value is the same as that of the mid-gap absorption observed in weakly doped $(CH)_x$, which would appear to be quite fortuitous. The fact that the frequencies of the IR modes remain unchanged upon doping is not surprising in view of a recent theory of Horovitz[16] who argues that the IR modes are not sensitive to changes in the charge configuration. Thus their frequencies will be essentially the same in the incommensurate limit as for a charged soliton.

We believe that the optical absorption spectrum, in particular around 0.5 eV, can be explained in a more satissactory way if disorder is taken into account. Indeed the dopant ions which are usually assumed to merely change the band-filling and to provide a pinning potential for charged solitons may be essentially involved in the local displacement patterns. Energetic considerations (condensation energy of 0.01 eV per CH group as compared to the strong Coulomb potential introduced by the dopants) suggest that the impurity potential will not simply bind the charged soliton as a whole, but strongly distort, if not destroy, its shape. Doping will then proceed by creating more and more of these defected regions without strongly affecting their internal structure. An alternative description of such an "island" would be in terms of a local incommensurate region (due to the charge transfer) with strong pinning of the phase of the complex order parameter at the impurity center.

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REFERENCES

1. See e.g. the proceedings of two recent conferences, Physics in One Dimension, ed. by J. Bernasconi and T. Schneider (Springer Series in Solid State Sciences, Vol. 23, Berlin, 1981) and Low-Dimensional Synthetic Metals (Helsingor, 10-15 August 1980) to be published in Chemica Scripta.
2. For a recent review see D. Baeriswyl, G. Harbeke, H. Kiess, and W. Meyer, in Electronic Properties of Polymers, ed. by J. Mort and G. Pfister (Wiley, New York, in press).
3. M.J. Rice, Phys. Lett. 71A, 152 (1979); W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. B 22, 2099 (1980).
4. W.P. Su, and J.R. Schrieffer, Proc. Natl. Acad. Sci. USA 77, 5626 (1980).
5. Y. Tomkiewicz, T.D. Schultz, H.B. Brom, T.C. Clarke, and G.B. Street, Phys. Rev. Lett. 43, 1532 (1979); Y. Tomkiewicz, T.D. Schultz, H.B. Brom, A.R. Taranko, T.C. Clarke, and G.B. Street, preprint 1981.

6. H. Kiess, W. Meyer, D. Baeriswyl, and G. Harbeke, J. Elec. Mat. 9, 763 (1980).
7. J.J. Ritsko, E.J. Mele, A.J. Heeger, A.G. MacDiarmid, and M. Ozaki, Phys. Rev. Lett. 44, 1351 (1980).
8. A.J. Epstein, H. Rommelmann, M.A. Druy, A.J. Heeger, and A.G. MacDiarmid, preprint 1981.
9. W.H. Meyer, this volume.
10. W.H. Meyer, Synth. Met. 4, 81 (1981).
11. R. Fincher Jr., M. Ozaki, M. Tanaka, D. Peebles, L. Lauchlan, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. B 20, 1589 (1979).
12. G. Harbeke, H. Kiess, W. Meyer, and D. Baeriswyl, Proc. 15th Int. Conf. Phys. of Semicond., Kyoto 1980, J. Phys. Soc. Japan 49, Suppl. 17, 856 (1980).
13. N. Suzuki, M. Ozaki, S. Etemad, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. Lett., 45, 1209 (1980), Erratum in Phys. Rev. Lett. 45, 1463 (1980).
14. S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M.A. Druy, A. Sivak, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. Lett. 45, 1123 (1980); M. Peo, H. Förster, K. Menke, J. Hocker, J.A. Gardner, S. Roth, and K. Dransfeld, Solid State Commun. 38, 467 (1981).
15. S. Etemad, A. Pron, A.J. Heeger, A.G. MacDiarmid, E.J. Mele, and M.J. Rice, Phys. Rev. B 23, 5137 (1981).
16. B. Horovitz, preprint 1981.