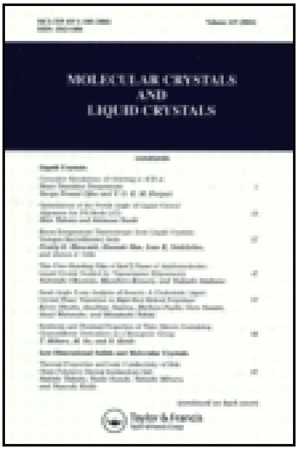

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Short Time Transport Phenomena in Polyacetylene

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SHORT TIME TRANSPORT PHENOMENA IN POLYACETYLENE

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Abstract High frequency AC (up to 10 THz) conductivity and short time photoconductivity (25 ps illumination, 100 ps resolution) measurements are reported. The conductivity is interpreted as hopping between localized states and it is argued that due to a variety of imperfections of polymeric samples these states can not be identified, especially not as solitons. In photoconductivity a fast transient, $\tau < 100$ ps, is observed and attributed to hot, non-thermalized carriers, followed by a ms tail, again due to hopping. The hopping origin of this tail is implied by the observation of similar experimental results in short-chain polyacetylene and in β-carotene.

INTRODUCTION

One of the most important properties of metallically conducting polymers is, of course, their conductivity. About seven years ago it has been discovered that upon doping with strong oxidizing agents like iodine or AsF_5, polyacetylene changes its conductivity by many orders of magnitude and at high doping concentrations values as high as 1000 S/cm are obtained[1]. Meanwhile this effect has been reproduced in a variety of other polymers with extended systems of conjugated double bonds and with various doping agents, both on the acceptor (oxidizing) and the donator (reducing) side. Although there seems to be agreement between experts that "extended" systems of conjugated double bonds are necessary for high electrical conductivity, it is not yet clear in which way the conjugation length enters into conductivity and to which extend charge transport along the conjugated polymer chains is more important than transport from one chain to another.

In polyacetylene the elementary cell of the polymer lattice is roughly known from structural analysis (typical samples have a crystallinity of about 80 %) and the band structure can be calculated[2]. From these calculations half-filled bands with a bandwidth of 10 eV parallel to the chain direction and some tenths of an eV perpendicular to it are obtained. Therefore one would expect a very anisotropic metallic conductivity with highest values along the chains. On the other hand this high anisotropy will lead to a quasi one-dimensional behaviour and to a Peierls insulator rather than to a 1d metal with half-filled band. Doping would change the band filling, we would move away from the half-filled case, and the Peierls distortion should be suppressed and the metallic state restored. But in addition, doping will create a large amount of disorder and most of the electronic states will become localized, localization being another typical 1d feature.

At low doping level the Peierls distortion should be suppressed only locally, via the creation of conjugational defects, which might show several of the fascinating properties of solitary waves ("solitons")[3]. Especially these solitons might be mobile and, if charged, they could contribute to the electrical conductivity[4].

Unfortunately typical polyacetylene samples are not only disordered, but there is a coexistence of several types of disorder: On a scale of some thousand Ångströms polyacetylene consists of a network of fibres with typical diameters of 100 - 1000 Å. Any macroscopic transport mechanism will be influenced by the contact resistance between these fibres (in polymers other than polyacetylene grain boundaries will lead to similar effects). Within each fibre there are crystalline and amorphous regions, where a typical crystallite diameter might be some hundred Ångströms, and within the crystallites there are many point defects, of which the conjugational defect (soliton) is just one. Some of these defects are shown in Figure 1. Most of them will have the tendency to localize the electronic states.

In view of this rich zoological garden of defects, it will be very difficult to estimate the importance of one particular species and its contribution to the electrical conductivity or resistivity. The present paper will summarize the results of high frequency measurements of the electrical conductivity and of the investigations of transient photoconductivity and discuss their implications on the mechanism of charge transport.

2. HIGH FREQUENCY CONDUCTIVITY

It is reasonable to assume that at high doping levels most localized states overlap and that, within a fibre, polyacetylene will behave like a highly disordered metal. Under these conditions the overall electrical conductivity will be dominated by the contact resistance between fibres and a mechanism of fluctuation induced tunneling should fairly well described the charge transport. This idea has been proposed by several authors[5] and Philipp et al.[6] and Ehinger[7] have well succeeded in fitting such theories, which had originally been developed for contact barriers in granular metals and carbon-polyvinylchloride composites, to their experimental data of polyacetylene.

At lower doping concentrations, e.g. below 5 % of iodine doping, the resistance within a fibre might be a greater obstacle to charge transport than the resistance across contacts between fibres. Since most electronic states will be localized some version of a hopping model for charge transport should be appropriate. An elegant proposition is Kivelson's mechanism of inter-soliton hopping[4]: In the ideal case the relevant defects are conjugational defects. Electrons hop between these defects each of which is associated with a localized state exactly at midgap, so that the density of states would be a δ-function at the Fermi level. Since neutral defects (solitons) are mobile they will migrate into the vicinity of charged defects, which are immobile because trapped by the Coulomb potential of the dopant ions (e.g. I_3^-). Therefore there occur only fairly small hopping distances. This model is consistant with most of the available experimental data of undoped and very weakly doped polyacetylene - with the exception of the imaginary part of the high frequency conductivity[8]. If one introduced interactions between defects this would modified the density of states and lead to a double peak instead of a δ-function and probably even better fits could be obtained.

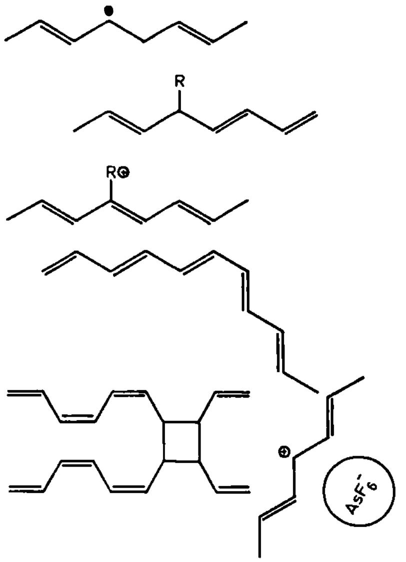

Figure 1: Some possible defects in polyacetylene

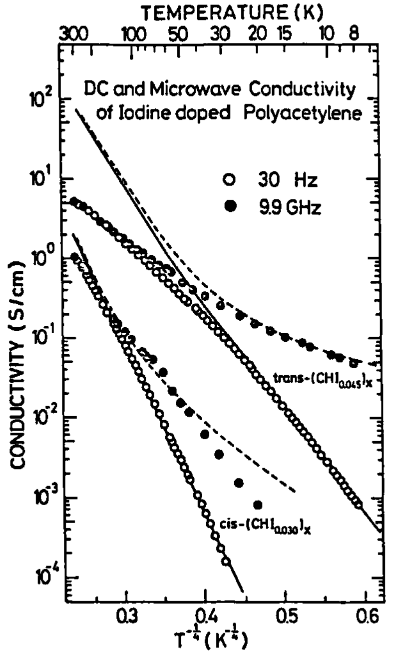

Figure 2: Hopping conductivity in moderately doped polyacetylene

Alternatively one can try to start from a constant density of states variable range hopping model, as it is used in disordered anorganic semiconductors[9]. Such an attempt has been made by Ehinger et al.[10] and is shown in Figure 2. The solid lines are calculated and correspond to the extended pair approximation to variable range hopping. The low temperature DC approximation to this approximation leads to Mott's famous $T^{-1/4}$ law. In this regime the parameters of the theory are adjusted (spacial extension of the localized wave function, frequency of the phonons assisting in the hopping process, and density of states around the Fermi level). At high temperatures the theory deviates upwards from $T^{-1/4}$, but the experimental data (full dots) deviate downwards. By introducing a cut-off in the density of states somewhat above the Fermi level the theoretical DC conductivity is reduced and can be made to fit the data. From the low-temperature DC parameters the AC conductivity (10 GHz microwaves) is calculated (dashed lines in the figure). For one sample shown excellent agreement is obtained, for the other sample, however, there is a considerable discrepancy. To make the calculated values coincide with the experimental data, the density of states has to be modified again: It turns out that a dip has to be introduced around the Fermi level.

This more general model has the advantage of being applicable both to undoped and to moderately doped samples, but after the respective modifications of the original density of states both models do not only describe well the experimental data but in addition they are nearly undistinguishable. Starting from a δ-distribution in one case (inter-soliton hopping) and from a constant in the other (semiconductor approach) the density of states has been modified in such a way that finally identical functions (Figure 3) are obtained (which in addition are allowed to vary from sample to sample and to change with sample history). At this state of the art it is impossible to identify the origin of the localized states and it is futile to argue whether in the ideal unmodified case there were solitons or some more general entities.

Recently, the AC conductivity of moderately doped polyacetylene has been measured not only at 10 GHz but up to 10 THz, well into the infrared regime. The result is shown in Figure 4 (ref.[11]). Very remarkable is the minimum at about 100 GHz in all samples and at all temperatures. This certainly must be due to a superposition of two mechanisms. One might be a free electron contribution to the conductivity, which falls off with frequency in a Drude-like manner ($\sigma = Ne\mu/(1+\omega^2\tau^2)$), perhaps originating from highly doped parts of the sample or from carriers thermally excited into extended states. Furthermore, for a broad distribution of hopping frequencies a $1/(1+\omega^2\tau^2)$ term will also appear in the hopping models. The second contribution, important above 100 GHz, would be a different type of hopping. But in addition, in this regime there are already several intramolecular and lattice modes, which might become IR active or enhanced by charged impurities (doping). Therefore, measurements of the very high frequency dielectric function do not seem to help very much in the selection of conductivity mechanisms, but they certainly provide ample information on the lattice dynamics of the polymer.

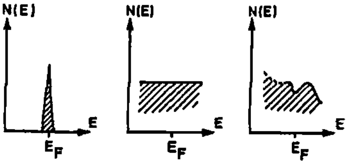

Figure 3 (above): Density of states in hopping models: Soliton approach (left), semiconductor approach (center), modified (right)

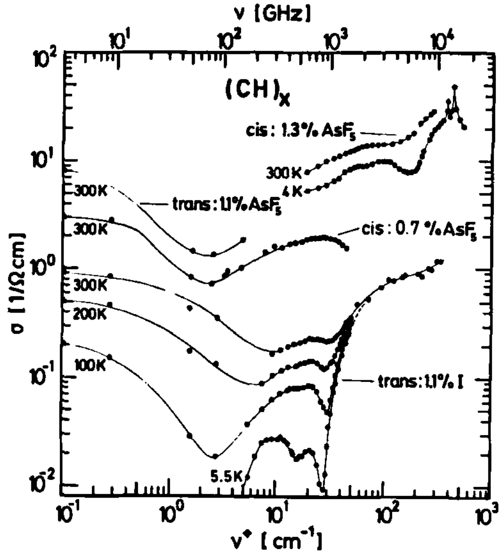

Figure 4 (right): Frequency dependence of the conductivity of doped polyacetylene up to 10 THz

3. TRANSIENT PHOTOCONDUCTIVITY

One might expect that in very fast transient experiment only the local properties of the polymer are important and that this might help to identify some of the defects, especially mobile conjugational defects (solitons). Since in photoconductivity charge carriers are created without doping, charged solitons are not trapped at charged counter-ions and might be as mobile as neutral solitons. During very short times they do not have to travel very far and perhaps some evidence of motion along a chain could be obtained.

We have carried out fast photoconductivity experiments with 25 ps light pulses and 100 ps time resolution[12] both on undoped trans-polyacetylene and on polydiacetylene (Figure 5). In both cases we observe a very fast transient signal, which at the maximum resolution presently accessible to us, has a relaxation time of 100 ps, and corresponds just to the electronic time constant of our system (fast transient recorder). So the real relaxation time is certainly $\tau < 100$ ps. This fast transient is followed by a 10 ns tail in polydiacetylene and by a much longer tail in polyacetylene, unvisible at the scale of Figure 5 and investigated in more detail in Figure 6. We assume the fast transient to be due to the initial creation of hot carriers. They have not yet had time to interact with the lattice and thermalize. (So they are not solitons, because they have not yet coupled to phonons.)

Figure 6 shows the long-time tails for polyacetylene on a ms scale. In this case the samples have been illuminated by ns pulses from a nitrogen laser and the signal has been recorded by photographing the screen of an ordinary oscilloscope. In agreement with other authors[13] we observe a decay of the photoconductivity of trans-polyacetylene within some ms. Figure 6 also shows the ms transient photoconductivity in modified polyacetylene, in a sample, were 12 % of the CH-groups have been replaced by CHD-groups, so that the conjugation is interrupted at every 8th lattice position on the average. This short chain length has been confirmed by Raman investigations[14]. As is clearly seen from the figure, the time constant of the photoconductivity in this short-chain sample is not much different from that of ordinary polyacetylene. Also shown in Figure 6 is the photoconductivity decay in β-carotene. This is a commercially available oligomere with 11 conjugated double bonds. Here also a time constant in the order of magnitude of ms is found. We do not expect continuous soliton motion in β-carotene and in short-chain polyacetylene. So we have to interprete the photoconductivity of these substances as due to hopping. By similarity we will imply that photoconductivity in ordinary polyacetylene is also due to hopping and not to continuous soliton motion. Therefore the short transient does not furnish us information on the nature of the defects because the carriers are not yet solitons, the long transient does not give this information because the carriers are no more solitons (they are trapped and move in a discontinuous hopping motion).

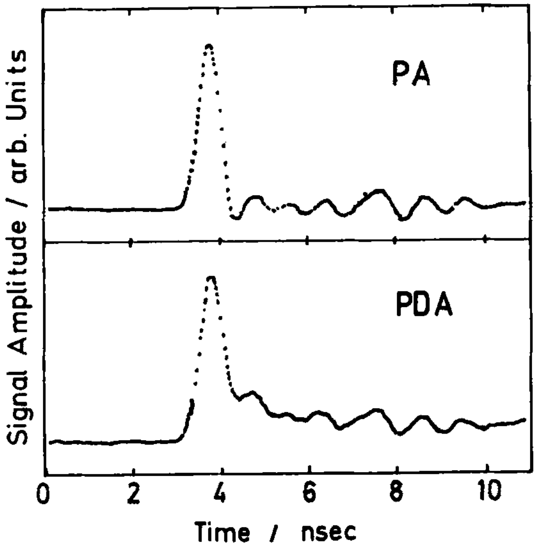

Figure 5:
Fast transient photoconductivity in polyacetylene and in polydiacetylene

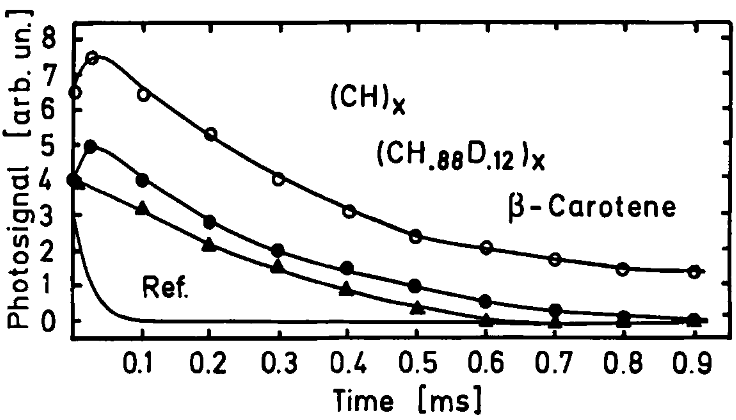

Figure 6: Transient photoconductivity measured on a millisecond scale

4. CONCLUSION

Transport phenomena in polyacetylene are mainly governed by the morphology and by imperfections of the samples. At high doping concentrations the main contribution to the electrical resistivity is the contact resistance between fibres, which can be described by a model of fluctuation-induced tunneling. In the moderate doping regime the macroscopic conductivity is determined by the resistivity within a fiber. For this situation a model of phonon assisted hopping between localized sites is appropriate. From the temperature and frequency dependence of the conductivity the energy distribution of the density of states can be deduced, but it is not possible to identify the localized states, in particular to decide whether some of them have soliton-like properties. To fit the experimental data both Kivelson's original assumption of a δ-distribution of states at midgap, characteristic for inter-soliton hopping, and the semiconductor approach of a constant density of states have to be modified in such a way, that the two models are finally indistinguishable.

In time-dependent photoconductivity experiments a fast transient of $\tau < 100$ ps is observed, probably due to initially created hot carriers, which seem to bear no information on particular defects, especially not on solitons. Millisecond tails of the photoconductive decay are due to hopping between chains and are not only found in ordinary polyacetylene, but also in short-chain polyacetylene and in β-carotene.

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