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42

ac CONDUCTIVITY OF SEMICONDUCTING *trans*-POLYACETYLENE

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ABSTRACT: The ac conductivity of semiconducting *trans*-polyacetylene has been measured over the frequency range 10 Hz to 10 MHz at room temperature. Both ohmic and blocking contacts were used on samples prepared at several doping levels below the metallic limit. The complex conductivity was found to be frequency independent for all levels of doping and for both types of contacts. A discussion is given regarding soliton motion and inhomogeneous doping and their possible effects on ac conductivity in *trans*-polyacetylene.

Transport effects in semiconducting and conducting *trans*-polyacetylene, t-$(CH)_x$, have lately been the object of active investigation. Although various models have been put forth to explain the measurements, definitive interpretation has been impeded by the high degree of both macroscopic and microscopic disorder in the samples. That is, scanning electron micrographs have revealed that t-$(CH)_x$ consists of a random fibrous network with fiber diameters ranging from several hundred to several thousand Angstroms.[1] Moreover, within the fibers themselves, diffraction studies have so far been unable to clearly determine basic crystallographic features such as atomic coordinates and bond lengths.[2] Recently, based on magnetic spin resonance measurements, it has been proposed that the doping of polyacetylene proceeds in an extremely inhomogeneous fashion, commencing with the nucleation of "metallic" regions at the very lowest dopant amounts which then grow at the expense of the surrounding insulating medium with the addition of more impurity material.[3] Results such as these encourage the application of ac conductivity techniques which in the past have been shown to be useful in the study of other disordered systems ranging from granular metals to interrupted polymers and amorphous semiconductors.[4] We report here our findings for the frequency dispersion of the complex conductivity between 10-10^7 Hz in t-$(CH)_x$ doped in the semiconducting regime using both ohmic and blocking contacts. Our conclusions are that from the perspective of the ac conductivity dispersion over the above frequency range, t-$(CH)_x$ at all semiconducting doping levels behaves much more like a homogeneous medium than would have been expected given the type of disorder discussed above. For much higher frequencies (e. g., 9 GHz), we show that a particular model of extreme inhomogeneous doping (discrete, highly conducting regions in a semiconducting matrix) can lead to dispersion in the ac conductivity.

Our *trans*-$(CH)_x$ samples were prepared following standard methods.[5] Films in the thickness range 1-5μ were grown on glass substrates containing pre-deposited metal electrodes. A subsequent metallization step followed resulting in a sandwich-like structure which provided for maximum capacitance and minimum resistance conditions. Separate gold-gold and gold-indium contact pairs were employed enabling both ohmic and blocking measurements to be made on the same film. The contact area was approximately 1 mm^2. Oxygen was used to achieve controllably light doping levels. It turned out that the effect of oxygen was almost completely reversible on overnight pumping in vacuum. For doping levels approaching, but not entering, the metallic region, we used AsF_5. Oxygen doping was carried out in situ on a previously measured undoped sample while the AsF_5-containing sample was doped before the top electrodes were deposited. Impedance measurements between 10-10^4 Hz were performed on a locally-constructed Schering bridge, while those between 10^4-10^7 Hz were done using a Hewlett-Packard 4275A LCR meter.

The experimental results are summarized in Figs. 1 and 2 which show the effective resistivity and dielectric constant as a function of frequency for three levels of doping, all less than 0.1 mole %, as estimated from the sample resistivity. We note that only very weak dispersion is observed for the ohmic contact pair with the undoped response beginning to roll off near 10^5 Hz and the AsF_5-doped near 10^6 Hz. It is tempting to ascribe this difference on the basis of some effective-medium model taking into account hopping activity or microscopic inhomogeneity. However, great care must be exercised to eliminate external circuit artifacts, which, as Street, Davies and Yoffe[6] have shown, can be surprisingly large. For example, if we consider the circuit under measurement to consist of some external lead or contact resistance in series with a parallel RC circuit repesenting the sample, and assume that all three elements are frequency independent, simple network analysis leads to a Debye-like impedance function with a half-power frequency (break point) given by $f_{1/2} = 1/2\pi\sqrt{R_L R_S C_S}$ for $R_L << R_S$ (here R_L is lead resistance; R_S, C_S are sample resistance, capacitance). For a gold stripe of the size used for our contacts, $R_L \sim 1\ \Omega$. In the AsF_5-doped case, $R_S \sim 10^3\ \Omega$ and $C_S \sim 20$ pf, giving $f_{1/2} \sim 250$ MHz, well beyond the range of our measurements. On the other hand, $R_S \sim 10^6\ \Omega$ for our undoped sample yielding a break point frequency of only 8 MHz, very close to that indicated by the data in Fig. 1. Therefore we conclude that the resistivity and dielectric constant of t-$(CH)_x$ are essentially frequency independent below 10 MHz for all doping levels in the semiconducting regime and that most, if not all, of the observed dispersion arises from the external circuit.[7]

Figures 1 and 2 also display the complex frequency response of the blocking contact pair on each sample. Indium has been shown to form a Schottky barrier to t-$(CH)_x$ and the I-V characteristics of our samples demonstrated clear rectifying

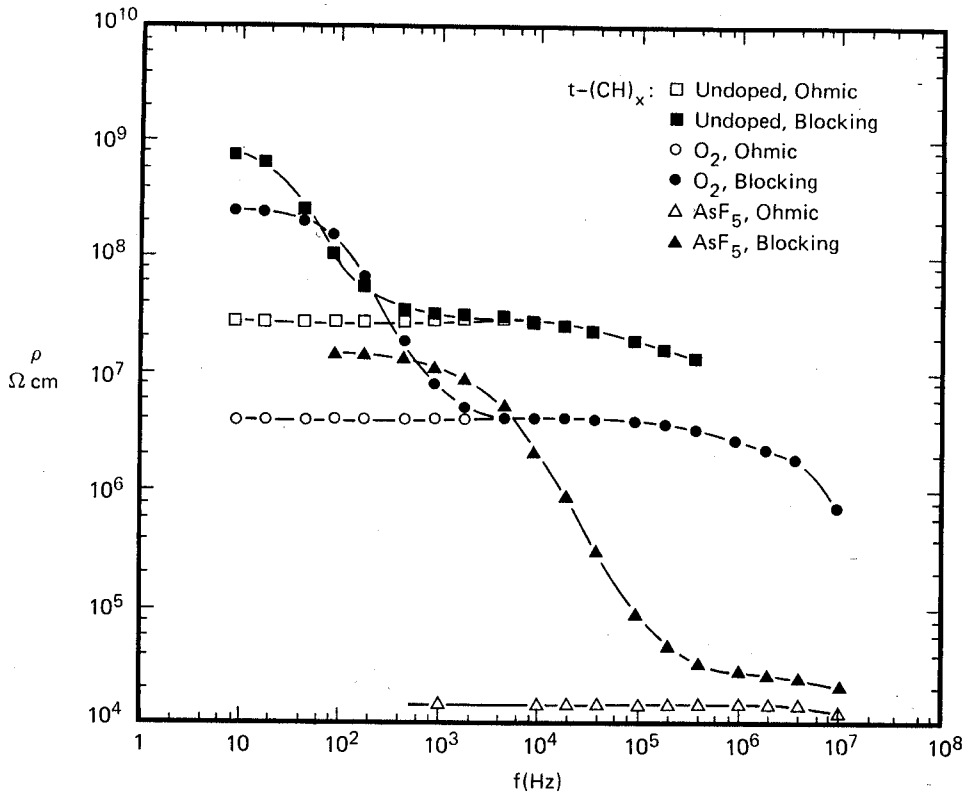

Figure 1. Frequency dependence of the resistivity of t-$(CH)_x$ for ohmic and blocking contacts to samples doped in the semiconducting range.

behavior at electrodes of this metal.[8] Unlike the ohmic measurements, the effective resistivity and dielectric constant for a blocking contact showed a strong frequency dispersion. The data were taken at zero bias with a modulation level of 50 mV or less. Since the built-in potential of an indium-t-$(CH)_x$ junction is typically 0.9 V, our measurements were in effect taken in the reverse characteristic region of the diode. More complete junction data will be presented in a forthcoming paper.[9] Again, one is tempted to attribute the observed frequency dependence of the junction to intrinsic barrier physics. However, as with the ohmic measurements, the junction results can be interpreted by the same simple equivalent circuit. We can model the sample as a parallel RC combination representing the thin depletion region under the indium contact in series with the remaining material in the sandwich configuration. The resistance of this latter portion can be approximated by the forward resistance of the diode. We may then apply our previous analysis with the subscript "S" now refering to the junction region and "L" to the sample bulk. For the AsF_5-doped sample, the appropriate numbers are R_S = 112 kΩ, C_S = 1200 pf and R_L = 1200 Ω resulting in a break frequency of 11.5 kHz. For light O_2-doping, we have R_S = 28 MΩ, C_S = 1000 pf and R_L = 160 kΩ giving $f_{1/2}$ = 75 Hz. Both of these frequencies agree reasonably well with the data thus demonstrating that the barrier properties, like those of the bulk, are essentially frequency independent below 10 MHz. It is important to note from the above observations that the unknown presence of blocking contacts can lead one to unwittingly deduce spuriously high dielectric constants at low frequencies. In our work, we have found that even gold forms rectifying contacts 5-10% of the time.

Many models have been put forward over the years to interpret the dispersion of ac conductivity in inhomogeneous media. Most of these fall into two general catagories: 1) Maxwell-Wagner,[10] in which macroscopically inhomogeneous systems are represented as a series of parallel RC circuits, and 2) Pollak-Geballe,[11] applicable to microscopic disorder (e.g., amorphous semiconductors in which averages are performed over appropriate distributions of the lifetime parameter of a Debye response function). In this latter case, for variable range hopping between localized states brought on by the disorder, one obtains $\sigma \sim f^{0.8}$ at a threshold of typically 10^4 Hz. The absence of any frequency dispersion in our measurements suggests that strong localization effects are not important at room temperature in semiconducting t-$(CH)_x$ despite diffraction evidence that appreciable short-range disorder exists. In addition to the dispersion experiments, a search was also made for non-linear behavior in the ac conductivity at low frequencies (100 Hz). For all-gold contacts, the ac conductivity was independent of modulating signal for field strengths between 5-1000 V/cm. Although we did not expect to observe non-linear behavior arising from thin-wire localization of the type proposed by Anderson, Abrahams and Ramakrishnan,[12] since our work was done at room temperature, other sources of low-field non-linearity in the ac conductivity of semiconducting polymers have been predicted.[13] Our null result indicates that, although such models may apply to some semiconducting polymers, they are not valid for t-$(CH)_x$. In view of our evidence that non-ohmic contacts can occur reasonably often in this material, attempts to measure non-linear effects should be undertaken cautiously and initial results treated suspiciously. Recently, Mortensen, *et al.*,[14] have

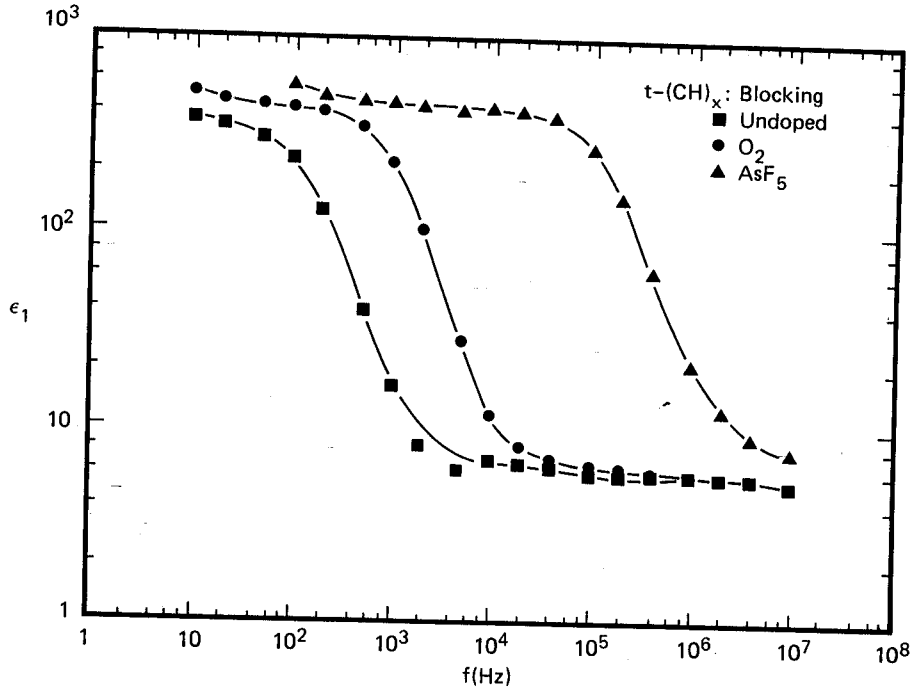

Figure 2. Frequency dependence of the dielectric constant of t-$(CH)_x$ with blocking contacts on the same samples used for the Fig. 1 data. The ohmic contacts yielded essentially the same ϵ_1 as did the blocking results in the high frequency limit. Note that the convergence of ϵ_1 at high frequencies in all samples implies a static dielectric constant $\epsilon \approx 5$.

reported non-linear resistances at low temperatures in *cis*-$[CH(AsF_5)_{0.005}]_x$ at fields above 10^4 V/cm. Whether these effects will occur in doped t-$(CH)_x$ samples such as ours remains an open question.

Although our results suggest t-$(CH)_x$ behaves as a homogeneous system below 10 MHz, there may nevertheless be some higher frequency at which dispersion will finally begin. We will now examine this question in terms of a simple doping model for t-$(CH)_x$ originally proposed by Tomkiewicz and coworkers.[3] This model views the doping of $(CH)_x$ as an extremely inhomogeneous process whereby finite, highly conducting regions form at the lowest doping levels and which increase in size at the expense of the insulating remainder as further doping progresses. This approach differs greatly from a perhaps more traditional picture of uniform dispersal of the dopant throughout the bulk of the material. Consider the particular implementation as shown in the insert to Fig. 3 in which we conceive the non-uniform doping as creating conducting and insulating segments in series within each fiber. In order to gain a tractable analytical form, we assume the length of each segment to be periodic along the fiber at a given level of doping. The lumped parameter equivalent circuit is depicted below the model and is isomorphic to that considered earlier for the ohmic and blocking contact problem. Here R_C is the resistance of the conducting region, and R_I, C_I are the resistance and capacitance of the semiconducting or insulating portion. We are interested in describing the ratio of ac to dc conductivity as a function of both frequency and doping. Straightforward analysis of our model gives the following relations:

$$\frac{\sigma_{ac}}{\sigma_{dc}} = 1 + \left(\frac{y_M}{y} - 1\right)\frac{\sigma_C}{\sigma_I}\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) , \qquad (1)$$

where

$$\tau = \left[1 + \left(\frac{y_M}{y} - 1\right)\frac{\sigma_C}{\sigma_I}\right]^{-1}\frac{\epsilon_0\epsilon_I}{\sigma_I} , \qquad (2)$$

and

$$y/y_M \equiv \ell_C/L . \qquad (3)$$

Implicit in this model is the assumption that the total length $L = \ell_I + \ell_C$ is invariant to doping; that is, the conducting parts grow at the same rate as the insulating ones shrink allowing the definition of the dopant concentration y as given by Eq. (3). y is then the doping level determined by weight while y_M is the highest doping level achievable for a particular dopant species; e.g., $y_M = 0.1$ for AsF_5 and 0.3 for iodine. Thus, in the conducting portion of the fiber, we always have the saturated doping condition. Choosing as optimal values $\sigma_C = 10^4$ $\Omega^{-1}cm^{-1}$, $\sigma_I = 10^{-9}$ $\Omega^{-1}cm^{-1}$ and $\epsilon_I = 5$, we see that at an upper limit concentration $y = 0.01$ (*i.e.*, 10% of the fiber volume metallic under AsF_5 doping), the lower break point frequency is roughly 5 GHz, far beyond the range of our data. On the other hand, σ_{ac}/σ_{dc} as a function of iodine concentration at 9 GHz has been measured by Mihaly, *et al.*,[16] who find a decrease from about 10^3 at $y = 0$ to around unity at $y = 0.03$. However, Fig. 3 contains a plot of Eq. (1) at this frequency which shows an increase in σ_{ac}/σ_{dc} with increasing y. Therefore, the Fig. 3 model of serial segregation into "metallic" and "insulating" regions predicts a behavior opposite to that observed experimentally. We should point out that actual doping activity probably proceeds as a diffusion of the dopant radially into the fiber rather than by the creation of axially isolated conducting/nonconducting regions. Such a process would in principle display a complete absence of ac conductivity dispersion because the equivalent circuit would remain a parallel RC network at all doping levels in the semi-

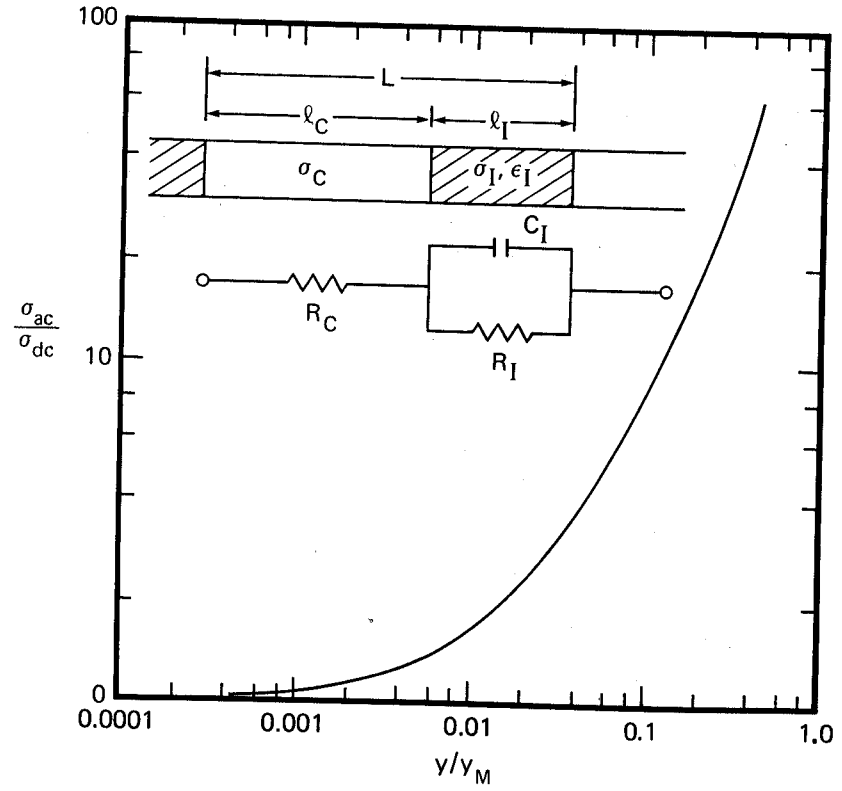

Figure 3. The insert shows the model used to simulate aggregate doping as a series of conducting and insulating regions within a fiber. The curve shows the dependence of the ac-to-dc conductivity ratio as a function of dopant concentration for the set of model parameters discussed in the text.

conductor range.[15] Thus, the observations of Mihaly, *et al.*,[16] are, as these authors suggest, much more in accord with hopping between localized states. It may be that this hopping occurs primarily in the insulating regions of the material and completely masks the weak opposing response due to doping aggregation.

We will now comment briefly on the possibility of charged soliton motion giving rise to dispersion in ac conductivity measurements. Most of the usual models for ac conductivity governed by microscopic processes require that these processes simulate in some way the motion of damped rotating dipoles and thus give rise to Debye-like response functions. The particular frequency dependence is generated by the specific average taken over the Debye lifetime parameter, an average which is chosen by the specific physics of the effective dipole generation and motion. The classic example is the Pollak-Geballe[11] model for partially compensated doped silicon. All models of the Debye type predict zero ac conductivity at zero frequency. The threshold frequency at which one begins to observe dispersion thus depends on the magnitude of the dc conductivity present in a given situation. In fact, the mathematical treatment leads to expressions exactly identical to the effective medium response functions discussed above. There are thus two conditions a soliton model for ac conductivity must meet: 1) a mechanism for generating effective dipole activity, and, 2) a knowledge of the dc conductivity magnitude so that an estimate can be made of the threshold frequency. With regard to the first condition, Park, *et al.*,[17] have pointed out that charged soliton transport is likely to be by hopping between impurity sites, a situation suitable for the effective dipole model. Experimentally, however, the second condition is more critical. All we can say at this time is that the level of dc conductivity at room temperature is sufficiently high throughout the semiconducting regime so that possible ac conductivity arising from charged soliton activity is unobservable below 10 MHz at room temperature.

In summary, we find the room temperature ac conductivity of *t*-$(CH)_x$ to be constant at frequencies below 10 MHz. The apparent frequency dependence of indium-*t*-$(CH)_x$ Schottky barriers can be explained by the relatively high forward resistance of these junctions. As we have seen, simple models of non-uniform doping predict either zero or relatively small upward departures from dc conductivity levels at frequencies in the gigahertz range, in contradiction to what is actually observed and is believed to be due to diffusive hopping. It is possible that charged soliton motion could contribute to the ac conductivity in *t*-$(CH)_x$, but a better theoretical understanding of the relative amounts of dc to ac soliton transport is needed before serious comparison to experiment can be made. The most important finding of the present work was the unexpected frequency independence of the ac conductivity below 10 MHz. Compared with other structurally disordered materials, *t*-$(CH)_x$ seems much more homogeneous than would appear warranted. We believe this to be a consequenceeither of essentially uniform doping throughout the fibers or of the radial doping process mentioned above, whereby the resulting equivalent circuit approximates a parallel RC network with frequency independent parameters in the range of our measurements.

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