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The conjugated organic polymer $(CH)_x$ has recently been the subject of extensive interest on two counts: 1) In pristine *trans*-$(CH)_x$, EPR and NMR evidence has been given for highly mobile spin carriers that carry no charge. These have been interpreted as arising from topological solitons (a localized reversal of the bond alternation pattern). The novelty of such spin carriers has stimulated much theoretical and experimental interest. 2) Upon doping, the conductivity of $(CH)_x$ increases by $\sim 10^{12}$ and undergoes an apparent insulator-to-metal transition at ~1% dopant concentration. The possibility that the doping produces charged solitons rather than band electrons and that with increasing density this soliton gas undergoes a phase transtion has also attracted much interest.

In this paper, these two aspects of $(CH)_x$ will be discussed. In the first part, spin-echo and CW EPR results for the undoped *trans* polymer will be presented. We shall show that both the magnitude and the temperature dependence of the diffusion rate as determined from the echo measurements should lead to a reconsideration of the soliton model. In the second part, magnetic and transport data obtained in the doped *cis* polymer will be presented showing that doping of $(CH)_x$ is very inhomogeneous. The doped and undoped parts of the polymer appear to be largely distinct, the doped regions being metallic. The conductivity changes that have previously been interpreted as arising from a transition *within* the doped region are attributed to a change in the topology of these regions, *i. e.*, the occurrence of a percolation threshold in which the metallic regions touch and form an essentially metallic continuum.

Spin Dynamics in *trans*-$(CH)_x$. Fig. 1 shows T_M of the electron spins in $(CD)_x$ as derived by spin-echo measurements[2] and T_2^* from CW EPR as functions of temperature. While T_2^* has a monotonic behavior as a function of temperature, T_M has a minimum value of 120 nsec at $T_{min} = 130$ K. For $T > T_{min}$, T_M is an increasing function of temperature and agrees well with T_2^*; for $T < T_{min}$, T_M is a decreasing function of temperature and has very different values from those of T_2^*, implying that the EPR line is inhomogeneously broadened for these temperatures. The monotonic temperature dependence of T_2^* was previously interpreted as an indication of a strong narrowing for all temperatures. The present measurements indicate that the strong narrowing regime is a proper description only for the temperature range $T > T_{min}$. Thus, the data presented show[3] that the diffusion rate of the motion is temperature-dependent and, if this temperature dependence can be represented by an activated process, then the activation energy is larger than 130 K.

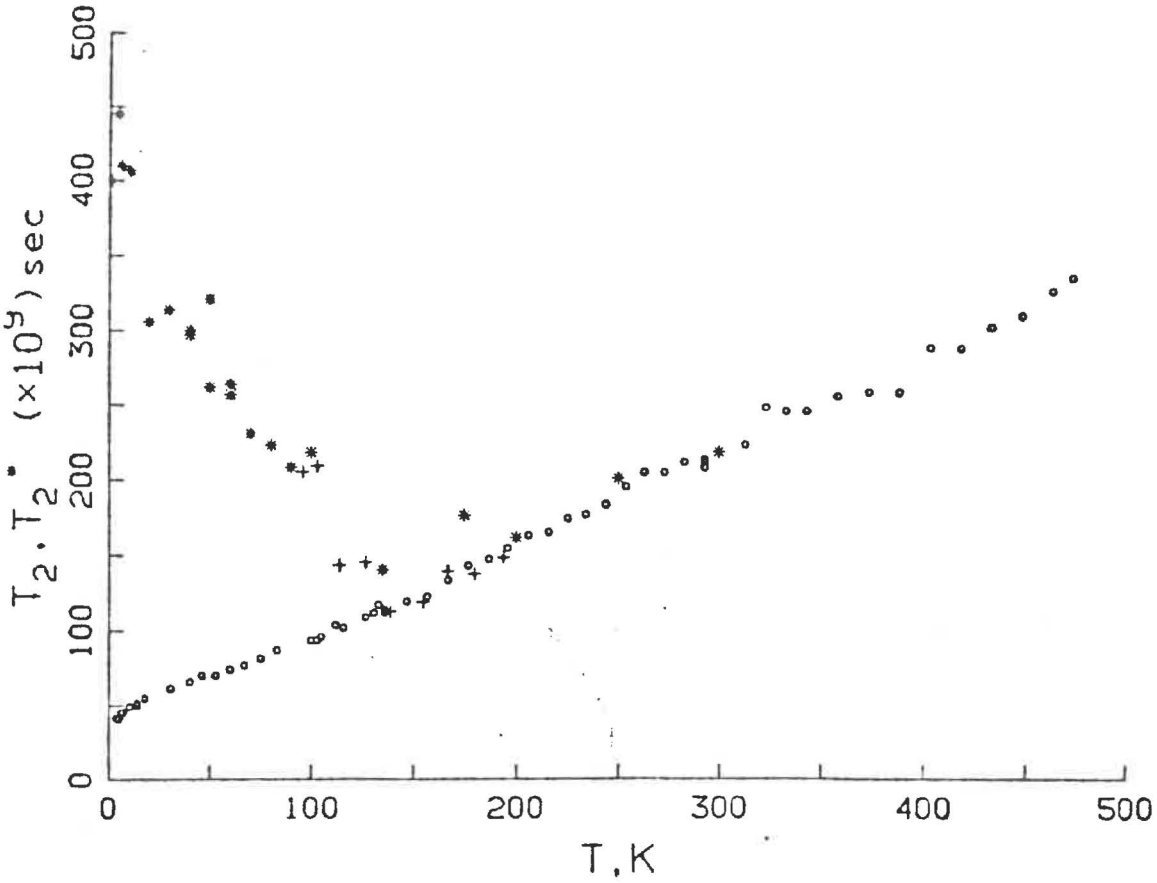

Fig. 1. T_M (as determined from spin-echo experiments) and T_2^* (as determined from CW EPR) as a function of temperature. The T_M data presented are on two different samples indicated by • and +. The T_2^* data are indicated by o.

At the position of the minimum in T_M, the determination of the diffusion rate D from the echo measurements has two advantages. First, the diffusion rate can be determined readily from the relationship

$$D\tau = C \tag{1}$$

where τ is the time separating the 90° and 180° pulses. Although the value of C depends on the details of the particular model used, for the commonly accepted models of either 1d or quasi-1d diffusion C = 6. Thus D as determined from (1) is independent of the model, *i. e.* of whether the motion is 1d or quasi-1d. This should be contrasted with the strong dependence on dimension of D as determined from the EPR linewidth, a variation by a factor of ~10. Second, any other technique for determining D requires knowledge of either the linewidth of static spins (EPR) or the hyperfine coupling between the proton and electron spins (NMR). In determining D from echo measurements at the position of the minimum, no additional parameters are required.

The determination of D at any temperature other than that corresponding to the minimum of T_M requires a specific model. Since the value of the diffusion coefficient at 293 K is a subject of extensive interest, we have determined an upper bound for D to be 6 × 10^9 sec^{-1}. This upper bound comes from using a 1d diffusion model in analyzing the echo data. We know this overestimates D because both the line shape and the echo decay

indicate that the diffusion is not one-dimensional. If one further modifies this estimate by assuming a spin delocalization over 15 sites, as required by the soliton model, the upper bound for the diffusion rate becomes $\sim 10^{11}$ sec^{-1}. Thus, even this upper bound, which must grossly overestimate the true rate, is lower by a factor of at least 100 than the rate of $\sim 10^{13}$ sec^{-1} inferred from NMR.

We may summarize the results of the spin-echo data experiments: 1) The spin diffusion rates are significantly lower than the values previously determined by NMR and expected by the soliton model. 2) The activation energy of the diffusion is of the order of hundreds of degrees at least, much higher than that expected from the soliton model. These results should lead to a reconsideration of the soliton model.

Insulator-to-Metal Transition of Doped $(CH)_x$. Fig. 2 shows the temperature dependence of the spin susceptibility of *cis*-$(CH)_x$ doped with various levels of AsF_5 in the temperature range $100 < T < 300$ K. For comparison, the susceptibility of pristine *cis*-$(CH)_x$ is also shown in this figure. It is clearly seen that doping *increases* the spin susceptibility and that the spin susceptibility generated by doping has hardly any temperature dependence in this temperature regime, even for the lowest concentration of dopant (0.3%). If doping were homogeneous, then at least for the lower concentrations the electrons would be expected to occupy localized, non-overlapping states, giving rise to a spin susceptibility having a Curie type of temperature dependence. Since the susceptibility is temperature-independent, banding apparently occurs. Thus, the impurity states must overlap even for the lowest dopant concentration, which would require inhomogeneity. Moreover, we find a linear relationship between the magnitude of the susceptibility and the dopant concentration over a broad range of concentrations (0.3% to 12%), suggesting that the effective transfer integral is concentration-independent. This would indeed be the case if metallic domains were formed in the $(CH)_x$ matrix. The effect of increasing the concentration would be to increase the size of these domains and/or to increase their number so that eventually enough would be in essential contact to create percolation paths. While the transition to such a situation would be expected to affect the transport properties considerably, no similar effect is expected for the magnetic susceptibility. And indeed, neither

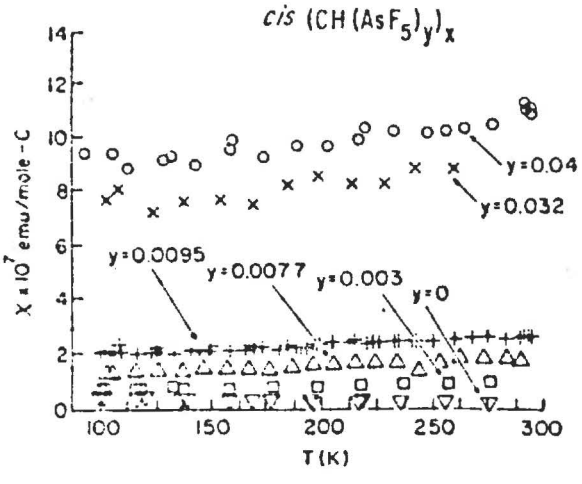

Fig. 2. Spin susceptibility as a function of temperature for *cis*-$(CH)_x$ doped with various levels of AsF_5.

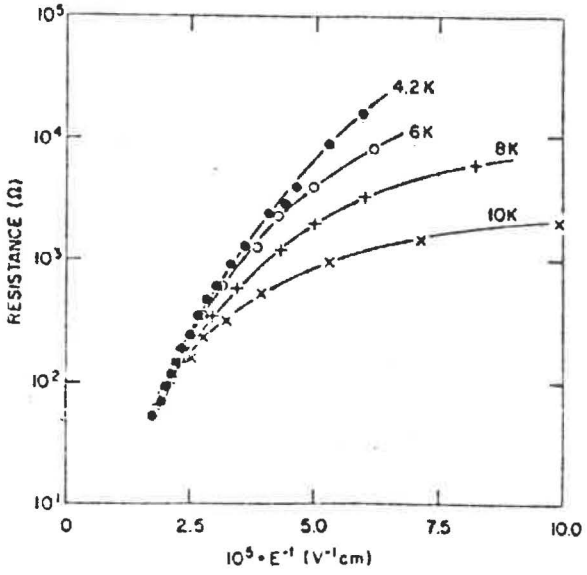

Fig. 3. Resistance as a function of 1/E for $[CH(AsF_5)_{0.005}]_x$ at several temperatures.

the temperature dependence of the susceptibility nor its magnitude shows any indication of the semiconductor-to-metal transition apparently seen in the conductivity at the level of about 1% doping.

As for the conductivity, in the low-concentration regime the low-field (ohmic) resistance has the temperature dependence[4] $\exp(T_0/T)^{1/2}$. At high electric fields, namely when the voltage drop between neighboring grains is much larger than the thermal energy, the resistance should have a field dependence given by the equation[5]

$$R = R_o \exp(E_o/E) \qquad (2)$$

Figure 3 shows the field dependence of the resistance in the temperature range 4.2–10 K. The field dependence follows equation (2) with a temperature-independent $E_0 \simeq 2 \times 10^5$ V/cm. By applying a similar analysis to that used for granular metals, we have determined the average separation of the metallic grains for the studied sample to be 60 Å. Thus, our studies on doped $(CH)_x$ for concentrations below the "insulator-to-metal transition" indicate the existence of metallic domains with high tunneling barriers between them, analogous to granular metals below the percolation threshold. Measurements on concentrations above this transition show a much weaker temperature and field dependence, indicating that barriers still exist but that they are much reduced and that both the temperature dependence and the field dependence of the conductivity can be understood by fluctuation-induced tunneling.

We may summarize the conclusions about doped materials. 1) The doping of $(CH)_x$ is inhomogeneous for all concentrations of dopant. A phase separation exists between the doped and undoped parts of the polymer and metallic clusters exhibiting Pauli-like susceptibility are formed in the doped parts. 2) The conductivity results, which were previously interpreted as indicative of an insulator-to-metal transition, can be understood in terms of the existence of two structural regimes: a) a dielectric regime in which isolated metallic particles are dispersed in the undoped polymer, yielding a low conductivity involving thermal activation, and b) a metallic regime where there are percolation paths *via* metallic domains that are very close and separated by only small barriers.

References

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2. The evaluation of T_{M} was done by fitting the echo amplitude data with a function of the form $Ae^{-T_M/2\tau}$

3. Even if two kinds of spins, localized and fast-moving, were to exist in the sample, as suggested by Holczer *et al.*, the only way the minimum in T_M would occur would be if above 130 K only the fast spins were observed. Thus, even in this situation our conclusions are still applicable.

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5. B. Abeles, Appl. Solid State Sci. 6, 1 (1976).