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Highly conducting polyacetylene: Three-dimensional delocalization

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We report the experimental results for magnetic susceptibility, thermopower, and magnetoresistance of highly conducting I_2-doped new polyacetylene, N-$(CH)_x$. These measurements deal with the density of states at the Fermi energy, its local structure, and conduction-electron relaxation time. We conclude that microscopic electronic phenomena in the highly doped N-$(CH)_x$ as compared with the earlier studied Shirakawa polyacetylene has not been changed; rather there is an increase in the relaxation time along the chain or interchain transfer that helps to avoid entrapment of the charge within a single chain. This leads to the three-dimensional delocalization of electrons responsible for the high conductivity.

Polyacetylene has been an important focus of research since 1977 when it was reported that the conductivity (σ) of insulating Shirkawa polyacetylene, S-$(CH)_x$, upon doping with iodine increased by 15 orders of magnitude to "metallic" values of ~ 200 (Ω%cm).[1,2] The temperature T dependence of σ varies as $\exp[-(T_0/T)^{1/4}]$, with T_0 a constant decreasing with increasing doping levels. Later some doped S-$(CH)_x$ samples were prepared with higher σ's $[\approx 10^3\ (\Omega\,\mathrm{cm})^{-1}]$ and weaker T dependence.[2,3] The report of preparation of new polyacetylene, N-$(CH)_x$, which when doped has a weakly T-dependent conductivity approaching that of copper at room temperature ($\sim 10^5$ S/cm) (Refs. 4–7) and an increasing anisotropy $(\sigma_{\parallel}/\sigma_{\perp})\approx 30$ raises questions concerning the origins of its high conductivity. Recently two other doped newly processed polyacetylenes have been reported to yield conductivities of 3×10^4 (Ref. 8) and $10^5\ (\Omega\,\mathrm{cm})^{-1}$ (Ref. 9) with maximum $(\sigma_{\parallel}/\sigma_{\perp})\approx 100$.[8]

We report the results of magnetic susceptibility, thermopower, and magnetoresistance studies of N-$(CH)_x$ (fully doped with iodine) and compare our results with earlier data for S-$(CH)_x$. We find that the microscopic electronic structure of doped N-$(CH)_x$ and doped S-$(CH)_x$ are nearly identical. Analysis of the 4.2 K magnetoresistance data leads to the conclusion that the relaxation time along the chain or interchain transfer are sufficiently large in doped N-$(CH)_x$ to enable three-dimensional delocalization of the electrons responsible for the high conductivity. This three-dimensional delocalization is critical for high conductivity in polymer materials with finite chain lengths and chain defects.

Procedures for synthesis, stretch orientation (to 500% elongation), and I_2 doping of N-$(CH)_x$ have been reported elsewhere.[4,7] The magnetic susceptibility data (after subtraction of the core diamagnetic contribution) obtained by the Faraday balance technique was analyzed to obtain the metallic Pauli susceptibility and localized Curie spin contribution.[7,10] Thermopower was measured using a technique that minimizes the thermal gradient across the sample.[11] Magnetoresistance was measured at 4.2 K for fields up to 70 kG both parallel and perpendicular to the chain orientation direction. Both S and magnetoresistance were reproducible among differing samples of the same type of preparation. The scatter in the data represents the reproducibility of the experiments for repeated measurements on an individual sample.

Figure 1 presents the density of states at the Fermi energy as a function of iodine doping for both S-$(CH)_x$ (Ref. 10) and N-$(CH)_x$ (Ref. 7) obtained utilizing $\chi^p=\mu_B^2 N(E_F)$, where μ_B is the Bohr magneton and $N(E_F)$ the density of states at the Fermi energy. At high-doping levels, χ^p is nearly identical for N-$(CH)_x$ and

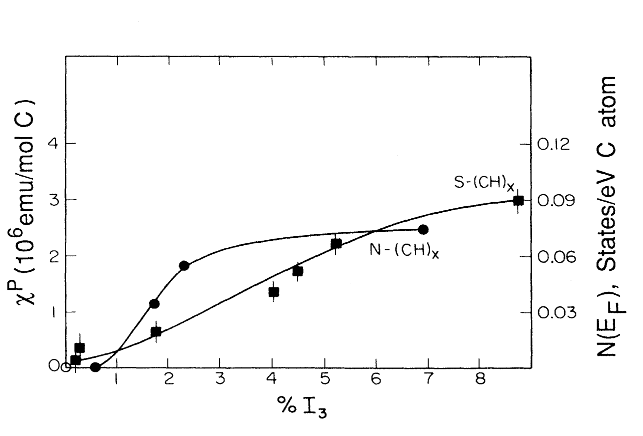

FIG. 1. Pauli magnetic susceptibility and $N(E_F)$ of S-$(CH)_x$ (Ref. 10) and N-$(CH)_x$ as a function of iodine doping.

S-(CH)$_x$, implying $N(E_F)\simeq 0.08$ states/eV C for both systems. The difference in magnetic behavior of N-(CH)$_x$ and S-(CH)$_x$ at low-doping levels likely reflects inhomogeneous doping of the more dense N-(CH)$_x$.

The thermopower of fully doped free standing fivefold stretched film of highly doped N-(CH)$_x$, Fig 2, is linear with temperature. These data are very similar to those of earlier studied[3] AsF$_5$-doped S-(CH)$_x$ and NbCl$_5$-doped newly processed (CH)$_x$ (Ref. 8), but are lower in magnitude and more linear in T than the thermopower of I_2-doped S-(CH)$_x$.[11]

Magnetoresistance of samples of 500% stretched highly doped N-[CH$(I_3)_y$]$_x$, $y>0.06$, was measured at 4.2 K with magnetic field in the range of 0–70 kG. Figure 3 shows data for two orientations of magnetic field: H perpendicular to the film and direction of current, and H in the plane of the film and parallel to current. Magnetoresistance is negative in both cases but nearly ten times smaller for H parallel to the current as compared with H perpendicular to the current. In small fields the relative change in resistivity was $(\Delta\rho/\rho)\propto -H^2$, with a gradual deviation from quadratic dependence at higher fields. The magnetoresistance of [N-CH$(I_3)_{0.55}$]$_x$ at 4.2 K was also negative, though the large resistivity of the sample precluded quantitative study. A similar negative magnetoresistance was reported for an early study of highly conducting AsF$_5$-doped S-(CH)$_x$.[3]

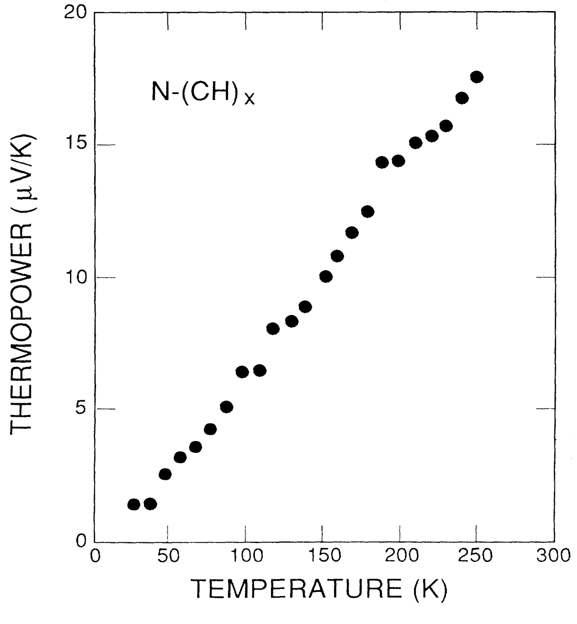

FIG. 2. Thermopower of I_2-doped 500% stretched N-(CH)$_x$ film vs temperature measured parallel to the stretch (chain) axis.

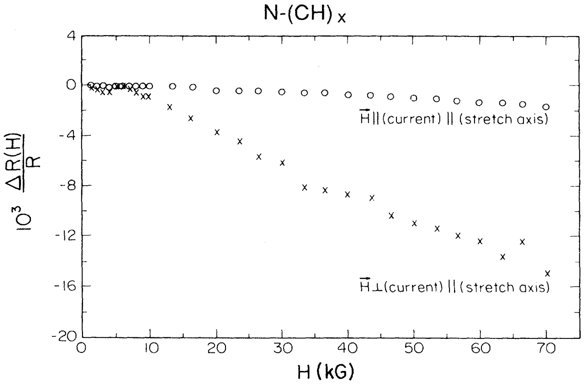

FIG. 3. Magnetoresistance of I_2-doped stretched N-(CH)$_x$ films vs magnetic field for two orientations of magnetic field. The current is along the stretch axis in both cases.

For homogeneous materials, values of χ^p, S, and magnetoresistance can be directly related to $N(E_F)$ and its structure in k space. That is, χ^p is proportional to $N(E_F)$ (Ref. 12) through

$$\chi^p=\mu_B^2 N(E_F)\;, \tag{1}$$

while S represents the change of the conductivity and hence $N(E)$ with energy:[13]

$$S=\left[\frac{\pi^2}{3}\right]\left[\frac{k_B^2 T}{e}\right]\left[\frac{dl\,n\sigma(E)}{dE}\right]_{E=E_F} \propto \left[\frac{dl\,nN(E)}{dT}\right]_{E=E_F}, \tag{2}$$

where in the last term we have assumed that mobility μ is independent of the energy ($\sigma=ne\mu$, where n is the charge-carrier density). The magnetoresistance is related to the curvature of $N(E)$ near E_F,[14] though this term is negligible except when the conductivity is a sharp function of energy.[15]

While σ (300 K)$\simeq 4\times10^4$ S/cm for heavy doped N-(CH)$_x$, σ decreases with dereasing T[5-7] in contrast with usual phonon limited metallic behavior,[12,13] and in accord with barrier limited conductivity.[5,6,7,16] The origins of the dramatically higher conductivity of heavily doped N-(CH)$_x$ as compared with S-(CH)$_x$ are of importance. Our results show that $N(E_F)$ is virtually unchanged for samples of $y>0.06$ as the conductivity increases from ≈ 50 S/cm to $\approx 50\,000$ S/cm. Similarly dN/dW is essentially the same in highly conducting AsF$_5$-doped S-(CH)$_x$ and I_2 N-(CH)$_x$.[17] Assuming that magnetoresistance predominantly represents d^2N/dE^2 in the conducting regions (and not barriers since phase coherent multiple tunneling through the barriers is unlikely to occur), then the curvature of $N(E_F)$ is also the same for highly conducting AsF$_5$-doped S-(CH)$_x$ and for I_2- doped N-(CH)$_x$. In the light of these similarities, the two orders-of-magnitude difference in their room-temperature conductivity is puzzling. We, therefore, reexamine the implications of magnetoresistance in light of the quasi-one-dimensional polymer structure.

For an isolated one-dimensional chain with randomly distributed scattering centers, the processes accounting for the momentum transfer during the motion of electrons along the chain may be represented as forward and backward scattering with corresponding relaxation times τ_1 and τ_2, respectively. The mean free path is $l=v_F\tau$, where τ is the total relaxation time. For weak disorder

($k_F l \gg 1$), the localization length is much greater than the repeat distance a, and one-dimensional localization occurs because of quantum interference due to multiple scattering.[18] Firsov[19] has considered the interesting situation of N isolated chains being bundled together to form a wire. This situation is very relevant to the case of polyacetylene polymer which has a fibrous structure. Each fiber consisted of many parallel one-dimensional (1D) chains with some overlap between neighboring chains. Structural defects such as chain breaks introduce sizeable barriers (strong backward scattering centers) while dopant ions (located between chains) mainly introduce forward scattering.[20] Firsov[19] showed that for the case of a quasi-one dimensional system there is a threshold interchain transfer integral ($t_{\perp c}$) such that the electronic system of a bundle of single chains abruptly transforms from localized to extended states. This critical value is estimated to be

$$t_{\perp c} \simeq \left[\frac{0.3\hbar}{2} \right] \left[\frac{\tau\tau_2}{2} \right]^{-1/2} \tag{3}$$

which depends not only on τ_2 (backward scatterng) but also on τ_1 (forward scattering). The influence of τ_1 could be understood on qualitative grounds because it leads to an additional disorder which should enhance the tendency towards localization.[19] It is assumed here that the mean free path is equal to the average separation between chain breaks. Taking $\tau_1 = \tau_2 = (\tau/2)$ (Ref. 19) simplifies Eq. (3) to $t_{\perp c} \simeq (0.3\hbar 2)(\tau^2/4)^{-1/2} \simeq 0.3\tau^{-1}$. Kivelson and Heeger[21] reached similar conclusions disregarding forward scattering altogether. They introduced a more stringent requirement if the charge transfer between chains is incoherent.

We now reexamine the magnetoresistance data. In the case of a metal with isotropic Fermi surface and for small fields, $(\Delta\rho/\rho) \simeq +(\omega_c\tau)^2$ (Ref. 22), which is opposite in sign to the magnetoresistance of doped N-$(\mathrm{CH})_x$. The case of magnetoresistance of disordered electronic systems has been considered recently. Hikami *et al.*[23] found that scattering by localized spins and spin-orbit interaction leads to positive magnetoresistance. Lee and Ramakrishnan[24] showed that for systems near metal-insulator transition, the sign of magnetoresistance could effectively distinguish between the importance of localization or electron-electron interaction. At low fields magnetoresistance is found to be linear in H^2 with negative (positive) contributions due to localization (*e-e* interaction), though the contribution of *e-e* interaction is smaller by a factor of $(1/k_F l)^2$.[24] Observation of negative magnetoresistance for a $(\mathrm{CH})_x$ polymer at high-doping levels indicates that localization effects are important. Kawabata[25] has estimated the value of $[\Delta\rho(H)/\rho]$ for three-dimensional systems for the case of electron delocalization by a magnetic field ($\omega_c\tau \ll 1$),

$$\left[\frac{\Delta\rho}{\rho} \right] = - \left[\frac{1}{12\sqrt{3}} \right] \left[\frac{\tau_\epsilon}{\tau} \right]^{3/2} (\omega_c\tau)^2 , \tag{4}$$

where τ (τ_ϵ) is the elastic (inelastic) scattering time and $\omega_c = (eH/mc)$ is the cyclotron frequency. Analyzing the data for a typical sample studied of $\sigma_\parallel$ (4.2 K) = 2700 S/cm [$\sigma_\parallel$ (295 K) = 15 000 S/cm], and utilizing 0.08 charge carriers per carbon, we estimate $\tau \simeq 2.7 \times 10^{-15}$ s ($\omega_e\tau \ll 1$), mean free path along the chain $l = v_F\tau \simeq 30$ Å, and $(\tau_\epsilon/\tau) \simeq 1600$. Because each electron will not spend more time than τ on a single chain, on the average it has jumped 1600 times between chains. This means that a cigar-shaped "metallic island" could be involved which is about 2000 Å long and $\sqrt{1600} \simeq 40$ chains in diameter. The higher conductivity then reflects a particularly large ratio of (τ/τ_ϵ). Further improvements of conductivity would then follow from improved purity and structure to further reduce scattering. Expectations of this model are consistent with the T independence of $\sigma_\parallel/\sigma_\perp$ and the increase of $\sigma_\parallel/\sigma_\perp$ with increasing conductivity. The model also predicts[19] that $\sigma_\parallel/\sigma_\perp$ will be frequency independent in accord with preliminary polarized infrared studies.[26]

In summary, we have measured three physical properties of highly doped new polyacetylene, which are directly related to density of states at Fermi level and its derivatives with respect to energy. Our measurements show marked differences with I_2-doped S-$(\mathrm{CH})_x$ and striking similarity with data for AsF_5-doped $(\mathrm{CH})_x$. We have used a theoretical model of bundles of coupled parallel 1D chains develops by Firsov to describe the transport mechanism in doped $(\mathrm{CH})_x$. This model predicts a transition of the electron system from localized to extended states as the interchain transfer integral increases above a threshold value. The increase of relaxation time along a single chain while maintaining a sufficiently large interchain coupling has a similar effect.[27] Increased order between chains and decreased sp^3 defects along a chain function in parallel in improving conductivity.

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