

Electron localization in polyaniline derivatives

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Electron localization in the methyl-ring-substituted derivative of polyaniline (PAN), poly(*o*-toluidine) (POT), has been investigated by transport and magnetic measurements. The HCl salt of POT shows greater electron localization than that of PAN due to decreased interchain diffusion rate caused by increased interchain separation and decreased interchain coherence. Each of these is attributed to the addition of one CH₃ to each C₆ ring. The general implications for control of dimensionality and conductivity are discussed.

Isolated chains of conducting polymers are one-dimensional (1D) entities. Models based on this 1D character have accounted for many of their unusual spectroscopic and magnetic phenomena, attributed to the presence of solitons and polarons.¹ However, it is well known that the interference of scattered electron waves causes all the electron states in a strictly one-dimensional disordered system (1D-DS) to be localized by any weak disorder.²⁻⁵ For a quasi-one-dimensional (Q1D) DS,^{5,6} if the interchain diffusion rate ω exceeds a threshold value ω_c , the states are extended; otherwise they are localized. In the localized regime, i.e., $\omega < \omega_c$, the interchain coupling tends to delocalize the electron states.⁵ In the weak interchain coupling case $\omega \ll \omega_c$, $\omega \propto 2\pi t_{\perp}^2 \tau_i / \hbar^2$ if the chains are packed into a perfect lattice⁶ (t_{\perp} is the interchain bandwidth, τ_i is intrachain mean free time, and \hbar is Planck's constant). If the chains are not packed into a perfect lattice, a smaller ω is expected due to the disorder.⁵ The value of ω depends, among others, on t_{\perp} which in turn is related to the overlap of the electron wave functions of two neighboring chains. This overlap is an exponentially decaying function of interchain distance. Hence the interchain separation is expected to be of considerable importance in the localization of a Q1D-DS. Since ω also depends on τ_i and interchain coherence length,^{5,6} these two parameters also play important roles in the electron localization. At low temperatures $k_B T \ll \hbar / \tau_i$, the conductivity of a Q1D-DS is due to variable-range hopping (VRH) among the localized states^{3,4,6} with the interchain conductivity $\sigma_{\perp} \propto \exp[-(T_0/T)^{1/2}]$ much smaller than the intrachain conductivity⁶ $\sigma_{\parallel} \propto \exp[-zT_0/16T]$ in the case of $t_{\perp} \tau_i / \hbar \ll 1$. Here $T_0 = 16a/N(E_F)k_B z$; a^{-1} is the decay length of the wave function, $N(E_F)$ the density of states at the Fermi energy E_F (for both signs of spins), e the electron charge, k_B the Boltzmann constant, and z is the number of nearest-neighbor chains. Because $\sigma_{\perp} \ll \sigma_{\parallel}$, the observed conductivity should have the same T dependence as σ_{\perp} . The hopping energies will be,⁶ respectively, $W_{\perp} \propto T^{1/2}$ and

$W_{\parallel} \propto T_0$. Since thermoelectric power³ $S(T) \propto (W^2/eT) \times [d \ln N(E)/dE]_{E=E_F}$, $S_{\perp}(T) = \text{const}$ and $S_{\parallel} \propto 1/T$. Also the dielectric constant is⁴ $\epsilon \approx 2.4 \times 16e^2 l_i^2 / \hbar v_F A$ for a sample without voids (compactness 1.0) at the $T=0$ K limit for frequencies $\nu \ll \tau_i^{-1}$ and the localization length $l_{\text{loc}} = 4l_i$ (Ref. 4) where v_F is the Fermi velocity, l_i is the mean free path, and A is the cross-section area.

In this Rapid Communication we report the consequences of this 1D nature for electron localization and conductivity, utilizing a systematic study of electron localization in the polyaniline (PAN) polymer system. With substitution of a larger methyl group (CH₃) for one hydrogen atom on each C₆ ring of the emeraldine salt form of PAN (PAN-ES) to form poly(*o*-toluidine) salt (POT-ES) (Ref. 7) (Fig. 1), there is a several percent increase in interchain separation,⁸ though crystallinity and coherence length are similar to those of PAN-ES.^{8,9} Within the crystalline regions there is greater disorder in the interchain separations,⁸ likely associated with the random location of CH₃ on *a* or *b* positions of the C₆ rings. Spectroscopic studies show that the POT-ES and PAN-ES have essentially the same electronic structures.⁷ We report here the results of magnetic susceptibility χ , dc conductivity σ_{dc} ,

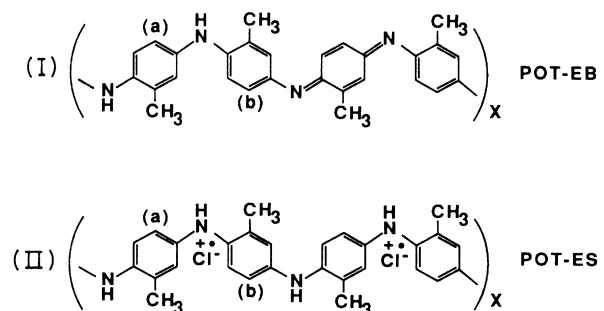


FIG. 1. Schematic structure of (I) POT-EB and (II) HCl salt of POT (POT-ES).

microwave conductivity σ_{mw} and dielectric constant ϵ , thermoelectric power $S(T)$, and EPR measurements which together reflect the increasing localization of charges associated with a decreased interchain diffusion rate and increased one dimensionality. The results are direct experimental verification of the mechanism of charge localization and provide guidelines for design of truly delocalized “metallic” polymers.

POT was synthesized in the base and salt form as described earlier.⁷ Pressed pellets were used for most of the transport measurements, with the exception of microwave studies where films cast from *N*-methyl-2-pyrrolidinone were used. A four-probe technique was utilized for σ_{dc} measurements.¹⁰ The “cavity perturbation” technique was adopted for the microwave measurement.¹¹ EPR *X*-band measurements utilized a Bruker EPS 300 spectrometer.¹² The static χ was measured by Faraday technique.¹³

Though the electronic structure of POT-ES and PAN-ES are essentially the same (as measured spectroscopically⁷), POT-ES has larger χ_{Curie} and smaller χ_{Pauli} with $N(E_F) = 1.76$ states/[eV (2 rings)] calculated from $\chi_{Pauli} = \mu_B^2 N(E_F)$ compared to 3.5 for PAN-ES,¹³ implying greater localization of the electrons.¹⁴ The larger EPR linewidth for POT-ES (0.7 vs 0.3 G for PAN-ES at 295 K) similarly suggests less motional narrowing¹⁵ and hence, increased localization. In contrast, *g* factors of POT-ES ($g = 2.0034$) and PAN-ES ($g = 2.0038$) are similar, indicating the spins are delocalized over at least one ring and nitrogen repeating unit (~ 5 Å) for both polymers, since the value of $g = 2.0034$ corresponds closely to the arithmetic mean of the *g* factors of the six *C* [$g \sim 2.0031$ (Ref. 16)] and one *N* [$g \sim 2.0054$ (Ref. 16)] in the repeat unit.

The experimental line shapes of POT-ES and PAN-ES are shown in Fig. 2, together with the 1D and 3D diffusion theoretical line shapes. For 3D spin diffusion the transverse magnetization $\Phi(t)$ varies such that $\Phi(t) \sim \exp(-t/t_0)$, resulting in a Lorentzian line shape;¹⁷ for

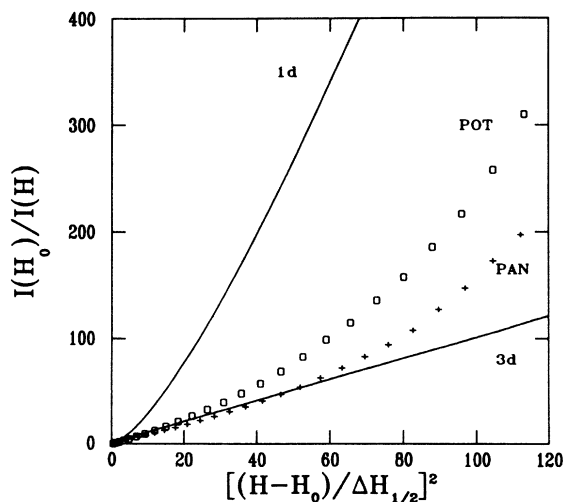


FIG. 2. The EPR line-shape data of POT-ES (\square) and PAN-ES ($+$) in comparison with the theoretical line shapes of 1D and 3D spin diffusion.

1D spin diffusion, $\Phi(t) \sim \exp[-(t/t_0)^{-3/2}]$.¹⁷ Comparison of the EPR line shapes shows that the spin diffusion in POT-ES is closer to 1D motion than that of PAN-ES, associated with the decreased interchain diffusion rate and the increased electron localization in POT-ES.

The increased localization in POT-ES is further reflected in much smaller σ_{dc} , and σ_{mw} and ϵ of POT-ES at 6.5 GHz [Fig. 3 and inset (a)] as compared with those of PAN-ES.¹¹ The *T*-dependent σ_{dc} of POT-ES (Ref. 18) varies as $\exp[-(T_0/T)^{1/2}]$ (Fig. 3) with $T_0 = 30000$ K much larger than 6000 K reported for PAN-ES,¹⁰ also indicating greater electron localization of POT-ES. The $S(T)$ can be decomposed into the sum of a constant and $1/T$ term [inset (b) of Fig. 3], suggesting Q1D VRH. Given a crystal structure with greater isolation between chains and the *T* dependence of $S(T)$, the σ_{dc} data are fit to Q1D-VRH model (the equation for σ_{\perp}). From the value of T_0 and $N(E_F)$ we estimate $a^{-1} \sim 0.88$ (2 rings) or roughly 9 Å, consistent with above *g*-factor analysis. Utilizing the equation for ϵ at $T = 0$ K and $N(E_F) = 2/\pi\hbar v_F$, assuming 0.7 sample compactness and averaging over random orientations of the polymer chains, we estimate $l_{loc} = 4l_i = 6.4$ Å for $\epsilon = 7.0 - 4.5 = 2.5$ [ϵ (EB) subtracted from ϵ (ES) (Refs. 11 and 19)]. This is in good agreement with the estimated 9 Å obtained from T_0 .

It is noted that the charging energy limited tunneling model²⁰ for granular metals also predicts $\ln\sigma \propto T^{-1/2}$, however the electric-field dependence of σ implies the size of metallic grains on the order of 1 μ m, too large for the application of the model.²¹ Similarly, 3D-VRH model in the presence of a Coulomb gap predicts $T^{-1/2}$ law.²² Within this model electron interactions cause the density of states $N(E)$ at the Fermi energy to vanish as $N(E) \propto (E - E_F)^2$. However, the finite difference of ϵ for POT-ES and POT-EB at the $T = 0$ K limit [inset (b) of Fig. 3] indicate $\epsilon - \epsilon_{\infty} \propto N(E_F) \neq 0$ (Refs. 11 and 23) (ϵ_{∞} is due to core polarization). The presence of finite χ_{Pauli} implying finite $N(E_F)$ also contradicts the application of this model.

The mechanism for the increased localization in POT as compared with PAN-ES has broad interest for both the theory of localization and the design of “metallic” polymers. The CH_3 groups induce a small increase in ring torsion angle and concomitant small decrease in the “metallic” energy bandwidth. Also, there is random CH_3 occupation of *a* or *b* position (due to ring flipping). Both effects decrease τ_i (Ref. 3) and hence ω .⁶ However, there is only less than 5% difference in bandwidth of PAN and POT with no significant broadening of the band edges observed spectroscopically.⁷ The important factors for the increased localization in POT are proposed to be the decreased interchain diffusion rate due to the decreased interchain bandwidth t_{\perp} caused by the larger transverse unit-cell length and the decreased coherence between the chains caused by greater interchain disorder within the crystalline regions. These results point to a methodology to synthesize materials of controlled one-dimensional character to further probe localization phenomena, through judicious increase or reduction in interchain coherence and separation. Similarly, the achievement of highly conducting metallic polymers then requires maxim-

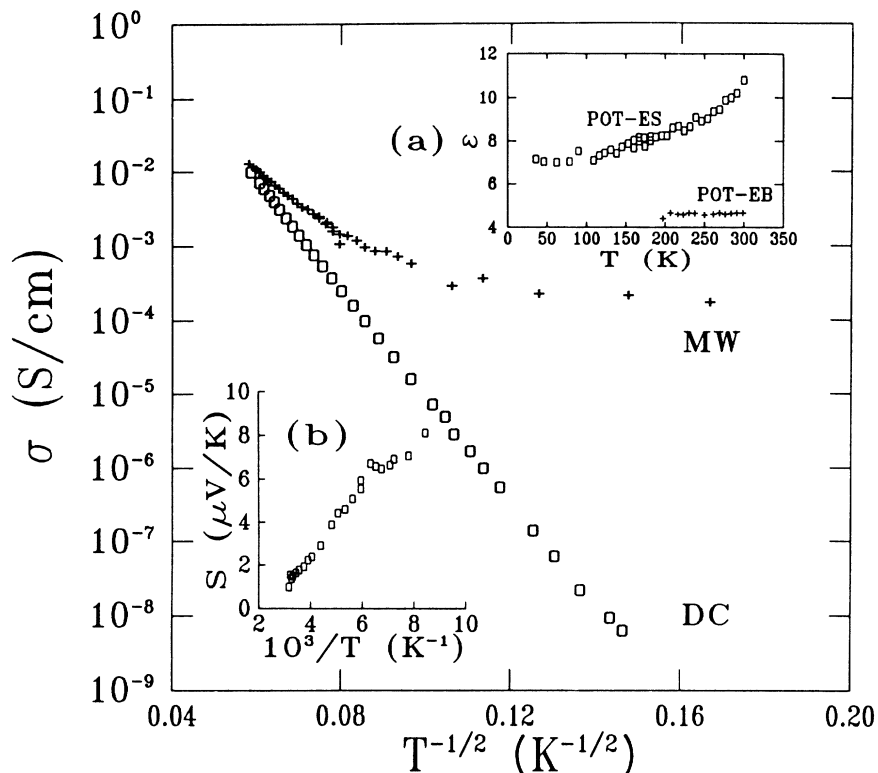


FIG. 3. T dependence of σ_{dc} (\square) and σ_{mw} (6.5 GHz) (+) for POT-ES. Inset is (a) $\epsilon(T)$ of POT-ES (\square) and POT-EB (+) and (b) $S(T)$ of POT-ES.

izing the interchain coherence and reduction of interchain separation. Increase of intrachain scattering time or conjugated length is also helpful. Hence addition of side groups to PAN and other polymers such as polypyrrole and polythiophene is likely to increase localization with concomitant decrease in conductivity in the absence of special crystal packing.

In conclusion, POT-ES shows more increased electron localization than PAN-ES. The key factor for this localization is the decreased interchain diffusion rate caused by (i) increased separation between neighboring chains and (ii) decreased coherence between the chains even within the crystalline regions. Both of these make this polymer

more 1D-like, hence more susceptible to localization. Study of various PAN derivatives enables probing of the important criteria for localization in solids and metallic behavior in polymers.

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