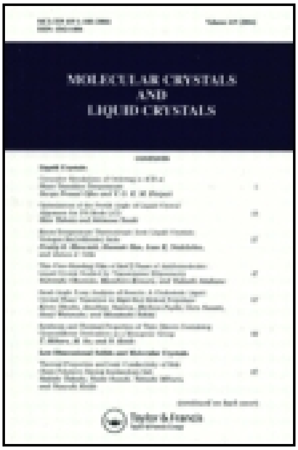

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Non-ohmic Conductivity: A Probe of the Localization Mechanism in Polyaniline Derivatives

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Non-ohmic Conductivity: A Probe of the Localization Mechanism in Polyaniline Derivatives

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Electron localization in the methyl ring-substituted derivative of polyaniline, poly(o-toluidine), has been investigated by electric field dependence of conductivity $\sigma(E)$. We found $ln\sigma(E) = KE^{1/2}$, with K varying as square root of temperature ($K \propto T^{-1/2}$). This result is in accord with quasi-one-dimensional variable range hopping of charge carriers localized along a one-dimensional chain, with an effective Coulomb barrier between adjacent sites. The measured non-ohmic conductivity is modeled by the Poole-Frenkel effect where the Coulomb potential between localized sites is lowered by the electric field. Model analysis yields an estimated effective barrier height of ~0.1 eV, corresponding to an effective charge carrier mass of the order of that of an electron. In contrast, the charging energy limited tunneling model predicts $ln\sigma \propto E^{-1}$, which is not consistent with the experimental results.

1. INTRODUCTION

Electron localization in the polyaniline (PAN) derivative poly(o-toluidine) (POT) (Figure 1) has been previously studied by transport and magnetic measurements.[1] Compared with the emeraldine salt form (PAN-ES) of PAN, the experiments showed increased electron localization in the conducting emeraldine salt form (POT-ES) of POT, as indicated by much smaller conductivity σ and dielectric constant

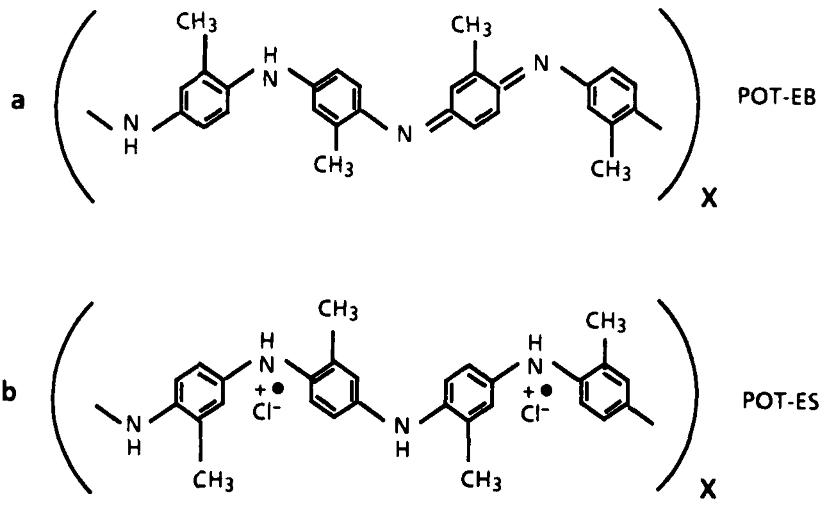

FIGURE 1 Schematic illustrations of the idealized (a) POT-EB and (b) POT-ES structures.

ϵ, different T dependence of thermoelectric power, much stronger temperature dependence of the DC conductivity σ_{DC}, smaller Pauli susceptibility χ_{pauli} and larger Curie susceptibility χ_{curie}, and larger EPR linewidth with lineshape reflecting quasi-one-dimensional spin diffusion.[1,2] The origin of the localization has been proposed[1] to be the decreased interchain diffusion rate[3], attributed[1] to the CH_3 groups on the C_6 rings which increase the separation between neighboring chains[4] due to its steric effect and induce a weak disorder in chain separations within the crystalline regions[1] since the CH_3 group flips randomly about the chain axis. Thus, the electrons are confined in segments of a chain by scattering due to limited coherence lengths along the chain and become localized.[3] At low temperatures, the electric conduction of these electrons has been attributed[1] to phonon-assistant variable range hopping in quasi-one-dimension (quasi-1d-VRH).[5]

The temperature dependence of σ_{DC} of POT was found[1] to vary as $ln\sigma_{DC} \propto T^{-1/2}$, similar to that of PAN-ES.[2] There are several models that yield this behavior, for example, charging energy limited tunneling model (CELT) for granular metals[2,6] and quasi-1d-VRH model.[5,7] In order to probe the localization phenomena we investigated the electric field dependence of the conductivity, $\sigma(E)$. Our experimental results show $\ln \sigma(E) = KE^{1/2}$ and $K \propto T^{-1/2}$. These data can be understood in terms of quasi-1d-VRH of electrons hopping among the localized states where the electrons have an effective Coulomb barrier between adjacent sites. The effective Coulomb barriers V are lowered by the applied electric field in a manner similar to the Poole-Frenkel effect. From our data we estimate that V is on the order of 0.1 eV corresponding to an effective charge carrier mass $m \sim m_e$. On the other hand, an attempt to fit the POT-ES data to CELT model gives the size of the metallic grains on the order of 1 μm, too large for the self-consistent application of this model. In Section 2 we will briefly describe the experimental techniques. In Section 3 two relevant models are compared. In Section 4 we will discuss the results and in Section 5 we present our conclusion.

2. EXPERIMENTAL TECHNIQUES

Poly(o-toluidine) (Figure 1) was synthesized in the base form as described earlier.[8] The polymer was doped to approximately 50% protonation (i.e., $x \equiv [Cl]/[N] = 0.5$) in 1 M HCl solution for at least 48 hrs and dried overnight in vacuum of 10^{-4} mba. Pressed pellets (under pressure of 9 Kba) from the dried powder were used for all measurements. Both 2-probe and 4-probe techniques were used. A sandwich geometry was adopted for the 2-probe measurements and co-planar geometry for the 4-probe studies. Sample thickness varies from 55 μ to 1 mm, and width and length from a few mm to 1 cm. Gold wires are attached to the sample surfaces either directly by conducting paste (Acheson 502 electrodag) or through thin gold films evaporated on the sample surfaces. The differences in results between the two kinds of contacts were negligible. A HP 214B Pulse Generator was used to apply voltage on the samples and a HP 7603 Oscilloscope was used for the measurements. Maximum average input power to the sample from the Pulse Generator was 10 μW and maximum voltage is 100 V, thus the maximum electric field was $E \sim 2 \times 10^4\ V/cm$ for sample thickness $d = 55\ \mu m$. The temperature was controlled by a LakeShore DRC 82C temperature controller. The displayed temperature fluctuation was on the order of 0.1 Kelvin, but due to the large size of a quartz block attached to the samples the actual temperature fluctuation of the samples was less than that.

To reduce sample heating effects due to the applied voltage, samples were in thermal contact with a block of single crystal quartz through GE 7031 varnish. The whole system was enclosed in a Janis DT dewar with He exchange gas. Although care was taken to avoid it, heating was still a serious problem in the experiment, especially for the small samples. During the experiment the width and the repetition rate of the pulses from the pulse generator were changed to monitor the heating effects.

3. MODELS

3.1 Charging Energy Limited Tunneling

The CELT model was proposed for application to granular metals.[6] This model predicts

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}] \tag{1}$$

for modest electric fields, and

$$\sigma = \sigma_0' \exp[-(E_0/E)] \tag{2}$$

in the high field regime, $e\Delta V > k_B T$, where ΔV is the voltage drop between two metallic grains. Here T_0, E_0, σ_0, σ_0' only weakly depend on T and E. The most probable separation between the centers of two metallic grains w is given by[2,6]

$$w = k_B T_0 / 4eE_0 \tag{3}$$

or

$$w = k_B T / eE_t \tag{4}$$

where E_t is the threshold electric field above which σ increases rapidly according to Equation (2) (high field regime) and k_B is the Boltzmann constant.

3.2 Quasi-One-Dimensional Variable Range Hopping

The quasi-1d-VRH model[5,7] also predicts a similar temperature dependence for the conductivity:

$$\sigma = \frac{\sigma_0}{T} \exp[-(T_0/T)^{1/2}] \tag{5}$$

where[5]

$$T_0 = \frac{8\alpha}{k_B N(E_F) z} \tag{6}$$

where $N(E_F)$ the density of states at the Fermi energy E_F, e the electron charge, k_B the Boltzmann constant, z is the number of the nearest chains and α^{-1} is the decay length of the localized state. For the case of strong localization a measure of α can be obtained from[7]

$$\alpha \approx \left(\frac{2mV}{\hbar^2}\right)^{1/2} \tag{7}$$

where V is the effective barrier height between localized sites, m is effective mass of the charge carriers. Now we consider a model in which electrons are trapped and localized in an effective potential U(r) centered at r = 0. With the application of electric field E, U is changed (Poole-Frenkel effect[9]) as

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 \epsilon r} - erE \tag{8}$$

The maximum barrier height $V = U_{\max}$ between adjacent sites will be lowered by

$$\delta V = \delta U_{max} = \left(\frac{e^3}{\pi\epsilon_0\epsilon}\right)^{1/2} E^{1/2} \tag{9}$$

Noting that α will change according to Equation (7), using Equation (5) and expanding V leads to

$$\begin{aligned} ln\sigma &\propto -(T_0(E)/T)^{1/2} \\ &\propto \frac{1}{4V}\left(\frac{T_0}{T}\right)^{1/2} \left(\frac{e^3}{\pi\epsilon_0\epsilon}\right)^{1/2} E^{1/2} \\ &= KE^{1/2} \end{aligned} \tag{10}$$

where

$$K = \frac{T_0^{1/2}}{4V}\left(\frac{e^3}{\pi\epsilon_0\epsilon}\right)^{1/2} T^{-1/2}$$

$$= K'T^{-1/2} \tag{11}$$

and

$$K' = \frac{T_0^{1/2}}{4V}\left(\frac{e^3}{\pi\epsilon_0\epsilon}\right)^{1/2} \tag{12}$$

where ϵ_0 is the vacuum dielectric constant.

The barrier height V and the effective localization length α^{-1} together can determine the tunneling mass of the moving charge carriers,

$$m = \frac{\alpha^2\hbar^2}{2V}. \tag{13}$$

4. RESULTS AND DISCUSSION

We first analyze the experimental data of POT-ES within the framework of the CELT model. POT-ES, similar to PAN-ES, has significant crystallinity (up to 50%).[4,10] The coherence length of the crystalline regions is approximately 50 Å.[4,10] There is greater disorder within the crystalline regions of POT-ES than in PAN-ES, likely associated with random orientation of the CH_3 groups. Based on studies of PAN-ES,[2,10] it is assumed that the crystalline regions are associated with highly conducting regions of the polymer ("metallic grains") and amorphous regions with lower conducting regions ("insulating media"). Hence w, the separation of the center of the "metallic grains," will be on the order of 100 Å. At T = 100 K, using Equation (4) we estimate $E_t = 8.6 \times 10^3 V/cm$. With maximum voltage 100 Volt and film thickness d = 55 μm, experiments can be carried out to a maximum $E \sim 2 \times 10^4 V/cm$, above the estimated threshold field so that the divergence predicted by Equation (2) should be observed.

The experimental results are plotted in Figure 2 as lnR^{-1} vs. $1/E$. Here R is the measured sample resistance (applied voltage/current). The data were taken by a 2-probe technique for sample of thickness 55 μ. Forcing a fit of the data to Equation (2) yields an unrealistic small value of $E_0 \sim 10^4$ V/cm, or equivalently unrealistic high value for w ($\sim$ 1 μm). This estimate of w is too large for the application of the CELT model. The CELT model assumes[6] that the charging energy which occurs when an electron hops from one neutral metallic grain to another one dominates the conduction. This charging energy is $E_c \sim e^2/\epsilon d$ where d is the dimension of the grain size. For $\epsilon \sim 7^1$ and $d \sim 1$ μm, E_c is negligibly small compared with k_BT, for the temperatures at which the experiment was executed. That is, the charging

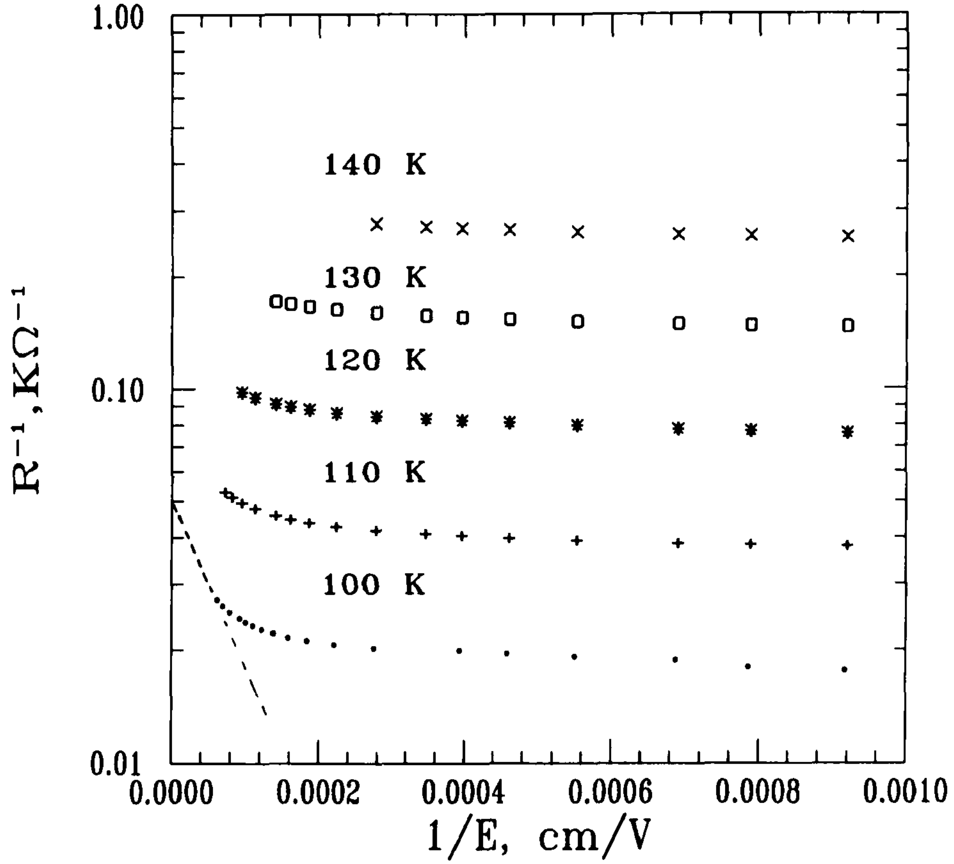

FIGURE 2 Electric field dependence of $\sigma(E)$ for a POT-ES sample at selected temperatures plotted as $ln\sigma(E)$ vs. $1/E$. The dashed line represent a slope of $E_0 \sim 10^4$ V/cm in Equation (2).

energy E_c is negligible[11] compared with thermal energy and hence cannot dominate the conduction. A slope 100 times larger than the dashed curve in Fig. 2 is necessary for consistent application of the CELT model.

Plotting the same data as lnR^{-1} vs. $E^{1/2}$, Figure 3 shows that the data fit Equation (10) reasonably well at the high field ($E > 2000$ V/cm). Calculating the slopes of each curve (inset of Figure 3) and assuming they vary as $T^{-1/2}$, we estimate $K' \approx 1.3 \times 10^{-2}(m/V)^{1/2}K^{1/2}$, using $T_0 = 35000K$ and $\epsilon \sim \epsilon_\infty = 4.5$[1,9] for POT. This gives $V \sim 0.12eV$. Using this value and $\alpha^{-1} = 7$ Å, obtained from application of Equation (5) to $\sigma(T)$,[1] we get $m \approx m_e$ according to Equation (13).

Figure 3 shows that $ln\sigma(E)$ deviates from $E^{1/2}$ at low fields ($E < 10^3V/cm$). Possible origins of this effect include field dependence of barriers and space-charge-limited injection of charges.[12]

To study the low field behavior of $\sigma(E)$ and to avoid space-charge injection effects, a 4-probe technique was utilized. Figure 4 shows $\sigma(E)$ measured by a 4-probe technique using either a direct current source or a pulsed source. Both curves could be fit into straight lines with the same slope, indicating $ln\sigma \sim E^{1/2}$ and that heating is not important. However the 2-probe $\sigma(E)$ in Figure (4) does not follow

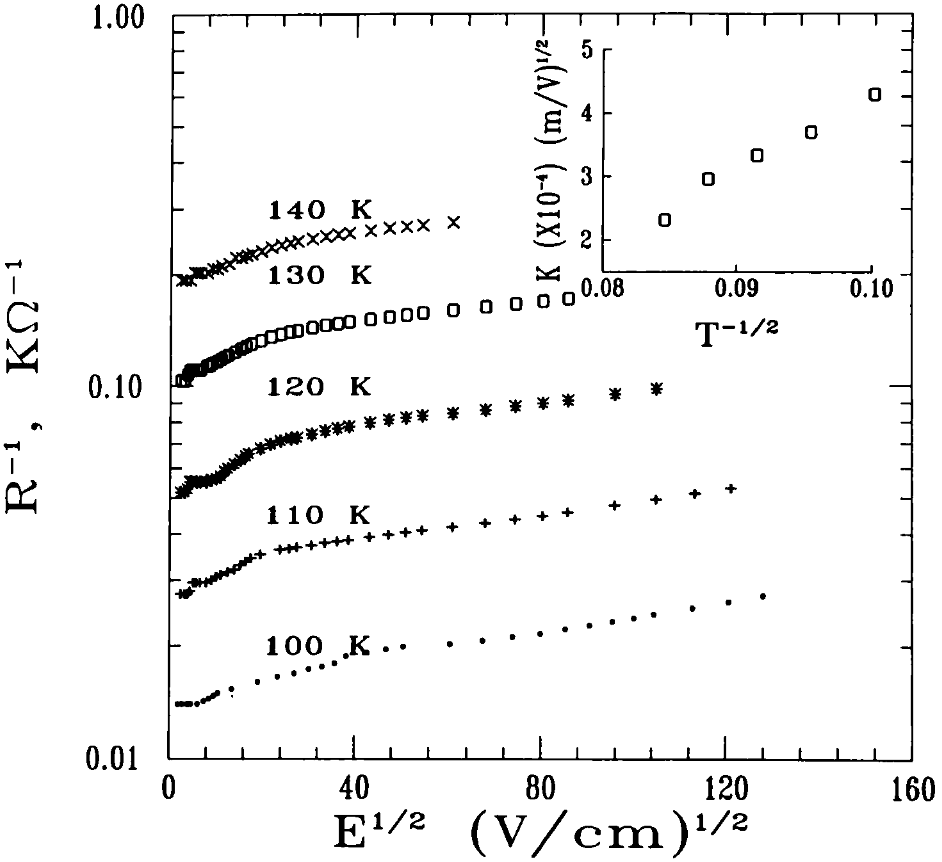

FIGURE 3 The same data of Figure 2 is plotted as $ln\sigma(E)$ vs. $E^{1/2}$. Inset is the slope K for each curve at high electric fields vs. temperature T.

the same behavior at low fields. Hence the 2-probe measurement data are not reliable in the low field region. (The 2-probe data at high field $E > 400V/cm$ may not be reliable either though we have no 4-probe data available in this regime to compare with).

The 4-probe $\sigma(E)$ at different temperatures T were studied and the change of their slopes K with T is shown in the inset of Figure 4. Assuming a linear relation between K and $T^{-1/2}$, we find $K' = 2.6 \times 10^{-2}(m/V)^{1/2}K^{1/2}$, in good agreement with $K' = 1.3 \times 10^{-2}(m/V)^{1/2}K^{1/2}$, obtained from high field measurements by the 2-probe technique. This value corresponds to $V = 60\ meV$ and effective mass $m \approx 1.3m_e$. Considering that the straight line in the inset of Figure 4 should go through the origin, we obtain a value $K' = 1.6 \times 10^{-2}(m/V)^{1/2}K^{1/2}$, and thus $V = 96meV$ and $m = 0.8m_e$. Combining all the data together we can conclude that the Coulomb potential barrier height is of the order of $0.1eV$ and the effective charge carrier mass is on the order of electron mass m_e. This result suggests that the moving charge carriers for POT-ES act as electrons in the dense band of

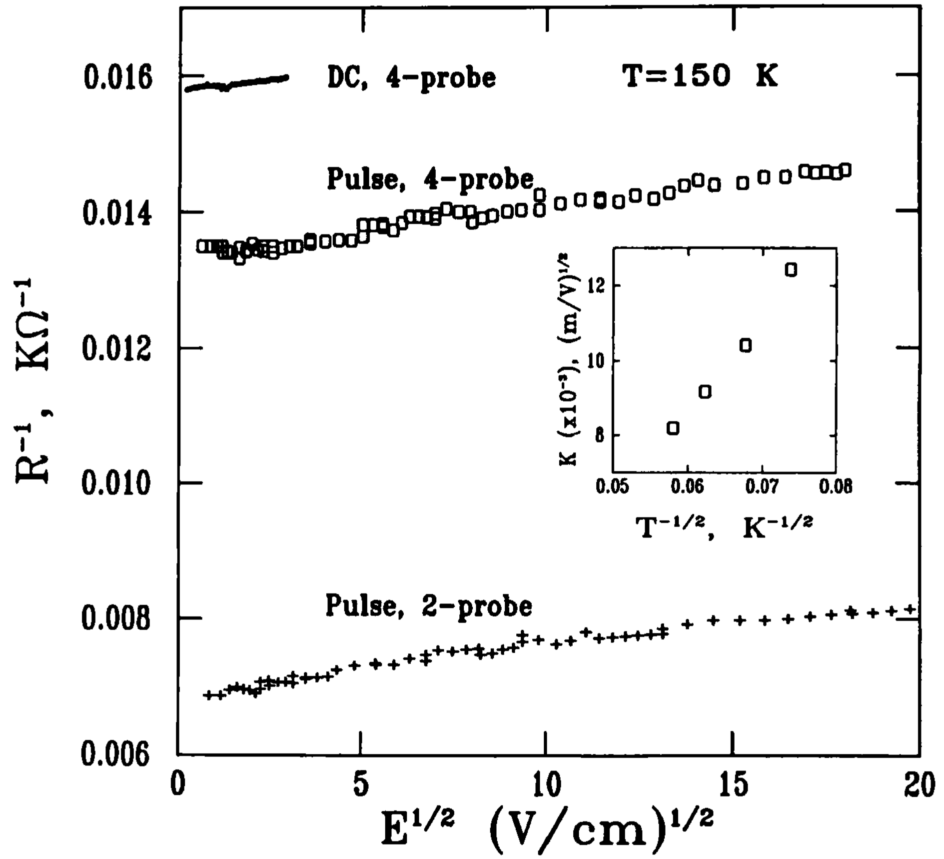

FIGURE 4 Four-probe measurements of $\sigma(E)$ in comparison with the results for two-probe measurements. The DC and pulse measurements are also compared. The inset shows the slope K of the four-probe measurements as a function of the temperature T.

localized states and hop without large C_6 ring motion characteristic of the massive polarons in lightly doped ES, EB and leucoemeraldine base.[13]

Note that although K' obtained from 2-probe $\sigma(E)$ at high field $E > 2000 V/cm$ and 4-probe $\sigma(E)$ at low field are in good agreement, the $K(T)$ are different. The values of $K(T)$ at high field are approximately one order smaller than those at low field. The difference may come from the contact resistance of 2-probe technique used in high field measurements. It is also possible that high field and low field data result from two different mechanisms. The qualitatively similar behavior was also observed in PAN-ES and other polyaniline derivatives.[15] Also the linear relation between $K(T)$ and $T^{-1/2}$ is not a unique fit of the data since the large errors in measuring $K(T)$ and the small temperature range covered by the experiment make it difficult to confirm this relation. Finally, we note that the qualitative field dependence of quasi-1d-VRH was also observed in PAN-ES at low temperatures ($10K \sim 20K$),[15] where localization is also expected to be important.[16]

The quasi-1d charge hopping has its origin in decreased interchain diffusion rate.[1]

Since CH_3 has larger steric effect than H, it increases the chain separation.[4] Due to the ring rotation CH_3 flips about the chain axis which induces a disorder in chain separation.[4] This in turn reduces the interchain coherence and further reduces the interchain diffusion rate. The latter may also induce an additional random potential which reduces intrachain mean free time τ_i and tends to localize the electron. This will also decrease the interchain diffusion rate.[1,5] The optical spectra of PAN-ES and POT-ES in aqueous 80% acetic acid solution are similar.[14] POT-ES spectra has a less than 5% shift in absorption peaks, the origin of which has been assigned[14] to a decrease of the polaron bandwidth caused by increased ring angles.[8,14] There is no significant broadening of the shoulders of the optical transitions.[14] Therefore the intrachain random potential due to varying location of the CH_3 is expected to be small.

5. CONCLUSION

The electric field dependence of conductivity of POT-ES was analyzed in terms of two localization mechanism: charging energy limited tunneling and quasi-1d-variable range hopping. Both models predict the temperature dependence of the conductivity as $ln\sigma \propto T^{-1/2}$ as observed.[1]. The $\sigma(E)$ data do not support the CELT model because the estimated size of the metallic grains would be on the order of 1 μm if this model were applied. This value is too large for a self-consistent application of this model. The $\sigma(E)$ can be understood in terms of quasi-1d-VRH model where the localized charges hop from one localized state to another along the chains. The observed $\ln \sigma(E) \propto E^{1/2}$ is modeled using the Poole-Frenkel approach where intersite potentials, assumed to be an effective Coulomb potential, are lowered by the applied electric field. The estimated potential height is about $0.1 eV$, corresponding to an effective mass of the charge carriers on the order of m_e. The origin of the increase charge localization in POT-ES was proposed to be the decrease in the interchain diffusion rate due to the increased chain separation and decreased coherence between chains caused by the CH_3 groups.[1] Our studies on the electric field dependence of the DC conductivity support this conclusion.

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