Transport studies of protonated emeraldine polymer: A granular polymeric metal system

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An experimental study of the temperature- (T) dependent dc conductivity σ , the electric field (E) dependence of σ , and the *T*-dependent thermopower *S* as a function of protonation level $(0.0 < x \equiv [H^+]/[N] \leq 0.5)$ of emeraldine polymer is presented. The conductivity $\sigma(300 \text{ K})$ varies from 10^{-10} to $10 \ \Omega^{-1}$ cm⁻¹ with increasing protonation, while $\sigma(T) \propto \exp[-(T_0/T)^{1/2}]$, with T_0 decreasing with increasing *x*. Above a threshold field E_t , $\sigma \propto \exp(-E_0/E)$, with E_0 constant. The thermopower *S* changes sign with increasing *x* and is proportional to *T* for $x \approx 0.5$. The transport properties are the first systematic evidence for the formation of a granular polymeric metal.

The mechanisms for formation of a metallic state and charge conduction in conducting polymers have been the subject of intensive study since the report of an insulatorto-metal transition occurring upon p- or n-type doping of polyacetylene,¹ and the subsequent proposal that soliton and polaron defects have a major role in these systems.²⁻⁵ The electronic state and conduction mechanisms of the emeraldine form of polyaniline have been of particular current interest.^{6,7} The polymer differs from previously reported conducting polymers in that the number of electrons on the polymer chain are held constant while the number of protons is varied. Recently, a metallic Pauli susceptibility approximately linearly proportional to the percent protonation was reported^{8,9} and a model of phase segregation into fully protonated (metallic) regions and unprotonated (insulating) regions was proposed.^{8,9} The transition to a metallic state was suggested^{8,9} to coincide with a change in the electronic structure to form a polaronic metal, Fig. 1.

Despite the metallic density of states, the conductivity reported⁶⁻¹⁰ for the fully protonated polymer is only ~ 1 S/cm. We have carried out an extensive series of transport studies of the emeraldine polymer as a function of the percent protonation in order to detect the formation of a metallic state. We report here the results of $\sigma(T,E)$ and S(T) for emeraldine as a function of protonation level, from that of unprotonated $(x \equiv [H^+]/[N] = 0.0, \text{ emeral-}$ dine base) to the fully protonated (x=0.5, emeraldine)salt) composition. At no composition does the conductivity appear truly metallic. At all compositions the conductivity is that of a granular metal and can be fit as transport via charging energy limited tunneling between conducting islands. The data are consistent with percolation among these metallic islands for $x \ge 0.3$ with the presence of an insulating layer surrounding each island above the percolation threshold. The size of these islands is estimated to be 200-300 Å.

The freestanding emeraldine films were prepared from chemically synthesized emeraldine base in aqueous acetic acid solution and subsequently treated with HCl of appropriate pH values to achieve the protonation level desired.¹⁰ The low-field four-probe $\sigma(T)$ and S(T) were measured using a previously described technique.¹¹ The electric field dependence was measured using a two-probe configuration with 10 mm² deposited gold on both sides of \sim 50-µm-thick film. Heating effects were eliminated by using 500-ns pulses with a low repetition rate. Equivalence of T dependence of two- and four-probe conductivity demonstrated the absence of contact effects. For all data presented here, the experiments were performed in vacuum on samples that were pumped on for a minimum of several hours to eliminate the effects of any absorbed moisture.

The $\sigma(T)$ of representative samples of protonated emeraldine is shown in Fig. 2 for 300 K > T > 20 K. The conductivity was measured on several preparations of each composition and was found to be reproducible at each composition. As seen in Fig. 2, the conductivity increases with increasing protonation to a maximum room-



FIG. 1. (a) Emeraldine base polymer (unprotonated); (b) polaron lattice on emeraldine salt polymer (fully protonated, x = 0.5).

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FIG. 2. $\log \sigma$ vs $T^{-1/2}$ for representative compositions of the emeraldine polymer. The inset shows the composition dependence of the slope T_0 of these curves. The solid line is a fit to $T_0 = 2500 \text{ K/x}$.

temperature value of -0.5 S/cm for samples of x = 0.5. The $\sigma(T)$ data for each x were fit to

$$\sigma = \sigma_0 \exp[-(T_0/T)^n] , \qquad (1)$$

with σ_0 a constant. In general, the best fit was achieved for n=0.5, shown in Fig. 2. Although the absolute value of the conductivity continued to increase as the protonation level increased beyond x = 0.3, the *T* dependence of σ did not change substantially for x > 0.3. The rapid variation of T_0 with x for $x \le 0.3$, and near constant value for x > 0.3 (inset of Fig. 2), reflects this behavior.

The data in Fig. 2 were taken at low fields. At high electric fields, the apparent resistance decreases rapidly, Fig. 3. For fields significantly exceeding the threshold value $E > E_t$ the apparent resistance varies as

$$R(E) = R_0 \exp(E_0/E) \tag{2}$$

with R_0 a constant. Similar behaviors are observed for all protonation levels. The 30-K data for x = 0.38 are shown in Fig. 3 while the inset in Fig. 3 shows the $\sigma(T,E)$ behavior for the fully protonated sample, x = 0.5. In all cases at high fields the resistance approaches the limiting resistance behavior given by Eq. (2), with E_0 being relatively independent of x for x > 0.3 and E_t increasing somewhat with increasing T (see inset, Fig. 3).

In light of the phase segregation into metallic and nonmetallic polymer regions demonstrated by the metallic Pauli susceptibility being approximately linear in composition x,^{8,9} the observed $\sigma(T, E)$ may be associated with the expectations of charging energy limited tunneling



FIG. 3. Sample resistance vs 1/E for a representative sample of emeraldine with x = 0.38. The temperature dependence of this field-dependent resistance for x = 0.5 composition is shown in the inset. The dashed line represents the limiting behavior, $\sigma \propto \exp - E_0/E$.

(CELT) between metallic particles embedded in a dielectric matrix.¹² The applicability of this model above a "percolation threshold" of $x \sim 0.3$ suggests the presence of an insulating boundary layer surrounding the "metallic" particles even beyond the percolation threshold. The rapid variation of T_0 for x < 0.3 is in agreement with percolation expectations.¹² Using the CELT model of Sheng,¹² the dimension of the small metal particles w including the insulating surface can be estimated as

$$w - \frac{k_B}{4|e|} \frac{T_0}{E_0} , \qquad (3a)$$

$$w = \frac{k_B T}{|e|E_l} , \qquad (3b)$$

where e is the electron charge and k_B Boltzmann's constant.

Using $T_0 = 6400$ K and $E_0 = 5 \times 10^4$ V/cm appropriate for x > 0.3, we obtain $w \sim 275$ Å from Eq. (3a). For a threshold field of 2000 V/cm at temperature of 50 K, we obtain $w \sim 200$ Å from Eq. (3b), consistent with the above estimate. A similar but independent value of the size of the metal particles has been obtained by assuming the Curie spins observed at low T were associated with localization of unpaired electrons (polarons) in the surface unit cells of the metal particles.^{8,9}

The *T*- and *x*-dependent thermopower provides an independent measure of the transport phenomena (Fig. 4). For fully protonated x = 0.5 emeraldine salt, S(300 K) $= -10 \mu \text{V/K}$, in agreement with the presence of a metallic density of states inferred from the magnetic susceptibil-



FIG. 4. Thermopower vs temperature for representative compositions of emeraldine polymer. The inset shows the variation of the room-temperature thermopower vs composition. The solid line is a fit to an effective medium theory model for thermopower; see text.

ity.^{8,9} As T decreases, S decreases linearly toward zero in agreement with expectations of a metallic behavior,

$$S = \frac{\pi^2}{3} \frac{k_B}{|e|} (k_B T) [d \ln \sigma(E)/dE]_{E_F} .$$
 (4)

Assuming energy-independent scattering and that the metallic polaron band is a symmetric half-filled onedimensional type binding band, the thermopower should be zero. The small nonzero value of the thermopower is in agreement with the asymmetric dispersion of the polaron band calculated by Stafstrom *et al.*,¹³ with predominantly electronlike curvature at the half-filled point.

The thermopower for somewhat less protonated x = 0.38 material is nearly identical to that of x = 0.50 compositions, that is, small and negative at room temperature and linearly decreasing with decreasing T. The tendency to deviate from linearity below 100 K may indicate the presence of phonon drag effects or an increasing contribution to the thermopower from the insulating regimes. For x < 0.3, the room-temperature thermopower changes sign in agreement with earlier results of Travers *et al.*⁷ There is simultaneously a change in the T dependence of S from linearly proportional to temperature, to nearly T independent for $x \sim 0.25$, to varying as $S \propto T^{-1}$ for x < 0.25.

The variation of the room-temperature thermopower with x (see inset, Fig. 4) is reminiscent of the variation of T_0 with x (inset, Fig. 2). In accord with the granular

metal model applied to the conductivity data, effective medium theory¹⁴ may be used to explain this variation of thermopower with composition. Assuming spherical metallic polymer particles embedded in the nonmetallic matrix, the effective medium theory model can be evaluated with few simple assumptions. It is assumed that the thermal conductivity of the conducting and nonconducting polymer regions is the same at high temperatures. As the measured conductivity is thought to be due to the charging energy limited tunneling between the metallic particles, the electrical conductivity of the metallic particles σ_m is assumed to be large while that of the insulating matrix σ_i between the metallic particles varies with x and is taken approximately as the measured conductivity of the composite. We, therefore, use $\sigma_m/\sigma_i = 2 \times 10^{11}$ for x near zero and 20 for x near fully protonated. Taking σ_m/σ_i varying with x as $\tanh[(x-x_c)/x_w]$ and $x_c \sim 0.1$ (concentration for most rapid increase in σ) and $x_c \sim 0.06$ in accord with $\sigma(x)$ data^{10,15} together with effective-medium theory,¹⁴ we obtain the solid line fit to the room-temperature thermopower (inset, Fig. 4). The temperature dependence of the thermopower of the composite polymer for x < 0.3 may be related to a presence of a small amount of protonation or impurities within the insulating regions of the polymer.

Preliminary diffraction experiments confirm that the protonated polymer has only limited short-range order.¹⁶ In the presence of the disorder, the formation of a Fermi glass¹⁷ and the role of a Coulomb gap¹⁸ may be expected, perhaps leading to $\sigma \propto \exp[-(T_0/T)^{1/2}]$ with T_0 inversely proportional to the localization length.¹⁸ Magnetic-susceptibility studies^{8,9} of emeraldine as a function of xshowed that the Pauli susceptibility was large (corresponding to a polaron bandwidth of 0.4 eV) and approximately linearly proportional to x in contradiction to the presence of a Coulomb gap. The systematic variation of the measured T_0 (including $T_0 = \text{const for } 0.3 < x \le 0.5$) with x together with the thermopower as a function of xsupports that the insulating regions between the small metal particles formed upon protonation dominate the transport and not the intrinsic disorder involved in the metallic particles. The origin of insulating regions may be a small nonstoichiometry in the ratio of the number of -NH-to-N= groups before protonation¹⁹ or contacts between the ~ 400 Å diameter, fibrils which make up the polymer films.²⁰

In summary, the transport studies presented here are in accord with a model of the formation of fully protonated metallic regions isolated by nonmetallic material as a function of protonation.

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