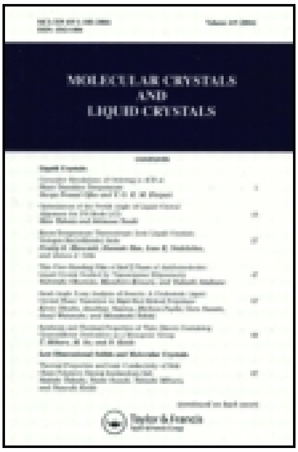

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Protonation of Emeraldine: Formation of a Granular Polaronic Polymeric Metal

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Protonation of Emeraldine: Formation of a Granular Polaronic Polymeric Metal

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A summary is presented of our recent work in the study of the physical properties of the emeraldine form of polyaniline as a function of protonation level. These studies show that upon protonation, the insulating emeraldine base becomes a conducting emeraldine salt polymer. The fully protonated form has been proposed to be a metallic polymer with an energy band formed from a lattice of polarons. Phase segregation of the partly protonated polymer into conducting and nonconducting regions leads to a conductivity dominated by charging energy limited tunneling among the "metallic" emeraldine salt regions.

I. INTRODUCTION

The polyaniline family of polymers has been known for over 75 years.[1] It has been of central interest lately because of the ability to control the electronic properties of this system through both protonation and oxidation, that is, through both a change in the number of protons per repeat unit and changes in the number of electrons per repeat unit.[2–7] The emeraldine base form of polyaniline has been proposed[5] to have equal numbers of reduced [—(C_6H_4)—(NH)—(C_6H_4)—(NH)—] and oxidized [—(C_6H_4)—N=(C_6H_4)=N—] repeat units, Figure 1a. Upon treatment of the emeraldine base form with acids of varying pH, protons are added to a fraction of the formerly unprotonated nitrogen sites

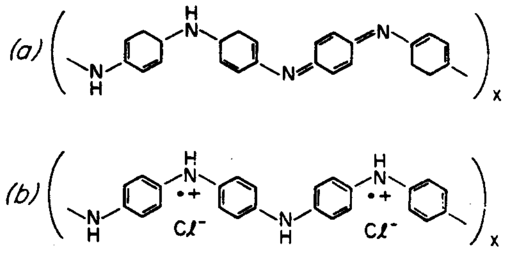

FIGURE 1 (a) Emeraldine base polymer (unprotonated); (b) polaron lattice on emeraldine salt polymer (fully protonated x = [Cl]/[N] = 0.5).

with a simultaneous increase in the electrical conductivity from the region of 10^{-10} S/cm for the base samples to $\sim$1 S/cm for the fully protonated form.[1-17] The origin of the ten orders of magnitude increase in conductivity together with the appropriate description of the electronic structure of this flexible class of materials is of fundamental interest. The relationship of the observed phenomena to the concepts relevent for nonlinear phenomena in polymers[7,18] with differing repeat units,[19] nondegenerate ground states,[20-23] and absence of charge conjugation symmetry is an aim of these studies.

In this paper we briefly review the results of coordinated chemical, electrochemical, optical, magnetic and transport studies of the emeraldine form of polyaniline as a function of protonation level. Together, these studies support that upon protonation, there is a transition to a polaronic metal with the presence of some disorder in the lattice. The conduction mechanism in these materials is dominated by the presence of barriers in the sample leading to charging energy limited tunneling among small metallic regions.

II. EXPERIMENTAL TECHNIQUES

The preparation of emeraldine base and its subsequent protonation are described elsewhere.[5,24,25] The physical studies reported here were performed in an anhydrous atmosphere or in a vacuum unless otherwise noted. The magnetic susceptibility was measured via a previously described[26] Faraday technique. The temperature dependent dc conductivity and the thermopower were measured using a previously described apparatus.[27] The techniques utilized for optical,[28] photoinduced optical,[29] audio frequency (10^1 to 10^5 Hz) conductivity,[30] and microwave (10^{10} Hz) conductivity and dielectric constant[31] are described elsewhere.

III. RESULTS AND DISCUSSION

The conductivity of emeraldine base at room temperature is $\sim 10^{-10}$ S/cm.[25,30] Upon exposure to an aqueous acid such as HCl, the conductivity increases toward a limiting value of ~1–10 S/cm.[25] Faraday and electron spin resonance studies as a function of degree of protonation and temperature demonstrate the presence of both a "Curie" type susceptibility and temperature independent Pauli susceptibility.[33] Figure 2 shows the Pauli susceptibility vs. protonation level for a number of emeraldine samples. The results are distinctly different from those for either *p* or *n*-type doping of polyacetylene.[26,32] For highest protonation level ([Cl]/[N] = 0.5) the Pauli susceptibility is approximately 7×10^{-6} emu/mole (C + N). This is more than twice the value observed in heavily doped polyacetylene ($\chi^{Pauli} = 3 \times 10^{-6}$ emu/mole-C). In addition, for doped polyacetylene, the Pauli susceptibility remains near zero until a doping level of ~0.05 charges per carbon is achieved. At that point, the susceptibility increases rapidly to the highly doped level value. For emeraldine base as a function of protonation, the susceptibility varies nearly linearly with concentration. This linear behavior has been suggested by Ginder, et al.[33] to be the result of phase segregation into metallic and nonmetallic regions. The phase segregation is in qualitative agreement with predictions of Choi and Mele.[34]

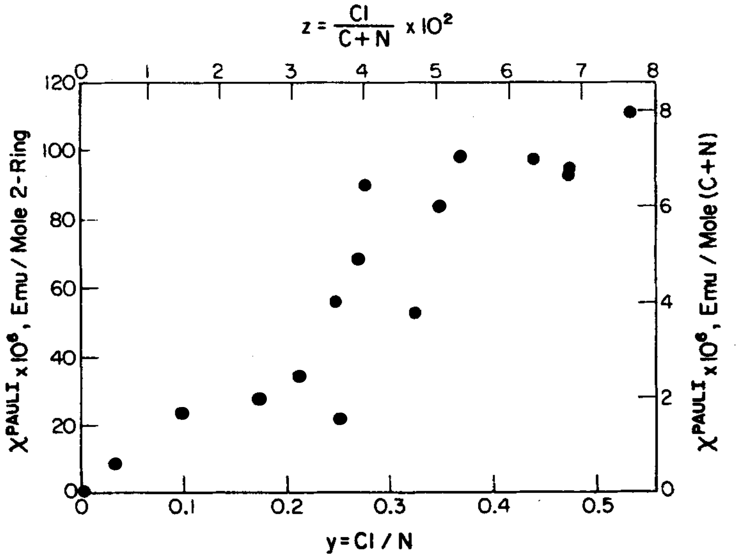

FIGURE 2 Pauli susceptibility vs. protonation level for emeraldine base polymer.

The metallic Pauli susceptibility is inconsistent with the electron distribution along the emeraldine polymer unchanged upon with addition of protons to the iimine (—N=) sites, since such an electronic structure would be spinless. It was proposed[33,35] that upon protonation of the iimine, the resulting doubly positive bipolaron type structure is unstable to formation of a nearly ordered array of polarons essentially equally spaced along the emeraldine chain, centered at, for example, every other nitrogen site. The origin of the transition from bipolaron to polaron lattice may be related to disorder, coloumb repulsion within the charged bipolaron, delocalization (kinetic) energy, dielectric screening and/or counter ion interactions. For comparison, it is noted that in a tetramer oligomer analog of emeraldine of the same oxidation state as the emeraldine salt, the charges are in equivalent of a bipolaron (spinless) ground state,[36] while doubling the length of the oligomer to an octomer leads to dissociation of the bipolaron to a state similar to that found in the polyaniline polymer.[37] Analysis of the Pauli susceptibility leads to an estimate of the density of states in emeraldine salt consistent with a polaron band width of approximately 0.5 eV.

Optical absorption studies[35,38] confirm the change in electronic structure of the emeraldine polymer upon protonation. The 2.0 eV absorption peak present in the emeraldine base (which has been assigned to the presence of an exciton[35,39]) disappears and two new optical absorptions centered at ~1.5 eV and 2.9 eV occur upon protonation. These latter two absorptions have been suggested as arising from transitions from the valance band to the polaron band formed in the gap.[35] Calculations by Stafström, et al. of a polaron band structure in protonated emeraldine[38] are consistent with the experimental results. Steady state photoinduced absorption studies of the emeraldine base polymer[29] are consistent with the formation of polarons in the band gap in the polymer upon excitation of hot excitons. Similar absorption[40] and photoinduced absorption[41] results are observed for the emeraldine base and salt polymers in solution.

Measurements of the conductivity of the emeraldine base polymer as a function of both protonation level and temperature[42] are inconsistent with dominance of three-dimensional variable range hopping.[12] Analysis of the temperature data taken at low electric fields combined with the measurement of the electric field dependence of the conductivity as a function of composition and temperature by Zuo, et al.[42] lead to the proposal of the role of charging energy limited tunneling[43] between conducting islands. The conductivity can be described as $\sigma(T) \propto \exp(-(T_0/T)^{1/2})$, with T_0 decreasing with increasing

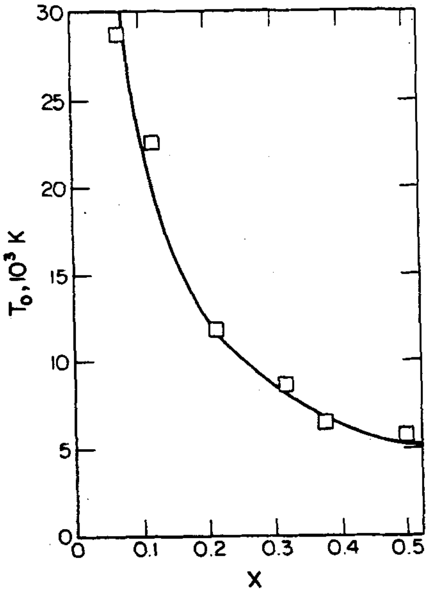

FIGURE 3 Composition dependence of slope T_0 of log σ vs. $T^{-1/2}$ for representative protonation levels of emeraldine base polymer.

protonation level, x. The variation of T_0 with x is summarized in Figure 3. The rapid variation of T_0 for $x < 0.3$ is in agreement with percolation expectations.[43] The constant value for T_0 for $x > 0.3$ suggests that barriers remain between the conducting islands even at compositions beyond the percolation threshold.

The temperature dependence of the thermopower as a function of composition is shown in Figure 4.[42] The variation of thermopower at room temperature is summarized in Figure 5.[42] The thermopower for the fully protonated $x = [\mathrm{Cl}]/[\mathrm{N}] = 0.5$ emeraldine salt, $S(300\mathrm{K}) = -10$ μV/K, is in agreement with the presence of a metallic density of states inferred from the magnetic susceptibility.[33] The linear temperature dependence of the thermopower for the $x = 0.5$ sample is also in accord with the metallic behavior of heavily protonated emeraldine. The variation of the room temperature thermopower with x, Figure 5, is reminiscent of the variation of T_0 with x, Figure 3. In agreement with the granular metal model applied to the conductivity data, an effective medium theory[44] has been used by Zuo, et al.[42] to explain this variation of thermopower with composition. Extension of the experimental studies to microwave frequency regime is in ac-

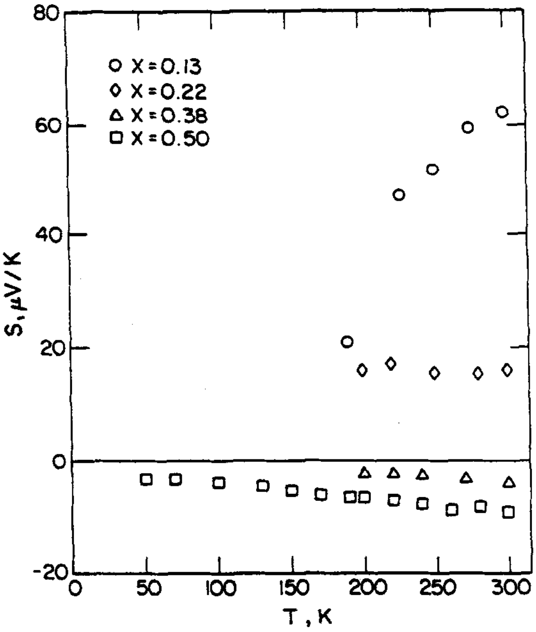

FIGURE 4 Thermopower vs. temperature for representative protonation levels of emeraldine base polymer.

cord with the granular polymeric metal nature of the emeraldine salt.[31] The variation of the measured dielectric constant with composition and temperature is in agreement with the granular polymeric metal description of emeraldine with additional indication of localization within the metallic grains at lower temperature.[31] Audio frequency conductivity studies of very lightly protonated emeraldine indicate that at low protonation levels, there is some protonation within the "insulating" regions in addition to the formation of segregated "metallic" grains.[30]

A significant variation of the measured conductivity with moisture content has been reported.[25,45] A study of the frequency (10^1 through 10^{10} Hz), composition, and moisture content variation of conductivity and dielectric constant indicates that the observed proton exchange among H_2O sites[45] does not play any significant role in determining the electronic conduction process.[46] It has been shown that the observed frequency and moisture content behavior is consistent with the continued role of barriers between the metallic polymer regions.[46]

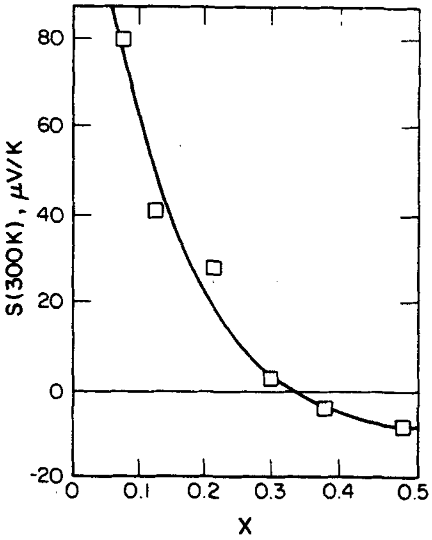

FIGURE 5 The variation of room temperature thermopower vs. protonation level of emeraldine base polymer. The solid line is a fit to an effective medium theory model for thermopower (see text).

SUMMARY

The variation of protonation level for the emeraldine base polymer produces a broad range of behaviors varying from insulating through "metallic." It has been shown that upon protonation, the polymer forms a granular polaronic polymeric metal. The polyaniline family of polymers remains intriguing in that derivitization of the polymer, for example, at either ring or nitrogen substituent positions[47] and/or elimination of barriers between the metallic grains may lead to substantially different stable states in this polymeric system.

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