

## Microwave transport in the emeraldine form of polyaniline

H. H. S. Javadi and K. R. Cromack

*Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106*

A. G. MacDiarmid

*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

A. J. Epstein

*Department of Physics and Chemistry, The Ohio State University, Columbus, Ohio 43210-1106*

(Received 1 June 1988)

The conductivity and dielectric constant of the emeraldine polymer are studied at a frequency of  $6.5 \times 10^9$  Hz as a function of temperature  $T$  and protonation levels spanning from insulating emeraldine base [ $\sigma_{dc}(295 \text{ K}) \approx 10^{-9} (\Omega \text{ cm})^{-1}$ ] to conducting emeraldine salt [ $\sigma_{dc}(295 \text{ K}) \approx 10^0 (\Omega \text{ cm})^{-1}$ ]. The microwave conductivity is larger than the dc conductivity by many orders of magnitude for the base but approaches that of dc for more conducting emeraldine salts. For lowly protonated emeraldine polymers the dielectric constant is small and almost temperature independent. For higher protonation levels the dielectric constant is linear in  $T$  with deviations observed at maximum protonation level. The dielectric constant increases monotonically with protonation for intermediate and higher-level protonated emeraldine salts. The temperature dependence of microwave conductivity differs from that of dc, especially at lower temperatures. In general, the data support the phase segregation of polymer into "metallic islands" and insulating background with localization prevailing at low temperatures. In view of the presence of barriers within the metallic islands and the increase of coherence length of the charge carriers with temperature, the phrase of "textured metallic islands" is introduced to describe the delicate role of temperature on the interplay between localization and delocalization. We review the relevance of some of the transport models to emeraldine polymers.

The polyaniline family of polymers<sup>1-4</sup> have been the focus of recent investigations.<sup>5,6</sup> The unusual properties of the emeraldine form of polyaniline, such as an insulator-to-metal transition as a result of protonation, have been investigated through magnetic,<sup>4,7,8</sup> optical,<sup>7,9</sup> photoinduced optical,<sup>10-12</sup> and transport [dc (Refs. 4, 7, and 13-18) to radio frequency<sup>14,15,18</sup>] studies. The variation of electrical, magnetic, and optical phenomena differ from studies of earlier investigated polymers such as polyacetylene, polypyrrole, and polythiophene<sup>1,2</sup> in three important aspects. First, polyaniline is not charge-conjugation symmetric; that is, the Fermi level and band gap are not formed in the center of the band so that valence and conduction bands are quite asymmetric. Second, both carbon rings and nitrogen atoms are within the conjugation path, forming a generalized "A-B"<sup>19</sup> polymer. Third, the electronic state of the polymer can be changed through variation of either the number of electrons per repeat unit or the number of protons per repeat unit.<sup>1-6,20</sup> The earlier studies of the effects of protonation on emeraldine base, inset of Fig. 1, lead to the proposal<sup>7,8,21</sup> of the transformation of the electronic structure of the emeraldine base (EB) to that of a granular polaron metal when it is protonated to form the emeraldine salt (ES). For intermediate protonation levels magnetic,<sup>8</sup> transport,<sup>13</sup> and optical<sup>7,9</sup> experiments supported the phase segregation<sup>22</sup> between highly conducting regions and insulating background. It has been proposed<sup>7,13</sup> that

the charge conduction is via charging-energy-limited tunneling<sup>23</sup> among the small granular polymeric grains.

The microwave data we present here also support these conclusions. The analysis indicates the presence of sizable barriers between "metallic" islands which prevent the samples from achieving higher conductivities even for protonation levels above the nominal percolation threshold. The importance of localization and microscopically detailed texture within the islands are revealed by our measurements at low temperatures.

Transport studies at high frequencies add a great deal of knowledge about the nature of conduction in many systems. The facts that transport measurements often involve placing contacts on the sample and contribution of the contact resistance and capacitance to the measurements are troublesome; therefore contactless probes are desirable. The "cavity perturbation method"<sup>24</sup> is a contactless measurement technique which has been utilized successfully in studies of many insulator-metal phase transitions.<sup>25-28</sup> Because of the distinct behavior of the dielectric constant for metals and insulators, the determination of dielectric constant by this technique is especially valuable.

We utilized a cylindrical  $\text{TM}_{010}$  cavity to study properties of this class of materials at resonance frequency of  $6.5 \times 10^9$  Hz. This system has been used by us for studies on other materials.<sup>27,28</sup> The cavity is made of oxygen-free high-conductivity copper; upper and lower plates were

placed on the cylindrical body of the cavity with indium O-rings as spacers and then pressed together. Application of O-rings guarantees uniform electric contacts between pieces and minimizes cavity loss due to surface current dissipation on the joints. The sample holder is made of a quartz tube (and on occasion thin-wall capillaries drawn from quartz). The microwave system with the sample holder inserted in the cavity is balanced in the absence of sample to enhance the observation of the small absorption introduced by the sample. The microwave source is a Hewlett-Packard model 8350B sweep generator. The cavity was slowly cooled from room temperature using a Janis Supravaritemp Dewar.

Samples were cut from films cast by dissolving powders of the emeraldine base form of polyaniline in solutions of acetic acid and subsequently converting them to the base form using ammonium hydroxide. These films are then protonated to the desired level using hydrochloric acid of appropriate pH.<sup>2</sup> The protonation level is described by the ratio of H<sup>+</sup> atoms added to N atoms, i.e.,  $x \equiv [\text{H}^+]/[\text{N}]$ . The formal maximum protonation level for ideal emeraldine,  $x=0.50$ , corresponds to one H<sup>+</sup> atom added to each —N= of the starting emeraldine base material. The samples were put in quartz sample holders and pumped for at least 1 h prior to filling the cavity with helium gas for measurement purposes. Our previous experience indicates that 1 h of pumping is sufficient to nearly eliminate the effect of moisture on conductivity and dielectric constant.<sup>14,16</sup>

All the measurements were performed within the range of validity of "depolarization-regime analysis," the sample thickness being less than the skin depth;<sup>24</sup> therefore electric field penetrates the sample uniformly. For some of the samples, the appropriate parameter for analysis ("metallic shift"<sup>24</sup>) was obtained from the experiment and no adjustable parameter was needed to analyze the data, but in others the parameter was chosen in accord with the predicted behavior for the conductivity, dielectric constant, and geometric estimation of this parameter. All the data are analyzed assuming 30% porosity for polymer films.

In view of the varying crystallinity and long-range order in emeraldine polymer,<sup>29</sup> the physics of disordered materials seems promising for interpretation of transport data. Lack of simple activated behavior of the dc conductivity rules out thermal excitation of carriers to extended bands above the Fermi level either from the valence band (semiconductorlike) or from the localized states at the edge of the valence band or inside the gap. Various models of hopping between localized states predict a  $T^{-n}$  dependence of  $\log_{10}\sigma$  ( $\frac{1}{4} < n < \frac{1}{2}$ ).<sup>30-38</sup> Magnetic-susceptibility measurements of polyaniline<sup>7,8</sup> revealed the presence of a finite density of states at the Fermi level  $D(E_F)$ . For localized states, the detailed energy dependence of  $D(E)$  at  $E_F$  determined the  $T^{-n}$  dependence;<sup>33</sup> e.g., depletion of  $D(E_F)$  as a result of electron correlation<sup>37</sup> predicts a  $T^{-1/2}$  dependence for three-dimensional (3D) systems as proposed by Efros and Shklovskii. Recently Nemeth and Muhlschlegel<sup>38</sup> have transferred ideas of Efros and Shklovskii about Coulomb correlations in disordered semiconductors to the case of

granular metals. They argued that  $\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}]$  behavior is only applicable for temperatures below a characteristic temperature  $T_c$ . Considering 50% protonated emeraldine salt, we estimated  $T_c$  to be less than a degree Kelvin<sup>16</sup> assuming metal islands with an average size of 100 Å.<sup>13</sup> Observation of the  $T^{-1/2}$  dependence of  $\log_{10}\sigma$  for intermediate to highly protonated emeraldine salts for  $T \gg T_c$  is not consistent with the model of Efros and Shklovskii. Sheng and Klafter<sup>33</sup> have proposed a model for hopping mechanisms in localized systems which could generate a  $T^{-n}$  law ( $\frac{1}{4} < n < \frac{1}{2}$ ) at different regimes. Their model of hopping between more conducting regions within the insulating background is consistent with the results of magnetic susceptibility,<sup>8</sup> which indicates an increase of  $D(E_F)$  with protonation level. According to Ginder *et al.*<sup>8</sup> upon protonation more "metallic islands" will be formed. This extends to a protonation level of  $x \equiv [\text{H}^+]/[\text{N}] = 0.50$  (maximum protonation level, i.e., the formal addition of one H<sup>+</sup> to —N=). The observation of "metallic islands" above the normal percolation level of ~33% in 3D systems (corresponding to  $x=0.165$ ) is reasonable in view of continued presence of structural defects such as broken bonds, chain ends, nonstoichiometric oxidation of emeraldine polymer, and double protonation of nitrogen sites. Results of microwave-conductivity and dielectric-constant measurements are interpreted in the spirit of the above. Given the limits of applicability of the numerous idealized models proposed for the electronic states and transport in materials with disorder, a description in terms of the phrase "textured metallic islands" is introduced to reflect the incomplete localization of charge even at lowest temperatures studied and the increase in the coherence length of charge carriers with increasing temperature. The concept of "textured metallic islands" is to describe qualitatively the delicate interplay between order, delocalization, Coulomb interaction, and temperature.

Figure 1 shows the microwave conductivity versus dc conductivity<sup>13</sup> for emeraldine polymers at room temperature. Emeraldine base and  $x=0.50$  protonated emeraldine salt (in the context of the polaron metal picture) are depicted in the inset. The difference in dc and microwave conductivity is much larger for samples with low protonation as indicated by the deviation of points from the straight line  $\sigma_{\mu w} = \sigma_{dc}$ . As samples become more conductive the dispersion becomes weaker and samples of higher protonation have frequency-independent conductivity up to microwave frequency. The detailed audio-frequency ( $10^1$ – $10^5$  Hz) measurements of Zuo *et al.*<sup>18</sup> are consistent with these results. Their studies of  $\sigma(\omega)$  show that the frequency at which the room temperature  $\sigma(\omega)$  deviates from  $\sigma_{dc}$ ,  $\omega_c$ , scales with the conductivity such that for emeraldine base  $\omega_c \sim 10^2$  Hz and for an  $x=0.08$  protonated sample  $\omega_c \sim 10^5$  Hz, increasing to higher frequencies for more conducting salts.

Although highly protonated samples have the same microwave conductivity as  $\sigma_{dc}$  at 300 K, their temperature dependencies are not the same. Figure 2 represents microwave and dc conductivity versus  $(1/T)^{1/2}$  for  $x=0.30$  and 0.50 protonated samples. Microwave and dc results

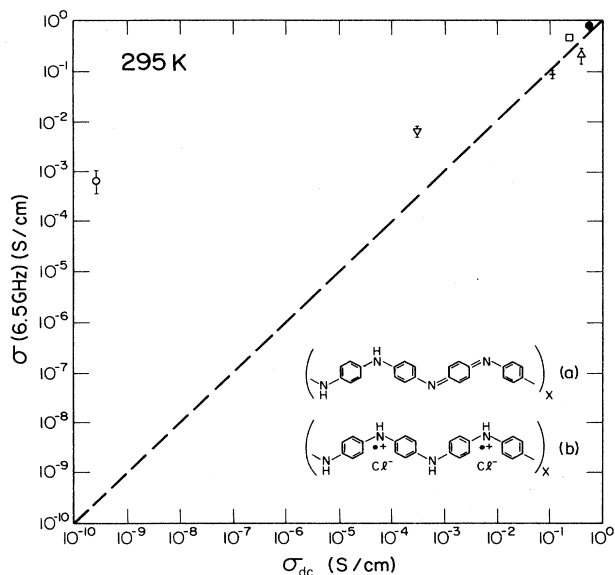


FIG. 1  $\log_{10}\sigma(6.5 \times 10^9 \text{ Hz})$  vs  $\log_{10}\sigma(\text{dc})$  at 295 K for emeraldine polymers of varying protonation level. The inset shows (a) the emeraldine base polymer and (b) the emeraldine salt polymer.

increasingly deviate at low temperatures. This behavior is expected for localized systems where motion within more conducting regions contributes to high-frequency transport. The texture of metallic islands becomes important at low temperatures as suggested by microwave data. Notice that for an  $x=0.50$  protonated sample mi-

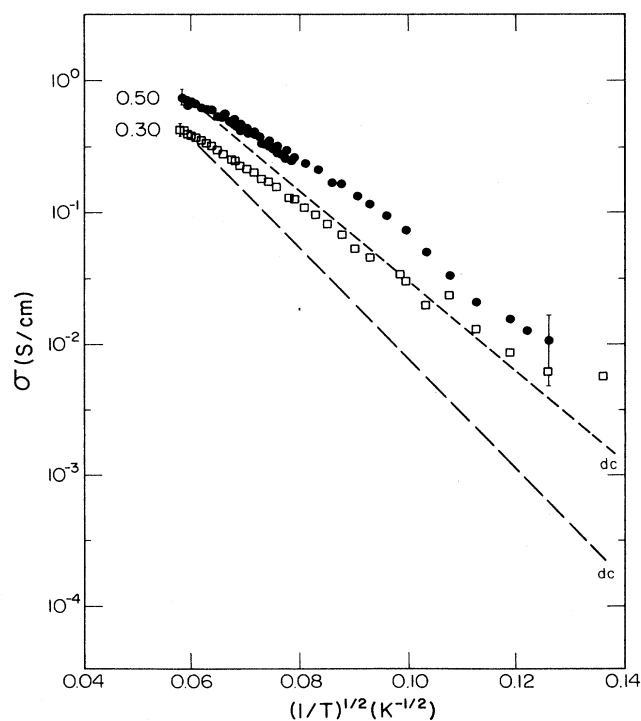


FIG. 2  $\log_{10}$  conductivity vs  $T^{-1/2}$  for emeraldine polymer of composition  $x=0.30$  and  $0.50$ . The symbols are the data at  $6.5 \times 10^9 \text{ Hz}$ , the dashed lines are data at dc (from Ref. 13).

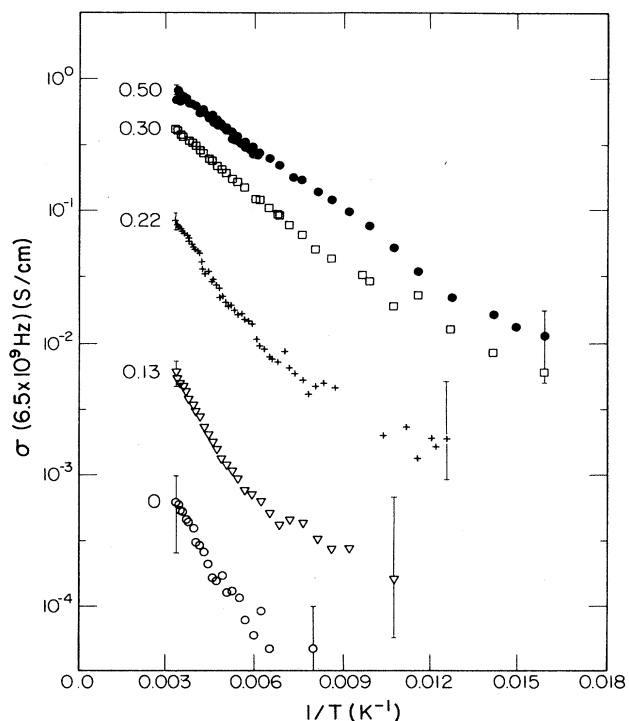


FIG. 3.  $\log_{10}\sigma(6.5 \times 10^9 \text{ Hz})$  vs  $T^{-1}$  for emeraldine polymer at representative protonation levels.

crowave and dc conductivity have slopes of comparable magnitudes. For lowly protonated samples not only is the microwave conductivity larger than the dc conductivity by many orders of magnitude, but it also has a much smaller slope.

Figure 3 is a plot of microwave conductivity versus

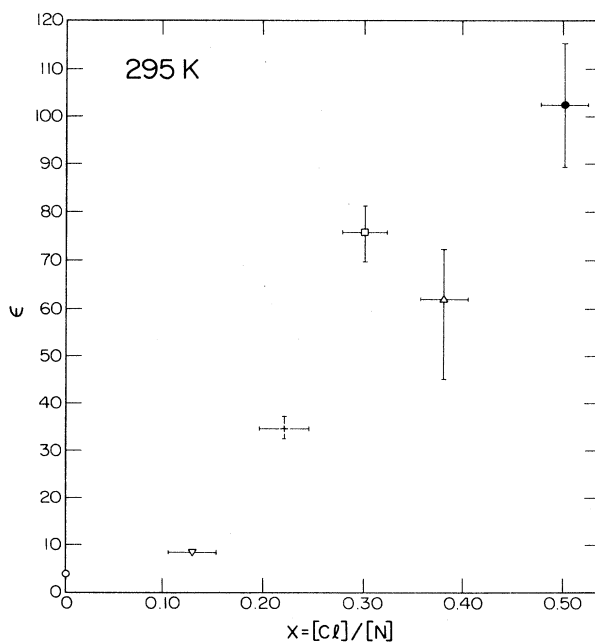


FIG. 4. Room-temperature dielectric constant vs protonation level for emeraldine polymer of representative compositions.

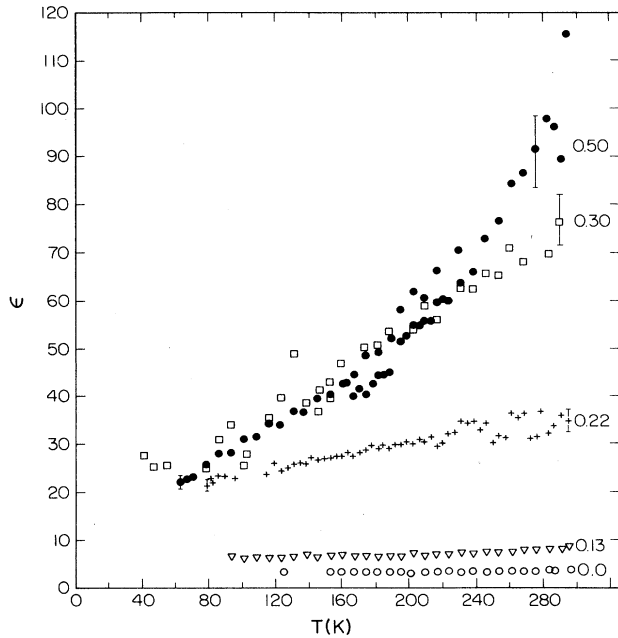


FIG. 5. Dielectric constant vs temperature for emeraldine polymer of representative protonation levels.

$1/T$  for  $x=0.0, 0.13, 0.22, 0.30,$  and  $0.50$  protonated emeraldine. It is apparent that for lowly protonated samples the curvature in the data starts at higher temperatures than for more highly protonated samples. Microwave data for the  $x=0.50$  protonated sample has a slope implying an activation energy of the order of 400 K.

Figure 4 represents the variation of the dielectric constant of the same samples at room temperature. In addition, the dielectric data for the  $x=0.38$  protonated sample is added. The dielectric constants for emeraldine base and  $x=0.13$  protonated samples are small, but  $\epsilon$  increases nearly linearly at higher protonation levels. Note that for intermediate protonation levels there is greater uncertainty in the absolute value of the data due to estimates of the depolarization factor. The error bars are indications of relative error (with respect to the other data in a temperature scan) rather than this absolute error. Figure 5 represents the temperature dependence of the dielectric constant for  $x=0.0, 0.13, 0.22, 0.30,$  and  $0.50$  protonated emeraldine polymer. A minimum dielectric constant of the order of 4 was found for emeraldine base. It has little temperature dependence and is in good agreement with a dielectric constant of approximately 5 reported for emeraldine base at  $10^5$  Hz and 78 K.<sup>18</sup> The dielectric constant changes little with protonation up to  $x=0.13$  and remains almost temperature independent for these compositions. The more protonated samples have an approximately linear increase in dielectric constant with temperature. The fully protonated emeraldine salt is an exception with stronger variation at high temperatures. The data for intermediate protonations are less accurate in their absolute values. The dielectric constants for the samples with  $x \geq 0.22$  have a larger value at lower temperatures than those with  $x < 0.22$ . This indicates a difference in underlying physics for lowly and highly pro-

tonated samples.

The dielectric constant data clearly distinguish two different behaviors for emeraldine polymers,—that for polymers of composition  $x \leq 0.13$  and that for those of composition  $x \geq 0.22$ . We concentrate first on the lightly protonated samples. The microwave and  $10^5$ -Hz measured dielectric constants are the same to within experimental error. [It is noted that at even lower frequencies at higher temperatures ( $T > 200$  K) there was a substantial increase in the dielectric constant that was attributed to a dipolar contribution to  $\epsilon$  from the hopping of electrons between isolated polaron and bipolaron states.<sup>18</sup>] The contribution to the dielectric constant that is frequency and temperature independent to  $6 \times 10^9$  Hz is likely due to electronic polarization of the emeraldine backbone. The small increase in  $\epsilon$  with protonation may reflect the contribution of isolated polarons and bipolarons formed at these doping levels oscillating about their pinning center. Assuming a pinning model<sup>39</sup> and averaging the dielectric constant over three directions,

$$\epsilon_p = \frac{4\pi}{3\epsilon_0} \frac{n_p}{V} \frac{e^2}{m_p^* \omega_0^2}, \quad (1)$$

where  $n_p = x$  is the number of polarons per ring,  $V$  the volume per ring,  $m_p^*$  the polaron effective mass, and  $\omega_0$  the polaron pinning frequency. For  $x=0.13$ , using  $V=125 \text{ \AA}^3$  and  $\epsilon_p = \Delta\epsilon = (6.7 - 3.5) = 3.2$ , and  $m_p^* \sim 50m_e$ ,<sup>12</sup> we obtain  $\omega_0/2\pi = 4.6 \times 10^{13}$  Hz or a pinning energy of 0.19 eV. Thus the polarons in emeraldine are substantially more pinned than the solitons in polyacetylene.<sup>40</sup> This is in accord with the amplitude-mode-formalism<sup>41</sup> analysis of the photoinduced and dopant-induced infrared activity in emeraldine.<sup>12</sup> The large value of  $\sigma_{\mu\omega}$  compared to  $\sigma_{dc}$  for  $x \leq 0.13$  at all  $T$  reflects the existence of some more probable hops that do not contribute to dc conductivity.<sup>35</sup>

For higher protonation levels, increase of dielectric constant with temperature is an indication of presence of potential barriers for polarizable species. A single relaxation process will yield Drude-like behavior for the dielectric constant

$$\epsilon = \epsilon_{\text{background}} + \epsilon_{\infty} + (\epsilon_{dc} - \epsilon_{\infty}) / (1 + \omega^2 \tau^2)$$

where  $\epsilon_{\text{background}} \simeq 5$  as measured for the emeraldine base,  $\epsilon_{dc}$  is the limiting value for  $\omega=0$  or  $\tau=0$ , and  $\epsilon_{\infty}$  is the high-frequency limit. An activated relaxation process  $\tau = \tau_0 \exp(\Delta/T)$  provides a model that accounts for  $\epsilon(T)$ .  $\epsilon(T) \propto T$  can be understood assuming a distribution of barrier potentials  $\Delta_{\min} < \Delta < \Delta_{\max}$  and a probability function belonging to one of Dyson's classic axioms<sup>42</sup> in random-diffusion problems. Stronger  $T$  dependence of  $\epsilon$  with increasing  $x$  may reflect a change in the distribution of  $\Delta$ 's with increasing protonation. In the limit of  $T=0$ , the dielectric constant will approach  $\epsilon_{\text{background}} + \epsilon_{\infty}$  irrespective of the frequency of measurement. Therefore observation of two different zero-temperature asymptotes for  $[\text{Cl}]/[\text{N}] > 0.13$  and  $< 0.13$  indicates the presence of more polarizable species for intermediate to highly protonated samples.

A likely origin of  $\epsilon$  in the intermediate to highly pro-

tonated regime is the effect of disorder on the motion of charge carriers. Assuming one-dimensional motion within a model of strands of metal wire,<sup>43</sup>

$$\epsilon = \frac{4\pi}{\epsilon_0} e^2 l_i^2 D(E_F), \quad (2)$$

where  $l_i$  is the effective coherence length ("mean free path") of charge carriers. From magnetic susceptibility measurements<sup>8</sup> we estimate  $D(E_F) \sim 1.5$  states/eV ring for  $x=0.50$  protonated emeraldine salt. A low  $T$  effective mean free path of  $\sim 0.7$  Å is calculated for  $x=0.50$  for a measured  $\epsilon \sim 15$ . Due to the presence of the depolarization effect in three-dimensional systems,<sup>44,45</sup> the dielectric constants reported here for the polyaniline salts are smaller than (expected) microscopic values for one-dimensional strands of wires [Eq. (2)]. Therefore the value of the coherence length of the order of 0.7 Å is an underestimate. The increased localization is reflected in the increased "Curie" susceptibility<sup>8</sup> and EPR linewidth<sup>45</sup> at low temperatures, although not all carriers need be this localized. The increase of dielectric constant with increasing temperature is again the result of the increase of the effective localization length with temperature. In the context of a strands-of-metal-wire model, barriers exist between neighboring metallic boxes. There is a broad distribution of barrier heights and at high temperatures charge carriers will not be affected by small barriers and have longer effective  $l_i$ . For example, Eq.(2) implies that the effective mean free path increases by a factor of 2.5 upon increase of  $T$  to room temperature. The linear increase of  $\epsilon$  with  $x$  for  $x > 0.22$  is in accord with the phase segregation into protonated "metallic" islands and insulating regions.<sup>13</sup>

The effective mean free path may be used to estimate a value for conductivity within the "metal islands" at low temperatures. Assuming free-carrier motion of electrons of mass  $m_e$  within a half-filled polaron band of width ( $4t_0$ ) 0.4 eV (Ref. 8) and a lattice repeat unit  $a$  of  $10$  Å, the Fermi velocity is  $v_F = 2t_0 a / \hbar \approx 3.0 \times 10^7$  cm/s and  $\tau = l_i / v_F \approx 2.3 \times 10^{-16}$  s<sup>-1</sup>. If all electrons in the polaron

band contribute to the conductivity,  $\sigma = ne^2\tau/m$  implies "intrinsic" conductivity within the "metallic islands" of  $\sim 250$  S/cm at low temperatures. Increasing effective mean free path with increasing  $T$  would lead to higher intrinsic conductivity at more elevated temperatures.

It is interesting to note that the protonated emeraldine form of polyaniline shows a large electric loss tangent at the microwave frequency of measurement. Moreover, this loss tangent increases monotonically with the protonation level of the polymer. At room temperature for  $x=0.22$ ,  $\tan\delta \equiv \epsilon''/\epsilon' \sim 0.8$ , increasing to  $\sim 1.5$  for  $x=0.30$  and further to a value of  $\sim 2.3$  for  $x=0.50$ . Moisture increases both the microwave conductivity and dielectric constant of  $x=0.50$  emeraldine salt<sup>16</sup> such that the loss tangent of a fully protonated emeraldine polymer under dynamic vacuum increases by a factor of  $\sim 3.5$  upon exposure to moisture. The values of the loss tangent should be compared to the value of  $\sim 1.2$  for commercially available carbon-filled insulating polymers.<sup>46</sup> Variation of the loss tangent with protonation level of emeraldine polyaniline makes this polymer a very fascinating material.

In summation, the temperature and composition behavior of the microwave-frequency conductivity and dielectric constant shows a systematic increase in dielectric constant and change in transport with increasing protonation level. At low protonation levels,  $x \leq 0.13$ , the charges are strongly pinned and the conductivity is by hopping. For higher protonation levels, the dielectric constant increases substantially and the microwave conductivity approaches the dc conductivity at room temperatures. Analysis of these data supports the increased delocalization of charge, reflecting the formation of "textured metallic islands" as well as the effect of localization and the delicate roles of temperature and local order in the balance between these opposing phenomena.

We thank F. Zuo and G. Mihaly for critical discussions. This work was supported in part by the Defense for Advanced Research Projects Agency through a grant monitored by the U.S. Office of Naval Research.

<sup>1</sup>A. G. Green and A. E. Woodhead, *J. Chem. Soc.* 2388 (1910).

<sup>2</sup>A. G. MacDiarmid, J.-C. Chiang, M. Halpern, W.-S. Huang, J. R. Krawczyk, R. J. Mammone, S.-L. Mu, N. L. D. Somasiri, and W. Wu, *Polym. Prepr.* **25**, 248 (1984); J. C. Chiang and A. G. MacDiarmid, *Synth. Met.* **13**, 193 (1986); A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *ibid.* **18**, 285 (1987).

<sup>3</sup>A. G. MacDiarmid, J.-C. Chiang, M. Halpern, W.-S. Huang, S.-L. Mu, N. L. D. Somasiri, W. Wu, and S. I. Yaniger, *Mol. Cryst. Liq. Cryst.* **121**, 173 (1985).

<sup>4</sup>J. P. Travers, J. Chroboczek, F. Devreux, F. Genoud, M. Nechtschein, A. Syed, E. M. Genies, and C. Tsintavis, *Mol. Cryst. Liq. Cryst.* **121**, 195 (1985).

<sup>5</sup>See, for example, Proceedings of the International Conferences on Synthetic Metals, Kyoto, 1986 [*Synth. Met.* **17-19** (1987)].

<sup>6</sup>See, for example, Proceedings of the International Conferences

on Synthetic Metals, Vadstena, 1986 [*Synth. Met.* **21** (1987)].

<sup>7</sup>A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H. S. Woo, D. B. Tanner, A. F. Richter, W.-S. Huang, and A. G. MacDiarmid, *Synth. Met.* **18**, 303 (1987).

<sup>8</sup>J. M. Ginder, A. F. Richter, A. G. MacDiarmid, and A. J. Epstein, *Solid State Commun.* **63**, 97 (1987).

<sup>9</sup>H. Kuzmány, N. S. Sariciftci, H. Neugebauer, and A. Neckel, *Phys. Rev. Lett.* **60**, 212 (1988).

<sup>10</sup>M. G. Roe, J. M. Ginder, P. E. Wigen, A. J. Epstein, M. Angelopoulos, and A. G. MacDiarmid, *Phys. Rev. Lett.* **60**, 2789 (1988).

<sup>11</sup>A. J. Epstein, J. M. Ginder, M. G. Roe, T. L. Gustafson, M. Angelopoulos, and A. G. MacDiarmid, in *Materials Research Conference Proceedings*, edited by A. J. Heeger, J. Orenstein, and D. R. Ulrich (MRS, Pittsburgh, 1988), Vol. 109, p.313.

<sup>12</sup>R. P. McCall, M. G. Roe, J. M. Ginder, T. Kusumoto, A. J.

- Epstein, E. M. Scherr, and A. G. MacDiarmid, *Synth. Met.* **29**, 433 (1989), and unpublished.
- <sup>13</sup>F. Zuo, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B* **36**, 3475 (1987).
- <sup>14</sup>H. H. S. Javadi, F. Zuo, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, *Mol. Cryst. Liq. Cryst.* **160**, 225 (1988).
- <sup>15</sup>T. Hayashi, Y. Hirai, H. Tanaka, and T. Nishi, *Jpn. J. Appl. Phys.* **26**, L1800 (1987).
- <sup>16</sup>H. H. S. Javadi, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.* **26**, 1 (1988).
- <sup>17</sup>B. Lundberg, W. R. Salaneck, and I. Lundström, *Synth. Met.* **21**, 143 (1987).
- <sup>18</sup>F. Zuo, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, preceding paper, *Phys. Rev. B* **39**, 3570 (1989).
- <sup>19</sup>M. J. Rice and E. J. Mele, *Phys. Rev. Lett.* **49**, 1455 (1982).
- <sup>20</sup>A. G. MacDiarmid, J.-C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Met.* **18**, 285 (1987).
- <sup>21</sup>S. Stafström, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, and A. G. MacDiarmid, *Phys. Rev. Lett.* **59**, 1464 (1987).
- <sup>22</sup>H.-Y. Choi and E. J. Mele, *Phys. Rev. Lett.* **59**, 2188 (1987).
- <sup>23</sup>B. Abeles, P. Sheng, M. D. Coutts, and Y. Arie, *Adv. Phys.* **24**, 407 (1975); *Phys. Rev. Lett.* **31**, 44 (1973).
- <sup>24</sup>L. Buravov and I. F. Shchegolev, *Prib. Tekh. Eksp.* **2**, 171 (1971).
- <sup>25</sup>W. J. Gunning, S. K. Khanna, A. F. Garito, and A. J. Heeger, *Solid State Commun.* **21**, 765 (1977).
- <sup>26</sup>G. Mihaly, G. Vancso, S. Pekker, and A. Janossy, *Synth. Met.* **1**, 357 (1979/80); A. Feldblum, Y. W. Park, A. J. Heeger, A. G. MacDiarmid, G. Wnek, F. Karasz, and J. C. W. Chien, *J. Polym. Sci.* **19**, 173 (1981).
- <sup>27</sup>H. H. S. Javadi, J. S. Miller, and A. J. Epstein, *Phys. Rev. Lett.* **59**, 1760 (1987).
- <sup>28</sup>H. H. S. Javadi, R. Laversanne, and A. J. Epstein, *Phys. Rev. B* **37**, 4280 (1988).
- <sup>29</sup>W. Fosong, T. Jinsong, W. Lixinag, Z. Hongfang, and M. Zhishen, *Mol. Cryst. Liq. Cryst.* **160**, 175 (1988). New x-ray diffraction studies have shown samples of emeraldine-base polymer of the type studied here to be essentially amorphous of structure EBI. Doping of EBI leads to the partially crystalline ESI structure [M. Jozefowicz, R. Laversanne, H. H. S. Javadi, A. J. Epstein, J. P. Pouget, X. Tang, and A. G. MacDiarmid (unpublished)].
- <sup>30</sup>A. J. Epstein, *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 2, p. 1041.
- <sup>31</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).
- <sup>32</sup>P. Nagels, in *Amorphous Semiconductors*, Vol. 36 of *Topics in Applied Physics*, edited by M. H. Brodsky (Springer-Verlag, Berlin, 1979), p. 114.
- <sup>33</sup>P. Sheng and J. Klafter, *Phys. Rev. B* **27**, 2583 (1983).
- <sup>34</sup>T. Chui, G. Deutscher, P. Lindenfeld, and W. L. McLean, *Phys. Rev. B* **23**, 6172 (1981).
- <sup>35</sup>N. F. Mott, *Philos. Mag.* **19**, 835 (1969).
- <sup>36</sup>V. Ambegaokar, B. I. Halperin, and J. S. Langer, *Phys. Rev. B* **4**, 2612 (1971).
- <sup>37</sup>A. L. Efros and B. I. Shklovskii, *J. Phys. C* **8**, L49 (1975).
- <sup>38</sup>R. Nemeth and B. Muhlschlegel, *Z. Phys. B* **70**, 159 (1988).
- <sup>39</sup>P. A. Lee, T. M. Rice, and P. W. Anderson, *Solid State Commun.* **14**, 703 (1974).
- <sup>40</sup>A. J. Epstein, H. Rommelmann, R. Bigelow, H. W. Gibson, D. M. Hoffman, and D. B. Tanner, *Phys. Rev. Lett.* **50**, 1866 (1983).
- <sup>41</sup>E. Ehrenfreund, Z. Vardeny, O. Brafman, and B. Horowitz, *Phys. Rev. B* **36**, 1535 (1987).
- <sup>42</sup>F. J. Dyson, *Phys. Rev.* **92**, 1331 (1953).
- <sup>43</sup>M. J. Rice and J. Bernasconi, *Phys. Rev. Lett.* **29**, 113 (1972).
- <sup>44</sup>S. Strassler, M. J. Rice, and P. Wyder, *Phys. Rev. B* **6**, 2575 (1972).
- <sup>45</sup>R. Laversanne, H. H. S. Javadi, E. Scherr, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.* **29**, 439 (1989), and unpublished.
- <sup>46</sup>See, for example, the catalogue of Emerson & Cuming, Inc., Woburn, MA 01888.