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# ac conductivity of emeraldine polymer

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

M. Angelopoulos and A. G. MacDiarmid
*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

A. J. Epstein
*Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1106*

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An experimental study of the temperature- ($T$-) dependent dc and audio-frequency conductivity ($\sigma$) as a function of protonation level ($0.0 \leq x \equiv [\mathrm{H}^+]/[\mathrm{N}] \leq 0.08$) of emeraldine polymer is presented. The dc conductivity varies from $10^{-10}$ S/cm for $x=0$ to $10^{-6}$ S/cm for $x=0.08$ and is proportional to $\exp[-(T_0/T)^{1/4}]$ with $T_0$ decreasing with increasing $x$. The temperature-dependent audiofrequency $f$ ($10^1$–$10^5$ Hz) conductivity varies as $f^s$ with $s \sim 0.9$ for $x=0$, decreasing with increasing $x$. For frequencies greater than $10^3$ Hz the dielectric constant agrees with the $T$-independent dielectric constant measured by microwave techniques. At lower frequencies and high temperatures the dielectric constant increases. A Cole-Cole analysis shows the presence of primarily a single thermally activated relaxation process in these materials with a dispersion in relaxation rates. These results are discussed in the context of models for dc and ac transport in polymers, with results supporting hopping of charge among positively charged polaron and bipolaron or neutral defect (polaron) states in the emeraldine polymer. A simple analysis yields estimates of $3.7 \times 10^{-3}$ bipolarons per polaron in the $x=0$ system, increasing with protonation to $7.9 \times 10^{-2}$ for $x=0.08$.

## I. INTRODUCTION

Mechanisms of charge conduction in conducting polymers have been of interest since the report of $p$ and $n$ doping of polyacetylene to the metallic state.[1–3] The presence of localized electronic states of energies less than the band gap arising from changes in local bond order, including the formation of solitons, polarons, and bipolarons have lead to the possibility of new types of charge conduction present in these polymer systems.[4–8] As a function of degree of $p$- or $n$-type doping the room-temperature conductivity of polyacetylene can be varied from $10^{-13}$ S/cm to $10^5$ S/cm.[9–12] For lightly doped *trans*-polyacetylene a novel electron hopping conduction model involving hopping among soliton states[13] was invoked to account for some of the unusual ac-conductivity results[14] for this polymer. This model required the presence of mobile neutral solitons. More usual variable-range-type hopping models[15,16] were applied to more insulating and disordered forms of polyacetylene[9] as well as to the *trans*-polyacetylene itself.[17,18] Doping polyacetylene to a level of 0.01–0.04 dopant ions per carbon atom lead to conductivities in the range of $10^{-1}$–$10^{+2}$ S/cm. Models that have been applied include variable-range hopping among states near the Fermi energy,[19–23] thermal activation of charge carriers to band-edge states,[24,25] diffusion of charged solitons,[26,27] and the interchain hopping of correlated soliton pairs.[28] At yet higher doping concentrations ($y > 0.05$) where the density of states becomes metal-like and the conductivity becomes much more metallic,[9,19,22,23,25,26] models of a gapless incommensurate Peierls semiconductor[29] and a transition to a polaronic metal[30] have been suggested. Most recently, use of a catalyst with additional reducing agents has led to a form of polyacetylene that, when doped with iodine, has conductivities up to $10^5$ S/cm at room temperature.[10,11] The origin of this high conductivity may lie in quasi-one-dimensional nature of the polymer electronic structure.[31]

The polyaniline family of polymers[32–35] has recently been the subject of intensive study.[3] The emeraldine-base (EB) form of the polymer, illustrated in Fig. 1(a), differs substantially from earlier studied polymers in several important aspects. First, it is not charge-conjugation symmetric; that is, the Fermi level and band gap are not formed in the center of the $\pi$ band so that the valence and conduction bands are very asymmetric.[36] Consequently, the energy-level positions of doping-induced[36,37] and photoinduced[38–40] absorptions differ substantially from those in charge-conjugation-symmetric polymers such as polyacetylene, polypyrrole, and polythiophene.[2,3] Second, both carbon rings and nitrogen atoms are within the conjugation path, forming a generalized "$A$-$B$" polymer.[4] Thus, the emeraldine polymer differs substantially from polypyrrole and polythiophene, whose heteroatoms do not contribute significantly to the $\pi$-band formation.[42] Third, the emeraldine base form of polyaniline can be converted from an insulating (conductivity $\sigma \sim 10^{-10}$ S/cm) to a "metallic" state [$\sigma$(295 K)$\sim$5 S/cm] if protons are added to the —N= sites while the number of

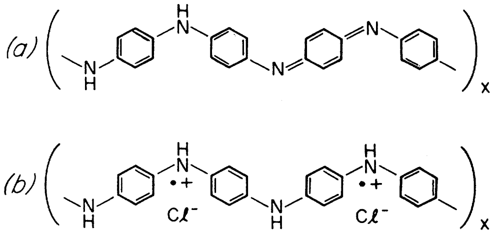

FIG. 1. Schematic illustration of (a) emeraldine base polymer (unprotonated); (b) polaron lattice on emeraldine salts polymer (fully protonated, $x=0.5$).

electrons in the chain is held constant.[33,34,37,43] For example, exposure of the emeraldine base polymer to a protonic acid such as HCl causes a transformation to the emeraldine salt (ES) form of polyaniline, Fig. 1(b). The salt polymer exhibits metallic properties including Pauli susceptibility,[43] a metallic thermopower,[44] and a free-carrier absorption typical of a metal.[37,45,46] It was proposed[37,43] that the transformation to the metallic state was due to formation of a polaron lattice in the material in subsequent agreement with band-structure calculations.[36] Partial protonation leads to phase segregation between protonated and unprotonated regions,[37,43–47] especially for $x>0.1$.

There has been increasing interest in the temperature and composition behavior of the conductivity of polyaniline and in the mechanisms of this conduction. Most studies have focused on the transport properties of the heavily protonated emeraldine salt materials.[35,48–54] A recent detailed study of Zuo *et al.*[44] of the $T$ dependence of $\sigma_{\text{dc}}$, the electric field dependence of $\sigma$, and the $T$ dependence of the thermopower as a function of protonation level $(0.13\leq x\leq 0.5)$ of emeraldine polymer established the first systematic evidence for the formation of a granular polymeric metal. That is, within this protonation regime the charge conduction is dominated by the phase segregation into primarily protonated and unprotonated regions leading to the importance of mechanisms such as charging-energy-limited tunneling.[55] The conductivity of the metallic emeraldine salt polymer is sensitive to the environmental humidity.[56–60] Frequency-dependent conductivity studies in the frequency range $10^1-10^{10}$ Hz (Refs. 59 and 60) demonstrated that the primary effect of moisture is on the barriers between the small metallic polymeric polymer grains. There are fewer studies of[61,62] of charge conduction in the more insulating forms of polyaniline. Frequency-dependent conductivity measurements of partly protonated emeraldine[62] were proposed to support the presence of an interpolaron hopping mechanism similar to the intersoliton hopping mechanism proposed earlier by Kivelson.[13] However, the limited composition range studied did not allow an adequate test for the model.

In view of the varying crystallinity and long-range order,[63] the physics of disordered materials is likely important for interpretation of transport data. Given the limits of applicability of the numerous idealized models proposed for electronic states and transport in materials with disorder, the phrase "textured metallic islands" was introduced to describe results of microwave-frequency $(6.5\times 10^9$ Hz) studies of the more highly conducting emeraldine compositions.[64] This phase reflects qualitatively the delicate interplay between order, delocalization, Coulomb interaction, and temperature.

We report here the results of an extensive study of the temperature dependence of the dc and ac $(10^1-10^5$ Hz) conductivity of the emeraldine polymer protonated in the range $0\leq x\leq 0.08$. Our results are inconsistent with a Kivelson-type interpolaron hopping between polaron and bipolaron sites. It is proposed that the dominant mechanism involves pairwise hopping of charges among polaron and bipolaron sites in the primarily "unprotonated" regions of the emeraldine base polymer.

In Sec. II we present a summary of the experimental techniques used as well as sample preparation methods. Section III is a presentation of our experimental results which are discussed in Sec. IV. A summary of our results are presented in Sec. V.

## II. EXPERIMENTAL TECHNIQUES

The ac- and dc-conductivity studies were carried out on both powders and films of emeraldine protonated to the appropriate level with nearly identical results. The emeraldine films were prepared from chemically synthesized emeraldine base in aqueous acetic acid solution and subsequently treated with HCl of appropriate $p$H to achieve the protonation level desired.[56,61] The powders were synthesized by previously described chemical technique.[33] The pressed pellet samples were compressed using a pressure of 15 Kpsi to obtain a sample of typical thickness of 0.5 mm. In the typical experimental configuration 1-cm-diam circular gold coatings were evaporated on opposite sides of the sample to act as electrodes. A gold-coated guard ring was also used to eliminate possible fringe effects. Conductivity data were acquired using a General Radio capacitance conduction bridge Model H21 in its three-terminal configuration. The dc conductivity was measured using a high-input-impedance Keithly model 617 electrometer on the same sample. For all data presented here, the samples were pumped for a minimum of several hours to eliminate the effects of any absorbed moisture. Temperature control in the range $78<T<375$ K was provided by a Delta "oven" model 5900.

## III. EXPERIMENTAL RESULTS

We present here the temperature dependence of the dc conductivity, audio-frequency conductivity, and audio-frequency dielectric constant for samples of composition $x=0.0$ (EB), 0.017, and 0.08. Experimental results for different samples of the same nominal composition were very similar. The dc conductivity is strongly $T$ dependent and varies in both magnitude and temperature dependence with composition. In order to enable comparison to the numerous models for transport in materials with disorder, the dc and ac data are presented in several formats. The Arrhenius plot, Fig. 2(a), is a modestly good fit to the data for the emeraldine base sample, especially at the higher temperatures. With increasing protonation the degree of curvature at low temperatures increases. For the $x = 0.0$ and 0.017 protonated samples, the high-temperature slope of $\log_{10}\sigma_{dc}$ versus $T^{-1}$ are large with an activation energy $E_a \sim 0.5$ eV (Table I) and

$$\sigma_{dc} = \sigma_0 \exp\left[\frac{-E_a}{k_B T}\right] . \quad (1)$$

A better overall fit to the dc conductivity is obtained using the variable-range-hopping formalism

$$\sigma_{dc} = 2\left[\frac{9\alpha N_0}{8\pi k_B T}\right]^{1/2} v_{ph} \exp[-(T_0/T)^{1/4}] , \quad (2)$$

where

$$T_0 = \frac{16}{k_B N_0 \alpha^3} . \quad (3)$$

Here $N_0$ is the density of states at the Fermi level, $v_{ph}$ is a (phonon) attempt frequency, and $\alpha$ is a three-dimensionally averaged characteristic decay length for the localized sites involved in the variable-range hopping. To facilitate comparison, the dc-conductivity data are re-

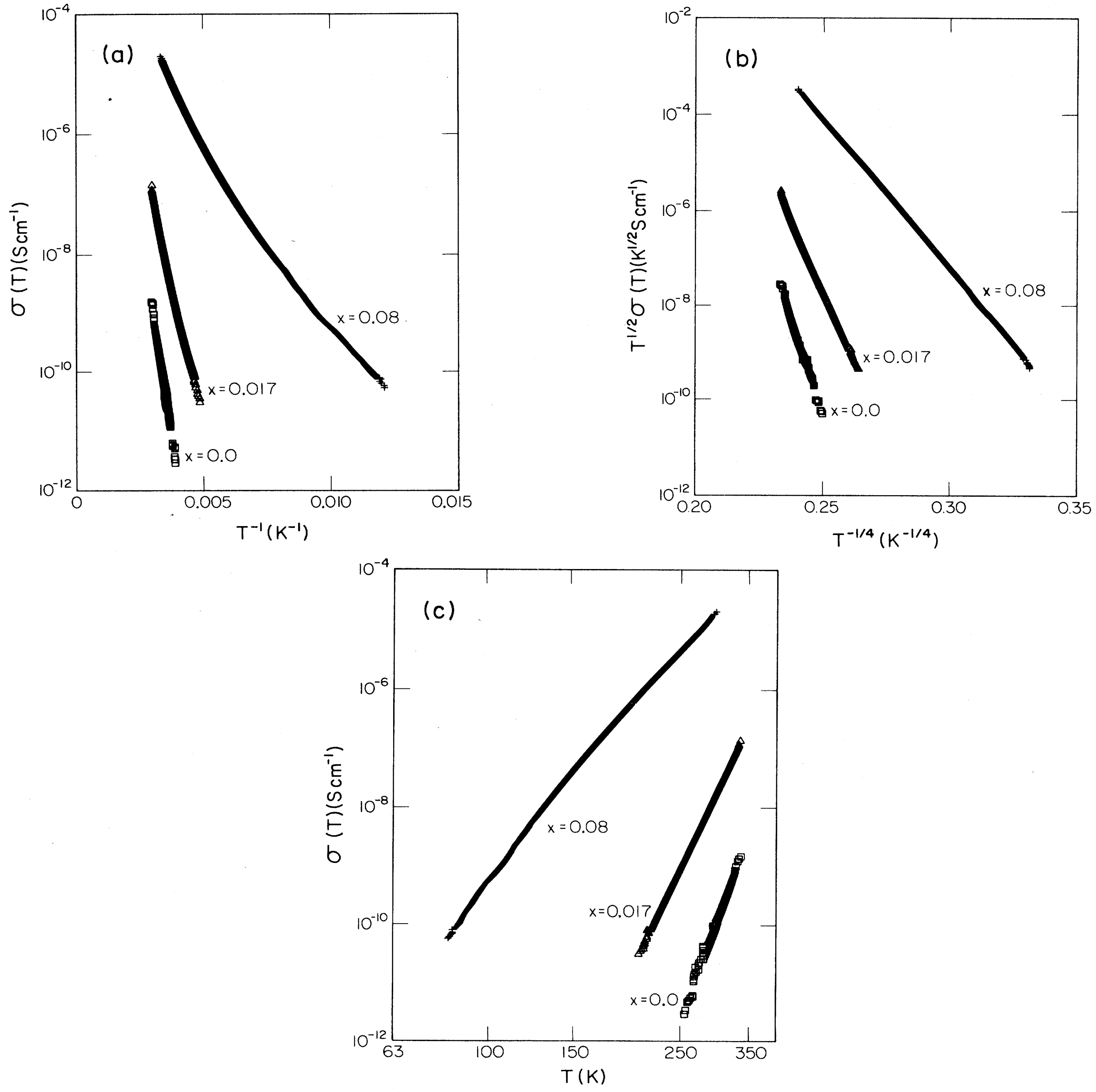

FIG. 2. (a) $\log_{10}\sigma$ vs $T^{-1}$; (b) $\log_{10}\sigma$ vs $T^{-1/4}$; and (c) $\log_{10}\sigma$ vs $\log_{10}T$ for representative compositions of unprotonated and lightly protonated emeraldine polymer.

TABLE I. Protonation dependence of conduction for emeraldine polymer.

| Protonation level $x$ | $\sigma_{dc}$(300 K) (S/cm) | $\epsilon$(300 K) (10 Hz) | $E_a$ (eV) | $E'_a$ (eV) | $T_0$ (K) | $n$ | $\alpha$ | $n_p$[a] per ring | $n_{bp}/n_p$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | $9.5\times10^{-11}$ | 10.2 | 0.56 | 0.46 | $1.87\times10^{10}$ | 22 | 0.96 | $2.0\times10^{-3}$ | $3.7\times10^{-3}$ |
| 0.017 | $1.6\times10^{-8}$ | 42 | 0.38 | 0.35 | $6.15\times10^{9}$ | 17 | 0.87 | $3.3\times10^{-3}$ | $1.1\times10^{-2}$ |
| 0.08 | $2.0\times10^{-5}$ | 370 | 0.13 | | $4.20\times10^{8}$ | 9.6 | 0.70 | $6.7\times10^{-3}$ | $7.9\times10^{-2}$ |

[a] References 43 and 45.

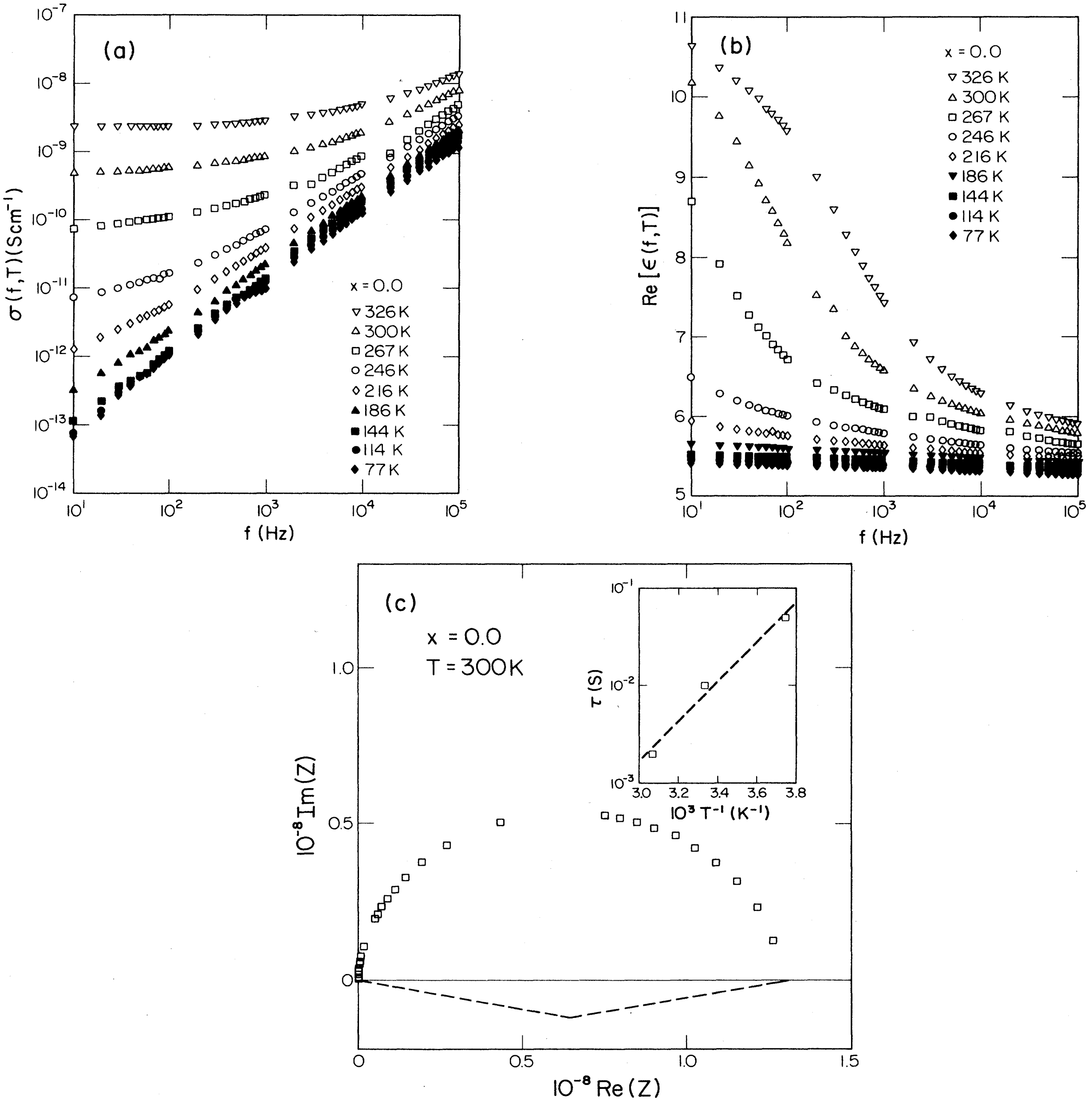

FIG. 3. (a) $\log_{10}\sigma$ vs $\log_{10}f$ at constant temperature; (b) real part of the dielectric constant, $\epsilon$, vs $\log_{10}f$ at constant temperature; (c) imaginary part of the impedance vs the real part of impedance at varying frequencies for a temperature of 300 K and for unprotonated ($x=0.0$) emeraldine polymer. The inset of (c) presents $\log_{10}\tau$ [determined from the maximum of plots of Im($Z$) vs Re($Z$)] vs $T^{-1}$ for the unprotonated emeraldine polymer. The dashed line in (c) indicates the center of curvature for the Cole-Cole analysis; the dashed line in the inset is the best fit to an Arrhenius expression, Table I. The "$\alpha$" obtained from the Cole-Cole plot is in agreement with that obtained from (a), as expected.

plotted in Fig. 2(b) as $T^{1/2}\sigma_{\rm dc}$ versus $T^{-1/4}$. The nearly linear curves indicate a good fit to the data with a composition-dependent $T_0$, Table I.

It is well known that analysis of dc conductivity is often not unique. For example, we show in Fig. 2(c) a plot of $\log_{10}\sigma_{\rm dc}$ versus $\log_{10}T$. The results indicate that a power-law behavior, $\sigma_{\rm dc}=AT^n$, also provides a reasonably good fit to the data with $n$ varying with sample composition as summarized in Table I.

Experimental ac conductivity for the emeraldine base sample is given in Fig. 3, together with the corresponding imaginary part of the conductivity measurements displayed as the dielectric constant derived from the actual measured capacitance of the sample. At lowest temperatures, the conductivity varies as $\sigma_{\rm ac}=Bf^s$, with $s\sim 0.98$ and temperature independent. At lower frequencies, an additional contribution to the conductivity can be seen to become increasingly important as the temperature is increased. The 10-Hz conductivity is in good agreement with the measured dc conductivity. At low temperatures the dielectric constant is frequency independent. At the higher temperatures studied, the dielectric constant for highest frequency approaches the low-temperature dielectric constant while at lower fre-

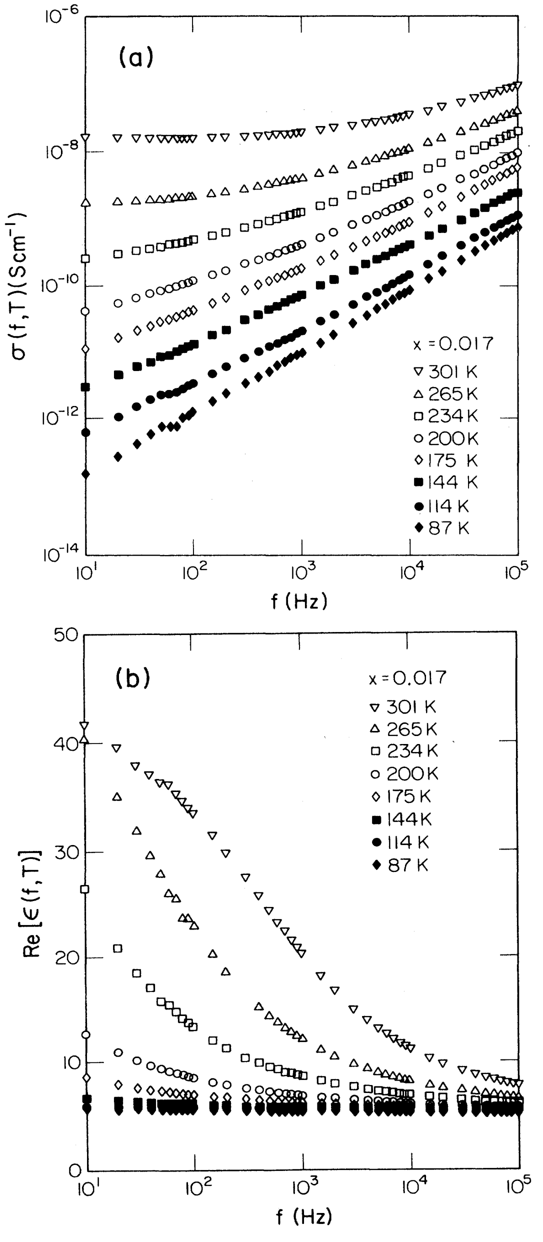

FIG. 4. (a) $\log_{10}\sigma$ vs $\log_{10}f$ for emeraldine polymer for protonation level $x=0.017$; (b) real part of the dielectric constant, $\epsilon$ vs $\log_{10}f$ at constant temperature for emeraldine polymer protonated to $x=0.017$.

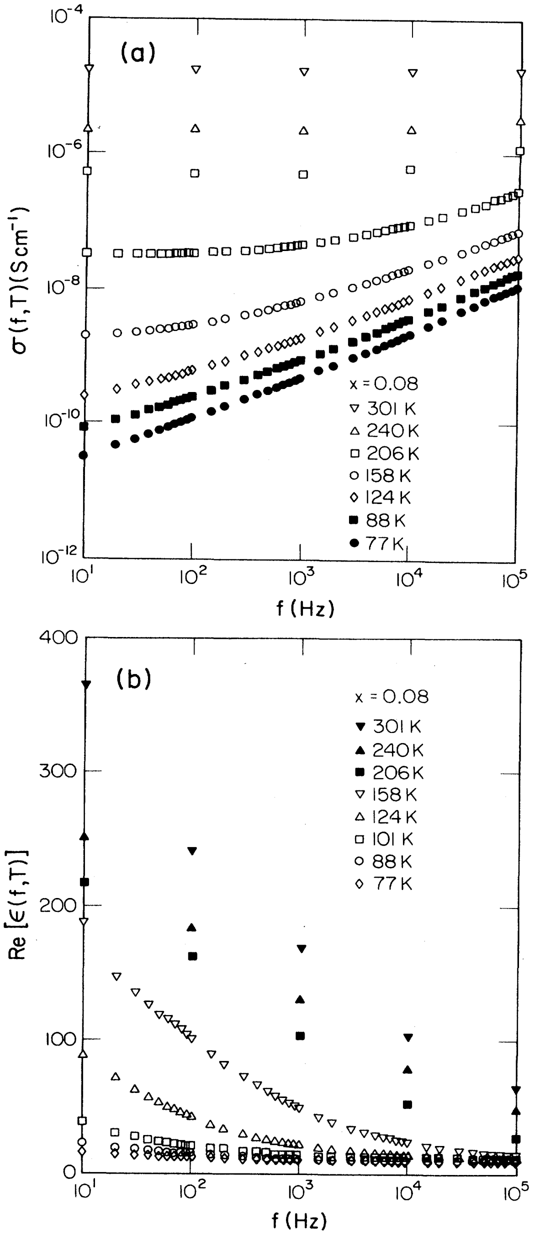

FIG. 5. (a) $\log_{10}\sigma$ vs $\log_{10}f$ at constant temperature for emeraldine polymer protonated $x=0.08$; (b) real part of the dielectric constant, $\epsilon$ vs $\log_{10}f$ at constant temperature for emeraldine polymer protonated to $x=0.08$.

quencies there is an increasing contribution to the dielectric constant. For all temperatures and compositions studied, the $10^5$-Hz dielectric constant approaches that measured at $6\times10^9$ Hz.[64] A Cole-Cole analysis[65,66] of the real and imaginary parts of the impedance can be done, Fig. 3(c). The nearly complete semicircle demonstrates an absence of contact effects and is reminescent of a simple Debye model[67] for noninteracting dipoles, although the incomplete nature of the semicircle indicates a dispersion in the relaxation rates, with an $\alpha$ similar to the $\alpha$ noted in the $\log_{10}\sigma_{\text{ac}}$-versus-$\log_{10}f$ plot. The characteristic relaxation time $\tau$ obtained from the Cole-Cole plot is temperature dependent. Assuming a simple Arrhenius expression for $\tau$ [Fig. 3(c) inset],

$$\tau=\tau_0\exp\left[\frac{E_a'}{k_bT}\right], \tag{4}$$

we find that for emeraldine base $\tau_0=1.6\times10^{-10}$ s and $E_a'\sim0.5$ eV.

Similar experiments have been performed for samples of composition $x=0.017$ (Fig. 4) and 0.08 (Fig. 5), with fitting parameters obtained summarized in Table I.

## IV. DISCUSSION

The origins of the conductivity and dielectric response in undoped and lightly doped emeraldine are of interest, especially in the context of the role of polaron and bipolaron defect states in this system. Although qualitatively $\sigma_{\text{dc}}$ and $\sigma_{\text{ac}}$ appear similar to those of other insulating materials, quantitatively the data are quite different from those reported for *trans*-polyacetylene,[14] *cis*-polyacetylene,[68] $NH_3$-compensated polyacetylene,[9] and amorphous silicon.[15,16] It had been suggested[62] that the conductivity of lightly protonated emeraldine could be described by a slightly modified Kivelson model; that is, the interpolaron hopping between polarons and bipolarons. An important aspect of the original intersoliton hopping model[13] is the isoenergetic nature of the hop. The temperature dependence of the hopping conductivity is controlled only by a phonon distribution whose temperature dependence is the transition rate $\gamma(T)$ independent of soliton concentration. According to Kivelson, $\gamma(T)\propto T^n$. This temperature dependence is independent of dopant concentration in the relevant regime for *trans*-polyacetylene.[14] In Fig. 2(c) $\sigma_{\text{dc}}$ of the emeraldine samples studied is plotted on a log-log plot. While the conductivity of each of the samples can be fitted to a power law, $T^n$, it is clear that $n$ decreases rapidly with protonation. Hence, the proposed generalization of the Kivelson intersoliton hopping model to form an interpolaron hopping model is not appropriate for the unprotonated and lightly protonated emeraldine samples. Similarily, the change in temperature dependence of the dc conductivity with protonation argues against the applicability of a model in which individual polarons hop independently of each other.[52,69]

Qualitatively dc conductivity reflects behavior often attributed to variable-range hopping. Earlier studies of the magnetic susceptibility of emeraldine with protonation[43] showed that the number of Cure-like spins (presumably positively charged polarons, see below) increases with protonation from $\sim1$ per 500 rings to $\sim1$ per 150 rings as the protonation level was increased from emeraldine base to $x=0.02-0.1$. Assuming the density of spins is the density of states available, together with Eqs. (2) and (3), a variation of localization length $\alpha$ with $x$ can be estimated. Use of this $\alpha(x)$ together with the experimental $T_0(x)$ yields estimates of absolute conductivity inconsistent with the measured values. It is suggested, therefore, that a modification of variable-range hopping, for example, extended pairwise hopping[17] may be more important in this system where they may be several different kinds of distinct energy levels within the energy gap (see below).

The Cole-Cole analysis of the ac conductivity shows the presence of a Debye-like relaxation with a modest dispersion in relaxation times. With increasing protonation, the dispersion increases. The high-frequency and low-temperature dielectric constants measured are in agreement with results of microwave-frequency studies of conductivity and dielectric constant in emeraldine.[59,60,64] The increase in magnitude of the frequency- and temperature-independent component of the dielectric constant with increasing $x$ supports that it is the sum of the dielectric response of the backbone emeraldine base polymer plus a term related to the contribution of isolated polarons and bipolarons formed at these doping levels oscillating about their pinning center. Assuming a pinning model[64,70] and averaging the dielectric constant over three directions,

$$\epsilon_p=\frac{4\pi}{3\epsilon_0}\frac{n_p}{V}\frac{e^2}{m_p^*\omega_0^2}, \tag{5}$$

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 $x=0.08$ using $V=125$ Å$^3$ and $\epsilon_p=\Delta\epsilon=(10.4-5.3)=5.1$, and $m_p^*\sim50$ $m_e$,[40] we obtain $\omega_0/2\pi=7.7\times10^{13}$ Hz or a pinning energy of 0.3 eV, in reasonable agreement with a pinning energy of 0.35 eV obtained from analysis[64] of the microwave-frequency dielectric-constant results and in accord with the amplitude-mode–formalism[71] analysis of the photoinduced and dopant-induced infrared activity in emeraldine.[40] Thus the polarons in emeraldine are substantially more pinned than the solitons in polyacetylene.[22]

The increase in dielectric constant at low frequencies and high temperatures show the presence of a second independent relaxation process. For emeraldine base, the characteristic frequency of this process is thermally activated with a thermal activation energy nearly the same as the thermal activation energy obtained from parametrization of $\sigma_{\text{dc}}$ is an Arrhenius expression. Also, the $\tau_0^{-1}$ obtained is a reasonable attempt frequency that might be expected in a solid with flipping rings.[40,72] These results suggest that this low-frequency dielectric process is, in fact, the charge hopping between allowed sites in the polymer.

The dielectric constant data can be used to estimate the distribution and types of sites in the system. From the magnetic-susceptibility data[43,45] the density of spins, presumably positively charged polarons, in the polymer varies from 1 per 500 rings for $x=0.0$ to 1 per $\sim 300$ rings for $x\sim 0.02$ to 1 per $\sim 150$ rings for $x\sim 0.10$. The number of localized spins (polarons) created is much less than the number of charges added through protonation due to phase segregation into primarily protonated and unprotonated regimes.[43,45] It is expected in the actual polymer, especially at low protonation levels when the volume fraction of protonated phase is small, that some isolated polarons would also form in the insulating phase and that there is a disproportionation of some of the polarons to form bipolarons or other spinless charged defects (such as — $\mathrm{NH_2}^+$—).[73–75]

The presence of a few doubly charged bipolarons [or even neutral defects (polarons) formed, for example, through the destabilization of some quinoid groups to form —N= based radicals[75]] among an array of singly charged polarons provides a charge-transport mechanism for the excess holes (e.g., second positive charge of a bipolaron) hopping among the polaron sites. With each hop a positive polaron $P^+$ is converted to a doubly positive bipolaron $\mathrm{BP}^{2+}$, while a $\mathrm{BP}^{2+}$ is transformed into a $P^+$. A classical dipole model[76] may be used to estimate the contribution to the dielectric constant of this polaron hopping

$$\epsilon=\frac{4\pi}{\epsilon_0}\left[\frac{n_p}{A}\right]\left[\frac{n_{\mathrm{bp}}}{n_p+n_{\mathrm{bp}}}\right]\frac{e^2L^2}{k_BT}\left[\frac{1}{1+\omega^2\tau^2}\right] . \tag{6}$$

Here $n_p$ is the number of polarons per ring of the polymer, $n_{\mathrm{bp}}$ the number of bipolarons per unit length of the polymer, $A$ the cross-sectional area of bipolaron chain, $L^2$ the mean-square average hopping distance between polarons. Assuming a density of one polaron per 500 rings[43] (or an average 50 Å apart) this equation can be solved in the $\omega \leq \tau$ limit to give the fraction of bipolarons in the polymer. The experimental low-frequency value of $\epsilon=12$ implies a concentration of approximately $3.7\times 10^{-3}$ bipolarons per polaron for $x=0$ increasing to approximately $1.1\times 10^{-2}$ for the $x=0.017$ sample with average separation between polarons of 42 Å. These low concentrations of bipolarons are reasonable in the context of available data on the polymer. For $x=0.08$, use of Eq. (6) (with an average separation between polarons of 33 Å) assuming negligible contribution from the isolated metallic islands being formed,[44] gives a concentration of $7.9\times 10^{-2}$ bipolarons per polaron. Thus, the dielectric constant can be understood within a picture of three-dimensional charge hopping among polaron sites. It is noted that the near-identical value of effective activation energy obtained for $\tau$ from dielectric constant and $\sigma_{\mathrm{dc}}$ supports this picture.

With increasing protonation much beyond the $x=0.1$ level, it is expected that the charge conduction becomes dominated by interaction among the granular metal islands formed.[44] The bipolaron-polaron hopping conduction mechanism is quite general and may be appropriate for other lightly doped nondegenerate conjugated polymers, for example, polypyrrole and polythiophene.

## V. SUMMARY

The experimental study of the $\sigma_{\mathrm{dc}}$, $\sigma_{\mathrm{ac}}$, and $\epsilon_{\mathrm{ac}}$ for emeraldine base and lightly protonated emeraldine polymer shows that the charge transport does not occur via the usual mechanisms attributed to insulating materials. Detailed analysis of these data in the context of other data for the polyaniline polymers supports the possibility of a new mechanism for charge conduction, charge hopping among fixed polaron states. This mechanism accounts for the magnitude and temperature dependence of the dc conductivity, frequency-dependent conductivity, and frequency-dependent dielectric constant. The characteristics of the model are such that it is likely applicable to other nondegenerate polymer states, including polypyrrole and polythiophene.

## ACKNOWLEDGMENTS

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[1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chaing, and A. J. Heeger, J. Chem. Soc. Chem. Commun. 578 (1977).

[2] See, for example, *Handbook of Conducting Polymers,* edited by T. Skotheim (Dekker, New York, 1986), Vols. 1 and 2.

[3] See, for example, Proceedings of the International Conference on Synthetic Metals, Santa Fe, 1988 [Synth. Met. (to be published)]; Proceedings of the International Conference on Synthetic Metals, Kyoto, 1986 [*ibid.* **17-19** (1987)]; Proceedings of the International Conference on Synthetic Metals, Albano Terme, 1984 [Mol. Cryst. **117-121** (1985)].

[4] J. A. Pople and S. H. Walmsley, Mol. Phys. **5**, 15 (1962).

[5] M. J. Rice, Phys. Lett. **71A**, 152 (1979).

[6] W. P. Su, J. R Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).

[7] S. A. Brozovskii and N. N. Korova, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 6 (1981) [JETP Lett. **33**, 4 (1981)].

[8] D. K. Campbell and A. R. Bishop, Phys. Rev. B **24**, 4859 (1981); Y. Onodera, Phys. Rev. B **30**, 775 (1984).

[9] A. J. Epstein, in *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 2. p. 1041.

[10] H. Naarmann and N. Theophilou, Synth. Met. **22**, 1 (1987).

[11] N. Theophilou, D. B. Swanson, A. G. MacDiarmid, A. Chakraborty, H. H. S. Javadi, R. P. McCall, F. Zuo, S. P. Treat, and A. J. Epstein, Synth. Met. **28**, 35 (1989).

[12] E. M. Conwell, IEEE Trans. Electr. Insul. **EI-22**, 591 (1987).

[13] S. Kivelson, Phys. Rev. B **25**, 3798 (1982).

[14] A. J. Epstein, H. Rommelmann, M. Abkowitz, and H. W. Gibson, Phys. Rev. Lett. **47**, 1549 (1981); Mol. Cryst. Liq. Cryst. **77**, 81 (1981).

[15] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).

[16] P. Nagles, in *Amorphous Semiconductors,* Vol. 36 of *Topics in*

*Applied Physics*, edited by M. H. Brodsky (Springer-Verlag, Berlin, 1979).

[17] J. A. Chroboczek and S. Summerfield, J. Phys. (Paris) Colloq. **44**, C3-517 (1983).

[18] D. Emin and K. L. Ngai, J. Phys. (Paris) Colloq. **44**, C3-471 (1983).

[19] A. J. Epstein, H. W. Gibson, P. M. Chaikin, W. G. Clark, and G. Grüner, Phys. Rev. Lett. **45**, 1730 (1980); Chem. Scr. **17**, 135 (1981).

[20] M. Audenaert, G. Gusman, and R. Deltour, Phys. Rev. B **24**, 7380 (1981); Phys. Rev. Lett. **51**, 2019 (1983).

[21] M. Audenaert, Phys. Rev. B **30**, 4609 (1984).

[22] A. J. Epstein, H. Rommelmann, R. Bigelow, H. W. Gibson, D. Hoffman, and D. B. Tanner, Phys. Rev. Lett. **50**, 1866 (1983); **51**, 2020 (1983).

[23] A. J. Epstein, R. W. Bigelow, H. Rommelmann, H. W. Gibson, R. J. Weagley, A. Feldblum, D. B. Tanner, J. P. Pouget, J. C. Pouxviel, R. Comes, P. Robin, and S. Kivelson, Mol. Cryst. Liq. Cryst. **117**, 147 (1985).

[24] E. M. Conwell, Synth. Met. **9**, 195 (1984); Mol. Cryst. Liq. Cryst. **117**, 155 (1985).

[25] A. J. Epstein, R. W. Bigelow, A. Feldblum, H. W. Gibson, D. M. Hoffman, and D. B. Tanner, Synth. Met. **9**, 155 (1984); A. Feldblum, R. Bigelow, H. W. Gibson, A. J. Epstein, and D. B. Tanner, Mol. Cryst. Liq. Cryst. **105**, 191 (1984).

[26] T. C. Chung, F. Moraes, J. D. Flood, and A. J. Heeger, Phys. Rev. B **29**, 2341 (1984).

[27] J. Dong, Ph.D. thesis, University of California, Santa Barbara, 1984.

[28] R. R. Chance, J. L. Bredas, and R. Silbey, Phys. Rev. B **29**, 4491 (1984).

[29] X. Q. Yang, D. B. Tanner, M. J. Rice, H. W. Gibson, A. Feldblum, and A. J. Epstein, Solid State Commun. **61**, 335 (1987).

[30] S. Kivelson and A. J. Heeger, Phys. Rev. Lett. **55**, 308 (1985).

[31] E. M. Conwell, Synth. Met. **20**, 289 (1987); S. Kivelson and A. J. Heeger, *ibid.* **22**, 371 (1988).

[32] A. G. Green and A. E. Woodhead, J. Chem. Soc. **97**, 2388 (1910).

[33] A. G. MacDiarmid, J.-C. Chiang, M. Halpern, W.-S. Huang, J. R. Krawczyk, R. J. Mammone, S. L. Mu, N. L. D. Somasir, and W. Wu, Polym. Prepr. **25**, 248 (1984); J. C. Chiang and A. G. MacDiarmid, Synth. Met. **13**, 193 (1986).

[34] 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).

[35] 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).

[36] 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).

[37] 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).

[38] M. G. Roe, J. M. Ginder, P. E. Wigen, A. J. Epstein, M. Angelopoulos, and A. G. MacDiarmid, Phys. Rev. Lett. **60**, 2789 (1988); M. G. Roe, J. M. Ginder, T. L. Gustafson, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein (unpublished).

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

[40] R. P. McCall, M. G. Roe, J. M. Ginder, T. Kusumoto, A. J. Epstein, G. E. Asturias, E. M. Scherr, and A. G. MacDiarmid, Synth. Met. **29**, 433 (1989); R. P. McCall, J. M. Ginder, M. G. Roe, G. E. Asturias, E. M. Scherr, A. G. MacDiarmid, and A. J. Epstein (unpublished).

[41] M. J. Rice and E. J. Mele, Phys. Rev. Lett. **49**, 1455 (1982).

[42] J. L. Bredas, B. Themans, J. G. Fripiat, J. M. Andre, and R. R. Chance, Phys. Rev. B **29**, 6761 (1984).

[43] J. M. Ginder, A. F. Richter, A. G. MacDiarmid, and A. J. Epstein, Solid State Commun. **63**, 97 (1987).

[44] F. Zuo, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **36**, 3475 (1987).

[45] A. J. Epstein, J. M. Ginder, F. Zuo, H.-S. Woo, D. B. Tanner, A. F. Richter, M. Angelopoulos, W.-S. Huang, and A. G. MacDiarmid, Synth. Met. **21**, 63 (1987).

[46] H. Kuzmany, N. S. Sariciftic, H. Neugebauer, and A. Neckel, Phys. Rev. Lett. **60**, 212 (1988).

[47] H.-Y. Choi and E. J. Mele, Phys. Rev. Lett. **59**, 2188 (1987).

[48] J. Langer, Solid State Commun. **26**, 839 (1978).

[49] J. P. Travers, C. Menardo, M. Nechtschein, and B. Villeret, in Proceedings of the European Symposium on Polymeric Materials, 1987 (unpublished).

[50] F. Wudl, R. O. Angus, Jr., F. L. Lu, P. M. Allemand, D. J. Vachon, M. Nowak, Z. X. Liu, and A. J. Heeger, J. Am. Chem. Soc. **109**, 3677 (1987).

[51] Y. W. Park, Y. S. Lee, C. Park, L. W. Shacklette, and R. H. Baughman, Solid State Commun. **63**, 1063 (1987).

[52] G. E. Wnek, Polymer Prepr. **26**, 277 (1985).

[53] P. M. McManus, S. C. Yang, and R. J. Cushman, J. Chem. Soc., Chem. Commun. 1156 (1985); P. M. McManus, R. J. Cushman, and S. C. Yang, J. Phys. Chem. **91**, 744 (1987); R. J. Cushman, P. M. McManus, and S. C. Yang, Makromol. Chem. Rapid Commun. **8**, 69 (1987).

[54] A. P. Monkman, D. Bloor, G. C. Stevens, and J. C. H. Stevens, J. Phys. D **20**, 1337 (1987).

[55] B. Abeles, P. Sheng, M. D. Coutts, and Y. Arie, Adv. Phys. **24**, 407 (1975); Phys. Rev. Lett. **31**, 44 (1973).

[56] M. Angelopoulos, A. Ray, A. G. MacDiarmid, and A. J. Epstein, Synth. Met. **21**, 21 (1987).

[57] J. P. Travers and N. Nechtschein, Synth. Met. **21**, 135 (1987).

[58] M. Nechtschein, C. Santier, J. P. Travers, J. Chroboczek, A. Alix, and M. Ripert, Synth. Met. **18**, 311 (1987).

[59] H. H. S. Javadi, F. Zuo, M. Angelopolous, A. G. MacDiarmid, and A. J. Epstein, Mol. Cryst. Liq. Cryst. **160**, 225 (1988).

[60] H. H. S. Javadi, M. Angelopolous, A. G. MacDiarmid, and A. J. Epstein, Synth. Met. **26**, 1 (1988).

[61] M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, M. Akhtar, Z. Kiss, and A. J. Epstein, Mol. Cryst. Liq. Cryst. **160**, 151 (1988); M. X. Wan, A. G. MacDiarmid, and A. J. Epstein, Solid State Sci. **76**, 216 (1987).

[62] T. Hayashi, Y. Hirai, H. Tanaka, and T. Nishi, Jpn. Phys. **26**. L1800 (1987).

[63] F. Fosong, T. Jinsong, W. Lixinag, Z. Hongfang, and M. Zhishen, Mol. Cryst. Liq. Cryst. **160**, 175 (1988); new x-ray diffraction studies have shown that 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).]

[64] H. H. S. Javadi, K. R. Cromack, M. Angelopolous, A. G. MacDiarmid, and A. J. Epstein, following paper, Phys. Rev. B **39**, 3579 (1989).

[65] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[66] R. M. Hill and A. K. Jonscher, Contemp. Phys. **24**, 75 (1983); A. K. Jonscher, Thin Solid Films **50**, 187 (1978).

[67] P. Debye, Z. Phys. **13**, 97 (1912); *Polar Molecules* (Dover, New York, 1945).

[68] A. J. Epstein, H. Rommelmann, and H. W. Gibson, Phys. Rev. B **31**, 2502 (1985).

[69] H. B. Schüttler and T. Holstein, Phys. Rev. Lett. **51**, 2337 (1983).

[70] P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. **14**, 703 (1974).

[71] E. Ehrenfreud, Z. Vardeny, O. Brafman, and B. Horovitz, Phys. Rev. B **36**, 1535 (1987).

[72] S. Kaplan, E. M. Conwell, A. F. Richter, and A. G. MacDiarmid, J. Am. Chem. Soc. **110**, 7647 (1988).

[73] F. Genoud, M. Guglielmi, M. Nechtschein, E. Genies, and M. Salmon, Phys. Rev. Lett. **55**, 118 (1985).

[74] E. M. Conwell, Phys. Rev. B **33**, 2465 (1986).

[75] J. M. Ginder, K. Cromack, A. G. MacDiarmid, and A. J. Epstein (unpublished).

[76] H. H. S. Javadi, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. **59**, 1760 (1987).