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Electrodynamics of the Conducting Polymer Polyaniline on the Insulating Side of the Metal Insulator Transition

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Abstract

Conducting polymer samples of Polyaniline (PANI) exhibit a dramatic change in their conductivity as function of protonation level, analogous with the changes in the transport properties of semiconductors upon doping. In this work PANI samples were prepared by protonating with varying concentrations of hydrochloric acid. The complex terahertz frequency-dependent conductivity and the dc conductivity of these samples were measured and analyzed in the framework of the disorder-driven, metal-insulator quantum phase transition. The samples were determined to all fall on the insulating phase of this phase transition. The frequency dependence of both the real and imaginary terahertz conductivity are found to be consistent with theories that include electronic correlation effects.

Introduction

A large fraction of polymers found in commercial applications, e.g. polypropylene, polyethylene and polystyrene, show unremarkable electrical and optical properties. However, over forty years ago it was discovered that conjugated polymers, i.e. those with alternating double and single carbon bonds, could be doped in a similar fashion to traditional semiconductors like silicon,¹ resulting in tunable electronic and optical properties.^{2,3} Polymers can be modeled in a similar fashion to traditional band-gap semiconductors like silicon where a HOMO-LUMO gap is used to describe the band gap in analogy to the valence band to conduction band gap used to describe classical semiconductors.⁴ Like the archetypical semiconductor silicon, polymers can be intentionally doped both with *n*-type and *p*-type dopants, providing the mechanism to utilize these materials in all industry applications where *p-n* junctions are currently being used in the semiconductor industry. Based on this principle, these conducting polymers have found numerous applications in technology due in large part to their unique ability to be tuned over such a wide range of conductivities along with their relative ease of synthesis and low cost. Conducting polymers are used in solar cells,⁵ field effect transistors,⁶ organic light-emitting diodes (OLEDs),⁷ and because of their strong absorption in the microwave and millimeter wave range, in absorbing paints in the defense industry.⁸

Polyaniline (PANI) has been widely studied and is referred to as either emeraldine base (EB) when the aniline monomers are combined to form an insulating polymer, and conversely is referred to as emeraldine salt (ES) when “protonated” to form a conductive polymer. The term emeraldine, stems from the greenish tint of PANI first observed in the early 1900s.⁹ PANI can be effectively systematically doped by synthesizing or treating the polymer in a solution with a varying molarity of an acid, such as hydrochloric acid (HCl) which was used in this study, to protonate the sample.^{10,11} Upon treatment or synthesis of varying molarity, *M*, of an acid solution, protons are added to a fraction of the formerly unprotonated Nitrogen sites on the PANI chain with the general trend of greater conductivity with

increasing protonation level.¹² The actual number of electrons on the chain is not altered and therefore the degree of protonation must change the electronic structure, i.e., the density of states at the Fermi level. Beyond an upper limit of the concentration, i.e., molarity of the acid, used in the protonation process, the polyaniline chains are saturated resulting in no further increase in conductivity and in certain cases a reduction in conductivity has been observed,^{3,13} phenomenologically similar to an upper limit on the level of increasing conductivity in amorphous metal semiconductor samples though for different reasons.¹⁴

Overall, PANI like many other conducting polymers, exhibit strong similarities with classic band gap semiconductor materials. Crystalline doped semiconductors, like phosphorous doped silicon, Si:P,¹⁵ and amorphous metal semiconductor alloys, like, amorphous niobium silicon, a-Nb_xSi_{1-x},^{16,17} have been shown to have universal properties consistent with the disorder driven metal-insulator transition (MIT), a type of quantum phase transition (QPT).¹⁸ These universal properties include unique features in the dc conductivity, $\sigma_{dc}(T)$, and the electrodynamic response, i.e., the complex frequency dependent conductivity, $\sigma_1(\omega)$, as samples are tuned through a critical dopant concentration, x_c , that separates quantum mechanical metallic and insulating systems. In the framework of the Anderson-like disorder-driven MIT, it is actually a tuning of the relative carrier density of states to the level of disorder in the system that changes a specific sample from being a metal to an insulator.^{19,20} Thus the ratio of the dopant atom concentration to the natural disorder of the host matrix, be it crystalline silicon or amorphous silicon are critical factors in determining whether a doped band-gap system falls on the metallic or insulating side of the MIT. For instance the critical concentration of dopant atoms for which samples cross over from the insulating to the metallic phase in the naturally much more ordered crystalline silicon is a factor of 10,000 less than in the highly disordered amorphous metal semiconductor alloys.⁷ One expects then that due to the high level of disorder in the polymer systems that these systems should show greater similarities with the amorphous metal semiconductor alloys, including, a higher effective charge carrier concentration required to tune the systems through the MIT.

The universal behavior found in both the crystalline systems and in the metal semiconductor alloys occurs for the lowest lying excitations of the system; in the metallic, the critical regime, and on the insulating side of the MIT. Previous studies of conducting polymers have mainly focused on dc conductivity, σ_{dc} ,²¹ and its dependence on temperature, applied magnetic field, and static pressure, where application of a magnetic field typically reduces the conductivity of a specific sample whereas increased pressure has the opposite effect.²² Similar magnetoconductance has in fact also been observed in amorphous metal semiconductor alloys, such as a-GdSi.²³ From the earliest reports the transport behavior of conducting polymer samples that fall on the insulating side of the MIT have been modeled using variable range hopping (VRH),²⁴ though the fits of the data over which this VRH occurs persist often to room temperature, which is quite different than insulating samples of metal semiconductor alloys which only exhibit VRH behavior up to approximately 20K and certainly much higher in temperature than doped crystalline semiconductor systems where VRH is observed up to even lower temperatures, depending on how far the sample is tuned into the insulating phase.²⁵

The low—energy electrodynamic properties of systems tuned close to a MIT offer a unique means to test many of the prevailing theories associated with fundamental transport mechanisms including the importance of electron-electron correlations or interactions that dictate the low temperature and frequency transport behavior. The low-energy here specifically refers to the photon energy being used, which need be less than that required to excite charge carriers from the dopant band into the conduction band or analogously the LUMO band, typically in the meV range. Furthermore, to appropriately analyze the system in terms of the disorder driven metal-insulator quantum phase transition, measurements of the frequency-dependent conductivity should be taken in the so-called quantum limit, $\hbar\omega \gg k_B T$ so that only the lowest lying excitations of the ground state of the system are probed.

Previous reports for measurements of $\sigma_1(\omega)$ that have been performed at these low photon energies come from low resolution, far-infrared FTIR measurements probing to 30 cm^{-1} ($\sim 1 \text{ THz}$), and utilizing a

Kramers-Kronig (KK) analysis.²⁶ In FTIR spectroscopy it is well known that the major contribution to the frequency-dependent optical properties derived from the KK analysis of the reflectivity data comes from the spectral range over which the reflectivity data is taken.²⁷ Thus as the spectrometer used in that study had an instrumental cutoff frequency in the spectral range, i.e., it did not actually measure reflectivity data in the THz region, those data are highly dependent on the method used to extrapolate the data set and therefore unreliable in ascertaining the frequency dependence of the conductivity in the THz spectral range. Another group has reported on microwave transport in the emeraldine form of PANI, having measured the temperature dependence of the complex frequency-dependent conductivity using a 6.5 GHz resonant cavity.²⁸ However these authors only report data down to ~40 K which is well outside the quantum limit, and as such, thermal excitations could likely still play a significant role in the observed behavior.

Our motivation in this study focused then on identifying whether these doped conducting polymers i.e. protonated PANI, would show similar universal electrodynamic properties as has been previously found in crystalline doped silicon and amorphous metal-semiconductor alloys. Specifically, the research we present is the first attempt to test the theories associated with photon-assisted hopping in conducting polymers in order to compare the results for this class of conducting polymer with inorganic doped semiconductors like crystalline silicon and amorphous metal semiconductor alloys. In this study, we determined the terahertz (THz) or millimeter-wave conductivity, $\sigma_1(\omega)$ directly using THz time-domain spectroscopy (which measures both amplitude and phase, and thereby eliminates the need for KK analysis) for PANI samples prepared at various same protonation level.

Background and Theory

Universal physics has been found in numerous types of doped semiconductors and in certain conducting polymers tuned close to the MIT. For instance, for samples tuned to the insulating side of the MIT, the

low temperature transport is referred to as variable range hopping (VRH). The original single-particle calculations, i.e., excluding electron-electron interactions, for VRH, performed by Mott predicted $\sigma_{dc} \propto e^{-(T'/T)^{1/(D+1)}}$, where T' is a characteristic “Mott Temperature” and D the dimensionality of the system, normally 3D,²⁹ but reduced to 2D or 1D depending on the relative geometry of the sample as compared to the localization length, ξ , of the charge carriers. Materials that follow this non-interacting transport behavior are referred to as insulating Fermi glasses, in reference to the similarity with the non-interacting Fermi liquid theory used to describe conductors.³⁰ Efros and Shklovskii (ES) re-calculated the VRH including electron-electron interaction or correlation effects. Including these interactions, the VRH is predicted to be $\sigma_{dc} \propto e^{-(T_{ES}/T)^{1/2}}$, where T_{ES} is a different characteristic temperature,³¹ and materials that obey this dependence are often referred to as Coulomb glasses. In practice, for traditional semiconductor materials, the VRH only becomes the dominant conduction mechanism at low temperatures, i.e. when thermal activation of charge carriers to a higher band is sufficiently suppressed, typically below 20K, and as such in those systems it has proven difficult to distinguish between the Mott and ES forms for VRH simply using the temperature-dependence of the σ_{dc} data due to the limited temperature range over which this VRH mechanism can be measured. It should also be noted that the exponent 1/2, which corresponds to VRH in Coulomb glasses and in 1D Fermi glasses is also expected for percolation models based on tunneling between mesoscopic metallic islands,³² as well as in a theory based on hopping between polaronic clusters.³³

However in many conducting polymers, analysis of the so-called reduced activation energy using a logarithmic derivative, $W = d(\ln \sigma)/d(\ln T)$, (where a negative slope for W indicates insulating behavior and a positive slope for W indicates metallic behavior, and the value of the slope is the power in the exponential form for the specific VRH mechanism, e.g., 1/2 or 1/4) has indicated that VRH behavior persists much higher in temperature. For instance, recent measurements on gated samples of the conducting polymer material poly(3-hexylthiophene), P3HT, have elegantly shown both $T^{-1/4}$ and $T^{-1/2}$

dependence in samples on the insulating side of the MIT using this logarithmic derivative method, with the VRH behavior persisting up to ~ 150 K and higher depending on how deep into the insulating regime the samples were tuned.³⁴ An apparent crossover between these two behaviors has been shown to occur with varying temperature in several materials, both in crystalline doped semiconductors³⁵ and in conducting polymers,³⁶ and models which attempt to recreate this observed crossover, including the Fogler-Teber-Shklovskii model, have been proposed.³⁷ Universal scaling, as a function of gate bias and temperature, has also been observed in these conducting polymers.³⁸

The lowest lying excitations can also be probed using optical techniques when the photon energy, $\hbar\omega$, lies within the dopant bandwidth. In practice the sample temperature must be low to eliminate any thermal excitations of the charge carriers and thus one probes the quantum ground state of the system, i.e., $k_B T \ll \hbar\omega$, where k_B is the Boltzmann constant. THz spectroscopy is then ideally suited to probe the lowest lying excitations in systems tuned close to the MIT as the THz spectral range satisfies both of these conditions in a typical laboratory set-up using a closed-cycle, helium cryostat. In this quantum limit, temperature independent, photon assisted hopping is predicted to occur. The real part of the complex frequency-dependent conductivity for intra-dopant band photon assisted hopping in insulating samples close to the MIT has a general temperature independent form,

$$\sigma_1(\omega) = Ae^2 N_0^2 \xi^5 \hbar \omega^2 \left[\ln(2I_0/\hbar\omega) \right]^4 \quad (1)$$

Here A is a constant close to unity, N_0 is the non-interacting density of states, ξ is the electronic wave function localization length, and I_0 is the prefactor of the wavefunction overlap integral between neighboring sites. I_0 is commonly taken to be the Bohr energy of the dopant, thus in the THz region, $\hbar\omega \ll I_0$ and we expect $\sigma_1(\omega) \propto \omega^\alpha$ where α is slightly less than 2 due to logarithmic corrections.

For the case where electron-electron interactions are relevant, two new characteristic energy scales emerge that dictate the frequency dependence of the complex conductivity; naturally the Coulomb

interaction energy between centers forming a resonant pair, U , and a resultant soft-gap that forms in the background density of states known as the Coulomb gap, Δ .³¹ The full form derived by Efros and Shklovskii is given by,

$$\sigma_1(\omega) = Ae^2 N_0^2 \xi^5 \omega [\ln(2I_0/\hbar\omega)]^4 [\hbar\omega + U(r_w)] \quad (2)$$

where the Coulomb interaction energy, $U(r_w) = e^2/\epsilon r_w$, is evaluated for the most probable hop distance, r_w , between pairs (ϵ is the dielectric constant).³¹ With the logarithmic corrections being only a minor contribution, again we expect, $\sigma_1(\omega) \propto \omega^\alpha$. In the case of $\hbar\omega < U < \Delta$, Eq. (2) predicts a slightly sublinear dependence on frequency, i.e., $\alpha \leq 1$ is expected, and in the special case of $U > \hbar\omega > \Delta$, Eq. (2) predicts a slightly superlinear frequency dependence and $\alpha \geq 1$.³⁹ Thus a measurement of $\sigma_1(\omega)$ in the THz spectral range for samples that fall on the insulating side of the MIT provides a clear test for both the role of electron-electron interactions as well as the relative magnitude of relevant energy scales, as opposed to $\sigma_{dc}(T)$ data alone, to determine the role of correlation effects for systems tuned close to a MIT.

Predictions for the frequency dependent conductivity for the models of tunneling between mesoscopic islands,³² and for hopping between polaronic clusters,³³ that also produce an exponent of $1/2$ in the dc conductivity, have not been reported. However, these latter theories, based on hopping transport mechanisms include Coulombic interaction charging energies of the clusters or islands and as such might be expected to show a hard gap in the density of states. Such a hard gap in the density of states would produce a sharp cutoff feature in the low energy excitation spectrum of the frequency-dependent conductivity, and only a soft gap as in the case of the Coulomb gap in the ES model would produce an frequency-dependent conductivity that goes to zero smoothly.

Thus far we have discussed the insulating side of the MIT, i.e. the Fermi glass and Coulomb glass behavior. In both the critical and the metallic regimes, the temperature and the frequency dependent transport are expected to follow power law behavior, e.g., $\sigma_{dc} \propto T^\beta$ and $\sigma_1 \propto \omega^\beta$ respectively, and temperature-frequency scaling behavior is also expected within the critical regime.¹⁶ In crystalline doped semiconductor systems like Si:P and in metal semiconductor systems like a-NbSi, the critical power has been found to be $\beta \approx 1/2$.¹⁶ Numerous types of conducting polymer samples tuned to the critical and metallic regimes have shown temperature dependent conductivity with $\beta \approx 1/3$,⁴⁰ however measurements of the frequency dependent conductivity in the critical or metallic regimes have also never been reported. In polyaniline, without application of external magnetic fields or pressure, conclusively metallic behavior has also never been reported.³⁴

Experiment Details and Results

Aniline Hydrochloride and Ammonium Peroxydisulfate were mixed to synthesize PANI powder filtered from solution.⁴¹ These powders were thoroughly rinsed in de-ionized water to remove monomers and other residue and then dried under vacuum. The PANI was then deprotonated using 0.2 molar Ammonium Hydroxide to the filtered powder which resulted in EB. These EB powders were also stored under vacuum. The final samples which were prepared for measurements were re-protonated by placing the EB powder into baths of varying molarity, i.e. concentration of HCl, from 0.02M HCl to 2.0M HCl and stirred vigorously for an extended period. The resultant filtered powder was thoroughly dried. At each stage the filtered residue was ground to create a uniformly consistent, fine, dried powder. The re-protonated PANI powder was then pressed into pellets using a hydraulic press at a pressure of 10 metric tons (just over 700 MPa). The pellets were 13 mm in diameter and ranged in thickness from 0.2 – 1.4 mm. No other material was added to the reprotonated PANI powder to enable binding when making the

pellets. When pressed into a pellet, the deprotonated PANI powder was characterized to have a room temperature conductivity of $10^{-8} (\Omega \cdot \text{cm})^{-1}$ consistent with results for PANI base.¹¹

The $\sigma_{dc}(T)$ was measured using a closed-cycle cryostat with a base temperature of 10K and using a standard four-probe configuration. Temperature fluctuations further limited the base temperature for which we could reliably measure the sample conductivity. Sample resistances up to $\sim 1 G\Omega$ were measured with this set-up. The high-input impedance setting of the DMM was another limiting factor for the highest resistance measurements at low temperatures for the most insulating samples.

Figure 1 – A) $\sigma_{dc}(T)$ for the PANI samples. Samples are denoted by the molarity, M , of the HCl solution in which the PANI was reprotonated. B) shows the data plotted on a $T^{-1/2}$ scale as expected for ES type VRH. C) selected sample data are shown for the reduced activation energy W indicating insulating behavior. The fits to the low temperature data indicate VRH exponents of approximately -0.2 and -0.5 for the most metallic and insulating samples respectively.

We treat the molarity of the acid in which the EB samples were reprotonated as analog to the dopant concentration used in studies of the MIT in Si:P and a-NbSi. As such Fig. 1 A) shows the expected trend of an overall increasing σ_{dc} with increasing acid molarity, M, for the HCl solutions in which the samples were prepared. The conductivity of the deprotonated PANI, e.g. the EB, was measured to have a room-temperature σ_{dc} of the order $10^{-9} (\Omega \cdot cm)^{-1}$ consistent with literature values.¹³ Figure 1 B) shows the dc conductivity for the PANI samples plotted vs $T^{-1/2}$ as would be expected for Coulomb glass-like behavior. Finally in Figure 1 C) we show the reduced activation energy for select samples. For all of the samples W shows a negative slope, which is appropriate for insulating behavior. However the lowest temperature data for our samples show slopes ranging from ~ -0.2 for the most metallic samples up to ~ -0.5 for the most insulating samples. We also note that in Figure 1C) we observe a crossover to Arrhenius-like activated behavior at higher temperatures similar to predictions from a Monte Carlo simulation of hopping in a Coulomb glass.⁴² Overall the dc conductivity data indicated that we had synthesized insulating PANI samples showing the correct magnitude of conductivity and the correct slope for W. The trend of a crossover in the actual slope of W, both as a function of temperature and as a function of proximity to the critical or metallic regime has been reported before for both inorganic doped semiconductors,¹⁵ and for conducting polymers.³³

The frequency-dependent conductivity was measured using a Terahertz Time-Domain Spectroscopy (THz TDS) system in a transmission configuration over the spectral range 0.1-1.5 THz.⁴³ The THz TDS system allows for determination of the amplitude and phase of the transmitted THz pulses, and thus the real, σ_1 , as well as the imaginary component, σ_2 , of the complex frequency-dependent conductivity of a sample can be simultaneously measured. The THz TDS system we used in this study is a Menlo Systems TERA K8 spectrometer with a C-Fiber 780 Er-doped fiber laser as the pump source and the samples were cooled to a base temperature of 10K in a closed-cycle cryostat.

Figure 2 – σ_1 for reprotonated PANI samples showing a distinctly linear (as opposed to quadratic) frequency. Inset shows the temperature dependence of σ_1 overlaid with the σ_{dc} for the 0.02M sample.

Fig. 2 shows σ_1 plotted as a function of frequency at the base temperature of 10K for selected PANI samples. Samples prepared in higher molarity solutions of the HCl show enhanced THz conductivity consistent with the dc conductivity results. We also note that the THz conductivity seems to be smoothly approaching zero in the dc limit, which is again consistent with the expected behavior for these insulating samples in the framework of Efros and Shklovskii and the notion of a soft Coulomb gap. The inset of the Figure 2 shows the THz conductivity for selected frequencies as a function of temperature overlaid on a plot of this sample's $\sigma_{dc}(T)$ indicating that the low temperature THz conductivity is temperature independent. This temperature independence of the THz conductivity at low temperature is indicative that at our lowest experimental temperatures, we are indeed probing the photon assisted hopping conductivity in our PANI samples that is expected to be temperature independent.³⁰ However we note here that the magnitude of the THz conductivity is much greater than the dc conductivity value, e.g., at ~ 20 K, the 200 GHz value of σ_1 is more than four orders of magnitude larger than the value for σ_{dc} for the most conducting sample measured and over eight orders of magnitude for the most insulating sample.

This is in stark contrast to results in Si:P and in a-NbSi, where the σ_1 data tracks the σ_{dc} data quite closely down to ~ 20 K before it flattens out, i.e., becomes temperature independent showing the photon assisted hopping behavior.¹⁷ We surmise that the reason may be linked to the as yet unexplained experimental result that VRH is observed to much higher temperatures (even room temperature) in conducting polymer samples as compared to the inorganic semiconductor systems. The large difference in the magnitudes of the THz conductivity and the dc conductivity that we observe in our PANI data is however consistent with the observed large difference between the measured microwave conductivity and the dc conductivity values reported by Javadi et al.²⁸

Discussion and Analysis

The $\sigma_1(\omega)$ was found to be consistent with the theoretical prediction put forth by ES, namely that the lowest lying electrodynamic excitations for samples on the insulating side of a metal insulator transition follows an approximately linear frequency dependence. This is the first reported study that uses THz conductivity to test this prediction in a conducting polymer sample tuned close to the MIT. This prediction is based on theories that take electron-electron interaction effects into account. The countervailing theory based on single particle dynamics that exclude electron-electron interactions predicts an approximately quadratic frequency dependence in the low-energy frequency-dependent conductivity.

Figure 3 – σ_1 and $|\sigma_2|$ data for the 0.02 Molar HCL PANI sample. Both σ_1 and $|\sigma_2|$ show an approximately linear frequency dependence (dotted line as guide to the eye for linear dependence). Analysis of the ratio of their magnitudes is shown in the upper inset and representative absorption spectra for a reference and sample are shown in the bottom inset.

We used the Kramers-Kronig compatible form for the complex frequency-dependent conductivity

$$\hat{\sigma} = \sigma_1 + i\sigma_2 = A(i\omega)^\alpha, \quad (3)$$

from which the power can be accurately determined from a ratio of the experimentally measured values for σ_1 and $|\sigma_2|$, i.e., $\alpha = (2/\pi) \tan^{-1} (|\sigma_2|/\sigma_1)$. Fig. 3, shows that both σ_1 and $|\sigma_2|$ follow a similar trend over the measured frequency range individually (we show the magnitude $|\sigma_2|$ as the imaginary

conductivity is negative, i.e., capacitive) and for all samples the magnitude of $|\sigma_2|$ is considerably larger than σ_1 which is consistent with our samples falling on the insulating side of the MIT. The results are summarized in Table I. The 2.0M sample was too opaque to obtain transmission data and thus no value of α was obtained.

Table I. The material parameters for the PANI samples. Uncertainty in α determined from the deviation from the mean for all data for the samples. α could not be determined for the most metallic sample. Localization lengths ξ determined from the characteristic Efros Shklovskii temperature, T_{ES} , fits to the low temperature dc conductivity data

Sample Molarity	α from Eq. (1)	ξ (Å) from T_{ES}
2.0	NA	23
0.5	0.78 ± 0.03	18
0.1	0.74 ± 0.05	11
0.05	0.89 ± 0.02	2
0.02	0.87 ± 0.02	2

In general, we found a sublinear frequency dependence in all of the measured samples. Furthermore we found a trend of increasing α for samples falling further into the insulating regime, i.e. at decreasing molarity. This latter trend is consistent with the observed behavior in other systems, e.g. Si:P, tuned close to the MIT.⁹ This can be explained by the fact that as the system is tuned closer towards the metallic and critical regimes, the frequency dependent conductivity is expected to cross over to a different power law dependence, $\sigma_1 \propto \omega^\beta$, with the power β , expected to fall in the range 1/2 to 1/3,^{16,36} depending on the critical scaling exponents and the universality class of the phase transition.⁴⁴ Thus assuming a slow crossover, the observed power α that we have determined experimentally is showing a subtle change from the ES predicted slightly sublinear form expected for photon assisted hopping deep in the Coulomb glass phase to a lower power that would reach the value of β if our samples could be tuned fully into the critical regime.

Another point to note from our experimentally determined values for α is that because the values are sublinear across the entire span of samples, this indicates that for our measured spectral range, $\hbar\omega < U < \Delta$, as discussed above, according to the theory of ES. This then sets an upper limit on both the Coulomb gap width and the electron-electron interaction energy of ~ 1 meV. This approximate value for the Coulomb gap width is consistent with tunneling results for the inorganic semiconductor Si:B,⁴⁵ however recent results on the organic polymer, poly(3-hexylthiophene), P3HT, have indicated a Coulomb gap width of 10-100 meV (with increasing values for Δ the deeper the samples were tuned into the insulating regime) on the insulating side of the MIT in that system.³⁴

The THz conductivity convincingly shows ES-type behavior indicating that our PANI samples fall under the classification of Coulomb glasses, indicating the importance of correlation effects for the lowest lying excitations. The lower panel in Fig. 1 shows the data we collected for a number of our protonated PANI samples plotted against $T^{-1/2}$. Even though the logarithmic derivative method indicates that $T^{-1/2}$ is not exactly appropriate, we fit the low temperature conductivity to determine relative values for the characteristic temperature in the Efros-Shklovskii model for VRH, $T_{ES} \cong 2.8e^2/k_B\epsilon\xi$,³¹ where ϵ is the dielectric constant, and ξ is the correlation or localization length used to parameterize how far a sample falls from the MIT in scaling theories associated with QPTs.⁴⁶ The approximate values for T_{ES} fall in the range of ~ 1000 K, consistent with values previously determined in PANI.²⁴ Values for ξ can in general be extracted from the ES characteristic temperature T_{ES} if the dielectric constant is known.

This highlights a further benefit of using THz TDS to analyze systems close the MIT, namely the fact that by directly measuring the amplitude and the phase of the transmitted THz pulses we can not only directly determine both the real part of the complex frequency-dependent conductivity, σ_1 , but also the frequency dependent dielectric constant for the material, $\epsilon_1 = \epsilon_{EB} + 4\pi\chi$, where ϵ_{EB} is background dielectric constant of the host material, i.e. emeraldine base, EB, and $4\pi\chi$ represents the divergent electric susceptibility contribution due to the charge carriers in the system.

Figure 4 – T=10 K ϵ_1 data as determined from σ_2 plotted vs. frequency showing divergent behavior. Inset shows an analysis of the dopant band contribution of the electric susceptibility portion of ϵ_1 as a function of sample molarity.

Figure 4 shows representative dielectric constant data for one of our measured samples. The sharp increase in ϵ_1 with decreasing frequency highlights the divergent behavior expected for the dielectric constant for samples tuned close to the MIT and in the dc limit. Using the 100 GHz value as a representative value for ϵ_1 , we extracted approximate values for the localization lengths for our samples from T_{ES} , which ranged from ~ 0.6 to ~ 6 nm from the most insulating to the highest molarity sample. The magnitudes of these localization lengths are consistent with previously reported values of ξ ,^{24,34} and represent appropriate length scales between the Nitrogen protonation sites on a polyaniline chain. Finally, the inset in Figure 4 shows an analysis of the electric susceptibility of the carriers with respect to the molarity of the protonation acid for our samples. Here we subtracted off the literature value of $\epsilon_{EB} = 6.9$ for aniline, the oligomers that make up the emeraldine base form of PANI.⁴⁷ In the theory of the disorder driven MIT, this susceptibility is predicted to diverge as $\chi = \chi_0(x_c - x)^{-\gamma}$, and though controversy remains regarding the precise value for the scaling exponent γ , it is often found to be close to unity.²⁹ In PANI we have the further complication due to the tuning mechanism of protonation not having a direct correspondence to the tuning parameter, x , when dopants introduce charge carriers in other MIT systems. However, the inset for Figure 4 shows a clear trend for the inverse susceptibility, and the

molarity at which the best fit line intercepts the horizontal axis represents point where the susceptibility would diverge, i.e. the critical molarity at which the MIT would potentially be expected to occur in this system, ~ 5 molar HCl. It is unclear why this plot shows the linear trend, however the value of ~ 5 molar HCl does corroborate the THz and dc conductivity data that our samples all fall on the insulating side of the MIT. As such it seems that in order to observe “metallic” like conductivity, PANI would need to be protonated beyond 5M HCl. However we found a saturation and eventual decrease in σ_{dc} (300K) for PANI prepared in high molarity acid solutions, as has been observed for PANI synthesized in other acids,¹³ which was interpreted as being due to structural changes in the polymer, thus indicating that a transition to critical or metallic-like behavior cannot be achieved in HCl protonated PANI.

Conclusion

In summary we have presented measurements for both $\sigma_{dc}(T)$ and the corresponding complex THz conductivity, $\sigma_1(\omega)$, for a series of insulating samples of a conducting polymer, PANI, tuned close to but not quite reaching the MIT. This is the first systematic study of the low energy electrodynamics of this type of disordered conducting polymer system. The THz conductivity data clearly shows the ES type sub-linear dependence on frequency for both σ_1 and $|\sigma_2|$, thus indicating that electronic correlations dominate the physics of these systems in the phase space close to the MIT. The observed sublinear dependence also sets an upper limit on the Coulomb Gap and electron-electron interaction strength of ~ 1 meV. These results strengthen the argument that insulating PANI is a Coulomb glass as we have demonstrated the same universal behavior in the THz conductivity as has previously been found in crystalline doped silicon and amorphous metal semiconductor alloys. The relative values for the localization lengths and the T_{ES} are consistent with values expected in these types of samples tuned close to the MIT, and analysis of the dielectric susceptibility seems to indicate a critical molarity of HCl of ~ 5 at which a transition to metallic behavior might be expected. Future studies using different acids to

protonate PANI or using different conducting polymers should be pursued in order to push the samples through the metal insulator transition and verify that the metallic and critical regime samples also display the same universal effects.

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