

Heat capacity, electron paramagnetic resonance, and dc conductivity investigations of dispersed polyaniline and poly(ethylene dioxythiophene)

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Abstract

Dispersible polyaniline (PANI) exhibits a dc conductivity $\sigma \approx 0.1$ S/cm when it's doped with poly(styrene sulfonic acid) (PSS) such that the number of sulfate ions per two-ring PANI unit (y) is 2. On increasing the dopant amount to $y = 12$ the conductivity σ drops to 10^{-5} S/cm. The EPR magnetic susceptibility results on these samples give nearly the same density of states at the Fermi level $N(E_F) \approx 0.65$ states/eV 2-rings. With y' defined as the number of sulfate groups per three-ring PEDOT unit, PSS doping of poly(ethylene dioxythiophene) (PEDOT) gives $\sigma \approx 10^{-1}$ S/cm at $y' = 5.7$ and $\sigma \approx 10^{-5}$ S/cm at $y' = 45.9$. Like PANI, $N(E_F) \approx 0.55$ states/eV 3-rings is same at both the doping levels. The EPR linewidth for these samples in the less conducting state is found to be large compared with the more conducting state, although the overall temperature dependence in the two states is qualitatively the same. These results are consistent with the inhomogeneous disorder models.

Keywords: polyaniline and derivatives, conductivity, Electron Spin Resonance, specific heat, magnetic measurements

1. Introduction

Conducting polymers in their doped state exhibit a rich variety of electrical, optical, magnetic and magnetic resonance properties primarily due to structural organization of the polymer chains into mesoscopically ordered and disordered regions [1,2]. Chain morphology that distinguishes polymers from both crystalline and amorphous solids leads to an electronic behavior that ranges from insulating through semi-conducting to metallic.

Conductivity of PSS doped PEDOT [3] can be varied over a wide range using different molar ratios of PEDOT and PSS [3]. The more conducting PEDOT ($\sigma \approx 0.1$ S/cm) has a particle size of around 90 nm, but the less conducting PEDOT ($\sigma \approx 10^{-6}$ S/cm) has a particle size of around 20 nm. Films made from aqueous dispersions of PEDOT find many applications depending upon their conductivity as, for example, an intermediate smooth layer of PEDOT deposited

on ITO (indium-tin oxide) prior to the semi-conducting polymer coating has been found to increase the durability and efficiency of light emitting devices [4]. It is the objective of the present paper to investigate the electronic behavior of PEDOT in its different conducting states.

We also report on the electronic behavior of dispersible polyaniline, which exhibits a range of conductivities depending upon the dopant level [5]. The primary particles in this type of polyaniline are found to have a size of around 10 nm. The primary particles are further comprised of smaller morphological units of size around 3.5 nm [6].

2. Experimental

The two dispersion-processed PEDOT samples were commercially obtained from H.C. STARCK (Bayer subsidiary) [3] under the trade names AI 4071 and CH 8000, and they were then dried into powders. With the formula

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units of PEDOT and PSS defined as $(-C_6H_4O_2S^-)_3$ and $-CH_2CH(C_6H_4SO_3^-)$, the molar ratio of PSS and three-ring PEDOT unit (y') is 5.7 for AI 4071 and 45.9 for CH 8000, respectively. We will henceforth abbreviate AI 4071 and CH 8000 as PEDOT6 and PEDOT46, respectively.

The PANI samples were obtained from Ormecon. With PANI formula unit defined as $(C_6H_4N-C_6H_5N)$, the two samples abbreviated as PANI2 and PANI12 have PSS to two-ring PANI unit molar ratios of 2 and 12, respectively.

A computer controlled X-band Bruker EMX 6/1 spectrometer (9.5 GHz) was used for EPR measurements. An Oxford ESR900 cryostat under ITC503 control was used for controlling temperature down to 4.2 K. The derivative intensity data following an EPR experiment were integrated twice. This result was divided by the double integral of the derivative EPR signal for a K_3CrO_8 standard to obtain a value for the magnetic susceptibility. The absolute uncertainty in the EPR obtained $N(E_F)$ values is primarily due to mass measurements of the K_3CrO_8 crystal and its solution in a capillary. This error is small and estimated to be approximately ten percent.

Calorimetric measurements were made using a thermal-relaxation type microcalorimeter in a He^3 cryostat the details of which were given in an earlier paper [7].

3. Results and Discussion

The room temperature conductivities of PEDOT6 and PEDOT46 are 0.1 S/cm and 2×10^{-5} S/cm, respectively, and for PANI2 and PANI12, they are 0.1 and 7×10^{-6} S/cm, respectively. Excess dopant clearly leads to significant decreases in conductivity. With the materials in the vicinity of Insulator-Metal (IM) transition, Figs. 1 and 2 show plots of reduced activation energy $W = \Delta \ln \sigma / \Delta \ln T$ as a function of temperature. The positive slope at low temperatures indicates that PEDOT6 and PANI2 are on the metallic side of the IM transition. On the other hand, PANI12 appears to be slightly on the metallic side and PEDOT46 is on the insulating side of the MI transition.

Figure 3 shows the EPR-derived magnetic susceptibility results as a function of temperature for PEDOT6 and PEDOT46. The dependence of χT on T is linear for both the samples and can be analyzed using $\chi = \chi_C + \chi_P$, where $\chi_C = N\mu_B^2 / k_B T$ and $\chi_P = \mu_B^2 N(E_F)$ are the Curie and Pauli susceptibilities. Slope of the χT ($= (N\mu_B^2 / k_B) + \mu_B^2 N(E_F)T$) versus T plot thus yields $N(E_F)$, the density of states at the Fermi level. The values of $N(E_F)$ obtained from the above plot are 0.5 ± 0.1 states/eV 3-rings for both PEDOT6 and PEDOT46. On the other hand, the number of Curie spins per formula unit is 0.004 and 0.001 for PEDOT6 and PEDOT46, respectively.

The magnetic susceptibility data in the form of a χT versus T plot are shown in Fig. 4 for PANI2 and PANI12. $N(E_F)$ values obtained from the above plot are 0.65 ± 0.10 states/eV 3-rings for both PANI2 and PANI12. On the other hand, the

number of Curie spins per formula unit is 0.003 and 0.005 for PANI2 and PANI12, respectively.

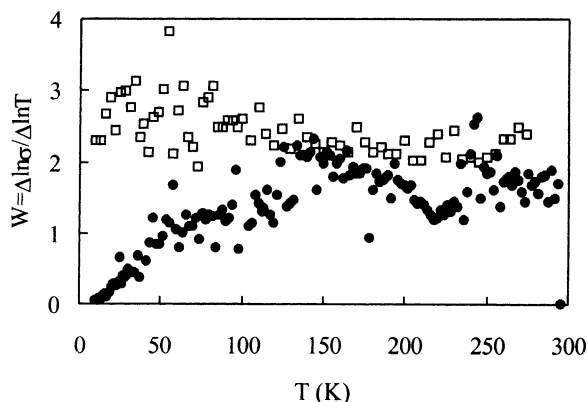


Fig. 1. W versus T for PEDOT6 (circles) and PEDOT46 (squares).

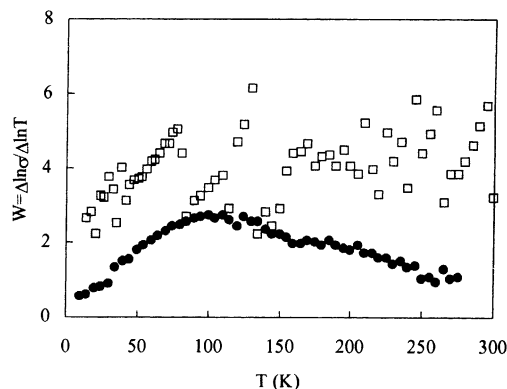


Fig. 2. W versus T for PANI2 (circles) and PANI12 (squares).

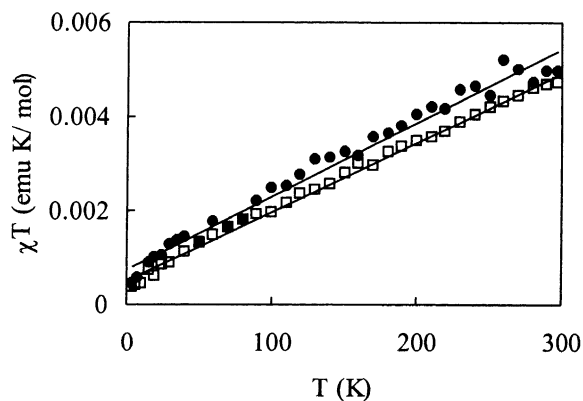


Fig. 3. χT versus T for PEDOT6 (circles) and PEDOT46 (squares). The straight lines correspond to linear regression of the χT data.

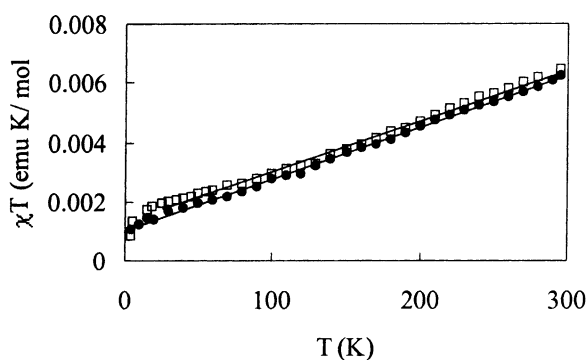


Fig. 4. χT versus T for PANI2 (circles) and PANI12 (squares). The straight lines correspond to linear regression of the χT data.

It seems clear that the excess dopant does not change the density of states at the Fermi level in either the PANI system or the PEDOT system. We investigate this issue further using the technique of heat capacity measurements.

The specific heat data for PEDOT6 and PEDOT46 are shown in Fig. 5 in the form of C/T versus T^2 plots. At sufficiently low temperatures the data normally follow a simple relation: $C/T = \gamma + \beta T^2$. The electronic specific heat coefficient γ is a measure of $N(E_F)$ (in states/eV formula unit) = 0.212γ (in mJ/mol K^2) per spin direction, while β is the lattice heat capacity coefficient.

Uncertainty in the high-temperature limit of the T^3 -dependence for lattice specific heat and anomalies at low temperature make it harder to obtain $N(E_F)$. A different approach is taken. We first calculate a value of γ ($= N(E_F)/0.424 = 1.2 \text{ mJ/mol K}^2$) from the EPR results. It is then used as the predetermined intercept for a straight line fit (in Figure 5) to each set of C/T versus T^2 data above the anomalous region.

For PANI2 and PANI12, the specific heat data are presented in Figs. 6 and 7. Same procedure as in analyzing data in Fig. 5 is applied to these systems with calculated γ ($= 1.50 \text{ mJ/mol K}^2$) for PANI2 and PANI12. Least squares fits of the data shown by straight lines are reasonable.

It is clear that EPR $N(E_F)$ values for dispersible PEDOT and for PANI that have been subjected to an additional dispersion step are the same in the more conducting and the less conducting states. This implies that majority of the additional anionic sulfate groups are not a part of the ordered regions, but are located instead in the disordered regions [8,9]. In other words, they may be located outside of the (metallic) primary particles where they help to disperse in aqueous media. Although the primary particle size in PANI is around 10 nm, agglomerates of the particles (secondary particles) are nearly always found. For

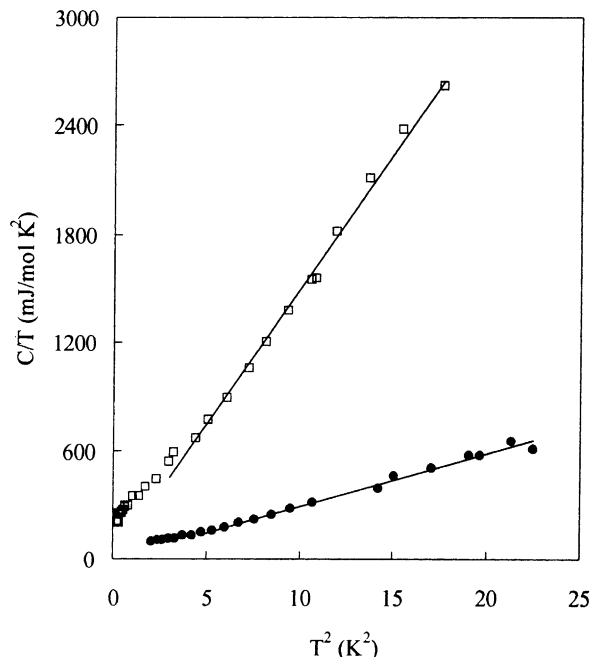


Fig. 5. C/T versus T^2 for PEDOT6 (circles) and PEDOT46 (squares). The straight lines correspond to linear regression of the C/T data.

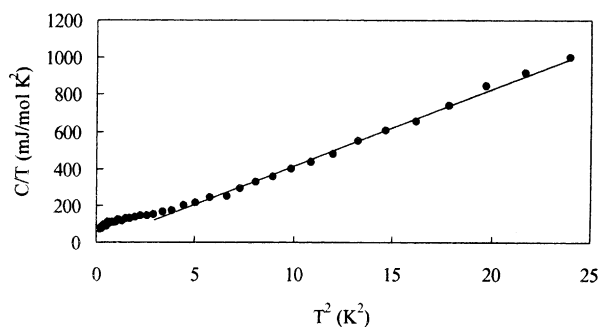


Fig. 6. C/T versus T^2 for PANI2. The straight line correspond to linear regression of the C/T data.

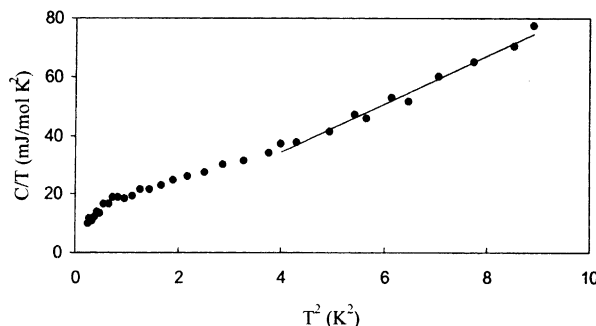


Fig. 7. C/T versus T^2 for PANI12. The straight line correspond to linear regression of the C/T data at higher temperatures.

PANI, an average size of 40 nm [5] is found. PEDOT, on the other hand, has a particle size in the range 80 – 100 nm for PEDOT6 and around 20 nm for PEDOT46 [3].

To obtain further insight, we present our results on the temperature dependence of the EPR linewidth Δ_{pp} in Figs. 8 and 9. While the linewidth increases with increase of temperature for the PEDOT system, it decreases for PANI. Since the low temperature linewidth for PEDOT6 and PEDOT46 is nearly the same, the increase with temperature is interpreted as due to interactions between the delocalized spins in the ordered regions and the localized spins in the disordered regions. For the PANI systems, the linewidth decrease is believed to be primarily due to motional narrowing.

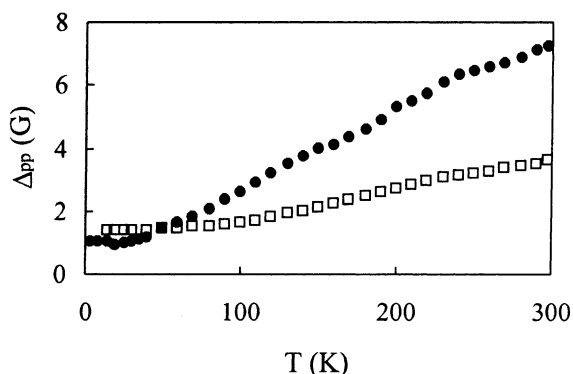


Fig. 8. Δ_{pp} as a function of T for PEDOT6 (circles) and PEDOT46 (squares)

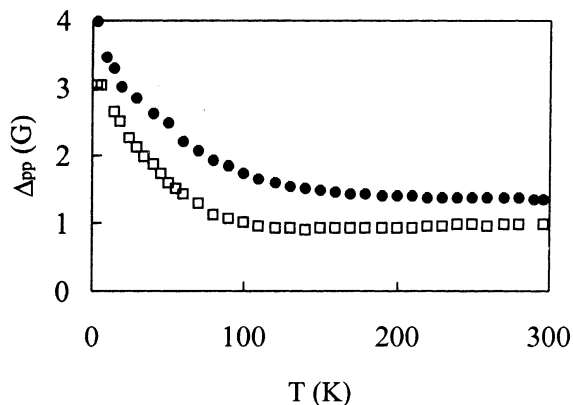


Fig. 9. Δ_{pp} as a function of T for PANI2 (circles) and PANI12 (squares)

We also wish to report that our EPR experiments give $N(E_F) = 0.7$ states/eV 3-rings for PTSA- (*p*-toluene sulfonic acid) doped PEDOT, which has one sulfonate group per two EDT rings and has a dc conductivity of 90 S/cm. On subjecting this sample to an extra dispersion step, the conductivity increases to 240 S/cm, but $N(E_F)$ stays the same around 0.7 states/eV 3-rings. Additionally, PTSA doped PANI when dispersed in poly(methyl methacrylate) gives the same $N(E_F) = 2.2$ states/eV 2-rings as undispersed PANI.

4. Conclusions

Polyaniline and poly(ethylene dioxythiophene) samples that are doped significantly more compared with their fully doped state have four orders of magnitude higher conductivity but the same value for the density of states at the Fermi level as the samples that are doped in slight excess. This is interpreted in the framework of the inhomogeneous disorder model according to which the doped material is comprised of nanosize “metallic” particles that are surrounded by disordered regions. The excess dopant is believed to be located outside the metallic core of the particles.

Acknowledgments

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