Conducting state of polyaniline films: Dependence on moisture

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The moisture dependence of the conducting properties of polyaniline films doped with camphor sulfonic acid is reported. Samples characterized as lying in the metallic and critical regimes of the metal-insulator transition have been studied for electrical resistivity in the temperature range 77–353 K under different thermal conditions. Thermal annealing is shown to increase the resistivity and also its temperature dependence. Additionally, the temperature above which the resistivity indicates metallic characteristics is shown to depend very sensitively on the presence of moisture. The results are interpreted using both the inhomogeneously and homogeneously disordered metal models.

I. INTRODUCTION

The conducting polymer polyaniline (PAN) has recently been the focus of intense investigations.[1–9] Beginning with insulating polyaniline in the emeraldine-base form (PAN-EB), one can obtain its conducting analog through either chemical/electrochemical oxidation or protonation with aqueous acids. The latter route involving protonation—especially with HCl—leads to emeraldine-salt polyaniline (PAN-Cl), which has moderately high conductivity in the range $1–10$ Ω^{-1} cm^{-1} and significantly large Pauli-like and Curie susceptibilities.[1,2] PAN-Cl is therefore characterized as an inhomogeneously disordered metal comprised of ''metallic islands'' separated by insulating barriers (also called the metallic-islands model).[2]

Polyaniline can also be synthesized in the conducting form with the use of functionalized acids.[10] Of particular interest to us in this paper is polyaniline doped with camphor sulfonic acid and cast from m-cresol (PAN-CSA). The temperature coefficient of dc resistivity in these films changes from positive to negative below 180 K or so.[11] This change is attributed to a disorder-induced localization in a homogeneously disordered metal. PAN-CSA is thus considered to be a disordered metal close to the metal-insulator (MI) boundary. Other features of metallic behavior seen in PAN-CSA include the negative dielectric constant[12] at microwave frequencies, linear temperature dependence of thermopower,[13] high reflectance in the far IR (Ref. 14) with a strong plasma resonance at 1.4 eV, and a temperature-independent Pauli susceptibility.[15]

The purpose of this paper is to show that absorbed moisture affects significantly the conducting state of PAN-CSA. It is a known fact that the presence of moisture in PAN-Cl increases its dc conductivity by as much as one order of magnitude, and significantly affects the other electronic properties.[16–27] While some water molecules in the polymer are rather tightly bound, others are found to be relatively free and mobile.[22] The enhancement of conductivity due to the presence of moisture is also reflected in the microwave-frequency conductivity and dielectric measurements of Javadi et al.[20] This increase in conductivity has been argued to be due to reduced potential barriers between metallic islands.

II. EXPERIMENT

The ratio of PAN-CSA to m-cresol was 2% by weight for one of the samples, henceforth denoted as PAN-CSA-2, and 4% by weight for the other (PAN-CSA-4). These two samples, provided by Y. Cao, have conducting properties characteristic of the metallic side of the MI transition. The sample prepared locally was about 3% by weight of PAN-CSA-3 and it lies on the critical side of the MI transition. Films of PAN-CSA-2 and PAN-CSA-4 were about 40 μm thick, while the PAN-CSA-3 film was approximately 15 μm thick. dc conductivity was measured using a four-probe technique. All measurements as well as thermal annealing were done in a vacuum of about 80 mTorr except when the sample was exposed to nitrogen and oxygen gases and moist air. Before each experiment the sample was pumped overnight to get rid of any superficial water. Data were recorded as the sample was cooled and also during warming. No hysteresis was observed upon thermal recycling and only the data taken during the cooling cycle are reported.

III. RESULTS

Figures 1 and 2 show the temperature dependence of resistivity of PAN-CSA-2 at various annealing temperatures. The resistivity is seen to have metallic characteristics with a positive temperature coefficient down to about 220 K for the sample kept at room temperature in vacuum. This temperature at which the resistivity reaches a minimum (T_m) is 180 K as measured by Reghu et al.[11] This difference could be due to a slight variation in the sample preparation and measurement techniques, and is not deemed significant as our primary purpose is to show the effect of thermal annealing or
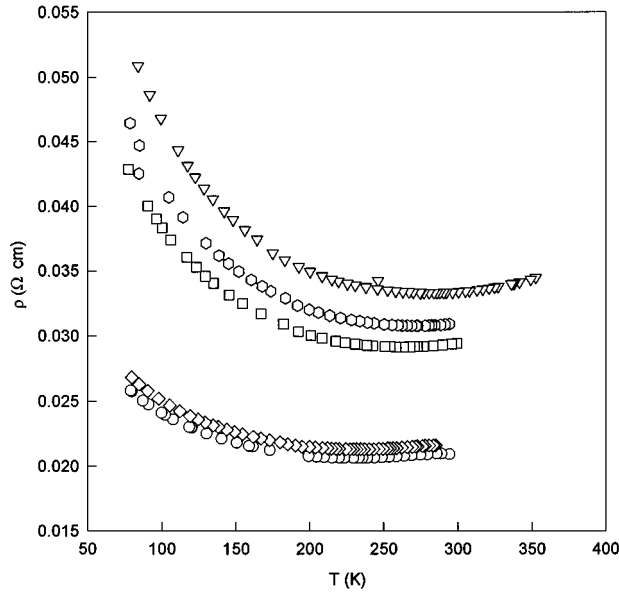
FIG. 1. Temperature dependence of dc resistivity of PAN-CSA-2 in the metallic regime of the metal-insulator transition. Various experimental conditions are as follows: (○) unannealed; (□) annealed overnight at 323 K; (⬡) annealed overnight at 333 K; (▽) annealed overnight at 353 K; (◇) exposed overnight to moist air.

moisture on the metallic nature of PAN-CSA. As seen in Figs. 1 and 2, the effect of annealing is first to increase the resistivity and second to shift the temperature of the minimum of the resistivity to higher temperatures. The sample was annealed at 323, 333, and 353 K for at least 12 h before being exposed to moisture. Each experiment performed subsequently resulted in the curves shown in Fig. 1. Figure 2 shows an expanded view of the resistivity data near T_m, clearly indicating that the minimum T_m moves to higher temperatures upon annealing. The temperature dependence of resistivity is also seen to increase upon annealing, indicating that the conduction mechanism has been affected and is more likely to be of an activation or variable-range-hopping type. As seen in Fig. 1, upon exposure to moisture, recovery of the temperature dependence of the resistivity is better than 85% and reflects the fact that water is replenished upon exposure to moisture nearly as rapidly as it is taken away due to annealing at elevated temperatures.

Figures 3 and 4 show the temperature dependence of resistivity of PAN-CSA-4 for various annealing temperatures. The resistivity is seen to have a positive temperature coefficient down to about 240 K for the sample kept at room temperature in vacuum. The sample was annealed at 323 K and then at 333 K. As seen in Fig. 3 the effect is similar to that obtained in PAN-CSA-2 viz, the resistivity increases as the annealing temperature is increased. After annealing the sample at 333 K the sample was then exposed to moisture. This resulted in a temperature dependence similar to that of the starting material. Once again the sample was annealed at 333 K to remove any absorbed moisture before exposing it to dry N_2 gas, and the experiment was repeated. The resistivity increases and exhibits a similar temperature dependence as when previously annealed at the same temperature, indicating excellent reproducibility. This is also a further proof that annealing at these temperatures leads primarily to the loss of
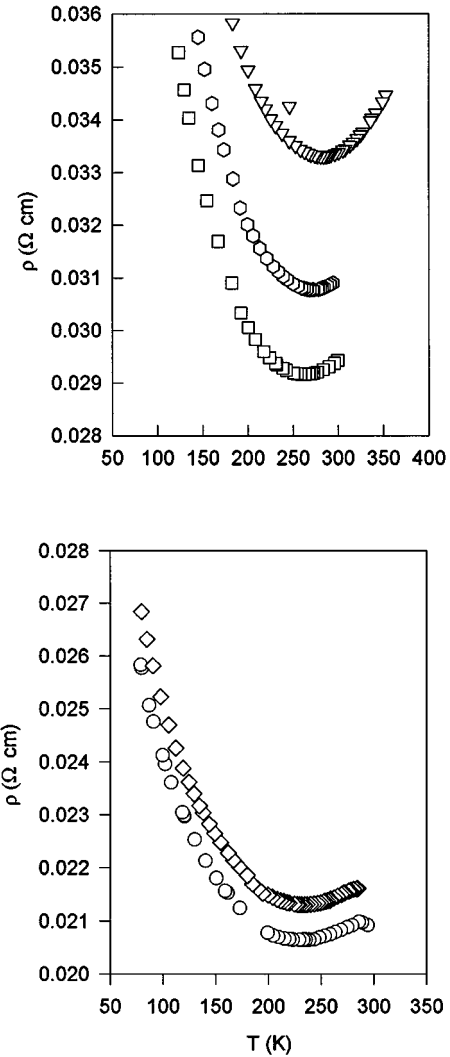

FIG. 2. Expanded temperature scale showing the shift of the minimum in the resistivity of Fig. 1 towards higher temperature. Symbols have the same meaning as in Fig. 1.

water. Then the sample was exposed to N_2 gas overnight at room temperature and the conductivity measured again. As can be seen from Figs. 3 and 4, the temperature dependence is very similar to that obtained upon annealing to 333 K, suggesting that N_2 does not affect the conductivity but rather that it is the water vapors in the surrounding medium that affect the temperature dependence of the conductivity. Upon exposure to moisture once again, the recovery of the temperature dependence of the resistivity data is better than 85%, which reflects the fact that the water lost due to annealing is replenished. Figures 3 and 4 show a gradual shift of T_m to higher temperatures upon annealing, an effect similar to that found in PAN-CSA-2.

Figure 5 shows the temperature dependence of conductivity for PAN-CSA-3. This sample has characteristics of the insulating regime of the metal-insulator boundary. As can be seen in the figure, the room temperature resistivity is larger than for PAN-CSA-2 and PAN-CSA-4. The temperature dependence, however, is much more dependent on annealing and the minimum of the resistivity is believed to have moved toward higher temperatures. Exposure to N_2 and O_2 gases
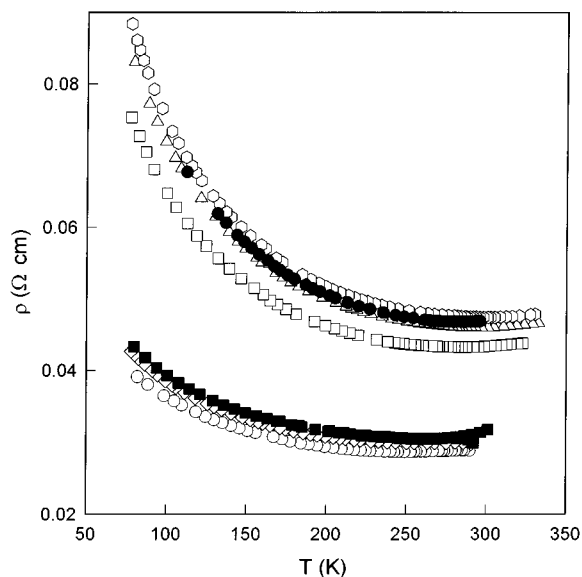
FIG. 3. Temperature dependence of dc resistivity of PAN-CSA-4 in the metallic regime of the metal-insulator transition. Various experimental conditions are as follows sequentially: (○) unannealed; (□) annealed overnight at 323 K; (△) annealed overnight at 333 K; (◇) exposed overnight to moist air; (⬡) annealed overnight again at 333 K; (●) exposed overnight to N$_2$ gas; (■) exposed overnight to moist air.

has no effect on the conduction mechanism. Exposure to moisture results in a recovery of the temperature dependence of the resistivity to better than 85%. Once again we see that it is the moisture that affects the conducting properties of this polymer.

IV. DISCUSSION AND ANALYSIS

It is known that the conductivity of PAN-Cl is greatly enhanced by the presence of water molecules present in the polymer matrix. Although the structure of PAN-CSA is more ordered at the mesoscopic level than PAN-Cl, water is seen to drastically change the transport properties in much the same way as it did for PAN-Cl, the results for which were analyzed earlier[8] using the model of metallic islands.[2] The results on PAN-CSA can therefore be explained using the same model.

We believe that the presence of water leads to additional spin and charge delocalization, most probably by solvating the Cl$^-$ anions and thereby reducing electrostatic interaction between the positive charge and the anions.[1,23] Recent calculations[27] on model oligomers of polyaniline also suggest that a strong interaction between the oligomers and polar water molecules causes the electron charge to delocalize along the polymer backbone. This charge distribution due to the presence of moisture has been argued to reduce polarization effects of the anion, and hence decrease scattering cross section due to the anions. We further believe that the metallic regions in PAN are physically bridged by relatively less ordered chains running through amorphous regions.[9] While the electronic wave function in an amorphous region is well localized, the wave function in a crystalline region is delocal-
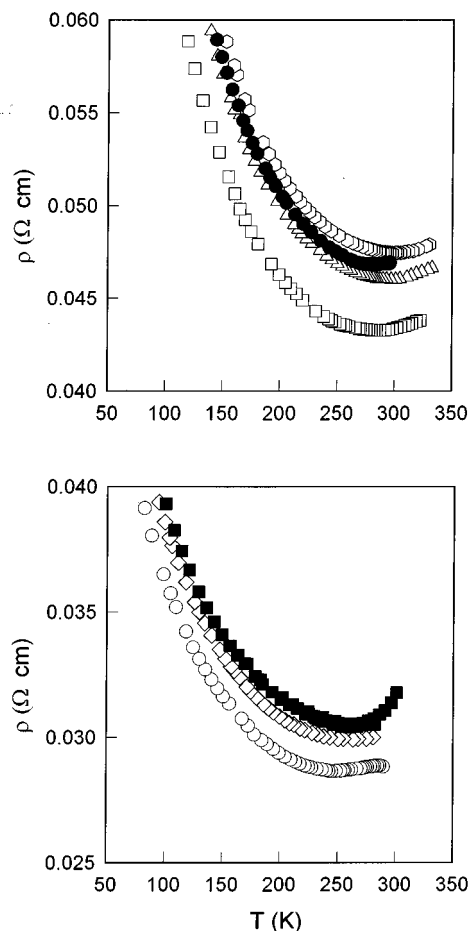

FIG. 4. Expanded temperature scale showing the shift of the minimum in the resistivity of Fig. 3 towards higher temperature. Symbols have the same meaning as in Fig. 3.

ized over 50–150 Å. The charge delocalization on bridging chains is believed to be less than that on chains in crystalline regions. As the dc conductivity is determined by charge transport through ''difficult'' regions, the size of the conduction barriers plays a crucial role in the metallic versus nonmetallic behavior of PAN. Since x-ray structural studies show no significant improvement of crystalline order in CSA doped poly(ortho)toluidine (POT) fibers compared to POT-HCl,[28,29] the higher conductivity in PAN-CSA over PAN-HCl therefore results from the combined effect of (i) smaller barriers due to the disordered regions and (ii) increased charge delocalization in the ordered regions.

The increase in resistivity of all the samples studied, as the annealing temperature is raised, can therefore be explained by assuming increased localization of the electronic wave function along polymer chains due to the loss of some bound water molecules; it is emphasized that the unannealed samples were pumped under vacuum overnight to remove free or loose water molecules. Liberation of water by thermal aging is thought to introduce more disorder through changes, for example, in the potential barriers close to the anion sites[23] or increased polarization effects due to the anions.[27] We also see that although the intrinsic metallic characteristics are not affected by moisture, T_m for all the samples studied moves towards higher temperatures as the annealing
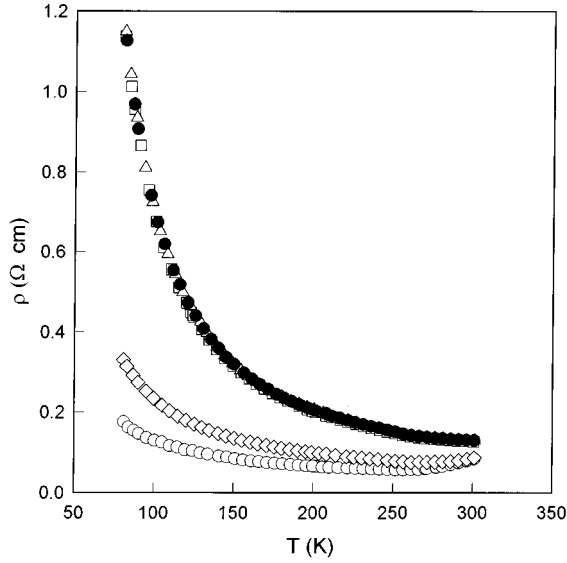
FIG. 5. Temperature dependence of dc resistivity of PAN-CSA-3 in the insulating regime of the metal-insulator transition. Various experimental conditions are as follows sequentially: ($\bigcirc$) unannealed; ($\square$) annealed overnight at 323 K; ($\triangle$) exposed overnight to O_2 gas; ($\bullet$) exposed overnight to N_2 gas; ($\blacksquare$) exposed overnight to moist air.

temperature is raised. Since the removal of water leads to disorder both within and between ordered regions, T_m is increased as now a higher temperature is required to overcome the increased barrier heights.

The results presented in Figs. 1–5 can also be interpreted in terms of a model which considers PAN-CSA as a homogeneously disordered three-dimensional metal.[30] In this model, samples with $r[=\rho(1.4\ \text{K})/\rho(300\ \text{K})]$ less than 2 belong to the metallic regime, those with $2<r<6$ are placed in the critical regime, and those with $r>6$ fall in the insulating regime of the MI transition. Furthermore, in the temperature range 100–200 K, the conductivity in this model is activated, viz., $\sigma(T)=\sigma_c \exp[-|E_F-E_c|/k_BT]$, where E_F and E_c are the Fermi energy and mobility edge respectively, σ_c is the conductivity at the mobility edge, and k_B is the Boltzmann constant. The data in Figs. 1, 3, and 5 were fit to the above expression in the temperature range 100 K $<T<$200 K and the fitting parameters are shown in Table I. It seems clear that annealing increases the separation between the Fermi

energy and the mobility edge. Since our data were taken at temperatures down to 77 K only, we find that the ratio, $r'=\rho(80\ \text{K})/\rho(300\ \text{K})$, for PAN-CSA-2 is 1.2 -for the data taken on the unannealed sample and 1.5 when the annealing temperature is raised to 353 K. Extrapolation of this data (corresponding to 353 K) to lower temperatures leads to $r=2$, and the sample can still be characterized as being on the metallic side of the MI transition. Annealing is thus seen not to affect the transport properties in this sample. For PAN-CSA-4, the value of r' is 1.3 for the data taken on the unannealed sample and 1.8 for the same sample annealed to 333 K. Extrapolation of the data leads to the ratio being slightly larger than 2 for the sample annealed at 333 K. This sample can thus be envisioned to make a transition into the critical regime of the MI transition. While the conductivity at room temperature for PAN-CSA-3 is not severely affected by the sample preparation, the activation energy is seen to be much higher than found for PAN-CSA-2 and PAN-CSA-4 under similar annealing temperatures. One possibility is that our sample was less crystalline than those furnished by Y. Cao, which would lead to noticeable changes in the electrical properties, especially at low temperatures. The values for r' for the unannealed and the annealed (at 323 K) samples are 2.4 and 8.8, respectively. In this sample, annealing is seen to induce a transition into the insulating regime.

V. CONCLUSIONS

We have shown that while the PAN-CSA samples are intrinsically metallic at temperatures larger than T_m, the value of T_m depends sensitively on the moisture content. The dependence of resistivity on temperature is not influenced by gases such as oxygen and nitrogen. The removal of moisture effected by thermal annealing has the effect of reducing the structural order between polymer chains in the ''crystalline regions'' (metallic regions) as well as on chains bridging the metallic regions. This disorder reduces the localization length of the electronic wave function, and leads simultaneously to increased resistivity and T_m. With increased charge localization, especially on the bridging chains, a delocalization-to-localization transition takes place and the system undergoes a metallic-to-nonmetallic transition. We have also analyzed our data in terms of the homogeneously disordered metal model in which thermal annealing is found

TABLE I. Parameters of PAN-CSA films (as described in the text) obtained from an analysis of the data in the temperature range $100<T<200$ K using a homogeneously disordered metal model.

Sample	Annealing temperature (K)	$|E_F-E_c|/k_B$ (K)	σ_c (S/cm)
PAN-CSA-2	295	30	56
PAN-CSA-2	323	49	42
PAN-CSA-2	333	52	40
PAN-CSA-2	353	58	38
PAN-CSA-4	295	43	42
PAN-CSA-4	323	68	30
PAN-CSA-4	333	73	28
PAN-CSA-3	295	141	30
PAN-CSA-3	323	247	17

to increase the separation between the Fermi energy and the mobility edge. From the present data we have no way of discriminating between these two models, although we tend to favor the former model over the latter. Nonetheless, the presence of moisture has been shown to play a significant role in defining the metallic state of PAN-CSA films.

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