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Counterion-induced processibility of polyaniline: Thermoelectric power

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The temperature dependence of the thermoelectric power was investigated for the emeraldine salt form of polyaniline protonated with camphor sulfonic acid (PANI-CSA) and for blends of PANI-CSA with poly(methyl methacrylate) (PANI-CSA/PMMA). The thermoelectric power (S) of PANI-CSA increases linearly in proportion to the temperature with $S \approx +10\ \mu\mathrm{V/K}$ at room temperature. This characteristic behavior persists when the fraction of PANI-CSA is diluted as a blend in insulating PMMA, even at volume fractions of PANI-CSA as low as about 1%. We discuss the PANI-CSA results in the context of transport at the metal-insulator boundary. The data from the blends are consistent with charge transport along the self-organized interconnected pathways of PANI-CSA in PMMA.

INTRODUCTION

The origin of the metallic state in the emeraldine salt form of polyaniline has been discussed for many years.[1-7] The formation of a polaron lattice was proposed by Stäfstrom *et al.*[1] based on the observation of a temperature-independent Pauli contribution to the magnetic susceptibility, and a broad absorption band in the near infrared.[3] The protonation-induced spin-unpairing mechanism[4,5] causes a rearrangement of the structure of polyaniline such that the formal repeat unit can be written as follows:

$$(\text{-}B\text{-NH-}B\text{-NH-})^{+\uparrow}(A^{-}) , \tag{1}$$

where B denotes a phenyl ring in the benzenoid form, A^{-} is the counterion, and the $(\,)^{+\uparrow}$ indicates that there is one unpaired spin in the π system and one positive charge in the σ system of the repeat unit. Although the conversion from the emeraldine base to the emeraldine salt does not involve charge transfer, the internal redox reaction leaves the electronic structure of the π system of the emeraldine salt with a three-quarter-filled band with one hole per (-B-NH-B-NH-) unit.[1,2]

The existence of one unpaired π electron per repeat unit implies that the electronic structure of the emeraldine salt will be that of a metal. It is well known, however, that disorder can result in localization of states; if the magnitude of the disorder potential is large compared with the bandwidth, all states become localized.[8] In such a case, even with one unpaired electron per repeat unit and a half-filled conduction band, the system will be an insulator. In such an insulator, there is no gap in the density of states; the material is an insulator since the Fermi level (E_F) lies in an energy interval in which all states are localized—the system is a Fermi glass. In a Fermi glass, the conductivity is activated; at high temperatures the activation energy is a measure of the energy difference between E_F (which lies in the region of localized states) and the mobility edge; at lower temperatures, variable range hopping transport results from the existence of unoccupied localized electronic states near E_F.

Although relatively highly conducting, transport measurements on the emeraldine salt form of polyaniline (PANI) with Cl^-, HSO_4^- etc. as counterions do not show typically metallic behavior. The electrical conductivity is dominated by hopping carrier conduction.[9] The thermoelectric power[9,10] does not show the characteristic linear dependence on temperature (T) expected for the entropy per carrier of a metal. Li, Cruz, and Philips[11] suggested that the U-shaped temperature dependence of thermopower observed, for example, in PANI-Cl,[9,10] could result from temperature-dependent tunneling between granular metallic islands.

The anamalous transport behavior observed in the emeraldine salt arises from a combination of mesoscale inhomogeneity (metallic islands) and microscopic disorder (localization of the electronic wave functions), both of which are indicative of the quality of the material. Thus, PANI has been characterized as a Fermi glass rather than as a true metal[4] or, alternatively, as a collection of metallic islands separated by insulating barriers.[9]

The development of homogeneous conducting polyaniline protonated with camphor sulfonic acid (CSA),[12-15] a surfactant counterion which induces solubility and processibility of PANI in its conducting form, has resulted in significant improvement of the electrical properties. The electrical conductivity of PANI-CSA (nonoriented; as cast from solution) is approximately 300 S/cm at room temperature (the resistivity ρ is about $3\times10^{-3}\,\Omega\,\mathrm{cm}$), an improvement over that obtained with conventional counterions by more than an order of magnitude.[13] The temperature dependence of the resistivity is correspondingly weaker, decreasing by only a small factor on cooling the sample from room temperature to 1 K.[13] The observation of a metallic temperature dependence for the resistivity above 200 K, a power-law dependence below 30 K, and a magnetic-field-induced crossover from power-law dependence to variable range hopping dependence demonstrated that films of PANI-CSA cast from solution in *m*-cresol are almost precisely on the metal-insulator boundary.[13]

The temperature-independent magnetic susceptibility obtained from electron-spin-resonance measurements[14] indicates the existence of a finite density of states at the Fermi energy. The low contribution to the susceptibility from Curie-law spins implies that the material is homogeneous with reduced disorder, compared with earlier data from samples with Cl^- and HSO_4^- as counterions.[3-5]

Composite polyblends of PANI-CSA with polymethylmethacrylate (PMMA) are electrically conducting at remarkably low volume fractions of the conducting component; the percolation threshold is at approximately 1% volume fraction of PANI-CSA.[12,15] The surfactant counterions lead to self-organization of the phase-segregated morphology during the course of liquid-liquid phase separation and the formation of an interconnected fibrillar network of conducting PANI-CSA in the PMMA host.[15] As a result, the conducting properties of PANI-CSA persist in the blends even at very low concentrations ($y \approx 1\%$), in agreement with the conclusion that the electronic structure remains like that of a metal (there is a finite density of states at E_F), as inferred from the Pauli contribution to the magnetic susceptibility.[14]

We report the temperature dependence of the thermoelectric power of PANI-CSA and PANI-CSA/PMMA polyblends with various PANI-CSA concentrations. The thermopower of PANI-CSA is *positive* and exhibits a linear temperature dependence; the data are qualitatively different from those obtained earlier with conventional counterions. Since orientation by tensile drawing has been shown to improve the structural order and to produce a shift toward positive values of $S(T)$ with greater linearity,[9] the thermopower data obtained for PANI-CSA imply a significant reduction in the disorder, even in undrawn samples. When the conducting PANI-CSA is diluted in the polyblend with insulating PMMA, the linear temperature dependence persists with unchanged magnitude. The sign change and U shape of $S(T)$ at low temperatures in the most dilute blends (2.43% PANI-CSA) are reminiscent of similar but much more exaggerated effects observed earlier for inhomogeneous PANI-Cl.[9-11]

EXPERIMENTAL DETAILS

PANI-CSA was prepared by dissolving the emeraldine base form of PANI and (±)-10-camphor sulfonic acid, in the molar ratio of 0.5 CSA to PANI repeat unit, in *m*-cresol.[12] PANI-CSA/PMMA polyblends were prepared by mixing various concentrations of the PANI-CSA complex into a 10% solution of PMMA in *m*-cresol.[12,14] Free-standing films were obtained by casting onto glass substrates and subsequently drying in air at 50 °C for 24 h.

The differential technique was used for the thermopower measurements.[16] Two isolated copper blocks were alternatively heated,[17] and the heating current was accurately controlled by computer. The temperature difference between the two copper blocks was measured by a chromel-constantan thermocouple and did not exceed 0.5 K at each thermal cycle. Samples were mounted across the copper blocks with pressure contacts, and the voltage difference across the sample was averaged for one complete cycle. Any temperature difference between sample and thermocouple was less than 10% of the temperature gradient across the sample; the thermometry was carefully calibrated for the entire temperature range ($5\ K < T < 300\ K$). The absolute thermopower of the sample was obtained from the absolute scale for lead.[18] The four-probe method was used for dc conductivity measurements.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of thermoelectric power of PANI-CSA. The room-temperature value is approximately 10 μV/K with small variations ($\pm 2\ \mu$ V/K) depending on the details of the sample casting process. The magnitude and sign of $S(T)$ are similar to results obtained from a number of partially doped *p*-type conducting polymers.[19,20] The positive sign of the thermopower is consistent with the calculated band structure of the metallic emeraldine salt; a three-quarter-filled π band with one hole per (-*B*-NH-*B*-NH-) repeat unit. The linear temperature dependence of $S(T)$ corresponds to the characteristic diffusion thermopower of a metal, or alternatively, to the entropy per carrier. Neither the phonon drag effect,[21] which is usually suppressed

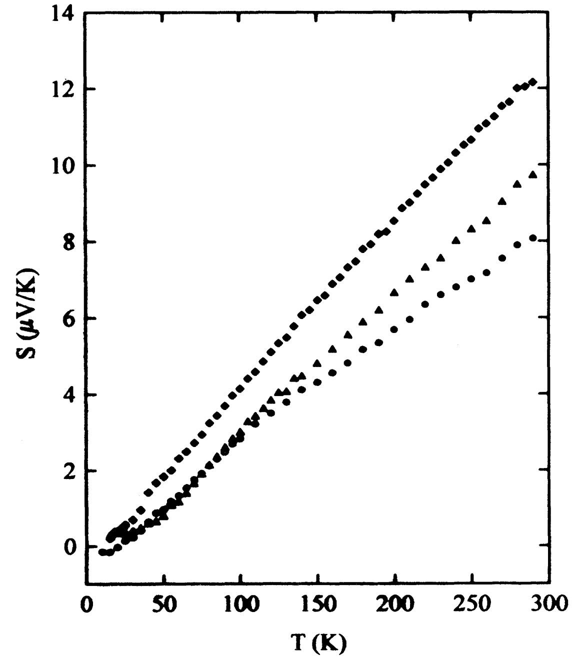

FIG. 1. The thermoelectric power of PANI-CSA; the samples (◆), (▲) and (●) are prepared in different casting conditions.

by disorder, nor the positive contribution due to the electron-phonon interaction,[22] were observed.

For a disordered system with a partially filled electronic band, there is a finite density of states at the Fermi energy. The electronic system is either a metal (weak disorder) with extended states at the Fermi energy, or a Fermi glass (strong disorder) with localized states at the Fermi energy. If the disorder is sufficiently weak that E_F lies in the regime of extended states, the temperature dependence can be expressed as follows:

$$S=\frac{\pi^2}{3}\frac{k_B}{e}k_BT\left|\frac{d\ln\sigma(E)}{dE}\right|_{E_F}, \tag{2}$$

where k_B is the Boltzmann constant, e is the electron charge, E_F is the Fermi energy, and the energy dependence of the conductivity, $\sigma(E)$, generally arises from both the band structure and the energy dependence of the scattering time. A relatively large magnitude of $S(T)$ in comparison with typical metals suggests that a relatively small bandwidth is responsible for the linear temperature dependence, rather than an energy-dependent scattering process. If we assume that $\sigma(E)$ is a slowly varying function in the vicinity of E_F, Eq. (3) is equivalent to the free-electron approximation result

$$S_m(T)=+(\pi^2/3)(k_B/|e|)k_BT(z/E_F)\ , \tag{3}$$

where the positive sign indicates that the π band is more than half-filled,[1,2] with one hole per (-B-NH-B-NH-) unit as noted above, and z is a constant determined from the band structure and energy dependence of the mean scattering time. Using $z=1$, $E_F\approx1$ eV,[1,2] and $T=300$ K, Eq. (3) yields $S(300\text{ K})\approx7.5\mu$V/K; i.e., close to the measured value. The density of states estimated from the magnitude of the thermopower[19] is 1.1–1.6 states per eV per two rings (assuming energy-independent scattering), consistent with the value of one state per eV per two rings obtained from magnetic susceptibility measurement.[14]

As shown in Fig. 2, the thermopower data in Fig. 1 are insensitive to the details of the temperature dependence of the resistivity. In Fig. 2, the most metallic sample (●) exhibits a weak temperature dependence at low temperature and a resistivity ratio ρ (1 K)/ρ(300 K) equal to 1.6; whereas the most disordered sample (♦) exhibits the temperature dependence characteristic of variable range hopping (VRH) in three dimensions,

$$\rho=\rho_0\exp(T_0/T)^{1/4} \tag{4}$$

at low temperature with a relatively high-resistivity ratio. The other sample in critical regime (▲) exhibits a power-law temperature dependence at low temperature and has a resistivity ratio of 3. These data and the related magnetic-field-induced crossover from power-law temperature dependence to VRH temperature dependence demonstrate that although the PANI-CSA samples are very near the metal-insulator boundary, the states at the Fermi level are localized.[13] The linear dependence of the thermopower for all three samples confirms the conclusion that PANI-CSA processed from solution in m-cresol is near the metal-insulator boundary.

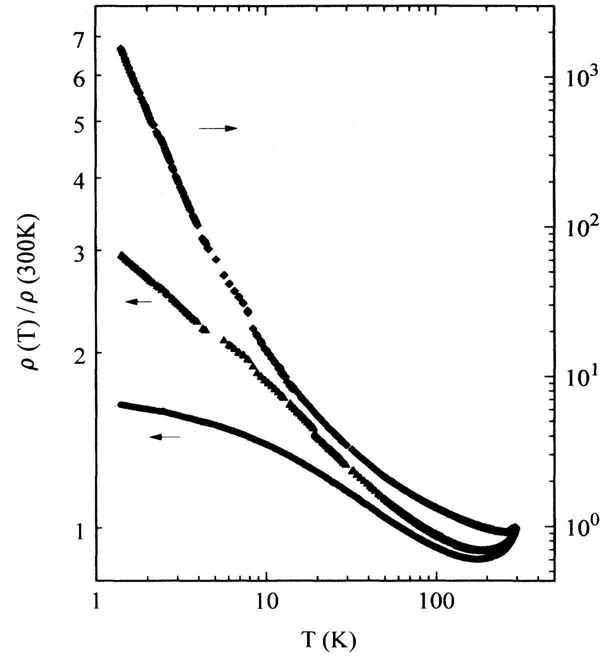

FIG. 2. The temperature dependence of the normalized resistivity for the same samples on which the thermopower was measured (Fig. 1); the values of $\rho(300\text{ K})$ for the three samples are essentially the same [(♦):3.6×10^{-3} Ω cm, (▲):3.1×10^{-3} Ω cm, and (●):4.5×10^{-3} Ω cm], whereas the low-temperature resistivities exhibit weak (●), power law (▲), and hopping (♦) temperature dependences, respectively.

For variable range hopping transport, the thermopower can be written as S_{hop},[8]

$$S_{\text{hop}}=-\frac{1}{2}\frac{k_B}{|e|}\frac{W^2}{k_BT}\left|\frac{d\ln N(E)}{dE}\right|_{E_F}, \tag{5}$$

where for VRH, $W^2/k_BT=k_B(T_0T)^{1/2}$ for variable range hopping in three dimensions. Thus, in the VRH regime, $S_{\text{hop}}(T)$ varies as $T^{1/2}$, tending to zero as T goes to zero. Comparing the hopping term (S_{hop}) with metallic thermopower (S_m),

$$\left|\frac{S_{\text{hop}}}{S_m}\right|\propto\left[\frac{T_0}{T}\right]^{1/2}. \tag{6}$$

Thus the hopping contribution to the thermopower would be expected to dominate the thermopower for $T\ll T_0$. The data shown in Fig. 1 remain linear over the entire temperature range for the sample for which the resistivity follows the VRH temperature dependence [Eq. (4)], even for $T<T_0\approx3\times10^4$ K.

The localization length (L_c) for the samples in insulating regime of M-I transition can be estimated both from the magnitude of T_0 and from the magnetic-field dependence of the resistivity,[13] resulting in $L_c\approx30\sim160$ Å. Since this value of L_c is obtained from an analysis of VRH in three dimension, the localization length along the chain is significantly greater than L_c. The linear temperature dependence of $S(T)$ therefore implies that the one-dimensional electronic structure of the PANI chains is very close to that of a metal even in the three-dimensional VRH regime close to the M-I transition.

The thermoelectric power data obtained from a series of PANI-CSA/PMMA blends are shown in Fig. 3. The data for all concentrations are similar; approximately linear above 100 K with a common room-temperature value, $S(300\text{ K}) \approx +8\ \mu\text{V/K}$, independent of concentration. The results imply a phase-separated morphology with little change in the electronic structure of the PANI-CSA component by dilution in PMMA. This is consistent with the interpenetrating network morphology observed by electron microscopy studies of the PANI-CSA/PMMA blends,[15] and with the measurements of the Pauli contribution to the magnetic susceptibility, χ_P,[14] which show that χ_P (per two-ring repeat unit) is independent of concentration.

The transport and microscopy data indicate that the percolation threshold in the PANI-CSA network is at approximately 1%. $S(T)$ remains linear above 100 K with little change in magnitude even for $y \approx 1\%$ (we were not able to extend the thermopower data to low temperatures for concentrations below 1% because of the high sample resistance). As the blends are diluted, the temperature dependence remains linear at high temperatures, but shows a clear deviation from linearity below 100 K; this deviation from linearity increases as y decreases. For the most dilute samples near the percolation threshold (e.g., 2.4% PANI-CSA), the low-temperature behavior is reminiscent of the characteristic U-shaped dependence well-known for HCl-doped polyaniline.[9–11] Note, however, that the magnitude of the U-shaped deviation from linearity in Fig. 3 is much smaller than reported for the emeraldine salt with Cl^-counterions.[9–11] Since the percolation threshold represents the contribution below which the conducting network breaks up into disconnected regions, we infer that the U-shape results from activated transport through the insulating regions. In this sense, the observation of a weak U-shaped contribution to $S(T)$ near the percolation threshold is consistent with the existence of large-scale inhomogeneity (metallic islands) in HCl-doped polyaniline.

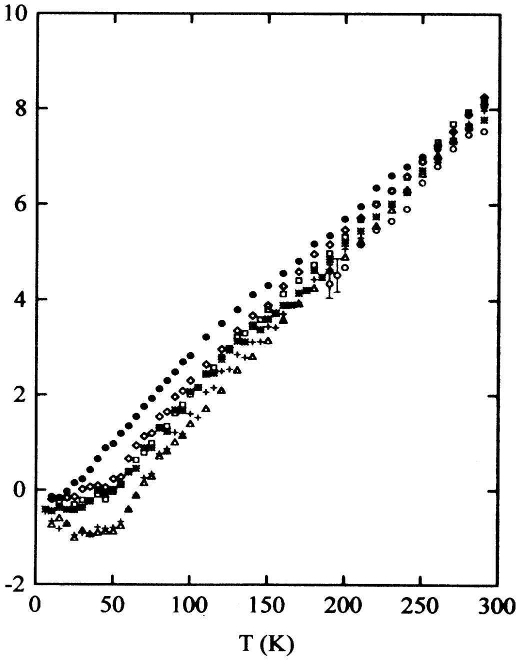

FIG. 3. The thermoelectric power of PANI-CSA/PMMA blends at various concentrations of PANI-CSA in PMMA: $y = 100\%$(●), 66.6%(◇), 33.3%(□), 9.09%(∗), 4.76%(+), 2.43%(△), and 1.24%(○).

The metallic temperature dependence of $S(T)$ observed at a surprisingly low concentration of PANI-CSA indicates that the microscopic conduction mechanism is not changed as PANI-CSA is diluted in PMMA. The electrical conductivity is strongly dependent on the number of connected pathways. However, once connected paths are formed above the percolation threshold ($y \approx 1\%$), $S(T)$ is insensitive to the change in the number of paths. As a zero current transport coefficient, the thermoelectric power is relatively insensitive to the conduction between phase-separated regions because the thermoelectric voltages add as long as most of the thermal gradients take place across the conducting paths.[21] In such a heterogeneous system, the additional contribution to $S(T)$ from transport between separated regions becomes important only when the average hopping distance is large, consistent with the data for dilute concentrations of PANI-CSA/PMMA blend in Fig. 3. The electrical conductivity is, however, especially sensitive to the existence of insulating barriers in a heterogeneous system. Thus the combination of the thermopower and conductivity results (and the existence of a Pauli contribution to the magnetic susceptibility) in the blends provides insight into the electronic structure of PANI-CSA in the dilute blends.

Detailed analysis of the temperature dependence of the conductivity near the percolation threshold implies superlocalization on the fractal structure.[23,24] These results, together with a more detailed analysis of the thermoelectric power in the superlocalization regime, will be reported in a subsequent publication.

SUMMARY AND CONCLUSION

In summary, the thermoelectric power of PANI-CSA increases linearly in proportion to the temperature with $S \approx +10\ \mu\text{V/K}$ at room temperature. This characteristic behavior persists when the fraction of PANI-CSA is diluted as a blend in insulating PMMA, even at volume fractions of PANI-CSA as a low as $\approx 1\%$. The PANI-CSA results are consistent with resistivity data which imply that the extent of disorder has been reduced to the point where the transport occurs essentially at the metal-insulator boundary. The data from the blends indicate charge transport along the self-organized interconnected pathways of PANI-CSA in PMMA. The observation of the linear temperature dependence for $S(T)$ indicates that the entropy per carrier is that of a degenerate Fermi system; since the resistivity in the same samples indicates hopping transport, PANI-CSA is a Fermi glass close to the metal-insulator transition. In the best samples, the data indicate that the disorder has been reduced to the point where the system has crossed over to the metallic side of the metal-insulator transition.

The demonstration that PANI-CSA cast from solution in *m*-cresol is on the boundary of the *M*-*I* transition provides a fixed point. Although improvement in material quality will quite generally improve electrical properties, reduction in disorder *within the metallic regime* will increase the mean free path for carriers in extended states. That this fixed point has been achieved in materials cast directly from solution without subsequent processing to optimize chain extension, chain alignment, and interchain order suggests that major improvements in electrical conductivity can be anticipated for polyaniline protonated with surfactant counterions.

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