BF$_3$-doped polyaniline: A novel conducting polymer

DEBANGSHU CHAUDHURI and D D SARMA

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

E-mail: sarma@sscu.iisc.ernet.in; sarmadd_in@yahoo.com

Abstract. We review the unusual structural, transport and magnetic properties of highly conducting polyaniline, doped with boron trifluoride. Our studies establish the unique conducting state of this system, which is in distinct contrast with the conventional proton-doped polyaniline samples.

1. Introduction

During the past two decades, both fundamental and applied research in conducting polymers has grown enormously [1]. Polyaniline (PANI) owing to its ease of synthesis, remarkable environmental stability, and high conductivity in the doped form, has remained one of the most thoroughly studied conducting polymers. While it is long known that proton-doping can make PANI conducting, the possibility of using non-protonic dopants such as electron-deficient Lewis acids was demonstrated only very recently [2–5]. Lewis acid-doped polymers are expected to be different from the conventional protonated PANI owing to a qualitatively different chemical interaction between the dopant and the polymer; for instance, the absence of any counterion in these systems may have a different influence on the properties. In this article, we review the transport and magnetic properties of a highly conducting PANI doped with boron trifluoride (BF$_3$).

2. Experimental

A detailed procedure for the synthesis of PANI and doping with BF$_3$ has been previously reported [2]. The sample was characterized for complete doping using routine spectroscopic techniques, like UV–visible absorption, FTIR and ^{11}B magic-angle-spinning (MAS) NMR spectroscopy. For the four-probe conductivity

measurements, the as-prepared powder samples were pressed into ~ 1 mm thick pellets. Magnetic susceptibility was measured on powdered samples, using a super-conducting quantum interference device magnetometer (Quantum Design MPMS).

3. Results and discussion

In figure 1, we present the X-ray diffraction (XRD) patterns of undoped and BF_3-doped PANI. We have also presented the data for HCl-PANI, adapted from ref. [6]. The XRD pattern reveals that BF_3-PANI is as amorphous as undoped PANI. This is in stark contrast with conventional HCl-doped PANI, as can be seen from the figure. It is known that undoped, amorphous PANI becomes partially crystalline upon proton-doping. It has been established that the delocalized charge carriers responsible for the sample's electrical conductivity are essentially associated with these crystalline domains. Considering that the intrinsic conductivities of BF_3-doped sample is much higher than that of the protonated PANI, as discussed later, this observation puts the present system in a unique class of amorphous and yet highly conducting polymers.

We now present the results of DC conductivity. As mentioned earlier, the room temperature conductivity of BF_3-PANI (35 S cm^{-1}) is an order of magnitude higher than that of HCl-PANI (~ 1 S cm^{-1}). This difference becomes even more prominent at lower temperatures. Temperature dependence of conductivity in doped PANI has been described using the relation

$$\sigma = \sigma_0 \, \exp[-(T_0/T)^\alpha], \tag{1}$$

where T_0 and α are independent of temperature. For most doped PANI systems, α is found to be 0.5. There are two different conduction mechanisms that lead
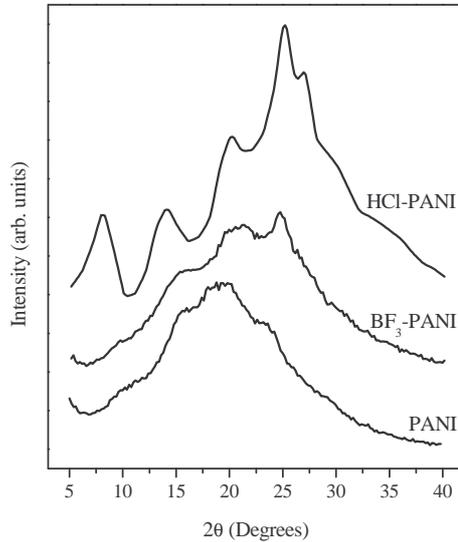

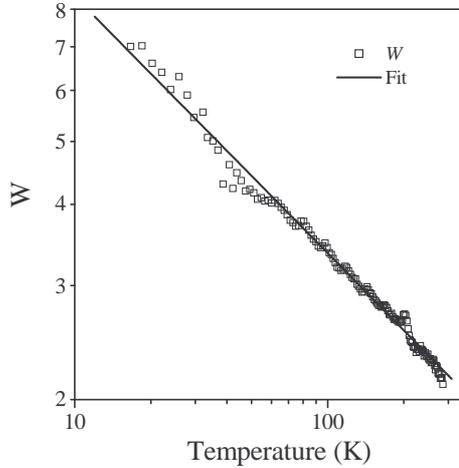**Figure 1.** The XRD patterns of undoped, BF_3-doped, and 50% HCl-doped PANI (reproduced from ref. [7]).

Figure 2. Variation of the reduced activation energy W as a function of temperature on a double-logarithmic scale, for the as-made BF$_3$-PANI sample.

to $\alpha = 0.5$; quasi-one-dimensional variable range hopping (Q1D-VRH) of charge carriers [7], and Sheng's model of charging energy limited tunnelling (CELT) of carriers between small metallic grains [8]. While the former mechanism has been the most widely accepted one in doped PANI systems, we have established that the dominant mechanism in BF$_3$-doped PANI is CELT. In figure 2, we present the variation of reduced activation energy (W) as a function of temperature, on a double logarithmic scale; the quantity W is defined as $(\mathrm{d}\ln\sigma/\mathrm{d}\ln T)$. For the systems obeying eq. (1), $\ln W$ vs. $\ln T$ plot must be linear with a slope of $-\alpha$. In the case of BF$_3$-PANI, we indeed find the dependence to be linear, however, the slope is -0.4. While such a deviation from $\alpha = 0.5$ cannot be accommodated within the framework of Q1D-VRH, CELT on the other hand, predicts the value of α to lie between 0.5 and 0.25. Therefore, the data presented in figure 2 seem to suggest that the conduction is mediated by CELT of charge carriers across small conducting grains.

To confirm this interpretation, we carried out a systematic study of the charge transport in large-grain BF$_3$-PANI samples, prepared by three different routes: thermal annealing of the as-prepared pellet (sample A), cast film of BF$_3$-PANI (sample B), and a pellet compressed in the presence of a solvent (sample C). In figure 3, we present the variation of W as a function of T for the three large-grain samples. In all the cases, we observe a clear departure from the linear behaviour that was seen for the small-grain, as-prepared sample. It is well-known that CELT in large grain samples obey the following temperature dependence [9]:

$$\sigma(T) = \sigma_0 \exp[-T_0/(T + T_1)], \tag{2}$$

where T_0 gives a measure of the barrier height. For samples obeying eq. (2), the slope of $\ln W$ vs. $\ln T$ curve is given by $1 - 2T/(T + T_1)$, and is therefore, expected to vary from -1 ($T \gg T_1$) to 0 ($T = T_1$). The result presented in figure 3 confirms this, as we find the slope of the three curves changing gradually from ~ 1 to 0 with decreasing temperature.
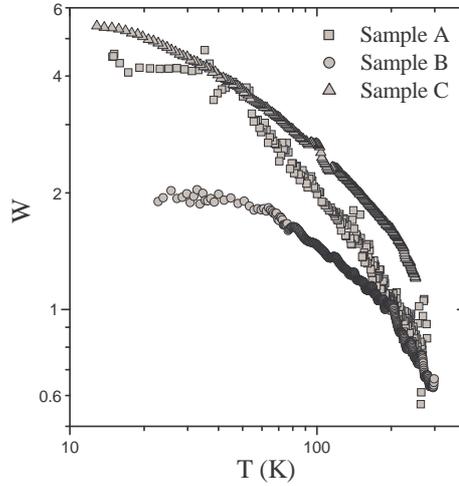
Figure 3. W vs. T for the three large grain samples, A, B and C.

From the above discussion, it is evident that the macroscopic resistivity of these doped PANI samples is influenced strongly by the presence of grain boundaries. In such a scenario, a measure of the intrinsic conductivity can be obtained from the magnetic properties. In figure 4, we present the results of temperature-dependent DC magnetic susceptibility (χ) for BF$_3$-PANI. χ for doped PANI has been described by [10]

$$\chi(T) = \frac{C}{T} + \chi_{\mathrm{P}}, \tag{3}$$

where χ_{P} is the temperature-independent Pauli paramagnetic contribution from the de-localized charge carriers, and C is the Curie constant arising from localized spins. While the low-temperature part of χT vs. T certainly looks linear, a closer inspection seems to suggest a deviation at $T \sim 210$ K. The increase in slope at 210 K suggests an increase in χ_{P}, and a simultaneous decrease in C. $\ln \chi$ vs. $\ln T$ plot in the same figure further accentuates this fact. This enhancement of χ_{P} at the cost of C with increasing T is possibly a consequence of the thermal activation of the localized spins into free carriers, indicating that the trapping potential is in the scale of the thermal energy in this system. This fact has also been established using electron spin resonance studies [2]. Density of states at the Fermi level, $N(E_{\mathrm{F}})$, derived from χ_{P} for BF$_3$-doped PANI is 11.4 states eV^{-1} (2-rings)$^{-1}$. The fact that this value is considerably higher than any known conducting PANI system [7] exemplifies the superiority of BF$_3$ over other dopants.

4. Conclusion

To conclude, we establish a very high intrinsic conductivity in BF$_3$-PANI. Macroscopic conductivity is dominated by CELT between highly conducting grains across
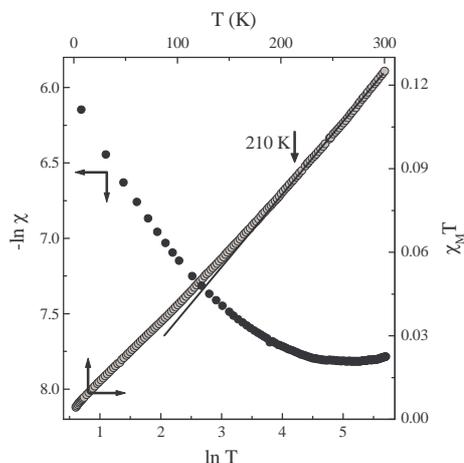
BF$_3$-doped polyaniline

Figure 4. Plots of χT vs. T. The solid line is a guide to the eye. $\ln \chi$ vs. $\ln T$ suggesting spin delocalization near 210 K.

the insulating grain-boundary layer. The energy scales associated with the trap potential for localizing spins were found to be in the order of the thermal energy scale. Additionally, the fact that BF$_3$-PANI is amorphous, puts it in a unique class of amorphous and yet metallic polymers.

Acknowledgement

References

[1] T A Skotheim, R L Elsenbaumer and J Reynolds, *Handbook of conducting polymers* (Marcel Dekker, New York, 1998)
[2] D Chaudhuri, A Kumar, I Rudra and D D Sarma, *Adv. Mater.* **13**, 1548 (2001)
[3] D Chaudhuri, A Kumar, D D Sarma, M García-Hernández, J P Joshi and S V Bhat, *Appl. Phys. Lett.* **82**, 1733 (2003)
[4] D Chaudhuri, P W Menezes and D D Sarma, *Appl. Phys. Lett.* **83**, 2348 (2003)
[5] D Chaudhuri, A Kumar, R Nirmala, D D Sarma, M García-Hernández, L S Sharath Chandra and V Ganesan, *Phys. Rev.* **B73**, 075205 (2006)
[6] M E Jozefowicz *et al*, *Phys. Rev.* **B39**, 12958 (1989)
[7] Z H Wang, C Li, E M Scherr, A G MacDiarmid and A J Epstein, *Phys. Rev. Lett.* **66**, 1745 (1991)
[8] L Zuppiroli, M N Bussac, S Paschen, O Chauvet and L Forro, *Phys. Rev.* **B50**, 5196 (1994)
[9] P Sheng, B Abeles and Y Arie, *Phys. Rev. Lett.* **31**, 44 (1973)
[10] A J Epstein *et al*, *Synth. Met.* **21**, 63 (1987)