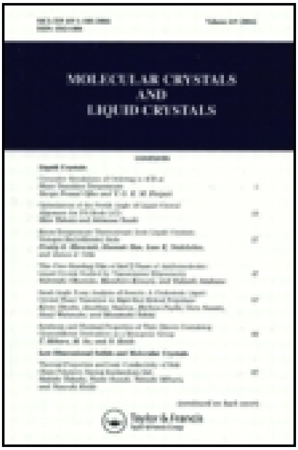

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Magnetic Properties of Organic Acid-Doped Polyaniline

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Magnetic Properties of Organic Acid-Doped Polyaniline

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Magnetization and magnetic susceptibility of pellets of polyaniline basic- EB and acid doped-ES(HCOOH) and ES(HCl) were measured as a function of the temperature and magnetic field. Few but large magnetic moments are responsible for the magnetism in these materials.

Keywords: polyaniline; magnetism; conducting polymers

1. INTRODUCTION:

Among several interesting conducting polymers, polyaniline (PAni) is distinguished by several reasons. Its conductivity depends simultaneously of the oxidation state of the main chain and the acid doping possibility of the imine nitrogen atoms. The rich variety of oxidized states and doping levels, which can be readily controlled by appropriate oxidation and protonation process makes the physical and chemical properties dependent of several experimental circumstances, such as oxidant used in the synthesis process, pH of solution and the acid used, temperature, pressure, humidity, final oxidation states, secondary doping process and so on. All this possibility makes PAni attractive because it allows developing materials with interesting properties changing the right parameters. While the study of conducting polymers has now progressed to the point of producing commercially viable products [1-2] there are few results presented on magnetic properties and applications. Materials having both electrical and magnetic properties (e.g. ferromagnetic properties) will be suitable for the application in electrical and magnetic shielding, microwave absorption and information recording. Recently PAni and its derivatives have attracted much attention for their ferromagnetic properties [3-5]. Although some results on high temperature organic magnets are controversial and linked to impurities of transition metals [6], there is evidence that ferromagnetic and antiferromagnetic properties of Pani are intrinsically due to the polymer chain. Experiments with doping and undoping with acid and base respectively have been done in order to show that the ferromagnetic property is really due to the polymer main chain. The ferromagnetic phase [4] is destroyed when the polymer is treated with base and it appears again when the samples are treated with hydrochloric acid, suggesting that the contribution from transition metal impurities would be not so important in that case. Because the solubility is an important factor for obtain a high polymer chain alignment, yielding a high spin state throughout the bulk, we investigate in this paper the magnetic properties of PAni in the undoped form (emeraldine base, EB), in the HCl-doped form (emeraldine hydrochloride, ES(HCl)) and in formic acid-doped form (emeraldine formiate, ES(HCOOH)).

2. EXPERIMENTAL PROCEDURE AND RESULTS

Except for aniline, purified by repeated distillations, all other reagents were used as received. Solutions were prepared with distilled/deionized water. PAni was chemically synthesized in a procedure adapted from literature [7]. As synthesized PAni was converted to the undoped form, emeraldine base (EB), by treatment with 1.0M ammonium hydroxide for 4 hours. Part of this powder was treated with 1.0M HCl for 4 hours, and another part was treated with 86% formic acid for 4 hours. The remaining material, which was treated neither with HCl nor with HCOOH was labeled simply EB. All samples were pressed into pellets at 5 ton using a Beckman 00-25 laboratory press. A SQUID magnetometer was used to measure the magnetization M and the susceptibility χ of samples. The temperature T was varied in the range 1.7-300 K and the magnetic field H was swept from –5 to +5 kOe. In Fig. 1a χ is plotted against the inverse of T. The solid lines are fit to the Curie type plus a temperature independent susceptibility ($=\chi_0+C/T$). A deviation from the Curie-law is observed at lower T. The EB and ES(HCl) samples showed approximately the same χ_0 while the ES(HCOOH) sample presented a much higher value. The Fig. 1a inset show a typical FC (field-cooled) and ZFC (zero-field-cooled) data for H = 500 Oe for the ES(HCOOH) sample showing some irreversibility. We notice that this irreversible behavior diminishes when H is increased.

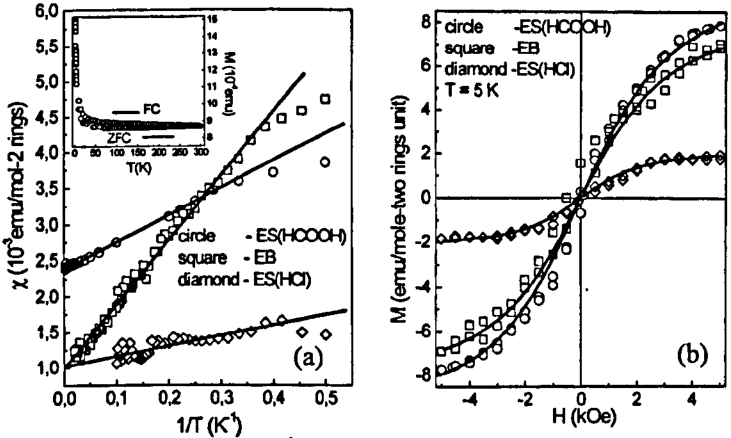

FIGURE 1 (a) χ vs. T^{-1} and (b) M vs. H curves. The inset in Fig. 1a shows ZFC and FC curves for the ES(HCOOH) sample.

Fig.1b shows M vs. H data for 5 K. Solid lines are Brillouin functions fitted to the data. The parameters N and p were independently obtained from the saturation magnetization M_S (Np) and the linear susceptibility χ ($Np^2/3k_BT$). A small hysteresis ($H_C \approx 50$ Oe) is also present in the data. The parameters obtained from the fit of the Curie-law (χ_0 and C) and from the Brillouin function (N and p) are shown in table 1.

TABLE1 Fitting parameters.

Sample/ Parameter	χ_0(emu/mol-2rings)	C(emu-K/mol 2-rings)	N (mol 2-rings)$^{-1}$	P(μ_B)
EB	1.10×10^{-3}	9.5×10^{-3}	1.70×10^{19}	61
ES(HCl)	0.96×10^{-3}	1.2×10^{-3}	0.30×10^{19}	85
ES(HCOOH)	2.40×10^{-3}	3.5×10^{-3}	1.95×10^{19}	119

3. DISCUSSIONS AND CONCLUSIONS

The values listed in Table 1 for N and p($=g\mu_B[J(J+1)]^{1/2}$), show that few but large magnetic moments are responsible for the magnetism in these samples. The clustering behavior, the coercive field, the non-Curie-type susceptibility plus the small irreversibility, suggest a superparamagnetic state with some long-range interaction. This magnetic state is typical of glassy materials, which, in the present case, could be expected because of the way the samples were prepared. Furthermore, it would be necessary to have of the order of 1 part in 10^3 impurities to account for our results assuming that they are due magnetic impurities. This number is well beyond the measured ones (through plasma spectrometry), which are in the ppm range. Work partially supported by FINEP, CNPq, CAPES and FACEPE.

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