

# Observation of ferromagnetism in polyaniline

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## Abstract

We discuss our observation on synthesis and characterization of ferromagnetic polyaniline by way of stabilizing spin carrying charge carriers generated during redox doping of polyaniline.

**Key words:** Polyaniline, Magnetic Measurements, Auger Electron Spectroscopy.

## Introduction

The topic of current interest in conjugated polymeric system is the construction of high spin polymeric system. A genuine organic ferromagnet p-nitrophenyl nitronyl nitroxide was successfully synthesized in 1991 [1]. A guiding principle concerning magnetic interaction among organic radical is Mc Connell proposal on spin exchange to give spin polarization effect in an open shell system like cyclophane [2]. The second scheme invokes stacking of donor and acceptors in an alternating arrangement.

Among conducting polymer, polyaniline is exceptional and each repeat unit can accommodate one polaron [3]. The recent proposal suggests that if the repeat unit of polymer has meta, para coupling it can yield a ferromagnetic spin alignment upon doping [4-5]. However, such systems have poor reproducibility and stability. It has been reported that to achieve extensive spin stabilization the synthesis can be carried out using branched oligomers to yield a two dimensional system with meta-para coupling [5]. However close examination of this work show that redox potentials of these system are high enough to destabilize any polaronic species to bipolaron [6-7]. In this communication we report our observations on use of large size functionalised dopant namely: 2-6 quinone disulphonic acid for obtaining conducting emeraldine salt which gets attracted to permanent magnet at room temperature.

## Experimental

Aniline polymerization was carried out at pH 1 as described in literature. The electrochemical polymerization was carried out at platinum electrodes by sweeping the

potential from -0.2V to 0.7V vs saturated calomel electrode (SCE). All solutions were purged with argon. The polymer was characterized by electrochemical, thermal analysis, powder x-ray diffraction, electronic and  $H^1$  NMR, vibrational spectra, XPS,  $^{13}C$  NMR and magnetic studies. The XPS measurement on ferromagnetic polyaniline was made on VG Mkii ESCA LAB spectrometer with a Mg- $K\alpha$ -X-ray source (1253.6 eV photons). All core level spectra are referenced to C 1s neutral carbon peak at 284.6 eV. The magnetic measurements were made on EG and G mode 155 VSM with sensitivity of  $\pm 0.01$  emu.  $^{13}C$ -CPMAS was recorded on DSX - 300 NMR spectrometer with TMS as reference.

## Results and Discussions

The host - guest interaction of polymer like polyaniline can be visualized as lock and key, which means that guest must penetrate into and wrapped by host matrix to yield a layered structure thus the doping emerges as a dedicated molecular interactions. The basic theory of coulombic forces explains the ion - dipole interaction has the same dependence on the dielectric environment as interaction between partners bearing charges but weaken on an absolute scale and falls off with distance more steeply. This implies the directional nature of host - guest chemistry and dipole depends on their mutual orientation. Thus the use of dopants with a co- planar orientation (aromatic sulphonic acids etc) yield a polyaniline which does not show any ferromagnetic behaviour. Thus the use of a dopant which is not only functionalised but has a vertical orientation not only yields a polyaniline which has a layered structure as indicated by growth of polyaniline by

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potential step technique, Fig.1, but also exhibits ferromagnetic behaviour at room temperature.

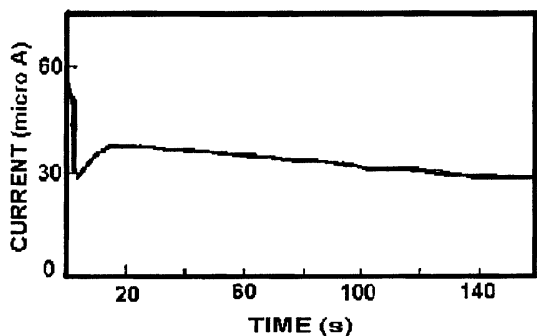


Fig.1: Growth of PAN at 0.75 V vs SCE

The steps in the growth curve indicates the formation of an layered structure which is not common in conductive polymers and growth pattern indicated by fall and rise in current which is the indicative of random nucleation [6]. The reason for observing this type of growth pattern can be ascribed to the orientation of the dopant molecules which has four functional group namely two keto and two sulphonic acid group in exactly opposite direction to each other thus this dopant molecule acts as a spacer cum ferromagnetic coupling unit. The perusal of cyclic voltammetry curve shows that the peaks are observed at 180 mV and 440 mV anodic cycle and +440 mV and +80 mV in the cathodic cycle. The difference in the 1st and II nd peak potential is 260 mV, whereas in sulfuric acid medium it is around 500 mV [6]. This cyclic voltammetric behaviour can be ascribed due to stabilization of polarons.

$^{13}\text{C}$  – CPMAS signals with respect to TMS were observed at 120, 125, 134, and 137 ppm due to benzenoid carbon. The signal due to non protonated carbon (quinoid) were observed at 152, 185, and 198 ppm entirely due to dopant suggesting that majority of polymer has benzenoid structure which is only possible if polarons gets stabilized.

The XPS signals for nitrogen 1s core level were observed at 398.50 eV with main signal centered at 400.32 eV with a satellite peaks at 401.28, 402.9 and 403.86, suggesting the charge at nitrogen atom.

The diffuse reflectance spectra gave a peak at 430 nm and 720 nm. The clear peak formation at 720 nm indicates that charge carriers are polarons. The magnetic measurements shows the clear loop formation between increasing and decreasing magnetic field suggesting that magnetism is due to spins Fig 2. At room temperature magnetization value is 10 emu /g.

The elemental analysis indicated that doping is 49.5 mole % per two repeat unit of aniline was essential to observe room temperature ferromagnetism.

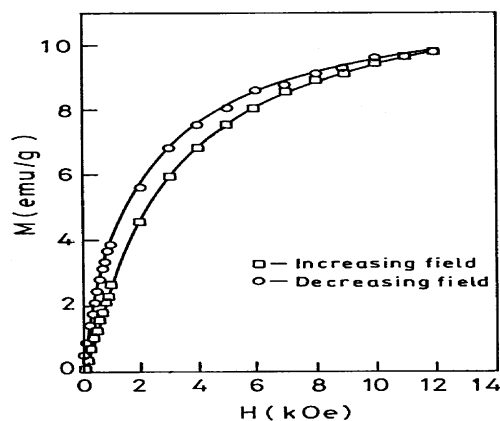


Fig. 2 Magnetization studies at 300 K

To determine any inorganic ferromagnetic impurities, doped polyaniline was decomposed at 700°C and the residue was 0.1% of total weight. The residue was subjected to analysis by atomic absorption using AAS 200 Varian and X – ray probe analysis. These analysis clearly indicated that ferromagnetic impurities were nil and residue was only sodium sulfate.

### Conclusion

Our observation suggest that the position of the self – trapped carriers are essentially due to the non-coplanar orientation of the dopant and therefore a competition between ferromagnetic (layered growth) and anti ferromagnetic (random nucleation) yields the material with a frustrated structure to give spin ordering thus the observation of ferromagnetism in polyaniline is due to spin glass structure.

### Acknowledgement

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