

# The Influence of the Morphology on the Magnetic Properties of Poly(3-hexylthiophene)

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Received: 3 August 2008 / Accepted: 15 June 2009 / Published online: 24 September 2009  
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**Abstract** The influence of the morphology on the magnetic properties of poly(3-hexylthiophene) has been studied and the results reported. The changes in the saturation magnetization were explained considering the polymer morphology prepared with different amounts of water in the solution during sample synthesis. The results show that the saturation magnetization is maximized for 200 ppm of the water in acetonitrile solution.

**Keywords** Ferromagnetism · Conducting polymers · Poly(3-Hexylthiophene) · Morphology

## 1 Introduction

Nowadays conducting polymers has been studied for the application in different fields. These materials become important because their electronic and optical properties are easily modified. More recently, conducting polymers have shown magnetic properties, which enabled its application in materials for spintronics. An example to this application is poly(3-hexylthiophene) [1] emerged as one of the most promising materials and is currently the subject of intense research. This polymer, in which ground state is nondegenerate, exhibits two possible configurations of charge carriers: polaron

(spin  $\frac{1}{2}$ ) and spinless bipolaron (a coupled pair of polarons). In special synthesis conditions, these polymers exhibit an intrinsic ferromagnetic phase at room temperature. This behavior is observed in poly(3-methylthiophene) [2, 3] and poly(3-hexylthiophene) [4]. Changes in the preparation conditions of the polymer, as reduction potentials [4] and pressure of pellets [3], lead to important modifications in magnetic properties. Additionally, the morphology may affect the stability of the polaron in the polymeric chain, leading to changes in the magnetic behavior, as in the saturation magnetization. One possible explanation for the magnetic ordering observed in these polymers could be exchange interaction among the magnetic moments, i.e., polaron (spin  $\frac{1}{2}$ ) in this case.

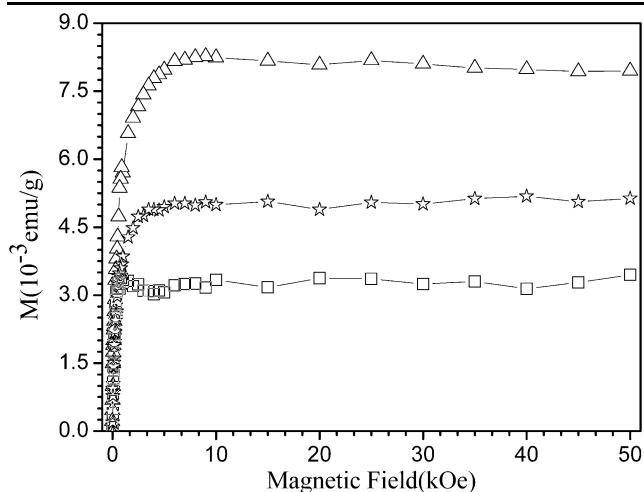
In this work, we present the results of the effects of water introduction in the acetonitrile solution on the morphology of the polymers, and as consequence, changes in the magnetic properties.

## 2 Experimental Details

Polymers sample were prepared electrochemically in a dry box filled with argon at 300 K with a constant potential of 1.60 V (referred to a quasi-reference silver electrode) and the addition of different amounts of water (0–200 ppm) in the solution during sample synthesis. These conditions were using the control of the water amounts during the synthesis. The monomer concentration was 0.2 M poly(3-hexylthiophene) and 0.1 M LiClO<sub>4</sub>. After the synthesis, the sample was electrochemically reduced until the open circuit potential to be 0.80 V and enclosed in a silicone die and isostatically pressed at 570 bar. These synthesis parameters were optimized in a previous work [4]. Magnetic measurements were performed using a Quantum Design

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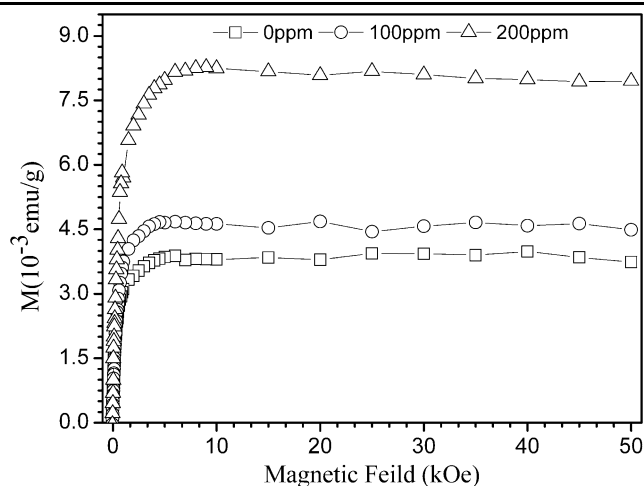
**Fig. 1** Magnetization versus field curves at 300 K for sample prepared with 200 ppm of water in acetonitrile solution taken just after synthesis (triangles) and the same sample measured two week later (stars) and four squares

SQUID magnetometer; model MPMS-5S for magnetic field up to 50 kOe at 300 K the morphological conditions were analyzed by micrographs performed by a scanning electron microscope, SEM, using an electron microscope ZEISS model DSM940A.

### 3 Results and Discussion

Figure 1 shows the magnetization as a function of an applied magnetic field performed at 300 K for samples prepared in acetonitrile in the presence of 200 ppm of water. We present the data for magnetization measured on the same day of the polymerization (triangles), two (stars) and four weeks later (squares). The diamagnetic contribution was subtracted in all curves. We observed a decrease in the saturation magnetization ( $M_S$ ) as the storage time increased. It is important to emphasize that the storage was in a vacuum ( $10^{-3}$  torr) and in absence of light. This behavior  $M_S$  was observed previously in poly(3-methylthiophene) samples [5], and in that case an even more aggressive condition was used once the same was stored in air. The present results are evidence that our samples are free of ferromagnetic metals particles and then the magnetic behavior is an intrinsic property of the sample.

Figure 2 shows the magnetization as a function of applied magnetic field at 300 K for a sample synthesized with the addition of different amounts of water in acetonitrile solution. These measurements were performed immediately on the same day of the sample polymerization. We observed that the  $M_S$  has a maximum value for those samples prepared in the presence of 200 ppm of water in a solution. It was observed that the diamagnetic susceptibility



**Fig. 2** Magnetization versus field curves at 300 K for sample with addition of different amount of water in the solution during the synthesis: (squares) 0 ppm; (circles) 100 ppm and (triangles) 200 ppm

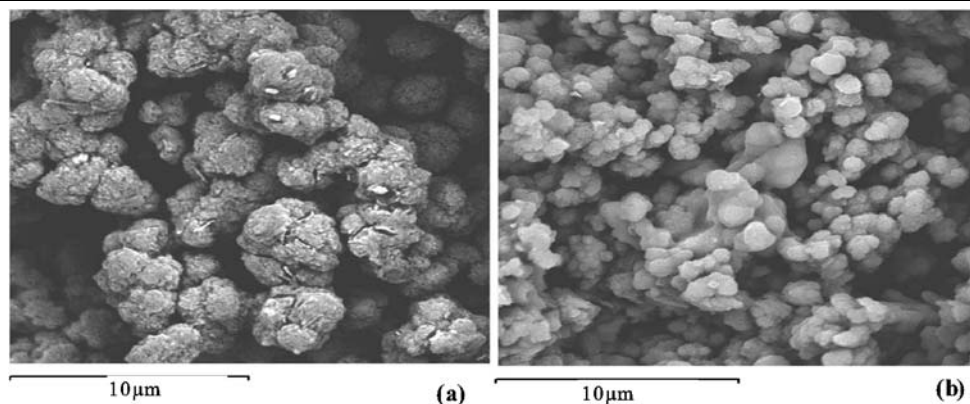
is  $-7.5 \times 10^{-7}$  emu/gOe for all samples prepared. The fact that this contribution does not change is an indication that the morphological changes affect only a portion of the samples which contribute to the formation of the ferromagnetic phase.

To investigate the correlation between the magnetic properties and the morphology, we performed SEM images measuring two different samples, as shown in Fig. 3. In Fig. 3a, we observed that the sample prepared in the absence of water in an acetonitrile solution exhibits grain size around 4  $\mu\text{m}$ . In Fig. 3b, where we introduced 200 ppm of water in the solution, it was observed that the grain size has a mean value of 1  $\mu\text{m}$ .

In the literature, the effect of water introduction in acetonitrile solution during the electropolymerization of conducting polymers has been discussed in different papers [6, 7]. These works show that the addition of small amounts of water in the solution during the synthesis could reduce the solubility of oligomers and lead to faster deposition on the electrode or act as a chain terminator agent for the polymer leading to a decrease in the electrical conductivity. This behavior could be attributed to reaction of the nucleophilic  $\text{OH}^-$  species with the radical cation during the polymer synthesis [6, 7]. The data is shown in Fig. 2, where the  $M_S$  increases with the increased water content in the acetonitrile.

The data shown in Fig. 2, where the  $M_S$  increases with the increased water content in the acetonitrile then could be associated with the stability of the polarons with the greater concentration of structural defects and reduction of the chain lengths [6–8]. The presence of structural defects and small conjugation lengths localize and limit the recombination of these polarons into bipolarons. As a consequence, the largest stability of polaron leads to a rise in saturation magnetization of the sample which the magnetic interaction mediated by polarons change. The presence of water modifies

**Fig. 3** Scanning electrical microscopic images for poly(3-hexylthiophene) sample with addition of different amount of water in the solution during the synthesis: **(a)** without the addition of water and **(b)** addition of 200 ppm of water



the morphology of the polymer and formed smaller chain polymers and a higher concentration of structural defects. The presence of smaller chains and structural defects stabilize and limit the recombination of polarons in bipolarons. As a consequence, this stability of a polaron leads to a rise in the saturation magnetization of the sample. This particular characteristic is important for applications in organic spintronics [9], because the stability of polarons over bipolarons is important since only polarons are related to spin transport.

#### 4 Conclusions

The results present in this work show that the effect of water in acetonitrile solution is important for the nucleation and growth mechanism in poly(3-hexylthiophene). As a consequence, the polymer morphology changes. The magnetic properties, in particular saturation magnetization, were also observed to change as the water content in the polymerization is modified. Our results show that the saturation magnetization at room temperature was optimized with the addition of 200 ppm of water in the solution indicating a cor-

relation between the sample morphology and the magnetic properties.

**Acknowledgements** We thank Professor L. Walmsley from the Universidade Estadual Paulista for useful discussions and suggestions and also to CNPq, CAPES, and FAPESP for the financial support.

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