

# Water effect on the morphology and magnetic properties of poly(3-hexylthiophene)

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## Abstract

Poly(3-hexylthiophene) magnetic characteristics and morphology prepared in acetonitrile solution by electrochemical techniques have been studied, and the results are reported. The results indicate that the films prepared in small amounts of water in the electrolyte solution show significantly different morphology and magnetic behavior. The differences in these properties are explained in terms of different functional groups introduced during polymer film preparation.

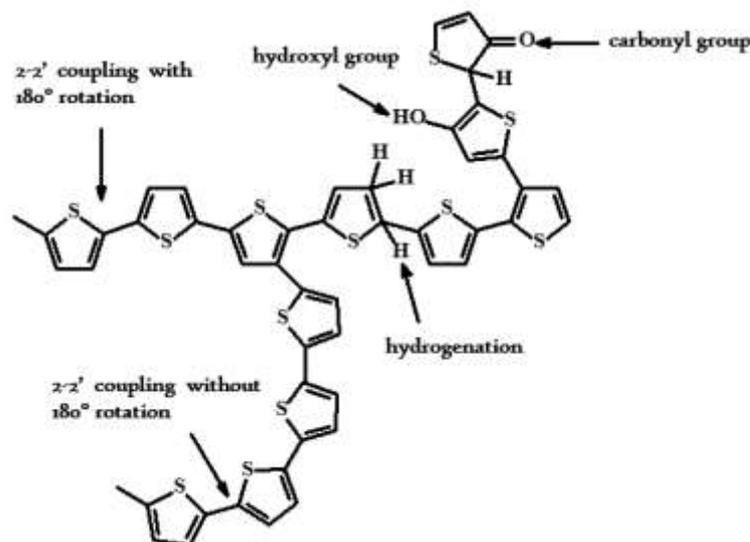
**Keywords:** Poly(3-hexylthiophene), polymers magnetic,  $\pi$ -conjugated system, organic ferromagnetism

## 1. Introduction

Since the first discovery in 1977 that chemical treatment with iodine converts electrically insulating polyacetylene into a highly conducting material with electrical conductivity above  $10^4 S/cm$  [1], conducting polymers are subject of great interest due to their outstanding electronic properties. A wide variety of electrically conducting polymers exhibiting nearly conductivity of metallic type have been investigated. Polyheterocyclics, particularly polythiophenes and derivatives are another class of electroactive polymers that are perhaps of more practical interest because of their ease of synthesis and architectural flexibility for appropriate chemical modification. Further, this polyheterocyclic is also thermally and environmentally stable. In addition to these advantages, polythiophene can be switched between conducting (oxidized) and nonconducting (neutral) states simply by electrochemical techniques. This technique is a handy feature for applications in which electrical conductivity and optical of material must be controlled [2-4].

The electrophysical properties of polythiophenes are determined by various factors such as the degree of polymerization, nature of dopants, and the heteroatom incorporated into the  $\pi$ -conjugated system of carbon atoms. The heteroaromatic and extended  $\pi$ -conjugated backbone structure of polythiophene provides stability and electrical conductivity, respectively. However, the  $\pi$ -conjugated backbone structure is not sufficient to produce appreciable conductivity about yourself. Partial charge extraction from the polymeric chain is also required, which is achieved by a chemical or an electrochemical process called doping. This doping process that coincides with polymerization of the polymer consists of incorporating of counteranions, present in the reaction medium, in the polymeric chains growing to maintain the polymeric system's neutrality. Upon extraction of a negative charge from the neutral segment of a polymeric chain by doping process a local deformation to the quinoid structure occurs since it is favored energetically. The positive charge and the unpaired spin are referred to as a polaron combined with the quinoid structure. The formation of a polaron induces two new intermediate states (bonding and antibonding) simultaneously, the bandgap while the unpaired electron occupies the bonding (low energy) state, thus giving the polaron a spin of 1/2. As oxidation continues further another electron has to be removed of the polymeric chain that already contains a polaron, resulting in the formation of a bipolaron which is energetically preferred to the formation of two polarons. A bipolaron is known to extend over about six thiophene rings [5]. The bipolaronic states lie further from the band edges. The lower energy state of the bipolaron is empty; thus, this species has a zero spin. As the degree of oxidation increases, the bipolaronic energy state overlaps, resulting in the narrow intermediate bandstructure formation. At high doping levels, bipolarons are predominant in the polymeric chain, and thus the charge carries in the conducting polymer has zero-spin.

In the formation of polarons and bipolarons regularity and order in polymer structure have a critical role. Maintain the regularity and order in polymer structure is a complex problem. For example, although the chain of polythiophene and its derivatives are intrinsically linear and planar, many defects structural and conformational can be formed during polymerization, as shown in Figure 1. The defects in the polymer chain break the planarity and linearity and reduce the extent of  $\pi$ -orbitals overlaps. The defects include conformational 2-2' coupling with nonregular 180° rotations of the monomer unit, defects such as 2-3' or 2-4' coupling, nonaromatic bonding and formation of carbonyl and hydroxyl groups on the polymeric chains.



**Figure1:** Chemical and conformational defects in polythiophene.

One of the synthesis variables that can influence the regularity and order in polymer structure is the presence of water in the synthesis solution. This parameter on polypyrrole polymerization in acetonitrile has been shown in several articles [6-8]. The results showed that water increases the polymerization rate, improves the film adherence and morphology of the film, and enhances the resulting polymer's conductivity. According to some authors, water contributes to pyrrole synthesis. Its greater dielectric constant (80 against 37 for acetonitrile) [9-11] reduces Coulomb's repulsion between radical cations, and facilitates radical-radical coupling.

There are few studies on the literature the effects of water on the physical properties of polythiophenes. Downard and Pletcher [12] studied water's influence on the mechanism of electropolymerization of polythiophene in acetonitrile. They observed that during the film deposit, water presence leads to a shift of the potential required for deposition to a more anodic and inhibits film formation due to the reaction of ions formed during the electropolymerization with water. Moreover, the presence of water forms a non-conductive layer and is passive at the electrode surface or on the polymer deposited and causes a negative effect in the conductivity and the structural characteristics in the films of polythiophene [13].

Hillman *et al.* [14] performed the polymerization of thiophene in acetonitrile, using the potential step method and observed an initial increase of current followed by a fall. The authors concluded that the oxidation of the monomer was blocked before the precipitation of the oligomers. This effect was related to the presence of water in the solvent, which had not undergone a withdrawal of water present in the solution. Barsch *et al.* [15] analyzed the superoxidation anodic of the polythiophene and poly (3-methylthiophene) in solution, containing acetonitrile and water. The authors observed that the degree of superoxide increases with the amount of water depending on the water reaction with the radical cation. The water's oxygen forms a double bond with the radical cation's sulfur while the input of another water molecule causes another double bond and posteriorly occurs the loss of SO<sub>2</sub>. Finally, with increasing water concentration, the conjugation of the polymer is broken, forming COOH-terminal groups. The effects of the water in poly (3-hexylthiopheno) were studied by Skompska *et al.* [16]. They observed that water in the solution of synthesis reduces the oxidation level and the thickness of the films formed.

As noted above, there are great difficulties in obtaining the polymerization of thiophene in aqueous media. One effect that contributes to this difficulty is related to the fact that the redox potential of thiophene is higher than the potential for the decomposition of water. Thus, due to the high reactivity of the thiophene

radical, the product of decomposition of water, e.g., hydroxyl, can react and block the polymerization, reducing the length of the polymeric chain.

In this paper, we report details of the influence of the water added in small amounts in the solution of synthesis on the magnetic properties and morphologic of the poly(3-hexylthiophene).

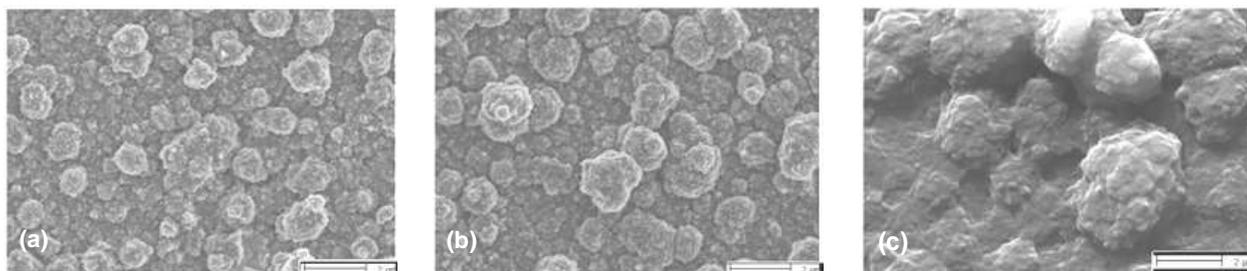
## 2. Experimental

The polymer was generated on the platinum electrode by the electrooxidation of 3-hexylthiophene according to the well established procedures already reported in the literature [17]. The polymerization was carried out under an inert atmosphere in a dry box at 297 K with a constant potential of 1.60 V (referred to as quasi-reference silver electrode) and a single compartment cell. The lithium perchlorate ( $LiClO_4$ ) was used as the supporting electrolyte, and acetonitrile as solvent. The synthesis solution added the monomer concentration of 0.2 M poly(3hexylthiophene), 0.1 M lithium perchlorate water ranging from 0 to 400 ppm. The deposition of the oxidized powdered polymer on the Pt electrode was performed up to a total charge of 40 C. Finally, after the polymerization the polymer was partially reduced the final value of open circuit potential ( $V_{oc}$ ) of 0.80 V. This process was performed in acetonitrile solution with 0.1 M ( $LiClO_4$ ) and without the presence of monomer where. In this  $V_{oc}$  the sample has the highest values of remanence (reference). After the electrochemical reduction, the sample was enclosed in a silicone capsule and isostatically pressed at 570 bar in the form of a pellet.

The samples' morphology was analyzed by micrographs performed by a scanning electron microscope, SEM, using an electron microscope ZEISS model DSM940A. The magnetic measurements were performed using a Quantum Design SQUID magnetometer, model MPMS-5S. Different magnetic measurements were performed to characterize the magnetic behavior of samples; magnetization as a function of the magnetic field and spontaneous magnetization as a function of temperature. In all the magnetization curves the diamagnetic contribution obtained by the linear fit ( $M(H) = \chi_D H$ ) in high magnetic fields and the room temperature was subtracted.

## 3. Results and Discussion

Figure 1 shows the micrographs of samples synthesized with different concentrations of water in the solution of synthesis. The films of poly(3-hexylthiophene) showed a nodular morphology. We can observe that increasing the amount of water increases the size of the nodules.

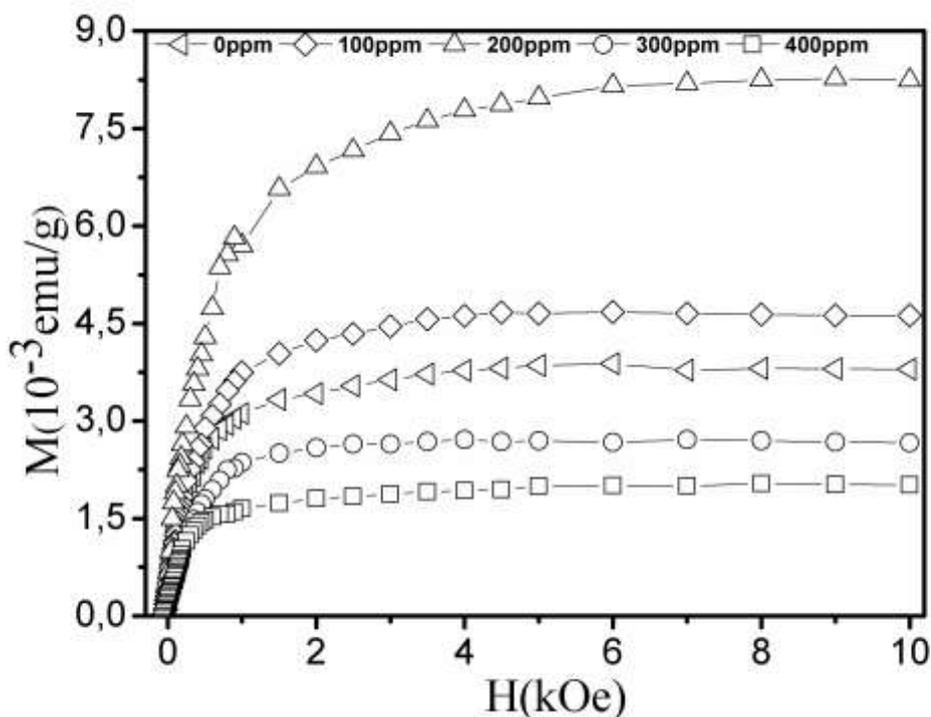


**Figure 2.** Scanning electrical microscopic images for poly(3-hexylthiophene) sample with addition of different amount of water in the solution during the synthesis:(a) without the addition of water, addition of 200 (b), and 400 ppm (c).

This result might be related polymer's to the nucleation rate, which is faster with the presence of water in the solution, or as described by Lemon et al. [18], the presence of oxygen in the working electrode.

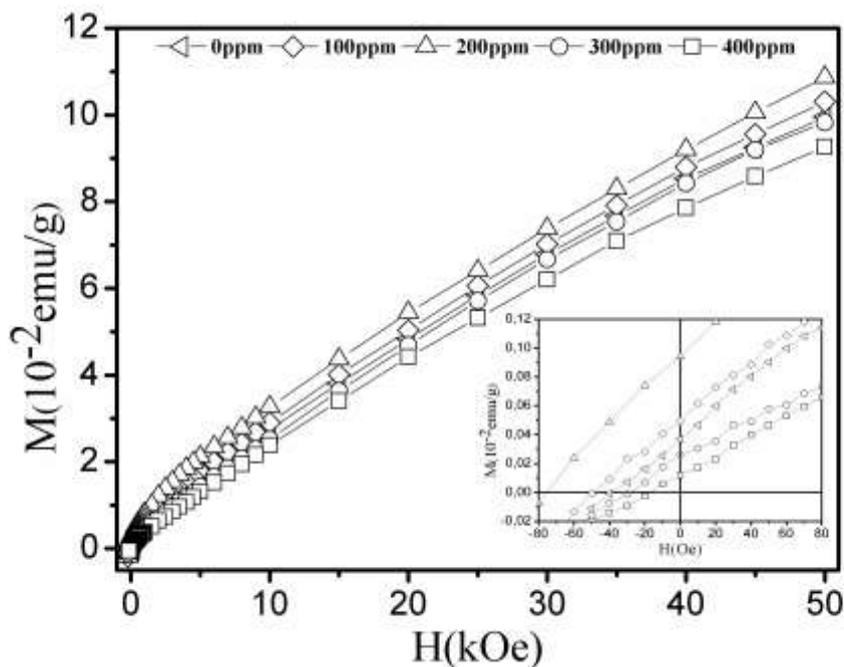
Besides the influence of the presence of water on the morphology of the polymer was also observed variations in magnetic properties of the samples studied. Figure 2 shows the magnetization curves versus the magnetic field at 300 K for samples synthesized with different water concentrations in the electrolyte solution. The diamagnetic contribution was obtained from the linear fit to the high magnetic fields regime and subtracted from all the samples' curves. These contributions are in Table 1. Figure 2 shows the effect of water in the solution of synthesis on the polymer's magnetic properties. The values of saturation magnetization, remanence, and coercive field, have their values optimized with 200 ppm of water in the

solution synthesis. However, as can be observed at concentrations higher than 200 ppm, these magnetic contributions are reduced.



**Figure 02.** Magnetization versus field curves at 300K for sample prepared with addition of different amount of water in the solution synthesis of poly(3-hexylthiophene) at 300 K without diamagnetic contribution.

Figure 3, we have the curves of magnetization versus magnetic field at 5 K. We found that the most significant magnetic contributions also occur for a 200 ppm of water concentration. With the decrease in thermal energy, we observe that these contributions are higher than those obtained at 300 K (see table 1).



**Figure 03:** Curve magnetization as a function of magnetic field at 5 K without diamagnetic contribution. Inset, details of the ferromagnetic hysteresis.

Considering the paramagnetic behavior, we can observe in figure 03 that the magnetic field does not suffice to reach the saturation state of the samples at low temperatures and therefore we have performed for magnetic fields above 5 kOe a fitting using the equation

$$M(H) = M_1 + M_2 \tanh(\alpha H).$$

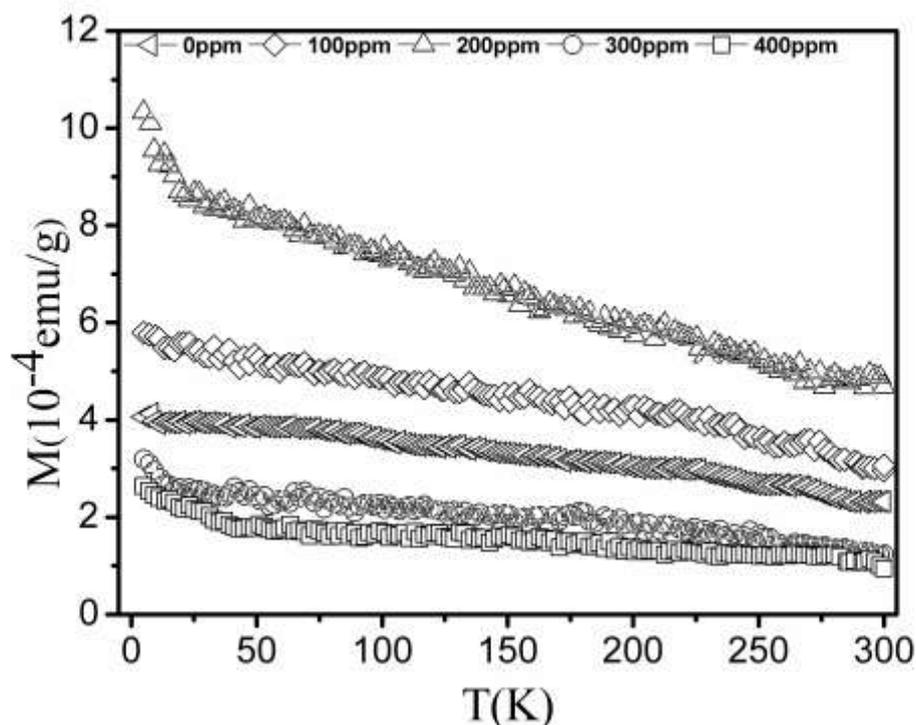
In the equation, the term  $M_1$  describe the ferromagnetic saturation at 300 K,  $M_2$  the paramagnetic saturation at 5 K,  $\alpha = \mu_B / \kappa_B T$ , and  $H$  the magnetic field. The fitting parameters at 5K and values obtained directly from the magnetization curve at 5K and 300K are shown in table 1.

Figure 3 shows the spontaneous magnetization as a function of temperature for samples synthesized with different water concentrations in the solution. The sample was cooled from 300 K a 5 K without an applied field. At 5 K a magnetic field of 50 kOe was applied for ten minutes and then removed. The data was collected, raising the temperature by 2K/min.

**Table 1:** Fitting parameters and values of curves magnetization as a function of magnetic field at 5 and 300 K. Remanent magnetization ( $M_{rem}$ ), coercive field ( $H_{coer}$ ), diamagnetic susceptibility ( $\chi_D$ ), ferromagnetic saturation ( $M_1$ ), and paramagnetic saturation ( $M_2$ ).

Water (ppm)	Temperature (K)	$M_1$ ( $\text{emu g}^{-1}$ )	$M_2$ ( $\text{emu g}^{-1}$ )	$M_{rem}$ ( $\text{emu g}^{-1}$ )	$H_{coer}$ (Oe)	$\chi_D$ ( $\text{emu g}^{-1} \text{Oe}^{-1}$ )
0	5	5.00	1.50	3.70	40	-
	300	$\times 10^{-3}$ 3.80 $\times 10^{-3}$	$\times 10^{-1}$ -	$\times 10^{-4}$ 3.00 $\times 10^{-4}$	35	$-7.80 \times 10^{-7}$
100	5	6.50	1.60	5.00	50	$-7.00 \times 10^{-7}$
	300	$\times 10^{-3}$ 4.70 $\times 10^{-3}$	$\times 10^{-1}$ -	$\times 10^{-4}$ 3.90 $\times 10^{-4}$	37	
200	5	10.00	1.75	9.50	76	$-7.50 \times 10^{-7}$
	300	$\times 10^{-3}$ 8.20 $\times 10^{-3}$	$\times 10^{-1}$ -	$\times 10^{-4}$ 5.10 $\times 10^{-4}$	40	
300	5	2.70,	1.50	2.50	30	$-7.26 \times 10^{-7}$
	300	$\times 10^{-3}$ 2.70, $\times 10^{-3}$	$\times 10^{-1}$ -	$\times 10^{-4}$ 2.30 $\times 10^{-4}$	32	
400	5	2.60	1.40	1.20	18	$-7.40 \times 10^{-7}$
	300	$\times 10^{-3}$ 2.10 $\times 10^{-2}$	$\times 10^{-1}$ -	$\times 10^{-4}$ 1.00 $\times 10^{-4}$	18	

We observed that the interaction between the magnetic moments occurs throughout the temperature range studied, with a more significant contribution at low temperatures. We can also observe the contribution of ferromagnetic behavior for the concentration of 200 ppm of water in the solution.



**Figure 3:** Spontaneous magnetization as a function of temperature for the sample cooled without a field from 300 to 5 K. at 5 K, a field of 50 kOe was applied for 10 min. and removed.

#### 4. Conclusion

According to the results found in this work, water in the synthesis solution plays an essential role in the morphology of the poly(3-hexylthiophene). The films have nodules on the surface that change in size due to the increase in water concentration. This variation may be associated with an increased rate of nucleation of the film due to water and the formation of oxygen balls in the working electrode. The oxygen present in the solution is due to the electrolysis of water during polymerization. This occurs because the polymer's potential polymerization is much more positive than the potential for water decomposition. Another consequence of water in the solution of synthesis is the change in the samples' magnetic behavior. Electropolymerized polymers in the absence of water allow that the polymer chains have greater length and a more minor structural defect. This framework promotes the formation and stability of bipolarons (spin 0) in the polymer chain [19], resulting in the reduction of the sample's magnetization. However, films prepared with small amounts of water contain carbonyl and/or hydroxyl groups on the polymeric chains. These groups leading the formation of smaller chains and of structural defects of the polymeric chain. Polarons located where these functional groups are present can better stabilize this carrier of the magnetic moment, leading to an increase in the samples' magnetization. The results showed that the ferromagnetic and paramagnetic contributions are optimized with the addition of 200 ppm of water in the electrolyte solution, however, for concentrations of 300 and 400 ppm of water, there is a reduction of these contributions. This result reveals a limit on the maximum number of defects in the polymer network and the chain length to allow for the existence and stability of polarons that effectively participate in the ferromagnetic and paramagnetic contribution.

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