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EFFECTS OF ISOSTATIC PRESSURE ON THE MAGNETIC PROPERTIES OF POLY(3-HEXYLTHIOPHENE)

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Abstract

We have observed the variation of the magnetic saturation, and Curie temperature (T_C) in samples of the poly(3-hexylthiophene) doped with ClO_4^- isostatically pressed. We attribute this behaviorto the continuous variation of the interchain interaction induced by different pressures used during the sample preparation. We believe that the pressure induces an increase in exchange interaction interchains because of the reduction of the distance interchain, contributing to the increase in the ferromagnetic behavior observed in the samples.

Introduction

Conducting polymers what exhibit collective magnetic behavior are interest not only because of possible attractive application in electronic device but also by the new form of magnetic ordering where the magnetic moments reside in the p orbital.In most cases, this interaction has proved to be weak so that the ferromagnetic behavior was only observed at low temperature[1-3]. However, some reports about weak ferromagnetic phase at room temperature can be found in the literature. Makarova et al. have observed ferromagnetic phase in C_{60}[4]. Torrance et al. [5]reported ferromagnetic phase below 400 K in poly(1,3,5-triaminobenzene) when oxidized with iodine andZaidi et al. reported ferromagnetic behavior with Tc around 350 K in polymers composed of polyaniline and an acceptor molecule, tetracyanoquinodimethane[6]. In the last years,much has been done in search ofnew conducting polymers that exhibit magnetic order at room temperature. In this case, heterocyclic polymers such as poly(3-hexylthiophene)[7] have received considerable attention in recent years. This polymer has a nondegenerate ground π-electron state which can form by the electron-phonon interaction a charged defect, polaron. The polaron has electronic charge $\pm e$ and spin ½ which plays an essential role in the formation of the magnetic moments and, therefore in the magnetic behavior of the polymer.

The ferromagnetic order in these organic systems is usually the result of exchange interactions interchain between the magnetic moments and therefore the distance between the chains of the polymer is of fundamental interest.

In this work, we present magnetic measurements in poly(3-hexylthiophene) isostatically pressed using different pressures. We investigate the influence of the pressure on the magnetic properties of the sample with particular interest in obtained magnetic order at room temperature.

Experimental Details

The polymer was prepared electrochemically with a constant potential of 1.60 V (referred to a quasi-reference solver electrode) in anelectrochemical cell filled with acetonitrile containing 0.1 M of $LiClO_4$, 0.2 M of poly(3-hexylthiophene) monomer and 200 ppm of water. The synthesis occurred in a dry box filled with argon at 297 K. 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 in an acetonitrile solution with 0.1 M $LiClO_4^-$ where a final value of V_{oc} was 0.80 V. In this V_{oc} the sample have the higher values of remanence. After the electrochemical reduction, the sample was enclosed in a capsule of silicone and isostatically pressed in the form of

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a pellet using different pressures up to 1000 bar. Magnetic measurements were performed using a Quantum Design SQUID magnetometer, model MPMS-5S.Different magnetic analyses were performed to characterize the magnetic behavior of samples; magnetization as a function of magnetic field and spontaneous magnetization as a function of temperature. In all the magnetization curves the diamagnetic contribution obtained by the linear fit in high magnetic fields and room temperature was subtracted.

Results and Discussion

Relevant information about the influence of pressure on magnetic properties of the poly(3-hexylthiophene) can be obtained by measurements of the dependence of the magnetic moment with temperature and magnetic field.Figure 1 exhibits the magnetization versus magnetic field at 300 K for samples isostatically pressed in the form of a pellet using different pressures up to 1000 bar. We observe in all samples an increase of the saturation and remanence magnetization as well as of the coercive field with increasing pressure.The saturation magnetization of the sample pressed at 1000 bar is approximately 20 times higher than the sample powder (0bar). One possible explanation is that the isostatic pressure applied in the polymer reduces the distance interchain allowing the increase in the intensity of the ferromagnetic interaction and of the magnetic domains in the samples. The increase in the coercive field suggests that pressure is contributing to the increasing the crystalline portion of the samples.
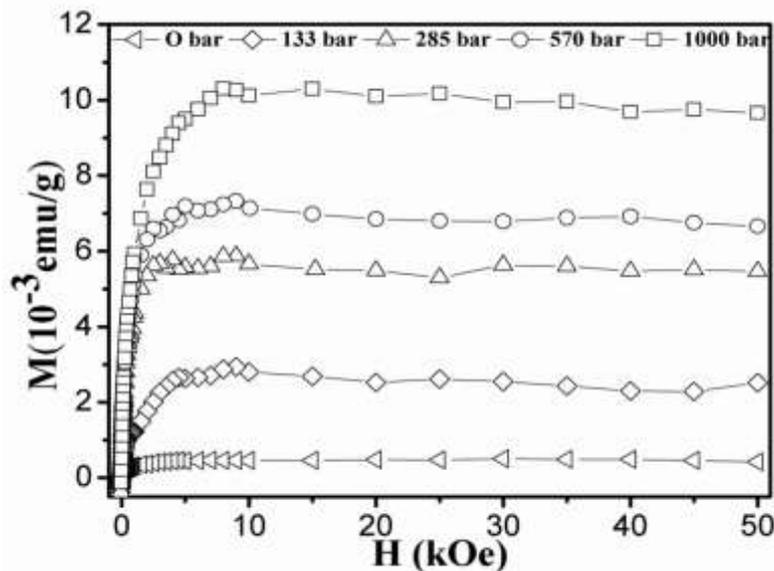

Figure 1: Magnetization versus field curves for sample isostatically pressured using different pressures up to 1000 bar at 300K. The diamagnetic contribution was subtracted from all curves.

Figure 2 we show the magnetization versus magnetic field curves at 5 K where we observe besides the ferromagnetic contribution, the paramagnetic contribution. As in 300 K, are noted variations in the ferromagnetic behavior of the samples as a function of pressure.

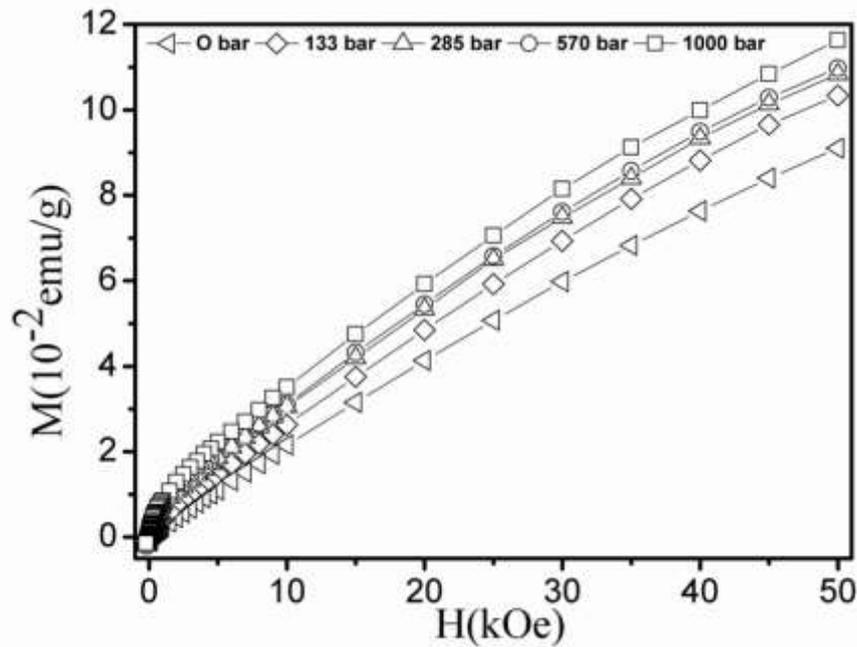# INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

Figure 2: Magnetization versus field curves for sample isostatically pressured using different pressures up to 1000 bar at 5K. The diamagnetic contribution was subtracted from all curves.

Consider now the behavior of paramagnetic spins in high magnetic fields and low temperatures. In such a case, the magnetization can be described by the following formula:

$$M = Ng J \mu_B B_J \left(\frac{g J \mu_B H}{\kappa_B T} \right)$$

where B_J is the Brillouin function

$$B_J(\alpha) = \frac{1}{J} \left[\left(J + \frac{1}{2} \right) \coth \left(J + \frac{1}{2} \right) \alpha - \frac{1}{2} \coth \frac{\alpha}{2} \right]$$

where

$$\alpha = \frac{g \mu_B H}{\kappa_B} J$$

B_J describes the saturation of paramagnetic moments of the total quantum number J. To have a better understanding of the data figure we have performed a Brillouin with spin ½ and $g = 2$. The Brillouin function can be approximated by

$$M(H) = M_0 \tanh(\alpha H)$$

with

$$M_0 = N \mu_B$$

and

$$\alpha = \mu_B / \kappa_B T$$

The fitting parameters at 5K and values obtained directly from magnetization curve at 5K and 300K are shown in table 1.

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Table 1:Fitting parameters and values of curves magnetization as a function of magnetic field at 5 and 300 K using different pressure. Remanent magnetization (M_{rem}), coercive field (H_{coer}), diamagnetic susceptibility (χ_D), ferromagnetic saturation ($M_{Fer.Sat.}$), and paramagnetic saturation ($M_{Par.Sat.}$).

Pressure (bar)	Temperature (K)	$M_{Fer.Sat}$ (emu g^{-1})	$M_{Par.Sat.}$ (emu g^{-1})	$M_{rem.}$ (emu g^{-1})	$H_{coer.}$ (Oe)	χ_D (emu g^{-1} Oe^{-1})
0	5	0.76×10^{-3}	1.50×10^{-1}	0.30×10^{-4}	10	-7.72×10^{-7}
	300	0.52×10^{-3}		0	0	
133	5	3.00×10^{-3}	1.52×10^{-1}	2.20×10^{-4}	30	-8.40×10^{-7}
	300	2.84×10^{-3}		0.60×10^{-4}	14	
285	5	6.20×10^{-3}	1.53×10^{-1}	5.60×10^{-4}	41	-8.44×10^{-7}
	300	5.82×10^{-3}		3.60×10^{-4}	23	
570	5	$6.37, \times 10^{-3}$	1.60×10^{-1}	7.33×10^{-4}	47	-8.38×10^{-7}
	300	7.23×10^{-3}		4.30×10^{-4}	25	
1000	5	9.24×10^{-3}	1.66×10^{-1}	9.80×10^{-4}	68	-8.90×10^{-7}
	300	10.3×10^{-2}		5.00×10^{-4}	32	

As shown in Table 1, the pressure exerts great influence on the magnetic properties of the polymer. However when we observe the paramagnetic contribution we found little variation when compared to variations of the ferromagnetic contributions. This result shows that pressure has great influence on the interaction between the magnetic moments existing in the sample and not on creating new.

Figure 3 show the spontaneous magnetization as a function of temperature for samplesisostatically pressed using different pressures up to 1000 bar. 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. We can also observe whatthe powder sample haslowest remanencein comparison withsamples pressed. This behavior occurs because the sample powder has few regions to establish ferromagnetic order. For the samples pressed at interchain distance is reduced, increasing the ferromagnetic interaction.
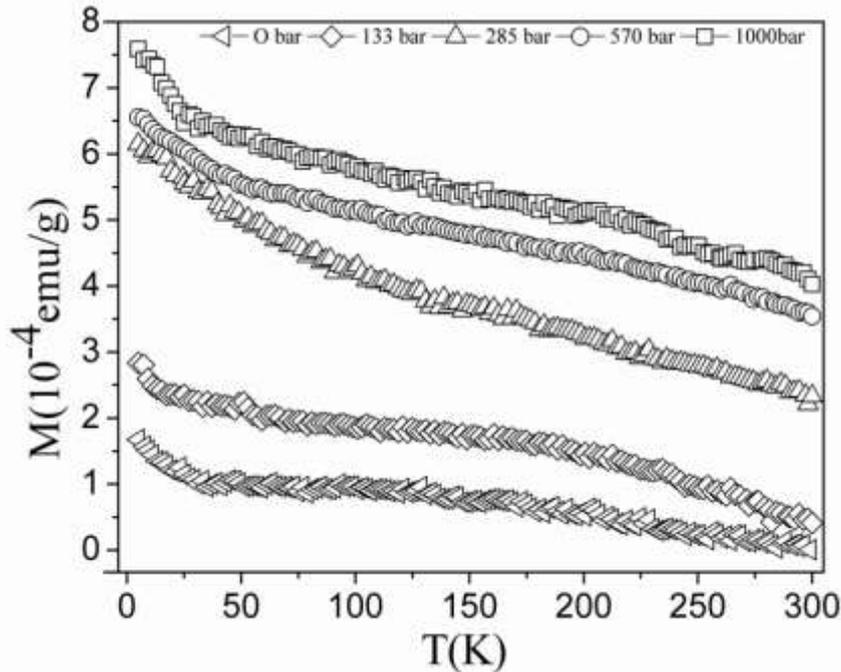
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Figure 3: Spontaneous magnetization as a function of temperature for the samplesisostatically pressured using different pressure up to 1000 bar. The sample was cooled without a fiel from 300 to 5 K at 5 K, a field of 50 Oe was applied for 10 min. and removed.

The spontaneous magnetization curveswere fit with a bidimensional behavior given by $M(H) = M(0) - bT$. The Curie temperatures (T_C) obtained from the fit was used to estimate the intensity of energy exchange between the magnetic moments with their nearest neighbor. We use the equation

$$J = \frac{3\kappa_B T_C}{2zJ(J+1)}$$

For the polymeric system studied $z = 2$e $J = 1/2$. The equation can be rewritten as

$$J = \kappa_B T_C.$$

The results are shown in figure 4.We observed that increasing the pressure in the preparation of the samples increases the energies of interaction between the magnetic moments.
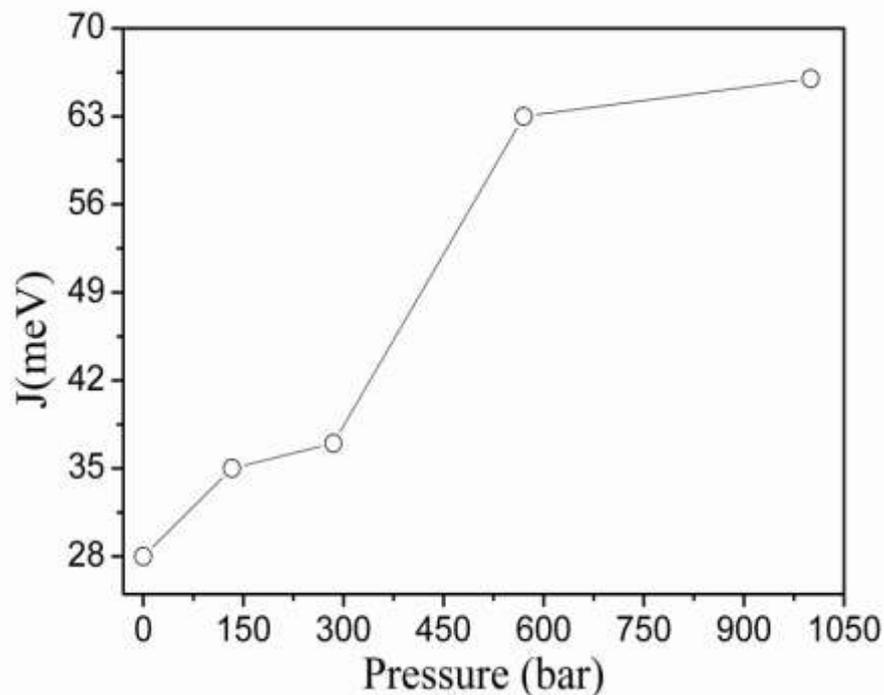
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Figure 4: Estimate the energy exchange(J) between magnetic moments and the nearest neighbors, determined from the critical temperature, obtained from the fit through the spontaneous magnetization given by equation $M(H) = M(0) − bT$.

Conclusions

The results obtained indicate that the magnetic behavior of the poly(3-hexylthiophene) is influenced by pressure used during the sample preparation. We observed that the ferromagnetic saturation, remanence, and coercive field increase with increasing of the pressure used in the preparation of the samples. However there were no significant variations in the paramagnetic contribution. This result shows that the pressure does not create new magnetic moments, but acts effectively in the interaction between magnetic moments. We also observed variations in the Curie temperature of the samples as a function of pressure. The Curie temperature increased from 320K for the powder sample to 760 K for the sample pressed at 1000 bar. This change represented an increase in the energy exchange of 28 meV (powder) to 66 meV (1000bar).

The variations observed in the magnetization of the sample as a function of pressure are related with increase in exchange interaction between the magnetic moments due torsions of the chain as well as a shortening of interchain spacing by the application of the pressure. This result gives us a way to obtain ferromagnetic order at high temperature in organic materials and also control this property..

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