

## Magnetic and Magneto-Optical Properties of Conjugated Polymers: A New Frontier

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### Introduction

Last 25 years have witnessed a tremendous growth in studies of conjugated polymers with interesting optical and electrical properties. These unusual optoelectronic properties allow these polymers to be used for a large number of applications, including non-linear optical devices, light emitting displays, all-plastic transistors, artificial actuators, sensing devices etc and owe their origin largely to the delocalization of electrons in a continuously overlapped  $\pi$  orbital along the polymer backbone. Figure 1 lists the repeat units and conductivities of a few common conjugated polymers.

Polymer (Year conductivity discovered)	Structure	$\pi$ - $\pi^*$ gap (eV)	Conductivity [1] (S/cm)
<b>I. Polyacetylene and Analogues</b>			
Polyacetylene (1977)		1.5	$10^3 - 1.7 \times 10^6$
Polypyrrole (1979)		3.1	$10^2 - 7.5 \times 10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
<b>II. Polyphenylene and Analogues</b>			
Poly(paraphenylene) (1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5 \times 10^3$
Polyaniline (1980)		3.2	30 - 200

Figure 1. Some conjugated conducting polymers

The mechanism behind the metal-like properties of these polymers is still a matter of debate and is generally believed to be dependent on the way the charge carriers are stabilized in the polymer chain. A few of these polymers possess intrinsic charge carriers or polarons, which can also be created by p- or n-type doping. Polythiophene presents a unique case of study because of its semiconducting properties at its native state. Through p-doping (oxidation) it can be made conducting whereas n-doping (reduction) can convert it to a complete insulator. Interestingly, polythiophenes also show subtle structure property relationship which have been exploited to tune its properties. Polyalkylthiophenes also undergo self assembly to form two-dimensional (2D) structures through strong interchain coupling which depends mainly on the length of the side chain and regioregularity of the polymer.[2] The regioregular (RR) substituted polythiophenes (P3AT), in which the alkyl side group is attached to the 3<sup>rd</sup> position of the thiophene rings in a head to tail stereoregular order, form thin films with nanocrystalline lamellae, resulting in high hole mobilities ( $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )[3,4] and strong interchain interaction. On the contrary, P3AT films of regiorandom stereo order do not show supramolecular structures, and the hole mobility is poor ( $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )[3,4]. It has been shown very recently that the polarons in RR P3AT thin films become delocalized over several polymer chains, consistent with the high hole mobilities.[5] This difference has been cleverly used in a recent report to construct efficient solar cells from this material[6] and magnetic field switchable electroluminescent devices[7].

Large dynamic 2D delocalization of charged carrier may create magnetic ordering in polythiophene derivatives and be easily perturbed by external magnetic fields. The strong interchain coupling also indicates a possible existence of polaron percolation in this material. These reasons prompted us to investigate magnetic and

magneto optical properties of polyalkylthiophenes. In this report we will discuss our recent experimental findings of magnetic and magneto optical investigations on polythiophene thin films.

### Experimental

**Materials.** Poly(3-dodecylthiophene) with RR > 99% (PDT) and degree of polymerization of 40 was used for this study. The synthesis, purification and characterization of materials and regioregularity has been published elsewhere.[8] The solvents used to fabricate thin and thick films were all of HPLC grade and was used as received.

**SQUID / EPR.** MPMS5S SQUID DC/AC magnetometer was used for SQUID (Superconducting Quantum Interference Device) studies. Multiple magnet resets were employed to attain small residual magnetic fields. Following the magnetization/susceptibility studies the samples were kept at room temperature and ambient condition for several weeks before repeating identical sequence of measurements to reproduce the measurements and check the magnetic stability of PDT. For CW x-band EPR (Electron Paramagnetic Resonance) studies on PDT powder a Bruker E580 epr spectrometer was used. The EPR data was collected at room temperature.

**Magneto Optics.** Magneto optical studies were carried out on thin films of PDT spin coated on optically polished BK7 substrates using a Faraday rotation geometry and a solenoid as the source of AC magnetic field.

### Results and discussion

**SQUID / EPR Results.** The plot of  $\chi$  versus T (dc susceptibility,  $\chi = M/H$ ) is shown in Figure 2A and shows a rapid rise till 5 K with a blocking temperature of 4.9 K. At 0.1 T of applied field and 4.8 K the  $\chi T$  value reaches a maximum of 6115 electromagnetic units (emu) K mol<sup>-1</sup> (of monomer). Very approximately this corresponds to an effective magnetic moment  $\mu_{\text{eff}} \sim 48,900 \mu_B$  and an average  $S \sim 25000$ , largest so far reported in any organic material.[9] These values may be viewed as lower bound estimates as the susceptibility was measured under high external magnetic field.

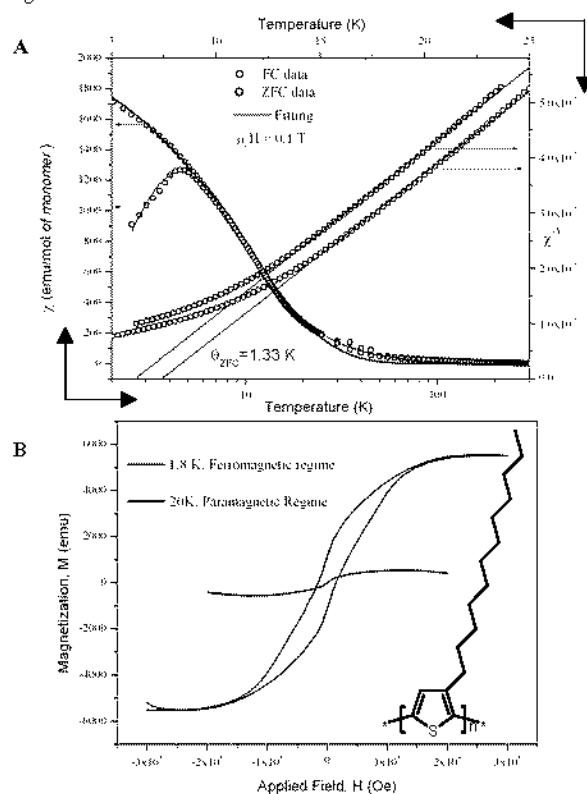


Figure 2. SQUID data on PDT: A. ZFC, FC and Curie-Weiss plots, arrows indicate the complimenting axes. B. M-H loops recorded at 1.8 and 20 K on PDT. Inset in plot B is the structure of PDT.

The paramagnetic region follows Curie-Weiss law with a Weiss constant of 1.33 K which indicates ferromagnetic coupling. More detailed studies of the temperature dependence at low temperature reveals that even at such high applied magnetic field the field cooled (FC) and zero field cooled data diverge below 5K indicating the slow relaxation (blocking) of the magnetization and ferromagnetic remanence. The M-H loop at 1.8K is shown in Figure 2B which shows that PDT possesses at this temperature a remanence of  $\sim 3000$  Oe, which is very large compared to organic ferromagnetic species[10]. EPR data at room temperature (not shown here) corresponds to spin concentration of  $1.254 \times 10^{19}$  g which is equivalent to one spin for every 190 monomer. This indicates that the delocalization is extended well beyond a single polymer chain, consistent with high hole mobility in this class of polymers.

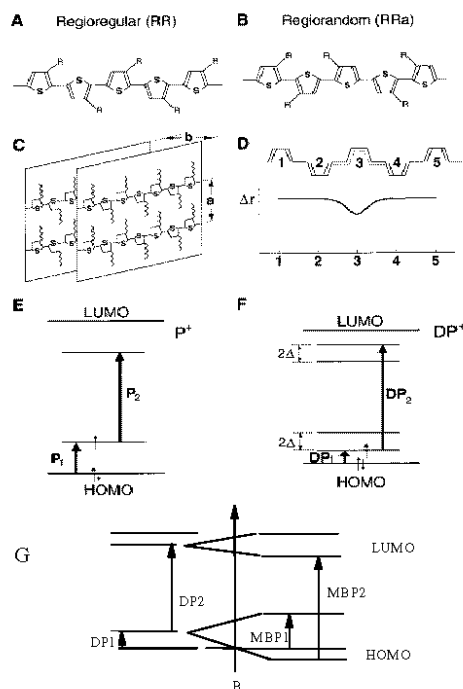
**Magneto Optical Studies.** Faraday rotation measurements on the spin coated thin films of PDT revealed large Verdet constant ( $V$ , expressed in degree/Tesla meter and constant at any certain wavelength) values at visible as well as near infrared wavelengths (see Table 1). Two types of figure of merit (FOM) has been calculated, one based on the absorbance,  $F1 = |V|/10^{-A}$  and the other on refractive index,  $F2 = |V|/n$  where  $A$  and  $n$  are the absorbance and refractive index respectively of the thin films of PDT at any particular wavelength. In Table 1 these values have been compared to those of TGG (terbium doped gallium garnet) single crystals. TGG single crystal is commonly used in commercial magneto optic devices. The Verdet constant of PDT are 100 to 150 times larger than that of TGG[11]. Our recent studies also show that the Verdet constant of PDT falls sharply with decreasing regioregularity.

**Table 1.** Verdet constant ( $V$ ) and FOM values ( $F1$  and  $F2$ ) of PDT thin films and TGG single crystals. Typical errors in these measurements are 5%.

	$\lambda$ (nm)	$10^5 \text{ Degree} \cdot \text{T}^{-1} \cdot \text{m}^{-1}$				
		528	633	789	830	980
PDT	$V$	-0.22	-2.9	-5.8	-2.8	4.14
	$F1$	0.023	1.51	5.27	2.63	4.0
	$F2$	0.128	1.73	3.52	1.7	2.6
TGG	$V$	-0.077		-0.046		-0.026
	$F2$	0.016		0.028		0.017

**Discussion.** The spin coated thin films of RR PDT were prepared using chloroform as solvent. The RR polymers (Figure 3A) (>99%, head to tail) self organized to form the lamellae (Figure 3C) perpendicular to the substrate. In the MO studies, these lamellae are also perpendicular to the applied magnetic field and to the propagation direction of light. PDT forms these lamellae with a grain size of 15 nm, interplane distance of 0.38 nm whereas the in-plane interchain distance varied from 1.3 to 2.7 nm. In a thin film of regiorandom polythiophene (Figure 3B) such a 2D structure is completely absent.[6] In a strictly 1D chain model, a single charge carrier added onto the polymer chain forms a spin -1/2 polaron (Figure 3D) with two localized states in the gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) (Figure 3E). The two localized states are shifted inside the gap caused by the polaronic relaxation due to the local electronic environment, bond dimerization ( $\Delta r$  in Figure 3D) and lattice structure; resulting in two allowed optical transitions for the polarons,  $P1$  and  $P2$ . Strong electron-phonon coupling in  $\pi$ -conjugated polymers, interplanar interaction and delocalized polarons in the RR ordered phase modify the molecular 1D energy states to generate 2D bound polarons and corresponding two allowed transitions  $DP1$  and  $DP2$  (Figure 3F) [5]. In the presence of external magnetic perturbation (B) the energy states of these 2D bound polarons undergo Zeeman type splitting resulting in large predominant paramagnetic MO transition (Figure 3E) and magnetic bound polarons (MBPs, Figure 3F). Qualitatively the presence of large Zeeman splitting explains the high Verdet constant values in PDT. A room temperature spin orbit coupling energy of  $52 \text{ cm}^{-1}$  calculated from Verdet constants is comparable to a value of  $86 \text{ cm}^{-1}$  calculated from the ZFC data from the fitting in the paramagnetic region at much lower temperature. The ZFC and FC data were fit using a 2D Ising model of an infinite spin chain of parallel and perpendicular susceptibilities. Although the physical origin of the ferromagnetic phase at low temperatures in

these materials remains unclear at this point, a 2D Ising type interaction among the bound polarons (the so called polaron percolation) is suspected. As antisite defects a bound magnetic polaron consists of one localized hole and a large number of independent or coupled spins. Even though the direct exchange interaction between the localized holes is antiferromagnetic, the interactions between the bound polarons may be ferromagnetic at large enough spin concentration [12].



**Figure 3.** Lamellar structure and energy states in thin films of PDT, see text for details.

## Conclusion

In conclusion, we have studied the magnetic and magneto optical properties of regioregular PDT and our experimental data show that organic polymer magnets with large effective magnetic moment in the ground state can be prepared. Large magneto optical effect also promises use of this material in first all-organic MO sensors and devices, probably in interesting in-fiber geometry and more compact form than the present day inorganic crystal based devices.

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