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Review

Magneto-optic Properties of Regioregular Polyalkylthiophenes[†]

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This paper reviews work on the magneto-optical properties of π-conjugated polymers, in particular regioregular poly(3-alkyl)thiophenes. We give an overview of the theoretical formalism that led to the first observation of Faraday rotation from thin films of poly(3-dodecyl)thiophene and experimental results, which include Faraday rotation studies from thin films composed of various polythiophene derivatives with varying degree of regioregularity We also discuss possible correlations of Faraday rotation and the supramolecular organization within the thin films of these polymers. When appropriate, we point out possible applications or suggest directions for further research. Organic magneto-optic polymer materials could reduce production costs for various magneto-optic devices, as these materials are solution processable and amenable to roll-to-roll processing.

Introduction

The last few decades have witnessed tremendous growth in studies of conjugated polymers with interesting optical and electrical properties.[1] These unusual optoelectronic properties allow these polymers to be used for a large number of applications, including nonlinear optical devices with large second- ($\chi^{(2)}$) and third-order ($\chi^{(3)}$) susceptibilities, organic light-emitting displays as both emitting and carrier-transporting medium, all-plastic transistors, artificial actuators, sensing devices, terahertz emitters, etc., and owe their origin largely to the delocalization of electrons in a continuously overlapped π orbital along the polymer backbone.[2] As carrier transporting material, π-conjugated polymers have also found applications in capacitors, electron beam lithography, organic bulk heterojunction solar cells, as electrochemically active materials in batteries and electrochromic devices, as highly conducting transparent replacement of indium tin oxide, in sensors and artificial muscles. Molecular self-assembly is the key mechanism behind efficient molecular packing that is known to critically impact on the electronic structure of these polymers in solid state and hence on the optical and charge transport properties. However, 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 and on interchain interactions.[3] A few of these polymers possess intrinsic charge carriers or polarons, which can also be created by p- or n-type doping. Polythiophene derivatives, like many other conjugated polymers, show semiconducting properties in its native state. Through p-doping (oxidation), it can be made conducting, whereas n-doping (reduction) may convert it to a complete insulator. However, it has been previously shown that excessive amounts of both oxidation and reduction may lead to insulating properties among conjugated polymers.[4] Interestingly, polythiophenes also show subtle structure–property relationships, 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.[5] The regioregular (RR) substituted polythiophenes (P3AT), in which the alkyl side group is attached to the third 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 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$)[6,7] and strong interchain interaction. On the contrary, P3AT films of regiorandom stereo order do not show supramolecular structures, and the hole mobility is poor ($10^{-5}\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$).[4,5] It has been shown very recently that the polarons in RR P3AT thin films become delocalized over several polymer chains, consistent with the high 2D hole mobilities.[8] This difference has been cleverly used in a recent report to construct efficient solar cells from this material[9,10] and magnetic field switchable electroluminescent devices.[11] Such large dynamic 2D delocalization of the 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 factors prompted us to investigate magneto-optical and magnetic properties of substituted polyalkylthiophenes.

Magneto-optical properties, in particular Faraday (FR) rotation, was studied in thin films of various polythiophene derivatives. Faraday rotation[12] is the rotation of the plane of polarization of linearly polarized light due to magnetic-field-induced circular birefringence of a material. In a

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nonabsorbing or weakly absorbing medium, a linearly polarized monochromatic light beam passing through the material along the direction of the applied magnetic field experiences circular birefringence, resulting in rotation of the plane of polarization. FR measurements are usually performed using AC and DC magnetic field in a geometry with k, $B||z$, where the FR angle is defined as $\theta = VBL = \pi \frac{\Delta n}{\lambda} L$ where Δn is the magnitude of circular birefringence (i.e., $n_{\mathrm{LCP}} - n_{\mathrm{RCP}}$) experienced by the medium under the applied magnetic field B, λ is the wavelength of light, and L is the length of the medium. The constant V, the Verdet constant (expressed in degrees/Tesla-meter, °/(T m)) is a materials property and a quantitative measure of the FR ability of the material. The Verdet constant is strongly wavelength dependent, decreasing dramatically away from resonance and in the case of a paramagnetic material, V also depends on the frequency of the magnetic field used.[13] The Verdet constant is usually measured by determining the amount of polarization rotation that linearly polarized light experiences when incident on a sample under an AC or DC magnetic field. Faraday active materials are used in high-end applications such as the optical isolator,[14] an important device that protects lasers from unwanted back reflection, highly sensitive magnetic field sensors,[15] and satellite altitude monitors,[16] among others. Faraday rotation measurements have also been used to estimate magnetic susceptibilities and carrier densities[17] in semiconductors where the effective mass of the carrier is known. Generally, Faraday rotation is at its strongest in inorganic substances containing paramagnetic ions or in superparamagnetic and magnetic materials.[18] Unfortunately, these materials are often very expensive and difficult to process, do not allow for miniaturization and hybrid integration, and/or are not suitable for applications at ambient temperatures. Organic or polymeric materials had not been investigated for efficient Faraday rotation until recently. Nevertheless, a significant advantage of organic materials would be their ease of processing, limited weight, and the fact that they can be custom designed and synthesized to meet specific device requirements. Recently, we have shown that conjugated polythiophenes are very promising materials for Faraday rotation.[19] We have shown that some of the polythiophene derivatives possess exceptionally high Verdet constants, 200−300 times larger than those of commercially used magneto-optic (MO) materials, such as, terbium-doped gallium garnet (TGG) crystals or substituted yttrium iron garnets (YIGs).[20] The potential applications of polymeric MO materials include attractive possibilities of more compact and integrable waveguide optical isolators and high-performance magnetic field sensors that can be readily inserted onto photonic integrated circuit platforms.[21]

In this review, we will limit ourselves to an overview of new and recent work in the field of magneto-optical activity, in particular Faraday rotation measurements in various poly-(3-alkyl) and poly-(3-alkoxy) derivatives. In addition where applicable, we discuss work of other groups that have made important contributions to the field. When appropriate, we will point out possible applications and directions for further research.

Magneto-optic Properties

In most inorganic crystals and glasses Faraday rotation derives from the presence of a significant density of free spins associated with magnetic ions containing triplet energy states, a mechanism that is not applicable to the polythiophenes. In these so-called "paramagnetic transitions", the time average of microscopic magnetic moments is nonzero at room temperature and is not time reversal invariant.[20] The basic mechanisms responsible for MO activity observed in diamagnetic materials involving diamagnetic transitions,[22] interband effects within spin-split Landau levels,[23] positive free carrier rotation,[24] and dynamic spin organization of magnetic polarons generated due to defects in semiconductors[25] are the known processes that are generally not very common in organic systems. In the electric dipole optical transition regime, the classical diamagnetic transition generally addresses the difference in oscillator strength experienced between the right and left circularly polarized light interacting with the excited multiplet caused by Zeeman splitting. The Zeeman energy, given by $\Delta E = g\mu_{\mathrm{B}}B$, where g is the Landé g factor and μ_{B} is the Bohr magneton, is only of the order of 1 μeV at a field of 100 gauss, and therefore much smaller than the thermal energy kT (~25 000 μeV) at the room temperature. Faraday rotation derived from degenerate Landau levels follows a similar mechanism to the diamagnetic transitions found specifically in semimagnetic semiconductor systems and can be estimated from the balance of thermal and Zeeman energy. Neither of these two traditional mechanisms allows any possible existence of large Faraday rotation in organic polymers. Recently, we have reported large magneto-optic activity (Faraday rotation) in several substituted regioregular polythiophene thin films with Verdet constants on the order of 1×10^4 to 1×10^5 ° T^{-1} m^{-1}, as large as those of commercial inorganic magneto-optical materials like terbium gallium garnet (TGG: $V = -7.68 \times 10^4$ ° T^{-1} m^{-1}).[19] There has been another recent report of large Faraday rotation from poly(aryleneethynylene) and poly(3-alkyl)-thiophene thin films indicating toward a supramolecular organization controlled mechanism responsible for the Faraday rotation, similar to our observation on substituted polythiophenes.[26] We have also shown that Faraday rotation depends strongly on the regioregularity of substituted polythiophenes. In semiconductor polymers, such as in polythiophene derivatives, absorption of photons would lead to formation of bound excitons, pair of holes and electrons with binding energy on the order of 0.1 eV. It has been shown that lifetimes of pairs of paramagnetic species (such as electrons and holes) are very sensitive to external magnetic fields.[27] The typical magnetic dipole fields between the pairs of electrons and holes is expected to be on the order of 100 gauss, which also suggests the possibility of forming spin-containing units under such low magnetic field excitations.[28] Possibilities of stronger spin−orbit coupling arising from such spin-containing

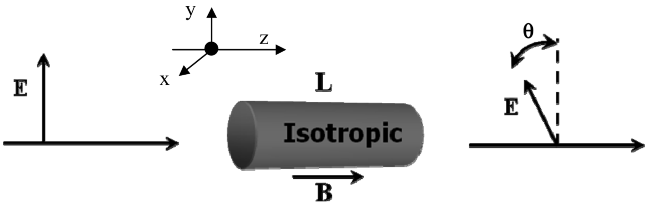

Figure 1. Faraday rotation measurement geometry and Cartesian coordinate system used to define tensor elements.

units not only supports our observations of Faraday rotation in these thin films under low magnetic fields and continuous wave excitation but also explains their dependence on the lamellae-type organization and strong interchain interactions. The exciton wave function generally extends over a number of repeat units along the chain. Depending upon the extent of interchain stacking, the wave function of the excited state can spread onto neighboring chains; in such a scenario, regioregularity in the polythiophene derivatives is expected to play a key role in Faraday rotation.

We consider an experimental configuration of Faraday rotation measurements where a laser beam with frequency ω is transmitted through a isotropic sample under magnetic field B (Figure 1). Electric field polarization inside the sample can be described as

$$\begin{gathered}\mathbf{P}(\omega;\omega,0) = \chi^{\mathrm{eem}}_{xyz}(\omega;\omega,0)\mathbf{E}_y(\omega)\mathbf{B}_z(0) \\ \text{and hence, } \mathbf{P}_i = \chi_{ij}\mathbf{E}_{\mathrm{j}} + \chi^{\mathrm{eem}}_{ijk}\mathbf{E}_j\mathbf{B}_k\end{gathered} \qquad (1)$$

where $B(0)$ is the magnetic induction field and χ is the electric dipole allowed susceptibility, the superscript in the susceptibility components associate the respective subscripts with electric dipole (e) and magnetic dipole (m) interactions. Both linear polarization and magnetization act as sources for Faraday rotation. Note that unlike χ^{eee}, χ^{eem} exists in all media,[29] isotropic and anisotropic, indicating phenomenological similarity with Faraday rotation. Equation 1 can be further reduced to

$$\mathbf{P} = \chi^{\mathrm{B}}\mathbf{E} \text{ with } \chi^{\mathrm{B}} = \begin{pmatrix} \chi_{xx} & \chi_{xyz}\mathbf{B} \\ \chi_{yxz}\mathbf{B} & \chi_{yy} \end{pmatrix} \qquad (2)$$

Using symmetry arguments in the geometry described in Figure 1, one can derive $\chi_{xyz} = -\chi_{yxz} = \chi^{\mathrm{eem}}$. Now Faraday rotation can be easily extracted as $\theta = VBL = \pi\frac{\Delta n}{\lambda}L = \left(\frac{4\pi^2}{n\lambda}i\chi^{\mathrm{eem}}\right)\mathrm{BL}$.[19] Using χ^{eem} value of 0.4 pm/V reported earlier for P3DT system,[27] Verdet constant V can be calculated as 1.8×10^5 °/(T m), an encouragingly large number that certainly has been a major driving force in our research over the last couple of years.

A critical part of this research has been to develop a robust highly sensitive instrumentation for Faraday rotation measurement (so-called magneto-optic polarimetry). The research in this area traditionally has been aimed at sensing of weak to extremely weak magnetic fields of low frequency (~4 to 60 Hz), i.e., those associated with the surveillance of military activities such as moving vehicles or underwater moving objects causing magnetic field fluctuations through interactions with the earth's magnetic field has been explored.[30] Ongoing investigations aim to improve the sensitivity enough to measure sub femto-tesla magnetic fields, a requirement for mapping biomagnetism such as that occurring in the human brain.[31] A highly sensitive Faraday rotation measurement system will also enable one to measure MO properties of organic materials, possibly to the single molecule level, opening a hitherto uncharted arena of MO materials. Methods to measure Verdet constants of materials using AC[32] or DC[33] magnetic fields involving either simple polarimetric or the more complex interferometric[34] approach in both free space and in-fiber[35] configurations have been reported in literature. Two techniques fairly common to these measurements are those based on balanced phase sensitive detection combined with polarization modulation and a heterodyne detection system coupled with a post modulation scheme generally operating in the RF regime. However, a benchtop interferometric setup requires circulation of higher laser power through larger area to attain shot-noise limited sensitivity and often organic polymer materials are susceptible to damage at high incident power. We have reported a simplified free space benchtop MO polarimeter using a magnetic field modulation technique and various optical and electronic noise cancellation schemes working together in ref 19c. We used this system for Faraday rotation measurements in reflection and transmission as well as by placing a nonmagnetic mirror behind any transparent sample in a two-pass configuration. A two pass configuration with AC magnetic field source and the detection system disposed perpendicular to each other is key in successful Faraday rotation measurements from thin films of polythiophene derivatives. To compare, a 1 μm thick spun coat film of regioregular poly(3-hexyl)thiophene with $V \approx 4.4 \times 10^4$ °/(T m) would generate as much Faraday rotation (0.44 mdeg) as in 200 μm thick BK7 plates ($V \approx 250$°/(T m)) under the same magnetic field (100 G) at 633 nm. We have shown that such measurements are possible with signal-to-noise ratio as high as 1000 (ref). Using phase-sensitive noise cancellation schemes Faraday rotations as low as 1 μdeg can easily be measured reproducibly in a wide range of magnetic field frequency (Figure 2). The data clearly shows the ability of this system to perform microdegree Faraday rotation measurements; the noise equivalent sensitivity of the setup is dependent on many factors, such as wavelength and optical power of the laser, measurement time and bandwidth, etc.; a detailed discussion of the sensitivity analysis is out of the scope of this report. With a minimum signal-to-noise ratio of 10, at 532 nm, the setup has a sensitivity of 1×10^{-6} °/$\sqrt{\mathrm{Hz}}$, when used with at least 2 mW of optical power, sensitivity increasing with optical power. In the absence of any standard MO materials, to evaluate repeatability and performance of the system at various wavelengths, Faraday rotation in a variety of materials, including glass, liquid solvents and crystals was measured and compared with the values available in literature. The comparison, presented in ref 19c, shows that the measurements are repeatable within 5% and compare well with the reported values. Efficient noise cancellation, high repeatability, and sensitivity of the setup have been the key factors in our ability to measure Faraday rotation from the ultrathin films of regioregular alkyl substituted polythiophenes reported here. Faraday rotation can also be measured using DC magnetic field with post polarization modulation as reported in ref 26 and premodulation reported by us in ref 36. However, both of these techniques are often susceptible to drift from the modulation source and are not as robust as the ac modulation technique described in ref 19c.

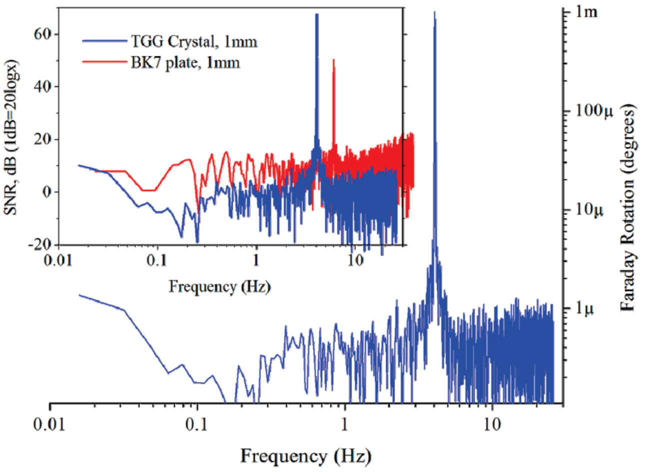

Figure 2. Fast Fourier transform of magneto-optic signal recorded using a controlled magnetic field of 100 μT at 4 Hz measured with 1 mm thick **TGG** crystal and BK7 glass plate showing a low frequency noise level 1 μ° Faraday rotation sensitivity.

Molecular structures of the polymers reviewed in this report are given in Figure 3. The key different candidates are poly(3-alkyl)thiophenes (PTs), poly(3-alkoxy)thiophenes (POTs) and poly(aryleneethynylene) (PAEs), the different chain lengths and regioregularity is also shown. Note that the PAE derivative is not an analogue to either of the polythiophene derivatives. However, in the solid state of the PAE derivative, the molecules are known to be self-assembled into a highly ordered face-to-face π-stacking structure, similar to regioregular PTs. In PAEs, π-interaction is considered to be stronger than the PTs and POTs, because of higher planarity of the molecular backbone.[37] As reported in ref 26, PAE derivatives show larger Faraday rotation than any of the PT derivatives studied so far. Table 1 lists wavelength dependent Verdet constants of the polymers reviewed in this report. Within the PT derivatives Faraday rotation measurements carried out on multiple spun-coat films of RRP3DT and RRP3HT, and their regiorandom counter parts show that the RR derivatives possess V on the order of 1×10^4 °/(T m) as predicted from the χ^{eem} comparison. The regiorandom derivatives are either Faraday inactive or the rotation is below the detection limit of our system. Within measurement error both the polythiophene derivatives show quite similar Faraday activity and also depend strongly on the crystallinity and the lamellae type structure of these polymers. When the spun-coat films were subjected to different processing conditions followed by rigorous Faraday rotation measurements, it was observed that the Faraday rotation drastically decreased when the films were fabricated using melt processing. Details of the Faraday rotation and X-ray diffraction studies of these thin films have been published by us previously in ref . It was shown that the phase change above 80 °C in the PT derivatives seems to be a critical factor influencing Faraday rotation indicating a strong dependence on processing conditions and interchain interaction. On the other hand, interchain charge transfers are known to be more robust in POT derivatives and we have previously shown that POTs show larger Faraday rotation than the PT derivatives (ref 19a). It has been also shown that the Faraday rotation from these materials is also a strong function of regioregularity (ref 38). Poly(3-alkoxythiophene)s with different degrees of regioregularity were prepared using

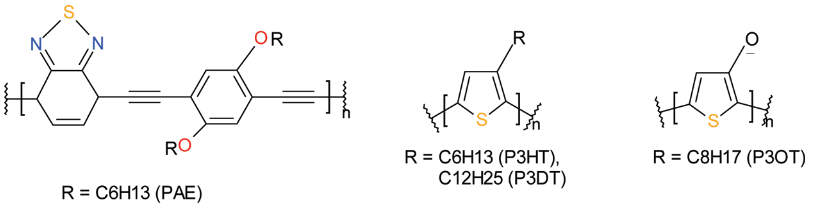

Figure 3. Molecular structures of the polymer systems reviewed in this report.

Table 1. V, Verdet Constant ($\times 10^4$ °/(T m)) of polymers PAE[a], RRP3DT, and RRP3HT at Different Wavelengths.[b]

	V					
	532 nm	633 nm	670 nm	980 nm	1310 nm	1550 nm
PAE		25[a]				
RRP3DT	+2.06 (0.3)	+2.6 (0.6) 11.4[a]	+2.2 (0.2)	+1.6 (0.3)	+1.2 (0.2)	+0.85 (0.04)
RRP3HT (spun-coat)	+6.25 (0.3)	+4.42 (0.2) 20.3[a]	+4.02 (0.2)	+2.01 (0.04)	+1.04 (0.2)	+0.84 (0.03)
RRP3HT (melt-processed)			+0.60 (0.002)	+0.43 (0.003)	+0.21 (0.001)	
BK7	+0.036	+0.025	+0.0223	+0.010	+0.0074	+0.0045
TGG[19]	−1.012	−0.813	−0.73	−0.34	−0.23	−0.15

[a] From ref 26. [b] Typically 200 nm to 1 μm films are used for these measurements. Standard deviations calculated from multiple independent measurements are shown in the bracket. The values are also compared to Verdet constants of BK7 glass and that of a TGG crystal.

Scheme 1. Synthetic Scheme for HT Coupled Highly Regioregular Poly(3-dodecyl)thiophene Using GRIM Methodology[38]

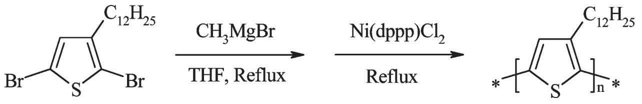

Table 2. ICP-ES data of RRP3DT and RRP3HT for Common Metal Impurities Found in Polythiophene Derivatives

sample	iron % (w/w)	cobalt % (w/w)	nickel % (w/w)
RRP3DT (65 mg)	< 0.01	< 0.005	0.010
RRP3HT (85 mg)	< 0.03	< 0.004	< 0.008

three different methodologies. It was shown that their Faraday rotation is highly dependent on the degree of regioregularity, and Faraday rotation was proposed to be a powerful technique to probe (small) variation in (supra)-molecular structure of chiral as well as achiral conjugated polymers. It is pertinent at this point to describe the synthetic methodology used to prepare the RR PT derivatives reported by us. The synthesis (see Scheme 1), purification, and characterization of P3DT were carried out using a procedure developed by this group.[38] The samples were characterized in detail for the presence of metal impurities and listed in Table 2. The polymer was prepared according to the GRIM methodology, starting from 2,5-dibromo-3-dodecylthiophene (10.0 mmol, 4.10 g); 1 mol % (0.1 mmol, 54.2 mg) Ni(dppp)Cl_2 was used. After polymerization, the polymer was purified through repeated precipitation using methanol followed by thorough washing with methanol, acetone, and hexane using a Soxhlet apparatus. Finally, the polymer was extracted with THF, reprecipitated in methanol, filtered off, and dried. Poly-(3-dodecyl)thiophene (P3DT) has only 70 monomers (note that the estimation of the number of monomers may be an upper bound estimate), with regioregularity for the chain (without the headgroup) > 99% as obtained from NMR. Yield = 1.61 g (64%) ^{1}H NMR δ (ppm): 6.99 (1H, s), 2.81 (2H, t), 1.72 (2H, m), 1.1−1.6 (18H, m), 0.88 (3H, t). M_n = 17.5 kg/mol (measured by GPC in THF toward polystryrene standards), D = 1.4 (measured by GPC in THF toward polystryrene standards), T_m = 145 °C (measured by DSC at a heating rate of 20 °C/min), T_c = 121 °C (measured by DSC at a cooling rate of 20 °C/min). The results of ICP (inductively coupled plasma emission spectrometry, ICP-ES) analysis on RRP3DT and RRP3HT are shown in Table 2 (weight of the samples used in the ICP analysis is indicated within the bracket). Minimal presence of metal impurities confirms that the origin of Faraday rotation in these polymers is not inorganic in nature. P3HT with different degree of regioregularity were obtained from different commercial sources and used to measure Faraday rotation from thin films (500 nm to 1 μm thick) prepared under identical conditions using spin coating technique. Faraday rotation measurements were carried out on multiple spun coat films of RRP3DT, RRP3HT and their regiorandom counter parts. The Verdet constants calculated from the measured Faraday rotation are shown in Table 3. The regiorandom derivatives are either Faraday inactive or the rotation is below the detection limit of our system and within the measurement errors both P3DT and P3HTs with similar regioregularity show quite similar Faraday activity. However, there appears that the Faraday rotation and hence the Verdet constant of P3HTs is a strong function of regioregularity, although a weaker trend compared to that reported in ref 38. Figure 4 shows the dependence of Verdet constant of P3HTs on regioregularity. The empirical fit indicates that the Verdet constant depends exponentially to the regioregularity. Note that such dependence is valid based on the assumption that the reported value of the regioregularity from the vendors are accurate within the measurement errors and the assumption that all samples had identical processing conditions. These observations further confirm that the Faraday rotation in this class of conjugated polymers depends strongly on the supramolecular organization in their thin films. Faraday rotation measurements on different π-conjugated polymers with varying degrees of band gap currently under study will be helpful in further elaborating the underlying mechanism.

Table 3. *V*, Verdet Constant (× 10^4 °/(T m)) of Polymers RRP3DT and RRP3HT with Different Extent of Regioregularity Measured at 532 nm from Spun-Coat Films (standard measurement error of ∼10% is expected)

	P3DT	P3HT						
% regioregularity	> 99.9	50	67	72	84	90	95	99
V (× 10^4 °/(T m))	+2.1	∼0	∼0	+0.64	+0.79	+3.5	+4.7	+8.8

In this review, we have summarized major advances in the description of parameters and processing conditions influencing magneto-optic properties of a class of regioregular poly(3-alkyl)thiophene derivatives. Presently emerging picture in this class of materials appears more complex in nature than the traditional inorganic crystalline magneto-optic materials; where inorganic garnets can usually be well-described using magnetic-field-induced splitting of free electron band structure. The magneto-optic properties in the polythiophene derivatives seem to depend on molecular structure, regioregularity, processing conditions for film preparation and cannot be explained in a fashion similar to the garnets. Being an absorption-mediated

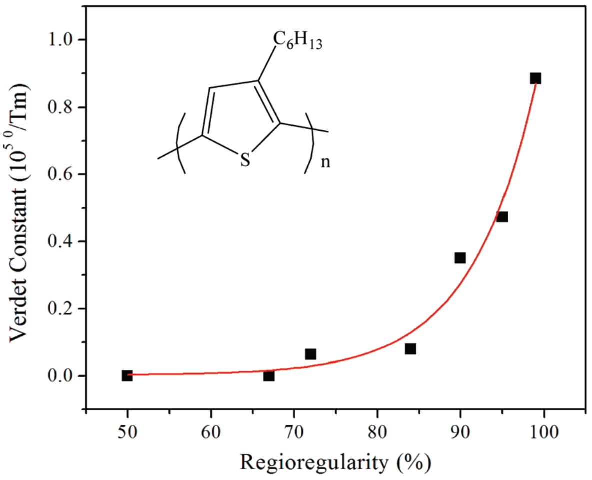

Figure 4. Dependence of Verdet constants on regioregularity in RRP3HT thin films. Inset shows the structure of P3HT.

process, Faraday rotation in both the polythiophene derivatives and garnets are strongly wavelength dependent. Following the experimental results summarized here, we can conclude that a comprehensive understanding of the underlying mechanism responsible for giant magneto-optic effects will emerge from (i) theoretical modeling based on both local as well as nonlocal electron−electron and electron−phonon coupling, (ii) over a much larger experimental system such as other semiconducting organic polymers than those that have been studied so far, (iii) study of influence from intrinsic and supramolecular chirality.

We hope that this review will provide the impetus for these experiments and synthesis to be undertaken.

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