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Insights into Magneto-Optics of Helical Conjugated Polymers

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ABSTRACT: Materials with magneto-optic (MO) properties have enabled critical fiber-optic applications and highly sensitive magnetic field sensors. While traditional MO materials are inorganic in nature, new generations of MO materials based on organic semiconducting polymers could allow increased versatility for device architectures, manufacturing options, and flexible mechanics. However, the origin of MO activity in semiconducting polymers is far from understood. In this paper, we report high MO activity observed in a chiral helical poly-3-(alkylsulfone)thiophene (**P3AST**), which confirms a new design for the creation of giant Faraday effect with Verdet constants up to $(7.63 \pm 0.78) \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$ at 532 nm. We have determined that the sign of the Verdet constant and its magnitude are related to the helicity of the polymer at the measured wavelength. The Faraday rotation and the helical conformation of **P3AST** are modulated by thermal annealing, which is further supported by DFT and MD simulations. Our results demonstrate that helical polymers exhibit enhanced Verdet constants, and expand the previous design space for polythiophene MO materials that was thought to be limited to highly regular lamellar structures. The structure property studies herein provide insights for the design of next generation MO materials based upon semiconducting organic polymers.

1. Introduction

Magneto-optic (MO) materials have broad utility in photonic devices including quantum memory,¹ optical isolators,² optical circulators,³ and magnetic insulators.⁴ They also find use in biomedical applications to create highly sensitive magnetic field sensors (MFS),⁵ which are able to detect extremely weak magnetic field fluctuations associated with real-time human brain activity. The Faraday effect, discovered by Michael Faraday two centuries ago, is a ubiquitous MO effect, describing the rotation of the plane polarized light traveling through a material along the axis of an applied magnetic field.⁶ This effect is quantified by a Verdet constant (V), which is wavelength dependent, and linearly correlated to the applied field and path length through the material. The most common materials used for MFS applications and other photonic devices are terbium gallium garnet (TGG)⁷ and other ferromagnetic, rare-earth metal based crystals.⁸ However, the utility of these paramagnetic materials is limited by their modest Verdet constants, which exhibit magnetic field saturation and appreciable temperature dependence.⁹ Moreover, they are rigid crystals that present difficulties for device integration and fabrication. Conjugated polymeric materials have been demonstrated to possess increased flexibility in fabrication, form-factor, and real-world applications.¹⁰ Furthermore, understanding the underlying mechanism of MO activity and developing new generations of polymeric transducers is a pressing demand and will enable the development of technologies.¹¹

The potential of semiconducting polymers to display extraordinary Faraday effects is a relatively recent and unexpected discovery that has precipitated a renewed interest in the development of new Faraday rotators.¹² Polythiophenes and polyalkoxythiophenes were found to possess large Verdet constants, on

the order of 10^4 - $10^5 \text{ deg T}^{-1} \text{ m}^{-1}$, that exceed those for TGG ($V = -1.0 \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$ at 532 nm and $-0.3 \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$ at 980 nm) and other inorganic materials.^{12c, 12e} The large Faraday rotation of these polymers is thought to be dependent on their crystallinity, and has been correlated to their high regioregularity and their organization into lamellae-type structures. However, polyalkoxythiophenes have limited oxidative stability and the crystalline lamellar structures, if not uniformly organized, are highly optically scattering.¹³ Electronically delocalized organic materials were further confirmed to be a general class of MO materials with the measurement of large Faraday rotations in poly(arylene ethynylene) and mesogenic organic molecules, which suggested that highly-ordered face-to-face π -stacking and the triplet excitation resonances were responsible for the observed Verdet constants.^{12b, 12d} Very recently, Prasad and coworkers reported a strategy for tuning the magneto-optic activity by using a chiral helical polymer doped with organic biradicals, and found that the Faraday rotation behavior differed substantially between the parent polymer and the blended material.^{5a, 12a} These previous investigations highlight the role of polymer conformation and supramolecular organization to affect the electronic delocalization and electromagnetic interactions in the polymer backbone and thereby modulate the Faraday effect. However, aside from these earlier studies, mechanisms to enhance MO activity in polymeric materials is still far from understood.

Polythiophenes with lamellar crystalline structures are typically highly scattering optical materials and are limited in potential applications. As a result, we have been interested in the performance of alternative polythiophene morphologies as MO materials. Chiral helical structures are particularly attractive

and also have prospects in molecular recognition and sensing.^{14,15} Herein, we report helical poly-3-(alkylsulfone)thiophenes (**P3ASTs**) with large Verdet constants and that the sign of Faraday rotation and the helical structure of polymers can be modulated by thermal treatment. Our results provide a basis for the design of new materials, shedding light on understanding the mechanism of MO activity in polymeric materials.

2. Material Design

Figure 1. One-dimensional potential energy surface (PES) scan with an increment of 2.5 ° along the S-C-C'-S' dihedral angle of dimers **D1** and **D2**, evaluated using DFT at the B3LYP/6-31G* level. The global minima at -37.4° for **D1** and -46.2° for **D2** are also included.

Non-resonant optical phenomena¹⁶ are generally enhanced by more polarizable heavy atoms and hence we targeted polythiophenes with sulfur containing substituents.¹⁷ The larger size of sulfide/sulfone groups were also attractive as we suppose that it will promote non-planar polymer backbones and promote tight helical structures. Our expectation was that high chirality will enhance the electronic delocalization along the polymer backbone and afford a higher sensitivity to magnetic fields.

Our investigations were guided by the computed geometries of thiophene dimers **D1** with sulfide alkyl chain and **D2** with sulfone alkyl chain, using density functional theory (DFT). A one-dimensional potential energy surface (PES) scan was conducted in the gas phase as a function of the torsional angle between two thiophene rings, defined as the S-C-C'-S' dihedral angle, and was computed from -180° to +180° (0°, *cis*-conformation; ±180°, *trans*-conformation) (Figure 1). Both dimers exhibit global potential energy minima at acute torsional angles of -37.4° for **D1** and -46.2° for **D2**. **D2** shows a slightly larger torsional angle than **D1**, which could lead to a tighter helix in the respective polymer. In both cases the torsional angles are shifted significantly from the planar structure, indicating the prospect for helical structures in the corresponding polymers. To evaluate the role of the alkyl sidechains on the formation of helical structures and on Faraday rotation, we synthesized a number of chiral and achiral poly-3-(alkylthio)thiophenes (**P3ATTs**) and poly-3-(alkylsulfone)thiophenes (**P3ASTs**) (Scheme 1).

The synthetic route to **P3ATTs** and **P3ASTs** is shown in Scheme 1, beginning with a lithium-halogen exchange reaction with 3-bromothiophene followed by quenching with sulfur to give 3-thiophenethiol. Using the corresponding nucleophilic

3. Results and Discussion

Scheme 1. Synthetic Route for Head to Tail Regioregular **P3ATTs** and **P3ASTs**

thiolate with bromo-alkanes provided facile access to 3-(alkylthio)thiophenes. Selective mono-bromination using NBS and ultrasound^{17b} afforded the mono-brominated products, which were used for a Kumada polymerization¹⁸ as the next step to produce regioregular polythiophenes in high yields. Knochel's base was used to deprotonate the monomer, and 0.5 mol% NiCl₂(dppe) was chosen as the catalyst to promote the polymerization. With this method, polymers of **P3ATTs** with racemic side chains (**S-P1**) and with chiral side chains (**(S)-S-P2**) were all synthesized for comparison in 64% yield and 44% yield, respectively. The physical data of these polymers are summarized in Table 1. **S-P1** was obtained with a *M_n* of 54.6 kDa and head to tail (HT-HT) regioregularity >96%, which is an improvement from previously published results.¹⁹ Different from the previous reported **P3ATTs** with *n*-alkyl side chains that are only soluble in CS₂, **S-P1** with branched side chain shows extraordinary solubility in most common organic solvents including hexane and silicon oil, which is desirable. **(S)-S-P2** is less soluble but can be completely dissolved in hot chloroform or *ortho*-dichlorobenzene (*o*-DCB). Its molecular weight based on the THF soluble portion at room temperature was estimated (by GPC) to be 11.8 kDa (*Đ* = 1.17), implying that the real molecular weight of **(S)-S-P2** is likely higher.

The oxidation of **P3ATTs** to sulfone containing polymers **P3ASTs** was accomplished using *m*-CPBA as the oxidant and proceeded in >99% conversion with excellent solubility in most organic solvents. The molecular weights of **SO2-P1** and **(S)-SO2-P2** are 32.7 kDa and 20.0 kDa respectively, with *Đ*s of 1.42 and 1.61. The effective molecular weight (based on GPC) of the sulfone polymer is smaller than its sulfide counterpart, which may be related to the conformation differences or undetected degradation from *m*-CPBA oxidation. ¹H NMR spectra (Figure S1-1) are well resolved, indicating the absence of polymer aggregation, and the polymers possess high levels of regioregularity. The protons of the CH₂ group adjacent to the sulfone group and protons on the remaining β-position of the thiophene rings shift to lower field, which reflects the electron-withdrawing nature of the sulfone group as compared to the original electron-donating sulfide group.

The thermal stabilities of the polymers were evaluated by thermal gravimetric analysis (TGA). The decomposition temperatures are in the range of 362–404 °C (Figure S7), starting with the loss of alkyl chains from the sulfide/sulfone groups. Differential scanning calorimetry (DSC) analysis of **S-P1** reveals a melting transition at 171 °C and a crystallization transition with cooling around 154 °C (scan rate 5 °C/min). In contrast, no obvious thermal transition of

SO2-P1 is observed in the range from 100 to 350 °C. **(S)-S-P2** has a melting transition at 205 °C and crystallizes at 191 °C with cooling (scan rate 5 °C/min). **(S)-SO2-P2** is in a metastable phase that melts at 118 °C and exothermically transforms to a new phase that melts at 203 °C. The low temperature crystalline phase forms again

with cooling to 107 °C (scan rate 5 °C/min). The melt processing of MO materials is attractive and hence the thermal transitions and stability of these polymers are highly relevant.

Table 1. Physical Properties of P3ATTs and P3ASTs

Polymer	Mn (kDa)/ Đ ^a	T _d ^b (°C)	T _m ^c (°C)	T _c ^d (°C)	λ _{max} Solution ^e (nm)	λ _{max} Film ^f (nm)	E _{ox} (V) ^g Vs Ag/Ag ⁺	E _g (eV) ^h
S-P1	54.6/1.37	365	171	154	542	553, 600	0.26	1.85
SO2-P1	32.7/1.42	404	179 ^j	1	411	414	1.46	2.49
(S)-S-P2	11.8/1.17 ⁱ	371	205	191	526	570, 622	0.34	1.84
(S)-SO2-P2	20.0/1.61	362	118, 203 ^k	107	403	414	1.30	2.27

^aEvaluated by gel permeation chromatography (GPC) in THF against a polystyrene calibration at room temperature. ^bDecomposition temperature. ^cMelting temperature. ^dCrystallization temperature. ^eIn CHCl₃ solution. ^fSpin-coated films with polymers dissolved in chloroform solution, without thermal annealing. ^gDetermined by Cyclic Voltammetry with polymers spin-coated on ITO glass. 0.1 M Bu₄NPF₆ in CH₃CN was used as the electrolyte, Pt wire as the counter electrode, Ag/AgNO₃ as the reference electrode. Ferrocene (E_{1/2} = 0.10 V) was used as external standard. ^hBandgap determined by the onset of UV-vis absorption of thin films. ⁱDetermined from the soluble part in THF at room temperature. ^jOnly observed for the first scan. ^kA low temperature meta-stable phase is observed- see text. ^lNo noticeable thermal transitions are observed.

The sulfide and sulfone motifs impart different optical and electronic properties to the polymers (Table 1). With the oxidation from sulfide to sulfone, the bandgap and the onset of oxidation (E_{ox}) increase as a result of the electron-withdrawing nature of the sulfone group and decreased conjugation arising from the twisting of the polymer backbone. The spectroelectrochemistry of polymers was studied with polymers spin-coated on ITO glasses (Figure S8). Both of **S-P1** and **(S)-S-P2** exhibit electrochemical behavior with reversible p-doping and de-doping process. The intensities associated with the UV-vis absorption bands of **(S)-S-P2** at 570 nm and 622 nm decrease with oxidation from 0 to 1.0 V (vs. Ag/AgCl), while the absorption around 850 nm increases (Figure S8f). Upon de-doping from 1.0 to 0 V, the absorption band intensities at 570 nm and 622 nm are re-established. This transition is accompanied by a change in color of the thin film from purple to a visually transparent state, which is reversible for hundreds of cycles. For polymer **(S)-SO2-P2**, the redox behavior is not reversible and a much higher E_{ox} potential of 1.30 V is required to oxidize the polymer as a result of the electron-withdrawing sulfone groups.

GI-WAXS and AFM Measurements

Grazing-incidence wide-angle X-ray scattering (GI-WAXS) and atomic force microscopy (AFM) were used to investigate the polymer organization and the morphology of thin films (Figure 2). X-ray patterns of **(S)-S-P2** and **(S)-SO2-P2** reveal inter-chain spacing consistent with proposed helical structures with d_{100} -spacings 23.5/25.6 Å (Figure S17) for **(S)-S-P2** and 24.1 Å for **(S)-SO2-P2**. These periodic organizations are considerably larger than the d_{100} -spacing of simple poly(3-alkylthiophene)s with C4 to C10 carbon chains that organize in lamellar structures with solution cast films (16.4–21.5 Å).^{19d} AFM images of both **(S)-S-P2** and **(S)-SO2-P2** show thin film morphologies with nano-fibrillar structures with different diameters that appear to depend on their helicity.²⁰ Interestingly, we noted that the (100) peak position of **(S)-SO2-P2** exhibits a slight shift towards smaller d_{100} -spacing when compared to **(S)-**

S-P2. Additionally, **(S)-S-P2** displays (200) and (300) x-ray reflections and larger diameter nano-fibrils in AFM images, suggesting that **(S)-S-P2** possesses a more regular structure. Furthermore, slow diffusion of non-solvents into dilute solutions²¹ of **(S)-S-P2** or **(S)-SO2-P2** creates micrometer-scale helical fibers and could be visualized by scanning electron microscopy (SEM) (Figure S18). Although GI-WAXS and AFM showed supports of the formation of helix, circular dichroism (CD) measurements was used to confirm the helicity of these chiral polymers.

Figure 2. GI-WAXS pattern and tapping-mode AFM image of (a) (*S*)-**S-P2** and (b) (*S*)-**SO2-P2**. Insets: proposed d_{100} -spacing between two helical structures. GI-WAXS was taken on polymer samples drop-cast with polymers dissolved in chloroform 10

mg/mL on zero-diffraction wafers; AFM was performed on spin-coated polymer films prepared from chloroform solution 5 mg/mL (1500 rpm) on highly oriented pyrolytic graphite (HOPG).

Circular Dichroism (CD) measurements

Figure 3. (a) Circular Dichroism (CD) and UV-vis spectra of (*S*)-**SO2-P2** in solutions of THF/MeOH (v/v), 0.2 mg/mL at 25 °C. (b) CD spectra of (*R*)-, (*S*)- and (*R+S*)-**SO2-P2** ((*R*)/(*S*) = 1/1) in THF/MeOH (40/60). (c) CD spectra of thin films with (*R+S*)-**SO2-P2** before and after thermal annealing (TA) at 150°C for 12 h under inert atmosphere. CD spectra of thin films with (*S*)-**SO2-P2** and (*R*)-**SO2-P2** (d) before thermal annealing, (e) and after thermal annealing. Polymers were dissolved in chloroform and spin-coated on glass slides.

The helicity of chiral polymers was then interrogated with the use of CD measurements taken in solution and thin film states (Figure 3). The CD measurements in solution showed strong bisignate Cotton effects for the π - π^* transitions in (*S*)-**S-P2** and (*S*)-**SO2-P2**, whereas no Cotton effect was observed for **S-P1** and **SO2-P1**. Figure 3a shows the UV-vis and CD spectra of (*S*)-**SO2-P2** when aggregated in solution.²² Specifically, when (*S*)-**SO2-P2** was dissolved in pure THF, no Cotton effect was observed. Upon addition of MeOH, a poor solvent, the polymer exhibited an increased CD signal corresponding to the formation of an ordered helical aggregation.²³ The zero-crossing wavelength in the bisignated CD band of (*S*)-**SO2-P2** correlates approximately with the wavelength of maximum absorption in UV-vis spectra, and shows a positive CD band around 540 nm and a negative one around 378 nm, implying its *P*-helicity with a right-handed chiral assembly of the polymer.^{14a, 24} The aggregation of (*S*)-**SO2-P2** is also reflected by its UV-vis absorption and causes a new lower-energy peak at 570 nm. The concentration independence of UV-vis absorption, with polymers dissolved in THF/MeOH (v/v) 50/50, suggests the same type of aggregates are formed and the aggregation takes place even at very low concentration (0.005 mg/mL) (Figure S5-2). Dissolving the polymer in different combinations of solvents shows the similar Cotton effect and handedness as is shown in THF/MeOH (Figure S9).²⁵

To confirm that the helicity of the supramolecular helix is dictated by the absolute configuration of the chiral center on the side chain, polymer (*R*)-**SO2-P2** bearing a chiral center with the opposite (*R*)-configuration was synthesized. As expected it displays a mirror-imaged CD spectrum to that of (*S*)-**SO2-P2**

when dissolved in THF/MeOH (40/60), indicating the formation of the opposite helicity of helical structure (Figure 3b). Moreover, when using a combination 1:1 mass portion of (*R*)- and (*S*)-**SO2-P2** polymers to make a mixed sample (*R+S*)-**SO2-P2**, no CD effect was observed.

CD responses were further studied with polymer thin films, a form in which magneto-optic devices would be constructed. The CD spectra were checked at different rotation angles to confirm that there was no optical anisotropy. The thin films of (*S*)-**SO2-P2** display chiroptical properties that vary depending on the deposition conditions and other treatments. The CD spectrum of a thin film of (*S*)-**SO2-P2** spin-coated from chloroform solution without thermal annealing displays a helically ordered supramolecular structure, which is very similar as in the solution phase. However, a bisignate CD response arising from chiral excitonic coupling reveals another type of helical structure with *M*-helicity after thermal annealing at 150 °C for 12 hours (Figure 3d and 3e).²⁶ This behavior suggests that thermal annealing promotes an alternate helicity which is thermodynamically favored and is accompanied by a redshift of the UV-vis, consistent with increased aggregation. To determine the generality of this behavior, thin films of (*R*)-**SO2-P2** were further investigated. The initial spin-coated (*R*)-**SO2-P2** film also shows a similar CD effect as in solution, and displays helical structures of *P*-helicity after thermal annealing (Figure 3e). The helicity change behaviors of polymer (*R*)- and (*S*)-**SO2-P2** after thermal treatment are further confirmed by high-temperature MD simulations (*vide infra*). Attempts to spin coat with pre-aggregated polymer solutions on glass slides resulted in cloudy and non-uniform thin films (Figure S11), which are not suitable for MO

measurements. As predicted, a thin film of mixed sample (**(R+S)-SO2-P2**) shows no CD response before and after being thermal annealed (Figure 3c).

To complement the ground state chiroptical properties of polymers provided by CD, circularly polarized luminescence (CPL) was also measured for thin films of (**R**)- and (**S**)-**SO2-P2** to investigate their excited state properties. Indeed, the change of helicity of polymers in thin films after thermal annealing was also observed in CPL measurements (Figure S12). The differential chiroptical behavior of (**R**)- and (**S**)-**SO2-P2** polymers reveals that their helical aggregations depend upon external thermal stimuli, and have provided us with an opportunity to investigate the correlations between helicities of polymers and the magnitude/sign of their Faraday rotations.

Faraday rotation measurement

The magneto-optic activities of the polymers were then evaluated via Faraday rotation measurements on polymer thin films, which were prepared by spin coating on thin glass substrates (substrate thickness ~ 170 μm ; sample thickness ~ 130 nm). Our home-built Faraday rotation measurement system is based on established designs,^{12b, 12d} and is fully described in the supporting information (Figure S19). The performance of the system was evaluated by measuring reference samples of BK7 and TGG (Table S1), giving results consistent with the literature values.^{12c, 27}

Figure 4. Verdet constants of polymers **S-P1**, **SO2-P1**, (**S**)-**S-P2**, (**S**)-**SO2-P2**, (**R**)-**SO2-P2** and (**R+S**)-**SO2-P2** were measured over applied magnetic fields of -0.5 T to $+0.5$ T at 532 nm. Polymers were dissolved in chloroform and spin-coated on 0.17 mm glass slides. Thermal annealed (TA) at 150°C for 12 h under inert atmosphere. Error bars represent the propagation of errors of background measurements, sample measurements, and film thickness measurements by AFM.

The MO properties were evaluated using a 532 nm laser diode light source. As shown in Figure 4a, the helical polymers show superior MO performance relative to non-helical analogs. Polymers (**S**)-**S-P2**, (**S**)-**SO2-P2**, and (**R**)-**SO2-P2** give absolute Verdet constants from $(6.90 \pm 0.97) \times 10^4$ to $(7.63 \pm 0.78) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$, and the achiral polymers **S-P1**, **SO2-P1** give Verdet constants from $-(1.77 \pm 0.42) \times 10^4$ to $-(3.09 \pm 0.66) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$. Thermal annealing did not affect the Faraday rotation of non-helical polymers, but gave dramatic changes for the chiral sulfone polymers. As shown in Figure S10, the CD response of (**S**)-**S-P2** remains the same without changing its helicity after thermal annealing, and it gives consistent Verdet constants of $(7.53 \pm 1.10) \times 10^4$ and $(6.23 \pm 0.78) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$ respectively. As shown in Figure 4b, (**S**)-**SO2-P2** displays

a Verdet constant of $(7.63 \pm 0.78) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$, but switches sign to $-(6.38 \pm 0.86) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$ with *M*-helicity after thermal annealing. A similar phenomenon was also discovered with (**R**)-**SO2-P2**, which gives a Verdet constant of $-(6.90 \pm 0.97) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$ and changes to $(7.71 \pm 1.20) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$ with *P*-helicity upon thermal annealing.

The influence of helicity on the sign of the Faraday rotation was further confirmed by using sample (**R+S**)-**SO2-P2**, which was found to show no CD effect both in solution and film state. The film of (**R+S**)-**SO2-P2** has a Verdet constant of $-(3.27 \pm 0.94) \times 10^4$ degree $\text{T}^{-1} \text{m}^{-1}$ which is approximately half of the value of the chiral ones, and is unchanged after thermal treatment. During the thermal treatment, the UV-vis absorption

of (*R*)-, (*S*)- and (*R*+*S*)-SO₂-P₂ all red-shifted approximately 100 nm as a result of the formation of more aggregated structures (Figure S6). Hence thermal annealing changed the aggregation patterns of polymers, which could contribute to the change of sign of Faraday rotation at 532 nm. The measured Verdet constants support our hypothesis that the high degree of electronic delocalization in a twisted helical polymer gives rise to an enhancement of MO activity. The dependence of the sign of the Verdet constant upon polymer helicity is notable, and we suggest this effect could be related to the transient magnetic dipole moment arising from the interaction of the chiral helix with resonant light.

DFT Calculation and MD Simulation

To better understand the molecular structures and electronic properties associated with our polymers, we constructed truncated decamer models and performed a combination of density functional theory (DFT) calculations²⁸ and molecular dynamics (MD) simulations²⁹ at the molecular level in the gas phase.

DFT (B3LYP/6-31G*) optimized geometries at 0 K reveal that the polymers with chiral side chains, (*S*)-S-P₂ and (*S*)-SO₂-P₂, favor helical conformations with *P*-helicities (Figure 5c, 5d), whereas achiral polymers S-P₁ and SO₂-P₁, are stable in random configurations (Figure 5a, 5b). In addition, sulfone-containing (*S*)-SO₂-P₂ shows tighter helix than the sulfide-containing (*S*)-S-P₂, (9 v.s. 10 repeating units in each helical period).

Figure 5. DFT-optimized geometries (0 K) of truncated decamers (a) S-P₁, (b) SO₂-P₁, (c) (*S*)-S-P₁ and (d) (*S*)-SO₂-S-P₁. Only the polythiophene backbones and the sulfonyl groups on the side chains are illustrated for clarity.

MD simulations were performed to confirm the helicities of (*S*)-S-P₂ and (*S*)-SO₂-P₂ at room temperature (298 K, initialized at DFT-optimized structures) and the helicity-switching during the thermal treatment (423 K and above). According to our MD simulations, within the first 1 ps after the temperature jump to 298 K, the decamers with chiral side chains are contracted into more compact helical structures with identical helicities obtained from DFT (Figure 6a, 6c). In contrast, those with achiral side chains, S-P₁ and SO₂-P₁, do not undergo any significant reconfiguration from their DFT-optimized geometries (Figure S14). Both DFT calculations and MD simulations at the molecular level suggest one possible mechanism of forming the helicity from the helical molecular configuration, which is induced by the steric repulsion from the branched, chiral side chain. It should be noted that the supramolecular aggregation of polymer chains is an additional source of helicity based on CD measurements with polymers in solution phase (Figure 3a).

High-temperature MD simulations further showed that the helicity-change behaviors of sulfone-containing helical polymers are consistent with our CD observations. The calculations were carried out at 423 K for (*R*)-SO₂-P₂, which was used for thermal annealing of the polymer thin films, and at 1023 K for (*S*)-SO₂-P₂ (for this polymer, the helical switch was not observed within the 2-ns simulation window at 423 K, and oligomer can stay “undissociated” within 2 ns at 1023 K). Both of the two polymers unfold themselves within 2 ns at the elevated temperatures, and then evolve to their thermodynamic minima with opposite helicities (Figure 6b, 6d). The helical structure of (*S*)-SO₂-P₂ switches from *P*-helicity at 298 K to *M*-helicity at 1023 K; while (*R*)-SO₂-P₂ switches from *M*-helicity at 298 K to *P*-helicity at 423 K. The unfolded “intermediate” structures are also observed during the transition from one helicity to the other (Figure S15).³⁰ To model the cooling process, room-temperature simulations were performed for another 2 ns using the final configurations from high-temperature simulations as the initial guesses, and these switched helicities are retained (Figure S16).

Figure 6. Geometries of the truncated decamers of (*S*)-SO₂-P₂ and (*R*)-SO₂-P₂ from final snapshots of MD simulations performed at the room and high temperatures. Only the polythiophene backbones and the sulfonyl groups on the side chains are illustrated for clarity. The experimentally observed switching of the helicity is reproduced by these simulations.

Conclusion

In summary, sulfone-containing chiral helical polymers were developed, and were found to exhibit tunable and large Faraday rotations with absolute Verdet constants up to $(7.63 \pm 0.78) \times 10^4$ deg T⁻¹ m⁻¹. These MO values rival the present record materials, and have moreover demonstrated the Verdet constants can be tuned that would be challenging to produce with present inorganic materials. The combination of experimentation and theoretical calculations point to a strong relationship between the helical structure of polymers and the sign/magnitude of Faraday rotation. The sulfone-containing helical polythiophenes reported herein provide an alternative to the lamellar structures that were shown previously to produce optimal results, and helical polymers have superior performance over non-helical analogs. Our results suggest promising routes to the creation of next generation MO materials with the performance metrics needed to enable transformative devices for the measurement of magnetic fields.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental procedures, details of the characterization of polymers and monomers, theoretical calculations, ^1H and ^{13}C NMR spectra.

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Notes

The authors declare no competing financial interest.

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SYNOPSIS TOC