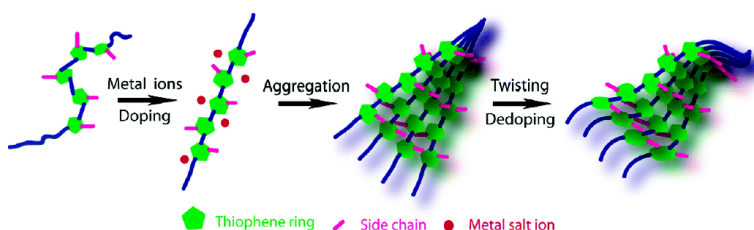


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Control of Chiral Ordering in Aggregated Poly{3-(S)-[2-methylbutyl]thiophene} by a Doping-Dedoping Process

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Abstract: The chiral ordering in aggregated poly(3-alkylthiophene) can be controlled by a metal salt-dependent doping-dedoping process. Enhancement or reduction in the chiral anisotropy factor depends on the doping level, such that doping driven by polymer–metal salt interactions, and dedoping driven by aggregate formation must be balanced in order to achieve maximal chiral ordering. This phenomenon provides a new basis to control chiral arrangement in conjugated polymer aggregates, relying solely on doping, and thus avoiding tedious modification of side-chain or main-chain structures.

Introduction

Chiral conjugated macromolecules have attracted much attention in recent material science research due to their potential applications in asymmetric catalysis, separation, and sensing, as well as for polarized light emission, wherein the chiral macromolecule has been further endowed with nonlinear electrical and optical properties.¹ A highly ordered chiral structure incorporated intramolecularly within each individual polymer chain, or induced intermolecularly by π – π or σ – σ stacking, is a prerequisite for a chiroptically functional polymer. Temperature,² solvent polarity,³ and the sample preparation process⁴ are crucial external factors in determining the chiral

ordering degree of a polymer, in addition to inherent factors such as the electronic and steric natures of the main chain or side chains, the distance from the chiral centers to the backbone,⁵ and the coupling sequence along the main chain (regioregularity).⁶

We here report a new, facile approach to enhance chirality in aggregates of a π -conjugated polymer, poly{3-[(S)-2-methylbutyl]thiophene} (PMBT), by the addition of a doping metal salt prior to aggregation. This approach may provide a general way to control the chiral arrangement of conjugated polymers because it does not depend stringently on the presence of particular structural elements in the main or side chains.

Experimental Section

Materials. Chemicals such as 3-bromothiophene (TCI), Ni(dppp)-Cl₂ (Kanto), anhydrous FeCl₃ (Kanto) and (S)-Methylbutyl bromide (Aldrich, $[\alpha]^{21} +4.5^\circ$, $c = 5$ in CHCl₃), were used as received.

Measurements. Molecular weights were estimated by size exclusion chromatography (SEC) on a Shodex KF806M column (eluent THF, 30 °C) using a Shimadzu liquid chromatograph equipped with a photodiode array detector and calibrated using polystyrene standards. Circular dichroism (CD) and simultaneous ultraviolet–visible (UV–vis) spectra were recorded using a JASCO J-725 spectropolarimeter (1 cm path length cell; sample concentration = 1.0×10^{-4} mol/L of the thiophene repeating units). NMR spectra were recorded on a Varian Unity 300 spectrometer relative to tetramethylsilane as internal standard in CDCl₃.

Preparation of Monomer. 3-[(S)-2-methylbutyl]thiophene (MBT) was prepared according to a literature method.⁷ (S)-2-Methylbutylmagnesium bromide (prepared from 0.12 mol (S)-2-methylbutyl

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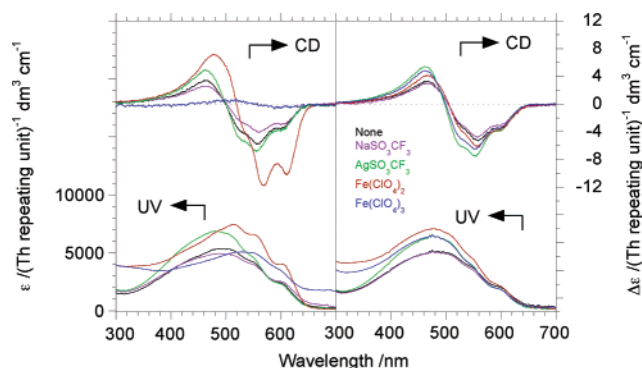


Figure 1. Metal salt effect on CD and UV-vis spectra of PMBT in Processes A (left) and B (right) at 20 °C (molar ratio between PMBT and metal salt is 1:1).

bromide) in 150 mL of diethyl ether was added to a 100 mL ethyl ether solution of 16.3 g (0.10 mol) of 3-bromothiophene in the presence of Ni(dppp)Cl₂ ([1,2-bis(diphenylphosphino)propane]dichloro-nickel(II)) at room temperature. The mixture was stirred for 4 h, and then gently refluxed for 8 h. 100 mL of 1.0 M HCl solution was added, and the water layer extracted using ethyl ether (2 × 50 mL). The organic layer was combined, washed with water (3 × 100 mL), and dried over magnesium sulfate. The product was purified by vacuum distillation. BP: 78–82 °C/8 mmHg, yield 58%, $[\alpha]_D^{24} = +7.37^\circ$ (neat). ¹³C NMR (CDCl₃, δ): 11.51, 19.12, 29.20, 36.03, 37.53, 120.68, 124.83, 128.76, 141.88.

Preparation of Polymer. The ferric chloride oxidation method was applied to synthesize the polymer.⁸ 1.5 g (10 mmol) MBT in 10 mL anhydrous chloroform was slowly added dropwise into a mixture of ferric chloride (40 mmol) in 90 mL chloroform with vigorous stirring under argon at room-temperature overnight. The reaction mixture was poured into 1 L methanol, and the solid formed was collected by filtration. This oxidized product was dissolved in 200 mL chloroform and washed with 3 × 100 mL 10% hydrazine aqueous solution. The chloroform layer was separated and dried over CaCl₂. Neutral state PMBT was obtained after removing the solvent. The polymer was purified by reprecipitation from chloroform and methanol. Yield, 70%; molecular weight, $M_w = 93\,600$, $M_n = 35\,260$; ¹³C NMR (CDCl₃, δ): 11.50, 19.24, 29.49, 35.97, 36.50, 120.60, 121.09, 133.58, 138.92. Regioregularity (head-to-tail coupling) was estimated to be about 80% based on ¹H NMR spectrometry using Rieke's method.⁹

Preparation of Aggregates. Process A: 0.5 mL of 1×10^{-3} M polymer in chloroform was placed in a 10 mL glass vial. With magnetic stirring (500 rpm), 0.1 mL of 5×10^{-3} M metal salt in acetonitrile was added rapidly. After 30 s, 4.4 mL of *n*-octanol was added at once. CD and UV-vis spectra were measured after 30 s. Process B: 0.5 mL of 1×10^{-3} M polymer in chloroform was placed in a 10 mL glass vial. With magnetic stirring (500 rpm), 4.4 mL of *n*-octanol was added rapidly. After 30 s, 0.1 mL of 5×10^{-3} M metal salt in acetonitrile was added at once. CD and UV-vis spectra were measured after 30 s. All measurements were repeated, and gave identical results.

Results and Discussion

The chiral anisotropy factor g_{abs} , defined as $\Delta\epsilon/\epsilon$, was determined to evaluate the extent of chiral ordering associated with the addition of metal salts. The CD and UV-vis absorption spectra of PMBT in a mixed solvent system (chloroform/acetonitrile/1-octanol) with a series of metal salts added prior to (Process A) and after (Process B) aggregation were measured (Figure 1). In Process A, Fe(ClO₄)₂ led to a remarkable increase

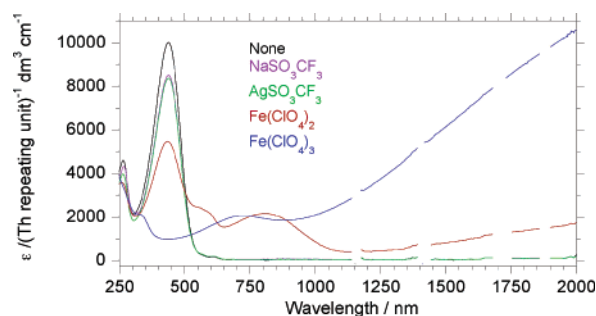


Figure 2. UV-vis and near-IR absorption spectra of PMBT in response to addition of metal salts before aggregation at 20 °C (molar ratio between PMBT and metal salt is 1:1).

in the g_{abs} factor (59%) (measured at the positive peak maximum in the CD), whereas Fe(ClO₄)₃ gave a dramatic decrease in g_{abs} (81%). NaSO₃CF₃ resulted in a slight decrease of the g_{abs} value (20%), and AgSO₃CF₃ produced a slight increase (9%). In contrast, in Process B no significant changes were observed in the CD spectra with any of the metal salts tested, establishing that the observed spectral changes were dependent on metal salt-polymer interaction preceding aggregation. In the absence of added metal salts, a 28 nm blue shift of λ_{max} in the UV-vis spectra (Process B, $\lambda_{\text{max}} = 475$ nm) was observed, which taken with the minimal change in the CD g_{abs} value of PMBT, indicates faster aggregation of the polymers due to the solvent polarity difference in Process B (chloroform/1-octanol) relative to Process A (chloroform/acetonitrile/1-octanol) at the initial state of aggregation. Interestingly, doping by Cu(SO₃CF₃)₂ of aggregated poly(3-arylthiophene) containing chiral oxazolinylium moieties was recently reported to cause loss of optical activity, a process cited as a novel example of chirality switching.¹⁰ These contrasting metal salt effects on polymer aggregates point to crucial roles for the side chain oxazolinylium groups (metal ion chelating) and benzene moieties (charge-transfer bridge) in polymer doping.

The UV-vis and near-infrared (near-IR) spectra of PMBT in chloroform after the addition of the metal salts, but prior to aggregation (addition of 1-octanol, Process A), were also recorded (Figure 2). Minimal changes in the absorption spectra of PMBT were observed upon addition of NaSO₃CF₃ or AgSO₃CF₃ before aggregation, while addition of Fe(ClO₄)₂ and Fe(ClO₄)₃ caused two new bands (~800 nm and in the near-IR region) to appear, accompanied by decreased intensity at 440 nm (original neutral band). This clearly demonstrates metal salt induction of a doping state, with Fe(ClO₄)₃ providing the larger effect. After aggregation, PMBT was completely dedoped when Fe(ClO₄)₂ was the dopant, whereas with Fe(ClO₄)₃ the band at ~800 nm persisted (Figure 1). Based on these results, it is clear that doping prior to aggregation is essential to effect chiral ordering in the aggregates, and the doping level, which depends on the oxidizing ability of the metal salts, is the decisive factor in determining whether the g_{abs} factor is ultimately increased or diminished.

To further develop this proposal, the CD and UV-vis spectra of PMBT were recorded after interaction with Fe(ClO₄)₂ at different ratios of doping salt to polymer. As shown in Figure 3, PMBT doping was dependent on the concentration of Fe-

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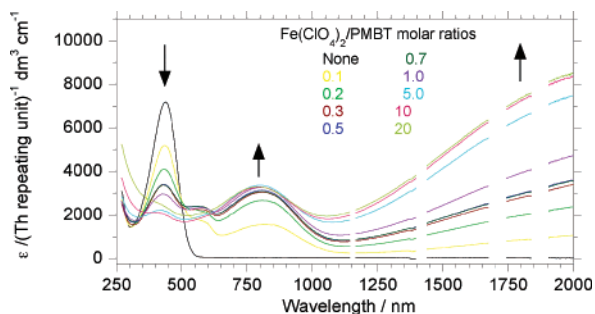


Figure 3. $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratio-dependent absorption spectra of PMBT in chloroform at 20 °C.

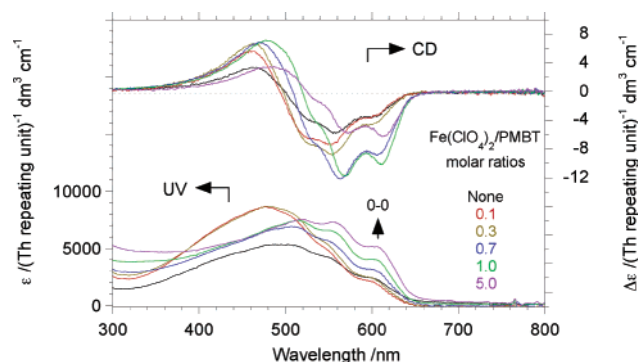


Figure 4. $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratio-dependent absorption and CD spectra of PMBT aggregates (Process A) at 20 °C.

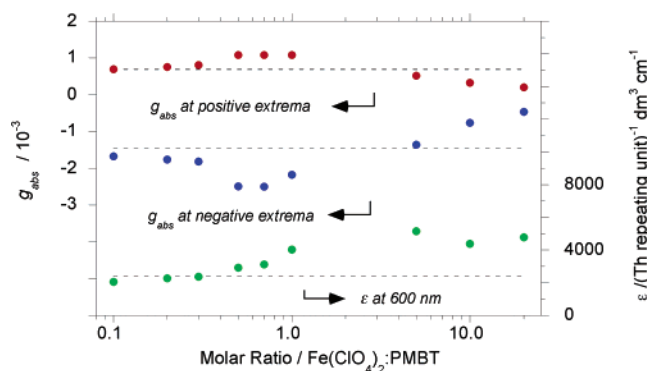


Figure 5. Absorption and CD spectral analyses of PMBT aggregates (Process A) at 20 °C (dashed lines correspond to the g_{abs} or λ_{max} value in the absence of added metal salts).

(ClO_4)₂ (in chloroform). At increasing relative concentrations of $\text{Fe}(\text{ClO}_4)_2$, the neutral transition band at 440 nm decreased in intensity, and simultaneously two new bands, one at ~ 800 nm and the other in the near-IR region, gained in intensity, suggesting formation of a polaron state¹¹ and an increase in doping level. The two new bands reached their maximal values when the $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratio exceeded 10.¹² It is evident that aggregation upon the addition of poor solvent led to complete dedoping of the polymer (Figure 4). It is also clear that the changes in g_{abs} values significantly depend on the $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratio, that is, at the low $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratios (0.1 \sim 1:1), the g_{abs} values increased, whereas it started to decrease when the ratio reached 5 (Figure 5). The greatest enhancement of chiral ordering in the aggregates occurred at

the $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratio of 0.7:1. Doping leads to a more planar polymer backbone, reducing the steric hindrance and therefore facilitating the approach of polymer chains during aggregation. Subsequent dedoping then produces cooperative twisting of the polymer backbones in the cases of low doping levels (low $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratios, 0.1 \sim 1:1), resulting in disruption of extended conjugation along each polymer chain, but with retention of a highly ordered chiral structure involving limited segments of interacting polymer main chains, induced by the *effective* chiral side chain interaction. At high doping levels (high $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratios, 5 \sim 20:1), the enhanced planarity due to increased double bonding between neighboring thiophene rings, may lead to rapid aggregation, which could result in a lowering of chiral ordering degree due to *ineffective* chiral side chain interactions, although the highly ordered structure (achiral) can still be formed.¹¹ This interpretation is consistent with the PMBT aggregates UV–vis spectra. The absorption bands at ~ 600 nm (0–0 transition¹¹) (Figures 4 and 5) have higher intensities at high doping levels ($\text{Fe}(\text{ClO}_4)_2$ /PMBT ratios 5 \sim 20:1) than at low ones ($\text{Fe}(\text{ClO}_4)_2$ /PMBT ratios 0.1 \sim 1:1), indicating a higher structural order in the aggregates in the former case, although the chiral ordering is decreased. It is also noted that in the absorption spectrum of PMBT with added $\text{Fe}(\text{ClO}_4)_3$ (Figure 2, blue line), the band at ~ 800 nm has less intensity, whereas the one in the near-IR region is more intense than the respective bands obtained by addition of $\text{Fe}(\text{ClO}_4)_2$ at an $\text{Fe}(\text{ClO}_4)_2$ /PMBT ratio of 20:1 (Figure 3), indicating the formation of bipolaron state and an even higher doping level¹¹ by $\text{Fe}(\text{ClO}_4)_3$. At such high doping levels, aggregation does not lead to PMBT dedoped completely (Figure 1, left blue line). In this case, the minimal chiral ordering in the aggregates could be caused by the disordering of the polymer chains owing to steric hindrance arising from strong association of some metal salt ions with the polymer chains, resulting in retention of the former during aggregation.

To further investigate the $\text{Fe}(\text{ClO}_4)_2$ doping-dedoping processes of PMBT, time-dependent CD and absorption spectra before and after aggregation were recorded. It is noted that the doping state formed was stable (no change within 2 days) at the lower doping levels ($\text{Fe}(\text{ClO}_4)_2$ /PMBT ≤ 1), whereas at the higher doping levels ($\text{Fe}(\text{ClO}_4)_2$ /PMBT ≥ 5), precipitation of the doped polymer occurred overnight, resulting in the disappearance of the absorption bands (spectra not shown). The subsequent dedoping process could not proceed, indicating that the driving force resulting from the addition of a poor solvent is inadequate to expel the metal ion from the polymer in the solid state. Time-dependent CD and UV–vis spectra of PMBT aggregates (Process A) with and without the addition of $\text{Fe}(\text{ClO}_4)_2$ were also recorded (Figure 6). The absorbance at negative maxima in the UV–vis spectra of PMBT aggregates without added metal salts showed a plateau at the early stage of aggregation, while that with the addition of $\text{Fe}(\text{ClO}_4)_2$ at the ratio of 1:1 decreased linearly, indicating that the aggregate in the former case is more stable. This result could be explained on the basis that the presence of $\text{Fe}(\text{ClO}_4)_2$ increases the solvent polarity, leading to faster aggregation. The formation of large particles resulted in the decrease in absorbance due to light-scattering. Minimal changes in g_{abs} values were observed in both cases (Figure 6), indicating a random aggregation between polymer chains and almost identical chirality in the aggregates,

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(12) Bound metal salt ions may shield the polymer, preventing other ions from approaching, resulting in apparent saturation of doping level.

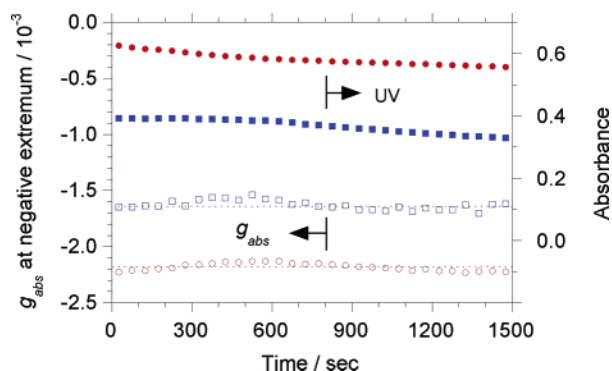


Figure 6. Time-dependent CD and UV–vis spectral analyses of PMBT aggregates (Process A) (blue, without metal salt; red, with the addition of $\text{Fe}(\text{ClO}_4)_2$ at the ratio of 1:1) at 20 °C.

consistent with a fast aggregation step at the initial stage due to the fast addition of poor solvent, even though PMBT has a broad molecular weight distribution ($M_w/M_n = 2.65$).

Conclusion

We have demonstrated a novel doping effect on chiral ordering in an aggregated conjugated polymer, in which (1)

doping prior to aggregation is a prerequisite for affecting the chiral ordering in the aggregates; (2) the doping level is the decisive factor in determining whether the g_{abs} is increased or diminished. To achieve maximal chiral ordering, doping driven by polymer–metal salt interactions and dedoping driven by aggregate formation must be balanced, the doping-produced planar polymer backbones facilitating aggregation, but with the efficient chiral side chain interactions still maintained to induce main chain chirality. This phenomenon provides a new basis to control chiral arrangement in conjugated polymer aggregates, relying solely on doping, and thus avoiding tedious modification of side chain or main chain structures.

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Supporting Information Available: CD and UV–vis spectral analyses of polymer PMBT aggregates with the addition of metal salts. This material is available free of charge via the Internet at <http://www.acs.org>.

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