

Expression of Supramolecular Chirality in Block Copoly(thiophene)s

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Abstract: Three block copolymers, **P3AT(*S*^{*})-*b*-P3AOT**, **P3AT(*R*^{*})-*b*-P3AOT(*S*^{*})** and **P3AT(*S*^{*})-*b*-P3AOT(*S*^{*})**, composed of an alkyl- and an alkoxy- substituted poly(thiophene) block, were synthesized using the living chain-growth polymerization of poly(3-alkylthiophene)s. One or both of the blocks are equipped with a chiral side-chain. The formation of the block copolymers was confirmed by GPC and ¹H NMR experiments. UV-vis, circular dichroism and emission spectroscopy were used to study the conformational and supramolecular behavior of these block copolymers in solution. This revealed that the block aggregating first upon addition of nonsolvent, has a major influence on the stacking and the chiroptical behavior of the other block.

Keywords: Conjugated block copolymers, chirality, self-assembly, supramolecular chemistry.

Introduction

Conjugated block copolymers have attracted a lot of attention in recent years. Especially rod-coil block copolymers, in which one of the blocks is a conjugated polymer, have been extensively studied.¹ However, reports on block copolymers composed of two different conjugated blocks, are rather limited.² Nevertheless these materials could lead to new promising applications, in *e.g.* solar cells. In this respect, an efficient supramolecular organization of the block copolymer is of tremendous importance, since the performance of these devices critically depends on this organization.

The supramolecular structure of a broad variety of conjugated (homo)polymers has already been investigated in detail. Lowering the solvent quality promotes π -stacking of the conjugated polymer, which can occur either intra- or intermolecularly. In the case of intramolecular π -stacking a regular macromolecular structure, for example a helix, can be formed; while in the latter case, a supramolecular, lamellar structure is formed. In this respect a distinction can be made between polymers with branched and linear side-chains. If a polymer is substituted with linear side-chains, the different polymer strands have the possibility to stack face-to-face on top of each other, giving rise to an optimal π -stacking. Polymer chains with asymmetrically branched (chiral) side-chains, cannot stack in a parallel way with respect to each other due to the sterical hindrance induced by the branching. These polymers stack in a helical way in which each polymer chain is slightly rotated towards the previous one. In this case the π -stacking is not optimal, but the system is in its lowest energy.

Circular dichroism (CD) spectroscopy has proven to be a very powerful tool to study the supramolecular and macromolecular structure of chiral conjugated polymers.³⁻¹¹ Chirality can give rise to (monosignate) Cotton effects located in the absorption band of the corresponding polymer. If, however, the chirally oriented transition dipole moments interact with each other, bisignate Cotton effects are observed. As a consequence, a chiral stacking of conjugated polymer chains, of which the transition dipole moments are oriented along the polymer backbone, typically results in bisignate Cotton effects.

In a previous manuscript, we reported the synthesis of a block copolymer, composed of an achiral poly(3-hexylthiophene) and a chiral poly[3-(3,7-dimethyloctyloxy)thiophene] and demonstrated a transfer of supramolecular chirality from the chiral to the achiral block.¹² This clearly shows that the chiral poly(3-alkoxythiophene) (P3AOT) block influences the supramolecular organization of the achiral poly(3-alkylthiophene) (P3AT) block.

This manuscript investigates whether the principles which govern the macromolecular and supramolecular behavior of conjugated (homo)polymers can also be used to explain the behavior of conjugated block copolymers. It will be investigated whether more general conclusions can be drawn concerning the aggregation behavior of conjugated block copolymers. In particular, the influence of both blocks on each other will be studied by using UV-vis and CD spectroscopy.

Therefore the polymers **P3AT(S*)-b-P3AOT**, **P3AT(R*)-b-P3AOT(S*)** and **P3AT(S*)-b-P3AOT(S*)** are synthesized and their properties are investigated. All the block copolymers are composed of an alkoxy and an alkyl substituted poly(thiophene) block, with chirality incorporated in one or both of the side-chains of these blocks. Block copolymer **P3AT(S*)-b-P3AOT** has a chiral alkyl-substituted block and an achiral alkoxy-substituted block, which is exactly the opposite as the already published block copolymer **P3AT-b-P3AOT(S*)** (Figure 1). Block copolymers **P3AT(R*)-b-P3AOT(S*)** and **P3AT(S*)-b-P3AOT(S*)** have two chirally substituted blocks, but in this case the enantiomer in the P3AT block is varied. All these block copolymers will be compared with each other in order to make more general conclusions concerning the influence of the blocks on each other.

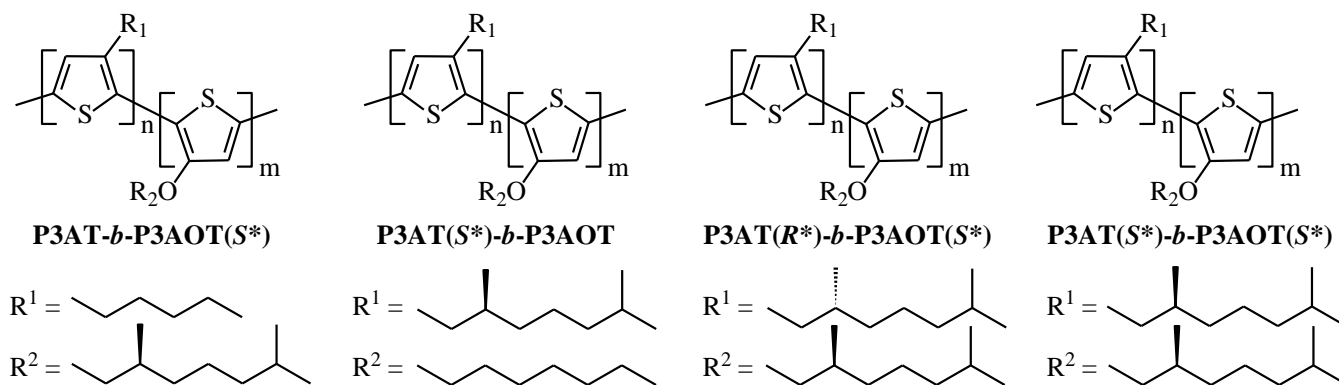


Figure 1. Structure of the block copolymers.

Experimental Section

Reagents and Instrumentation

All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka and Avocado. Reagent grade solvents were dried and purified by distillation.

Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ^1H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. UV-vis and CD spectra were recorded with a Varian Cary 400 and a JASCO 62 DS apparatus respectively. The fluorescence measurements were done on a PTI Photon Technology International apparatus. The samples were excited near the absorption wavelength. The optical rotations were measured with a polAAR 20 apparatus; the solvent used and concentration (in g/100 mL) are given in parenthesis.

2-Bromo-3-((*S*)-3,7-dimethyloctyl)thiophene ((*S*)-**1**)^{3b}, 2-bromo-3-octyloxythiophene (**3**)¹³ and 2-bromo-3-((*S*)-3,7-dimethyloctyloxy)thiophene ((*S*)-**3**)⁴ were synthesized according to literature procedures. 2-Bromo-3-((*R*)-3,7-dimethyloctyl)thiophene ((*R*)-**1**) was synthesized completely analogously to 2-bromo-3-((*S*)-3,7-dimethyloctyl)thiophene ((*S*)-**1**).

Monomer synthesis

Synthesis of (+)-2-bromo-5-iodo-3-((*S*)-3,7-dimethyloctyl)thiophene ((*S*)-2**)**

A solution of (*S*)-**1** (4.00 mmol, 1.23 g) in CH_2Cl_2 (10 mL) was cooled to 0 °C and iodine (0.903 mmol, 0.229 g) and iodobenzene diacetate (0.978 mmol, 0.314 g) were added. After stirring for 4 h at room temperature, an aqueous NaHSO_3 -solution was added and the mixture was extracted with diethylether and washed with a NaHCO_3 -solution. The organic layer was dried over MgSO_4 and the solvent and iodobenzene were removed in vacuo. The crude product was purified by column chromatography (silica gel, eluent: hexane) and isolated as a colorless oil.

Yield: 1.53 g (89%).

^1H NMR (CDCl_3): $\delta = 6.96$ (s, 1H), 2.52 (m, 2H), 1.52 (m, 1H), 1.28 (m, 6H), 1.14 (m, 3H), 0.91 (d, 3H), 0.87 (d, 6H).

^{13}C NMR (CDCl_3): $\delta = 144.5, 138.0, 111.6, 71.1, 39.4, 37.0, 36.9, 32.5, 28.1, 26.9, 24.7, 22.8, 22.7, 19.6$.

MS: $m/z = 429$ (M^+).

$[\alpha]_{\text{D}}^{20^\circ\text{C}} = +2.54 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL}$ ($c = 3.2$ in CHCl_3).

Synthesis of (-)-2-bromo-5-iodo-3-((*R*)-3,7-dimethyloctyl)thiophene ((*R*)-2)

The same procedure as for (*S*)-2 was followed, using (*R*)-1 (1.63 mmol, 0.495 g).

Yield: 0.584 g (83%).

$[\alpha]_{\text{D}}^{20^\circ\text{C}} = -2.54 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL}$ ($c = 3.1$ in CHCl_3).

Polymer synthesis

Synthesis of poly(3-((*S*)-3,7-dimethyloctyl)thiophene)-*b*-poly(3-octyloxythiophene) (P3AT(*S**)-*b*-P3AOT)

A solution of (*S*)-2 (1.00 mmol, 0.429 g) in dry THF (5 mL) was cooled to 0 °C and *i*PrMgCl (1.00 mmol, 0.5 mL, 2 M in THF) was added. The reaction mixture was stirred for 1 h at 0 °C and then transferred to a suspension of Ni(dppp)Cl₂ (66.7 μmol, 35.2 mg) in dry THF (6.5 mL). The volume of the polymer solution was adjusted to exactly 12 mL and after stirring for 2 h, this solution was divided in two parts. The first part (4.8 mL) was quenched with HCl (1 M in methanol), precipitated in methanol and filtered off. To the other part (7.2 mL) the second monomer (see below) was added and the polymerization mixture was allowed to react overnight. The polymer solution was then poured into methanol and the formed precipitate was filtered off and subsequently extracted with acetone, pentane and THF. The THF-fraction was precipitated in methanol, filtered off and dried.

For the preparation of the second monomer, freshly prepared lithium diisopropylamide (2.70 mmol in THF (2.5 mL)) was added to a solution of **3** (1.80 mmol, 0.524 g) in dry THF (5 mL) at -78 °C. After stirring for 30 min at room temperature, the solution was added to a suspension of MgBr₂ (2.70 mmol, 0.497 g) in dry THF (6 mL) and stirred for another 30 min.

m (THF-fraction) = 30.7 mg.

$$[\alpha]_{\text{D}}^{20^{\circ}\text{C}} = 7,800 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL} \text{ (} c = 6.4 \cdot 10^{-4} \text{ in CHCl}_3\text{)}.$$

Synthesis of poly(3-((*R*)-3,7-dimethyloctyl)thiophene)-*b*-poly(3-((*S*)-3,7-dimethyloctyloxy)thiophene) (P3AT(*R*^{*})-*b*-P3AOT(*S*^{*}))

The same procedure as for P3AT(*S*^{*})-*b*-P3AOT was followed, using (*R*)-2 (1.00 mmol, 0.429 g) and (*S*)-3 (1.80 mmol, 0.574 g).

m (THF-fraction) = 43.6 mg.

$$[\alpha]_{\text{D}}^{20^{\circ}\text{C}} = 53,000 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL} \text{ (} c = 1.1 \cdot 10^{-3} \text{ in CHCl}_3\text{)}.$$

Synthesis of poly(3-((*S*)-3,7-dimethyloctyl)thiophene)-*b*-poly(3-((*S*)-3,7-dimethyloctyloxy)thiophene) (P3AT(*S*^{*})-*b*-P3AOT(*S*^{*}))

The same procedure as for P3AT(*S*^{*})-*b*-P3AOT was followed, using (*S*)-2 (1.00 mmol, 0.429 g) and (*S*)-3 (1.80 mmol, 0.574 g).

m (THF-fraction) = 20.3 mg.

$$[\alpha]_{\text{D}}^{20^{\circ}\text{C}} = 18,000 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{g}^{-1}\cdot\text{mL} \text{ (} c = 7.6 \cdot 10^{-4} \text{ in CHCl}_3\text{)}.$$

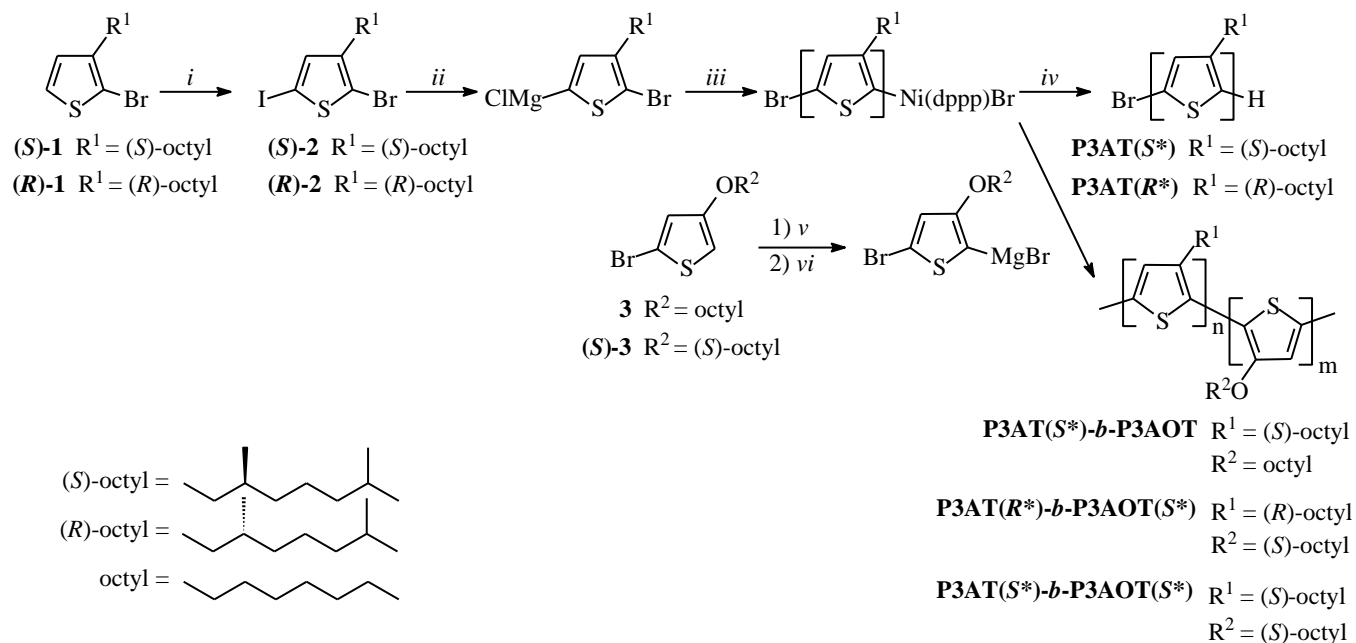
Results and Discussion

Polymer Synthesis

Since regioregularity is of tremendous importance for a good lamellar supramolecular organization, the polymers were prepared by polymerization methodologies which result in regioregular, HT-coupled poly(thiophene)s. For this purpose, the appropriate alkyl¹⁴ and alkoxy-substituted⁴ thiophene derivatives were prepared. This was accomplished by making use of an iodo-bromo-substituted alkythiophene ((*S*)-2 or (*R*)-2) and a 2-bromo-4-alkoxythiophene (**3** or (*S*)-3), which are prepared by reported methods.

The block copolymers were synthesized by the sequential addition of the two different monomers, exploiting the living character of the Ni(dppp)Cl₂-mediated polymerization of P3ATs. Since the polymerization of P3ATs proceeds by a living chain-growth mechanism¹⁵, which is probably not the case for P3AOTs¹⁶, the alkyl-substituted monomer was polymerized first (Scheme 1). After one hour,

the polymerization mixture was divided in two parts: one was quenched with HCl and precipitated in methanol, while to the second part the alkoxy-substituted monomer was added. This mixture was allowed to react overnight and subsequently precipitated in MeOH. To remove possible dead or unreacted P3AT chains, the sample was washed with acetone and pentane and finally extracted with THF. This THF-fraction was precipitated in methanol and dried in vacuo.



Scheme 1. Synthesis of the block copolymers. Conditions: *i*) I_2 , $PhI(OAc)_2$; *ii*) $iPrMgCl$; *iii*) $Ni(dppp)Cl_2$; *iv*) HCl ; *v*) LDA ; *vi*) $MgBr_2$.

GPC and NMR analysis

Both the quenched P3ATs and the block copolymers were characterized by gel permeation chromatography (GPC). The degree of polymerization of the first block of all the block copolymers could be estimated at 9-10. The appearance of only one, unimodal peak in the chromatogram of the block copolymers at a lower elution volume in comparison with the first block confirms the successful formation of the block copolymer (Supporting Information Figure S4-6). A second proof for the formation of the block copolymer was delivered by recording the GPC chromatogram at 600 nm - a wavelength corresponding to the absorption maximum of P3AOT but at which P3AT hardly absorbs. The GPC profiles measured at 254 and 600 nm are situated at the same elution volume, confirming that not a mixture of the homopolymers but a block copolymer was formed.

The ^1H NMR spectrum shows signals arising from both the alkyl- and alkoxy-substituted blocks (Supporting Information Figure S1-3). From the relative integration of the signals it could be calculated that the alkoxy-substituted blocks have a degree of polymerization of around 14-16. No traces of regioirregularity are observed in the P3AT nor in the P3AOT block, as the $\alpha\text{-CH}_2$'s show a rather clean singlet. In principle, the aromatic protons would be more suited for this purpose, but the overlap of both signals impedes such estimation.

These combined GPC and ^1H NMR data show that all three synthesized block copolymers and the previously prepared block copolymer (**P3AT-*b*-P3AOT(S*)**) have more or less the same molecular weight and the same ratio of P3AT/P3AOT. As a consequence, their similar molecular structure allows for a comparison of their supramolecular behavior.

UV-vis and CD analysis

Next, the conformational and supramolecular behavior of the block copolymers was studied by gradual addition of methanol to a chloroform solution using UV-vis and CD spectroscopy (Figure 2). For comparison also the spectra of **P3AT-*b*-P3AOT(S*)** are incorporated.¹² In a good solvent, two absorption bands can be observed for all block copolymers: one near 450 nm and one near 575 nm, corresponding to the $\pi - \pi^*$ transition of the more twisted P3AT and the rather planar P3AOT block, respectively. The fact that the spectra are no superposition of the respective homopolymers points at a mutual electronic influence of the blocks, which can be correlated with the fact that they are directly attached to each other. Upon decreasing the solvent quality, the P3AOT block - the least soluble block - starts to stack first. If **P3AT-*b*-P3AOT(S*)** is taken as an example, this is expressed by the small red-shift in the UV-vis spectra and the occurrence of Cotton effects. The bisignate nature of the CD signal with a zero-crossing in the center of the absorption band of the P3AOT block reveals that the polymer strands stack in a chiral way. Further addition of nonsolvent promotes also planarization and stacking of the P3AT chains, which is clearly expressed in the significant red-shift in the UV-vis spectra. Interestingly, also the CD spectrum changes: the intensity triples and the zero-crossing displays an important blue-shift. In fact, the CD spectra are composed of two bisignate Cotton effects originating

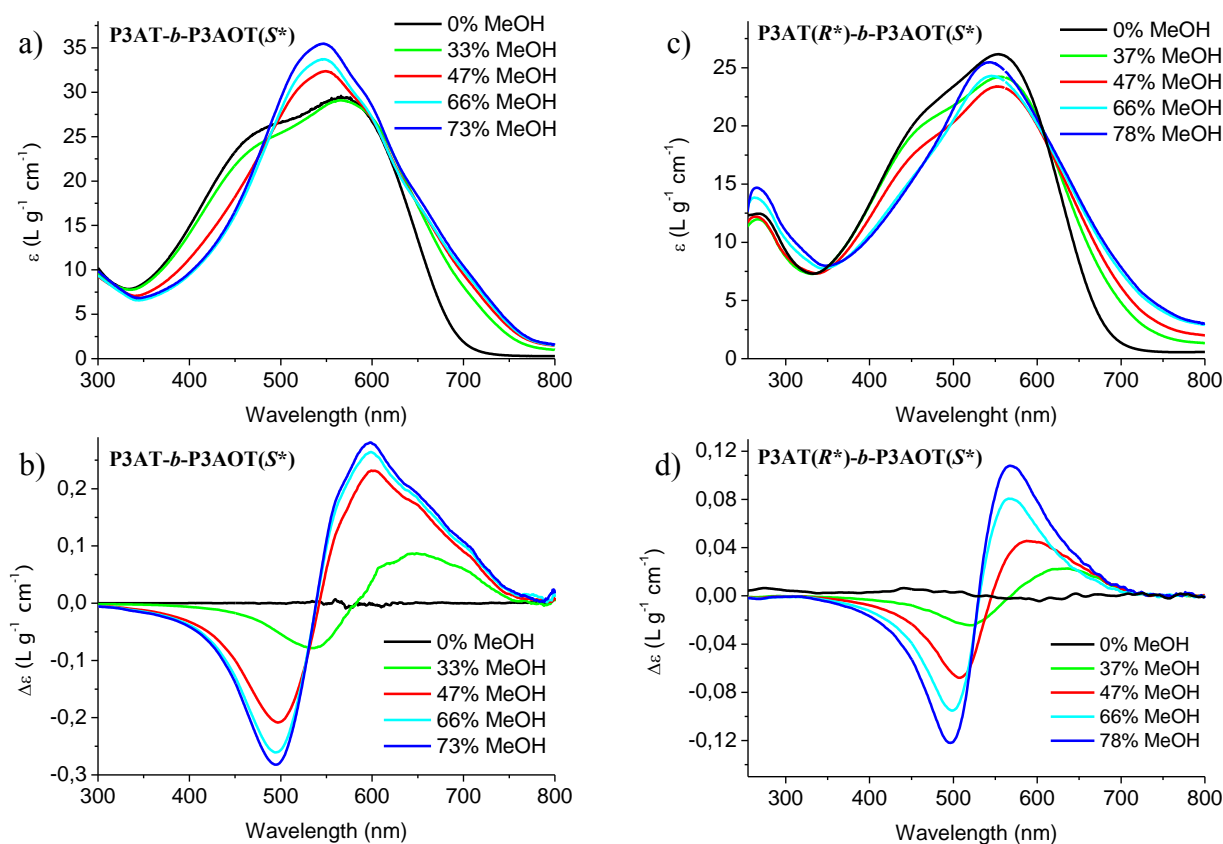
from the P3AOT and P3AT block. This reveals that the P3AT polymer chains, although being equipped with achiral side-chains, stack in a chiral way, in which the polymer chains adopt a rotated and not a parallel orientation towards each other. This contrasts with the supramolecular organization of the achiral P3AT homopolymer, in which the polymer chains are parallel stacked with respect to each other, maximizing the π -interactions. The behavior of the block copolymer can be understood taking into account the fact that the P3AT chains are directly connected to the P3AOT block: the P3AOT block dictates its chiral, helical lamellar supramolecular organization to the P3AT block, transferring its chirality. The as-formed supramolecular organization of the P3AT block is less stabilized than in the homopolymer due to the less efficient π -interactions, but the formation of this structure in the block copolymer is on the other hand not impeded by possible steric hindrance from the (linear) side-chains. Note that the sign of the bisignate Cotton effect – positive – is similar to that of the P3AOT homopolymer¹², showing that both blocks adopt a right-handed helical structure.

A similar behavior is observed for **P3AT(*R**)-*b*-P3AOT(*S**)** and **P3AT(*S**)-*b*-P3AOT(*S**)**: addition of methanol initially invokes the appearance of bisignate Cotton effects in the P3AOT transition, while further addition of nonsolvent results in spectra composed of bisignate Cotton effects in both blocks. Again, it can be concluded that both blocks chirally stack into a right-handed helical supramolecular structure. Nevertheless, some difference in intensity of the Cotton effects can be observed. **P3AT-*b*-P3AOT(*S**)**, in which the linear hexyl group poses no restriction on the stacking of the P3AT chains, shows the largest effects ($|g_{\text{abs}}| = 1 \times 10^{-2}$; $g_{\text{abs}} = \Delta\epsilon/\epsilon$), while **P3AT(*R**)-*b*-P3AOT(*S**)** ($|g_{\text{abs}}| = 6 \times 10^{-3}$) and **P3AT(*S**)-*b*-P3AOT(*S**)** ($|g_{\text{abs}}| = 4 \times 10^{-3}$) display smaller effects. This can be correlated with the Sol-Rel, Sed-Rod alternation rules, which have already been reported for chiral P3ATs by Langeveld-Voss *et al.*¹⁷ These rules predict that in stacks of poly(thiophene)s in which the (alkyl) substituent adopts an all-*trans* conformation, a change of the enantiomer (*S* or *R*) or a shift of the position of the asymmetric C-atom by one atom reverses the sense of the helical supramolecular structure (left- or right-handed) and therefore changes the sign of the CD spectrum. Applied on the block copolymers, the linear hexyl group in **P3AT-*b*-P3AOT(*S**)** poses no restriction to the steric stacking of the P3AT chains: it

can be assumed that more or less the same supramolecular organization is adopted in both the P3AT and P3AOT block, *i.e.* right-handed and rotated by approximately the same angle. In contrast, the asymmetric C-atom in the P3AT block in **P3AT(S*)-b-P3AOT(S*)** is shifted one position (due to the absence of the O-atom) compared with the P3AOT block. As a consequence, the substituent in both blocks promotes different helical senses. Applied on **P3AT(S*)-b-P3AOT(S*)**, the P3AT block is forced to adopt a helical supramolecular stacking of the same handedness as the P3AOT block, as this block is the first to aggregate, but the stacking (in the P3AT block) is far from as efficient as in **P3AT-b-P3AOT(S*)**, which is reflected in the smaller intensities of the Cotton effects. In **P3AT(R*)-b-P3AOT(S*)**, finally, both homopolymers form helical stacks of the same handedness, as the change of configuration (*R* versus *S*) is compensated by the shift of the position of the asymmetric C-atom by one atom. Therefore, the chiral stacking of the P3AT and P3AOT blocks in **P3AT(R*)-b-P3AOT(S*)** matches better than in **P3AT(S*)-b-P3AOT(S*)**, which is expressed in the increased intensity of the Cotton effects. Nevertheless, although both blocks in **P3AT(R*)-b-P3AOT(S*)** form helices of the same handedness, the exact helical structure with the lowest energy can be assumed to be different. This explains why **P3AT(R*)-b-P3AOT(S*)** shows smaller Cotton effects than **P3AT-b-P3AOT(S*)**: the linear hexyl chain in **P3AT-b-P3AOT(S*)** poses no steric restriction at all to the helical stacking, while the branched alkyl chain in **P3AT(R*)-b-P3AOT(S*)** does.

If the same experiment is repeated for **P3AT(S*)-b-P3AOT**, a completely different outcome is found. In a good solvent the UV-vis spectrum is still composed of two bands, none of which are displaying chirality, and addition of nonsolvent promotes aggregation of the P3AOT block, which is visualized in the UV-vis spectrum. Naturally, since the P3AOT block is substituted with achiral (octyloxy) chains, no (bisignate) Cotton effects are observed because the P3AOT chains stack in a parallel fashion, maximizing the π -interactions. However, upon further addition of nonsolvent, the conformation of the P3AT chains drastically changes, which can be concluded from the red-shift in the UV-vis spectra, but the shape of the spectrum at the highest methanol concentration slightly contrasts with that of the other block copolymers and the formation of this spectrum also requires a much higher methanol content.

Moreover, the corresponding CD spectra show a *monosignate* Cotton effect. Clearly, the addition of nonsolvent to a **P3AT(S*)-b-P3AOT** solution does not result in chiral aggregation of both blocks. Instead, the behavior can be explained by assuming that the P3AOT chains indeed stack, but in a parallel, achiral fashion. In contrast to the previous block copolymers, the P3AOT cannot impose its supramolecular organization on the P3AT block, since parallel stacking of the P3AT chains is sterically prohibited by the (chirally) branched alkyl side-chains. Therefore, further addition of methanol does not result in (chiral) aggregation of the P3AT chains, which would result in bisignate Cotton effects, but instead a chiral, probably helical (i.e. twisted ribbon) conformation is formed.



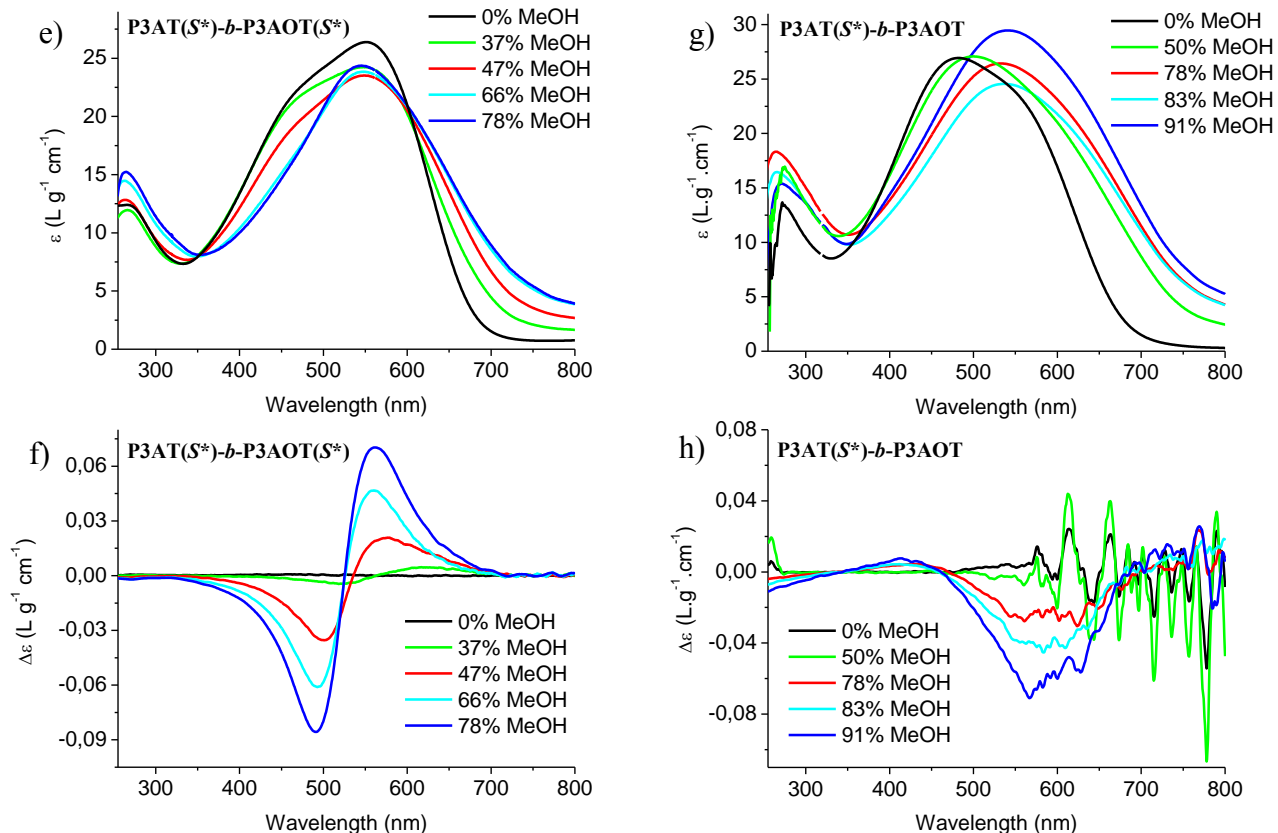


Figure 2. Influence of the addition of methanol to a chloroform solution of the block copolymers. (a) UV-vis and (b) CD spectra of **P3AT-*b*-P3AOT(*S*^{*})** ($c_{\text{start}} = 0.088$ g/L); (c) UV-vis and (d) CD spectra of **P3AT(*R*^{*})-*b*-P3AOT(*S*^{*})** ($c_{\text{start}} = 0.102$ g/L); (e) UV-vis and (f) CD spectra of **P3AT(*S*^{*})-*b*-P3AOT(*S*^{*})** ($c_{\text{start}} = 0.092$ g/L); (g) UV-vis and (h) CD spectra of **P3AT(*S*^{*})-*b*-P3AOT** ($c_{\text{start}} = 0.192$ g/L).

Emission spectroscopy

The emission spectra of all block copolymers in different solvent mixtures are displayed in Figure 3. The polymers were excited at 460 and 550 nm, corresponding to the absorption of the P3AT and P3AOT block, respectively. Only excitation at 460 nm results in emission, which is moreover situated in the P3AT emission region, but of a somewhat lower intensity compared to the P3AT homopolymer (Supporting Information Figure S7 and S9). If these findings are combined with the fact that the P3AOT homopolymer relaxes non-radiatively (Supporting Information Figure S8), it can be concluded that excitation of the P3AOT block in the copolymers results in non-radiative decay, while excitation of the P3AT block partly results in a radiative decay and partly in energy transfer to the P3AOT block, which

relaxes non-radiatively. This partial energy transfer to the P3AOT block, which serves as a trap, accounts for the lower P3AT emission in the block copolymers.

If the nonsolvent content is increased (chloroform/methanol (1/1)), in which conditions the P3AOT chains aggregate but the P3AT chains are still unaffected,¹⁸ a more or less equal emission intensity is observed which originates from the coiled P3AT chains. Unfortunately, since P3AOT decays non-radiatively, emission spectroscopy cannot provide direct information on the P3AOT block.

A further decrease of the solvent quality (chloroform/methanol (1/9)) - conditions in which also the P3AT block undergoes macro/supramolecular changes -¹⁸ results in an almost complete quenching of the fluorescence. The remaining emission still exclusively originates from the P3AT block. Moreover, the shape and position of this emission band reveals that it originates from residual coiled polymer chains with the same conformation as in good solvent and not from aggregated P3AT chains.

The fact that a similar decrease of the emission is observed for all block copolymers demonstrates that in all cases the P3AOT block serves as a trap. In this respect, the quenching of the P3AT emission can be correlated to the conformation of the two thiophenes linking the P3AT and P3AOT block. In fact, this corresponds to a head-to-head (HH) coupling, composed of an alkyl and alkoxy substituent. In case of HH-coupled dialkylthiophenes, steric hindrance is such that the two thiophenes are severely twisted in all conditions, disrupting the conjugation,¹⁹ while for HH-couplings in dialkoxythiophenes a rather planar conformation is adopted even in conditions in which stacking is not promoted.²⁰ As a consequence, a HH-coupling composed of an alkyl- and an alkoxy-substituted thiophene, as is the case in the linkage of the two polymer blocks in these copolymers, might be expected to show an intermediate behavior: a twisted conformation, disrupting the conjugation in a good solvent, and a more planar conformation in conditions which evoke planarization. Therefore, this linkage serves as a molecular valve for the conjugation between both blocks, which can be tuned by the solvent conditions. This hypothesis explains both the absorption and emission properties of the block copolymers. In a good solvent, the conformation around the two thiophenes linking the two blocks is rather twisted, resulting in a poor, but not completely disrupted conjugation. As a consequence, a small mutual electronic influence

of both blocks can be observed in the UV-vis spectra and the P3AT emission is only partially quenched by the P3AOT trap. As the solvent quality is decreased, the conformation around the two thiophenes is planarized, increasing the conjugation between both blocks. The UV-vis spectra of the block copolymers differ significantly from the constituting homopolymers and the emission is almost completely quenched.

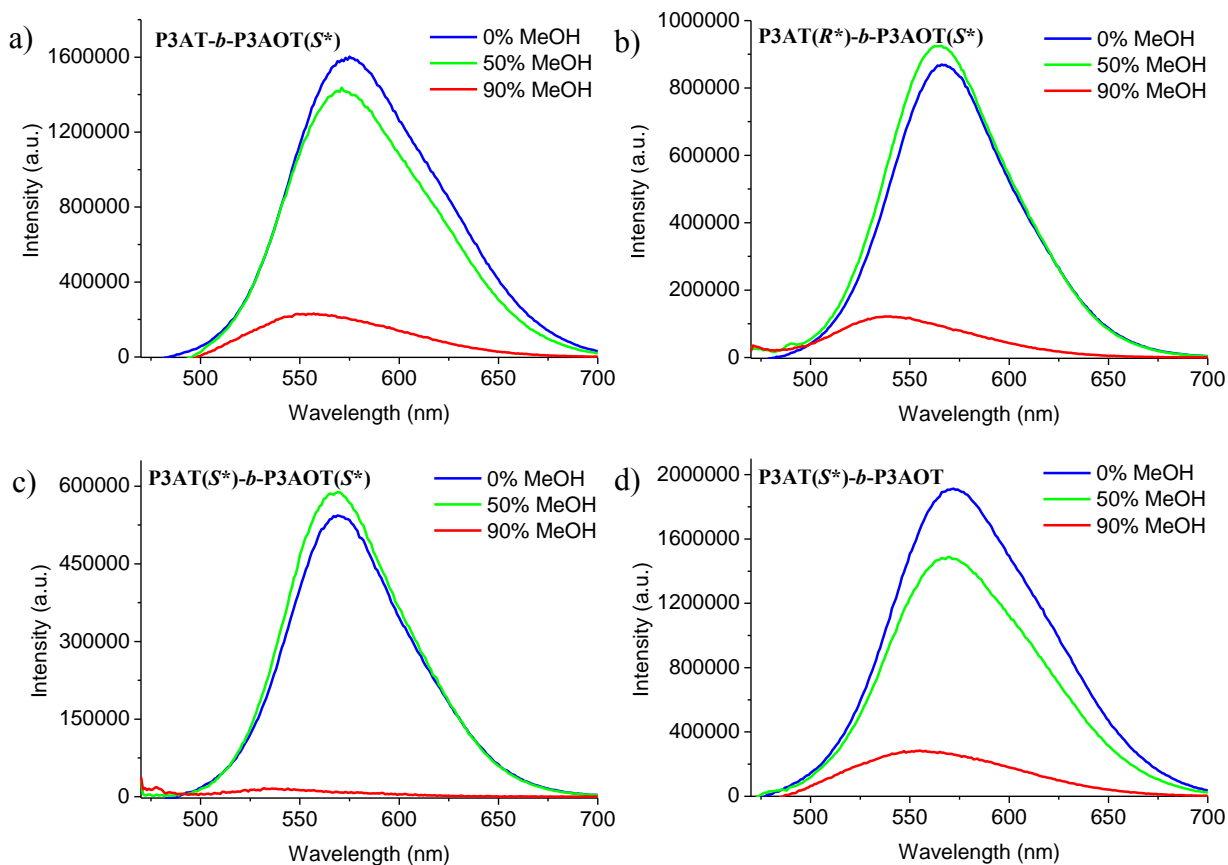


Figure 3. Influence of the solvent quality on the emission ($\lambda_{\text{ex}} = 460 \text{ nm}$) of the block copolymers (a) **P3AT-*b*-P3AOT(*S*^{*})** ($c = 3.7 \text{ mg/L}$), (b) **P3AT(*R*^{*})-*b*-P3AOT(*S*^{*})** ($c = 4.1 \text{ mg/L}$), (c) **P3AT(*S*^{*})-*b*-P3AOT(*S*^{*})** ($c = 2.8 \text{ mg/L}$) and (d) **P3AT(*S*^{*})-*b*-P3AOT** ($c = 3.2 \text{ mg/L}$). All intensities were corrected for the absorbance.

Conclusion

In conclusion, three fully conjugated block copolymers, **P3AT(*S*^{*})-*b*-P3AOT**, **P3AT(*R*^{*})-*b*-P3AOT(*S*^{*})** and **P3AT(*S*^{*})-*b*-P3AOT(*S*^{*})**, were synthesized exploiting the living chain-growth polymerization of P3ATs. The aggregation behavior and the supramolecular structure of these polymers

and the already synthesized **P3AT-*b*-P3AOT(*S*^{*})** were studied by UV-vis, CD and emission spectroscopy. **P3AT-*b*-P3AOT(*S*^{*})**, **P3AT(*R*^{*})-*b*-P3AOT(*S*^{*})** and **P3AT(*S*^{*})-*b*-P3AOT(*S*^{*})** all display the same supramolecular behavior. Lowering the solvent quality, results in chiral aggregation of the P3AOT block, being the least soluble of the two blocks. Upon further addition of nonsolvent, also the P3AT block aggregates, hereby adopting the same helical supramolecular organization as the P3AOT block, despite the nature of the substituent. Although the P3AOT block dictates its helical supramolecular structure to the P3AT block, the substituent on P3AT can complicate the stacking, as expressed by the intensity of the CD spectra. The chiroptical behavior of **P3AT(*S*^{*})-*b*-P3AOT** significantly contrasts with that of the previous polymers. The achiral P3AOT block aggregates in an achiral way. The sterical hindrance resulting from the branched substituents prevents an analogous stacking in the P3AT blend; instead the P3AT block forms a chiral, probably helical, conformation. Fluorescence experiments revealed that only the P3AT block emits. Its intensity depends on the conformation of the diade connecting the two blocks: a planar conformation allows an efficient energy transfer to the P3AOT block, which acts as a trap, quenching the fluorescence. These studies revealed that, for all the block copolymers, the block aggregating first upon addition of nonsolvent, has a major influence on the stacking and the chiroptical behavior of the other block.

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Supporting Information Available: ¹H NMR spectra, GPC spectra of all the block copolymers, emission spectra of **P3AT** and **P3AOT**, emission spectrum of **P3AT(*R*^{*})-*b*-P3AOT(*S*^{*})** at $\lambda_{\text{ex}} = 550$ nm and comparison of the UV-vis spectrum of **P3AT-*b*-P3AOT(*S*^{*})** and the constituting homopolymers. This material is available free of charge via the internet at <http://pubs.acs.org>.

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