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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 ^{1}H 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.

Introduction

Conjugated block copolymers have attracted a lot of attention in recent years. In particular, 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, for example, solar cells. In this respect, an efficient supramolecular organization of the block copolymer is of tremendous importance because 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 intermoleculary. In the case of intramolecular π-stacking, a regular macromolecular structure, for example a helix, can be formed, whereas 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 because of the sterical hindrance induced by the branching. These polymers stack in a helical way in which each polymer chain is slightly rotated toward 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, 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 that 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 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 of 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 of these block copolymers will be compared with each other to make more general conclusions concerning the influence of the blocks on each other.

Experimental Section

Reagents and Instrumentation. All reagents were purchased from Aldrich Chemical, 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. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out

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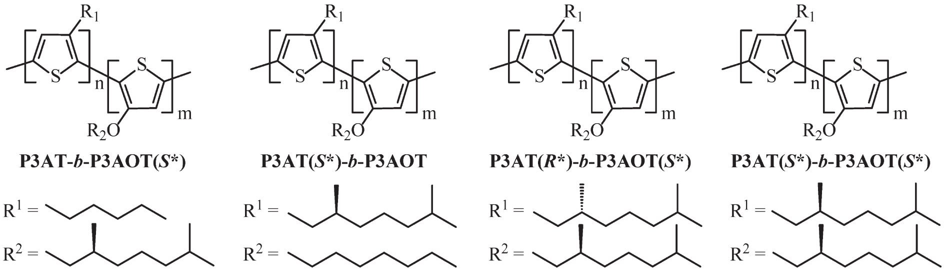


Figure 1. Structure of the block copolymers.

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 parentheses.

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%). ^{1}H NMR ($CDCl_3$, δ): 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 ($CDCl_3$, δ): 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^+). $[\alpha]_D^{20\ ^\circ C} = +2.54$ deg·dm^{-1}·g^{-1}·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 that for (***S***)**-2** was followed using (***R***)**-1** (1.63 mmol, 0.495 g). Yield: 0.584 g (83%). $[\alpha]_D^{20\ ^\circ C} = -2.54$ deg·dm^{-1}·g^{-1}·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)Cl_2 (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 in 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 $MgBr_2$ (2.70 mmol, 0.497 g) in dry THF (6 mL) and stirred for another 30 min. m (THF fraction) = 30.7 mg. $[\alpha]_D^{20\ ^\circ C} = 7800$ deg·dm^{-1}·g^{-1}·mL ($c = 6.4 \times 10^{-4}$ in $CHCl_3$).

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 that 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. $[\alpha]_D^{20\ ^\circ C} = 53{,}000$ deg·dm^{-1}·g^{-1}·mL ($c = 1.1 \times 10^{-3}$ in $CHCl_3$).

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 that 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. $[\alpha]_D^{20\ ^\circ C} = 18\,000$ deg·dm^{-1}·g^{-1}·mL ($c = 7.6 \times 10^{-4}$ in $CHCl_3$).

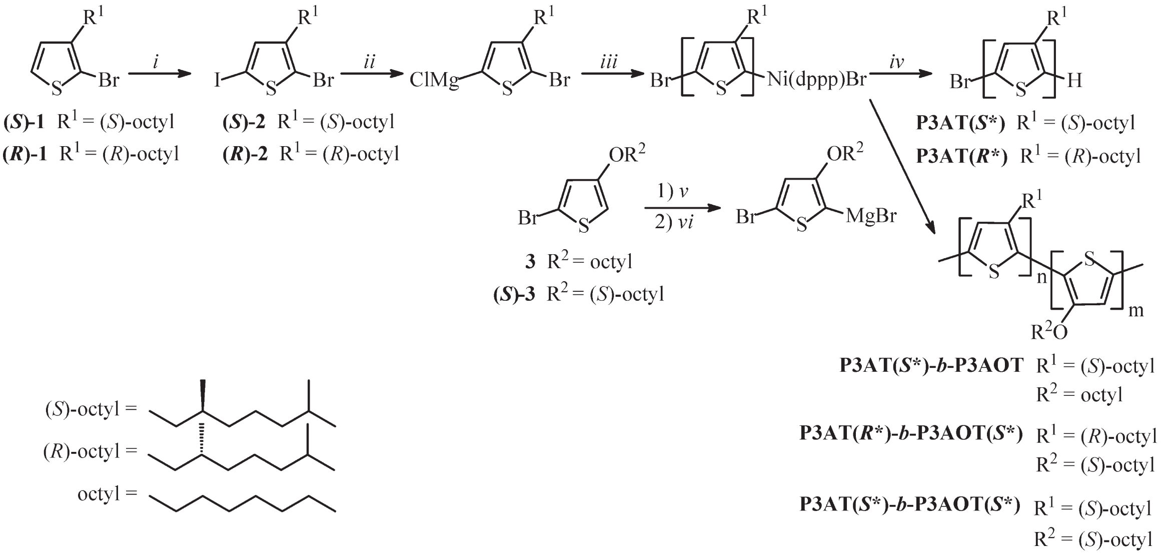
Results and Discussion

Polymer Synthesis. Because regioregularity is of tremendous importance for a good lamellar supramolecular organization, the polymers were prepared by polymerization methodologies that result in regioregular, HT-coupled poly(thiophene)s. For this purpose, the appropriate alkyl-[14] and alkoxy-substituted[4] thiophene derivatives were prepared. This was accomplished by making use of an iodo-bromo-substituted alkylthiophene ((***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)Cl_2-mediated polymerization of P3ATs. Because the polymerization of P3ATs proceeds by a living chain-growth mechanism,[15] which is probably not the case for P3AOTs,[16] the alkyl-substituted monomer was polymerized first (Scheme 1). After 1 h, the polymerization mixture was divided in two parts: one was quenched with HCl and precipitated in methanol, whereas 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.

GPC and NMR Analysis. Both the quenched P3ATs and the block copolymers were characterized by GPC. The degree of polymerization of the first block of all block copolymers could be estimated at 9 to 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 Figures S4−S6). 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.

Scheme 1. Synthesis of the Block Copolymers[a]



[a] Conditions: (i) I_2, $PhI(OAc)_2$; (ii) *i*PrMgCl; (iii) $Ni(dppp)Cl_2$; (iv) HCl; (v) LDA; (vi) $MgBr_2$.

The ^{1}H NMR spectrum shows signals arising from both the alkyl- and alkoxy-substituted blocks (Supporting Information Figures S1−S3). 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 because the α-CH_2's show a rather clean singulet. 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 ^{1}H 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, the spectra of **P3AT-*b*-P3AOT(*S**)** are also 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 and 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, the CD spectrum changes: the intensity triples and the zero-crossing also displays an important blue-shift. In fact, the CD spectra are composed of two bisignate Cotton effects originating from the P3AOT and P3AT blocks. 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 toward 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 by 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 that in the homopolymer because of the less efficient π-interactions, but the formation of this structure in the block copolymer is 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 homopolymer,[12] 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, whereas 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 ($|g_{abs}| = 1 \times 10^{-2}$; $g_{abs} = \Delta\varepsilon/\varepsilon$), whereas **P3AT(*R**)-*b*-P3AOT(*S**)** ($|g_{abs}| = 6 \times 10^{-3}$) and **P3AT(*S**)-*b*-P3AOT(*S**)** ($|g_{abs}| = 4 \times 10^{-3}$) 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,

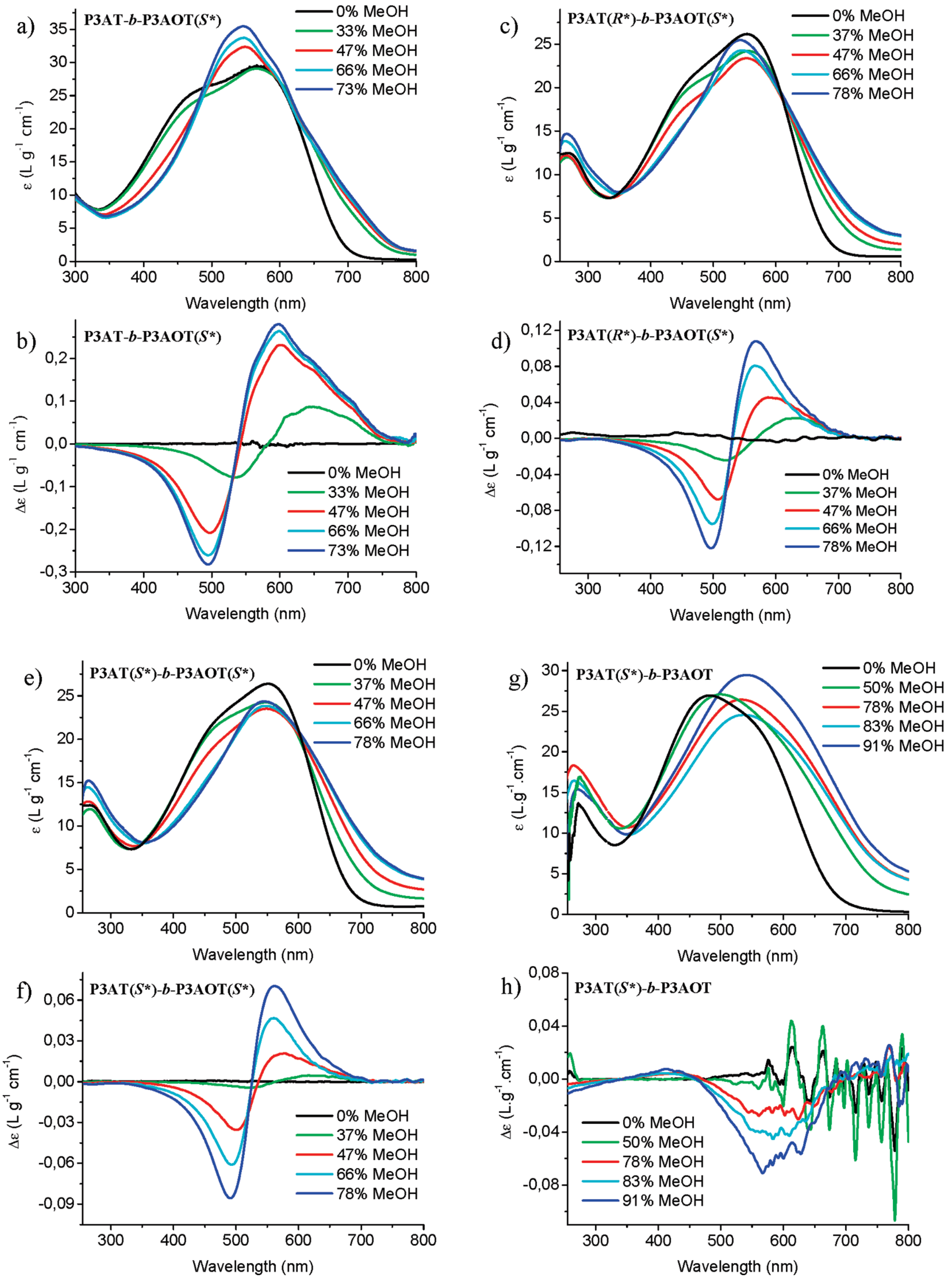


Figure 2. Influence of the addition of methanol to a chloroform solution of the block copolymers. (a) UV–vis and (b) CD spectra of **P3AT-*b*-P3AOT(*S**)** (c_{start} = 0.088 g/L); (c) UV–vis and (d) CD spectra of **P3AT(*R**)-*b*-P3AOT(*S**)** (c_{start} = 0.102 g/L); (e) UV–vis and (f) CD spectra of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

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 blocks, that is, 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 because 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

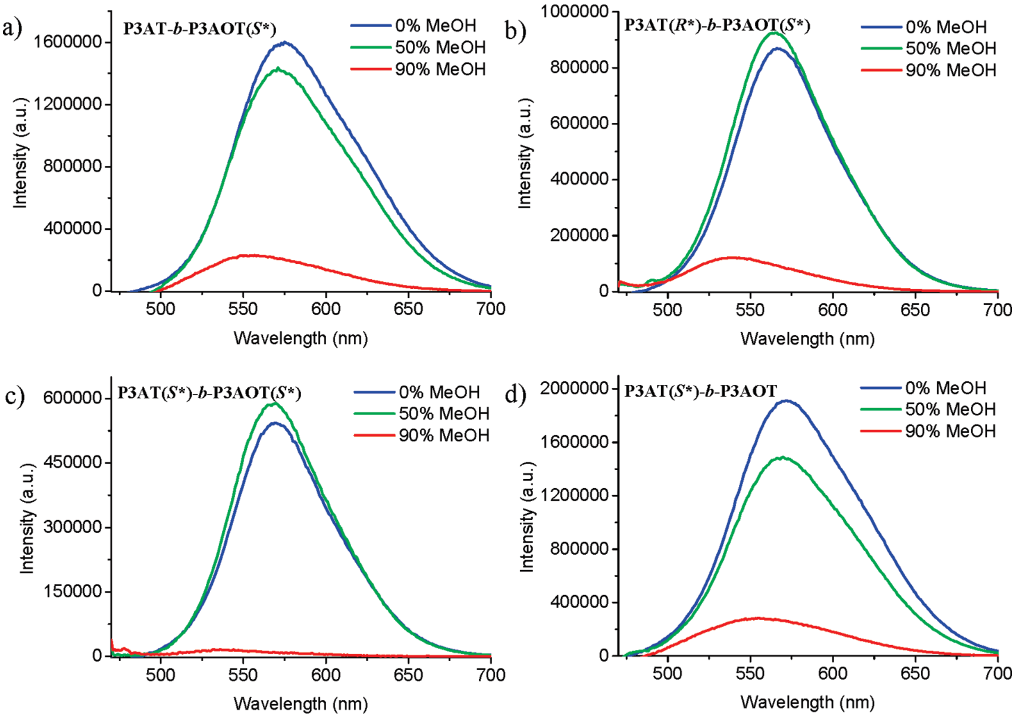


Figure 3. Influence of the solvent quality on the emission (λ_{ex} = 460 nm) of the block copolymers: (a) **P3AT-*b*-P3AOT(*S**)** (c = 3.7 mg/L), (b) **P3AT(*R**)-*b*-P3AOT(*S**)** (c = 4.1 mg/L), (c) **P3AT(*S**)-*b*-P3AOT(S*)** (c = 2.8 mg/L), and (d) **P3AT(*S**)-*b*-P3AOT** (c = 3.2 mg/L). All intensities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

the same handedness, the exact helical structure with the lowest energy can 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, whereas the branched alkyl chain in **P3AT(*R**)-*b*-P3AOT(*S**)** does.

If the same experiment is repeated for **P3AT(*S**)-*b*-P3AOT**, then 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, because 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 with the previous block copolymers, the P3AOT cannot impose its supramolecular organization on the P3AT block because 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.

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 with the P3AT homopolymer (Supporting Information, Figures S7 and S9). If these findings are combined with the fact that the P3AOT homopolymer relaxes nonradiatively (Supporting Information, Figure S8), then it can be concluded that excitation of the P3AOT block in the copolymers results in nonradiative decay, whereas excitation of the P3AT block partially results in a radiative decay and partially results in energy transfer to the P3AOT block, which relaxes nonradiatively. 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)), under 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, because P3AOT decays nonradiatively, emission spectroscopy cannot provide direct information on the P3AOT block.

A further decrease in the solvent quality (chloroform/methanol (1/9)) (conditions under which the P3AT block also 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 that in good solvent and not from aggregated P3AT chains.

The fact that a similar decrease in 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 blocks. In fact, this corresponds to a head-to-head (HH) coupling composed of an alkyl and alkoxy substituent. In the case of HH-coupled dialkylthiophenes, steric hindrance is such that the two thiophenes are severely twisted under all conditions, disrupting the conjugation,[19] whereas for HH-couplings in dialkoxythiophenes, a rather planar conformation is adopted, even under 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 under conditions that 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.

Conclusions

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, the P3AT block also 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 block; 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 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: ^{1}H NMR spectra, GPC spectra of all block copolymers, emission spectra of **P3AT** and **P3AOT**, emission spectrum of **P3AT(R*)-b-P3AOT(S*)** at $\lambda_{ex} = 550$ 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.

References and Notes

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