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ARTICLE

Influence of the Presence and Length of an Alkyl Spacer on the Supramolecular Chirality of Block Copoly(thiophene)s

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ABSTRACT: Three block copolymers, P3AT-1-*b*-P3AOT, P3AT-2-*b*-P3AOT, and P3AT-6-*b*-P3AOT, composed of an alkyl- and alkoxy-substituted poly(thiophene) block which are connected by a nonconjugated flexible alkyl spacer of variable length, were synthesized by coupling the azide- and acetylene-functionalized homopolymers using the click reaction. GPC and ^{1}H NMR analysis confirmed the formation of the block copolymers. Next, the influence of the presence and length of the alkyl spacer on the electronic properties was investigated with UV−vis and emission spectroscopy. Also, the influence of the length of the alkyl spacer on the aggregation behavior was studied with UV−vis and CD spectroscopy, which is possible due to the chirally substituted P3AOT block. All these experiments revealed that the supramolecular structure of the P3AT block is affected by the P3AOT block, but if a long alkyl spacer is present between the blocks, an additional reorganization of the P3AOT block is possible, which is not the case for shorter alkyl spacers or in the absence of a spacer.

Introduction

During the past decade, the approach of designing conjugated block copolymers has been very promising, especially in the field of solar cells and nanoelectronics.[1,2] Until now, however, research has mainly focused on partly conjugated block copolymers, while reports on all-conjugated block copolymers remain rather limited.[2] The supramolecular behavior of the latter materials is therefore still mainly unexplored. In this respect, the implementation of chirality has been proven to be very useful in probing the aggregation process of these materials through powerful chiroptical techniques, such as CD (circular dichroism) spectroscopy.

We previously reported the synthesis and the chiroptical characterization of block copolymers composed of a poly(3-alkylthiophene) (P3AT) and a poly(3-alkoxythiophene) (P3AOT) block.[3] These block copolymers were prepared by the successive addition of the different monomers, and consequently, the blocks were directly attached to each other without disrupting the conjugation. Using chiroptical techniques, it was shown that the block aggregating first upon addition of nonsolvent has a major influence on the stacking and the chiroptical behavior of the other block.

This article describes the synthesis and the chiroptical properties of a series of block copolymers, constituted of the same P3AT and P3AOT blocks, but separated from each other by a nonconjugated, flexible alkyl spacer of variable length. Because both blocks are not directly attached to one another, the conjugation is interrupted between them, which is in contrast with the previously reported, fully conjugated block copolymers. Since only the P3AOT block is equipped with chiral side chains, CD spectroscopy is used to probe a transfer of supramolecular chirality from the chiral to the achiral block during a solvatochromism experiment. In this way, it is investigated (i) whether the introduction of an alkyl spacer between the blocks affects the electronic properties of the block copolymers and (ii) what the influence of the length of the alkyl spacer is on the aggregation behavior of the block copolymers.

Therefore, three different block copolymers—P3AT-1-*b*-P3AOT, P3AT-2-*b*-P3AOT, and P3AT-6-*b*-P3AOT (Figure 1)—are investigated and compared with the analogous block copolymer without an alkyl spacer (P3AT-*b*-P3AOT). The block copolymers are prepared in a two-step process. In a first step, the P3AT and P3AOT homopolymers, bearing an azide or acetylene end-group, are prepared. Next, the homopolymers are coupled using azide−acetylene click chemistry. Finally, the chiroptical behavior of the polymers is measured using UV−vis, CD, and emission spectroscopy.

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. ^{1}H 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 at 460 nm.

1,[4] **3a**,[5] P3AOT-ace,[6] P3AT-2-N_3,[7] and P3AT-2-*b*-P3AOT[7] were prepared according to literature procedures.

Synthesis of the Homopolymers. *Synthesis of 6-(4-Bromo-3-methylphenoxy)hexanol* (**5**). A solution of **4** (10.0 mmol, 1.87 g) in dry DMF (10 mL) was added to a suspension of NaH (15.0 mmol, 0.360 g) in dry DMF (10 mL) under an argon atmosphere. After stirring for 1 h, NaI (2.00 mmol, 0.300 g) and a

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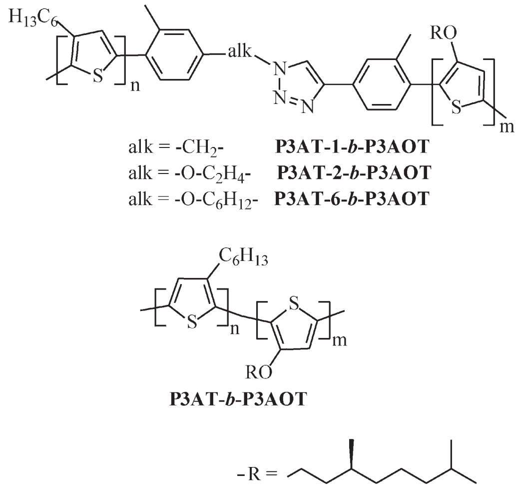


Figure 1. Structures of the block copolymers.

solution of 6-chloro-1-hexanol (20.0 mmol, 2.73 g) in dry DMF (20 mL) were added, and the reaction was followed by TLC (SiO_2, eluent: EtOAc). After the reaction was finished, water was added and the mixture was extracted with hexane. The organic layer was washed with a NaOH solution (30%) and dried over $MgSO_4$. The solvent and the excess of 6-chloro-1-hexanol were removed in vacuo. The product was isolated as a yellow oil. Yield: 1.23 g (43%). ^{1}H NMR ($CDCl_3$): δ = 7.37 (d, J = 8.7 Hz, 1H), 6.78 (d, J = 2.8 Hz, 1H), 6.60 (dd, J = 8.7 Hz, J = 2.8 Hz, 1H), 3.91 (t, 2H), 3.66 (t, 2H), 2.35 (s, 3H), 1.78 (m, 2H), 1.60 (m, 2H), 1.46 (m, 4H), 1.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ = 158.4, 138.9, 132.9, 117.2, 115.3, 113.6, 68.1, 63.0, 32.8, 29.3, 26.0, 25.6, 23.3. MS: m/z = 286 (M^+), 269 ($M^+ - OH$), 186 ($M^+ - (CH_2)_6OH$), 107 ($M^+ - (CH_2)_6OH{-}Br$).

*Synthesis of 1-Bromo-2-methyl-4-[6-(tert-butyldimethylsilyloxy)-hexyloxy]benzene (**6**).* An argon-purged solution of *tert*-butyldimethylsilyl chloride (6.45 mmol, 0.972 g) in dry DMF (10 mL) was added to a solution of **5** (4.30 mmol, 1.23 g) in dry DMF (10 mL) under an argon atmosphere. Next, a solution of imidazole (12.9 mmol, 0.878 g) in dry DMF (20 mL) was added at 0 °C. The reaction mixture was stirred at room temperature, and the reaction was monitored by TLC (SiO_2, eluent: CH_2Cl_2/EtOAc 1/1). After complete conversion, water was added and the mixture was extracted with hexane. The organic layer was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (SiO_2, eluent: CH_2Cl_2). Yield: 1.43 g (84%). ^{1}H NMR ($CDCl_3$): δ = 7.37 (d, J = 8.6 Hz, 1H), 6.77 (d, J = 3.0 Hz, 1H), 6.59 (dd, J = 8.6 Hz, J = 3.0 Hz, 1H), 3.90 (t, 2H), 3.61 (t, 2H), 2.35 (s, 3H), 1.77 (m, 2H), 1.54 (m, 2H), 1.42 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ = 158.4, 138.9, 132.9, 117.2, 115.3, 113.6, 68.2, 63.3, 32.9, 29.4, 26.1, 26.0, 25.7, 23.3, 18.5, −5.1. MS: m/z = 401 (M^+), 269 ($M^+ - OTBDMS$), 215 ($M^+ - Br{-}CH_3{-}C_6H_3{-}O^+$).

*Synthesis of Bromo-[2-methyl-4-[6-(tert-butyldimethylsilyloxy)-hexyloxy]phenyl]bis(triphenylphosphine)nickel (**3b**).* A solution of **6** (2.00 mmol, 0.803 g) in dry toluene (20 mL) was added under an argon atmosphere to $Ni(PPh_3)_4$ (1.80 mmol, 1.99 g). After stirring for 2 days, the reaction mixture was added dropwise to hexane (200 mL), and the formed precipitate was filtered off. The filtrate was concentrated by rotary evaporation to a volume of 10 mL and precipitated in methanol (100 mL) at 0 °C. The precipitate was filtered off and dried in vacuo. Finally, a yellow solid material was obtained. Yield: 0.621 g (32%); mp: 120 °C. ^{1}H NMR (CD_2Cl_2): δ = 7.51 (m, 12H), 7.35 (d, J = 7.2 Hz, 6H), 7.25 (d, J = 7.2 Hz, 12H), 6.84 (d, J = 8.4 Hz, 1H), 5.97 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 5.64 (d, J = 2.4 Hz, 1H), 3.59 (m, 4H), 2.03 (s, 3H), 1.60 (m, 2H), 1.50 (m, 2H), 1.36 (m, 4H), 0.87 (s, 9H), 0.02 (s, 6H). ^{31}P NMR (CD_2Cl_2): δ = 22.0, 21.2 (calibrated toward H_3PO_4).

Synthesis of P3AT-1-OTBDMS. *i*PrMgCl (2 M in THF, 2.18 mmol, 1.09 mL) was added to a solution of 2-bromo-3-hexyl-5-iodothiophene (2.00 mmol, 0.746 g) in dry THF (20 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred for 1 h at 0 °C. Meanwhile, an argon-purged mixture of **3a** (0.100 mmol, 0.0898 g) and dppp (0.200 mmol, 0.0825 g) in dry THF (10 mL) was stirred for 30 min at room temperature. In a next step, the solution with the Grignard reagent was added to the second mixture and stirred for 3 h at room temperature. The polymerization was then quenched by adding a few drops of HCl in THF, and the polymer was precipitated in methanol and filtered off. The polymer was washed with acetone and subsequently extracted with chloroform. This chloroform-soluble fraction was precipitated in methanol, filtered off, and dried in vacuo. Yield: 136 mg (41%).

Synthesis of P3AT-1-OH. A solution of P3AT-1-OTBDMS (0.800 mmol, 133 mg) in THF (50 mL) was purged with argon and shielded from light. $TBAF \cdot 3H_2O$ (1.00 mmol, 0.3155 g) was added, and the reaction was stirred overnight. The mixture was then concentrated to a volume of 10 mL and precipitated in methanol, filtered off, and dried in vacuo. Yield: 128.8 mg (96%).

Synthesis of P3AT-1-N_3. A solution of P3AT-1-OH (0.770 mmol, 128 mg) and diphenylphosphorylazide (DPPA) (15.4 mmol, 4.23 g) in dry THF (200 mL) was cooled to 0 °C, and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) (15.4 mmol, 2.34 g) was added. The mixture was stirred overnight, and after concentrating to a volume of 10 mL, it was precipitated in methanol and filtered off. The polymer was thoroughly washed with water and methanol and then dried in vacuo. Yield: 102.8 mg (80%).

Synthesis of P3AT-6-OTBDMS. The same procedure as described for P3AT-1-OTBDMS was followed, using **3b**. Yield: 100 mg (30%).

Synthesis of P3AT-6-OH. The same procedure as described for P3AT-1-OH was followed, using P3AT-6-OTBDMS (0.601 mmol, 100 mg). Yield: 70.0 mg (70%).

Synthesis of P3AT-6-N_3. A solution of P3AT-6-OH (0.371 mmol, 61.8 mg) and di-*p*-nitrophenylphosphorylazide (0.804 mmol, 0.294 g) in dry THF (10 mL) was brought under an argon atmosphere, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.804 mmol, 0.122 g) was added. This was stirred for 60 h. In a second reaction vessel, a mixture of TBAF (0.804 mmol, 0.254 g) and trimethylsilylazide (0.804 mmol, 0.0926 g) in dry THF was stirred for 15 min and then added to the first reaction. After stirring overnight, the reaction mixture was extracted with toluene. The organic layer was concentrated to a volume of 10 mL and precipitated in methanol. The polymer was filtered off and dried in vacuo. Yield: 48.0 mg (69%).

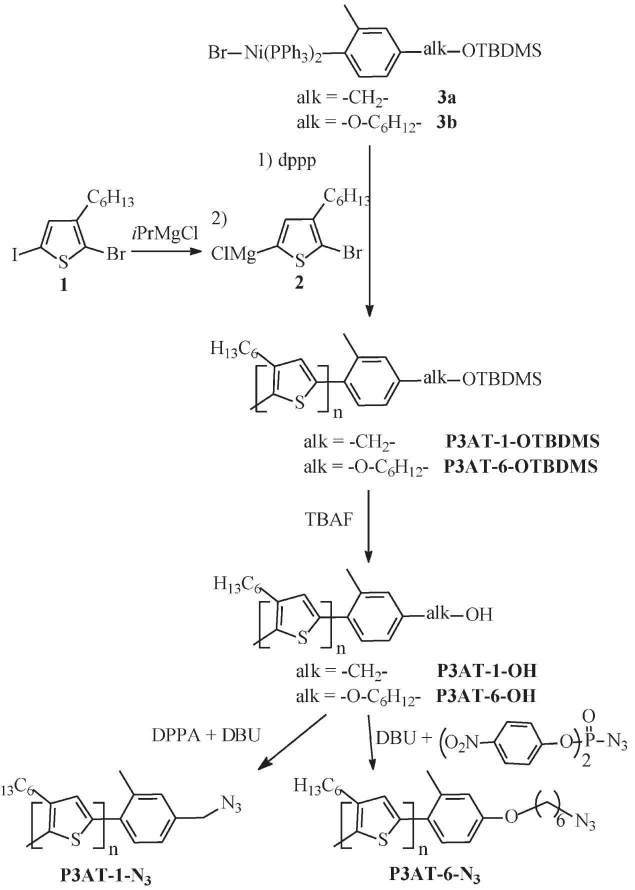
Synthesis of the Block Copolymers. *Synthesis of P3AT-1-b-P3AOT.* An argon-purged solution of PMDETA (11.0 μmol, 1.91 mg) in dry THF (8 mL) was added to a suspension of CuBr (8.82 μmol, 1.26 mg) and dry THF (8 mL). To this mixture, a solution of P3AOT-ace (0.187 mmol, 44.7 mg) and P3AT-1-N_3 (0.234 mmol, 39.0 mg) in dry THF (20 mL) was added, and the reaction is stirred overnight under an argon atmosphere. Then, chloroform and an aqueous solution of NH_3 were added, and the mixture was extracted. The organic layer was dried over $NaSO_4$ and concentrated to a volume of 10 mL, which was precipitated in methanol and filtered off. The polymer was purified by Soxhlet extractions with pentane, hexane, heptane, and finally with chloroform. The chloroform solution was precipitated in methanol, filtered off, and dried in vacuo. Yield: 25.0 mg.

Synthesis of P3AT-6-b-P3AOT. The same procedure as described for P3AT-1-*b*-P3AOT was followed, using P3AT-6-N_3 (0.0578 mmol, 9.62 mg). The heptane-soluble fraction was used. Yield: 5.65 mg.

Results and Discussion

Synthesis of the Polymers. *Synthesis of the Homopolymers.* The synthesis of the block copolymers requires four

Scheme 1. Synthesis of the Homopolymers P3AT-1-N_3 and P3AT-6-N_3



homopolymers, either equipped with an acetylene (P3AOT-ace) or azide (P3AT-1-N_3, P3AT-2-N_3, and P3AT-6-N_3) end-group. All functionalized homopolymers were prepared from a functionalized Ni catalyst.[5,6] After polymerization, the functional group present was converted into the appropriate functionality (acetylene or azide for the P3AOT and P3ATs, respectively) by postpolymerization reactions.

P3AOT-ace[6] and P3AT-2-N_3[7] were prepared as described elsewhere. The synthesis of P3AT-1-N_3 and P3AT-6-N_3 is depicted in Scheme 1 and starts from a Ni catalyst, bearing also a tetrabutyldimethylsilyl (TBDMS) protected alcohol (**3**). First the PPh_3 ligands were exchanged in situ by dppp, after which 2-bromo-5-chloromagnesio-3-hexylthiophene (**2**) was added. This ligand exchange was performed since the Ni-mediated polymerization of P3ATs is only living if dppp is used instead of PPh_3.[5,8b,9] **2** was prepared from **1** by a selective Grignard metathesis reaction. After polymerization, the TBDMS protecting group was removed with tetrabutylammonium fluoride (TBAF). In a final reaction, this alcohol functionality was converted into an azide using diphenylphosphorylazide (DPPA)[10] (P3AT-1-OH) or di-*p*-nitrophenylphosphorylazide[11] (P3AT-6-OH) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The latter conditions were chosen for P3AT-6-OH because the reaction with DPPA stopped at the formation of the phosphonate.

The postpolymerization reactions were monitored by ^{1}H NMR spectroscopy. The part of the spectra of P3AT-1-OTBDMS, P3AT-1-OH, and P3AT-1-N_3 displaying the CH_2 group adjacent to the benzene ring and the region of the silyl protecting group is depicted in Figure 2 (left). The conversion of the OTBDMS group to an alcohol functionality is accompanied by a small NMR shift of the CH_2 protons; in addition, the disappearance of the signals arising from the methyl and *tert*-butyl groups of the protecting group delivers a second proof for the successful reaction. Transformation of the alcohol end-group into an azide gives rise to a clear shift in the spectrum. Second, an IR spectrum of the azide shows a clear signal around 2094 cm^{-1}. The quantitative conversion of P3AT-6-OTBDMS to P3AT-6-N_3 was similarly shown (Figure 2, right).

The synthesis of initiator **3b** is shown in Scheme 2. In a first step, 4-bromo-3-methylphenol is reacted with 6-chlorohexanol. The alcohol functionality is then protected by treating **5** with *tert*-butyldimethylsilyl chloride (TBDMSCl) in the presence of imidazole. In a next step, the initiator is formed by reaction of **6** with $Ni(PPh_3)_4$. It is worthwhile mentioning that the methyl group in *ortho* position was preferred to ensure sufficient stability of the Ni-complex in solution.[5,8]

Synthesis of the Block Copolymers. The block copolymers were synthesized by a coupling reaction of the acetylene-terminated P3AOT with each of the azide-terminated P3AT (Scheme 3). The click reaction was performed in the presence of Cu(I)Br and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDTA), using an excess of the P3AT. After reaction, the mixture was precipitated in methanol and purified by successive Soxhlet extractions with pentane, hexane, and heptane to remove unreacted P3AT. Because of the large excess of P3AT, no unreacted P3AOT-ace could be detected after reaction, which facilitated the purification.

GPC and NMR Analysis. The molar masses of the homopolymers were determined by GPC and are shown in Table 1. From the measured $\overline{M}_n$, the degree of polymerization (DP) could be calculated. However, it is known that GPC, calibrated toward polystyrene standards, typically overestimates the molar mass of polymers that adopt a more rigid conformation, as in the case of P3ATs and P3AOTs. Therefore, ^{1}H NMR was also used to estimate the number of monomeric units in one polymer chain, which was done by relative integration of the signals of terminal and inner α-methylenes.

The molar mass of the block copolymers was determined by GPC as well, and the results are shown in Table 2. The molar masses of P3AT-1-*b*-P3AOT and P3AT-2-*b*-P3AOT match rather well with the expected values. The deviation from the expected $\overline{M}_n$ for P3AT-6-*b*-P3AOT, however, is likely to originate from a more thorough fractionation of the block copolymer, required to remove all unreacted homopolymer. This is also in line with its smaller polydispersity.

The appearance of only one, unimodal peak in the chromatogram, situated at a lower elution volume in comparison with the homopolymers, confirms the successful formation of the block copolymers. An example is shown for P3AT-1-*b*-P3AOT in Figure 3. Another proof for the formation of the block copolymers is delivered by recording the GPC chromatogram at 600 nm—a wavelength corresponding to the absorption maximum of P3AOT, but at which P3AT does not absorb. The fact that the GPC profiles can be measured at both 254 and 600 nm (and at the same elution volume) confirms the incorporation of the P3AOT block.

Also, the ^{1}H NMR spectra deliver a proof for the formation of the block copolymers. Indeed, signals arising from both P3AT and P3AOT blocks are found. The fact that the *o*-methyl groups on the benzene unit from each homopolymer both have the same integration shows that equal quantities of the blocks are present, confirming the presence of a block copolymer rather than a mixture of homopolymers. From ^{1}H NMR, also the relative amounts of P3AT and P3AOT repeating units present in the block copolymer could be

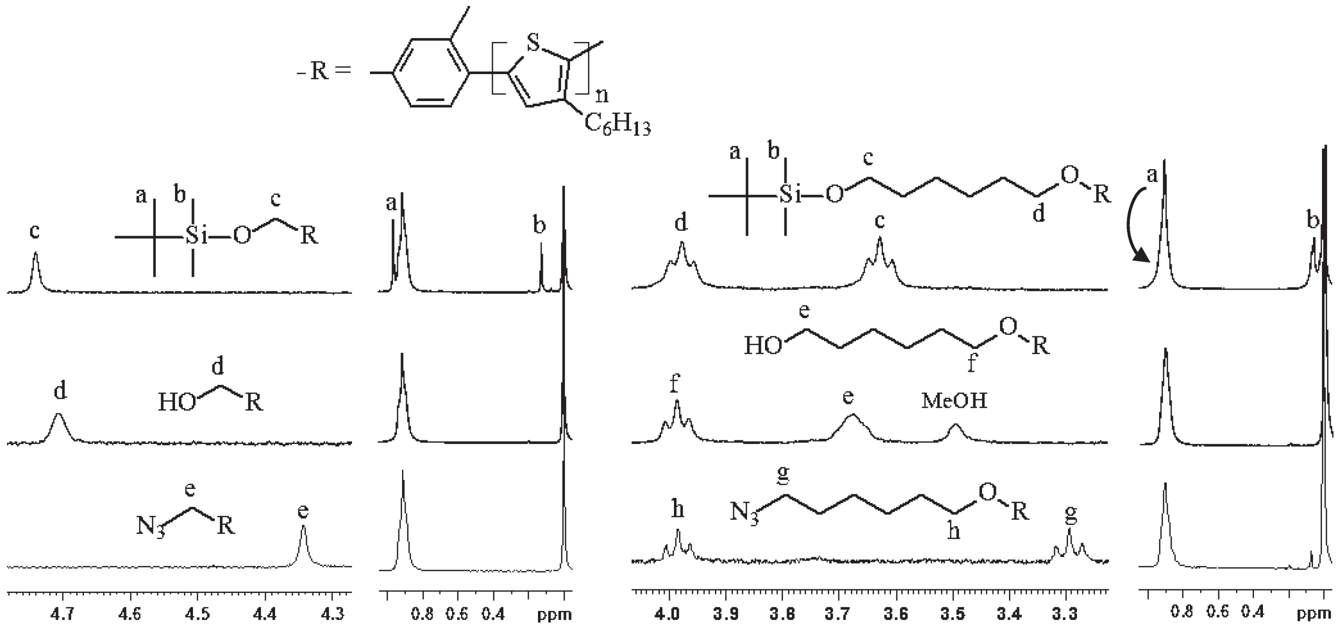


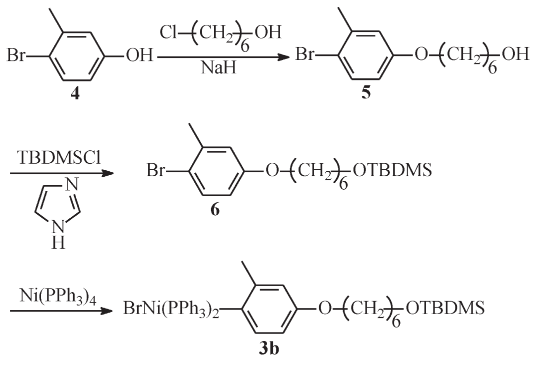
Figure 2. Part of the ^{1}H NMR spectra of P3AT-1-OTBDMS and P3AT-6-OTBDMS to P3AT-1-N$_3$ and P3AT-6-N$_3$ in CDCl$_3$, evidencing the quantitative postpolymerization reactions.

determined by the relative integration of the CH_2 and OCH_2 unit directly attached to the thiophene ring. This ratio is given in Table 2 and corresponds rather well with the degree of polymerization of the respective homopolymers.

Influence of the Alkyl Spacer on the Electronic Properties. Next, the influence of the presence and length of an alkyl spacer between the conjugated blocks on the electronic properties of the block copolymers is investigated. Therefore, the UV−vis spectra of the block copolymers in a good solvent were recorded and compared with a superposition of the UV−vis spectra of the corresponding P3AT and P3AOT homopolymers (Figure 4 and Supporting Information). For the block copolymers with the alkyl spacer, the spectrum of the superposition was composed of the spectrum of the corresponding azide-functionalized P3AT and P3AOT-ace. For P3AT-*b*-P3AOT, the superposition was calculated using the spectra of two homopolymers with the same degree of polymerization as the blocks in the block copolymer.[3]

The UV−vis spectra clearly show two separate absorption bands: one near 450 nm and one near 600 nm, corresponding to the $\pi-\pi^*$ transition of the P3AT and the P3AOT block, respectively. In contrast to P3AT-*b*-P3AOT, the spectra of the block copolymers with alkyl spacer match rather well the superposition of the two homopolymers. This confirms that no electronic influence between the blocks of these block copolymers is present in the ground state due to the presence of the nonconjugated alkyl spacer, which disrupts the conjugation. In P3AT-*b*-P3AOT, however, conjugation between the blocks is present, and the blocks electronically differ from the constituting homopolymers.

Scheme 2. Synthesis of the Ni-Initiator 3b



Second, the emission of the block copolymers is studied. As reported previously, P3AOTs relax nonradiatively and, consequently, the emission of block copolymers composed of P3AT and P3AOT originates from the P3AT block.[3b] Moreover, energy transfer from the P3AT to the P3AOT block occurs, which therefore quenches the fluorescence. For P3AT-*b*-P3AOT, the efficiency of this energy transfer depends on the conformation and supramolecular structure of the block copolymer. More in particular, the conformation of the bond connecting the polymer blocks is decisive in this respect: a planar conformation allows a good conjugation between the blocks and, consequently, an efficient energy transfer. Naturally, energy transfer via this pathway cannot occur in the block copolymers with alkyl spacer. Alternatively, also Förster energy transfer between the blocks can take place. Again, the supramolecular structure plays a crucial role in its efficiency. As a consequence, emission spectroscopy is a very suitable technique to probe differences and conformational changes in the excited state. The emission spectra of P3AT-1-*b*-P3AOT, P3AT-2-*b*-P3AOT, and P3AT-6-*b*-P3AOT and a P3AT homopolymer [$\overline{M}_n$ = 4.1 kg mol^{-1}, according to GPC in THF toward polystyrene] in chloroform, excited at 460 nm, are displayed in Figure 4c. All spectra are corrected for differences in absorption. Note that the lower λ_{ex} in P3AT-2-*b*-P3AOT and P3AT-6-*b*-P3AOT can be attributed to their lower degree of polymerization. From these spectra, it is clear that the emission of the block copolymers arises from the P3AT block and that energy transfer to the P3AOT occurs, which accounts for the drop of emission intensity compared with the P3AT homopolymer. Therefore, it can be concluded that although the conjugation between the two blocks is disrupted by the alkyl group, the electronic properties in the excited state are still affected by (through-space) energy transfer. Second, P3AT-6-*b*-P3AOT differs from P3AT-1-*b*-P3AOT and P3AT-2-*b*-P3AOT, demonstrating that the energy transfer is more efficient in

Scheme 3. Synthesis of the Block Copolymers

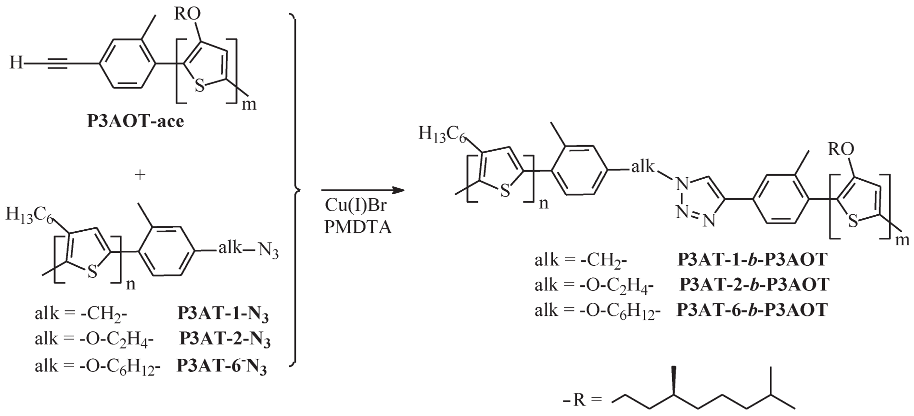


Table 1. Number-Averaged Molar Mass ($\overline{M}_n$), Polydispersity (*D*), and Degree of Polymerization (DP) of the Homopolymers

homopolymer	$\overline{M}_n$(GPC) (kg mol^{-1})	*D* (GPC)	DP (GPC)	DP (NMR)
P3AT-1-N$_3$	4.4	1.2	26	14
P3AT-2-N$_3$	2.0	1.2	12	10
P3AT-6-N$_3$	2.0	1.1	12	8
P3AOT-ace	10.3	1.5	43	n/a

Table 2. Number-Averaged Molar Mass ($\overline{M}_n$) and Polydispersity (*D*) of the Block Copolymers Measured by GPC and the Ratio P3AOT/P3AT Determined by ^{1}H NMR

block copolymer	$\overline{M}_n$(GPC) (kg mol^{-1})	*D* (GPC)	P3AOT/P3AT (NMR)
P3AT-1-*b*-P3AOT	14.1	1.4	2.1/1
P3AT-2-*b*-P3AOT	12.5	1.3	2.3/1
P3AT-6-*b*-P3AOT	15.3	1.2	2.8/1

P3AT-6-*b*-P3AOT. This can be correlated with the flexibility of the alkyl spacer between the two polymer blocks. In P3AT-1-*b*-P3AOT and P3AT-2-*b*-P3AOT, the two polymer blocks are somewhat restricted in the possible orientations they can adopt toward each other. More in particular, they cannot fold back, but instead, they must rather point away from each other, increasing the distance between the blocks and, hence, diminishing the energy transfer. This hypothesis is also supported by the CD study (see further). In P3AT-6-*b*-P3AOT, in contrast, the two blocks can fold back, allowing a more efficient energy transfer. Therefore, it can be concluded that the electronic properties of the block copolymers in the ground state are a superposition of the constituting homopolymers but that the emission spectra significantly differ due to energy transfer, which efficiency depends on the length of the connecting alkyl spacer.

Influence of the Length of the Alkyl Spacer on the Supramolecular Properties. Finally, the influence of the length of the alkyl spacer on the aggregation behavior of the block copolymers is investigated. For this purpose, the block copolymers are dissolved in a good solvent (chloroform) and a nonsolvent (methanol) is gradually added (Figure 5). UV−vis and CD spectroscopy are used to monitor the conformational and supramolecular changes of the block copolymer. As already mentioned, in a good solvent, two distinct absorption bands can be observed for all block copolymers, originating from both blocks. Upon decreasing the solvent quality, the least soluble block, being the (chiral) P3AOT block, starts to aggregate first. This aggregation is expressed by a very small red shift of the P3AOT band in the UV−vis spectrum and the appearance of a bisignate Cotton effect centered in the absorption band of the P3AOT block in the CD spectrum, showing that the P3AOT chains stack in a chiral way. By further decreasing the solvent quality, also the P3AT block aggregates, which is expressed by a large red shift in the UV−vis spectrum (Figure 5k). The CD intensity significantly increases and the zero crossing of the accompanying CD spectrum blue shifts toward ~550 nm. In fact, the observed CD spectra are composed of two bisignate Cotton effects—one from the (chiral) P3AOT block and the other one from the P3AT block—indicating that also the P3AT polymer chains, although being equipped with achiral side chains, stack in a chiral way. It can therefore be concluded that the already aggregated P3AOT block imposes its supramolecular structure to the P3AT block, transferring its chirality to the P3AT block.

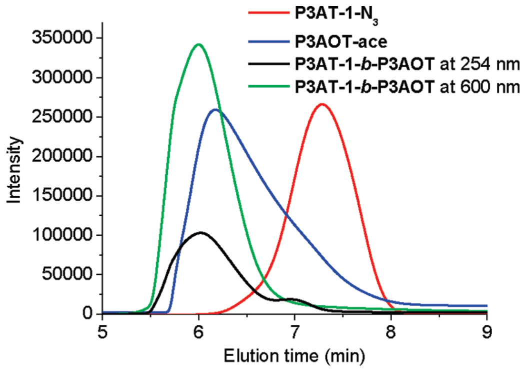


Figure 3. GPC spectra of P3AT-1-*b*-P3AOT and its constituting homopolymers.

However, the CD spectra of the three block copolymers show some subtle differences. Upon continuous addition of nonsolvent, the intensity of the Cotton effect in P3AT-1-*b*-P3AOT and P3AT-2-*b*-P3AOT increases up to ~60% of methanol. At that stage, a maximum intensity is reached, and the addition of more methanol does not affect the CD signal. In contrast, the CD spectra of P3AT-6-*b*-P3AOT reach a maximum (at ~60% of methanol), but then the intensity of the signal decreases again. Apart from a change in intensity, also the zero-crossing displays a blue shift. These two differences point at a decrease in intensity of the bisignate Cotton effects of the P3AOT block. It is interesting to note that if a chiral P3AOT homopolymer is subjected to a similar experiment (Figure 5i,j), exactly the same behavior is found. In fact, the evolution of the CD spectra upon decreasing the solvent quality is determined by both the number of aggregates and their individual CD, which, on its turn, depends on the angle

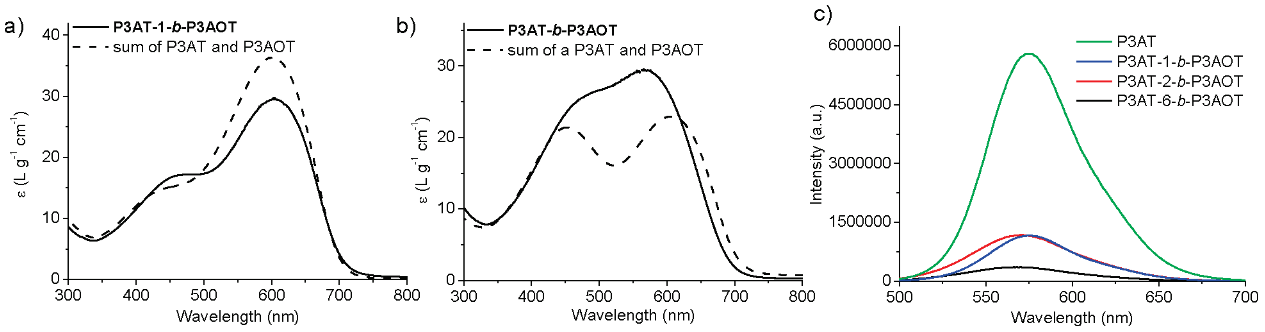


Figure 4. Comparison of the UV−vis spectrum of a sum of a P3AT and a P3AOT with (a) P3AT-1-*b*-P3AOT and (b) P3AT-*b*-P3AOT. (c) Emission spectra of P3AT (c = 2.8 mg/L), P3AT-1-*b*-P3AOT (c = 3.6 mg/L), P3AT-2-*b*-P3AOT (c = 4.0 mg/L), and P3AT-6-*b*-P3AOT (c = 5.3 mg/L) in chloroform (λ_{ex} = 460 nm). The spectra were corrected for differences in absorption.

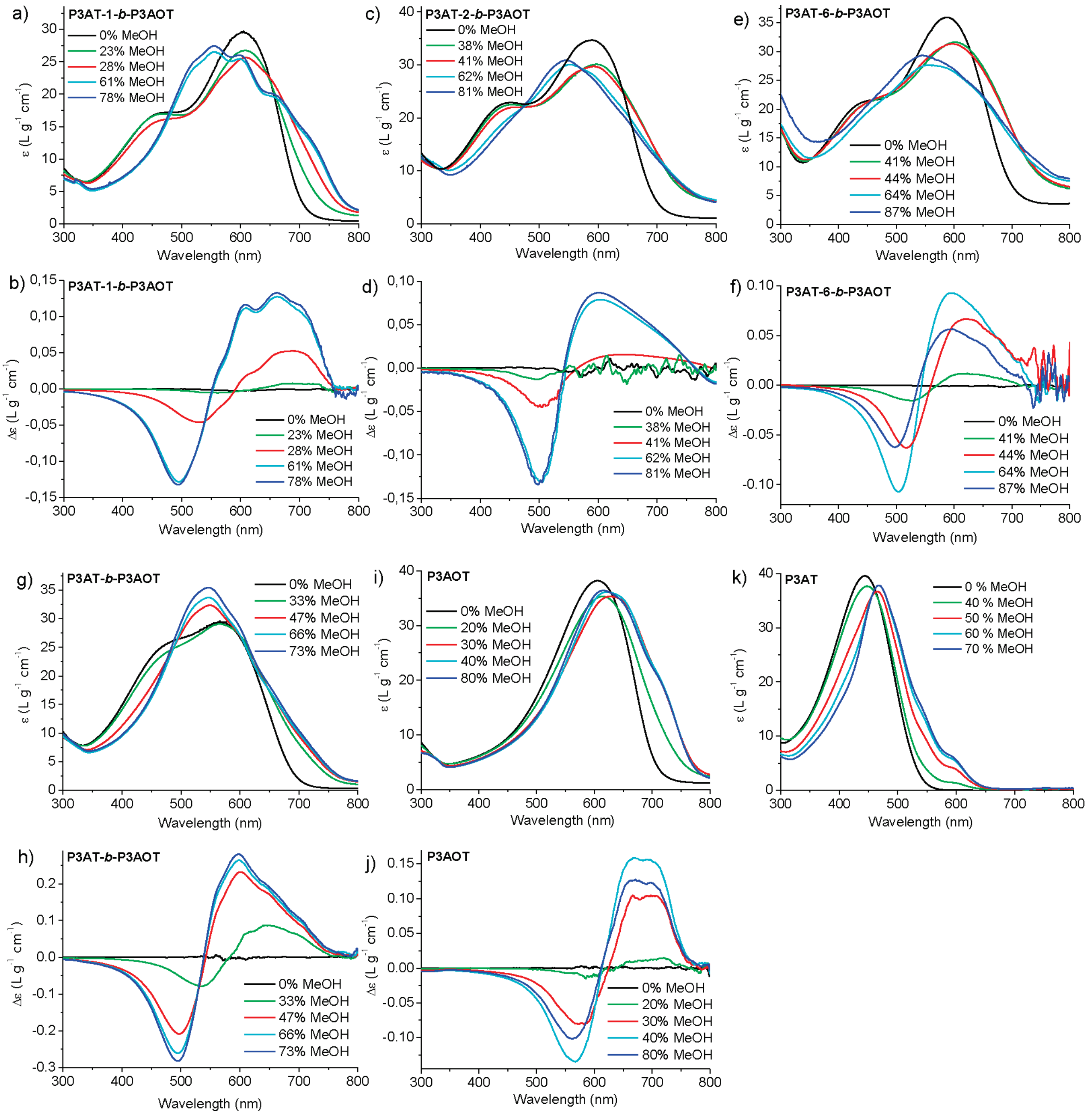


Figure 5. Influence of the addition of methanol to a chloroform solution of the block copolymers: (a) UV−vis and (b) CD spectra of P3AT-1-*b*-P3AOT (c_{start} = 0.094 g/L); (c) UV−vis and (d) CD spectra of P3AT-2-*b*-P3AOT (c_{start} = 0.089 g/L); (e) UV−vis and (f) CD spectra of P3AT-6-*b*-P3AOT (c_{start} = 0.113 g/L; (g) UV−vis and (h) CD spectra of P3AT-*b*-P3AOT (c_{start} = 0.088 g/L); (i) UV−vis and (j) CD spectra of P3AOT (c_{start} = 0.100 g/L); (k) UV−vis spectra of P3AT (c_{start} = 0.020 g/L).

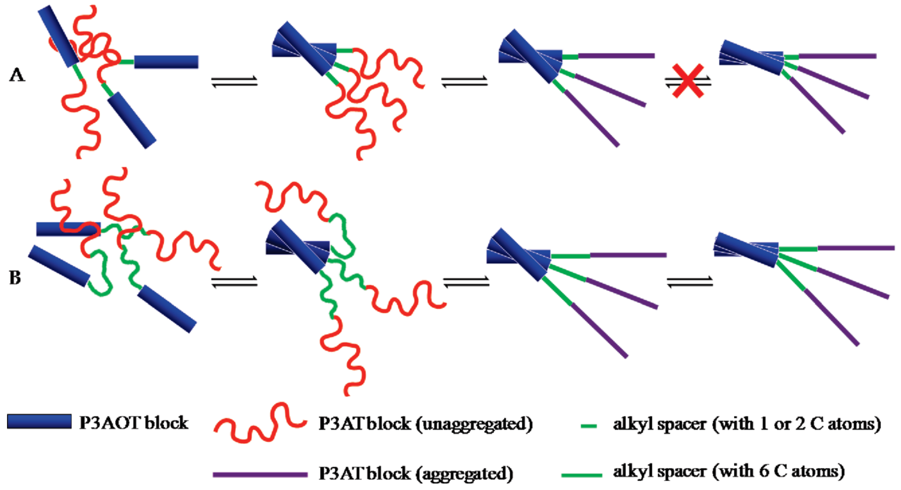


Figure 6. Schematic presentation of the influence of the addition of methanol to a chloroform solution of (A) P3AT-1-*b*-P3AOT and P3AT-2-*b*-P3AOT and (B) P3AT-6-*b*-P3AOT.

by which the stacked polymer chains are rotated toward each other. Therefore, the drop of CD intensity at high nonsolvent content originates from a more parallel orientation, induced by the decrease of the solvent quality.

The chiroptical properties of the block copolymers can therefore be explained as follows (see also Figure 6). Upon the addition of nonsolvent to a chloroform solution, first the P3AOT block stacks in a chiral way, as can be concluded from the bisignate Cotton effect in the absorption band of the P3AOT block. In case of long, flexible alkyl spacers, the alkyl chain can fold back, decreasing the distance between the P3AT and P3AOT blocks, which allows a more efficient energy transfer from the P3AT to the P3AOT chains. When the nonsolvent content is further increased, also the P3AT block stacks. Because of steric restrictions, the P3AT chains cannot stack parallel, but they adopt the chiral supramolecular structure of the P3AOT. This chiral stacking of the P3AT chains gives also rise to a bisignate Cotton effect in their absorption band. The observed CD is a superposition of both signals and has therefore a higher intensity with a zero-crossing which is intermediate between both λ_{max}. Upon further decreasing the solvent quality, the angle by which the P3AOT chains in P3AT-6-*b*-P3AOT are rotated is slightly reduced. As a consequence, the contribution of the P3AOT block to the overall Cotton effect is diminished, accounting for the drop in intensity and shift of the zero-crossing toward the absorption band of P3AT. This reorganization within the P3AOT block is not observed for P3AT-1-*b*-P3AOT and P3AT-2-*b*-P3AOT. In these polymers the alkyl spacer is much shorter and therefore less flexible, making the reorganization impossible. The same behavior was observed for P3AT-*b*-P3AOT, where no (flexible) alkyl spacer is present and thus also no reorganization is observed.

Conclusion

In conclusion, three block copolymers—P3AT-1-*b*-P3AOT, P3AT-2-*b*-P3AOT, and P3AT-6-*b*-P3AOT, with a nonconjugated, flexible alkyl spacer of variable length between the blocks—were studied. The polymers were prepared in a two-step process, coupling the homopolymers using click chemistry. The chiroptical properties were studied and compared with a previously synthesized block copolymer which lacks this alkyl spacer. It was shown by UV−vis and emission spectroscopy that the introduction of an alkyl spacer between the blocks does not affect the electronic properties of the block copolymer in the ground state but that energy transfer occurs. Depending on the length of the alkyl spacer, the polymer strands can fold back, decreasing the distance between both blocks and allowing a more efficient energy transfer. The aggregation behavior and the supramolecular structure of the block copolymers were studied by UV−vis and CD spectroscopy. Lowering the solvent quality results in chiral aggregation of the P3AOT block. Upon the further addition of more nonsolvent, also the P3AT block aggregates and adopts the same chiral, helical supramolecular organization as the P3AOT block. However, depending on the length of the alkyl spacer, some subtle differences were found. Upon continuous addition of more nonsolvent to the block copolymer solution, a longer alkyl spacer allows the P3AOT block to additionally reduce the angle between the stacked chains, which is reflected in a decrease of intensity of the CD signal and a blue-shift of the zero-crossing. This reorganization is not possible for the block copolymers with a shorter or no alkyl spacer.

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Supporting Information Available: Comparison of the UV−vis spectra of the block copolymers and the sum of the spectra of their constituting homopolymers and synthetic details for P3AT-2-*b*-P3AOT. This material is available free of charge via the Internet at http://pubs.acs.org.

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