Transfer of Supramolecular Chirality in Block Copoly(thiophene)s

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Conjugated block copolymers have received considerable attention in recent years, as they hold promise, for instance for solar cells and nanoelectronics.^[1-3] Block copolymers consisting of one conjugated block and one or more nonconjugated, usually coil-like blocks, have been shown to possess a variety of defined morphologies which differ from those of the parent conjugated homopolymers.^[1] However, since the nonconjugated segments do not contribute electronically to the material, their role remains restricted to the self-assembly. In contrast, different morphologies and unique electronic properties can be expected for conjugated block copolymers composed of two, electronically different blocks.^[2] For instance, Tu *et al.* showed that conjugated block copolymers can form morphologies which differ from those of a blend of their homopolymers and that the morphology and corresponding optical properties of amphiphilic block copolymers depend on the solvent conditions.^[3] Here, we show that the electronic properties and the supramolecular organization of one conjugated block can also be influenced by the other conjugated block.

The block copolymer studied in this paper, is composed of a regioregular, head-to-tail coupled, (achiral) poly(3-hexylthiophene) (P3HT) and a chiral, regioregular, head-to-tail coupled poly(3-(3,7-dimethyloctyloxy)thiophene) (P3OOT). Although both polymers are composed of the same polythiophene backbone, they electronically differ significantly: for instance, λ_{max} in film varies from ~500 nm for P3HT^[4] to ~630 nm for P3OOT.^[5]

Circular dichroism (CD) spectroscopy provides a very powerful tool in the study of the supramolecular organization of

(chiral) conjugated polymers. Langeveld-Voss *et al.* have demonstrated that bisignate Cotton effects, commonly observed in films and poor solvent mixtures of regioregular polythiophenes, arise from chirally aggregated, coplanar polymer strands.^[6] Since these Cotton effects are located in the absorption band of the corresponding polymer, CD spectra can deliver ambiguous evidence for the presence of supramolecular chirality in the respective blocks of conjugated block copolymers, provided that both polymer blocks show a significantly different λ_{max} . As a consequence, CD spectroscopy can probe a transfer of supramolecular chirality from the chiral P3OOT to the achiral P3HT block, as this would induce a bisignate Cotton effect in the absorption band of the achiral P3HT block.

The block copolymer was prepared by successive addition of the alkyl-substituted and alkoxy-substituted thiophene monomers, taking advantage of the living character of the Ni-catalyzed polymerization of **2** (Scheme 1).^[7] Special care was devoted to the regioregularity of the resulting polymer blocks, since this is a requisite for efficient supramolecular stacking, which was accomplished by the use of reported polymerization methods.^[8] For the P3OOT block, this requires the exclusive formation of **5**, being the most stable monomeric isomer.^[6] Since the polymerization of **2** in the presence of Ni(dppp)Cl₂ (dppp = 1,3-bis(diphenylphosphino)propane) has been shown to proceed via a living chain-growth mechanism,^[7a,9] while it is uncertain whether this is also the case for alkoxy-substituted thiophenes,^[10] first the P3HT block was formed, from which the P3OOT block was grown. The ratio [2]/[Ni(dppp)Cl₂] = 15. In order to verify the living nature of the P3HT block at the moment the second monomer was introduced and to characterize the P3HT block formed, the reaction mixture was divided in two parts. A first aliquot was quenched with HCl (1 M in methanol), rendering **P3HT₁**. **5** was added to the second batch. The actual concentration of **5** was determined by quenching a small sample of the reaction mixture with D₂O and analyzing it with ¹H NMR spectroscopy. This revealed that **5** was formed in 50% (the remainder being **4**), which corresponds to [5]/[3] = 23. After polymerization, also the second batch was quenched with HCl (1 M in methanol), rendering **P3HT-*b*-P3OOT**.

The polymers were subjected to MALDI-TOF mass spectrometry and GPC. According to MALDI-TOF, the degree of polymerization (P_n) of **P3HT₁** amounts 9.5, which corresponds to a conversion of ~63%; GPC analysis resulted in somewhat higher values (M_n = 2,8 kg/mol). The polymer solely consists of H/Br

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end-groups, which is expected for the living polymerization of **2**.^[7a,9] Unfortunately, we failed in analyzing **P3HT-*b*-P3OOT** using MALDI-TOF spectrometry. Nevertheless, the absence of **P3HT₁** in the GPC profile of **P3HT-*b*-P3OOT** demonstrates that all **3** initiated the polymerization of **5** and its unimodal GPC profile at smaller elution volumes delivers a final proof of the living nature of **3**. Moreover, the fact that the peak strongly absorbs at both 430 nm, at which P3HT strongly absorbs but P3OOT less, and at 600 nm, at which P3OOT absorbs but P3HT not, confirms that it must originate from a block copolymer composed of both a P3HT and a P3OOT block. Fortunately, P_n of **P3HT-*b*-P3OOT** could conveniently be calculated from its ¹H NMR spectrum by relative integration of signals arising from the P3HT block (9.5 units) and the P3OOT block, which revealed that the P3OOT block has P_n of ~14.

In order to investigate whether the polymer blocks influence their mutual supramolecular organization, the solvent quality of a solution of **P3HT-*b*-P3OOT** was systematically decreased, which was accomplished by gradual addition of methanol to a chloroform solution, and the influence on the UV/Vis and CD spectra was evaluated. In a chloroform solution, P3HT is present as poorly conjugated coils, while P3OOT rather adopts a strongly conjugated, planar conformation.^[11] Importantly, the UV/Vis spectrum of the block copolymer is not a superposition of the constituting homopolymers; it rather corresponds to a superposition of P3OOT and a P3HT of higher P_n . This demonstrates that both conjugated blocks do influence each other electronically.

At 30% nonsolvent content, the P3OOT block is aggregated, which is evidenced by the appearance of bisignate Cotton effects in the absorption band of the P3OOT block (Figure 1a-b). Since P3OOT is already strongly conjugated in chloroform solution, its aggregation is accompanied by a limited gain in conjugation and moderate red-shift (~30 nm), resulting in only a slight change of the UV/Vis spectrum. At this point, the P3HT block is still present in its unaggregated, poorly conjugated conformation. However, at 60% methanol, also the P3HT block is aggregated, as evidenced by the UV/Vis spectra, which evolve to a combination of P3OOT and P3HT blocks, both in their planar and aggregated state. However, the spectra are no superposition of their constituting homopolymers, demonstrating the mutual electronic influence of the two blocks.

Importantly, the zero-crossing of the CD spectrum displays a blue-shift (from ~600 to ~550 nm) and its intensity almost triples (from $g_{abs, \lambda = 550 \text{ nm}} = -2 \cdot 10^{-3}$ to $g_{abs, \lambda = 480 \text{ nm}} = -10^{-2}$). In fact, it is a superposition of two bisignate Cotton effects – one near 600 nm and one near 500 nm – originating from, respectively, chirally aggregated P3OOT and P3HT. Therefore, this experiment indicates that the chiral supramolecular organization of P3OOT invokes supramolecular chirality in the achiral P3HT block.

Next, the same experiment was repeated with blends of **P3OOT** ($M_n = 22 \text{ kg/mol}$, GPC)^[12] and P3HTs of different molar masses. Blends, composed of **P3HT₂** ($M_n = 2,4 \text{ kg/mol}$, GPC) which is similar to the P3HT block, could not be used, since the methanol content required to induce aggregation exceeds the highest attainable content with the protocol used. **P3HT₃** ($M_n = 4,1 \text{ kg/mol}$, GPC), on the other hand, better resembles the P3HT block of **P3HT-*b*-P3OOT** both electronically and in the methanol

content required to induce aggregation. At 30% methanol, **P3OOT** chirally stacks, while **P3HT₃** is still present as unaggregated, random coils. At 60% methanol, also **P3HT₃** aggregates, as evidenced by the UV/Vis spectra. On the other hand, the CD spectra do not gain intensity ($g_{abs, \lambda = 550 \text{ nm}} = -4 \cdot 10^{-3}$) and the zero-crossing displays a small blue-shift which is similar to that of **P3OOT** but clearly different from the block copolymer, showing that a contribution of **P3HT₃** is absent. As a consequence, it must be concluded that the two polymers separately aggregate and do not influence their mutual supramolecular organization in the blend, but that transfer of supramolecular chirality is present in the block copolymer.

It is clear that blends of **P3HT₃** and **P3OOT** form separate aggregates and that chirality is absent in the P3HT aggregates because no chiral P3OOT chains are incorporated in the P3HT aggregates. However, Langeveld-Voss *et al.* demonstrated that blending achiral and chiral poly(3-alkylthiophene)s which aggregate at the same methanol content, results in mixed aggregates in which a sergeant-and-soldiers behavior is present.^[13] To investigate whether this is also the case for P3HT-P3OOT blends or that both polymers inherently segregate, the aggregation of **P3HT₄** ($M_n = 4.1 \text{ kg/mol}$, GPC) and **P3OOT**, which aggregate at the same methanol content, was studied. The CD spectra, in particular the zero-crossing around 550 nm, indicate that both polymers are chirally stacked. Therefore, it can be concluded that the aggregates contain both achiral **P3HT₄** and chiral **P3OOT** chains. On the other hand, the intensity is somewhat lower ($g_{abs, \lambda = 550 \text{ nm}} = -1.5 \cdot 10^{-3}$), which may point at a more complicated stacking if the aggregates are composed of chains of a different nature. Importantly, the different behavior of the **P3HT₃-P3OOT** and **P3HT₄-P3OOT** blends again confirms the unique supramolecular behavior of the block copolymer.

In a next experiment, films of **P3HT-*b*-P3OOT** were spincoated. The samples were annealed by heating them at progressively increasing temperatures for 1 min. After each heating cycle, the samples were quenched to room temperature and their UV/Vis and CD spectra were immediately recorded. At 110 °C, the UV/Vis and CD spectra resemble well those in a poor solvent mixture, indicating that both polymer blocks are chirally aggregated. At higher temperatures, the contribution of the P3HT block vanishes, which can be associated with the melting of the P3HT block.

Then, a film, annealed at 110 °C, was oxidized by exposure to I₂ vapor (Figure 2). Although the CD spectrum of the oxidized block copolymer is less defined, it is clear that chirality is still present ($g_{abs} = -10^{-1}$; $\lambda = 460$ and 700 nm). Interestingly, I₂-doped polythiophenes tend to de-dope – the rate of reduction being dependent on the electronic nature of the polythiophene. Indeed, after 5 weeks the original spectra are restored, indicating that the supramolecular chiral organization is preserved during oxidation and back reduction. A similar behavior has also been found for chiral poly(dithienopyrrole)s^[14] and poly(3,4-dialkoxythiophene)s^[15]. Since P3HT is much faster dedoped than P3OOT, the P3HT block is first reduced, followed by the P3OOT block. Unfortunately, since the UV/Vis and CD spectra of **P3HT-*b*-P3OOT** are not a simple superposition of contributions of the two blocks, the individual contributions could not be calculated.^[16] Nevertheless, it is clear that the spectra of **P3HT-*b*-P3OOT** after 4 days are a combination of oxidized (chiral)

P3OOT and neutral, chirally aggregated P3HT. This again demonstrates that the achiral P3HT block shows supramolecular chirality, imposed by the chiral P3OOT block.

In conclusion, we have prepared a block copolymer, composed of (achiral) P3HT and chiral P3OOT and demonstrated that the P3OOT block influences the supramolecular organization of the P3HT block, as is expressed by transfer of supramolecular chirality to the achiral P3HT block. Further research will focus on the morphology of films of the block copolymer.

Experimental Section

Synthesis of P3HT₁ and P3HT-*b*-P3OOT.

A solution of **1** (0.50 mmol, 0.186 g) in dry THF (2.5 mL) was cooled to 0 °C and *i*PrMgCl (0.50 mmol, 0.25 mL, 2 M in THF) was added. The reaction mixture was stirred for 1 h at 0 °C and then cannulated to a suspension of Ni(dppp)Cl₂ (33.1 μmol, 17.5 mg) in dry THF (3.5 mL). The volume of the polymerization reaction was adjusted to 7 mL. After stirring for 2 h, a small aliquot (1.4 mL) was withdrawn and quenched with HCl (1 M in methanol) (P3HT₁). **5** (~0.60 mmol in THF) was added to the remaining part and the reaction mixture was stirred overnight. After being quenched with HCl (1 M in methanol), the polymer was precipitated into methanol, filtered off and dried (P3HT-*b*-P3OOT). For the preparation of **5**, freshly prepared lithium diisopropylamide (1.32 mmol in 3 mL of THF) was added to a solution of **4** (1.20 mmol, 0.383 g) in dry THF (3 mL) at -78 °C. After stirring for 30 min at RT, the solution was added to a suspension of MgBr₂ (1.80 mmol, 0.331 g) in dry THF (4 mL) and stirred for another 30 min.

The homopolymers (P3OOT^[5], P3HT₂₋₄^[9]) were prepared according to literature procedures.

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Captions to scheme and figures

Scheme 1. Synthesis of the homo- and block copolymer.

Figure 1. UV/Vis and CD spectra of **P3HT-*b*-P3OOT** (a, b), a blend of **P3HT₃** (c = 74 mg/L) and **P3OOT** (c = 40 mg/L) (c, d) and a blend of **P3HT₄** (c = 29 mg/L) and **P3OOT** (c = 24 mg/L) (e, f). (— 0 % methanol, ---- 30 % methanol, 60 % methanol).

Figure 2. UV/Vis and CD spectra of the oxidation (I_2) and back reduction of **P3HT-*b*-P3OOT** (— before oxidation, --- after oxidation, ... after 4 days, ---- after 5 weeks).

Entry for the Table of Contents

Block-copolymers

Karliën Van den Bergh, Jorgen Huybrechts, Thierry Verbiest, Guy Koeckelberghs* Page – Page

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chiral block transfers its supramolecular chirality to the achiral block, demonstrating that the blocks influence their mutual supramolecular organization.