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Transfer of Supramolecular Chirality in Block Copoly(thiophene)s

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Conjugated block copolymers have received considerable attention in recent years because 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 that 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 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 that 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] Herein, 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 differ significantly electronically, for instance, λ_{max} in a film varies from around 500 nm for P3HT[4] to around 630 nm for P3OOT.[5]

Circular dichroism (CD) spectroscopy is 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 block to the achiral P3HT block, because 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**, which is the most stable monomeric isomer.[6] Since the polymerization of **2** in the presence of [$NiCl_2$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) has been shown to proceed by 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 of the concentration of **2**/[$NiCl_2$(dppp)] was 15. 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. The first aliquot was quenched with HCl (1 M in methanol) to form P3HT$_1$. Compound **5** was added to the second batch. The actual concentration of **5**

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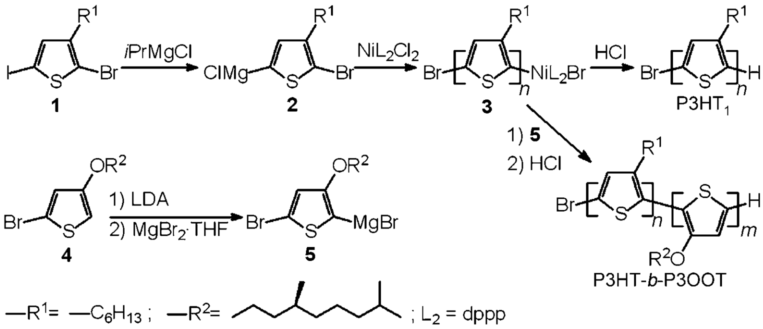

Scheme 1. Synthesis of the homopolymer and the block copolymer.

was determined by quenching a small sample of the reaction mixture with D_2O and analyzing it by ^{1}H NMR spectroscopy. This revealed that **5** was formed in 50 % yield (the remainder was **4**), which corresponds to a concentration ratio of **5**/**3** of 23. After polymerization, the second batch was also quenched with HCl (1 M in methanol) to form P3HT-*b*-P3OOT.

The polymers were subjected to MALDI-TOF mass spectrometry and gel permeation chromatography (GPC). According to MALDI-TOF mass spectrometry results, the degree of polymerization (P_n) of $\mathrm{P3HT_1}$ amounts to 9.5, which corresponds to a conversion of around 63 %; GPC analysis resulted in somewhat higher values (M_n = 2.8 kg mol^{-1}). The polymer solely consists of H/Br end groups, which is expected for the living polymerization of **2**.[7a,9] Unfortunately, we failed to analyze P3HT-*b*-P3OOT by using MALDI-TOF mass spectrometry. Nevertheless, the absence of $\mathrm{P3HT_1}$ in the GPC profile of P3HT-*b*-P3OOT demonstrated that all of **3** initiated the polymerization of **5** and its unimodal GPC profile at smaller elution volumes delivers final proof of the living nature of **3**. Moreover, the fact that the peak strongly absorbs at both 430 nm, at which P3OOT absorbs but the absorbance of P3HT is stronger, and at 600 nm, at which P3OOT absorbs but P3HT does not, confirms that it must originate from a block copolymer composed of both P3HT and P3OOT blocks. Fortunately, P_n of P3HT-*b*-P3OOT could be conveniently calculated from its ^{1}H 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 a P_n value of around 14.

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 solution in chloroform, and the influence on the UV/Vis and CD spectra was evaluated. In a solution in chloroform, P3HT is present as poorly conjugated coils, whereas P3OOT adopts a strongly conjugated, planar conformation.[11] Importantly, the UV/Vis spectrum of the block copolymer is not a superposition of the constituent homopolymers; rather it corresponds to a superposition of P3OOT and P3HT with a higher P_n value. 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, its aggregation is accompanied by a limited gain in conjugation and a moderate redshift (~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, the P3HT block is also 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 not a superposition of their constituent homopolymers, demonstrating the mutual electronic influence of the two blocks.

Importantly, the zero-crossing of the CD spectrum displays a blueshift (from ~600 to ~550 nm) and its intensity almost triples (from $g_{\mathrm{abs},\,\lambda=550\,\mathrm{nm}}=-2\times10^{-3}$ to $g_{\mathrm{abs},\,\lambda=480\,\mathrm{nm}}=-10^{-2}$). In fact, it is a superposition of two bisignate Cotton effects (one near 600 nm and one near 500 nm) originating from chirally aggregated P3OOT and P3HT, respectively. 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 kg mol^{-1}, GPC)[12] and P3HTs of different molar masses. Blends composed of $\mathrm{P3HT_2}$ (M_n = 2.4 kg mol^{-1}, 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. $\mathrm{P3HT_3}$ (M_n = 4.1 kg mol^{-1}, 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 $\mathrm{P3HT_3}$ is still present as unaggregated, random coils. At 60 % methanol, $\mathrm{P3HT_3}$ also aggregates, as evidenced by the UV/Vis spectra. On the other hand, the CD spectra do not gain intensity ($g_{\mathrm{abs},\,\lambda=550\,\mathrm{nm}}=-4\times10^{-3}$) and the zero-crossing displays a small blueshift, which is similar to that of P3OOT but clearly different from the block copolymer, showing that a contribution of $\mathrm{P3HT_3}$ 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 $\mathrm{P3HT_3}$ and P3OOT form separate aggregates and that chirality is absent in the P3HT aggre-

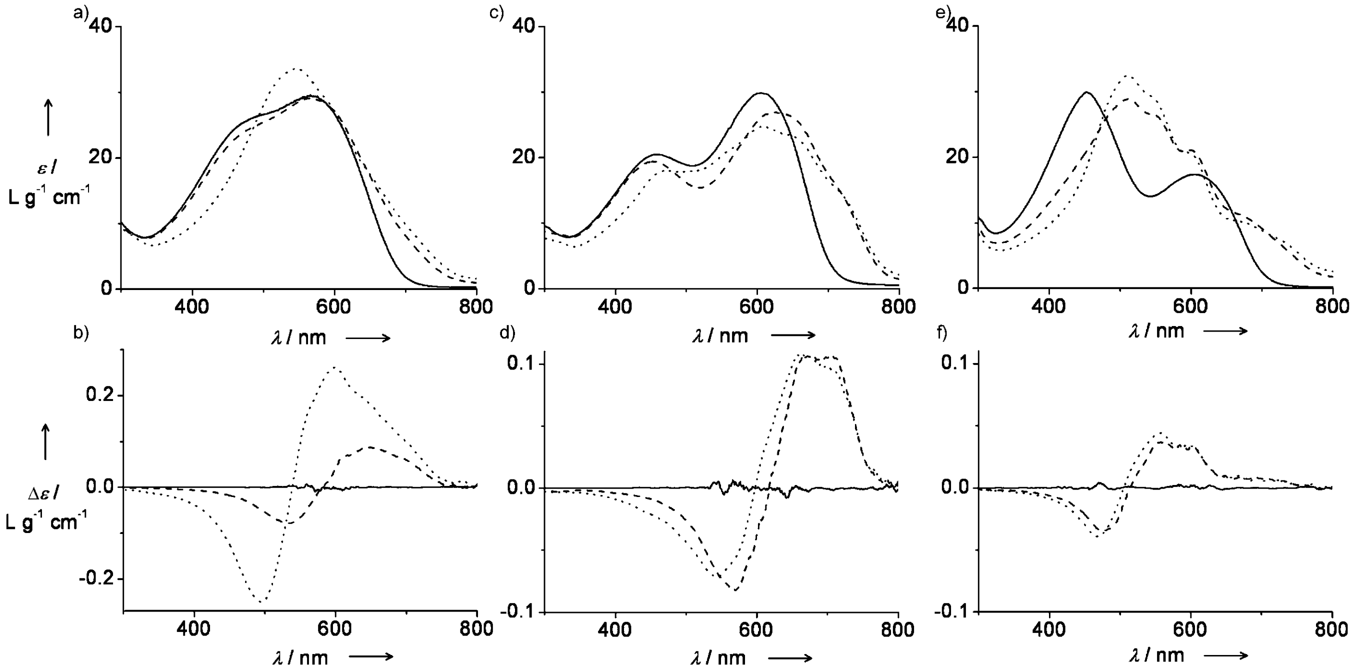

Figure 1. UV/Vis and CD spectra of P3HT-*b*-P3OOT (a, b), a blend of $P3HT_3$ ($c = 74\ mg\,L^{-1}$) and P3OOT ($c = 40\ mg\,L^{-1}$) (c, d), and a blend of $P3HT_4$ ($c = 29\ mg\,L^{-1}$) and P3OOT ($c = 24\ mg\,L^{-1}$) (e, f). (0 % methanol (——), 30 % methanol (-----), 60 % methanol (•••••)).

gates 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 sergeant-and-soldiers behavior is present.[13] To investigate whether this is also the case for P3HT–P3OOT blends or whether both polymers inherently segregate, the aggregation of $P3HT_4$ ($M_n = 4.1\ kg\,mol^{-1}$, 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 $P3HT_4$ and chiral P3OOT chains. On the other hand, the intensity is somewhat lower ($g_{abs,\,\lambda=550\ nm} = -1.5\times10^{-3}$), which may point to a more complicated stacking if the aggregates are composed of chains of a different nature. Importantly, the different behavior of the $P3HT_3$–P3OOT and $P3HT_4$–P3OOT blends again confirms the unique supramolecular behavior of the block copolymer.

In a subsequent 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 I_2 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, I_2-doped polythiophenes tend to dedope; the rate of reduction is dependent on the electronic nature of the polythiophene. Indeed, after five 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 dedoped much faster then

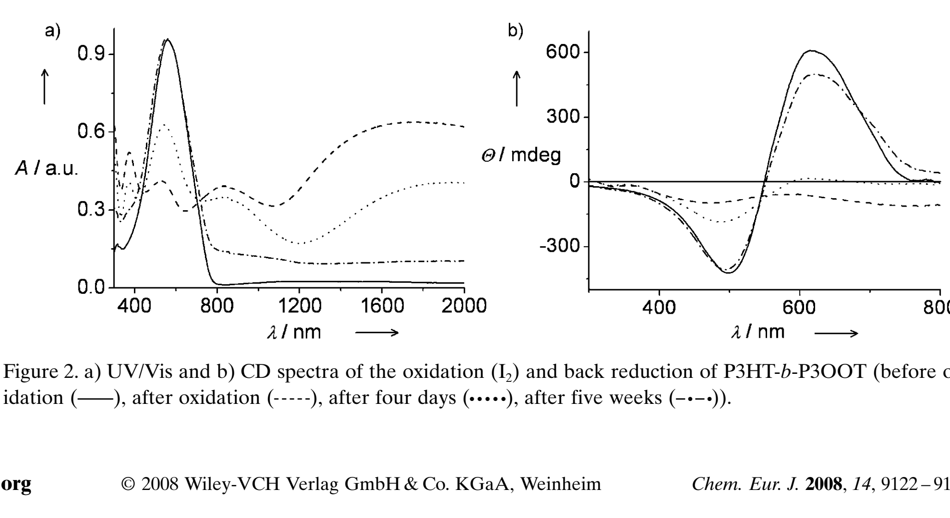

Figure 2. a) UV/Vis and b) CD spectra of the oxidation (I_2) and back reduction of P3HT-*b*-P3OOT (before oxidation (——), after oxidation (-----), after four days (•••••), after five weeks (–•–•)).

P3OOT, the P3HT block is reduced first, 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 after four days the spectra of P3HT-*b*-P3OOT are a combination of oxidized (chiral) P3OOT and neutral, chirally aggregated P3HT. This again demonstrates that the achiral P3HT block shows supramolecular chirality, which is 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 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 P3HT$_1$ 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 into a suspension of [NiCl$_2$(dppp)] (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) (P3HT$_1$). Compound **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 THF (3 mL)) 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 MgBr$_2$ (1.80 mmol, 0.331 g) in dry THF (4 mL) and stirred for another 30 min.

The homopolymers (P3OOT,[5] P3HT$_{2-4}$[9]) were prepared according to literature procedures.

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[12] Due to the rigid, rodlike conformation of poly(3-alkoxythiophene)s, a large overestimation of the molar mass by using GPC toward polystyrene standards can be expected. MALDI-TOF spectroscopy on the P3OOT homopolymer resulted in $M_n = 5\,\mathrm{kg\,mol^{-1}}$, $P_n = 20$, which corresponds rather well to the P3OOT block in the block copolymer.

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