Rational design of poly(fluorene)-*b*-poly(thiophene) block copolymers to obtain a unique aggregation behavior

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ABSTRACT

In poly(thiophene) (PT) block copolymers, aggregation features can be transferred from one block to the other. In this paper, it is investigated whether this is also possible in block copolymers consisting of blocks with different electronic properties, i.e. PT and poly(fluorene) (PF), in order to obtain a polymer with a unique combination of aggregation properties. By combining a PT block with chiral side chains with a PF block with a linear octyl side chain, it is probed to obtain a polymer in which chiral expression (arising from the PT with chiral side chains) and β -phase aggregation (arising from the PF with linear octyl side chains) are brought together. This combination is not possible in homopolymers, since chiral aggregation implies chiral, branched side chains and β -phase aggregation is only possible for PF with linear side chains. In a stepwise approach, the right conditions are elucidated to obtain both characteristics in one polymer. For this purpose, three block copolymers were synthesized via Suzuki catalyst transfer condensative polymerization (SCTCP), i.e. poly(9,9-dioctylfluorene)-*b*-poly(3-((*S*)-3,7-dimethyloctyl)thiophene) (**POF-*b*-P3OT***), poly(9,9-dihexylfluorene)-*b*-poly(3-((*S*)-3,7-dimethyloctyl)thiophene) (**PHF-*b*-P3OT***) and poly(9,9-dioctylfluorene)-*b*-poly(3-((*S*)-2-methylbutyl)thiophene) (**POF-*b*-P3BT***), and their aggregation behavior is studied via solvatochromism experiments. It is concluded that the side chains of the PF block should be 8 C-atoms long to ensure maximal β -phase aggregation and that the side chains of the PT block should be short to ensure this block aggregates first in a chiral way. In this way, the PT block can transfer its chirality to the PF block and a polymer is obtained in which β -phase aggregation and expression of chirality are combined in one PF, something which is impossible for homopolymers.

Introduction

Conjugated polymers are promising materials towards a wide variety of applications, e.g. photovoltaic cells and organic light-emitting diodes.¹⁻⁵ While the fine-tuning of the chemical structure of the polymers can lead to improved properties, also the morphology is of utmost importance for the final characteristics of the material.⁶⁻⁸ In applications different types of conjugated polymers, e.g. donor and acceptor polymers, are usually necessary and to avoid problems related to phase separation in blends, block copolymers can be a good alternative.⁹⁻¹² In fact, due to the covalent bond between the different polymer blocks, only microphase separation can occur. This can give rise to special morphologies, which cannot be obtained via (blends of) homopolymers, and even enhanced properties.^{13,14} Moreover, as the different polymer blocks are covalently bonded to each other, not only can they influence each other's properties more easily than in polymer blends, one polymer block can also transfer its properties to another one. A well-known example is the aggregation behavior of PT block copolymers.¹⁵⁻²² In these block copolymers, the block that aggregates first imposes its structure on the second block. For example, if the first aggregating block has chiral side chains, it aggregates in a chiral way and the block that aggregates secondly will aggregate in the same manner, independently of the (a)chirality of its side chains. As such, the first block introduces features in the second block that are not possible in any other way. This principle is already observed many times, but always in block copolymers built up from monomeric units that have similar electronic properties and aggregate in the same way, i.e. thiophene and thiophene or thiophene and selenophene units.^{15-17,23}

In this research, it is investigated whether it is also possible to transfer aggregation properties to polymers with different electronic properties, e.g. PT and PF.³⁻⁵ The aggregation behavior of

PTs is already well described in literature and depending on the (a)chirality of the side chains, linear or helical stacks of planarized PTs are obtained upon aggregation.^{24,25} The aggregation behavior of PFs is less documented, but it is accepted that there are three types, i.e. α -, α' - and β -phase.^{26–30} In the α - and α' - phase the PF chains aggregate in twisted ribbons (5_2 helices) and this is possible for PFs with all types of side chains. However, the β -phase is only possible for PFs with linear octyl (and to a lesser extent heptyl and nonyl) side chains and is obtained when the PF chains aggregate in flat ribbons (2_1 helices).³¹ Therefore, it is never possible to design a homopolymer in which chirality is combined with β -phase aggregation, as chirality implies branched side chains and this is not compatible with β -phase aggregation. However, it is hypothesized that *block copolymers* can be designed in which these properties can be united, since they can exhibit properties other than the sum of the properties of the homopolymers. By combining *PTs with short, chiral side chains* and *PFs with linear octyl side chains*, it is probed to create a polymer in which chiral expression (arising from the PT with chiral side chains) and β -phase aggregation (arising from the PF with linear octyl side chains) are brought together. It is hypothesized that the side chains of the PTs should be short to ensure this block aggregates first in a chiral way (in order to transfer its chirality to the PF block) and that the side chains of the PFs should be 8 C-atoms long to ensure maximal β -phase aggregation.

Results and discussion

In order to validate these hypotheses, three different block copolymers were synthesized, i.e. **POF-*b*-P3OT***, **PHF-*b*-P3OT*** and **POF-*b*-P3BT*** (Figure 1). The aggregation behavior of the first block copolymer was investigated to confirm that the chiral side chain of the thiophene units must be short in order to obtain an aggregation of the PT block prior to the PF block. The second

block copolymer was synthesized in order to validate that the side chains of the fluorene units must be 8 C-atoms long in order to enable β -phase aggregation of the PF block. The final block copolymer was synthesized to confirm that, by choosing the right side chains, chiral expression and β -phase aggregation can be combined in one polymer and that block copolymers can be designed in such a way that they display properties that can never be achieved with homopolymers.

Figure 1: Representation of the synthesized block copolymers.

For the synthesis of the block copolymers, the SCTCP was chosen (Scheme 1). For this polymerization, the controlled character was already demonstrated for PFs^{32–34} as well as for PTs^{34–36} and is therefore ideal to synthesize the predefined block copolymers. Due to the controlled character of the polymerization, sequential monomer addition can be used to obtain block copolymers, but because the blocks are built up from monomers with different electronic properties, the order of the monomer addition is important. During the polymerization, the strength of the complexation of the catalytic species to the growing polymer chain must always increase or remain the same. So only when the most electron rich monomer is polymerized last, block copolymers are obtained.^{37–40} Applied to the proposed systems, this means that the

fluorene monomer must be polymerized before the thiophene monomer.^{41,42} It was chosen to synthesize block copolymers in which the PT block has (approximately) double the number of monomer units compared to the PF block. In this way, the two blocks will be comparable in length, since the fluorene monomer is of approximately the double length of the thiophene monomer. In order to be able to determine the chain length of the synthesized polymers and to prevent the formation of BAB block copolymers due to random catalyst walking^{17,43,44}, external initiator **2** was used (Scheme 1). It was generated *in situ* from the commercially available palladacycle **1** and 4-bromotoluene.³² The latter was chosen for two reasons. First, to enable the determination of the degree of polymerization via ¹H NMR and second, to obtain an endgroup that resembles the adjacent monomer units. This is important since endgroups have severe implications on the properties of the adjacent blocks.²⁰ For this reason, also endcappers that resemble the adjacent monomer units were chosen to minimize their influence on the aggregation behavior of the block copolymer. Therefore, the block copolymers were endcapped with **4**. However, a small fraction of the polymerization mixture was also endcapped with **3** before the second monomer was added. In this way, the poly(fluorene) block could be analyzed separately.

Scheme 1: Representation of the block copolymerization.

The monomers that were used for the synthesis of the polymers were synthesized according to adapted literature procedures (Scheme 2).⁴⁵ For the first step in the conversion of **5a** and **5b** to **6a** and **6b**, tri(*tert*-butyl)magnesium lithium·lithium chloride ($((t\text{Bu})_3\text{MgLi}\cdot\text{LiCl})$) was used instead of *isopropyl*magnesiumchloride·lithium chloride ($i\text{PrMgCl}\cdot\text{LiCl}$), because the conversion with the latter is not complete, leading to lower yields.⁴⁵ Since boronic esters are preferred over boronic acids for stability reasons, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added in the second step, leading to the final monomers.⁴⁶ For the first step in the conversion of **7a** and **7b** to **8a** and **8b** $i\text{PrMgCl}\cdot\text{LiCl}$ was used, because for 2-bromo-5-iodo-3-alkylthiophene compounds complete conversion can be obtained with this reagent.⁴⁷

Scheme 2: Reaction scheme for the monomer synthesis.

As mentioned above, all polymers were synthesized via SCTCP (Scheme 1) and for **POF-*b*-P3OT**, **PHF-*b*-P3OT*** and **POF-*b*-P3BT*** monomers **6a** and **8a**, **6b** and **8a** and **6a** and **8b** were used, respectively. As can be derived from the GPC (gel permeation chromatography) elution chromatograms, not all polymer chains grew upon addition of the second monomer (Figure S1-S3). To ensure that only the aggregation behavior of the block copolymers was studied, and not that of a mixture of block copolymers, homopolymers and monomers, the synthesized materials were purified via Soxhlet extraction and preparative GPC. After the purification, a GPC analysis was performed at the wavelength of maximal absorbance for the PF (380 nm) and PT (440 nm) block (Figure S1-S3). Based on mixtures of **POF-*b*-P3BT*** and **POF** with decreasing percentage of **POF**, amounts as low as 1.25% of homopolymer can be detected via this technique (Figure S14). Since both curves overlap completely for each block copolymer, it can be concluded that no contamination with homopolymer is present after the purification. The M_n and $\bar{D}$ for all the polymers can be found in Table 1. ^1H NMR was used to determine the length of each block separately (Figure 2 and Figure S4-S5). The methylene group of the initiator (A) was used to calibrate the integration values and the degree of polymerization (DP) was calculated based on the β - and α -methylene protons of the side chains of the fluorene (B) and thiophene (C) monomer unit, respectively. The obtained DP for each block can also be found in Table 1.

Although the polymerization was not completely controlled, the aimed ratio of one fluorene monomer towards two thiophene monomers was still approximately retained. Also, the degree of polymerization of the PF and PT blocks were similar for the different polymers. Only the PT block of **PHF-*b*-P3OT*** is somewhat larger, but this poses no problem, as will be explained later on.

Figure 2: Determination of degree of polymerization for **POF-*b*-P3OT***.

Table 1: Overview of the number average molar mass, dispersity and degree of polymerization of the separate blocks of the synthesized block copolymers.

	M_n (kg/mol) ¹	$\bar{D}$ ¹	DP PF block ²	DP PT block ²
POF-<i>b</i>-P3OT*	11.7	1.2	10	17
PHF-<i>b</i>-P3OT*	21.3	1.1	11	27
POF-<i>b</i>-P3BT*	13.9	1.1	9	18

¹ M_n and $\bar{D}$ are calculated with GPC calibrated towards polystyrene standards.

² DP was calculated with ¹H NMR.

The aggregation behavior of the polymers was studied via solvatochromism experiments, whereby the polymer was dissolved in a good solvent, chloroform, and gradually more poor solvent, methanol (MeOH), was added to induce aggregation. The hypothesis that was tested was that the chiral PT block must aggregate first to be able to transfer its chirality to the PF block. With **POF-*b*-P3OT*** the opposite behavior was provoked, as the branched side chains in the PT

block increase the solubility of this block compared to the PF block, not taking differences in rigidity of the polymer backbone into account. This is confirmed by the solvatochromism experiments (Figure 3). The first event is the aggregation of the PF block (39% MeOH), visible in the absorption spectrum (A) by the decreasing signal around 380 nm and the appearance of a signal around 430 nm, which can be attributed to β -phase aggregation.^{48,49} No signal is yet visible in the circular dichroism (CD) spectrum (B), which was expected since the PF block has no chiral side chains. When more MeOH is added, also the PT block starts to aggregate (42% MeOH), visible by the increasing signal in the region between 500 and 700 nm in the absorption spectrum and the appearance of a bisignate signal in the same region in the CD spectrum. No chiral expression for the PF block is obtained, because the PT cannot enforce its chirality onto the PF block without breaking the previously formed achiral PF aggregates. From the behavior of this polymer, it can be concluded that the chiral PT block must aggregate first in order to be able to transfer its chirality to the PF block.

Figure 3: Absorption (A) and CD (B) spectra of the solvatochromism experiments for **POF-*b*-P3OT***. The complete data set can be found in Figure S8 and S9.

To verify the second hypothesis - the linear side chains of the PF block must be 8 C-atoms long to allow β -phase aggregation - the aggregation behavior of **PHF-*b*-P3OT*** was studied. As

can be derived from Figure 4, the same sequence of aggregation events in the solvatochromism experiment can be distinguished for **PHF-*b*-P3OT*** as for **POF-*b*-P3OT***. First, the PF block starts to aggregate (35% MeOH), visible in the absorption spectrum (A) by the decrease and broadening of the signal around 380 nm. Upon the addition of more MeOH (from 39% MeOH), also the PT block aggregates, visible by the increasing signal and appearance of fine structure between 500 nm and 700 nm in the absorption spectrum and by the appearance of a bisignate signal in the same region in the CD spectrum (B). However, no extra signal around 430 nm was observed upon the aggregation of **PHF-*b*-P3OT***, indicating that no β -phase aggregation occurred. This confirms the hypothesis that the length of the linear side chains on the fluorene units matters to obtain β -phase aggregation, as is the case for PF homopolymers.³¹ As mentioned above, the degree of polymerization is slightly higher for this polymer compared to the others, but this should not pose a problem since the sequence of aggregation events was still the same as intended.

Figure 4: Absorption (A) and CD (B) spectra of the solvatochromism experiments for **PHF-*b*-P3OT***. The complete data set can be found in Figure S10 and S11.

With the first two block copolymers, the formulated hypotheses were tested in a negative way (what would happen if the criteria are not met), but this forms no complete proof for the validity

of these hypotheses. Therefore, the aggregation behavior of the third block copolymer **POF-*b*-P3BT*** was studied. In this polymer, the two previous hypotheses were merged. It combines short and chiral side chains for the PT block, ensuring that this is the least soluble block, with linear octyl side chains for the PF block, allowing maximal β -phase aggregation. In the solvatochromism experiments for this block copolymer, the first signs of aggregation are visible upon the addition of 33% of MeOH (Figure 5). In the absorption spectrum (A) an increase of the signal between 450 and 650 nm, combined with a small decrease of the signal around 390 nm from 0% to 33% MeOH, is visible, indicating aggregation of the PT block. The appearance of a bisignate signal in the same region in the CD spectrum (B) confirms this. When gradually more MeOH is added up to 37%, the PT block is almost fully aggregated and the characteristic signal for β -phase aggregation of the PF block, a sharp peak at 430 nm, starts to appear in the absorption spectrum. This is accompanied by the appearance of a bisignate and monosignate signal for the PF block in the CD spectrum. This points towards a different type of aggregation behavior than is already observed for PF homopolymers. For α -phase aggregated PF (Figure 6A) and for β -phase aggregated PF (Figure 6B), a monosignate signal and no CD signal is anticipated, respectively. The sharp monosignate signal at 430 nm points towards a helical transition dipole moment perpendicular to the polymer backbones, indicating that the different polymer backbones are closely stacked in a helical manner (Figure 6C). This is possible in the β -phase, because the polymer backbone is planar and the side chains can intertwine. The bisignate Cotton effect arises from the helical orientation of transition dipole moments along the polymer backbones of (at least two) PF blocks, confirming the helical stacked structure for the PF blocks. This shows that the PT block is able to transfer its chirality and alter the aggregation behavior of the PF block. Surprisingly, a shift towards a more monosignate signal in the PT region is visible

in the CD spectrum, showing that not only does the PT block influence the aggregation behavior of the PF block, but also that the PF block influences the supramolecular structure of the aggregated PT block. The aggregation behavior of this block copolymer proves that it is possible to design block copolymers in such a way that properties can be combined, in this case a β -phase aggregation and chiral expression of PFs, which could never be obtained together with only homopolymers.

Figure 5: Absorption (A) and CD (B) spectra of the solvatochromism experiments for **POF-*b*-P3BT***. The complete data set can be found in Figure S12 and S13.

Figure 6: Representation of the packing of PF chains in the α -phase (A), β -phase (B) and helical stacks in **POF-*b*-P3BT*** (C). For the clarity in this schematic drawing, the side chains are omitted and only the PF backbone is represented, whereby C atoms are drawn in green and H atoms in blue.

Conclusions

Three different conjugated PF-*b*-PT copolymers were synthesized via SCTCP and characterized via GPC and ¹H NMR spectroscopy. The aggregation behavior of the synthesized polymers was studied via solvatochromism experiments in order to confirm the hypothesis that block copolymers can be designed to exhibit a set of properties which cannot be achieved in homopolymers by transferring properties of one block to the other. The set of properties chosen in this research was chiral expression and β -phase aggregation of PFs and it was probed that those could be combined in PF-*b*-PT copolymers with linear side chains for the PF block (allowing β -phase aggregation) and chiral side chains for the PT block (allowing chiral expression). A stepwise approach was chosen to confirm the hypothesis. With the aggregation behavior of **POF-*b*-P3OT***, it was elucidated that if the chiral PT block does not aggregate first, it cannot transfer its chirality to the PF block. With the aggregation behavior of **PHF-*b*-P3OT***, it was confirmed that not just any linear side chain can be used for the PF block to obtain β -phase aggregation. In the last polymer, **POF-*b*-P3BT***, those two conditions were successfully combined and a polymer was obtained in which chiral expression and β -phase aggregation of PFs were combined. This proves the possibility to design block copolymers in such a way that they can exhibit properties that transcend the properties of the homopolymers that they consist of, by transferring properties of one block to the other. Further research will be done to determine whether also other properties can be transferred and whether this can also be the case in block copolymers consisting of other monomeric units other than thiophene and fluorene.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Materials and instrumentation; experimental procedures; determination of the degree of polymerization; additional GPC elution chromatograms; additional absorption and CD spectra; ^1H NMR spectra of the monomers and polymers, ^{13}C NMR spectra of new compounds (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CD, circular dichroism; DP, degree of polymerization; GPC, gel permeation chromatography; MeOH, methanol; PFs, poly(fluorene)s; PTs, poly(thiophene)s; **PHF-*b*-P3OT***, poly(9,9-dihexylfluorene)-*b*-poly(3-((*S*)-3,7-dimethyloctyl)thiophene); **POF-*b*-P3BT***, poly(9,9-dioctylfluorene)-*b*-poly(3-((*S*)-2-methylbutyl)thiophene); **POF-*b*-P3OT***, poly(9,9-dioctylfluorene)-*b*-poly(3-((*S*)-3,7-dimethyloctyl)thiophene); SCTCP, Suzuki catalyst transfer condensative polymerization; (*t*Bu)₃MgLi·LiCl, tri(*tert*-butyl)magnesium lithium·lithium chloride.

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Rational design of poly(fluorene)-*b*-poly(thiophene) block copolymers to obtain a unique aggregation behavior

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