The influence of the sequence in conjugated triblock copolymers on their aggregation behavior

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ABSTRACT

Conjugated diblock copolymers can exhibit very promising properties, often based on microphase separation. However, both blocks can influence each other's aggregation behavior, which might lead to a suboptimal aggregation behavior of the consecutive blocks. Herein, we investigate whether the introduction of a third, non-aggregating block can render triblock copolymers where the two blocks do not influence the aggregation behavior of one another. Different triblock copolymers consisting of solely thiophene units, as well as triblock copolymers containing selenophene and (a)chiral thiophene units were designed to investigate the influence of the sequence of the blocks, the initiating unit and the non-aggregating block on the aggregation behavior of the resulting triblock copolymers. The conjugated triblock copolymers were synthesized via a controlled Kumada catalyst transfer condensative

polymerization (KCTCP) and their aggregation behavior was investigated via UV-vis and circular dichroism (CD) spectroscopy. For all synthesized polymers it was observed that when two aggregating blocks are separated from each other by a non-aggregating block, they do not influence each other's aggregation behavior and aggregate separately. However, when the two aggregating blocks are situated next to each other, they influence each other's aggregation behavior strongly and aggregate as one block.

Introduction

Conjugated polymers can be used for a wide variety of applications, for example organic photovoltaics (oPVs).¹ Besides their electronic properties, also their aggregation behavior is very important and can determine whether or not a specific polymer can be used. For oPVs, usually two types of conjugated polymers are necessary and in the past, just a blend of the desired homopolymers was used.^{2,3} Due to their different (electronic) properties, those blends often phase separate, possibly resulting in suboptimal conditions for applications. Later on, diblock copolymers of the necessary conjugated polymers were designed to tackle this problem.^{4,5} These polymers exhibit microphase separation instead of phase separation and this can even enhance the properties of the material.⁶ A possible downside of these conjugated diblock copolymers is that the adjacent blocks can affect each other's aggregation behavior, again resulting in a possible suboptimal aggregation behavior of each block. This change in aggregation behavior was for example demonstrated in diblock copolymers of poly(3-alkylthiophene)s (P3ATs) and poly(3-alkoxythiophene)s (P3AOTs).^{7,8}

In this paper, a possible solution to combine the microphase separation, observed in diblock copolymers, with the unaffected aggregation behavior of each block, observed in a blend of

homopolymers, is explored. For this purpose, triblock copolymers are designed containing two aggregating blocks and one non-aggregating block. By separating the aggregating blocks by a non-aggregating block, we aimed to exclude the influence of both blocks on each other. As a reference, also the triblock copolymers with the aggregating blocks next to each other were included in this research. The polymers were synthesized via a controlled KCTCP and, for the first time, the aggregation behavior of conjugated triblock copolymers was characterized via UV-vis and CD spectroscopy.

Results and discussion

To study the influence of the sequence of the blocks, triblock copolymers were designed consisting of two aggregating blocks (A and B) and one non-aggregating block (C). To rule out all the other influences, four combinations need to be prepared, namely ACB, BCA, CAB and CBA. Both ACB and BCA have the aggregating blocks at the two terminal sites and those are separated from each other by the non-aggregating block. As KCTCP with an external initiator will be used for the synthesis of the triblock copolymers, *vide supra*, an initiating group will be present at the beginning of the polymer chain. However, this group can influence the aggregation behavior of the adjacent block.⁹ To eliminate the influence of this end group, ACB and BCA will be compared to each other. In CAB and CBA the initiating group is placed next to the non-aggregating block. In this way it will not influence the aggregation behavior and the reverse combinations are not necessary. Since both aggregating blocks are situated next to each other in these combinations, the comparison of CAB and CBA reveals whether the non-aggregating block also influences the adjacent block or that the location in the middle rather than at the end is important. When ACB and BCA are compared towards CAB and CBA, it can be investigated

whether the aggregating blocks influence each other differently when they are separated from or placed next to each other.

KCTCP is used for the synthesis of the triblock copolymers. Via this controlled chain growth polymerization well-defined diblock copolymers can be synthesized⁷ and an external initiator ensures that only unidirectional growth is possible¹⁰. The first series of triblock copolymers consists of only thiophene based polymers. For those polymers it is known that they can be incorporated in multiblock copolymers in a controlled way.¹¹ Poly(3-dodecylthiophene) (P3DT) and poly(3-hexylthiophene) (P3HT) were chosen as aggregating blocks (A and B) and poly(3-(2-octyldodecyl)thiophene) (P3ODT) as non-aggregating block (C). P3DT and P3HT aggregate in the same manner when the aggregation is induced by the gradual addition of a poor solvent, since they are both thiophene based, but the aggregation of P3DT will take place at a higher percentage of poor solvent compared to P3HT due to the larger side chain. P3ODT is not able to aggregate because of the large steric hindrance of the side chain.¹¹ The four synthesized combinations and the polymerization scheme are represented in Scheme 1. Since a controlled chain growth polymerization is used, the monomers can be added sequentially, resulting in well-defined triblock copolymers. Each monomer was polymerized during 1 hour in order to ensure all monomer was built in, but no termination could occur. For each block, a block length of 20 units is attempted by choosing the monomer over initiator ratio equal to 20. In this manner the total degree of polymerization is low enough to ensure the controlled character of the polymerization, but the block length is high enough to allow aggregation of the separate blocks.

Scheme 1. A) Representation of the synthesized thiophene based triblock copolymers. B) Polymerization scheme shown for **P1**.

The otolyliinitiator (**2**) used in the polymerization was prepared in situ from **1** by a ligand exchange with 2 equivalents of 1,3-bis(diphenylphosphino)propane (dppp)¹² and monomers **3**¹³, **4**¹¹ and **5**¹⁴ were synthesized according to literature procedures. From the elution curves for the four polymerizations, shown in Figure 1, it can be derived that all the polymers were able to perform a chain extension twice. To ensure that the final triblock copolymers are not contaminated with homopolymers or diblock copolymers, they were purified via a Soxhlet

extraction and preparative gel permeation chromatography (GPC). The chromatograms after purification can be found in Figure S10.

Figure 1. GPC elution curves for **P1** (A), **P2** (B), **P3** (C) and **P4** (D). a and b are used to indicate the polymer after polymerization of respectively the first and second monomer.

The purified polymers were characterized by GPC analysis to estimate the number average molar mass ($\bar{M}_n$) and dispersity ($\bar{D}$) and via ^1H NMR analysis to determine the total degree of polymerization (DP) (Table 1). The latter can be calculated from the integration of the methyl protons of the initiating *o*-tolyl unit compared to the integration of the α -methylene protons of the thiophene units (Figure 2 for **P1**, Figure S1-S3 for **P2**, **P3** and **P4**).

This procedure can be used since only the signal arising from H-terminated thiophene units is present and no signal from Br-terminated thiophene units.⁸ This implies that no transfer nor termination occurred during the polymerization and that every polymer chain has an *o*-tolyl unit and a H-terminated thiophene unit at the chain ends. The degree of polymerization of the separate blocks could not be calculated, since as well the aliphatic as the aromatic signals of the different blocks overlap.

Table 1. Overview of the results of the GPC ($\bar{M}_n$ and Đ) and ^1H NMR (DP) analysis for **P1**, **P2**, **P3** and **P4** after purification.

	$\bar{M}_n$ (kg/mol)	Đ	DP
P1	18	1.08	58
P2	22	1.07	63
P3	21	1.07	56
P4	25	1.08	68

Figure 2. Assignment of ^1H NMR signals in the aliphatic region in order to determine the total degree of polymerization for **P1**.

In order to unravel the influence of the sequence of the blocks on the aggregation behavior in the synthesized triblock copolymers, solvatochromism experiments were conducted (the most relevant data can be found in Figure 3, the complete data set in Figure S15-S18). The polymers were dissolved in a good solvent (CHCl_3) and gradually a poor solvent (methanol (MeOH)) was added. Clear differences can be seen between the polymers where the aggregating blocks are separated from each other (**P1** and **P2**) and the polymers where the aggregating blocks are situated next to each other (**P3** and **P4**). First, a difference in shape of the absorption spectrum of the aggregated polymers (46% MeOH) can be observed. For **P3** and **P4**, the fine structure in the absorption band of the aggregated polymers is much more pronounced compared to **P1** and **P2**. Second, the onset of aggregation is postponed for **P1** (31% MeOH) and **P2** (29% MeOH) compared to **P3** (24% MeOH) and **P4** (24% MeOH). Both observations are an expression of the same feature. The higher the molar mass of P3ATs, the less soluble they are and the more fine structure is present in the absorption spectrum upon aggregation. Therefore, we hypothesize that when the aggregating blocks are separated from each other, they will also aggregate separately and behave like a block of approximately 20 units in terms of solubility and fine structure. However, when the aggregating blocks are situated next to each other, they will behave as one block of double length, resulting in a lower solubility and more fine structure in the absorption spectrum upon aggregation. The presence of a clear isosbestic point for the absorption spectra of **P3** and **P4**, and the lack thereof for **P1** and **P2**, support this hypothesis, since this indicates that only one type of aggregates is formed for **P3** and **P4** and two (or more) (slightly) different types of aggregates for **P1** and **P2**. Because the aggregation behavior of **P1** is similar to **P2** and that of **P3** similar to **P4**, the influence of respectively the otolyl functionality and the non-aggregating block is negligible for these polymers.

Figure 3. Absorption spectra of the solvatochromism experiments for **P1** (A), **P2** (B), **P3** (C) and **P4** (D).

To investigate whether these principles are also valid for triblock copolymers not solely consisting of thiophene monomers, a new series of triblock copolymers was designed. As aggregating blocks (A and B) poly(3-octylselenophene) (P3OSe) and P3HT were chosen and the non-aggregating block (C) was again P3ODT (Scheme 2). The P3OSe was selected because it can be synthesized via KCTCP in a controlled manner, like P3ATs, leading to well-defined triblock copolymers.¹⁵ Also, it shows a similar aggregation behavior as P3HT, but a different absorption spectrum upon aggregation.^{16,17} In this way, the blocks will be able to aggregate together (or separately) and the aggregation events can be more easily monitored via UV-vis spectroscopy.

Scheme 2. Representation of the synthesized triblock copolymers containing a P3OSe block.

P5, **P6**, **P7** and **P8** were synthesized under the same conditions as the previous triblock copolymers and the newly incorporated monomer 2-bromo-5-magnesiochloro-3-octyl selenophene **6** was synthesized via literature procedures¹⁸. From the elution curves for the four polymerizations, shown in Figure 4, it can be derived that most of the polymers were able to perform a chain extension twice. Only for **P5** dead chains of the first block are clearly present. This loss of control over the polymerization can be attributed to the gelation of the P3OSe homopolymer, which resulted in the fact that only intensive shaking was sufficient to mix the polymerization mixture. This, on its turn, resulted in polymer chains sticking at the sides of the polymerization tube, which were not able to grow any further. However, this poses no problem, since all the final triblock copolymers were purified via a Soxhlet extraction and preparative GPC. The chromatograms after purification can be found in Figure S11. To ensure that no homopolymers or diblock copolymers are present after the purification, GPC analysis was performed at the wavelength of maximal absorbance for P3AT (440 nm) and P3OSe (490 nm) (Figure S12). Since both curves overlap completely for each polymer, it can be concluded that only the triblock copolymers are present after purification.

Figure 4. GPC elution curves for **P5** (A), **P6** (B), **P7** (C) and **P8** (D). a and b are used to indicate the polymer after polymerization of respectively the first and second monomer.

The purified polymers were further characterized by GPC analysis to estimate $\bar{M}_n$ and dispersity and via ^1H NMR analysis to determine the total DP and DP of each block (Table 2). The total DP is determined based on the integration of the α -methylene protons of the three blocks compared to the methyl protons of the initiating *o*-tolyl unit (Figure 5 for **P5**, Figure S4-S6 for **P6**, **P7** and **P8**). The DP of each block can roughly be calculated from the integration of the methyl protons of the initiating *o*-tolyl unit compared with the integration of the aromatic signal of the thiophene and selenophene units (Figure 5 for **P5**, Figure S4-S6 for **P6**, **P7** and **P8**). When the total DP, obtained via the aliphatic signals, and the sum of the DPs of each block, obtained via the aromatic signals, are compared, it can be seen that they completely concur.

Table 2. Overview of the results of the GPC ($\bar{M}_n$ and Đ) and ^1H NMR (DP) analysis for **P5**, **P6**, **P7** and **P8** after purification.

	$\bar{M}_n$ (kg/mol)	Đ	Total DP	DP P3OSe	DP P3ODT	DP P3HT
P5	18	1.13	58	20	19	19
P6	18	1.07	60	19	20	21
P7	19	1.08	61	21	21	19
P8	18	1.07	59	14	20	25

Figure 5. Assignment of ^1H NMR signals in the aliphatic and aromatic region in order to determine the total degree of polymerization and the degree of polymerization of each block for **P5**.

For the second series of triblock copolymers, the same solvatochromism experiments were conducted as for the first series in order to investigate if the aggregation behavior is changed upon the introduction of a P3OSe block (the most relevant data can be found in Figure 6, the complete data set in Figure S19-S22). The polymers were dissolved in a good solvent (CHCl_3) and gradually a poor solvent (MeOH) is added. Unlike the first series of triblock copolymers, no

clear difference can be observed for **P5** and **P6** compared to **P7** and **P8**. The onset of aggregation and the amount of MeOH needed to reach the maximal aggregation are for all polymers almost the same. The only small difference that is visible is situated around 700 nm. At this wavelength, P3OSe homopolymers have a characteristic peak that originates from π -stacking¹⁶ and only for **P5** and **P6**, in which the P3OSe block is separated from the P3HT block, this is clearly visible. This could point into the direction of the previously postulated hypothesis that when the aggregating blocks are separated from each other, they also aggregate separately. However, when the aggregating blocks are situated next to each other, they aggregate together. This result might seem contradictory to previous literature, where it was described that diblock copolymers of poly(3-alkylselenophene) (P3ASe) and P3AT exhibit microphase separation.^{15,16,19} However, this result was obtained for (annealed) polymer films and a recent publication describes the possibility of cocrystallization for P3ASe-*b*-P3AT when no annealing is applied.²⁰ During the solvatochromism experiments described here, no annealing is performed and cocrystallization is possible. For the polymers where the aggregating blocks are situated next to each other, the absence of a clear peak around 700 nm of P3OSe can be explained by cocrystallization. The resulting polymer crystals will exhibit intermediate characteristics of the two polymers, resulting in a less pronounced peak around 700 nm.

Figure 6. Absorption spectra of the solvatochromism experiments for **P5** (A), **P6** (B), **P7** (C) and **P8** (D).

Unfortunately UV-vis spectroscopy solely is not sufficient to completely elucidate the aggregation behavior of triblock copolymers containing a P3OSe block. Therefore, a second, widely used technique to study the aggregation behavior of conjugated polymers, namely CD spectroscopy, will be used.²¹ In order to use this technique, chiral centers must be present. Therefore a new series of triblock copolymers was designed, containing a poly(3-((*S*)-2-methylbutyl)thiophene) (P3BT*) and a P3OSe block as aggregating blocks and a P3ODT block as non-aggregating block (Scheme 3). The aggregating thiophene block (and not the selenophene block) was chosen to be chiral, since, based on the aggregation behavior of the homopolymers and diblock copolymers, it is expected that, if the blocks aggregate separately, the P3OSe block will aggregate first.^{16,17} In this way, a clear distinction can be made whether the aggregating

blocks aggregate separately or together. When they aggregate separately, first a red shift in the absorption spectrum will be visible, indicating that the achiral P3OSe block aggregates, and at a later stage a CD signal will arise, indicating the aggregation of the chiral P3BT* block. However, when the blocks aggregate together, the red shift in the absorption spectrum and the appearance of a CD signal will take place at once.

Scheme 3. Representation of the synthesized triblock copolymers containing a chiral P3BT*, an achiral P3ODT and P3OSe block.

P9, **P10**, **P11** and **P12** were synthesized under the same conditions as the previous triblock copolymers and the newly incorporated monomer 2-bromo-5-magnesiochloro-3-((*S*)-2-methylbutyl)thiophene **7** was synthesized via literature procedures²². From the elution curves for the four polymerizations, shown in Figure 7, it can be derived that most of the polymers were able to perform a chain extension twice. To overcome the solubility problems associated with the P3OSe block that occurred in the second series of triblock copolymers, the monomer concentration was halved. By this measure, no gelation occurred during the synthesis of **P9**, resulting in a more controlled character of the polymerization. For **P11** and **P12** a small amount of termination is visible, but this poses no problem for the further experiments, since all the final triblock copolymers were purified via a Soxhlet extraction and preparative GPC. The

chromatograms after purification can be found in Figure S13. The GPC analysis at the wavelength of maximal absorbance for P3AT (440 nm) and P3OSe (490 nm) shown that only the triblock copolymers were present after purification (Figure S14).

Figure 7. GPC elution curves for **P9** (A), **P10** (B), **P11** (C) and **P12** (D). a and b are used to indicate the polymer after polymerization of respectively the first and second monomer.

The purified polymers were further characterized by GPC analysis to estimate the $\bar{M}_n$ and dispersity. ^1H NMR analysis was used to determine the total DP and DP of each block and the same method was used as for **P5-P8** (Table 3). The assignment of the aromatic and aliphatic protons for **P9** can be found in Figure 8 (Figure S7-S9 for **P10**, **P11** and **P12**). When the total DP, obtained via the aliphatic signals, and the sum of the DPs of each block, obtained via the aromatic signals, are compared, it can be seen that the sum of the DP renders a slightly lower

value than the total DP. This discrepancy can be attributed to the slower relaxation of the aromatic protons compared to the aliphatic proton, resulting in a smaller integration value.

Table 3. Overview of the results of the GPC ($\bar{M}_n$ and $\bar{D}$) and ^1H NMR (DP) analysis for **P9**, **P10**, **P11** and **P12** after purification.

	$\bar{M}_n$ (kg/mol)	$\bar{D}$	Total DP	DP P3OSe	DP P3ODT	DP P3BT*
P9	20	1.06	61	18	19	19
P10	22	1.07	63	19	20	18
P11	21	1.08	60	23	13	21
P12	24	1.06	62	19	21	21

Figure 8. Assignment of ^1H NMR signals in the aliphatic and aromatic region in order to determine the total degree of polymerization and the degree of polymerization of each block for **P9**.

For the third series of triblock copolymers, as well UV-vis spectroscopy as CD spectroscopy was used to characterize the aggregation behavior during the solvatochromism experiments (most relevant data can be found in Figure 9, the complete data set in Figure S23-S30). Again a clear difference can be observed between the triblock copolymers with the aggregating blocks separated (**P9** and **P10**) and the aggregating blocks next to each other (**P11** and **P12**). For **P9** and **P10**, the red shift in the absorption spectrum starts at 27% of MeOH, although a CD signal is only visible from 35% of MeOH. This indicates that, when the aggregating blocks are separated by the non-aggregating P3ODT block, the P3OSe block aggregates first (at 27% of MeOH) and the P3BT* starts to aggregate later (at 35% of MeOH). In contrary, when the aggregating blocks are situated next to each other, as is the case for **P11** and **P12**, the red shift in the absorption spectrum and the appearance of a CD signal occur together at 19% of MeOH. As for the triblock copolymers consisting of solely thiophene monomers, the triblock copolymers with the aggregating blocks next to each other start to aggregate at a lower percentage of MeOH (19%) compared to the triblock copolymers with the aggregating blocks separated (27% of MeOH). This confirms again the hypothesis that when the aggregating blocks are placed next to each other, they aggregate as one block of double length, but when they are separated, they also aggregate separately. For **P11** also a blue shift of the zero crossing of the CD signal can be noted. This can be attributed to the gradually higher amount of thiophene units incorporated in the aggregates as the percentage of MeOH rises. The low CD signal of **P12** compared to the other polymers can be assigned to the relative position of the chiral P3BT* block. In **P12** this block is situated in the middle of the polymer, possibly resulting in a lower capability to express its chirality. To support this data, photoluminescence measurements were performed, but unfortunately no extra information was obtained from these results (Figure S31-S32).

Figure 9. Absorption (left) and CD (right) spectra of the solvatochromism experiments for **P9** (A), **P10** (B), **P11** (C) and **P12** (D).

From these results it is clear that the block sequence has a large influence on the aggregation behavior of triblock copolymers: separated aggregating blocks show no influence on each other's aggregation behavior and neighboring aggregating blocks exhibit such a strong influence on each other that they aggregate as one block.

Conclusions

As well triblock copolymers consisting of solely thiophene units, as triblock copolymers containing selenophene and (a)chiral thiophene units were synthesized via KCTCP in a controlled manner. The synthesized triblock copolymers were characterized by GPC and ^1H NMR analysis. For the first time, the aggregation behavior of conjugated triblock copolymers was studied and this was done via UV-vis and CD spectroscopy. For all synthesized polymers it was observed that when two aggregating blocks are separated from each other by a non-aggregating block, they do not influence each other and aggregate separately. However, when the two aggregating blocks are situated next to each other, they influence each other's aggregation behavior strongly and aggregate as one block. With this in mind, triblock copolymers can be designed by changing the block sequence in conjugated triblock copolymers depending on which type of aggregation behavior is desired.

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 curves; additional absorption and CD spectra; ¹H NMR spectra of the polymers (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CD, circular dichroism; dppp, 1,3-bis(diphenylphosphino)propane; GPC, gel permeation chromatography; KCTCP, Kumada catalyst transfer condensative polymerization; MeOH, methanol; oPVs, organic photovoltaics; P3AOTs, poly(3-alkoxythiophene)s; P3ASe, poly(3-alkylselenophene); P3ATs, poly(3-alkylthiophene)s; P3BT*, poly(3-((S)-2-

methylbutyl)thiophene); P3DT, poly(3-dodecylthiophene); P3HT, poly(3-hexylthiophene); P3ODT, poly(3-(2-octyldodecyl)thiophene); P3OSe, poly(3-octylselenophene);

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