The influence of the end-group on the chiral self-assembly of all-conjugated block copolymers

M.-P. Van Den Eede^a, A. Bedi^a, J. Delabie^a, J. De Winter^b, P. Gerbaux^b and G. Koeckelberghs^{a,*}

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The self-assembly of all-conjugated block copolymers is an effective way to obtain well-ordered structures at the nanoscale. Although these polymers possess an end-group and a lot of research has been done on their self-assembly, the influence of the end-groups has hardly been considered. Both the nature of the blocks as well as the degree of polymerization (DP) play a crucial role in the solubility of the different blocks in a conjugated block copolymer. Here, we hypothesize that also the end-group is of importance: bulkier end-groups increase the solubility of that particular preceding block and thus will have an influence on the self-assembly. This hypothesis is validated using three series of all-conjugated block copolymers in which the blocks are composed of the two enantiomers of a chiral monomer.

Introduction

The many emerging applications of conjugated polymers (CP) have rapidly expanded their research. The optical and electronic properties of CP makes them suitable materials for optoelectronic applications such as organic photovoltaics¹, organic light emitting diodes² and organic field effect transistors^{3,4}. Since the device performance depends on both the electronic properties as well as on the nanoscale morphology, understanding and controlling this morphology is of great importance.^{5–7} Various strategies were explored to design nanoscale aggregates in a controlled way. The most popular approach for the fabrication of reproducible nanoscale aggregates relies on the self-assembly of CP.⁸ Different routes were tested to control the self-assembly of these materials, but block copolymers provide the most interesting results.^{9–21} For example, compared to blends, block copolymers are of special interest due to their preferable self-assembly and the better control of the nanoscale domain sizes of their aggregates. In order to obtain the desired variety in conjugated block copolymers, different synthetic routes were explored.^{22–25} A well-known, and by far the most popular route to obtain well defined AB-block copolymers makes use of sequential monomer addition.²⁶ This method makes it also possible to introduce functional end-groups: when a chain-growth polymerization is initiated by a functionalized external initiator, all chains will bear the functional group at the beginning of the

polymer chain. Although conjugated copolymers used in various applications possess an end-group, and a lot of research has been done on their self-assembly, the influence of the end-groups has hardly been considered.²⁷

We have demonstrated that the less soluble block of a block copolymer aggregates first and imposes its stacking to the second, more soluble block, whether this stacking is expected for the homopolymer of that second block or not.^{26,28–32} Apart from the nature of the blocks, also their degree of polymerization (DP) plays a role: a higher DP results in a lower solubility. Finally, we hypothesize that also the end-group is of importance. This will be shown in block copolymers, in particular a regioregular poly(3-alkylthiophene) in which both blocks consist of the same chiral monomers, but of different enantiomers. If the end-group has no influence on the solubility and aggregation behaviour, the solubility of the blocks depends only on the DP of the respective blocks: the longest block has the lowest solubility, aggregates first and dictates the supramolecular structure (Figure 1A–B). In contrast, if the sterically demanding end-group has an influence, it increases the solubility of the first block. Hereby, the handedness of the helical stacking and the sign of the CD spectra, depends both on the DPs of both blocks and the bulkiness of the end group. If the end-group is not too bulky and the first blue block has a much higher DP, that block remains the dominant one (situation 2A). The same happens for situation 2B, were the second green block with higher DP will dominate. However, if the bulky end-group has an influence and the first block does not have a much higher DP, the second block becomes dominant, despite its shorter chain length (situation 2C). According to this hypothesis, a larger end-group will have a larger influence which means that the ratio of the DP of the blocks at which the second, shorter block becomes dominant is determined by the bulkiness of the end-group.

^a Laboratory for Polymer Synthesis, KU Leuven, Celestijnenlaan 200F - Box 2404, B-3001 Heverlee, Belgium.

^b Organic Synthesis and Mass Spectrometry Laboratory, Interdisciplinary Center for Mass Spectrometry, University of Mons-UMONS, 23 Place du Parc, 7000 Mons, BELGIUM

*E-mail: guy.koeckelberghs@kuleuven.be

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Figure 1 – Schematic visualization of the influence of sterically different end-groups (red spheres) on the self-assembly of conjugated block copolymers.

Scheme 1 – Schematic representation of the polymers with sterically different end-groups and chiral side chains.

The synthesis of (new) external initiators allows the incorporation of sterically different end-groups: *o*-tolyl, *o*-ethylphenyl and *o*-*i*-propylphenyl (Scheme 1.1). The synthesis of block copolymers of which both blocks are the same but consist of a different enantiomer (Scheme 1.2), enables us to visualize the self-assembly of the block copolymer, and more specifically which block aggregates first and imposes its stacking.³² More precisely, block copolymers with a different percentage of (*R*) monomer compared to (*S*) monomer are synthesized for each different end-group (Scheme 1.3).

Results and discussion

Synthesis of the precursor initiators

The different external precursor initiators (**1**, **2** and **3**, Scheme 2) were prepared in dry toluene following the reported procedure by mixing $\text{Ni}(\text{PPh}_3)_4$ with the corresponding arylbromide at room temperature (Supporting Information S4).^{26,31}

Synthesis of the polymers

All polymers were synthesized using a $\text{Ni}(\text{dppp})$ (dppp = bisdiphenylphosphinopropane) mediated Kumada catalyst transfer condensative polymerization KCTCP (Scheme 2). The two monomers (**S**) and (**R**) were prepared *in situ* by a Grignard Metathesis (GRIM) reaction on the corresponding 3-alkyl-2-bromo-5-iodothiophene precursor monomer (**4** and **5**).²⁶ The different precursor initiators (**1**, **2** and **3**) underwent a ligand exchange with dppp in order to form the desired initiators **In M**, **In E** and **In iP**. Exploiting the living nature of the polymerization, the block copolymers (**M-P(2-5)b**, **E-P(2-5)b** and **iP-P(2-5)b**) were obtained by adding the (**R**) monomer to the reaction mixture after the first (**S**) monomer has been consumed. The polymerization reactions were terminated with acidified (HCl) THF in order to prevent disproportionation.³³ As shown in

Scheme 2 – Synthesis overview of polymers **M-P(1-5)a**, **E-P(1-5)a** and **iP-P(1-5)a**, and block copolymers **M-P(2-5)b**, **E-P(2-5)b** and **iP-P(2-5)b** using the *o*-tolyl (**In M**), *o*-ethylphenyl (**In E**) and *o*-*i*-propylphenyl (**In iP**) Ni initiators.

scheme 2 (dashed arrow), a known amount of the first block of all polymers (**M-P(1-5)a**, **E-P(1-5)a** and **iP-P(1-5)a**) was isolated in order to determine the degree of polymerization of the first block. This made it possible to calculate the monomer ratio in the block copolymers.

Using GPC in THF and poly(styrene) standards an initial indication of a successful block polymerization was obtained. However, GPC is not able to produce absolute data since it is calibrated toward poly(styrene) standards, and therefore overestimates the molar masses. For all polymers low dispersities were observed. Using ^1H NMR spectroscopy the DP as well as the monomer ratio of all polymers were calculated. This is done via the assignment of separated signals originating from internal monomer units as well as the end-groups of the isolated first blocks and the block copolymers (Scheme 3).

Scheme 3 – Assignment of ^1H NMR signals in the aromatic region in order to determine the chain length as well as the monomer ratio of the different polymers.

Scheme 4 – Assignment of ^1H NMR signals in the aliphatic region in order to determine the chain length as well as the monomer ratios of the different polymers.

The number average molar mass ($\bar{M}_n$) and dispersity ($\bar{D}$) of the different polymers obtained with GPC and the monomer ratios for each polymer series obtained with ^1H NMR are shown in table 1. When the DP calculated with ^1H NMR and GPC are compared, an overestimation of an average of 1.2 for the GPC results is obtained. This is in accordance with the size-exclusion quantification already performed on polythiophenes.³⁴

The controlled nature of the polymerization, in terms of molar mass and end-groups reliability, was further confirmed using MALDI-ToF analysis. The MALDI-ToF spectra of the polymers (supporting information S50) possess signals which can be assigned to polymer chains that contain end-groups corresponding to the initiator and hydrogen. This confirms that the initiators have efficiently played their role. Only in the lower molar mass region fractions of initiator/Br and H/Br terminated chains are visible. However, this lower molar mass region is not visible on GPC and can thus be considered as negligible as the ions with low molar mass are usually overestimated.^{35,36} The obtained control in the end-groups makes it also possible to determine the DP via the assignment of peaks in the aliphatic

region of the ^1H NMR spectra. This is done via the assignment of separated signals originating from the initiators as well as the signals of the α -methylene protons of the isolated first blocks and the block copolymers (Scheme 4). The DPs calculated in this way are in accordance with these obtained via the aromatic region (Scheme 3).

Solvatochromism experiments

Next, the actual self-assembly of the synthesized polymers was investigated in order to unravel the influence of the different end-groups. The polymers were dissolved in CHCl_3 , a good solvent for poly(3-alkylthiophenes), in which the polymer chains adopt a random coil-like, achiral structure. At this stage, no chiral response is measured with Circular Dichroism (CD). Next, methanol (non-solvent) was added stepwise. At a critical amount of non-solvent, the polymer chains start to stack in a chiral way, hereby mimicking a one-handed helix (M- or P-helix),

Figure 2 – Absorption and CD spectra of the solvatochromism experiment on the polymer series with the *o*-tolyl end-group (**M-P1a**, **M-P(2-5)b**).

block copolymer in which the two blocks possess a different solubility, the block that aggregates first imposes its stacking to the second block. This means that between 23% and 29% of (**R**) monomer in the block copolymer, the second (**R**) block becomes dominant. Since the (**R**) block has a lower DP than the (**S**) block, it can be concluded that the (**S**) block, which is directly attached to the bulky end-group, has a higher solubility. This experiment was also applied on **E-P1a**, **E-P(2-5)b** and **iP-P1a**, **iP-P(2-5)b** polymer series. Since the signal change of the bisignate Cotton-effect is of importance, these are summarized in table 1 for all series. For polymer series **E-P1a**, **E-P(2-5)b** a signal change between 4% and 20% of (**R**) monomer is obtained, while for polymer series **iP-P1a**, **iP-P(2-5)b** a signal change between 0% and 6% is observed. This is the case for all three different measurements (table 1).

In order to better visualize this important signal change, the CD signals of the different polymers of the three series at a content

of 45% of methanol were plotted in figure 3. In the series with the *o*-tolyl end-group the three first polymers show a negative CD signal, while the last two polymers show a positive CD signal. For the *o*-ethylphenyl end-group only the two first polymers show a negative CD signal and for the *o*-*i*-propylphenyl end-group only the first homo (**S**) chiral polymer. From table 1 and figure 3 we can conclude that the switch in the signal of the bisignate Cotton-effect takes place at lower percentage of (**R**) monomer if more bulky end-groups are present in the polymer chain. Since the (**S**) homopolymers of the three series possess the same sign of the bisignate Cotton-effect, the switch in sign cannot originate from the nature of the end-group. Note also that in case of the *o*-tolyl and *o*-ethylphenyl the zero-crossing shifts, which may indicate a difference in conjugation length. A very interesting phenomenon occurs with **M-P5b**, which contains 50% (**S**) and (**R**) monomers, hence no excess of chiral monomers is present. From figure 3 it is clear that a very strong

chiral response is present – even the strongest response of all polymers! This enables us to conclude that a presence of the end group is enough to break the symmetry and allows the strong expression of chirality. To the best of our knowledge, this is the first example that chirality can be expressed due to the presence of an end-group.

end-group governs the self-assembly of CP. This shows the importance of the end-group, a feature that is often overlooked. Finally, the presence of an end-group proved to be sufficient to dictate a strong chiral response in a block copolymer that contains no excess of chiral monomers.

Conflicts of interest

There are no conflicts of interest to declare

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Figure 3 – $\Delta\epsilon$ at a 45% methanol content plotted for the three different polymer series (M-P1a, M-P(2-5)b; E-P1a, E-P(2-5)b; iP-P1a, iP(2-5)b) as a function of the wavelength.

Conclusions

Three series of all-conjugated polymers in which both blocks consists of the enantiomers of a chiral monomer were prepared starting from an external initiator. The polymers vary in the ratio of the DPs of the two blocks and the bulkiness of the end group installed by the external initiator. Using CD, that reveals which block aggregates first, it could be concluded that not only the nature of the block and DP, but also the bulkiness of the

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