

Effect of the Nature and the Position of Defects on the Chiral Expression in Poly(3-alkylthiophene)s

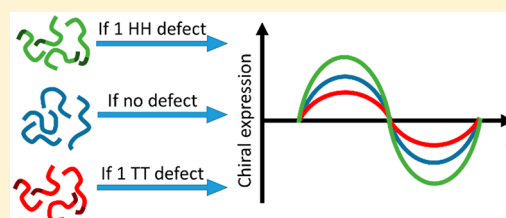
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Supporting Information

ABSTRACT: Polymers produced with the most used controlled polymerization method with the simplest initiators, namely the Kumada catalyst transfer condensation polymerization (KCTCP) with Ni²⁺ salts, all have one regiodeflect distributed along the polymer backbones. The irregularity created by these defects can be split up into three components, i.e., the nature of the defect, the position of the defect, and the additional inhomogeneity created by mixing polymers with the defect at different positions. In this research, the influence of these three parameters on the chiral expression of poly(3-alkylthiophene)s (P3ATs) is investigated separately for the first time. A series of chiral P3ATs with one tail-to-tail (TT) or head-to-head (HH) defect in different positions is synthesized by means of the Pd(RuPhos) protocol, and their chiral expression and that of their mixtures are studied via UV–vis and circular dichroism (CD) spectroscopy. For the polymers with an HH defect, it is found that the position at the very beginning of the polymer chain is the most optimal to obtain the largest chiral expression, and the obtained signal is even the highest ever reported for PTs in chloroform and MeOH solutions. When a TT defect is incorporated into the polymer, the chiral expression is much weaker, and the most optimal position of the defect is a little shifted toward the middle of the chain compared to their HH analogues. For the mixtures of the polymers with an HH defect, a weighted average of the signals of its constituents is obtained, but for the mixtures of the polymers with a TT defect different results are obtained. When 25% of each polymer is mixed, no chiral response is obtained, and when more of the polymers with the defect more toward the chain ends are incorporated, a chiral response higher than that of any of the component polymers is recorded. This shows that the chiral expression is not only influenced by the nature or the position of a defect, but also by the mixing of polymers with a defect in different positions.



INTRODUCTION

In the past decade, the field of conjugated polymers expanded rapidly, introducing new polymers, polymerization, and processing techniques.^{1–5} Although many polymer systems have been thoroughly studied, poly(3-alkylthiophene) (P3AT) remains the benchmark conjugated polymer. This can be attributed to its fairly easy and diverse synthesis routes, allowing the controlled synthesis of polymers with different chain lengths, end groups, and number of regiodeflects combined with a narrow dispersity.^{6–14} In this way, tailor-made polymers can be synthesized to investigate the intrinsic influence of each polymer characteristic on the final properties of the material. For instance, the influence of the chain length, side chains, end groups, and regiodeflects on the aggregation behavior is now well understood.^{9,15–19} Closely related to the aggregation behavior is the chiral expression. It was found that end groups can be used to tune the chiral response in block copolymers, and also the influence of the number of regiodeflects was investigated.^{9,16,20} Although maybe counter-intuitive, it was found that a small amount of defects increases the chiral response. This can also be extended to other irregularities. For example, in some cases when a block copolymer is synthesized with an achiral and a chiral block, the

chiral response is higher compared to the fully chiral homopolymer.²¹ A second example can be found in block copolymers with blocks of equal length but opposite chirality. When no end group is present, no chiral response is observed. However, when an end group different than H is introduced, the chiral response is even higher compared to the chiral homopolymer.^{16,22}

As mentioned above, different studies have been executed to understand the influence of the number of regiodeflects on the chiral expression of poly(thiophene)s (PTs),^{9,20} but no one investigated whether the position of these defects also plays a role. However, the polymers produced with the most used controlled polymerization method with the simplest initiators, namely, the Kumada catalyst transfer condensation polymerization (KCTCP) with Ni²⁺ salts, all present one regiodeflect somewhere along the polymer backbones.¹⁷ This is due to the formation of a tail-to-tail (TT) dyad during the initiation, combined with random catalyst ring walking, causing new monomers to be built in on either side of this TT dyad.²³ This

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results in a different final position of the TT dyad for each polymer chain. Therefore, the irregularity in these polymers is not only due to the presence of a defect but also due to the position of this defect and the additional inhomogeneity created by mixing polymers with the defect at different positions.

In this research, these three parameters are investigated separately for the first time. A series of chiral P3ATs with one TT or head-to-head (HH) defect in different positions is synthesized, and their chiral expression and that of their mixtures are studied via UV–vis and circular dichroism (CD) spectroscopy to address this issue. To control the position of the defect, block copolymers of the different regioisomers are synthesized in which the defect (TT or HH) is introduced at the transition from the first to the second block. However, not just any polymerization method can be used to obtain the intended polymers because control over the molar mass, dispersity, and position of the regiodefect is necessary. These criteria can only be met if a controlled polymerization with an external initiator is used that incorporates HH and TT couplings as readily as head-to-tail (HT) couplings. A controlled polymerization is necessary to obtain well-defined block copolymers and will also result in control over the molar mass. An external initiator must be used to only induce unidirectional growth, so only diblock copolymers and not triblock copolymers are formed. To exclude any effect of end groups,¹⁶ the aromatic moiety of this catalyst must be the same as the monomer unit. The last prerequisite is necessary to ensure that the propagation rate of the second block is equal to (or less than) the initiation rate to obtain a low-dispersity polymer. The Pd(RuPhos) protocol is the only polymerization procedure that meets all criteria and is therefore chosen to synthesize the required block copolymers.⁹

RESULTS AND DISCUSSION

To make well-defined block copolymers of the regioisomers, the monomers were synthesized via the adapted GRIM method, followed by a transmetalation reaction with ZnBr₂ (Scheme 1). In this way, only one regioisomer is formed from each precursor monomer. As mentioned above, the aromatic moiety of the external initiator must be the same as the monomer unit to eliminate an end group effect. Therefore, initiators **6a** and **6b** were used. The precursor monomers **3a**

and **3b** and initiator **6a** were synthesized via literature procedures.^{9,24} Initiator **6b** was synthesized via the same procedure as **6a**, but starting from **5b** instead of **5a** (Scheme 1).

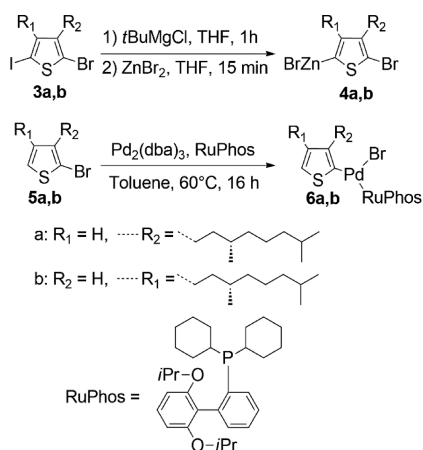
To evaluate the influence of the nature and the position of the defect on the chiral aggregation behavior, nine polymers were synthesized (Scheme 2). Four polymers with an HH defect were prepared from initiator **6a** and monomers **4a** and **4b** for the first and second block, respectively. Whereas the degree of polymerization (DP) of the polymer was kept constant, the DP of each block was modified to sample different positions of the defect. In the nomenclature of the polymers, the letters stand for the type of defect and the first and second number for the DP of the block before and after the defect, respectively. Because the aromatic moiety of the initiator becomes the first monomer unit in the final polymer, no first block of monomer **4a** was incorporated to obtain HH 1+19. Similar to the HH polymers, four polymers with a TT defect were synthesized from initiator **6b** and monomers **4b** and **4a** for the first and second block, respectively. In addition, a perfectly regioregular (rr) polymer was synthesized from initiator **6a** and monomer **4a** for comparative purposes.

As discussed above, the polymers were synthesized via the Pd(RuPhos) protocol (Scheme 2). This requires anhydrous conditions because each protic impurity can react with the monomer, creating a transfer reagent and canceling the controlled nature of the polymerization. Therefore, the precursor monomers, **3a** and **3b**, and ZnBr₂ were dried under reduced pressure in the presence of P₂O₅ and heat, respectively. Prior to the addition of the second monomer, a small aliquot of the polymerization mixture was withdrawn for analysis. In this way, the growth of the polymer chain can be monitored with gel permeation chromatography (GPC) (Figures S1–S9A). Although not all chains were able to incorporate the second monomer, all the dead chains of the first block were removed during the purification of the final polymers to investigate the properties of the pure block copolymer (Figures S1–S9B). The molar mass and dispersity of the purified polymers were also determined with GPC (Table 1). Because the GPC is calibrated toward polystyrene standards, the calculated molar mass is not absolute, and therefore also ¹H NMR was used to determine the DP (Table 1). For rr-PT, this can be done via the integration of the signals of the aliphatic or aromatic protons (Figure 1).²² When the aliphatic protons are used, the α -methylene protons of the external thiophene units (A) can be used to calibrate the spectrum because they have a slightly different chemical shift compared with the α -methylene protons of the internal thiophene units (B). The DP can be calculated with

$$DP = 4(A + B)/2A \quad (1)$$

In the aromatic region, the proton in the 5-position of the first thiophene unit (C) has a distinct chemical shift and can be used for calibration. To determine the DP, the presence of H- and Br-terminated chains must be considered. This is inherent to the Pd(RuPhos) protocol because, during the polymerization, the catalyst can diffuse away from the growing polymer chain and, later, reinsert in an available C–Br bond.²⁵ When the polymerization is quenched with acid, the polymer chains with the catalyst inserted in the terminal C–Br bond will react with the acid and result in H-terminated chains, while the polymer chains without the catalyst inserted in the C–Br bond will not react and result in Br-terminated chains. Because the

Scheme 1. Reaction Scheme of the Monomer and Initiator Synthesis



Scheme 2. Representation of the Polymerization Procedure

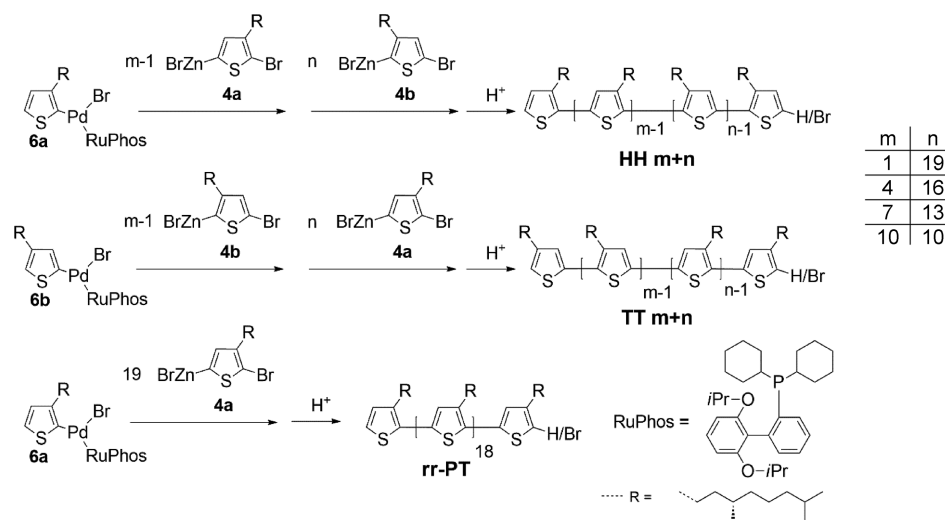


Table 1. Overview of the Properties of the Synthesized Polymers

| | M_n^a (kg/mol) | \mathcal{D}^a | DP^b |
|----------|------------------|-----------------|-----------------------|
| rr-PT | 5.0 | 1.4 | 17 (19 ^c) |
| HH 1+19 | 5.1 | 1.3 | 21 |
| HH 4+16 | 5.0 | 1.4 | 26 |
| HH 7+13 | 5.8 | 1.3 | 27 |
| HH 10+10 | 5.7 | 1.3 | 26 |
| TT 1+19 | 3.5 | 1.3 | 16 |
| TT 4+16 | 3.7 | 1.3 | 20 |
| TT 7+13 | 4.0 | 1.4 | 22 |
| TT 10+10 | 3.9 | 1.4 | 22 |

^a M_n and \mathcal{D} are calculated with GPC calibrated toward polystyrene standards. ^bDP was calculated with ¹H NMR based on the aliphatic signals. ^cDP was calculated with ¹H NMR based on the aromatic signals.

aromatic protons of the initial thiophene unit (C) and the Br-terminated thiophene (E) unit have different chemical shifts, the DP can be calculated with

$$DP = (D - C + 2E)/C \quad (2)$$

The DPs obtained via the two methods are slightly different. This can be attributed to the partial overlap of the aliphatic signals, complicating the correct integration. For the other polymers, the aromatic protons cannot be used to determine the DP because it is impossible to calculate the amount of Br-terminated chains. This is due to the similarity of the two chain ends, which is not the case for rr-PT. Therefore, only the aliphatic protons are used to determine the DP (Figure 2 for HH 4+16 and Figures S10–S17 for the other polymers). The α -methylene protons of the external thiophene units and the thiophene units next to the defect (A) have slightly different chemical shifts compared with the internal thiophene units (B) and can be used to calibrate the spectrum. The DP can again be calculated with

$$DP = 8(A + B)/2A \quad (3)$$

To minimize the error on the calculated DPs, the same regions were always integrated. An overview of the obtained DPs can be found in Table 1. The DPs of the polymers with an HH defect are slightly higher compared with the polymers with a

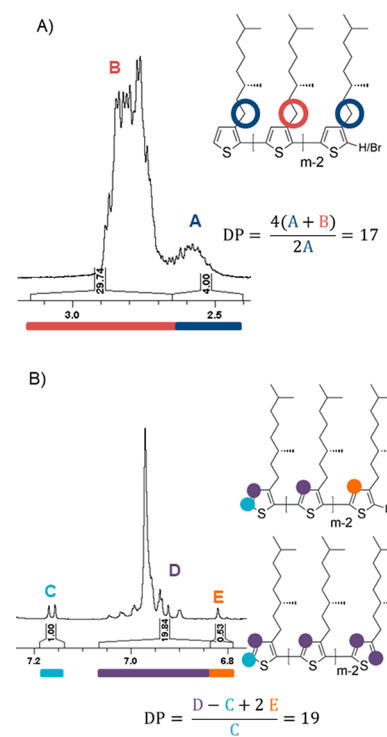


Figure 1. Determination of the degree of polymerization for rr-PT based on the aliphatic (A) and aromatic (B) signals.

TT defect. This can be attributed to the higher amount of polymer chains that did not react upon the addition of the second monomer for the polymers with an HH defect. Thereby, more monomers per growing chain were present and the DPs of the purified polymers are higher. Also, the DPs of the polymers with the defect at the beginning of the chain are slightly lower compared to the rest of the series.

To confirm the presence (or absence) of a TT or HH defect in the synthesized polymers, the aromatic region of the ¹H NMR spectrum was studied. As described by Barbarella et al., the chemical shift of the aromatic protons depends on the triad in which they are located (HT-HT, HT-TT, HT-HH, or TT-HH triad).²⁶ For the synthesized polymers, the assignment of the different triads can be found in Figure S19. Because of the

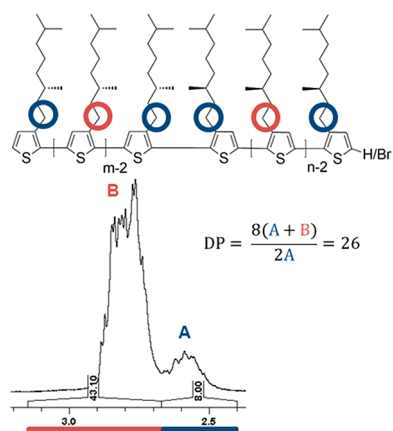


Figure 2. Determination of the degree of polymerization for HH 4+16.

overlap of the different signals and the more intense signal of the HT-HT triad, it is impossible to integrate the different contributions separately. However, it is visible that the contribution of the HH-HT (for the polymers with an HH defect) or TT-HT (for the polymers with a TT defect) triad is similar for all polymers, indicating that the same number of defects is present for all polymers. For rr-PT, negligible contributions are present of HT-TT, HT-HH, and TT-HH triads, confirming the high regioregularity of this polymer.

The polymers were further characterized by MALDI-ToF (matrix-assisted laser desorption/ionization time-of-flight) analysis to determine the nature of the end groups (Figures S20–S29). H/H and H/Br polymers were mostly detected, as anticipated. Also, the higher molar mass of the polymers with the HH defect compared with rr-PT and the polymers with the TT defect was confirmed.

To evaluate the effect of the nature and the position of a defect on the chiral response, solvatochromism experiments were performed on the synthesized polymers. The polymers

were dissolved in chloroform, i.e., a good solvent, and methanol (MeOH), i.e., a poor solvent, was gradually added. Because the chiral response is very sensitive toward all environmental factors, precautions were taken to keep all parameters constant for each polymer. For example, the stirring speed (1200 rpm) and the rate of MeOH addition (0.20 mL/min) were kept constant. The changes in organization upon the addition of MeOH were monitored by UV–vis and CD spectroscopy to probe the formation of supramolecular structures and *chiral* supramolecular structures, respectively. The most relevant UV–vis and CD spectra obtained for each polymer are shown in Figures 3, 4, and 5

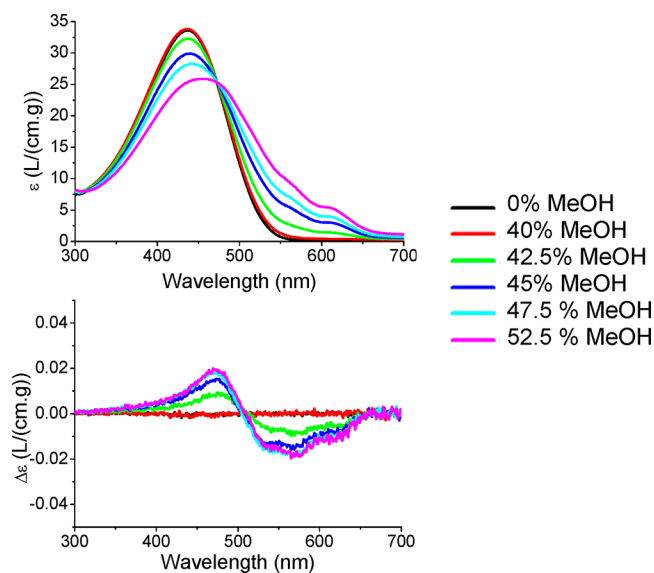


Figure 4. Absorption (top) and CD (bottom) spectra of the solvatochromism experiments for rr-PT. The complete data set can be found in Figures S31 and S32.

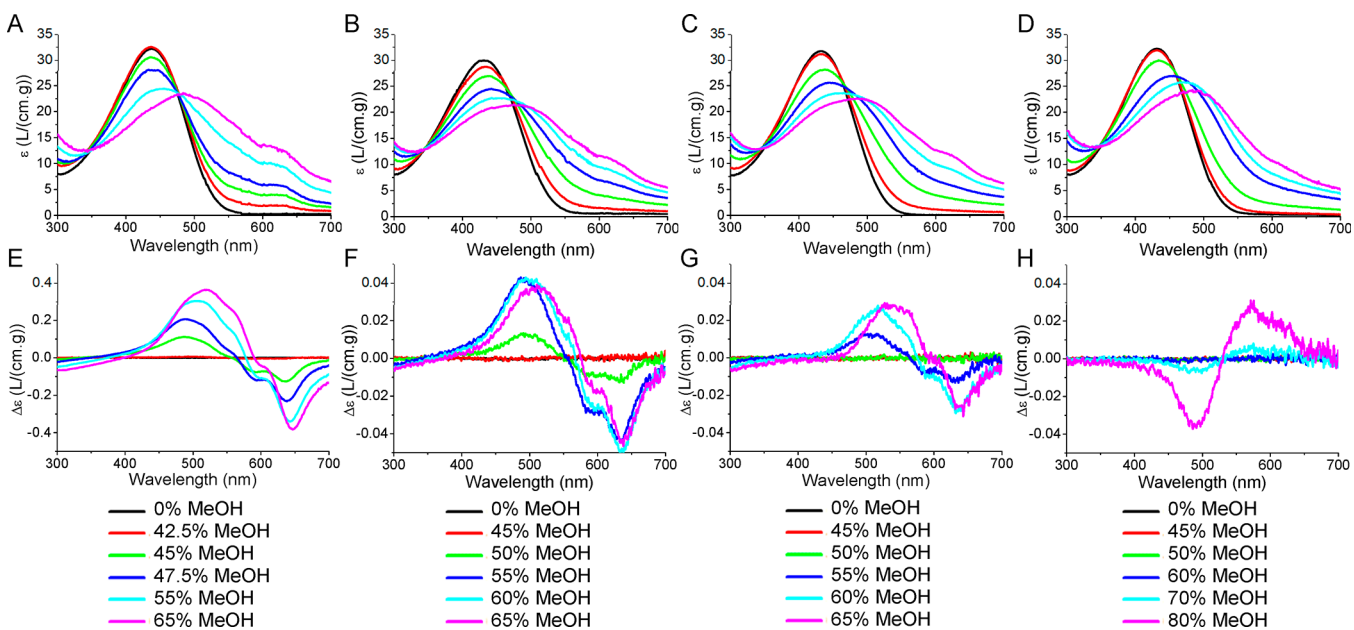


Figure 3. Absorption (A–D) and CD (E–H) spectra of the solvatochromism experiments for HH 1+19 (A, E), HH 4+16 (B, F), HH 7+13 (C, G), and HH 10+10 (D, H). The complete data set can be found in Figures S19–S29.

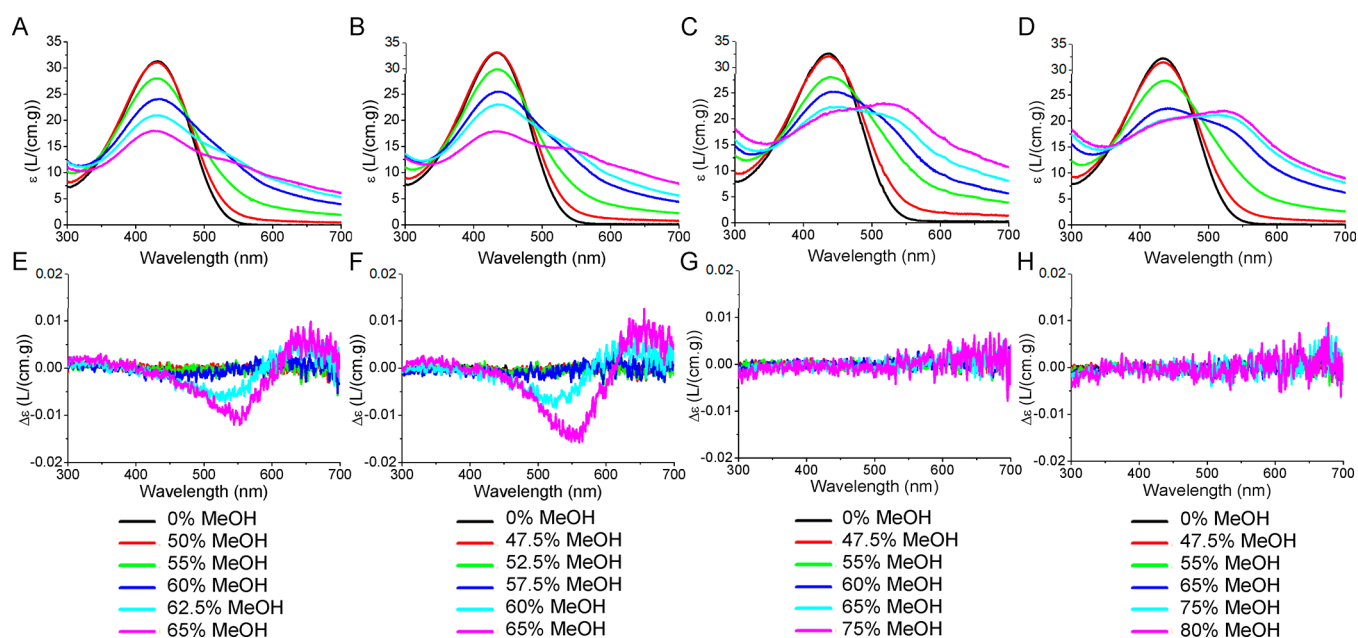


Figure 5. Absorption (A–D) and CD (E–H) spectra of the solvatochromism experiments for TT 1+19 (A, E), TT 4+16 (B, F), TT 7+13 (C, G), and TT 10+10 (D, H). The complete data set can be found in Figures S34–S43.

(the complete data set can be found in Figures S30–S54). For each polymer, MeOH was added until no changes in absorption and CD signal were observed or until the polymer visually flocculated.

When the chiral responses of the polymers with the HH defect (Figure 3) are compared with the one of the complete regioregular PT (Figure 4), the chiral response of the latter is observed to be the weakest. This is in line with previous research, where it was found that a small amount of defects can increase the chiral response.^{9,20} This can be explained by the larger conformational flexibility created by the defects, lowering the possibility that the polymer chains get trapped in supramolecular structures with less efficient chiral expression during the aggregation process. In this way, the defect can enhance the chiral response. For the synthesized polymers, additional observations can confirm this hypothesis. The rr-PT already visibly flocculates upon the addition of 55% MeOH, while the polymers with the HH defect flocculate only upon the addition of 70% MeOH or more, indicating the faster aggregation of complete regioregular PT. When the polymers with the HH defect are compared with each other, it can be observed that the start of the bathochromic shift in the absorption spectra occurs after the addition of similar amounts of MeOH (42% MeOH–50% MeOH). However, the vibronic fine structure becomes less pronounced as the defect is placed more toward the middle of the chain. This means that the planarization of the chains occurs under similar conditions but that more defined supramolecular structures are formed if the defect is situated closer to the chain ends. The latter is also reflected in the CD signal. The more the defect is moved toward the middle of the polymer, the higher the MeOH concentration must be to form a chiral supramolecular structure and the lower the final CD signal. Remarkable is the switch of the sign of the CD signal from HH 7+13 to HH 10+10, as this indicates a switch from a left-handed helix (negative bisignate Cotton effect) to a right-handed helix (positive bisignate Cotton effect). This can be attributed to the less defined supramolecular organization of the latter, which is

also reflected in the absence of vibronic fine structure in the absorption and CD spectra. As the sign of the CD signal is very sensitive toward environmental factors, this small difference can already result in an opposite sign.

To verify whether the decrease of the CD signal is due to a supramolecular structure with a *less efficient* chiral expression or just a *lower amount* of aggregated chains, $g_{\text{abs}} = \Delta\epsilon/\epsilon$ was calculated for all the polymers (Figures S30–S44). The higher this value, the more efficient the chiral expression for the same amount of aggregated polymer chains is. In Figure 6, the

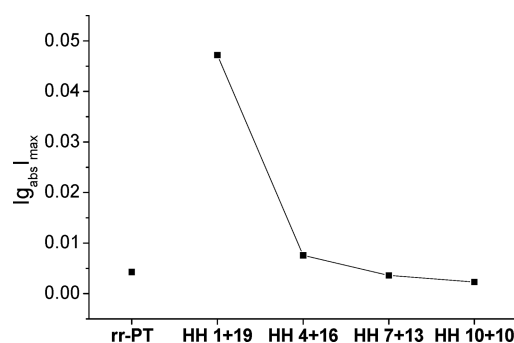


Figure 6. Comparison of $|g_{\text{abs}}|_{\text{max}}$ for rr-PT and the polymers with an HH defect.

highest absolute value for each polymer is represented for comparison, and this also shows a decay when the defect is moved toward the middle. This means that the decrease in CD signal is not due to less aggregated polymer chains but due to a less efficient chiral packaging upon aggregation. Similar as for the amount of defects,^{9,20} it is visible that there is also an optimum for the position of the defect, which can be explained by the same principles. A small amount of irregularities increases the conformational flexibility, leading to an increased chiral response, as described above. Nevertheless, when the incorporated irregularities are too large, the efficient packing is too much hindered. When the defect is moved toward the

middle of the chain, the amount of irregularity is increased by shortening the longest regioregular part of the polymers, similar to when the number of defects is increased. For the HH defect, the optimal position is at the very beginning of the chain. This is not very surprising because an HH defect provides already a large backbone distortion.^{27,28} The $|g_{\text{abs}}|_{\text{max}}$ value obtained for **HH 1+19** is also, to the best of our knowledge, the highest reported for PTs in chloroform and MeOH solutions.^{9,16,29} This is probably because in the past only polymers with multiple defects, one TT defect distributed along the backbones or one HH defect in the middle of the chains, were investigated. The large $|g_{\text{abs}}|_{\text{max}}$ value for **HH 1+19** is probably due to the large distortion at the beginning of the chain, whereby the conformational flexibility is increased while maintaining large defect-free backbone parts, a combination which leads toward very efficient supramolecular structures. This new insight can be of importance in the search for materials for chiral photonics and metaphotonics, as systems with a high chiral expression can result in materials with a negative, zero, or near-zero refractive index.³⁰

The second investigated type of defect is a TT defect. From **Figure 5**, it is visible that the bathochromic shift in the absorption spectra starts after the addition of similar amounts of MeOH (50% MeOH–55% MeOH), independent of the position of the defect. This indicates that the planarization of the chains occurs under similar conditions, as was the case for the polymers with an HH defect. However, (almost) no vibronic fine structure is observed in the absorption spectrum, indicating the formation of less defined supramolecular structures. This is also reflected in the CD signal. For **TT 1+19** and **TT 4+16**, a CD signal smaller than and with a sign opposite to **rr-PT** is recorded. As explained above, the opposite sign can be attributed to the less defined supramolecular organization for the polymers with the TT defect. For **TT 7+13** and **TT 10+10** even no CD signal is obtained. So in contrast to an HH defect, a TT defect has a negative influence on the chiral response of PTs. Also remarkable is the increase in maximal CD signal from **TT 1+19** to **TT 4+16**. To elucidate whether this arises from a *higher amount* of aggregated chains or from *more efficient* chiral supramolecular structures, g_{abs} values were calculated (**Figures S45 and S54**), and the highest absolute value for each polymer is represented in **Figure 7**. Because the $|g_{\text{abs}}|_{\text{max}}$ value also increases from **TT 1+19** to **TT 4+16**, it can be concluded that more efficient chiral supramolecular structures are formed for the latter. The optimal position of a TT defect for obtaining the most chiral supramolecular structure is therefore different than for an HH

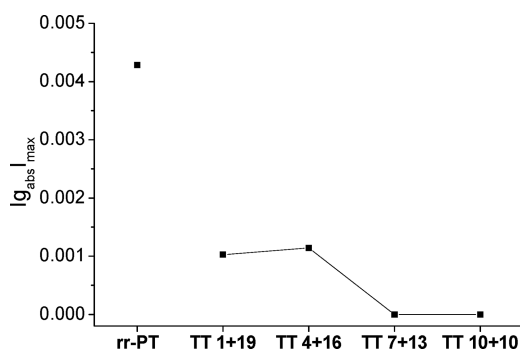


Figure 7. Comparison of $|g_{\text{abs}}|_{\text{max}}$ for **rr-PT** and the polymers with a TT defect.

defect. This can be attributed to the amount of deformation created by each defect. The adjacent monomers of an HH defect have a torsion angle of at least 40° due to enlarged steric hindrance, while the adjacent monomers of a TT defect experience less steric hindrance and can become coplanar upon aggregation.^{27,28} The amount of irregularity created by the defect itself is thus smaller for a TT defect, and therefore a more optimal situation can be reached by increasing this amount. This can be obtained by placing the defect more toward the middle of the chain, as explained above.

The observation that all the polymers with a TT defect have no vibronic fine structure in the absorption spectra and a small or no CD signal upon the addition of MeOH is surprising as polymers synthesized via KCTCP with Ni^{2+} salts, which also have one TT defect in each polymer chain, do exhibit vibronic fine structure and a clear CD signal upon aggregation.³¹ A possible explanation for this discrepancy is the higher amount of irregularities for the latter since not only the presence of the defect and the position of this defect increase the amount of irregularities but also the inhomogeneity created by mixing polymers with the defect in different positions. To investigate whether this mixing has an influence on the chiral expression, two different mixtures for each type of defect were prepared and analyzed. **Mix 1** is a mixture with equal proportions of each synthesized polymer, and in **Mix 2** more of the polymers with the defect more toward the chain ends are incorporated. The following percentages were chosen: 52% of **1+19**, 25% of **4+16**, 14% of **7+13**, and 9% of **10+10**. In this way, the obtained mixture of the polymers with the TT defect resembles the polymer obtained via KCTCP with Ni^{2+} salts.¹⁷ The chiral response of the polymer mixtures was evaluated with the same solvatochromism experiments as for the pure polymers, and the results can be found in **Figures 8 and 9** (the complete data set can be found in **Figures S55–S66**). For **Mix HH 2**, the absorption spectra, CD spectra, and $|g_{\text{abs}}|_{\text{max}}$ value are intermediate to those of **HH 1+19** and **HH 4+16**, which could be expected because the mixture consists of 52% of **HH 1+19** and 25% of **HH 4+16**. For **Mix HH 1**, consisting of 25% of each polymer, the $|g_{\text{abs}}|_{\text{max}}$ value is intermediate to those of **HH 4+16** and **HH 7+13**, as could be expected when the additionally introduced irregularity is not considered. The fact that the maximal obtained CD signal for this mixture is somewhat larger than that of **HH 4+16**, indicates that this additionally introduced irregularity has an, albeit small, influence on the chiral response. This is more clearly visible for the mixtures of the polymers with a TT defect. For **Mix TT 1**, almost no CD signal is recorded, indicating that too much irregularity was added to obtain a well-defined chiral supramolecular structure. For **Mix TT 2**, in which the added irregularity was lower, the opposite is true. The amount of vibronic fine structure in the absorption spectra, the maximal CD signal, and $|g_{\text{abs}}|_{\text{max}}$ value are all higher for the mixture compared to any of the individual polymers. This indicates that adding irregularity by mixing different types of polymers can also be used to increase the chiral response in PTs. It also explains the more efficient chiral expression of polymers synthesized via KCTCP with Ni^{2+} salts compared with all the TT polymers synthesized in this work. Not the presence of a TT defect, nor the position of this defect, but especially the mixture of chains with the defect in different positions gives rise to the chiral expression.

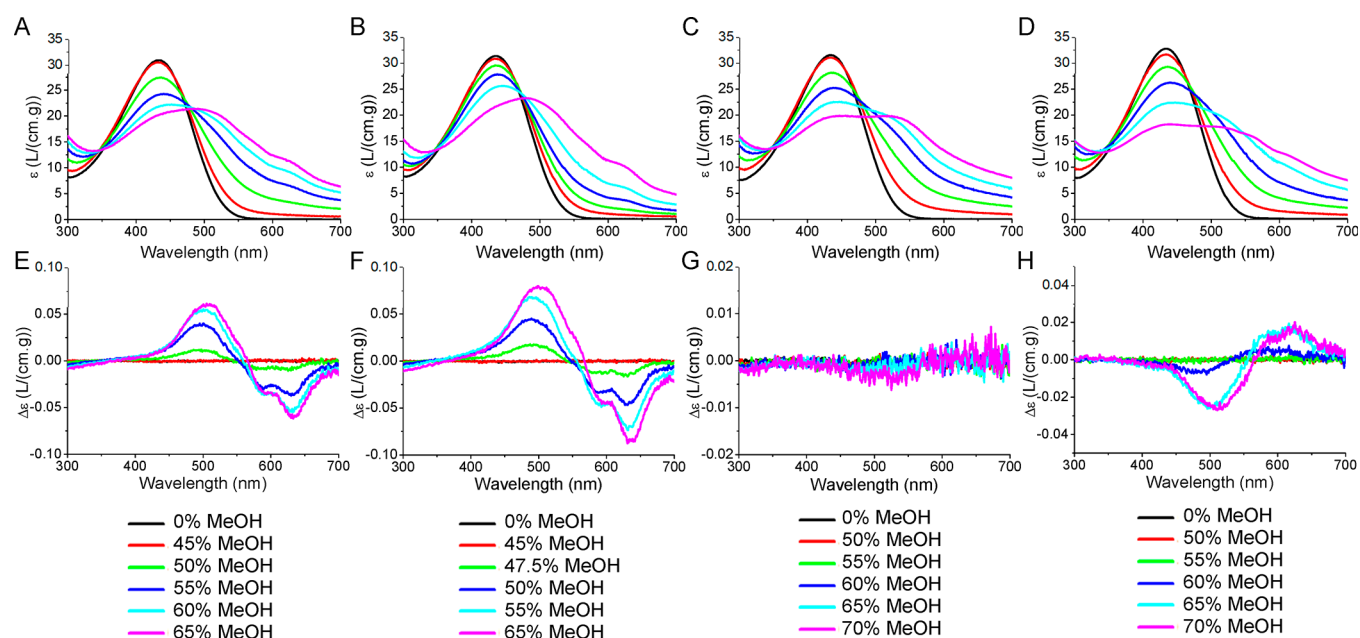


Figure 8. Absorption (A–D) and CD (E–H) spectra of the solvatochromism experiments for Mix HH 1 (A, E), Mix HH 2 (B, F), Mix TT 1 (C, G), and Mix TT 2 (D, H). The complete data set can be found in Figures S44–S55.

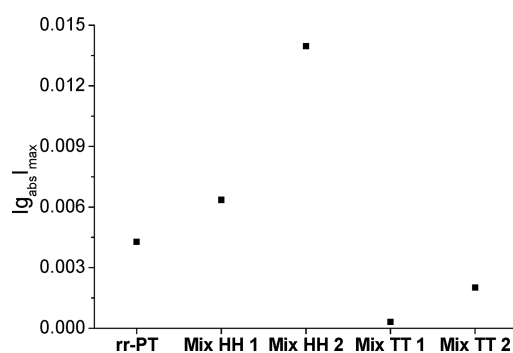


Figure 9. Comparison of $|g_{\text{abs}}|_{\text{max}}$ for rr-PT and the polymer mixtures.

CONCLUSIONS

Via the Pd(RuPhos) protocol, nine different polymers were synthesized to investigate the influence of the nature and the position of defects on the chiral expression in PTs. One fully regioregular PT and eight polymers with one defect, i.e., an HH or a TT coupling, placed in a predetermined position were prepared. The polymers were characterized with GPC and ^1H NMR, and their chiral expression was investigated with solvatochromism experiments, followed by UV–vis and CD spectroscopy. For the polymers with an HH defect, it was found that the position at the very beginning of the polymer chain is the most optimal to obtain the largest chiral expression. The obtained signal was higher compared with the complete regioregular PT and even the highest ever reported for PTs in chloroform and MeOH solutions. When the defect was displaced toward the middle of the chain, the chiral response rapidly decayed. When a TT defect is incorporated into the polymer, the chiral expression was lower compared with the regioregular polymer, and the most optimal position of the defect was a little shifted toward the middle of the chain compared with their HH analogues. All these observations can be explained by an effect that was

previously reported, namely, that a small amount of irregularity can increase the chiral response.^{9,20}

Besides the effect of the nature and the position of the defect on the chiral expression, also the effect of mixing polymers with a defect in different positions was investigated. For the mixtures of the polymers with an HH defect, a weighted average of the signals of its constituents was obtained, indicating no significant influence. However, for the mixtures of the polymers with a TT defect, different results were obtained. When 25% of each polymer was mixed, no chiral response was obtained, and when more of the polymers with the defect more toward the chain ends were incorporated, a chiral response higher than that of any of the component polymers was recorded. This reveals that not only the nature or the position of a defect influences the chiral expression but also the mixing of polymers with a defect in different positions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b01858.

Materials and instrumentation; experimental procedures; additional GPC elution chromatograms; determination of the degree of polymerization; additional absorption and CD spectra; ^1H NMR spectra of new compounds and polymers, ^{13}C NMR spectra of new compounds, ^{31}P NMR spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CD, circular dichroism; DP, degree of polymerization; GPC, gel permeation chromatography; GRIM, Grignard metathesis; HH, head-to-head; HT, head-to-tail; KCTCP, Kumada catalyst transfer condensation polymerization; MALDI-ToF, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; MeOH, methanol; rr, regioregular; P3ATs, poly(3-alkylthiophene)s; PTs, poly(thiophene)s; TT, tail-to-tail.

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