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Influence of Heterogeneity on the Chiral Expression of Star-Shaped Conjugated Polymers

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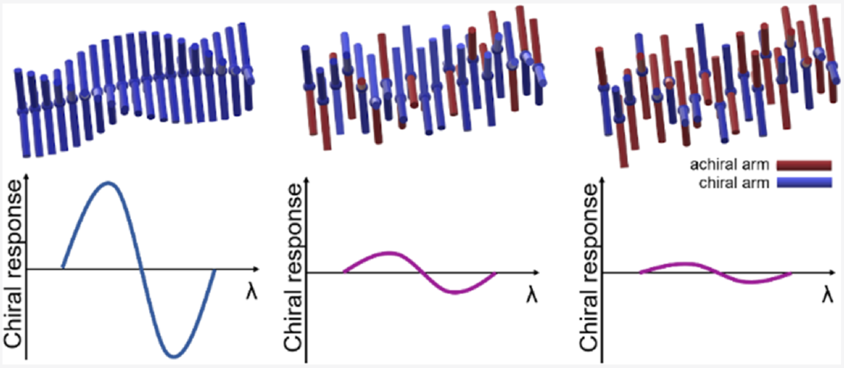

ABSTRACT: In this report, the influence of heterogeneity on the chiral expression of star-shaped conjugated polymers is investigated. For this purpose, two heterogeneous star-shaped conjugated polymers, i.e., one with two chiral arms and one achiral arm and the other one with one chiral arm and two achiral arms, are synthesized by combining Kumada catalyst transfer condensative polymerization, efficient post-polymerization reactions, and a two-step click reaction. The supramolecular organization and chiral expression of these systems are investigated by combining UV−vis, circular dichroism, differential scanning calorimetry, and atomic force microscopy. Three different hypotheses concerning the (chiral) supramolecular organization are postulated, i.e. the sergeants-and-soldiers-like principle, the "defect effect", and hampered organization. The results of the measurements exclude the first two hypotheses as a much lower chiral expression is obtained compared to the C3-symmetric chiral star-shaped polymer and revealed that replacing one chiral arm with one achiral arm was a too-large defect, resulting in a hampered organization.

INTRODUCTION

In the past decade, conjugated polymers (CPs) have gained a lot of attention as they possess unique optoelectronic properties and could, therefore, be promising materials for optoelectronics, such as oLEDs, oFETs, and oPVs.[1−3] The optoelectronic properties of CPs are closely linked to their supramolecular structure.[4−6] As a consequence, profound knowledge of the supramolecular organization of CPs is important, and extensive research concerning this topic has been conducted.[7−13] The incorporation of chiral substituents into the polymer creates a powerful tool for the investigation of the supramolecular structure since the chiral expression of CPs is directly related to their (chiral) supramolecular organization.[14]

Since poly(3-alkylthiophene) (P3AT) remains the benchmark polymer within CPs, the chiral expression of linear P3ATs has already been extensively investigated, and several principles have been established.[15−22] If, for instance, chiral and achiral polymer chains are randomly mixed into aggregates, then a positive nonlinear relationship is observed between the fraction of chiral polymer chains and the expected chiral response. This principle mimics the sergeants-and-soldiers principle, originally discovered by Green et al. in poly(isocyanates).[23] Further research on the chiral expression of P3ATs has revealed that there are several important parameters that can influence the chiral expression, such as the presence of end groups, the presence of defects, e.g., head-to-head or tail-to-tail couplings, in the polymer chain,[24−26] or co-crystallization in the supramolecular structure.[27] In the former case, depending on the position and nature of the defect, the chiral expression can be enhanced compared to the defect-free polymer, resulting in a larger chiral response compared to the defect-free polymer. The reason for the increase in chiral

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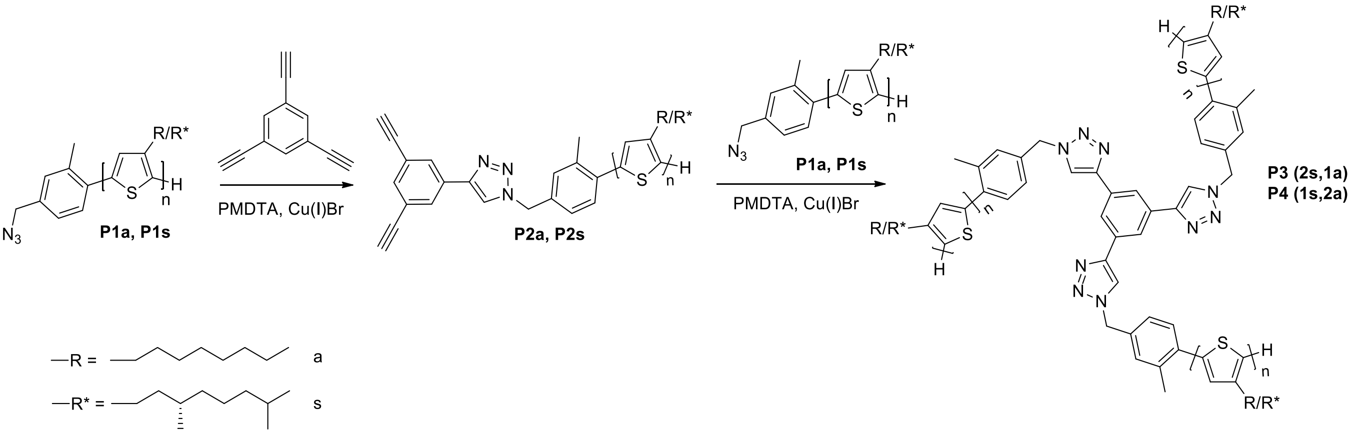
Scheme 1. Overview of the Synthetic Pathway of the Heterogeneous Star-Shaped P3ATs (P3 and P4)



response is the fact that the defect causes a larger twist between two aggregated polymer chains in the supramolecular helix, resulting in a higher chiral response compared to the defect-free polymer.[25,26]

A previous research indicated that CPs with a more complex topology, such as star-shaped systems, could obtain a more ordered morphology.[28] In contrast to the extensive library of manuscripts on the supramolecular organization of linear CPs, studies on star-shaped CPs remain scarce. The main reason thereof is that there is no efficient synthesis route available for the synthesis of well-defined star-shaped polymers. Recently, our group introduced the synthesis of well-defined star-shaped P3ATs with a controlled molar mass and low dispersity.[29] This revealed that star-shaped P3ATs have a more pronounced supramolecular organization than observed for any other linear P3AT. The corresponding chiral response of the C3-symmetric chiral star-shaped P3AT was 100-fold larger than the chiral response of the single, linear P3AT arm, indicating a considerably stronger chiral organization than that of linear P3ATs.[29]

In this research, the chiral expression of these intriguing star-shaped polymers is further unraveled by investigating the chiral response of heterogeneous star-shaped polymers. For this purpose, two heterogeneous well-defined star-shaped P3ATs are synthesized, one consisting of two chiral arms and one achiral arm and one with one chiral arm and two achiral arms, and the supramolecular organization and chiral expression are investigated. This mixing of different (chiral and achiral) arms can either result in a sergeants-and-soldiers-like behavior, a "defect effect", or a hampered organization. First, a sergeants-and-soldiers-like behavior expresses itself as a positive nonlinear trend of the chiral response as a function of the amount of chiral entity (in this case, the number of chiral arms) present in the heterogeneous star-shaped polymers. A true sergeants-and-soldiers experiment consists of mixing chiral and achiral entities, in which both the chiral and achiral entities adopt helical macro- or supramolecular structures, i.e., in the case of chiral entities, a one-handed helix is obtained, while in the case of achiral entities, a racemic mixture of helices is found. As a result, mixing chiral and achiral conjugated polymers is not a true sergeants-and-soldiers experiment as the sergeants (the chiral entities) form helical stacks, while the soldiers (the achiral entities) do not. Clearly, the polymers might form mixed aggregates, and all this might end up with graphics found in true sergeants-and-soldiers experiments, but it remains a different experiment. Therefore, we call this sergeants-and-soldiers-like behavior. Applied on the heterogeneous stars, a prerequisite for the sergeants-and-soldiers-like principle is that the aggregated chiral and achiral polymer chains do not phase-separate into separate chiral and achiral domains, but that they are randomly mixed into co-crystals. If the aggregated achiral and chiral polymers do phase-separate, a linear trend of the chiral response as a function of the number of chiral polymer chains would be visible. However, in the newly designed heterogeneous star-shaped polymers, the chiral and achiral polymer arms are attached to the same core, rendering phase-separation impossible. If the heterogeneous star-shaped polymers would aggregate in a similar way as the homogeneous C3-symmetric chiral star-shaped polymers do, then the chiral chains become randomly distributed in the crystal, and a sergeants-and-soldiers-like experiment would be realized.

Second, if the incorporation of the defect (in this case, the incorporation of the achiral arm), results in a larger chiral response than expected for the C3-symmetric chiral star-shaped polymer, then the "defect effect" is established. Third, and last, if the introduced defect is too large, then the (chiral) organization is hampered, resulting in a negative nonlinear trend of the chiral response as a function of the amount of chiral entity (in this case, the number of chiral arms) or even in no chiral response at all.

To investigate whether the supramolecular organization and the chiral response is enhanced or hampered by the incorporation of the defect, two heterogeneous star-shaped P3ATs are synthesized using a two-step copper(I)-catalyzed alkyne-azide cycloaddition (Cu(I)AAC). Afterward, the supramolecular organization is characterized using UV−vis and circular dichroism (CD) spectroscopy, differential scanning calorimetry (DSC), and atomic force microscopy (AFM) in order to reveal the effect of the heterogeneity on the supramolecular organization and the chiral response.

■ RESULTS AND DISCUSSION

In order to examine the effect of the heterogeneity on the (chiral) supramolecular organization of the star-shaped polymers, two heterogeneous star-shaped P3ATs, one with two chiral arms and one achiral arm and one with one chiral arm and two achiral arms, are synthesized using the grafting-onto method, in which the end-functionalized polymer chains are coupled to a central core. First, the two linear P3ATs,

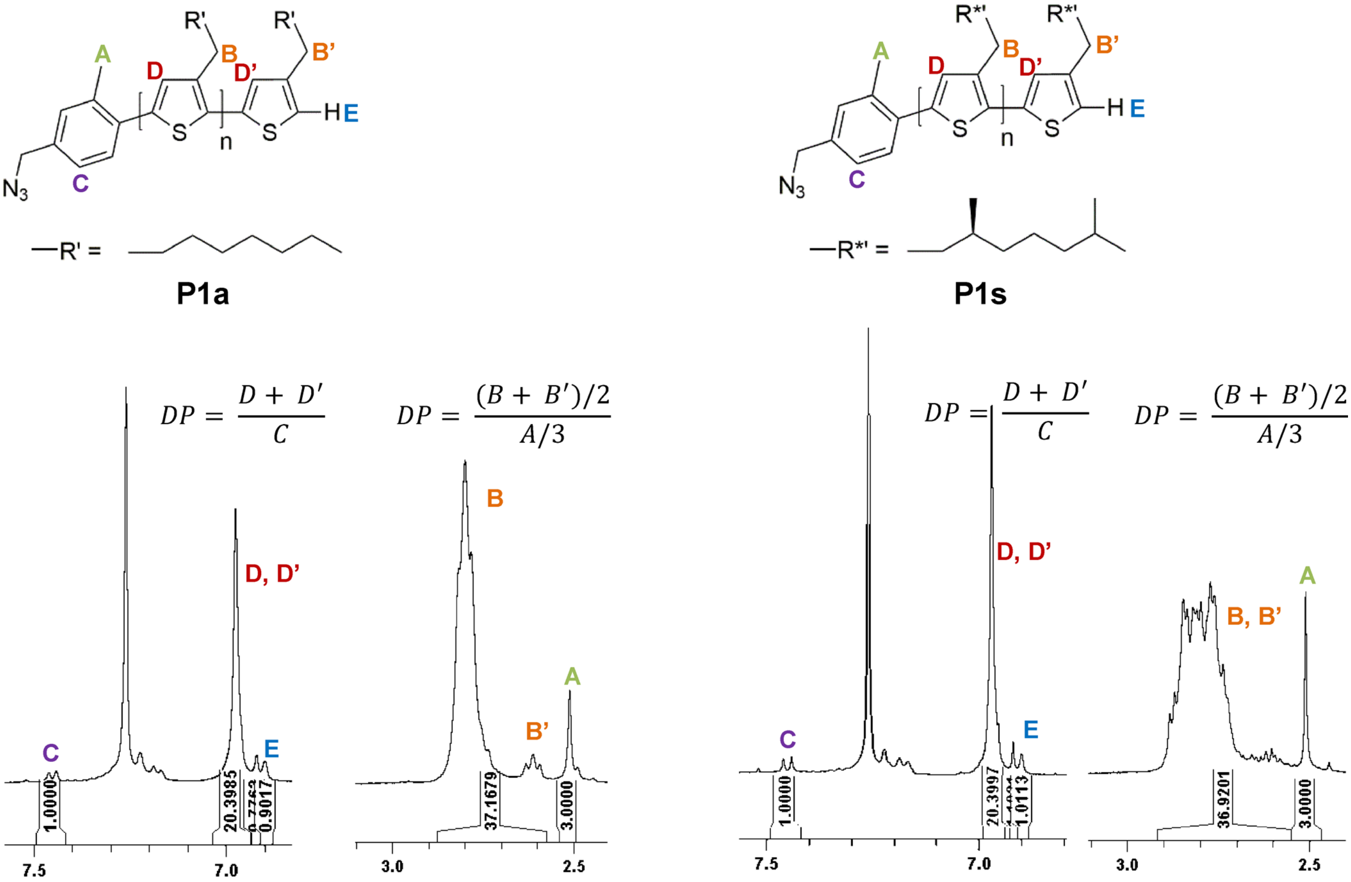


Figure 1. Assignment of ^{1}H NMR signals in the aromatic and aliphatic region in order to determine the degree of polymerization of **P1a** and **P1s**.

poly(3-octylthiophene) (P3OT) and poly((*S*)-3-(3,7-dimethyloctyl)thiophene) (P3DMO$^{(S)}$T) are synthesized according to literature procedures using the controlled Kumada catalyst transfer condensative polymerization (KCTCP) mechanism starting from a functionalized initiator.[29] The end group of the linear P3ATs is then modified according to literature procedures to an azide group via efficient post-polymerization reactions,[29] which allows the functionalized P3ATs to be coupled to the central 1,3,5-triethynylbenzene core in a two-step process (Scheme 1). The controlled character of KCTCP allows the synthesis of well-defined linear P3ATs with a low dispersity and with control over the molar mass and end-group functionalization.[30−33] The latter is of importance as only the P3ATs that bear the functional group will be incorporated in the star-shaped system. The degree of polymerization (DP) of the two P3ATs is set on 18, the reason thereof is twofold. First, a previous research has revealed that from a certain DP, the polymer chain ends will not continue to adopt a linear stack but will start to fold back, which can lead to a decreased supramolecular organization.[34] Second, a too-low DP will prevent efficient aggregation of the polymer chains.

P1a and **P1s** were analyzed by size exclusion chromatography (SEC) to estimate the number-average molar mass (M_n) and the molar mass dispersity ($Đ_M$). The DP of **P1a** and **P1s** can be calculated via ^{1}H NMR spectroscopy by comparing the signal of methyl protons of the end group of the polymer chains with the signal of the α-methylene protons of the monomer units (Figure 1) or by comparing the signal of an aromatic proton of the initiator with the signal of the aromatic proton of the thiophene units (Figure 1). These two methods are only valid if every polymer chain is initiated by an *o*-tolyl unit and has a H-terminated thiophene unit, implying that no transfer and no termination occurred during the polymerization. From the ^{1}H NMR spectrum of **P1a** and **P1s** in Figure 1, it can be derived that the aromatic *o*-tolyl signal and the aromatic thiophene signal are present in a 1:1 ratio, indicating that every polymer chain contains an *o*-tolyl unit and a H-terminated thiophene unit. The determination of the DP according to the aforementioned methods is therefore valid. This is further evidenced by the matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) spectra of **P1a** and **P1s**, which display negligible amounts of Br-terminated thiophene units (Supporting Information, Figures S1 and S2).

The estimated M_n and the molar mass dispersity ($Đ_M$) of **P1a** and **P1s**, obtained via SEC, and the DP of **P1a** and **P1s**, calculated via ^{1}H NMR spectroscopy, are shown in Table 1.

For the synthesis of the final heterogeneous star-shaped PATs, the azide-functionalized arms, **P1a** and **P1s**, are coupled

Table 1. Overview of the M_n, $Đ_M$ (Obtained via SEC) and the DP (Calculated via ^{1}H NMR Spectroscopy)

polymer	M_n (kg/mol)[a]	$Đ_M$[a]	DP[b]	DP[c]
P1a	4.6	1.2	18	20
P1s	5.2	1.2	18	19

[a] Determined via SEC calibrated toward poly(styrene) standards. [b] DP calculated via ^{1}H NMR spectroscopy in the aliphatic region. [c] DP calculated via ^{1}H NMR spectroscopy in the aromatic region.

in a two-step process to the central 1,3,5-triethynylbenzene core via a Cu(I)AAC click reaction. First, one arm, **P1a** or **P1s**, is coupled to the central 1,3,5-triethynylbenzene, using *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA) and Cu(I)Br, resulting in **P2a** and **P2s**, respectively (Scheme 1). A large excess of the core was used to ensure that only one arm was attached to the core. This click reaction was monitored by ^{1}H NMR spectroscopy as a clear shift of the methylene signal should occur (Figure 2). A possible side reaction that can occur is the coupling of two acetylene functions, i.e., the coupling of two cores, also known as Glaser coupling. This side reaction results in an extra SEC signal at double molar mass of the desired product (Figure 3, black curve). **P2a** and **P2s** were purified using preparative SEC in order to remove the coupled product (Figure 3, red curve). MALDI-ToF measurements confirmed the absence of coupled product (Supporting Information, Figures S3−S6).

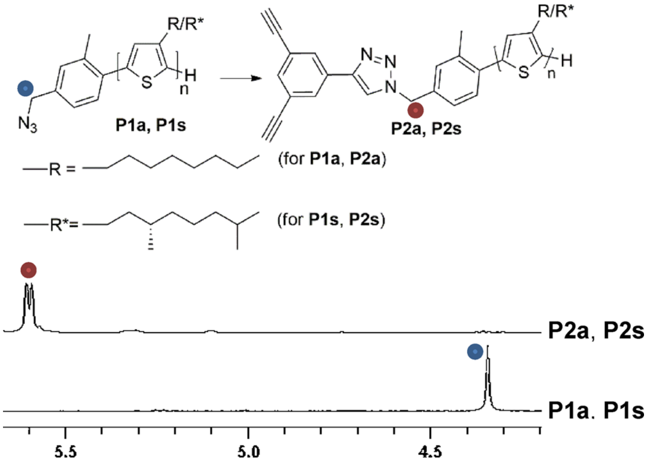


Figure 2. Overview of ^{1}H NMR spectra of the first Cu(I)AAC click reaction of **P1a** and **P1s** with the 1,3,5-triethynylbenzene core, indicating a small shift of the signal of the methylene protons.

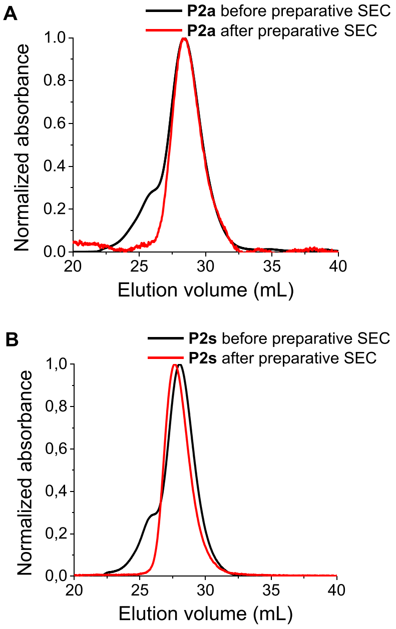


Figure 3. SEC elution curves of (A) **P2a** and (B) **P2s** before (black curve) and after (red curve) preparative SEC.

In the last step, the synthesis of the heterogeneous star-shaped polymers is finalized by coupling **P1s** and **P1a** to the two remaining acetylene functionalities of **P2a** and **P2s** via the Cu(I)AAC click reaction, resulting in the heterogeneous star-shaped polymers **P3** and **P4**, respectively. This last click reaction was again monitored by ^{1}H NMR spectroscopy as the signal of the acetylene proton at 3.1 ppm should disappear during the coupling of the P3AT arms to the core (Figure 4).

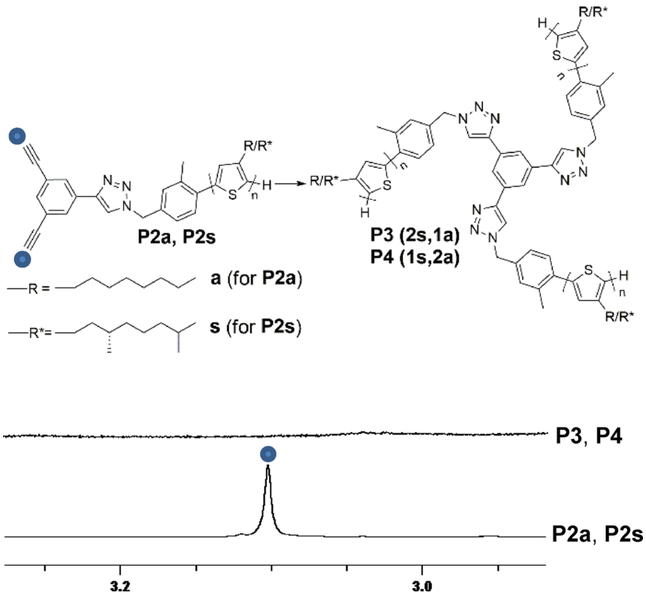


Figure 4. Overview of ^{1}H NMR spectra of the second and last Cu(I)AAC click reaction of **P1a** and **P1s** with **P2a** and **P2s**, indicating full conversion as the signal of the acetylene proton disappeared.

The signal of the methylene protons of **P2a** and **P2s** does not shift during the second Cu(I)AAC click reaction (Figure 5).

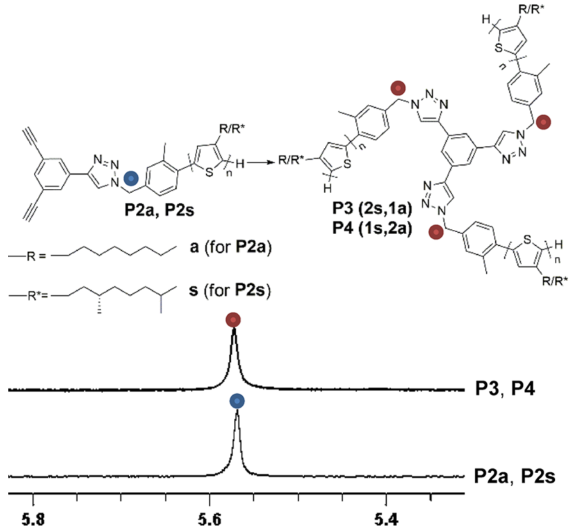


Figure 5. Overview of ^{1}H NMR spectra of the second and last Cu(I)AAC click reaction of **P1a** and **P1s** with **P2a** and **P2s**, indicating that no electronic influence is present between the polymer arms as the signal of the methylene of **P2a** and **P2s** does not shift upon the formation of **P3** and **P4**.

This indicates that no electronic influence is present between the polymer arms. In this second coupling step, a large excess of **P1a** and **P1s** is used to ensure the functionalization of both the acetylene functionalities. The excess of **P1a** and **P1s** is removed using preparative SEC in order to obtain the pure star-shaped polymers **P3** and **P4** (Figure 6). Note that these polymers are the first heterogeneous star-shaped all-conjugated polymers ever prepared.

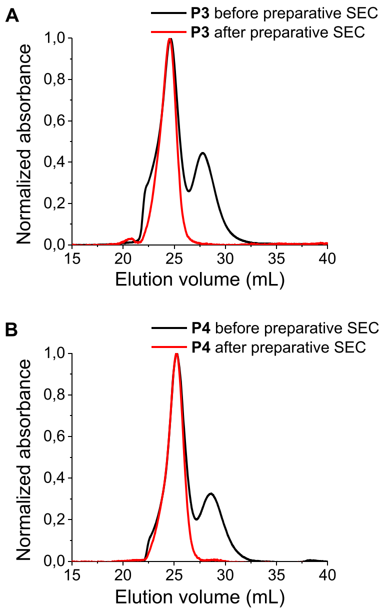


Figure 6. SEC elution curves of (A) **P3** and (B) **P4** before (black curve) and after (red curve) preparative SEC.

To verify which one of the three hypotheses discussed in the Introduction (sergeants-and-soldiers-like principle, “defect effect”, or hampered organization) holds, solvatochromism experiments were performed. For these experiments, three different ways to introduce aggregation are used. First, a non-solvent (methanol (MeOH)) is added step-wise to a solution of the polymers in a good solvent (chloroform). UV−vis and CD spectra were recorded directly after each addition of a non-solvent. To ensure the reproducibility of these measurements, the non-solvent is added with a constant speed of 0.20 mL/min via an automatic syringe pump. At a certain amount of MeOH, the polymer chains start to aggregate. This aggregation is visualized by a bathochromic effect and the appearance of a fine-structure in the absorption band. If the polymers start to organize in a chiral way, then apart from the redshift in the UV−vis spectra and the appearance of a fine-structure, a bisignate Cotton effect appears in the CD spectra. The UV−vis and CD spectra of **P3** and **P4** are shown in Figure 7.

As can be derived from the UV−vis spectra of **P3**, the polymer chains start to organize at a MeOH content of 40% (Figure 7). For **P4**, the UV−vis spectra indicate that the polymer chains already start to organize at 35% MeOH. This difference is due to the fact that achiral P3AT has a higher tendency to organize than the bulkier chiral P3AT, and since **P4** is equipped with two achiral P3AT arms and **P3** with only one achiral P3AT arm, **P4** organizes at a lower non-solvent content. Compared to the C3-symmetric chiral star-shaped polymer (Figure 8, left), the fine-structure in the UV−vis spectra of **P3** and **P4** is less pronounced, which indicates a less ordered supramolecular organization.[29] These results indicate that hypothesis three, i.e., hampered organization, is the most probable so far. However, a less-ordered supramolecular organization does not always result in less chiral organization

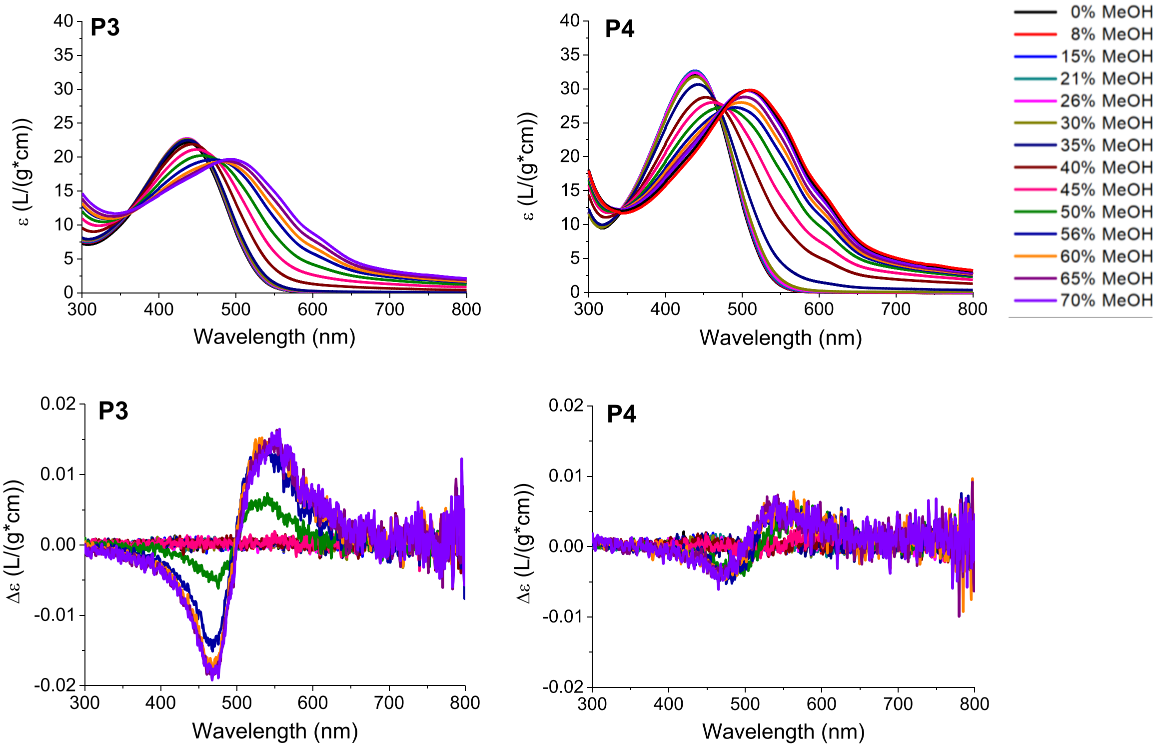


Figure 7. UV−vis spectra (top) and CD spectra (bottom) of the solvatochromism experiments for **P3** and **P4**. Concentration of the starting solution in chloroform: **P3** = 0.057 mg/mL, **P4** = 0.055 mg/mL; cell path length = 1 cm; temperature = 298 K.

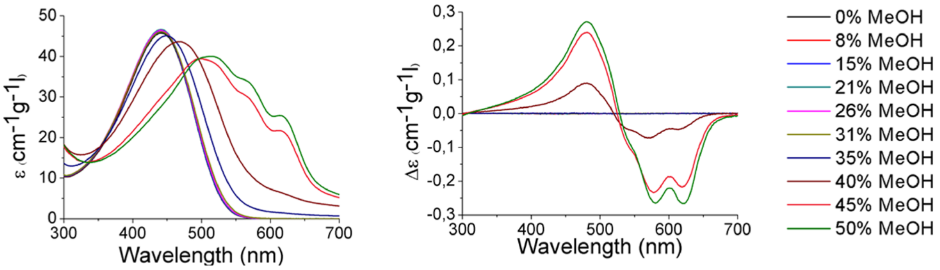


Figure 8. UV−vis spectra (left) and CD spectra (right) of the solvatochromism experiments for the C3-symmetric chiral star-shaped P3AT. Reprinted in part with permission from ref 29. Copyright 2018 American Chemical Society.

and thus a lower chiral expression. In order to evaluate the chiral organization, and thus the hypothesis of the sergeants-and-soldiers-like principle and the "defect effect", CD spectra were recorded in addition to the UV−vis spectra (Figure 7). For **P3** and **P4**, a weaker bisignate Cotton effect is observed compared to the C3-symmetric chiral star-shaped polymer (Figure 8, right).[29] The reason thereof can be twofold. First, this weaker CD signal could indicate that there is indeed less chiral organization within the aggregated polymer chains or second, that the overall organization of the polymer chains is less ordered, but that the chiral expression per aggregated unit is the same or even higher. The less-pronounced fine-structure in the UV−vis spectra of **P3** and **P4** already implies a less-ordered organization. To evaluate if there is indeed less organization, or solely less chiral organization, the $g_{\mathrm{abs,max}}$ (= $\Delta\varepsilon/\varepsilon$) value was calculated, resulting in a value of 0.001 $\pm$ 1 $\times$ 10^{-4} for **P3** and 0.0002 $\pm$ 7 $\times$ 10^{-5} for **P4**. For the C3-symmetric chiral star-shaped polymer, however, this value was 10−50 times higher ($g_{\mathrm{abs,max}} = 0.01 \pm 8 \times 10^{-5}$),[29] respectively, than the value of **P3** and **P4**, indicating that for the same amount of organization, **P3** and **P4** indeed show less chiral organization compared to the C3-symmetric chiral star-shaped polymer. Furthermore, **P4** has an even lower $g_{\mathrm{abs,max}}$ value than **P3**, indicating that the heterogeneous star-shaped polymer with only one chiral arm has the weakest chiral organization. Figure 9 displays the chiral response of the star-shaped polymers as a function of the amount of chiral entity present the polymers. If a sergeants-and-soldiers-like behavior would be obtained for these systems, then a positive cooperative effect would be present, and a positive nonlinear trend should be observed for the chiral response. For the "defect effect"-hypothesis, a steep increase in chiral expression is expected at low defect incorporation (high % of chiral entity), and the chiral expression of the small defect polymer would be even larger than for the defect-free polymer. If, on the other hand, no positive cooperative effect is present and the chiral expression is the result of solely the amount of chiral P3AT arms present, then the chiral expression would scale linearly with the amount of chiral entity, meaning the chiral response of **P3** and **P4** would be two-third and one-third of the chiral response of the C3-symmetric chiral star-shaped P3AT, respectively. However, from Figure 9, it can be derived that the chiral response does not follow any of these trends; on the contrary, the chiral response of the two heterogeneous star-shaped polymers is significantly smaller than is expected if no positive cooperative effect is present. These results indicate that the introduced heterogeneity is a too-large defect (33% in **P3** and 66% in **P4**) and instead of enhancing the chiral response, the supramolecular organization is hampered, leading to a much lower than expected chiral response. These results, therefore, eliminate the sergeants-and-soldiers-like principle and "defect effect" hypothesis and verify the hampered organization hypothesis. This is contrary to what is observed for linear P3ATs, in which sergeants-and-soldiers-like behavior has been established.[22] It is, however, in agreement with a broader trend, also present in linear P3ATs, in which the incorporation of a too-large defect results in a considerably lower chiral response compared to the defect-free polymer.[25,26]

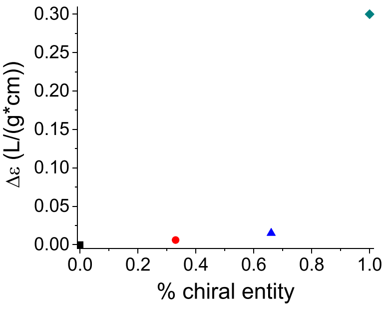


Figure 9. Plot of the chiral response of the different star-shaped polymers (achiral star-shaped P3AT (black square), **P3** (blue triangle), **P4** (red dot), and the C3-symmetric chiral star-shaped P3AT (green diamond)) as a function of the amount of chiral entity present.

Besides induction of aggregation through the addition of a non-solvent, the induction of aggregation through a variable temperature experiment is also investigated using CD spectroscopy. **P3** and **P4** were dissolved in 1-hexanol at 105 °C, the sample were then cooled down to 20 °C at 2 °C/min, and a CD spectrum was recorded every 2.5 min (Figure 10). The results obtained differ strongly from the results of the solvatochromism experiments discussed earlier. The effects are weaker and, more importantly, the shape does not correspond to a positive bisignate Cotton effect, which is a signature of chirally stacked (planar) polymer chains. The absence of the "right" shape of the CD spectra shows that this way of inducing aggregation is not suited to evaluate the chiral expression in these star-shaped polymers as a different supramolecular structure is formed. Note that obtaining a different supramolecular organization if the conditions to induce aggregation differ is not at all surprising. Moris et al. have found that the aggregation process of star-shaped but homogeneous, all-chiral polythiophenes follows a different path depending on the conditions used to induce aggregation (temperature, solvent quality, etc.) and that the aggregates formed have a different structure (although these particular structures were not revealed).[13,35] The results obtained for the variable temperature experiment can therefore not be

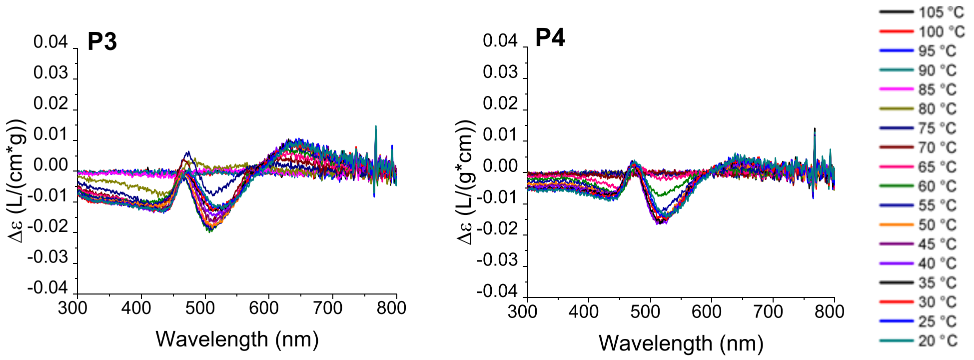


Figure 10. CD spectra of the variable temperature aggregation experiments for **P3** and **P4**.

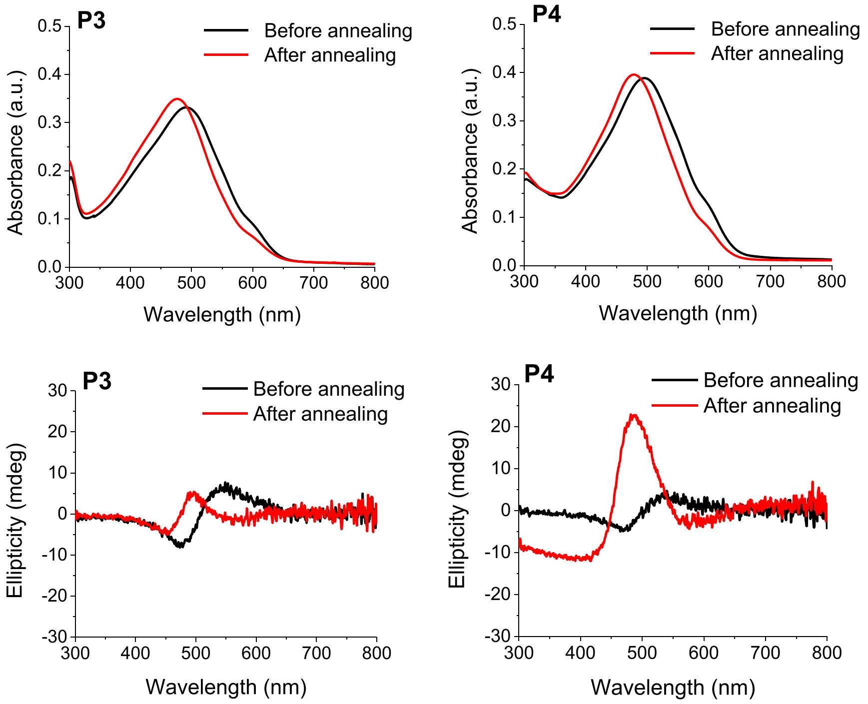


Figure 11. UV–vis spectra (top) and CD spectra (bottom) of the spin-coated films of **P3** and **P4** before (black curve) and after (red curve) thermal annealing. The films were prepared by spin coating solutions (1 mg/mL) of **P3** and **P4** in chloroform. The annealing temperature was 108 °C for **P3** and 123 °C for **P4**.

compared to the results obtained for the solvatochromism experiment using the gradual addition of a non-solvent.

Furthermore, UV–vis and CD experiments were conducted on spin-coated films of **P3** and **P4** before and after thermal annealing (Figure 11). The UV–vis and CD results of the spin-coated films before thermal annealing correspond to the results of the solvatochromism experiments—the same intensity and, more importantly, the same shape—indicating that the hampered organization hypothesis also holds for **P3** and **P4** in the solid state. After thermal annealing, the chiral response of **P3** is smaller than that before annealing, while the chiral response of **P4** has increased with a factor of 5 compared to the non-annealed film. More importantly, the shape becomes totally different (no bisignate Cotton effect anymore). In addition with the UV–vis spectra that are losing their vibronic fine-structure, this points again at a different organization.

DSC measurements were performed to study the thermal properties of the heterogeneous star-shaped polymers in the solid state. These thermal properties are closely related to the supramolecular organization of the star-shaped polymers in the solid state. For both **P3** and **P4**, clear melting peaks and crystallization peaks were visible. As expected, the peak melting temperature of **P3** (T_m = 117.8 °C) and **P4** (T_m = 133.2 °C) is the weighted average of the peak melting temperature of the C3-symmetric chiral star-shaped polymer (T_m = 108.9 °C) and the achiral star-shaped polymer (T_m = 142.9 °C).[29] Note that since only one peak at the averaged temperature is found, microphase separation of the two arms can be excluded. However, when considering the melt enthalpy (ΔH_m), **P3** (ΔH_m = 4.7 J/g) and **P4** (ΔH_m = 5.1 J/g) appear to have a lower melt enthalpy than the C3-symmetric chiral star-shaped polymer (ΔH_m = 7.5 J/g) and the achiral star-shaped polymer (ΔH_m = 7.7 J/g), indicating a weaker supramolecular organization for **P3** and **P4**, which is also confirmed by the UV–vis analysis (vide supra). These results further evidence the hampered organization hypothesis. The thermograms of **P3** and **P4** can be found in the Supporting Information (Figures S7 and S8).

Furthermore, AFM was performed in order to obtain more information on the supramolecular organization and morphology of the star-shaped polymers in the solid state. AFM imaging was performed on films obtained by drop casting a diluted solution of the star-shaped polymers in toluene on a highly oriented pyrolytic graphite (HOPG) substrate. For **P3** and **P4**, fibrous structures were clearly visible (Figure 12). The lamellar structures shown in Figure 12 are characteristic of P3AT films.[9,36,37] These structures consist of π-stacked polymer chains perpendicular to the axis of the fibers. Therefore, the length of a fiber is an indication of the strength of the $\pi-\pi$ stacking of the star-shaped polymers and thus of the supramolecular organization. Figure 13 shows the AFM images of the achiral and C3-symmetric chiral star-shaped P3ATs. **P3** forms fibers that have an average length of a few hundreds of nanometers; **P4**, on the other hand, forms fibers with an average length of a few micrometers, implying that **P4** has a stronger supramolecular organization. This is confirmed by the higher melting temperature and slightly higher melt enthalpy for **P4** obtained by DSC measurements. The UV−vis spectra of the organized **P4** polymer chains do not clearly imply a stronger organization for **P4** compared to **P3**. This can, however, be due to the fact that UV−vis is less sensitive toward differences in the supramolecular organization or due to the fact that the supramolecular organization obtained from solution experiments can differ from solid-state experiments. Furthermore, compared to the C3-symmetric chiral (14.8 ± 1.4 nm)[29] and achiral (14.8 ± 2.6 nm)[29] star-shaped polymer, a clear difference in the fiber width is observed for the heterogeneous star-shaped polymers **P3** (20.0 ± 1 nm) and **P4** (26.0 ± 3 nm) (see the Supporting Information, Figures S9 and S10, for the details). In the case of the C3-symmetric chiral and achiral star-shaped polymer, these experimentally obtained fiber widths confirmed the theoretically calculated fiber width of the proposed supramolecular organization in which the fibers consist of stacks of single, star-shaped polymers.[29] The larger fiber widths of **P3** and **P4** indicate that the star-shaped polymers do not perfectly aggregate on top of each other into fibers, but that the different aggregated star-shaped polymers are more shifted relative to each other and thus form broader fibers. This confirms the hypothesis of a more-hampered (chiral) supramolecular organization, which is further evidenced by UV−vis, CD, and DSC measurements.

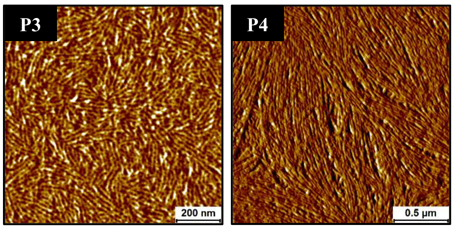


Figure 12. AFM phase images of dry films of **P3** and **P4** drop casted from toluene on a graphite substrate.

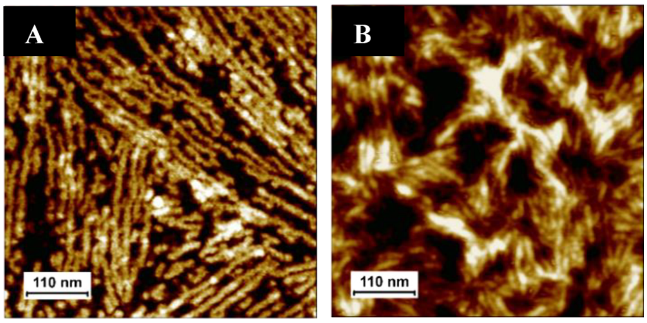


Figure 13. AFM topography images of dry films of the (A) achiral and (B) C3-symmetric chiral star-shaped P3AT drop casted from chloroform on a graphite substrate. Reprinted in part with permission from ref 29. Copyright 2018 American Chemical Society.

■ CONCLUSIONS

Two newly designed, well-defined heterogeneous star-shaped polymers with a low dispersity were successfully synthesized by combining KCTCP, efficient post-polymerization reactions, and Cu(I)AAC click reactions. Different techniques were combined to unravel the influence of the heterogeneity on the supramolecular organization and chiral expression of these peculiar star-shaped polymers. Three hypotheses concerning the (chiral) supramolecular organization were proposed, i.e., the sergeants-and-soldiers-like principle, "defect effect", and hampered organization. UV−vis and CD measurements revealed a weaker supramolecular organization and an even weaker chiral expression compared to the C3-symmetric chiral star-shaped polymer. From these results, it could be concluded that a negative nonlinear relationship is present between the amount of chiral entity present in the heterogeneous star-shaped polymers and the chiral expression, indicating that the (chiral) supramolecular organization is hampered by the introduction of the heterogeneity. These results thus eliminate the validity of the sergeants-and-soldiers-like hypothesis and the "defect effect". In the case of the latter, the absence of the "defect effect" is presumably due to the extent of the introduced defect. The "defect effect" only holds for the incorporation of a small defect, the replacement of one chiral arm with one achiral arm already accounts for a 33% defect in the polymer, which most probably is too large. DSC and AFM measurements were performed to evaluate the supramolecular organization in the solid state. The lower melt enthalpies for the heterogeneous star-shaped polymers, compared to the melt enthalpies of the C3-symmetric chiral and achiral star-shaped polymers, support the weaker supramolecular organization observed in the UV−vis and CD spectra. Furthermore, AFM images illustrate that the heterogeneous star-shaped polymers organize into well-defined fibers. However, the fiber width of the heterogeneous star-shaped polymers is broader compared to those of the C3-symmetric chiral and achiral star-shaped polymers, supporting the hypothesis that the introduced defect is too large and thus hampers the (chiral) supramolecular organization. In conclusion, the introduction of the heterogeneity has a negative influence on the supramolecular organization of these heterogeneous star-shaped polymers. This implies that the principles valid in linear P3ATs, such as the sergeants-and-soldiers-like principle, may no longer be valid in more complex structures, such as star-shaped polymers. To evaluate the validity of the "defect effect" in these more complex star-shaped systems, further research could be conducted on newly designed star-shaped polymers with at least six arms, so the replacement of one chiral arm by an achiral arm is more related to "the small defect effect" valid in linear P3ATs.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00901.

Materials and instrumentation, experimental procedures, MALDI-ToF spectra, DSC thermograms, AFM measurements, and ^{1}H NMR of the polymers (PDF)

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Notes

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ABBREVIATIONS

CPs, conjugated polymers; oLEDs, organic light-emitting diodes; oFETs, organic field-effect transistors; oPVs, organic photovoltaics; P3AT, poly(3-alkylthiophene); KCTCP, Kumada catalyst transfer condensative polymerization; Cu(I)AAC, copper(I)-catalyzed alkyne-azide cycloaddition; MALDI-ToF, matrix-assisted laser desorption/ionization time-of-flight; CD, circular dichroism; DSC, differential scanning calorimetry; AFM, atomic force microscopy; P3OT, poly(3-octylthiophene); P3DMO$^{(S)}$T, poly((*S*)-3-(3,7-dimethyloctyl)-thiophene); DP, degree of polymerization; SEC, size exclusion chromatography; PMDTA, *N*,*N*,*N*′,N″,N″-pentamethyldiethylenetriamine; MeOH, methanol; HOPG, highly oriented pyrolytic graphite

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