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ARTICLE TYPE

Poly(3-alkylthiophene) with tuneable regioregularity: synthesis and self-assembling properties

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This work reports on a synthetic strategy to generate poly(3-alkylthiophene)s (P3ATs) with joint-simultaneous control of the molar mass and the regioregularity. A series of chiral P3ATs with different regioregularities is synthesized using a Pd(RuPhos)-catalyzed chain-growth polymerisation. All polymers have molar masses and polydispersities (PDI) that lie within a narrow region. Furthermore, it is shown that the Pd-catalyst forms all kinds of couplings [head-to-tail (HT), tail-to-tail (TT) and head-to-head (HH)] to a similar extent, which allows to insert predictable amounts of regio-irregularities into the polymer chain. This enables a thorough study of the influence of the regioregularity on the properties of P3AT, which was performed using UV-vis and circular dichroism (CD) spectroscopy, differential scanning calorimetry (DSC) and atomic force microscopy (AFM) measurements. Unexpectedly, it is found that in “kinetic” conditions the highest crystallinity, π -stacking, supramolecular organisation and chiral expression are not obtained for fully regioregular P3AT with 100% HT couplings, but that a small amount of regio-irregularity increases these properties and the chiral expression. In “thermodynamical” conditions (after annealing, very slow solvent evaporation or very slow cooling from the melt), this effect is less pronounced or not found. This behaviour can be explained by a higher degree of motional freedom within the non-perfect polymer chains due to the increased steric repulsion from the HH-couplings, which leads to a more easy stacking in “kinetic” conditions.

Introduction

Poly(3-alkylthiophene)s (P3ATs) have become the fruitfly of the research area of conjugated polymers, both in terms of fundamental studies and application-oriented research. For example, organic solar cells using regioregular (rr), HT-P3ATs as the donor material have reported efficiencies over 6.5%.^{1,2} The reason for this popularity is mainly their relatively easy production and the formation of semicrystalline, lamellar microstructures.³ However, the advantageous properties are strongly dependent on features like the type of side chain,^{4–8} the molar mass,^{9–13} the polydispersity¹⁴ and the regioregularity. The latter is possibly the most critical parameter of all, as it has been shown that the regioregularity influences a vast amount of polymer properties: a higher regioregularity leads to higher crystallinity,^{15,16} interchain interactions,¹⁷ specific capacitance,¹⁸ charge mobility,¹⁹ photostability,²⁰ intramolecular order^{21,22} and a lower bandgap.²³ Furthermore, it influences the lamellar thickness of the aggregated polymer chains²⁴ and it has also been shown that a higher regioregularity results in higher morphological order.²⁵ For all these properties, it is generally believed that the higher the regioregularity, the better the properties. Regioregularity is also a crucial parameter for the application of P3ATs in organic photovoltaics (OPV). A high

percentage of HT-couplings is necessary to obtain high efficiencies^{26–29} while strongly regio-irregular (rir) P3ATs are not suited for use in OPVs, because of their amorphous structure. Nevertheless, a few reports indicate that a small amount of disturbance in the conjugated backbone, by e.g. HH-couplings, does not deteriorate the efficiency in the specific case of bulk heterojunction (BHJ) solar cells and can even lead to an increase thereof.^{30–32} The BHJ solar cells made from P3AT with small amounts of “defects” are believed to have lower crystallinity, resulting in less phase separation leading to a higher thermal stability.^{33–35} Therefore, the increased efficiencies of P3AT with lower %HT-couplings are not ascribed to a better organisation of the polymer chains, but to the fact that these defects slow down the “demixing tendency” of the active layer.

In those studies, the rir-P3ATs are usually synthesized using an oxidative polymerisation using for instance FeCl₃, or by other non-controlled polymerisation mechanisms, like Pd(PPh₃)₄-catalyzed Suzuki or Stille couplings.^{36–39} Unfortunately, those methods do not allow a good control of the degree of polymerisation and the polydispersities of these polymers are always fairly high (2 or above). Therefore, it is very difficult to adequately compare P3ATs with different degrees of regio-irregularity, because they always differ not only in the %HT-couplings, but also in other important parameters like the molar mass and the polydispersity. rr-P3ATs, on the contrary, are

typically synthesized using a controlled chain-growth Ni(dppp)-mediated polymerisation mechanism (dppp = 1,3-bis(diphenylphosphino)propane). If Ni(dppp)Cl₂ is used as an initiator, this results in HT-P3AT with one TT-defect.^{40,41}

Recently, 100% HT-P3AT, without a TT-defect, was synthesized using a 3-alkylthiophene Ni(dppp)-initiator.¹⁶ It was shown that this 100% HT-P3AT has an increased crystallinity compared to P3AT with only one TT-defect. HT-P3ATs obtained via the

Scheme 1 Synthesis of the precursor monomers and the initiator.

Scheme 2 Synthesis of the polymers P1-P7.

Ni(dppp)-catalyzed method possess well-determined molar masses and narrow polydispersities. However, starting from a monomer mixture of both isomers, it is impossible to synthesize *rr*-P3AT with this method, since HH-couplings are not formed in the absence of LiCl. Addition of LiCl to the polymerisation mixture promotes the formation of a HH-coupling,^{42,43} but the reaction rate of this HH-coupling is, however, still much lower compared to the formation of a HT-coupling, resulting in regioregular P3AT, with only one additional HH-defect. Therefore, it must be concluded that it is not possible to efficiently tune the %HT-couplings in P3AT using the Ni(dppp)-based polymerisation method.

From these arguments, it can be stated that a thorough study of the influence of the regioregularity on the polymer properties has not been possible up to now because of the synthetic limitations described above. Such a thorough study requires that (i) P3ATs are synthesized using a controlled polymerisation mechanism, to obtain materials with equal molar mass and polydispersities, and (ii) predictable amounts of non-HT-couplings can be introduced into the polymer chain. In this way, a clear view of the influence of the regioregularity on the P3AT properties can be obtained. This could be done by copolymerizing the two regio-isomers of the monomer, which are, ideally, randomly built in. With such an approach, the composition of the polymer does not vary and is similar to that of the monomer feed.

Recently, we reported a controlled chain-growth polymerisation mechanism for the synthesis of HT-P3AT, poly(fluorene) and their block-copolymers in both directions.⁴⁴ This mechanism is based on Negishi-couplings and uses a Pd-catalyst. Regioregularity was obtained by using only one isomer of 3-alkylthiophene (*i.e.* 2-bromo-5-bromozincio-3-alkylthiophene). However, Pd-based catalysts have already proven in the past to result in *rr*-P3ATs, albeit via step-growth polymerisations.^{45,46} It can therefore be speculated that, if both 3-alkylthiophene isomers (2-bromo-5-bromozincio-3-

alkylthiophene and 2-bromozincio-5-bromo-3-alkylthiophene) are added to the catalyst, both isomers will be consumed, resulting in regiorandom P3ATs. Furthermore, Bryan *et al.* have recently shown that HH-couplings are also formed in a chain-growth polymerisation if a Pd catalyst with *N*-heterocyclic carbene ligands is used for the copolymerisation of both isomers of 3-alkylthiophene.⁴⁷ However, they found that HT-couplings were still preferred over other types. Nonetheless, to be able to synthesize P3AT with predicted %HT-couplings, it is necessary that all different types of couplings (HT, HH and TT) are built in with (more or less) equal probability, meaning that the copolymerisation of both isomers needs to be statistical in nature.

In this paper, we investigate whether it is possible to use the abovementioned polymerisation protocol to obtain a controlled chain-growth polymerisation of P3ATs with tunable degrees of regioregularity. Polymers with varying %HT-couplings are synthesized by combining different ratios of the two 3-alkylthiophene isomers and it is analyzed whether statistical copolymerisations are obtained. We then characterize the crystallinity, the aggregation behaviour and the chiral expression of these polymers, using DSC, UV-vis-spectroscopy, AFM and CD-spectroscopy, to gain a detailed insight in the influence of the regioregularity on the polymer self-assembly and the resulting optical and electrical properties. Finally, the electrical properties of thin film deposits are studied using a Scanning Probe derived technique (*i.e.* Conducting Atomic Force Microscopy – C-AFM) able to map the current at the nanometer scale.^{48,49}

Results and Discussion

Synthesis

The uncommon isomer 5-bromo-2-iodo-3-((*S*)-3',7'-dimethyloctyl)-thiophene (**3**) was synthesized starting from **1** in a procedure similar to that reported previously by Boyd *et al.*⁵⁰ The starting product was converted to a Li-salt using a sterically hindered Li-reagent, lithium tetramethylpiperidine (LiTMP),

Table 1 Polymer composition and molar mass.

Polymer	% 10 in the feed	%HT-couplings ^a	%HH-couplings ^a	%TT-couplings ^a	$\bar{M}_n$ (kg/mol) ^b	PDI ^b
P1	100	100	0	0	8.5	1.45
P2	100	100	0	0	8.8	1.25
P3	99	95	3	2	9.1	1.45
P4	97	92	4	4	8.1	1.50
P5	95	89	5	6	8.0	1.35
P6	90	83	8	9	7.9	1.40
P7	50	56	21	23	8.4	1.40

^a Determined by ¹H NMR spectroscopy.^b Determined by GPC in THF towards poly(styrene) standards. **Scheme 3** Probability for the formation of the different dyads assuming a statistical copolymerisation.

followed by quenching with CBr_4 , which results in **2**. That molecule was then further treated with I_2 and $\text{PhI}(\text{OAc})_2$, yielding the “reverse” isomer **3**. The initiator (**5**) was synthesized by reaction of 2-bromo-3-((*S*)-3',7'-dimethyloctyl)thiophene (**4**) with $\text{Pd}_2(\text{dba})_3$ and RuPhos (Scheme 1).

The polymerisation of P3ATs with different degrees of regioregularity was approached as a random copolymerisation of the two isomers of the monomer (**8** and **10**) (Scheme 2). To obtain P3AT with a certain amount of HH-couplings, the relative quantities of the two isomers were varied. An increasing amount of isomer **8** should lead to an increase in HH-couplings, until a maximum is obtained if equal amounts of the two isomers are used. In the polymerisation reaction, the precursor monomers **3** and **6** were first converted to their Grignard-equivalent (**7** and **9**, respectively), after which they were reacted with dried ZnBr_2 , thereby forming the corresponding organozinc monomers **8** and **10**. Subsequently, predetermined quantities of these two isomers were combined, after which they were added to a solution containing 4 mol% of the initiator **5**. Using this method, a series of 7 polymers was synthesized. In order to be able to confirm the properties of the fully regioregular P3AT, the polymer with 100% HT couplings was prepared twice. The molar masses and polydispersities of all synthesized polymers were analyzed using gel permeation chromatography (GPC) (Table 1). All polymers have comparable molar masses and polydispersities. Taking into account that the molar masses obtained by GPC are

overestimated, the degree of polymerisation can be estimated to be ~ 25 , consistent with the amount of initiator that is used (4 mol%).

Next, we verified whether the two monomers are statistically incorporated into the polymer backbone, which would allow to predict the %HT-couplings in the resulting polymer for a given composition of the monomer feed. Since this polymerisation is in fact a copolymerisation of monomers **8** and **10**, the amount of the monomers in the polymer backbone, and related with this the %HT-couplings, depends on the copolymerisation parameters (r_1 and r_2). Their exact quantification requires the determination of the composition of the polymers after small conversions starting from different feed compositions. However, the purpose of our investigation is not the exact quantification of the copolymerisation parameters, but the verification of whether the polymerisation proceeds statistically. This can also be done by assuming that the polymerisation indeed proceeds statistically and verifying whether the predicted %HT-, %HH- and %TT-couplings in the series of copolymers is reflected in the experimentally prepared polymers. If the polymerisation proceeds statistically, all rate constants are equal, *i.e.* $k_{11} = k_{12} = k_{21} = k_{22}$ and $r_1 = r_2 = 1$, and both the feed and the polymer composition are the same and remain constant during the polymerisation. Hence, if the feed ratio of **8** equals x and that of **10** equals $(1-x)$, the probability that **8** is incorporated as monomer i (and $i+1$, $i+2$, etc) in the polymer chain is x , while the probability that **10** is incorporated on these positions is $(1-x)$. The formation of a HT-coupling requires that monomer **8** is on both i^{th} and $(i+1)^{\text{th}}$ position; as a consequence, the probability for its formation is x^2 (Scheme 3). The probability for the other dyads can be calculated likewise.

Since a HT-coupling is indistinguishable from a TH-coupling, we find that, assuming the polymerisation proceeds statistically:

$$\%HT = x^2 + (1-x)^2 = 2x^2 - 2x + 1$$

$$\%HH = \%TT = (1-x)x = -x^2 + x$$

Note that if the polymerisation does not proceed statistically, but that *e.g.* HH-couplings are more slowly formed, these equations do not hold. In that case, the %HH would be lower and the %HT would be higher. At high conversion, all monomers can be incorporated and, hence the monomer ratio in the feed corresponds to the ratio in the polymer, but the regioregularity is different.

The relative amounts of the respective dyads can be experimentally determined by ¹H NMR- spectroscopy. Barbarella

Fig. 1 ^1H NMR assignment of the different triads in P3AT (**P7**).

Fig. 2 Comparison of the experimental values of the different types of couplings with the theoretical values, assuming a random incorporation of both monomers (upper line = theoretical %HT-couplings; lower line = theoretical %HH- and TT-couplings).

Fig. 3 (a) Deconvolution of the UV-vis spectrum of **P1**, highlighting the aggregation-related band; (b) CD-spectra of **P1** for different $\text{CHCl}_3/\text{MeOH}$ mixtures. All measurements were performed with a concentration of 20 mg/L.

et al. have assigned the aromatic region of the four different triads (Fig. 1).⁵¹ As a consequence, the experimentally observed values for the possible couplings are:

$$\%HT = \frac{2A + B + C}{2(A + B + C + D)}$$

$$\%HH = \frac{C + D}{2(A + B + C + D)}$$

$$\%TT = \frac{B + D}{2(A + B + C + D)}$$

where A, B, C and D are the integration values of the respective ^1H NMR-signals.

In Fig. 2, the experimentally found values are compared with the predicted ones, in which a statistical polymerisation is assumed. First, it is clear that the presence of both monomers in the feed results in regio-irregular polymers. Moreover, the experimental results nicely follow the theoretical curves; only a small deviation is found for **P7**. This demonstrates that our assumption is valid and that the use of the $\text{Pd}(\text{RuPhos})$ catalyst results in a statistical copolymerisation, allowing to prepare P3AT with a predictable %HT-couplings. Taking the controlled nature of the polymerisation into account,⁴⁴ the method based on the $\text{Pd}(\text{RuPhos})$ catalyst constitutes the first method that combines a controlled polymerisation mechanism with a

Fig. 4 Relative intensity of the aggregation-related band as a function of the %HT-couplings (a) in poor solvent, (c) in film before annealing and (e) in film after annealing; g_{abs} -values ($\Delta\epsilon/\epsilon$) in function of the %HT-couplings (b) in poor solvent, (d) in film before annealing and (f) in film after annealing.

predictable %HT-couplings.

5 Chiroptical Properties

UV-vis and CD spectroscopy measurements were first performed in different solvent qualities (different ratios of CHCl_3 /methanol) to obtain insight in the aggregation behaviour of the polymers (see Electronic Supplementary Information (ESI)). From the spectra, it is clear that no aggregation takes place in **P7** (56% HT), reflected by the absence of any fine structure in the UV-vis spectrum and no CD-signal, although an increase in λ_{max} is observed, probably due to some planarisation of single polymer chains. For the other polymers (**P1-P6**), a clear red shift is observed in UV-vis spectroscopy, accompanied by the appearance of a fine structure, as commonly observed for π -P3ATs. Also a CD-signal is observed, indicating chiral aggregation.

In order to compare them with each other, the UV-vis spectra of the polymers obtained in 4/1 methanol/ CHCl_3 were deconvoluted into 5 constituting bands using a linear programming method, as shown in Fig. 3a for **P1** (see ESI for the other deconvoluted spectra).^{11,52}

For each polymer, the area of the band that can be correlated with the π -stacking,⁵³ indicated in red in Fig. 3a, is calculated. This area was compared with the total area of the UV-vis spectrum. These results can give a clear insight in the degree of π -stacking in the polymers. To analyze the chiral aggregation behavior, the CD-signals in different solvent mixtures (CHCl_3 /MeOH) are measured (Fig. 3b for **P1**). Note that in the spectra of **P1**, optomotorotation is observed when decreasing the solvent quality.⁵⁴ For each polymer, the spectrum in the chloroform/methanol mixture that gave the most intense signal was used to calculate the g_{abs} -values ($\Delta\epsilon/\epsilon$). These g_{abs} -values are a measure of the intrinsic chirality of the polymers and can be used directly to compare the chiral behaviour of the different polymers. The g_{abs} -value at 600 nm was used in the analysis.

In Fig. 4a-b, the values obtained from the UV-vis and CD-analysis of the polymers in a nonsolvent are plotted as a function of the %HT-couplings in the polymer. These graphs show a clear increase in both the relative intensity of the aggregation band, probing aggregation, and the g_{abs} -values as a function of the %HT-couplings, measuring chiral aggregation. It is important to note that even for **P6** (with only 82% HT-couplings) (chiral) organisation is still present, demonstrating that a relatively high amount of non-HT-couplings is tolerated. In contrast to what could be expected, both graphs (Fig. 4a-b) show a maximum for a %HT-couplings below 100%. Concerning the UV-vis data, it is clear that the largest relative contribution is obtained for **P3** (95% HT-couplings). **P1** and **P2**, with 100% HT-couplings have a smaller π -stacking contribution. The g_{abs} -values show a maximum value for **P4**, with 92% HT-couplings, after which a decreasing trend is observed with increasing %HT-couplings. From this graph, it can be concluded that the regioregularity also strongly influences the chiral behaviour of the different polymer chains and that the highest chiral response is obtained for polymers with some non-HT-defects in these conditions. We suspect that this better (chiral) aggregation can be related to an increase in conformational flexibility of the polymer chains, caused by the defects. This flexibility can reduce the occurrence of situations in which polymer chains get “trapped” during aggregation in a supramolecular structure with less efficient π -stacking. The presence of some defects would thus allow for a better chain ordering, generating a higher level of aggregation in a poor solvent, compared to fully regioregular P3ATs. The fact that the optimal results are not found for a 100% HT-P3AT and that a small amount of defects increases the π -stacking and chiral properties might be correlated with a more general trend that indicates that small amounts of molecular irregularities can result in a better (chiral) organisation of conjugated polymers. Indeed, this effect has been previously observed for several other alkylthiophene-based systems, in both random and block

Fig. 5 Melting enthalpies (ΔH^0) as a function of the %HT-couplings (a) after fast (10 °C/min) and (c) slow (1 °C/min) cooling; melting temperature (T_m) as a function of the %HT-couplings (b) after fast (10 °C/min) and (d) slow (1 °C/min) cooling.

copolymers^{55,32,56,57} and poly(3-alkylsulfanylthiophene)s.⁵⁸

Next, the experiments were repeated in the solid state. For this purpose, films were spincoated from chloroform solution and analyzed both directly after spincoating and after annealing at 100 °C for 1 minute. The results are summarized in Fig. 4c-f. They show that before annealing, *i.e.* in “kinetic” conditions, in which the polymers are likely to be “trapped” in a not-optimized structure, no clear differences are observed between polymers **P1-P5**, and higher regioregularity does not lead to an increased (chiral) aggregation. When the films are annealed and a more stable organisation is reached (*i.e.* in more “thermodynamic” conditions), the crystallinity of the polymer films increases, as the relative contribution of the π -stacking band increases (from $\approx 2.5\%$ in Fig. 4a,c to $\approx 5\%$ in Fig. 4e) and the chiral expression in general increases as well. However, the trend that optimal values are found with high, but not 100% amounts of HT-couplings is not repeated: while the trend of the g_{abs} -value is less clear, the UV-vis analysis reveals that the most intense π -interactions are present in **P1-P2**, although the difference between 95% and 100% HT-couplings is within the experimental error.

Differential Scanning Calorimetry

To gain further insight into the crystalline properties of the polymers, DSC measurements were performed on polymer powder samples. First, the samples were heated well above the melting point, kept for 15 minutes at this temperature under an inert atmosphere and then cooled down at 10 °C/min. The polymers were then measured in the heating scan; the measurements were repeated twice starting from new material. For **P7**, no peak was observed in the DSC-spectra, indicating the absence of crystallinity for this compound, in line with the UV-vis and CD spectra. Again, the experiments show that quite a high degree of regio-irregularity is tolerated to obtain order,

although a lower degree of crystallinity is found in the rather regio-irregular **P6**. The values of the melting enthalpies (ΔH^0) as well as those of the melting temperature (T_m) as a function of the %HT-couplings are plotted in Fig. 5 (a and b, respectively). The trend that was observed in the analysis of the UV-vis and CD-spectra in “kinetic” conditions is also present in these results: T_m and ΔH^0 increase with increasing %HT-couplings, up to maximal values, which are obtained for **P3**, after which the T_m and the ΔH^0 -values decrease for higher %HT-couplings (**P1-P2**). The T_m -values of the polymers give insight into the quality of the polymer crystals. The results indicate that the best crystals are obtained in **P3** and *not* **P1-P2**. The ΔH^0 -values are an indication of the degree of crystallinity that is present in the polymers, leading to the conclusion that, besides the higher crystal quality, also the percentage of crystallinity is the highest for **P3**. Next, the same thermal treatment (15 minutes above the melting temperature under an inert atmosphere) was performed on new samples, but afterwards, they were slowly cooled down (1 °C/min), which corresponds to “thermodynamic” conditions. Again, this results in a less clear outcome: concerning the melting enthalpy, the highest value is clearly found at 95% HT, while, within experimental errors, the same melting temperature is found for **P1-P2** and **P3** (Fig. 5 c-d).

These results are in contradiction with the observations made by Kohn *et al.* for a fully regioregular P3HT and a P3HT prepared by the conventionally initiated Ni(dppp)-catalyzed protocol with one TT-defect.¹⁶ They found that superior π -stacking was present in the fully regioregular sample. However, there are differences between the studies, which might explain the different outcome. First, in their study, the thiophene backbone bears hexyl side-chains, whereas in our study chiral branched side chains are used. This difference in side chain impacts steric

Fig. 6 Tapping-mode AFM phase images of thin deposits of **P1** (left), **P6** (middle) and **P7** (right) (scan size: $1 \times 1 \mu\text{m}^2$).

Table 2 Typical dimensions of the fibers for P3ATs with different %HT-couplings and hole mobility values extracted from the C-AFM measurements.

Polymer	Width (nm)	Length	μ ($10^{-6} \text{ cm}^2/\text{V.s}$)
P1	14.3 ± 1.7	$> 1 \mu\text{m}$	6.8 ± 1
P3	15.5 ± 1.4		4.4 ± 1
P5	13.8 ± 1.3		1.6 ± 1
P6	13.4 ± 1.4	$< 1 \mu\text{m}$	0.28 ± 1

Fig. 7 (a) Schematic representation of the C-AFM measurement. (b) $4 \times 1.5 \mu\text{m}^2$ current image obtained on **P1** when gradually increasing the bias voltage (0 - 3 V). (c) Current-voltage curves obtained by line averaging of the current images for **P1**, **P3**, **P5** and **P6**.

factors and, therefore, the probability that the polymer is “trapped” in conditions with smaller π -stacking and crystallinity.

Second, the molar masses and polydispersity of the polymers differ, affecting the crystalline properties of P3HT. Third, their study evaluated the polymers in thin films, whereas our chiroptical/DSC study covers both the behaviour in solution (poor solvent) and in thin films. Finally, the aggregation is analyzed differently from the UV-vis spectrum. Their study analyzed the

measurements by comparing the first (550 nm) and second progression (610 nm) in the absorption spectra, whilst we deconvoluted the absorption spectra and compared the π -stacking band area to the total area of the absorption spectrum. Concerning the DSC measurements, Kohn *et al.* used an isothermal crystallisation, while we used a very slow cooling.

Atomic Force Microscopy

Finally, AFM was used to study the microscopic morphology of thin deposits of the polymers, which were prepared from solutions in chlorobenzene, a good solvent, at a concentration of 0.2 mg/mL . The deposits were generated by drop-casting $25 \mu\text{L/cm}^2$ of the solutions on glass substrates and allowing the solvent to evaporate overnight in a solvent-saturated atmosphere. This process provides films with a thickness below 20 nm. The slow evaporation allows to generate morphologies approaching “thermodynamic” conditions. A fibrillar morphology is clearly observed for **P1**, **P3**, **P5** and **P6**. A typical AFM phase image obtained for **P1** is shown in Fig. 6, where a few fibrillar layers are observed on the substrate. Such an organisation is very often observed in thin films of poly(3-alkylthiophene)s.^{59,60} It originates from the π -stacking of the conjugated backbones, in such a way that the chains are perpendicular to the fibril axis and the plane of the conjugated backbone is perpendicular to the substrate. The width of the fibrils is within the experimental error the same for all polymers, reflecting the similar molar mass. The same morphology is observed for **P1**, **P3** and **P5** with fibers of similar lengths (Table 2). This indicates that the capacity of these P3ATs chains to aggregate into well-defined assemblies is not significantly affected by the presence of coupling defects in the polymer chains, at least down to 89% HT-couplings.

This is consistent with the optical measurements on the films obtained in “thermodynamic” conditions (after annealing). Further decreasing the regioregularity, a fibrillar morphology is maintained for **P6**, but shorter fibers are generally observed, below $1 \mu\text{m}$ in length (Fig. 6). Finally, no specific morphology is detected on **P7** deposits, indicating that those chains cannot assemble regularly on the long range, consistent with the optical measurements.

Conductive AFM characterisation was then performed to study the impact of the regioregularity on the charge transport. C-AFM

measures the current flowing between a conductive probe and a sample upon dc bias and with a sensitivity in the pA range. A tip coated with PtIr5 (work function ~ 5.2 eV) was used as the anode to inject holes into the HOMO of P3AT while a tin-doped indium oxide (ITO) cathode (work function ~ 4.7 eV) was used to collect those holes. Therefore, in this configuration C-AFM is used to characterize the hole transport in the P3AT deposits. The current imaging was performed close to, but not directly above, the cathode to avoid the risk of short-circuits (see Fig. 7a). Fig. 7b presents a current image over a 4x1.5 μm² area on a **P1** deposit. A linear variation of the tip potential was applied from 0 to 3 V while scanning the area from top to bottom. Consistently, the current gradually increases while increasing the tip potential, and the P3AT fiber morphology clearly appears in the image (similar images were obtained with **P3**, **P5** and **P6**). In order to quantify this current increase, the current is averaged line by line and plotted versus the tip potential; the resulting current-voltage curves are shown in Fig. 7c. A parabolic variation of the current is observed (see fitting curves), which is attributed to a space charge limited current (SCLC) regime. This behaviour, where the current is space charge limited, is in agreement with the results obtained with other polythiophene compounds.^{48,49} The SCLC behaviour is observed for **P1**, **P3**, **P5** and **P6**, while no current is detected on the amorphous **P7** deposits.

A model has been proposed to extract the hole mobility from those data,⁴⁸ assuming that the current-voltage variations are driven by the contact resistance, with the relation

$$I = \pi \epsilon_0 \epsilon_r \mu r_a \frac{V^2}{z^2}$$

where ϵ_0 is the vacuum permittivity, ϵ_r the relative dielectric constant of the film (~3.2), μ the charge carrier mobility, r_a the radius of the tip (~25 nm), and z the radius across which the voltage drops between the probe and the ITO electrode, which is at most in the order of the tip radius r_a . The extracted hole mobility values are presented in Table 2. **P1** and **P3** present similar mobility values and it is very difficult to distinguish those two polymers in terms of charge transport since their curves are very close to each other. However, going to **P5**, the mobility value decreases significantly despite the fact that **P5** deposits present the same morphology as **P1** and **P3**. This suggests that the fiber structures formed by **P5** have packing defects due to the lower regioregularity, which somewhat hampers charge transport. Consistently, going to **P6** the hole mobility value further decreases (by about one order of magnitude), due to the lower regioregularity and to the shorter fibrillar structures, which limits intra-chain hole transport and forces the holes to move through the slower inter-chain hopping.

Conclusion

By applying a Pd(RuPhos)-catalyzed polymerisation mechanism, a series of chiral P3ATs with different %HT-couplings were synthesized. The polymerisation was approached as a copolymerisation of two 3-alkylthiophene isomers. It was shown that the copolymerisation is statistical in nature and that therefore, the %HT-couplings can be predicted by varying the relative amounts of the isomers in the feed. Furthermore, the molar masses and PDIs of the polymers are situated in a narrow range,

allowing a direct comparison of the polymers, to obtain an insight in the effect of the regioregularity on the polymers' properties. This approach thus allows to control simultaneously the molar mass and the regioregularity of the polymers.

Studies using UV-vis and CD spectroscopy as well as DSC and (C-)AFM measurements indicate that a fairly high amount of non-HT-couplings can be present without preventing (chiral) aggregation and long-range self-assembly. If the samples are prepared under "kinetic" conditions, it was found that the highest crystallinity and stacking and the most perfect crystals are present in P3ATs with a small amount of non-HT-couplings (~5%) and not in a fully regioregular 100% HT-P3AT. This indicates that in these conditions a small amount of regio-irregularities improves the polymer chain ordering and crystallinity. In "thermodynamic" conditions, the effect of the regioregularity is less clear, but a clear trend that increasing regioregularity continuously results in increasing crystallinity, π -stacking, chiral expression and supramolecular organisation was not found. Likewise, the charge transport properties do not suffer from the presence of a small number of non-HT couplings.

It seems that, under "thermodynamic" conditions, small amounts of regio-defects have little influence on the polymers' self-assembling properties. The fact that in "kinetic" conditions the self-assembly is more efficient in polymers with <100 % HT-couplings might be related with the fact that the defects allow for an increased local conformational flexibility along the polymer chain. As a consequence, the higher degree of freedom may aid in preventing that non-perfect packing situations are 'frozen' during the aggregation process, eventually resulting in a more efficient π -stacking, higher crystallinity, etc. This hypothesis is further supported by the fact that in poly(3-alkylsulfanylthiophene)s, which are less flexible than P3ATs and thus more prone to be kinetically trapped, the highest crystallinity and chiral response is always observed in compounds with <100% HT-couplings.⁵⁸ These results also fit within recent studies, in which it was observed that small amounts of molecular irregularities do not deteriorate and can even improve the overall supramolecular organisation.

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[†] Electronic Supplementary Information (ESI) available: Experimental details, NMR-spectra of all new compounds and polymers, all measured

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UV-vis and CD-spectra and deconvoluted UV-vis spectra. See DOI: 10.1039/b000000x/

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