Steering poly(thiophene) properties by incorporation of phenyl groups

Tine Hardeman, Guy Koeckelberghs*

Laboratory for Polymer Synthesis, Division of Polymer Chemistry & Materials, KU Leuven,

Celestijnenlaan 200F, 3001 Heverlee (Leuven), Belgium

In order to tune the optical properties of poly(3-alkylthiophene)s, varying amounts of phenyl groups were incorporated more or less randomly along the backbone of this polymer. Because a living random copolymerization of thiophene and phenyl monomers is not possible in standard conditions, a specially designed biaryl monomer was used. The degree of randomness of this incorporation could be estimated by an in-depth ^{1}H NMR analysis. The effect on the bandgap was remarkable, since a linear relation between the bandgap and the percentage of introduced phenyl rings was observed. This enables the synthesis of conjugated polymers with tunable and predictable bandgaps. Aggregation and crystallization behavior were also affected by the introduction of phenyl rings. Aggregation was still possible with 20% of phenyl rings, albeit in a small extent, while crystallization was already completely inhibited at that point.

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INTRODUCTION

The field of conjugated polymers underwent a large evolution since its discovery, both with regards to the synthesis as well as the applications. From the synthetical point of view, McCullough[1] and Yokozawa[2] independently realized a major breakthrough by discovering a Ni-catalyzed polymerization that proceeds via a controlled chain-growth mechanism. This discovery enabled the synthesis of conjugated polymers with control over the molar mass, molecular structure and opened the doors towards the synthesis of block copolymers. Applications of these materials can nowadays be found in transistors, photovoltaics, light-emitting diodes, etc.[3–5]

A variety of conjugated polymers is available for these applications, each with their distinct set of properties. However, it can be interesting to fine-tune the properties of a certain polymer in order to obtain exactly the right set of characteristics. For non-conjugated polymers, this is often done by adding additives to the polymer, or by randomly introducing a second monomer in the polymer backbone. The second approach is generally preferred because the desired properties are then inherent to the material. A similar line of thought can be used for conjugated polymers. Although the focus in this field is often placed on block copolymers and alternating copolymers, the (semi-)random introduction of a second monomer in the polymer backbone has also been investigated. Because the bandgap lies at the heart of most applications of conjugated polymers, the goal is often to tune this property. A first method to prepare (semi-)random conjugated polymers is via polycondensation. Although ADMET[6,7], Yamamoto couplings[8,9] and Suzuki[10] couplings are also used, Stille couplings are generally preferred for these polymerizations. Two different dibromo monomers are then combined with one[11–20] or two[21,22] ditin monomers, resulting in semi-random conjugated polymers. This procedure allows for tuning the bandgap,

but the control over the polydispersity and molar mass of the polymer is limited and completely random polymers are not accessible through this method because of the alternating nature of the polymerization. These issues can be overcome when a chain-growth polymerization is used. In this way, random copolymers of thiophenes with different side-chains have been synthesized[23–26], but it is clear that its properties will hardly differ from the respective homopolymers, because of the similarity between both monomers. Hollinger *et al.* and Palermo *et al.* have both succeeded in making a nearly random thiophene-selenophene copolymer, which showed considerably different solid-state properties with respect to the block copolymer, but no variation in the bandgap was observed.[27,28] Bronstein *et al.* have already been able to tune the HOMO and LUMO levels of poly(thiophene)s by introducing varying amounts thiazoles in the backbone.[29] However, since *both* levels were up to 0.45 eV deeper, the bandgap was hardly affected. Also, one thiazole could be introduced every two or three repeating units, but further variation would prove to be very tedious following the same synthetic procedure. Only very recently, a first random conjugated polymer that enables variation of the bandgap by varying the monomer feed is synthesized via a chain-growth mechanism.[30] Our goal is to also exploit the benefits of a chain-growth polymerization and obtain copolymers with a quantifiable randomness that allow to predictively tune the bandgap.

A logical starting point for this study is poly(3-alkylthiophene) (P3AT), as it is still the benchmark conjugated polymer. In order to tune the bandgap of this polymer, a number of requirements have to be met. As indicated above, a more or less random incorporation of the second monomer is necessary, because block copolymer-like structures result in two absorption bands instead of one shifted band. The other requirements are related to the second monomer itself: it should (i) be aromatic and allow electron delocalization with thiophenes, so that the

benefits of fully conjugated polymers are maintained; (ii) not behave as an actual electron acceptor, since this would lead to a charge transfer band, not a shift of λ_{max}; (iii) result in a polymer with a considerably different bandgap compared to P3AT, to ensure that the effect of the incorporation of the monomer is large enough. Taking these requirements into account, a phenyl monomer was chosen. Hence, we would like to make poly(thiophene)s in which varying amounts of phenyl groups can be built in randomly. For small molecules, it was shown that this combination can indeed result varying bandgaps, further confirming our choice.[31] In order to maintain control over the molar mass of the polymer, efforts will be made to enable polymerization through a controlled chain-growth mechanism.

EXPERIMENTAL SECTION

Reagents and instrumentation. All reagents were purchased and used without further purification. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). 2-Bromo-3-((S)-3,7-dimethyloctyl) thiophene (**1**)[32] , 2-bromo-5-iodo-3-((S)-3,7-dimethyloctyl)thiophene (**5**)[33] and 1,4-dibromo-2,5-dimethoxybenzene[34] were synthesized according to literature procedures.

^{1}H-NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer. Size exclusion chromatography (SEC) measurements were carried out on a Shimadzu 10A GPC system. The column is a PLgel 5μm mixed-D type column and the detection system consists of a differential refractometer and a UV-vis spectrophotometer. The SEC system is calibrated towards polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF (c ≈ 1 mg/mL) and filtered over a pore size of 0.2 μm. Mass spectra are recorded using an Aligent HP5989. UV-vis and CD measurements were performed on a Perkin-

Elmer Lambda 900 UV-Vis NIR and a JASCO 62 DS apparatus, respectively. DSC samples were put in Tzero Aluminium Hermetic pans and the spectra were recorded in a TA Instruments Q2000 DSC, calibrated towards indium. A heating rate of 10°C/min was used.

Synthesis of 3. A solution of 2-bromo-3-((S)-3,7-dimethyloctyl)thiophene (**1**) (20.0 mmol, 6.07 g) in dry THF was cooled to -78°C and purged with argon. *n*-BuLi (2.5 M in hexane, 20.0 mmol, 8.00 mL) was added to the solution and the reaction was allowed to reach room temperature during 1h. Afterwards, a solution of trimethyltin chloride (22.0 mmol, 4.38 g) in dry THF was added to the reaction mixture. After a reaction time of 1h, the solvent and excess of trimethyltin chloride were evaporated under reduced pressure. Then, hexane was added and the precipitated salts were filtered off. Hexane was subsequently removed under reduced pressure and the crude stannylated compound was used without further purification. It was combined with 2,5-dibromo-1,4-dimethoxybenzene (40.0 mmol, 11.8 g) and dissolved in dry THF. This solution was added to $Pd(PPh_3)_4$ (1.00 mmol, 1.15 g) and the reaction mixture was refluxed overnight. Then, H_2O was added and the mixture was extracted with dichloromethane. The organic layer was washed with a saturated $NaHCO_3$-solution, dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified with column chromatography and a viscous yellow oil was obtained (SiO_2; eluens: heptane/DCM (60/40)). Yield: 1.18 g (13%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29 (d, 1H), 7.15 (s, 1H), 6.97 (d, 1H), 6.85 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 2.46 (m, 2H), 1.60-1.00 (m, 10H), 0.84 (d, 6H), 0.80 (d, 3H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 151.7, 149.8, 140.9, 132.1, 128.6, 124.5, 123.3, 116.7, 115.3, 111.3, 56.9, 56.4, 39.3, 37.8, 37.1, 32.7, 28.0, 26.7, 24.7, 22.7, 22.6, 19.5, 14.1. MS (EI): 440/438 ($M^{•+}$), 314/312 ($M^{•+}$- C_9H_{19}), 232 ($M^{•+}$- C_9H_{19}-Br)

Synthesis of 4. 3 (2.68 mmol, 1.18 g) was dissolved in dichloromethane, shielded from light, brought under argon atmosphere and cooled to 0°C. Iodobenzene diacetate (1.34 mmol, 0.431 g) and iodine (1.34 mmol, 0.339 g) were added to the reaction mixture and the solution was stirred at room temperature during 4h. Afterwards, the mixture was extracted with diethyl ether and washed with a $NaHSO_3$-solution. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was subsequently heated under reduced pressure in order to remove the iodobenzene which is formed during the reaction. The product was then purified using column chromatography (SiO_2; eluens: heptane/ethyl acetate (96/4)) and a viscous yellow oil was obtained. Yield: 1.36 g (90%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.14 (s, 1H), 7.10 (s, 1H), 6.79 (s, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 2.41 (m, 2H), 1.60-1.00 (m, 10H), 0.84 (d, 6H), 0.79 (d, 3H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 151.4, 149.8, 142.8, 138.4, 138.3, 122.0, 116.7, 115.8, 111.9, 72.5, 56.9, 56.3, 39.3, 37.6, 37.1, 32.6, 28.0, 26.4, 24.6, 22.7, 22.6, 19.5. MS (EI): 566/564 ($M^{\bullet+}$), 440/438 ($M^{\bullet+}$-I), 358 ($M^{\bullet+}$- C_9H_{19}-Br), 232 ($M^{\bullet+}$- C_9H_{19}-Br-I)

General polymerization procedure. The precursor monomers **4** and **5** are put in separate flasks under an argon atmosphere and dissolved in dry THF. To these solutions, 1 equivalent of *i*PrMgCl.LiCl is added and they are reacted for 30 min. Afterwards, the solutions of both monomers are combined and this monomer mixture is added to Ni(dppp)Cl$_2$ in dry THF. After 1 hour, the polymerization is quenched with acidified THF and precipitated in methanol. The polymer was then filtrated and purified by Soxhlet extraction with methanol and chloroform. The chloroform-soluble fraction was precipitated in methanol, filtered off and dried in vacuo.

Polymer 1: The used monomer was **4** (0.500 mmol, 0.283 g) and the catalyst is Ni(dppp)Cl$_2$ (33.0 μmol, 17.8 mg). Yield: 96 mg (54 %)

Polymer 2: The used monomers were **4** (0.426 mmol, 0.242 g) and **5** (0.142 mmol, 60.9 mg); the catalyst is Ni(dppp)Cl$_2$ (23.0 μmol, 12.5 mg). Yield: 94 mg (51 %)

Polymer 3: The used monomers were **4** (0.350 mmol, 0.198 g) and **5** (0.350 mmol, 0.150 g); the catalyst is Ni(dppp)Cl$_2$ (35.0 μmol, 18.9 mg). Yield: 64 mg (34 %)

Polymer 4: The used monomers were **4** (0.138 mmol, 78.7 mg) and **5** (0.417 mmol, 0.178 g); the catalyst is Ni(dppp)Cl$_2$ (32.0 μmol, 17.1 mg). Yield: 52 mg (36 %)

Polymer 5: The used monomer was **5** (1.00 mmol, 0.429 g) and the catalyst is Ni(dppp)Cl$_2$ (33.0 μmol, 17.8 mg). Yield: 187 mg (84 %)

RESULTS AND DISCUSSION

Monomer design. Even though thiophene and phenyl groups are rather common and often used in the synthesis of conjugated polymers, their combination in one single polymer is rare. They can both be polymerized in a controlled chain-growth fashion using a Kumada Catalyst Transfer Polycondensation (KCTP)[1,2,35], but simply combining both monomers in one reaction would not lead to a random copolymer because of the differing affinity of the Ni-catalysts towards both monomers. As was evidenced by Yokozawa and coworkers, the catalyst prefers to be associated with the more electron-rich thiophene and transfer to a phenyl ring with less π-donor ability is difficult.[36] This also results in the fact that thiophene-phenylene block copolymers can only be synthesized properly when poly(phenylene) is implemented as the first block. However, the group of Bielawski was able to combine both monomers via the synthesis of a novel biaryl monomer in which a thiophene and phenyl group are combined.[37] Using this

monomer, an alternating thiophene-phenyl copolymer could be synthesized in a controlled way. Also block-copolymers with P3HT could be made, although there was a clear preference in the order of polymerization. When the first block consisted of the alternating copolymer, the formation of the second block proceeded much more smoothly than when the order was reversed.

To obtain the desired copolymers, a regular 2-bromo- 5-chloromagnesio- 3-alkylthiophene monomer is combined with such a biaryl monomer. In order to enable the growing polymer chain to react equally fast with both monomers, they are equipped with similar reaction sites for the transmetalation, which is known to be the rate determining step for both thiophene and phenyl Ni(dppp)-catalyzed polymerizations.[35,38] The equal rate constants for reaction with both monomers is essential, because it is a requisite for a random copolymer. Hence, the reactive chloromagnesio group of the biaryl monomer is located at the thiophene ring and the same alkyl chain is located at the 3-position as for the regular thiophene monomer. It is chosen to introduce a chiral side-chain so that the aggregation behavior of the resulting polymers could be investigated more extensively with Circular Dichroïsm (CD) spectroscopy. Methoxy groups are placed on the phenyl ring in order to make the latter more electron-rich. We expect that this will aid the Ni-catalyst to 'walk' over the phenyl ring and engage in the necessary oxidative addition in the C-Br bond there. Although it might take more time for the Ni-catalyst to perform this oxidative addition at a biaryl monomer compared to a thiophene monomer, this does not compromise the formation of a random copolymer. To obtain the latter, it is only necessary that the growing polymer chain –independent of which monomer was built in previously- has no preference for reaction with either one of the monomers. It should be noted that while it is possible to obtain a random copolymerization of the thiophene and biaryl monomer, this is not

the same as a random copolymer of thiophene and phenyl rings, because the formation of two consecutive phenyl rings is for example impossible in the present case. Nevertheless, a random copolymerization of our two monomers will result in a more or less statistical distribution of the phenyl rings along the backbone, especially because very high phenyl contents are not used.

Monomer synthesis. The biaryl monomer is synthesized by converting 2-bromo-3-((S)-3,7-dimethyloctyl) thiophene (**1**) into its stannylated analogue (**2**) and coupling the latter with 2,5-dibromo-1,4-dimethoxybenzene in a Stille coupling. The resulting compound (**3**) is subsequently iodinated using PhI(OAc)$_2$ and I$_2$ (Scheme 1).
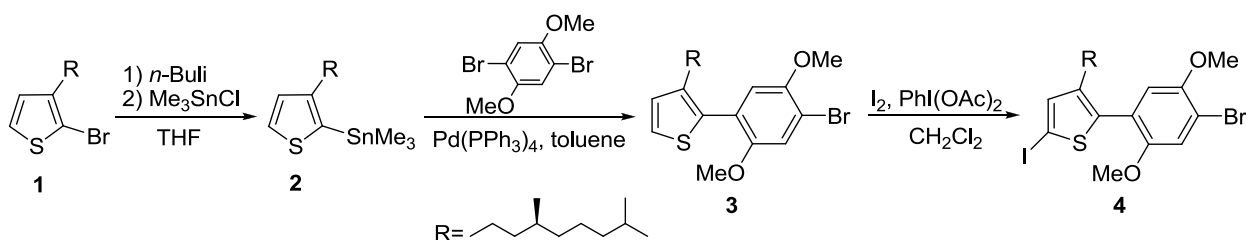
Scheme 1. Synthesis of the biaryl monomer

Polymer synthesis. Before polymerization, the synthesized precursor monomers are converted to the actual monomers using iPrMgCl.LiCl. This is done separately for each monomer. Afterwards, the monomers are combined in varying ratios and then added to the Ni(dppp)Cl$_2$ catalyst (Scheme 2). The polymerization continues for one hour and is subsequently terminated with acidified THF, which replaces the Ni-catalyst by a proton. A total of 5 polymers are synthesized, with an aimed phenyl content of 0, 20, 33, 40 and 50% respectively.
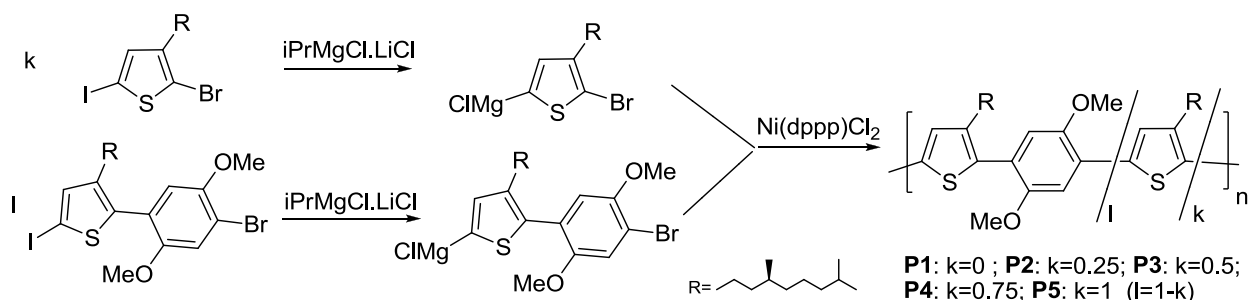
Scheme 2. Overview of the general polymerization procedure. The monomer ratios of 0, 0.25, 0.5, 0.75 and 1 give rise to polymers with respective phenyl contents of 50%, 40%, 33%, 20% and 0%.

GPC analysis showed the formation of polymers with a monomodal size-distribution and relatively low polydispersity indexes (PDI). The number average molar mass and PDI of all polymers are shown in Table 1.

Table 1. Overview of the actual phenyl content in each polymer, the molar mass, polydispersity, % of phenyl at chain end (ratio of phenyl at chain end to total phenyl content), relative amounts of AA (thiophene-thiophene), BB (biaryl monomer-biaryl monomer), A/B (thiophene-biaryl or biaryl-thiophene) couplings (p_{AA}, p_{BB} and $p_{A/B}$ respectively). p_{AX} and p_{BX} represent the respective fractions of A and B in the polymer. R is the calculated degree of randomness.

Polymer	phenyl content feed (%)	actual phenyl content (%)	Mn (kg/mol)	PDI	phenyl at chain end (%)	p_{AA}	p_{BB}	$p_{A/B}$	p_{AX}	p_{BX}	R
P1	50	50	12.7	1.4	9.3	0.00	1.00	0.00	0.00	1.00	0.0
P2	40	42.6	9.5	1.5	14	0.09	0.62	0.29	0.23	0.77	0.8
P3	33	33.6	9.6	1.6	20	0.29	0.31	0.40	0.49	0.51	0.8

P4	20	18.7	6.5	1.3	37	0.74	0.10	0.16	0.82	0.18	0.6
P5	0	0	12.6	1.1	///	1.00	0.00	0.00	1.00	0.00	0.0

The polymers are subsequently analyzed using 600 MHz ^{1}H NMR (Figure 1). A first

observation is that the ratio of both monomers in the feed is transferred well to the polymer

composition. This can be calculated by determining the ratio of the integral values of the doublet

at 2.5 ppm (originating from α-methylene protons of thiophene in a biaryl monomer) and the

doublet at 2.8 ppm (same protons in a regular thiophene monomer). It is calculated that the

aimed phenyl contents of 0, 20, 33, 40 and 50% are approximated by respectively 0, 18.7, 33.6,

42.6 and 50%. It can also be observed that the side-peak originating from a methoxy-group at a

phenyl chain-end becomes relatively more intense along the polymer series (going from **P1** to

P5). As a consequence, one can conclude that phenyl end-groups occur more than proportional

considering the monomer feed. This can be ascribed to the fact that reaction with the next

monomer takes more time if a biaryl monomer is located at the end of the growing polymer

chain. This is a reasonable assumption, because of the longer distance the catalyst has to 'walk'

over before the oxidative addition and the less favorable interaction with the phenyl ring that

needs to be overcome. The slower reaction results in a longer lifetime of these biaryl chain-ends

with respect to thiophene chain-ends, making them more abundant at the moment of termination

with acidified THF. As stated earlier, this does not affect the randomness as long as the reaction

of the polymer chain with each monomer occurs equally fast. In fact, the large variety of peaks in

the aromatic region already provides strong indications that the incorporation occurred in a more

or less random fashion, because the formation of a block copolymer-like structure would result

in a spectrum resembling an overlay of the spectra of the homopolymers, together with a few

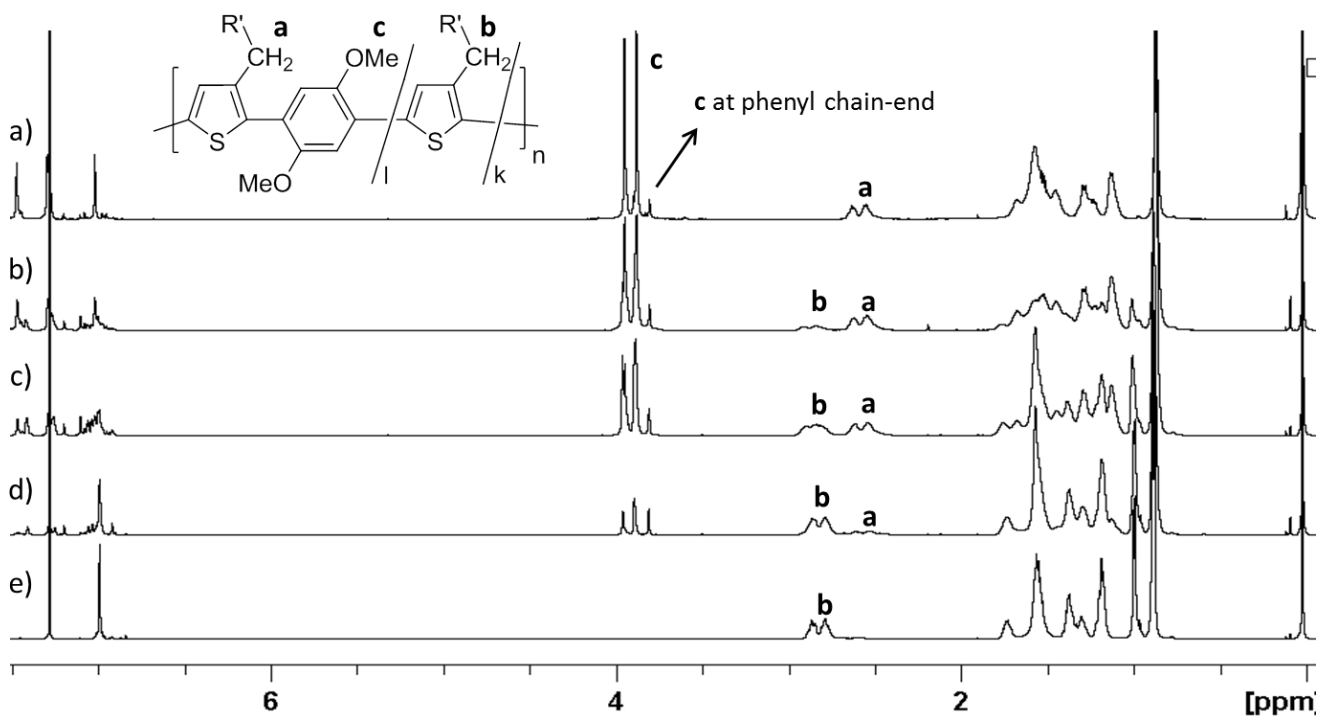small side peaks originating from the link between both blocks.

Figure 1. 600 MHz ^{1}H NMR spectrum of the 5 polymers: a) **P1**; b) **P2**; c) **P3**; d) **P4**; e) **P5**.

However, a more in-depth analysis enabled the determination of the degree of randomness

(R). R equals 1 for a random copolymer, while R<1 is observed for blocky structures, R=0 for

homopolymers, R=2 for alternating copolymers and R>1 for polymers with shorter sequence

lengths. In a copolymer with monomers A and B, R can be calculated using the following

equations.[39,40]

$$p_{A/B} = p_{AB} + p_{BA} \qquad (1)$$

$$p_{AX} = \frac{p_{A/B}}{2} + p_{AA} \qquad (2)$$

$$p_{BX} = \frac{p_{A/B}}{2} + p_{BB} \qquad (3)$$

$$R = \frac{p_{A/B}}{2p_{AX}p_{BX}} \tag{4}$$

Here p_{AA}, p_{BB}, p_{AB} and p_{BA} are the relative amounts of the respective couplings. Although the aromatic region of the three copolymers **P2**, **P3** and **P4** is rather complex, it is possible to extract p_{AA} (thiophene-thiophene), p_{BB} (biaryl-biaryl) and $p_{A/B}$ (thiophene-biaryl or biaryl-thiophene) from this region (Figure 2). By comparing with spectra from the homopolymers, the peak at 7.00 ppm can be ascribed to the thiophene proton in a thiophene-thiophene coupling, while the peaks at 7.46, 7.29 and 7.02 ppm can be ascribed to the phenyl and thiophene protons in a biaryl-biaryl coupling. However, these last three signals only represent one coupling, so only one of these three signals is required for the determination of p_{BB}. Because the peak at 7.46 ppm is most suited for proper integration, this peak is chosen. All peaks except the aforementioned ones are thus related to A/B couplings, or possibly to side-peaks arising from the chain-ends. Because it is very difficult to correctly assign each peak separately, especially in the 'thiophene area', the attention is shifted to the 'phenyl area' around 7.4-7.5 ppm. We already assigned the peak at 7.46 to a phenyl proton in a BB coupling, and analysis of the aromatic region of the homopolymer also reveals that the signal at 7.44 ppm is originating from a phenyl proton at a chain-end. Hence, the peak at 7.42 ppm is ascribed to a phenyl proton in an AB or BA coupling, providing us with a value for $p_{A/B}$. This assignment is further supported by the fact that the integration values of this peak vary as expected with differing monomer feeds, and therefore exclude the possibility that it originates from an end-group. Consequently, all the required fractions p_{AA}, p_{BB} and $p_{A/B}$ are known. In addition, further guidance is provided by the fact that p_{AX} and p_{BX} cannot only be calculated from p_{AA}, p_{BB} and $p_{A/B}$, they are by definition also equivalent to the molar fractions of monomers A (thiophene) and B (biaryl). These values are already determined via analysis of the

2.5-3 ppm region through a straightforward integration. Knowledge of p_{AA} and p_{BB} is however still necessary in order to know which fraction of the total is represented by A/B couplings. All relevant numbers can be found in Table 1. The randomness of **P2** and **P3** is found to equal 0.8, while R equals 0.6 for **P4**. The lower value for the latter can be understood by the relatively low amounts of phenyl rings that are still present in the polymer chain and their higher occurrence at the chain-end. Nevertheless, we observe that a nearly-random incorporation of both monomers is achieved by using this biaryl monomer, something which could not be achieved via simple phenyl monomers.
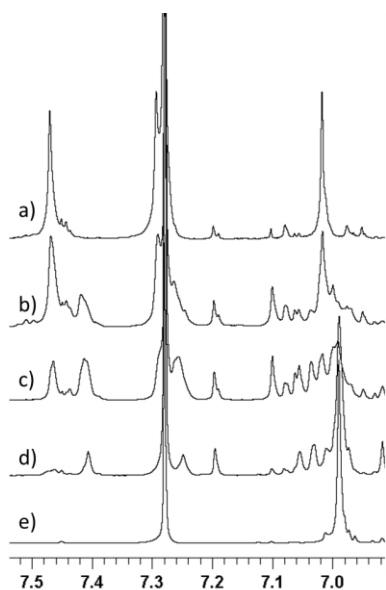

Figure 2. Aromatic region of the 600 MHz ^{1}H NMR spectrum of a) **P1**; b) **P2**; c) **P3**; d) **P4**; e) **P5**

Optical properties. Next, UV-vis absorption spectra are recorded of the five polymers in order to check how the bandgap is affected by the introduction of phenyl rings. As can be seen in Figure 3, there is a clear shift in λ_{max} towards lower values when an increasing amount of phenyl is incorporated. By processing this data and plotting the bandgap in function of the phenyl

content in each polymer, a linear trend is observed. Extending this curve with the bandgap

determined for poly(p-2,5-dialkoxyphenylene)[41] shows that this trend is even continued to 100%

phenyl content. This means that we are not only capable of tuning the bandgap, but also to do

this in a predictive manner. The obtained curve indicates which amount of phenyl rings is

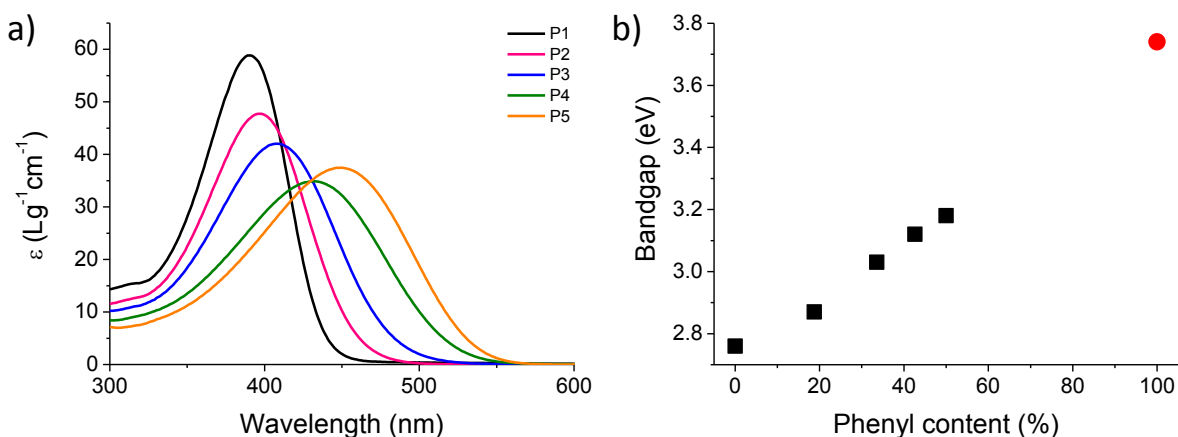necessary to obtain a certain bandgap within this region.

Figure 3. a) Absorption spectra of the polymers in CHCl$_3$ (c=0.025 mg/mL). A red-shift is

observed when the phenyl content is decreased. b) The bandgap of the polymers (calculated via

λ_{max}) in function of the phenyl content (%). (■: measured; ●: from literature[41])

Also the fluorescence of these polymers is investigated (Figure 4) at an excitation wavelength

of 380 nm. A similar increasing trend in λ_{max} with lower phenyl content can be observed. In fact,

this trend also confirms our hypothesis of a more or less random incorporation of the phenyl

rings: in the process of fluorescence, the absorbed energy will be transferred to the longest

thiophene sequences present, which will then fluoresce.[42] Hence, if the copolymerization is not

random and rather long sequences of only thiophenes are present, the fluorescence of all these

polymers would resemble poly(thiophene) fluorescence a lot more. As a consequence, the observed trend is evidence of the opposite.
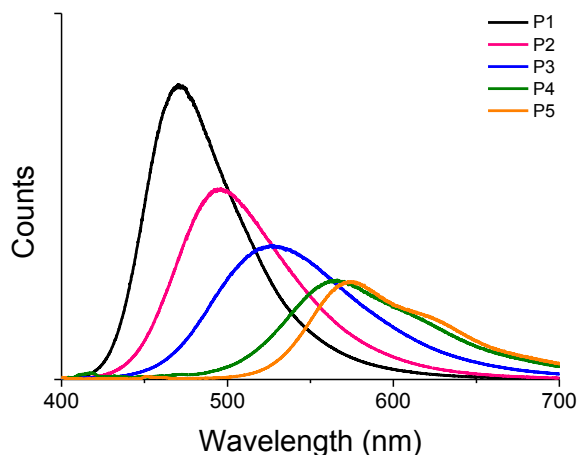

Figure 4. Fluorescence of the polymers in chloroform (λ_{ex} = 380 nm). The intensities are corrected for absorption at 380 nm.

Aggregation and solid state properties. Since the alkyl side-chains on the thiophene units of our polymers are chiral, aggregation behavior can be investigated using chiroptical techniques. Via circular dichroïsm measurements, chiral stacking of the polymers upon addition of increasing amounts of nonsolvent (eg. poor solvent) can be monitored by the appearance of a bisignate Cotton effect. As shown below (Figure 5), such chiral aggregation can only be observed for regular P3AT (**P5**) and to a lesser extent for the polymer with 20% of phenyl rings (**P4**). Both in the absorption spectrum and the CD spectrum of P3AT, a small extra band can be observed around 620 nm. This band is known to originate from long range order in the aggregates. It is clear that such a band is absent for **P4**, indicating this polymer shows no order on a larger scale.
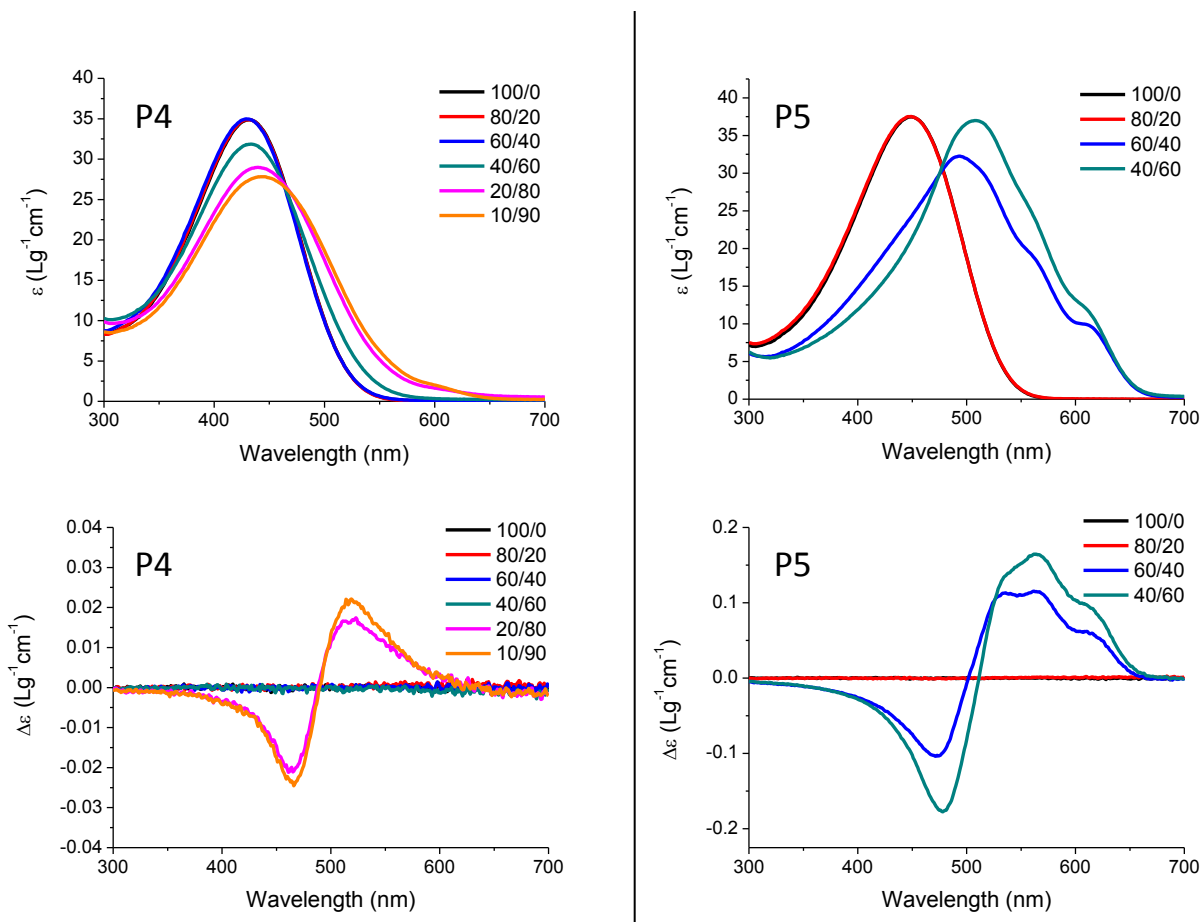
Figure 5. Results of the solvatochroïsm experiments. Above: evolution of the absorption spectra upon the addition of poor solvent (x/y = chloroform/methanol ratio). Below: Circular Dichroïsm spectra. Chiral aggregation was only observed for **P4** (c = 25 mg/L, left) and **P5** (c = 25.3 mg/L, right).

Finally, also melting and crystallization of these polymers are studied using DSC. However, only for P3AT melting and crystallization are observed. The fact that this is not observed for **P4** is in perfect agreement with the solvatochroïsm experiments, as they already indicated that no long range order was present for this polymer. It is believed that the linearity of the phenyl rings affects the conformation of the polymers and inhibits the formation of aggregates and crystalline structures.

CONCLUSION

Varying amounts of phenyl rings were introduced in a poly(thiophene) backbone in order to be able to tune the properties of the latter. To enable the introduction these phenyl rings in a random way -something which could not be achieved so far by use of the traditional thiophene and phenyl monomers- a biaryl monomer combining a thiophene and a phenyl ring was designed. Via ^{1}H NMR, we were able to show that the incorporation of our monomers occurred in an approximately random way. It is shown that the bandgap increases linearly with phenyl content, making it possible to synthesize polymers with predictable and tunable bandgaps. The chiral aggregation of these polymers is inhibited when more than 20% of phenyl rings are introduced. In order to prevent crystallization, even less than 20 % of phenyl rings is sufficient.

AUTHOR INFORMATION

Corresponding Author

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

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Steering poly(thiophene) properties by incorporation of phenyl groups

Tine Hardeman, Guy Koeckelberghs*