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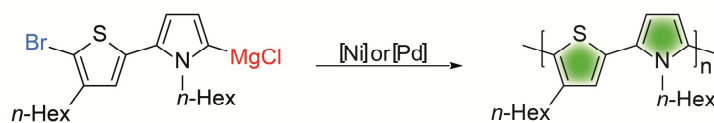
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## Graphical Abstract

### Synthesis of Poly(thiophene-*alt*-pyrrole) from a Difunctionalized Thiénylpyrrole by Kumada Polycondensation

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## Synthesis of Poly(thiophene-*alt*-pyrrole) from a Difunctionalized Thienylpyrrole by Kumada Polycondensation

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### ABSTRACT

A difunctional thienylpyrrole monomer with a bromide on the thienyl moiety and a magnesium halide on the pyrrole moiety was prepared via chemo-selective magnesium-iodine exchange. Based on this monomer, a  $\pi$ -conjugated alternating poly(thiophene-*alt*-pyrrole) **PTP** was synthesized via nickel and palladium catalyzed Kumada polycondensation. The optical and thermal properties of this polymer have been investigated. The optical and thermal properties suggested a wide band gap polymer, with a very low  $T_g$  for such polymers.

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### Introduction

Conjugated polymers have attracted extensive attention because of their potential industrial applications, due to their unique semiconducting and optoelectronic properties.<sup>1-3</sup> Among the conjugated polymers, polythiophenes and polypyrroles are centrally important and have been widely investigated as potential materials for organic electronics.<sup>4-8</sup> The properties of polythiophene and polypyrrole are different: polypyrrole has a larger band gap (ca. 3 eV<sup>9</sup> compared to ca. 2 eV for polythiophene<sup>10</sup>), resulting in a relatively low conductivity;<sup>11,12</sup> and has a lower oxidation potential,<sup>13,14</sup> which makes it highly reactive toward oxygen. As the copolymerization of the monomer containing several distinct units can lead to an interesting combination of the properties observed in the corresponding homopolymers,<sup>15-18</sup> it is interesting to obtain copolymers that contain both heterocycles simultaneously. Cava and coworker described the poly(thienylpyrrole) showed tailored electroactive properties.<sup>19</sup>

Copolymers of thiophene and pyrrole have mainly been prepared via electrochemical polymerization of 2,5-di(thiophen-2-yl)-1*H*-pyrrole derivatives.<sup>20-30</sup> However, this method may lead to significant branching and regioirregular polymers. In addition,

organometallic polycondensations have recently been employed to obtain copolymers via a bis(trimethylstannyl)thiophene monomer and a dibromo pyrrole monomer.<sup>31-33</sup> However, the polymers obtained by the Stille polycondensation had a very low molecular weight. There was no report on preparing poly(thiophene-*alt*-pyrrole) via a single monomer which contains a metal functional group and a halogen group. However, this kind of monomer is highly desirable as it has the potential to proceed via a quasi-living chain growth mechanism.<sup>34-43</sup> Herein, we report the highly chemo-selective synthesis of difunctional thienylpyrrole monomer containing a metal functional group and a bromo group. Based on the monomer,  $\pi$ -conjugated alternating poly(thienylpyrrole) was prepared via palladium catalyzed Kumada polycondensation.

### Results and Discussion

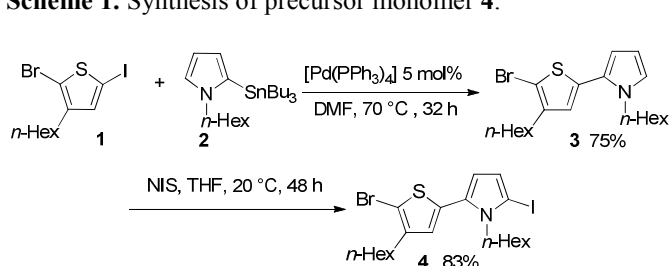
#### Synthesis of the pre-monomer **4**

The precursor monomer **4** was synthesized by an electrophile-selective Stille cross-coupling<sup>44</sup> between the 2-bromo-3-hexyl-5-iodothiophene **1** and the tributyltin substituted pyrrole **2**, followed by iodination of the pyrrole unit with an excess *N*-iodosuccinimide (NIS) in a yield of 62% over two steps.

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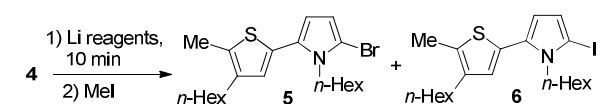
Although we initially planned to use **3** directly as a monomer precursor by lithiation through deprotonation as a lithiated monomer or followed by lithium-metal exchange if required, several metalation experiments using lithium diisopropylamide (LDA), and 1-lithio-2,2,6,6-tetramethyl-piperidine (LTMP) failed (For details see in the SI).

### Scheme 1. Synthesis of precursor monomer **4**.



A more reliable route seemed the lithiation of **4** by iodine-lithium exchange using different alkyl lithium reagents such as *n*-BuLi, *t*-BuLi or MeLi under different conditions (Table 1) (For details see the SI). In order to analyze the success of the lithiation procedure, the lithiated heterocycles were quenched with MeI, which could be easily identified by gas chromatography-mass spectrometry (GC-MS) and <sup>1</sup>H NMR spectroscopy. However, lithiation and quenching with MeI did not give the product 2-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-5-methyl-1*H*-pyrrole; on the contrary, 2-bromo-1-hexyl-5-(4-hexyl-5-methylthiophen-2-yl)-1*H*-pyrrole **5** was obtained as main product. This suggests a “halogen dance reaction”,<sup>45</sup> in which the initial iodo-lithium exchange on the pyrrole moiety was followed by bromination from the brominated thiophene moiety. This observation is unusual because in hexylthiophene, a bromide substituent is much more favoured in the 2 position adjacent to the *n*-hexyl group, but metallation is favoured in the 5 position (which in **4** is blocked by the pyrrole).<sup>46-48</sup> In addition, *n*-BuLi and *t*-BuLi (entries 1-3) also gave another byproduct 1-hexyl-2-(4-hexyl-5-methylthiophen-2-yl)-5-iodo-1*H*-pyrrole **6**. This is a consequence of a bromo-lithium exchange without a halogen dance. Although MeLi just gave trace amount of **6** (entry 4), other unidentified compounds was shown from the NMR (For details see in the SI).

**Table 1.** Lithiation of precursor monomer **4**.



entry	lithium reagents	solvents	T (°C)	ratio <sup>a</sup> <b>5</b> : <b>6</b>
1	<i>n</i> -BuLi	THF	-78	6 : 1
2	<i>n</i> -BuLi	THF	-100	10 : 1
3	<i>t</i> -BuLi	Me-THF	-129	0.5 : 1
4	MeLi	THF	-78	>99:1 <sup>b</sup>

<sup>a</sup> Estimated by <sup>1</sup>H NMR spectroscopy and identified by GC-MS.

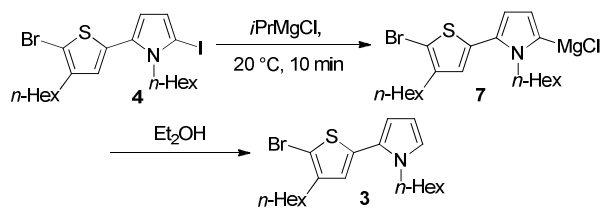
<sup>b</sup> A trace amount of compound **6** was detected only by GC-MS.

### Synthesis of the Grignard type monomer **7**

Surprisingly then, the Grignard-type monomer **7** could be synthesized by treating the precursor monomer **4** with 1 equiv of *i*PrMgCl at 20 °C for 10 min via a fast magnesium-iodine exchange reaction (100% yield based on analytical GC with

analysis of the protonated species **3** (Scheme 2). The metalation occurred selectively at the  $\alpha$ -position of the thiophene, leaving the aryl bromide intact.

### Scheme 2. Synthesis of Grignard-type monomer **7** by magnesium-iodine exchange.

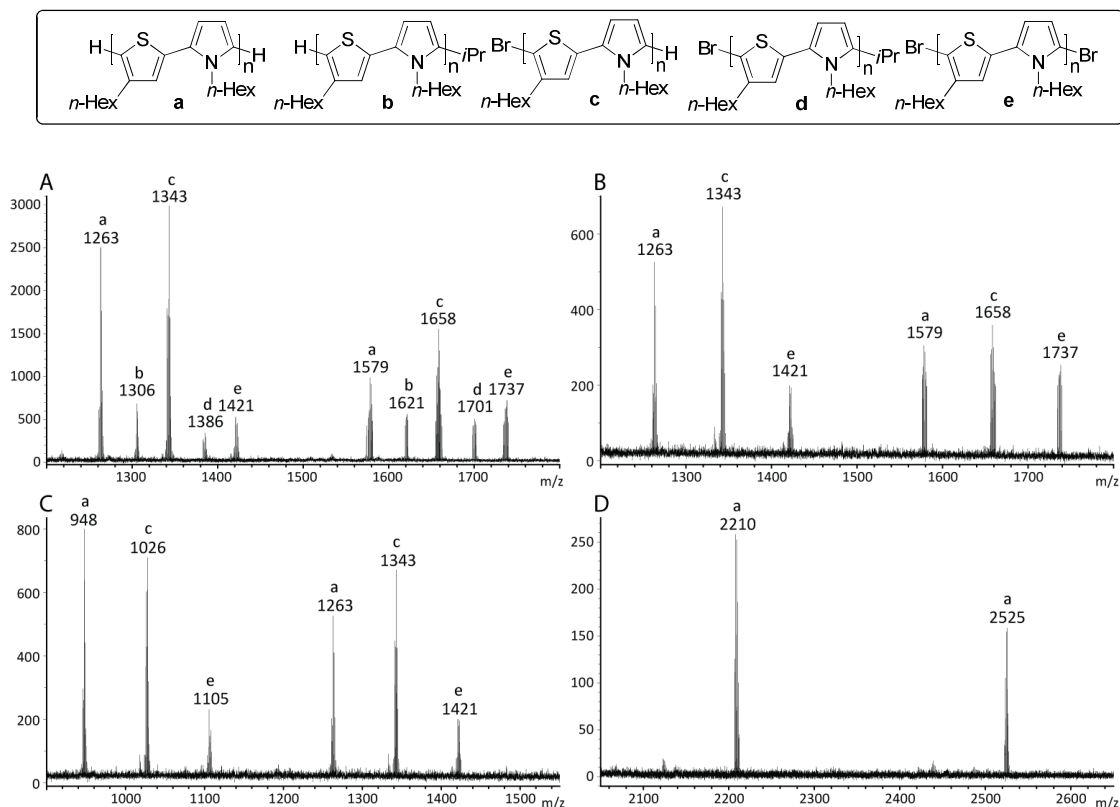


### Synthesis of poly(thiophene-*alt*-pyrrole) (PTP) with **7**

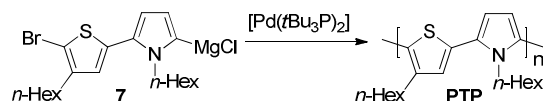
Based on the Grignard-type monomer **7**, polymerization was carried out firstly by the addition of 2 mol% of [Ni(dpp)Cl<sub>2</sub>] at 20 °C for 24 h. These conditions are well established for the synthesis of well-defined poly(3-hexylthiophene) by Kumada catalyst-transfer condensation polymerization.<sup>34,35</sup> However, the yield was only 65% and the molecular weight of the polymer ( $M_n = 3.9$  kDa,  $M_w/M_n = 1.5$ , GPC calibrated against polystyrene) was also quite low. Analysis of the polymer by MALDI-TOF revealed a series of peaks suggesting an isopropyl end group (Figure 1A). This could arise from quenching the metallated monomer by isopropyl iodide, which is the product from the previous magnesium-iodine exchange. In view of the fact that this reaction was not observed without a transition metal catalyst, also it is more likely that this end group arises as a cross-coupling product. This problem has been reported for other polymers, such as poly(9,9-dioctylfluorene).<sup>49</sup> In that case, the use of the magnesium complex [tBuMgCl·LiCl·15-crown-5] as the metallating species prevented any further substitution most likely because the *tert*-butyl cation is more stable compared to isopropyl cation. Treatment of **4** with 1 equiv of [tBuMgCl·LiCl·15-crown-5] at 20 °C for 10 min in THF gave **7** (100% yield based on analytical GC-MS with analysis of the protonated species **3**). The polymerization was then carried out by adding of 2 mol% of [Ni(dpp)Cl<sub>2</sub>] to the reaction mixture. After 24 h at 20 °C the polymer was obtained in a yield of 43% ( $M_n = 6.3$  kDa,  $M_w/M_n = 1.5$ , with a conversion of 99%). The MALDI-TOF MS spectra of the oligomer showed no evidence for a *tert*-butyl end group, with H/H, H/Br and Br/Br being the major end groups (Figure 1B). The obtained Br/Br terminated polymer was presumably as a result of the dissociation of the associated Ni<sup>0</sup>-arene  $\pi$  complexes according the proposed mechanism by Yokozawa<sup>50-53</sup> and McClough.<sup>54,55</sup> Although preventing the quenching reaction of polymerization, the relatively high polydispersity and only moderate yield led us to analyze further reaction conditions.

Palladium catalysts are generally less reactive than nickel catalysts for Kumada coupling with alkyl halides. In this instance, we decided to use [Pd(*t*Bu<sub>3</sub>P)<sub>2</sub>] as catalyst as it has been shown to be a suitable catalyst for chain growth polymerization of alternating copolymers based on Stille or Suzuki coupling reactions.<sup>56,43</sup> Although inefficient at 20 °C, (Table 2, entry 1) this catalyst was more efficient at 50 °C. The reaction was performed in the etheral solvents MTBE, DME, THF, and dioxane (Table 2, entries 2-5). In all cases, polymeric products were obtained. The highest molecular weight polymer was obtained by using MTBE as solvent (Table 2, entry 3) with a weight average molecular weight of  $M_n = 7700$ . However, in all cases, the polymers' polydispersities were relatively high

**Figure 1.** MALDI-TOF MS spectra of the poly(pyrrole-*alt*-thiophene): (A) polymer synthesized with *i*PrMgCl and [Ni(dppp)Cl<sub>2</sub>]; (B) polymer synthesized with *t*BuMgCl·LiCl, 15-crown-5 and [Ni(dppp)Cl<sub>2</sub>]; (C) polymer synthesized with *i*PrMgCl and [Pd(*t*Bu<sub>3</sub>P)<sub>2</sub>] (Table1, entry 6); (D) polymer synthesized with [*i*PrMgCl·LiCl] and [Pd(*t*Bu<sub>3</sub>P)<sub>2</sub>] (Table1, entry 10).



**Table 2.** Polymerization of **7** with various ether solvents and different catalyst loadings<sup>a</sup>



entry	cat. loading [mol%]	solvent	T (°C)	time (h)	yield (%)	$M_n^b$	$M_w/M_n^b$	Expected $M_n^c$
1	2	MTBE	20	24	-	-	-	15700
2	2	MTBE	50	18	91	7700	1.6	15700
3	2	DME	50	18	38	4000	1.5	15700
4	2	THF	50	18	49	5000	1.6	15700
5	2	Dioxane	50	18	73	5600	1.6	15700
6	2	MTBE	50(MW)	6.5	94	13200	2.2	15700
7	1	MTBE	50(MW)	5	14	1700	1.4	31500
8	2	MTBE	50(MW)	5	27	2100	1.4	15750
9	5	MTBE	50(MW)	5	97	17800	2.8	6300
10	5	MTBE/LiCl	50(MW)	5	99	29500	4.6	6300

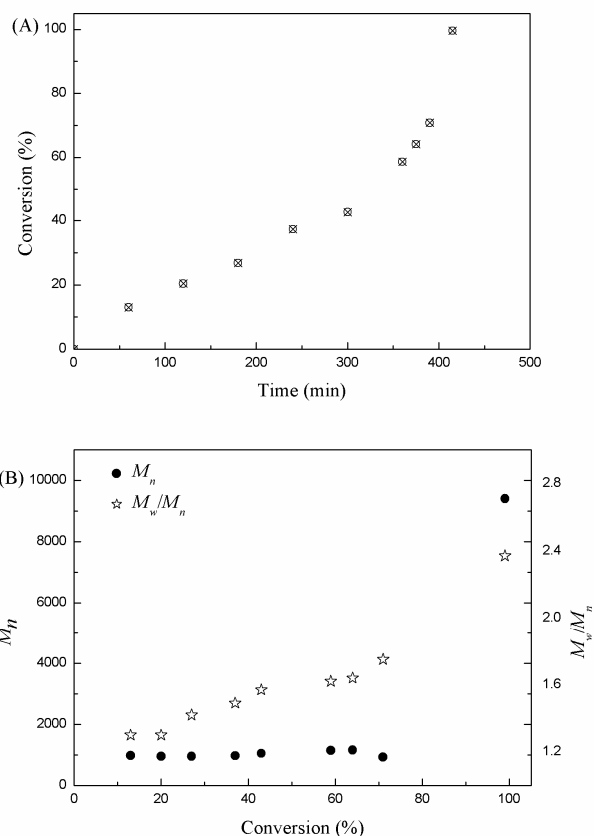
<sup>a</sup> The polymerizations were carried out by treatment of **4** with 1.0 eq. of *i*PrMgCl at 20 °C for 10 min to form **7**, followed by addition of [Pd(*t*Bu<sub>3</sub>P)<sub>2</sub>].

<sup>b</sup> Estimated by GPC calibrated against a polystyrene standard (eluent: CHCl<sub>3</sub>, 1 mL/min).

<sup>c</sup> If the polymerization was a quasi-living chain-growth polymerization.

between 1.5 and 1.6 and molecular weights stayed behind the expected molecular weights, which should not be expected for living polymerizations. To increase the rate of polymerization, the reaction in 4 mL of MTBE was conducted under microwave irradiation at 50 °C for 6.5 h. The conversion was 100% and 94% of the polymer was obtained with a higher molecular weight than under thermal conditions ( $M_n = 13.2$  kDa,  $M_w/M_n = 2.2$ ) (Table 2, entry 6). Different catalysts loadings (1, 2, 5 mol%) were also investigated for the polymerization catalyzed by  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  at 50 °C for 5 h under microwave irradiation (Table 1, entry 7-9), 5 mol% of  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  afforded the longest polymer chain ( $M_n = 17.8$  kDa,  $M_w/M_n = 2.9$ ). In general, higher catalyst loadings gave higher yields and polymers with higher molecular weights, but also with increased polydispersities ( $M_w/M_n$ ), which is counter indicative of a quasi-living chain growth polymerization. The polymers synthesized with  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  also had H/H, H/Br and Br/Br end groups (Figure 1C), which proves the polymerization process did not undergo the quenching with isopropyl iodide. However, the dissociation of the associated  $\text{Pd}^0$ -arene  $\pi$  complexes occurred, which could lead to the Br/Br terminated polymer. Stefan and coworkers reported the palladium-mediated polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene proceeded by a step-growth mechanism and with lower regioirregularity as various side reactions of dissociated  $\text{Pd}(0)$  catalyst.<sup>57</sup> It has been shown the addition of LiCl to Kumada catalyst transfer polycondensation could have beneficial effects on the chain-growth polymerization characteristics of aryl-Grignard monomers.<sup>41,36</sup> Bielawski and coworkers reported the addition of LiCl led to controlled chain-growth polymerization of 2-(4-bromo-2,5-bis(2-ethylhexyloxy)phenyl)-5-chloromagnesiothiophene to afford poly(thiophene-*alt-p*-phenylene).<sup>41</sup> However, in our case, LiCl did not show this effect; on the contrary, the  $M_w/M_n$  (4.6) value was much higher with much bigger  $M_n$  (29500) (Table 2, entry 10). The polymer had only H/H as the main end group in the presence of LiCl (Figure 1D). Based on these results, the best reaction conditions for the polymerization of **7** was 2 mol% of  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  in MTBE as the solvent at 50 °C for 6.5 h under microwave irradiation.

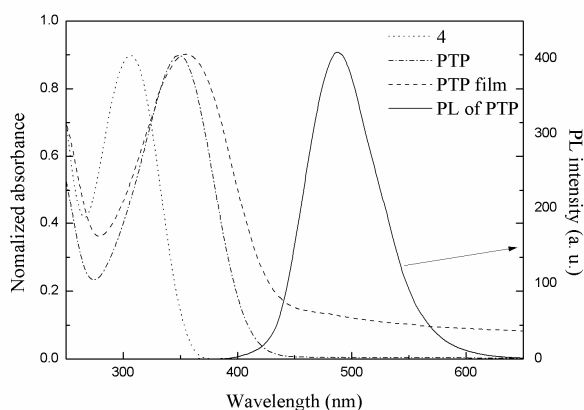
The conversion vs. time plot (Figure 2A) shows that the polymerization of **7** catalyzed by 2 mol% of  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  in 5 mL of MTBE at 50 °C under microwave conditions went smoothly in the first 390 min, up to a conversion of about 70%. However, after 390 min, the apparent conversion increased sharply and reached 100% in 25 min. The  $M_n$  and  $M_w/M_n$  values of the crude **PTP** (without purification by precipitation and fractionation) at each conversion in this polymerization were analyzed by GPC to evaluate the polymerization in detail. The  $M_n$  values did not increase in proportion to the conversion, and the  $M_n$  increased sharply toward the end of the reaction. Both of these observations suggest a step-growth polymerization. The  $M_w/M_n$  values of the collected polymer samples increased along with the consumption of monomer.



**Figure 2.** Conversion vs. time (A), and  $M_n$  and  $M_w/M_n$  vs. conversion (B) plots for the polymerization of **7** with 2 mol% of  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  in MTBE ( $[\mathbf{4}]_0 = 0.1$  mol/L) at 50 °C under microwave conditions. The conversion was defined as amount of compound **3** (from the quenching of a sample with ethanol) and determined by GC using naphthalene as internal calibration standard.

#### Optical Properties of **PTP**

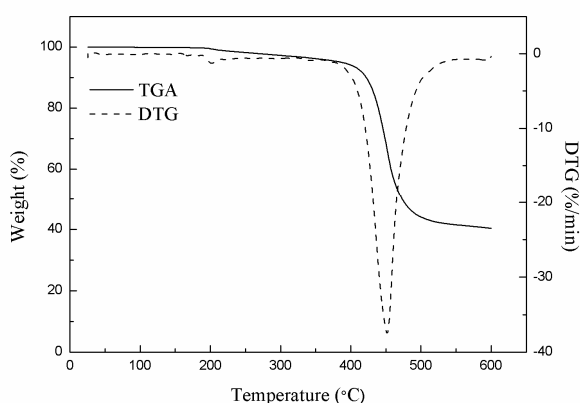
The polymer samples were analyzed with respect to their absorption properties and their photoluminescence spectra (Figure 3, a representative example of a polymer prepared under the conditions of Table 2, entry 6). The absorption spectra of **4** in diethyl ether solution showed maximal peaks at 306 nm. The absorption peaks of the polymers **PTP** (Table 2, entries 6, 9 10) in diethyl ether solution were all observed at ca. 348 nm, largely irrespective of the chain length obtained. If the polymers were processed as a film prepared by spin-coating, the absorption peaks were all at ca. 354 nm. The absorption bands of the polymer **PTP** in both solution and processed as a film were relatively narrow compared to regioregular poly(3-alkylthiophene) (**rr-P3AT**) ( $\lambda_{\text{max}} \approx 450$  nm).<sup>58</sup> This may be attributed to the effect of steric interactions of neighboring *n*-hexyl groups that reduce the conjugation length of the polymers. In fact, DFT calculations suggest a torsion angle between the planes of the two heterocycles of ca.  $-143^\circ$  in the *anti*-conformation of thiophene and pyrrole and  $46^\circ$  for the *syn*-conformation. These values are similar in the tetramers in all possible conformations (see Supporting Information). Irrespective of the chain length obtained (Table 2, entries 6, 9 10), the ether solutions of **PTP** all give a bright-green fluorescence with the maximum emission wavelength of ca. 487 nm, corresponding to the onset of  $\pi$ - $\pi^*$  transition of the electronic absorption spectra, which is at significantly higher energy than the **rr-P3AT** ( $\lambda_{\text{max}} \approx 570$  nm).<sup>58</sup>



**Figure 3.** UV-vis spectra of **4** and **PTP** in diethyl ether and as a film, PL spectra ( $\lambda_{\text{exc}} = 348 \text{ nm}$ ) of **PTP** in diethyl ether.

#### Thermal behavior of the polymer **PTP**

The thermal stability of the polymer (a representative example of a polymer prepared under the conditions of Table 2, entry 6) was studied by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) under  $\text{N}_2$  at a heating rate of  $4 \text{ }^\circ\text{C}/\text{min}$  (Figure 4). The polymer showed a 2% weight loss at  $201 \text{ }^\circ\text{C}$  and a 38% weight loss at  $451 \text{ }^\circ\text{C}$ . The first mass loss might be traced back to the removal of volatile species from the polymer, whereas the second mass loss can be due to the decomposition of the polymer. On the other hand, a DSC thermogram suggested a glass transition temperature at ca.  $-14 \text{ }^\circ\text{C}$  (see SI), which is quite low comparing to other semiconducting polymers. This lower transition temperature may be caused by the torsion between thiophene and pyrrole, which renders the material very flexible.



**Figure 4.** TGA and DTG curves of **PTP**.

#### Conclusions

A difunctional thienylpyrrole monomer containing a magnesium group and a bromo group was synthesized via a chemo-selective halogen-magnesium exchange. All halogen lithium exchange reactions on the dihalogenated starting material (with bromide on the thiophenyl moiety and iodide on the pyrrole moiety) proved unselective, leading to halogen dance or quenching with the alkyl halide that forms in situ. By using a magnesiated monomer, alternating copolymers **PTP** containing 3-alkylthiophene and *N*-alkylpyrrole was prepared by palladium catalyzed Kumada polycondensation. The molecular weights were high and a moderate polydispersity was found. The  $M_n$  vs. conversion plot indicated that the polymerization proceeded via a step-growth mechanism, presumably due to the dissociation of

the associated  $\text{Pd}^0$ -arene  $\pi$  complexes. The absorption bands of the polymer **PTP** in both solution and processed as a film were relatively very narrow due to the effect of steric interactions of neighboring *n*-hexyl groups that reduce the conjugation length of the polymers. This study highlights the difficulties for introducing pyrroles into semiconducting polymers. It points out optimal reaction conditions for the selective metallation of pyrroles in spite of the presence of competing thiophenes. The optical and thermal properties suggest a wide band gap polymer, with a very low  $T_g$  for such materials.

#### Experimental section

##### General Methods and Materials

All syntheses were carried out using standard Schlenk techniques or in glovebox under a dry and inert nitrogen atmosphere unless stated otherwise. Glassware and NMR-tubes were dried in an oven at  $200 \text{ }^\circ\text{C}$  for at least 2 h prior to use. Reaction vessels were heated under vacuum and purged with nitrogen three times before adding reagents.

All solvents that were used for reactions were used freshly distilled after refluxing for several hours over the specified drying agent under nitrogen and were stored in a J. Young's tube. If no drying agent is noted, the solvents were used for chromatography only and distilled for purification purposes.

##### Instruments and measurements

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 300 K.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX 500 (500 MHz) spectrometer.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX 500 (125 MHz) spectrometer. All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were referenced against the residual solvent peak. The exact assignment of the peaks was proved by  $^1\text{H}$ ,  $^{13}\text{C}$  DEPT and two-dimensional NMR spectroscopy such as  $^1\text{H}$  COSY,  $^{13}\text{C}$  HSQC or  $^1\text{H}/^{13}\text{C}$  HMBC when possible.

IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer with a A531-G Golden-Gate-ATR-unit. Ultra High resolution EI mass spectra were run on a VG Analytical Autospec apparatus. MALDI-MS analyses were performed using Bruker Daltonics UltrafleXtreme 2. The analyte (DCM, 1 mg/ml) was pre-mixed with the Dithranol matrix (MeOH, 10 mg/ml) in a 1:1 (v/v) ratio immediately prior to analysis. UV/Vis spectra were recorded on a Perkin Elmer Lambda14 spectrometer. Luminescence spectra were recorded on a Perkin Elmer LS55 spectrometer.

$M_n$  and  $M_w$  were determined on a Viscotek GPCmax VE2001, equipped with a Viscotek VE3580 RI detector (columns: ViscotekLT5000L 300 x 7.8 mm and LT4000L 300 x 7.8 mm).

The DTA-TG measurements were performed in  $\text{Al}_2\text{O}_3$  crucibles using a Netzsch STA-409CD instrument. All measurements were performed under  $\text{N}_2$  and were corrected for buoyancy and current effects. The instruments were calibrated using standard reference material, DSC was performed in a Perkin Elmer Pyris apparatus.

GC-MS analysis was performed on a Hewlett Packard 5890A gas chromatograph, equipped with a Hewlett Packard 5972A mass selective detector and an Agilent Technologies dimethylpolysiloxane column (19091S-931E, nominal length 15 m, 0.25 mm diameter, 0.25  $\mu\text{m}$  grain size).

GC analysis was performed on an Agilent Technologies 6890N gas chromatograph, equipped with an Agilent Technologies 7683 Series Injector, an Agilent Technologies

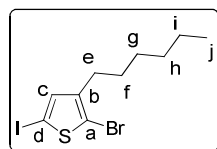
(5 %-phenyl)-methylpolysiloxane column (19091J-413, nominal length 30 m, 0.32 mm diameter, 0.25  $\mu$ m grain size) and a flame ionization detector (FID).

Reactions under microwave irradiation were carried out using a Biotage® Initiator+ SP Wave synthesis system, with continuous irradiation power from 0 to 300 W (Organic Synthesis Mode). The temperature was measured with an external IR sensor during microwave heating. All reactions were carried out in 5 mL oven-dried Biotage microwave vials sealed with an aluminum/Teflon® crimp top, which can be exposed to a maximum of 250 °C and 20 bar internal pressure.

For chromatographic purifications, silica gel (Macherey-Nagel Inc., grain size 0.040 - 0.063 mm) was used. Thin layer chromatography was performed using pre-coated plates from Macherey-Nagel Inc., ALUGRAM®Xtra SIL G/UV254. Chromatographic purification for compounds (**3**, **4**, **5**, **6**, **8**) were carried out using an Interchim Puriflash 430 system, where cartridges by Interchim (silica HC, grain size 50  $\mu$ m, 40g, 80 g or 120 g) were used.

### Synthesis

#### 2-Bromo-3-hexyl-5-iodothiophene (**1**)

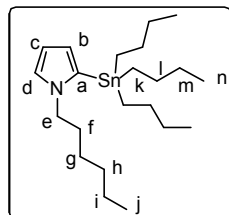


2-Bromo-3-hexyl-5-iodothiophene was prepared similarly to a method described by Koeckelberghs and co-workers<sup>59</sup> and was modified as followed: 2-bromo-3-hexylthiophene (5.00 g, 20.2 mmol) (For the synthetic procedure and

analytic data see in the SI) was dissolved in a mixture of chloroform (100 mL) and acetic acid (50 mL) and shielded from light under an air atmosphere. Then, *N*-iodosuccinimide (6.75 g, 30.0 mmol) was added in one portion. The reaction was stirred for 16 h at 20 °C. The solution was poured into water (100 mL) and the water phase was extracted with *n*-hexane (3 x 100 mL). The combined organic phases were washed with aqueous NaOH (2 M, 1 x 500 mL), water (2 x 200 mL), brine (1 x 100 mL) and were dried over MgSO<sub>4</sub>. After the solvent was removed *in vacuo*, the crude product was purified by Kugelrohr distillation (110 °C, 1.7 x 10<sup>-1</sup> mbar) to get 6.8 g (89%, lit.<sup>59</sup> 78%) of the product as yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.96 (s, 1 H, H-c), 2.52 (t, <sup>3</sup>*J* = 7.6 Hz, 2 H, H-e), 1.59-1.50 (m, 2 H, H-f), 1.37-1.24 (m, 6 H, H-g, h, i), 0.89 (t, <sup>3</sup>*J* = 6.7 Hz, 3 H, H-j) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.3 (C-b), 138.0 (C-c), 111.7 (C-a), 71.0 (C-d), 31.6, 29.6, 29.2, 28.8 (C-e, f, g, h), 22.6 (C-i), 14.1 (C-j) ppm. HRMS (EI-sector) *m/z*: [M]<sup>+</sup> Calcd for [C<sub>10</sub>H<sub>14</sub>BrIS]<sup>+</sup> 371.9044; Found 371.9032. IR (ATR):  $\tilde{\nu}$  = 2953 (m), 2923 (s), 2854 (s), 1534 (w), 1456 (m), 1403 (m), 1377 (w), 1275 (w), 1261 (w), 1191 (w), 1095 (w), 995 (s), 909 (w), 826 (s), 750 (s), 724 (m), 694 (w), 650 (w), 578 (w), 470 (s) cm<sup>-1</sup>.

#### 1-Hexyl-2-(tributylstannyl)-1*H*-pyrrole (**2**)



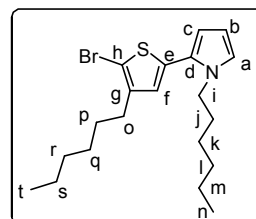
(For the synthetic procedure and analytic data see in the SI) was added dropwise to the solution at this temperature over the course of 10 min. The reaction mixture was allowed to warm up to 20 °C and stirred for 18 h. The reaction mixture was cooled back

*n*-Butyllithium (12.48 mL, 31.20 mmol, 2.50 M in hexanes) was added to a stirred solution of *N,N,N,N*-tetramethyl-ethane-1,2-diamine (4.710 g, 31.20 mmol) in *n*-hexane (90 mL) at 0 °C within 5 min. The reaction mixture was stirred for 1 h at 0 °C. *N*-(*n*-hexyl)-pyrrole (3.620 g, 24.00 mmol)

to 0 °C and tri-*n*-butyltin chloride (10.28 g, 36.00 mmol) was added dropwise over the course of 20 min and warm up to 20 °C and stirred for another 8 h. Then the reaction was quenched with saturated NH<sub>4</sub>Cl aqueous solution (50 mL). The aqueous layer was extracted with *n*-hexane (3 x 50 mL) and the combined organic phases were washed with water (3 x 100 mL). The organic phase was dried over MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was filtered over silica gel (which was pretreated by stirring it in a 5% Et<sub>3</sub>N in *n*-hexane solution to deactivate it). After removal of the solvent, the mixture was purified by bridge distillation (190 °C, 5 mbar) to receive 9.7 g (91 %) of colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.90 (t, <sup>3</sup>*J* = 1.9 Hz, 1 H, H-d), 6.32-6.15 (m, 2 H, H-b, c), 3.83 (t, <sup>3</sup>*J* = 7.6 Hz, 2 H, H-e), 1.77-1.71 (m, 2 H, H-f), 1.55-1.49 (m, 6 H, H-k), 1.36-1.28 (m, 12 H, H-g, h, i, l), 1.06-1.02 (m, 6 H, H-m), 0.90 (t, <sup>3</sup>*J* = 7.3 Hz, 12 H, H-j, n) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 131.6 (C-a), 123.9 (C-d), 118.6 (C-b/c), 108.5 (C-b/c), 51.5 (C-e), 32.4, 31.6 (C-f, g), 29.1 (C-k), 27.3, 26.7, 22.5 (C-h, i, l), 13.9, 13.6 (C-j, n), 10.3 (C-m) ppm. <sup>119</sup>Sn NMR (187 MHz, CDCl<sub>3</sub>):  $\delta$  = - 64.0 ppm. HRMS (EI-sector) *m/z*: [M]<sup>+</sup> Calcd for [C<sub>22</sub>H<sub>43</sub>NSn]<sup>+</sup> 441.2434; Found 441.2418. IR (ATR):  $\tilde{\nu}$  = 2955 (m), 2925 (s), 2854 (m), 1510 (w), 1462 (m), 1417 (w), 1376 (w), 1282 (m), 1072 (m), 1001 (w), 960 (w), 864 (w), 765 (m), 749 (m), 710 (s), 690 (m), 665 (m), 613 (w), 596 (m), 504 (m) cm<sup>-1</sup>.

#### 2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-1*H*-pyrrole (**3**)



[Pd(PPh<sub>3</sub>)<sub>4</sub>] (866 mg, 750  $\mu$ mol) was added to a solution of 1-hexyl-2-(tributylstannyl)-1*H*-pyrrole (6.60 g, 15.0 mmol) and 2-bromo-3-hexyl-5-iodothiophene (5.60 g, 15.0 mmol) in DMF (60 mL) at 20 °C. The reaction mixture was stirred at 70 °C for 32 h and then poured into water (100 mL). The aqueous layer

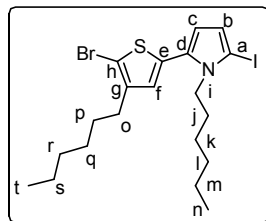
was extracted with diethyl ether (3 x 50 mL) and the combined organic phase was washed with water (3 x 80 mL) before drying over MgSO<sub>4</sub>. The volatiles were removed *in vacuo*. The crude product was purified by column chromatography over silica gel (*n*-hexane/DCM 14:1, R<sub>f</sub> = 0.51) to obtain 4.50 g (76%) of a yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.73 (t, <sup>3</sup>*J* = 2.2 Hz, 1 H, H-a), 6.67 (s, 1 H, H-f), 6.23 (dd, <sup>3</sup>*J* = 3.6 Hz, <sup>4</sup>*J* = 1.7 Hz, 1 H, H-c), 6.14 (t, <sup>3</sup>*J* = 3.2 Hz, 1 H, H-b), 3.94 (t, <sup>3</sup>*J* = 7.5 Hz, 2 H, H-i), 2.55 (t, <sup>3</sup>*J* = 7.5 Hz, 2 H, H-o), 1.72-1.66 (m, 2 H, H-j), 1.62-1.56 (m, 2 H, H-p), 1.38-1.22 (m, 12 H, H-k, l, m, q, r, s), 0.91-0.84 (m, 6 H, H-n, t) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.2 (C-g), 134.6 (C-e), 126.5 (C-f), 125.8 (C-d), 122.9 (C-a), 110.4 (C-c), 107.9 (C-b), 107.7 (C-h), 47.5 (C-i), 31.7, 31.5, 31.4 (C-j, k, l), 29.7, 29.6 (C-o, p), 28.9, 26.4, 22.6, 22.5 (C-m, q, r, s), 14.1, 14.0 (C-n, t) ppm. HRMS (EI-sector) *m/z*: [M]<sup>+</sup> Calcd for [C<sub>20</sub>H<sub>30</sub>BrNS]<sup>+</sup> 395.1282; Found 395.1275. IR (ATR):  $\tilde{\nu}$  = 2955 (m), 2925 (s), 2854 (m), 1573 (w), 1525 (w), 1457 (m), 1432 (m), 1408 (w), 1377 (w), 1291 (m), 1195 (m), 1113 (w), 1071 (m), 1032 (w), 1002 (w), 835 (m), 783 (m), 750 (m), 710 (s), 643 (w), 612 (m), 584 (w), 497 (w), 478 (w) cm<sup>-1</sup>.

#### 2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-iodo-1*H*-pyrrole (**4**)

*N*-Iodo-succinimide (896 mg, 4.00 mmol) was added in one portion to a stirred solution of 2-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1*H*-pyrrole (794 mg, 2.00 mmol) in THF (15 mL) at 20 °C. The reaction was stirred at 20 °C for 48 h. The reaction mixture was quenched with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (1





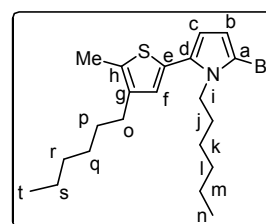
oil.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.78 (s, 1 H, H-f), 6.33 (d,  $^3J$  = 3.8 Hz, 1 H, H-c), 6.23 (d,  $^3J$  = 3.8 Hz, 1 H, H-b), 4.02 (t,  $^3J$  = 7.8 Hz, 2 H, H-i), 2.59 (t,  $^3J$  = 7.5 Hz, 2 H, H-o), 1.64-1.57 (m, 4 H, H-j, p), 1.38-1.21 (m, 12 H, H-k, l, m, q, r, s), 0.91-0.86 (m, 6 H, H-n, t) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.7 (C-g), 135.8 (C-e), 129.6 (C-d), 128.5 (C-f), 119.8 (C-c), 114.1 (C-b), 109.3 (C-h), 72.8 (C-a), 49.0 (C-i), 32.8, 32.4, 32.1 (C-j, k, l), 30.8, 30.4, 29.8 (C-o, p, q), 27.1 (C-m), 23.7, 23.5 (C-r, s), 14.4, 14.3 (C-n, t) ppm. HRMS (EI-sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $[\text{C}_{20}\text{H}_{29}\text{BrINS}]^+$  521.0249; Found 521.0238. IR (ATR):  $\tilde{\nu}$  = 2954 (s), 2924 (s), 2854 (s), 1573 (w), 1521 (w), 1455 (s), 1402 (s), 1375 (m), 1288 (m), 1199 (m), 1102 (w), 1035 (w), 1002 (w), 967 (w), 867 (w), 839 (m), 754 (s), 725 (m), 661 (w), 584 (w), 475 (w)  $\text{cm}^{-1}$ .

#### Typical procedure of lithiation of precursor monomer 4

4 (261 mg, 0.50 mmol) was added in one portion to THF (15 mL) and the solution was cooled to  $-78^\circ\text{C}$ .  $n\text{-BuLi}$  (0.2 mL, 0.50 mmol, 2.5 M in hexanes) was added dropwise to the solution over the course of 1 min and stirred for 10 min. Then MeI (426 mg, 0.2 mL, 3 mmol) was added in one portion and stirred for 2 h at  $-78^\circ\text{C}$ . The reaction was quenched with water (5 mL) and the aqueous phase was extracted with ether (2 x 15 mL). The combined organic phase was dried over  $\text{MgSO}_4$ . The solvent was removed *in vacuo* and the crude product was checked by GC-MS and NMR. The isolated products are shown as follows:

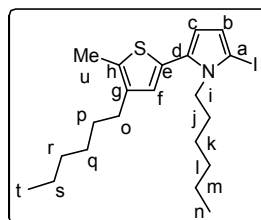
#### 2-Bromo-1-hexyl-5-(4-hexyl-5-methylthiophen-2-yl)-1H-pyrrole (5)



$^1\text{H}$  NMR (500 MHz, MeOD):  $\delta$  = 6.72 (s, 1 H, H-f), 6.14 (d,  $^3J$  = 3.8 Hz, 1 H, H-b/c), 6.11 (d,  $^3J$  = 3.8 Hz, 1 H, H-b/c), 4.05-3.95 (m, 2 H, H-i), 2.53 (t,  $^3J$  = 7.5 Hz, 2 H, H-o), 2.34 (s, 3 H, H-u), 1.65-1.54 (m, 4 H, H-j, p), 1.38-1.19 (m, 12 H, H-k, l, m, q, r, s), 0.93-0.83 (m, 6 H, H-n, t) ppm.  $^{13}\text{C}$  NMR (126 MHz, MeOD):  $\delta$  = 139.8 (C-g), 133.7 (C-h), 131.1 (C-e), 129.3 (C-a/d), 129.2 (C-f), 111.6 (C-b/c), 111.4 (C-b/c), 103.7 (C-a/d), 46.9 (C-i), 31.8 (C-j/p), 31.6 (C-j/p), 29.0 (C-o), 32.9, 32.4, 30.0, 27.1, 23.7, 23.6 (C-k, l, m, q, r, s), 14.4, 14.3 (C-t, n), 12.7 (C-u) ppm. HRMS (EI-sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $[\text{C}_{21}\text{H}_{32}\text{BrNS}]^+$  409.1339; Found 409.1442. IR (ATR):  $\tilde{\nu}$  = 2954 (s), 2924 (s), 2855 (s), 1458 (s), 1428 (m), 1402 (w), 1377 (m), 1289 (m), 1194 (m), 1158 (w), 1109 (w), 1030 (w), 961 (w), 892 (w), 839 (m), 750 (vs)  $\text{cm}^{-1}$ .

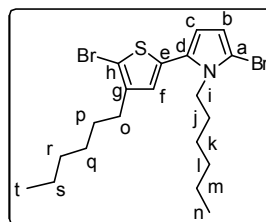
#### 1-Hexyl-2-(4-hexyl-5-methylthiophen-2-yl)-5-iodo-1H-pyrrole (6)

$^1\text{H}$  NMR (500 MHz, MeOD):  $\delta$  = 6.70 (s, 1 H, H-f), 6.29 (d,  $^3J$  = 3.7 Hz, 1 H, H-b/c), 6.16 (d,  $^3J$  = 3.7 Hz, 1 H, H-b/c), 4.03-3.98 (m, 2 H, H-i), 2.53 (t,  $^3J$  = 7.5 Hz, 2 H, H-o), 2.34 (s, 3 H, H-u), 1.65-1.53 (m, 4 H, H-j, p), 1.38-1.19 (m, 12 H, H-k, l, m, q, r, s), 0.93-0.83 (m, 6 H, H-n, t) ppm.  $^{13}\text{C}$  NMR (126 MHz, MeOD):  $\delta$  = 139.7 (C-g), 133.9 (C-h), 131.1 (C-d/e), 131.1 (C-d/e), 129.2



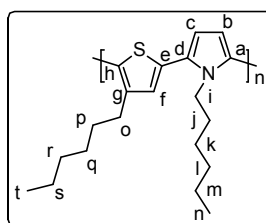
(C-f), 119.5 (C-b/c), 113.2 (C-b/c), 71.2 (C-a), 49.0 (C-i),  $^{60}$  32.1 (C-j/p), 31.6 (C-j/p), 29.0 (C-o), 32.9, 32.4, 30.0, 27.1, 23.7, 23.6 (C-k, l, m, q, r, s), 14.4, 14.3 (C-t, n), 12.7 (C-u) ppm. HRMS (EI-sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $[\text{C}_{21}\text{H}_{32}\text{INS}]^+$  457.1300; Found 457.1292. IR (ATR):  $\tilde{\nu}$  = 2954 (s), 2924 (s), 2855 (s), 1458 (s), 1420 (m), 1396 (w), 1376 (m), 1289 (m), 1194 (m), 1158 (w), 1102 (w), 1030 (w), 961 (w), 889 (w), 839 (m), 752 (vs)  $\text{cm}^{-1}$ .

#### 2-Bromo-5-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole (8)



$^1\text{H}$  NMR (500 MHz, MeOD):  $\delta$  = 6.80 (s, 1 H, H-f), 6.22 (d,  $^3J$  = 3.8 Hz, 1 H, H-b/c), 6.16 (d,  $^3J$  = 3.8 Hz, 1 H, H-b/c), 4.06-4.01 (m, 2 H, H-i), 2.63-2.56 (2 H, H-o), 1.67-1.57 (m, 4 H, H-j, p), 1.41-1.20 (m, 12 H, H-k, l, m, q, r, s), 0.94-0.84 (m, 6 H, H-n, t) ppm.  $^{13}\text{C}$  NMR (126 MHz, MeOD):  $\delta$  = 143.8 (C-g), 135.8 (C-e), 128.5 (C-f), 127.9 (C-d), 112.4 (C-b/c), 112.0 (C-b/c), 109.0 (C-h), 105.0 (C-a), 46.9 (C-i), 32.8, 32.4, 31.8, 30.8, 30.4, 29.9, 27.1, 23.7, 23.6 (C-j, k, l, m, o, p, q, r, s), 14.4, 14.3 (C-t, n) ppm. HRMS (EI-sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $[\text{C}_{20}\text{H}_{29}\text{Br}_2\text{NS}]^+$  473.0388; Found 473.0411. IR (ATR):  $\tilde{\nu}$  = 2955 (s), 2925 (s), 2856 (s), 1577 (w), 1524 (w), 1461 (s), 1411 (m), 1378 (w), 1290 (m), 1202 (m), 1111 (w), 1034 (w), 971 (w), 869 (w), 839 (m), 751 (vs)  $\text{cm}^{-1}$ .

#### General procedure for polymerization of 7



In a microwave vial,  $i\text{PrMgCl}$  (0.25 mL, 2.00 M in THF, 0.50 mmol) was added dropwise to a solution of precursor monomer 4 (261 mg, 0.50 mmol) in dry MTBE (3.0 mL) via a hamilton syringe in the glove box at  $20^\circ\text{C}$  over the course of 1 min. After stirring the reaction mixture for 10 min at  $20^\circ\text{C}$ , a solution of  $[\text{Pd}(t\text{Bu}_3\text{P})_2]$  (5.11 mg, 10.0  $\mu\text{mol}$ ) in MTBE (1.0 mL) was added to the reaction mixture. The reaction mixture was heated up to  $50^\circ\text{C}$  under microwave irradiation and stirred for 5 h. Then the reaction mixture was quenched with  $\text{H}_2\text{O}$  (10 mL) and the aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL) and dried with  $\text{MgSO}_4$ . The volatiles were removed *in vacuo* to give the crude product. This was dissolved in diethyl ether (0.5 mL) and the solution was added dropwise into methanol (200 mL) with vigorous stirring to remove the low molecular weight compounds. The precipitated polymer was extracted by soxhlet extractor with MeOH (200 mL) for 5 h. For removal from the Soxhlet extractor, the solid polymer was refluxed by diethyl ether (100 mL). The volatiles were removed *in vacuo* and product was dried under reduced pressure for 16 h give the polymer as orange to red brown viscous solid.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.97 (s, 1 H, H-f), 6.41 (d,  $^3J$  = 3.6 Hz, 1 H, H-b/c), 6.26 (d,  $^3J$  = 3.6 Hz, 1 H, H-b/c), 4.17-3.92 (m, 2 H, H-i), 2.66-2.46 (m, 2 H, H-o), 1.64-1.51 (m, 4 H, H-j, p), 1.35-1.09 (m, 12 H, H-k, l, m, q, r, s), 0.88 (t,  $^3J$  = 6.8 Hz, 3 H, H-n/t), 0.81 (t,  $^3J$  = 7.1 Hz, 3 H, H-n/t) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 142.8 (C-g), 134.9 (C-e), 128.1 (C-a/d), 127.6 (C-h), 126.7 (C-a/d), 126.3 (C-f), 112.0 (C-b/c), 110.0 (C-b/c), 45.3 (C-

i), 31.7 (C-k/l/m/q/r/s), 31.2 (C-k/l/m/q/r/s), 31.0 (C-j/p), 30.7 (C-j/p), 29.1 (C-o), 29.1 (C-k/l/m/q/r/s), 26.3 (C-k/l/m/q/r/s), 22.6 (C-k/l/m/q/r/s), 22.4 (C-k/l/m/q/r/s), 14.1 (C-n/t), 13.9 (C-n/t) ppm. IR (ATR):  $\tilde{\nu}$  = 2953 (s), 2923 (s), 2854 (s), 1458 (s), 1402 (m), 1376 (m), 1308 (m), 1193 (m), 1033 (m), 873 (w), 839 (m), 762 (m), 723 (m), 684 (w), 637 (w), 567 (w)  $\text{cm}^{-1}$ .

#### Procedure for the kinetics study

In a microwave vial, *i*PrMgCl (0.25 mL, 2.00 M in THF, 0.50 mmol) was added dropwise to a solution of precursor monomer **4** (261 mg, 0.50 mmol) and naphthalene (64.1 mg, 0.50 mmol, used as an internal standard for GC analysis to analyze the conversion) in dry MTBE (3.0 mL) via a hamilton syringe in the glove box at 20 °C over the course of 1 min. After stirring the reaction mixture for 10 min at 20 °C, a solution of [Pd(*t*Bu<sub>3</sub>P)<sub>2</sub>] (5.11 mg, 10.0  $\mu\text{mol}$ ) in MTBE (2.0 mL) was added to the reaction mixture. After the 60 min, 120 min, 180 min, 240 min, 300 min, 360 min, 375 min, 390 min, 415 min, 440 min, a sample (0.3 mL) was taken out of the reaction mixture. 0.1 mL of the solution was quenched with 2 droplets of ethanol. The quenched solution was diluted with 3 mL of THF, 2 mL of the solution was filtered with a syringe filter (0.45  $\mu\text{m}$ ) and used for GC analysis. The other 0.2 mL of reaction mixture was quenched with ethanol (1 mL) and diluted with Et<sub>2</sub>O (4 mL) and water (2 mL). After shaking the vial, the layers were separated. The organic phase was dried over MgSO<sub>4</sub> and filtered with a syringe filter (0.45  $\mu\text{m}$ ). Half of the solvent was removed *in vacuo*, diluted in chloroform (HPCL grade, 2 mL) and used for GPC analysis. The other half of the solvent was removed *in vacuo*, diluted in deuterated benzene for NMR analysis.

#### Acknowledgement

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