

Towards Perfect Control of End Groups and Polydispersity in Poly(3-hexylthiophene) via Catalyst Transfer Polymerization

*Ruth H. Lohwasser, Mukundan Thelakkat**

Applied Functional Polymers, Department of Macromolecular Chemistry I, University of Bayreuth
Universitätsstraße 30, 95444 Bayreuth, Germany.

mukundan.thelakkat@uni-bayreuth.de

Experimental Section

Materials and Characterization

¹H-NMR spectra were recorded in chloroform on a Bruker Avance 250 spectrometer at 300 MHz. Coupling constants are given in Hz. The spectra were calibrated according to the solvent signal at 7.26 ppm. Size exclusion chromatography (Poly-SEC) measurements were performed utilizing a Waters 515-HPLC pump with stabilized THF as the eluent at a flow rate of 0.5 mL/min. A 20 μ L volume of a solution with a concentration of approximately 1 mg/mL was injected into a column setup, which consists of a guard column (Varian, 50 \times 0.75 cm, ResiPore, particle size 3 μ m) and two separation columns (Varian, 300 \times 0.75 cm, ResiPore, particle size 3 μ m). The compounds were monitored with a Waters UV detector at 254 nm. Polystyrene was used as external standard and 1,2-dichlorobenzene as an internal standard for calibration. Matrix assisted laser desorption ionizations spectroscopy with time of flight detection mass spectroscopy (MALDI-TOF MS) measurements were performed on a Bruker Reflex III using Dithranol as matrix and a mixture of 1000:1 (Matrix:Polymer). The Laser intensity was

set to around 70%. The reflection mode was calibrated with a fullerite mixture from Sigma–Aldrich (CAS 131159-39-2).

The monomer 2,5-dibromo-3-hexylthiophene and the catalyst 1,3-bis(diphenylphosphino)propanenickel(II) chloride [Ni(dppp)Cl₂] were synthesized according to the literature.¹ All glass apparatus for polymerization were heated and cooled down under argon. Dry THF was distilled over calcium hydride and potassium. *t*-BuMgCl (1.7 M in THF) was purchased from Acros and titrated according to Krasovskiy and Knochel.² Hexamethyldisilazane (HMDS) (99% Aldrich) for the OFETs was used as received. LiCl puriss p.a. water free was purchased from Fluka and dried prior to use.

General Procedure for the Synthesis of P3HT

In a dry schlenk flask 1.5 g (4.6 mmol) 2,5-dibromo-3-hexylthiophene was dissolved in 9 ml THF and 3.6 ml (4.41 mmol) of *t*-BuMgCl were added with a syringe. After complete active Grignard monomer formation the solution was diluted with 33 mL of dry THF and the reaction was initiated with Ni(dppp)Cl₂ (96 mg, 0.18 mmol) suspended in 1 ml THF. For kinetic studies samples of ca. 0.5 mL were withdrawn quenched in HCl and washed with MeOH. The polymerization was stopped by adding 5 ml of 5N HCl. After precipitation in Methanol the polymer was filtered into a Soxhlet thimble and extracted with methanol over night to wash away the monomer and low molecular impurities. The pure polymer was gained by dissolving the polymer in chloroform and precipitation in methanol.

P3HT 1: GPC $M_p = 4400 \text{ g mol}^{-1}$, $M_n = 4000 \text{ g mol}^{-1}$, $M_w = 4300 \text{ g mol}^{-1}$, $M_w/M_n = 1.10$; δ_H (300 MHz; CDCl₃) 6.98 (1 H, s, H_{ar}), 2.80 (2 H, t, J_{ab} 7.6, α -CH₂), 1.85–1.50 (2 H, m, β -CH₂), 1.50–1.10 (6 H, m), 1.0–0.75 (3 H, m, CH₃); FTIR ν_{max} (film)/cm⁻¹ 3056w, 2955s, 2927s, 2857s, 1512w, 1456m, 1378m, 821m, 726w.

General Procedure for the Synthesis of P3HT using LiCl

In a schlenk flask LiCl was dried under vacuum at 140°C for 4h. After cooling to room temperature dry THF was added and stirred over night to form at 0.5 M LiCl solution. In a dry schlenk flask 1.5 g

(4.6 mmol) 2,5-dibromo-3-hexylthiophene was dissolved in 9.2 ml of 0.5 M LiCl solution and 3.6 ml (4.41 mmol) of *t*-BuMgCl were added with a syringe. After complete active Grignard monomer formation the solution was diluted with 33 ml THF. The polymerization was initiated with a suspension of 98 mg (0.18 mmol) Ni(dppp)Cl₂ in 1 mL THF. The polymerization was stopped by adding 5 ml of 5N HCl. After precipitation in Methanol the polymer was filtered into a Soxhlet thimble and extracted with methanol over night to wash away the monomer and low molecular impurities. The pure polymer was gained by dissolving the polymer in chloroform and precipitation in methanol.

OFET Preparation and Measurements

OFET substrates were purchased from Fraunhofer IMPS, Dresden. The geometry of the device was a bottom gate top electrode type, with n-doped (doping at wafer surface: $n \approx 3^{17} \text{ cm}^{-3}$) silicon as gate electrode and a 230 nm SiO₂ layer as gate dielectric. The source and drain electrodes were ITO (indium tin oxide) (10 nm) as adhesion layer with a high work function and gold (30 nm). The analysed channel length was 20 μm and the width was 10 mm. The substrates were cleaned with acetone, H₂O₂/H₂SO₄ (15 min), VE-water, acetone (ultrasonic bath, 15 min), *i*-propanol (ultrasonic bath, 15 min) and rinsed with hexane. The H₂O₂/H₂SO₄ solution should be handled with care because it is highly corrosive. After plasma etching for 15 min the substrates were hydrophobized with hexamethyldisilazane (HMDS) vapour for 3 hours. Excess HMDS was washed off with hexane. All following steps were done under inert gas atmosphere in a glovebox. The active polymer layers were spin coated at 2000 rpm from a 1 wt% solution in CHCl₃. Output and transfer characteristics were measured with a Hewlett Packard 41555A semiconductor parameter analyser. The hole transport mobilities were determined from the transfer characteristics according to equation 1.³ Since the mobility did not reach a saturation regime for all devices, all the given mobilities are for a fixed gate voltage of -40 V.

$$\mu_{\text{sat}} = \left(\frac{\partial \sqrt{I_{\text{SD}}}}{\partial V_{\text{G}}} \right)^2 \frac{2L}{WC_i} \quad (1)$$

Additional MALDI-TOF MS Spectra

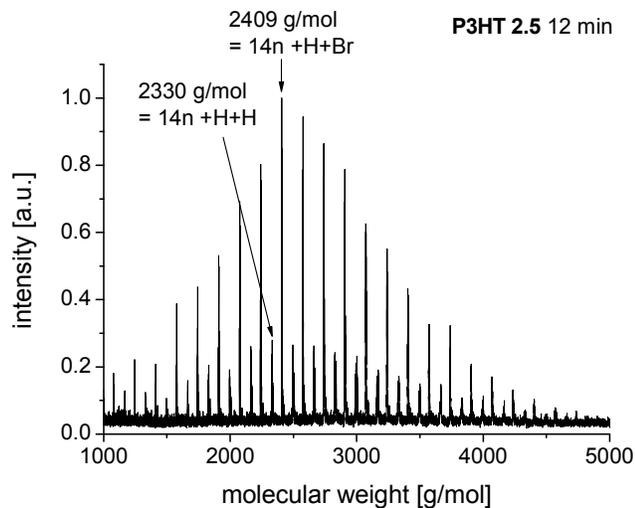


Figure SI-1: MALDI-TOF MS spectrum of P3HT 2.5 with incomplete active Grignard monomer formation after 12 min of polymerization. Two peak series H/Br and H/H are observed. The amount of chain with H/Br end groups is ca 80%.

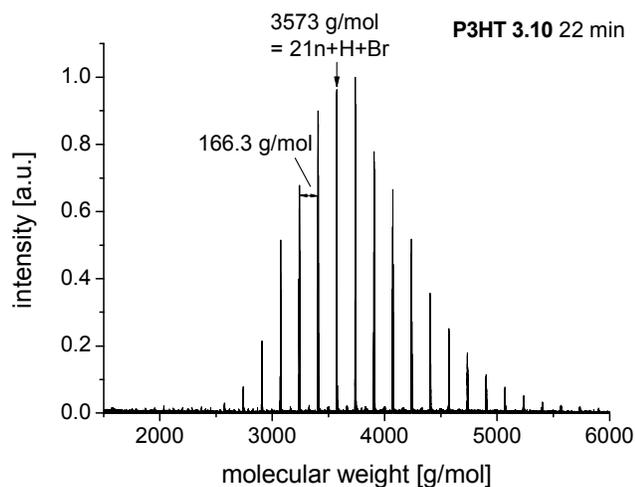


Figure SI-2: MALDI-TOF MS spectrum of P3HT 3.10 polymerized with LiCl as an additive and after complete active Grignard monomer formation after 22 min of polymerization. Only one peak series for polymer with H/Br chain ends is observed.

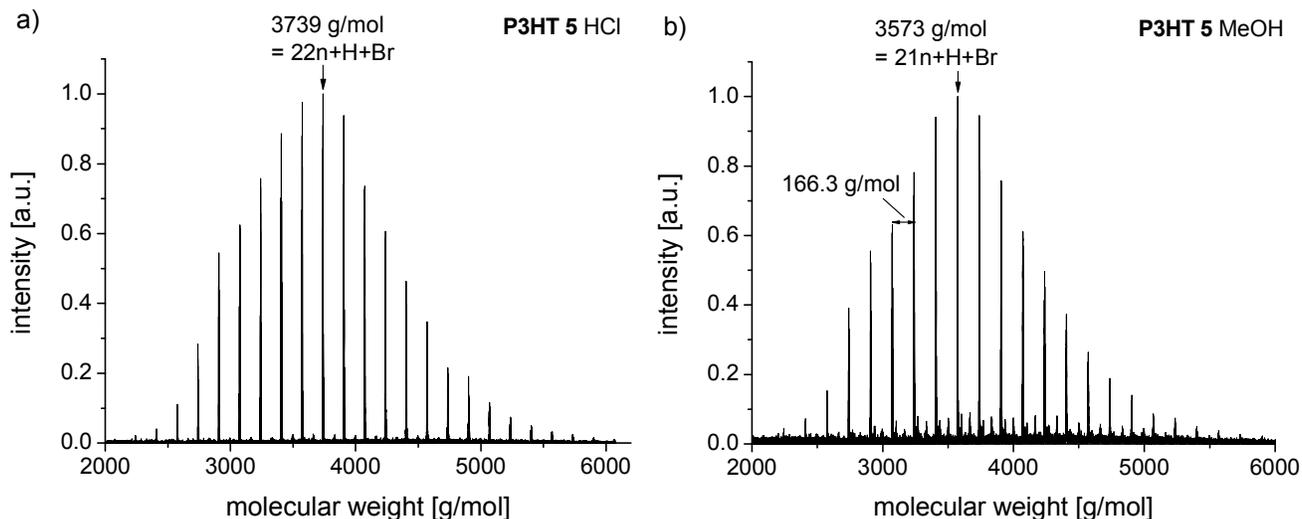


Figure SI-3: MALDI-TOF MS spectra of P3HT 5 polymerized with LiCl as an additive and a) quenched with HCl and b) MeOH. Only one main peak series for chains with H/Br end groups are observed. A monomodal distribution for the P3HT 5 sample quenched with MeOH shows that coupled chains observed in SEC are not visible in MALDI-TOF MS.

Output Characteristics of P3HT 4 and P3HT 5

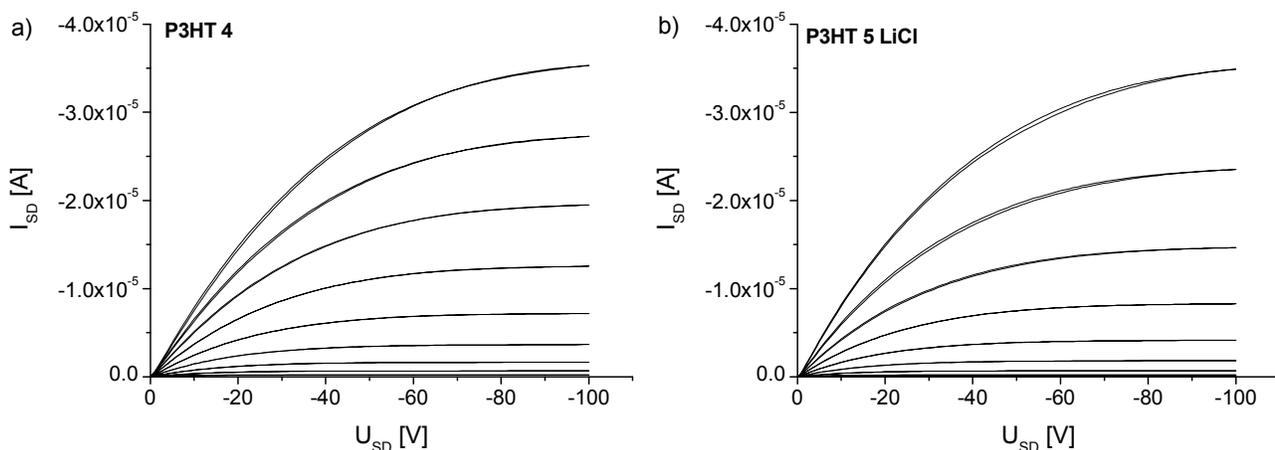


Figure SI-4: Output characteristics (I_{DS} - U_{DS}) of organic thin film transistors of a) P3HT 4 synthesized without LiCl and b) P3HT 5 synthesized with LiCl. The geometry was a bottom gate device with SiO₂ as gate dielectric coated with a hexamethyldisilazane (HMDS) layer. The gate Voltage U_G was varied in -10 V steps from 0 V to -80 V.

^1H NMR spectra of two different molecular weights of P3HTs synthesized with and without LiCl

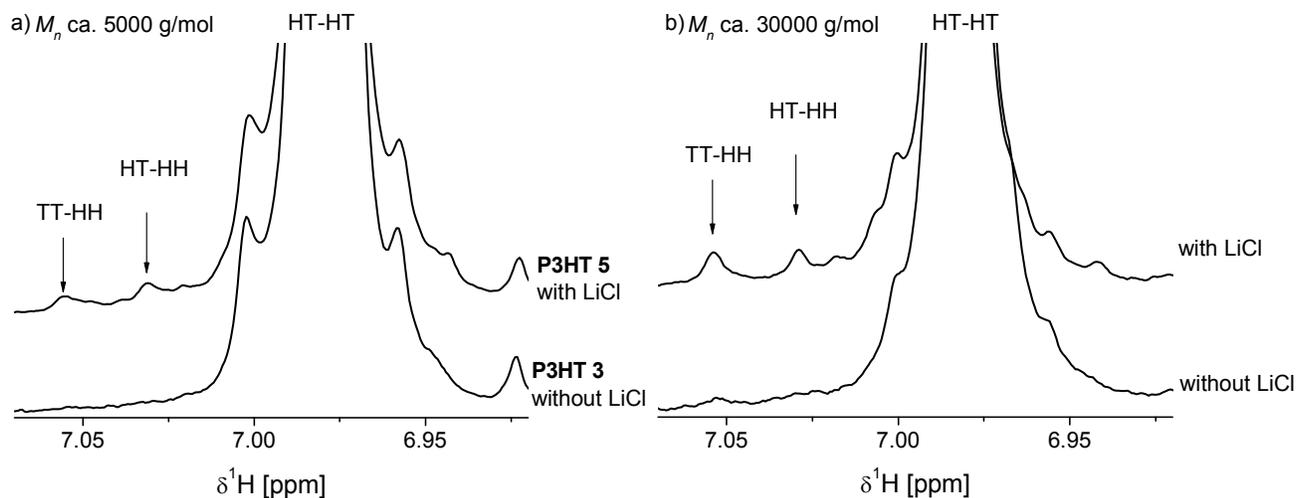


Figure SI- 5: Enlarged aromatic region of relevance for regioregularity in the ^1H NMR spectra of P3HTs synthesized with and without LiCl as an additive for samples with a M_n of a) ca. 5000 g/mol and b) ca. 30000 g/mol. While no irregular couplings are observed for P3HTs which were polymerized without adding LiCl, TT-HH and HT-HH couplings are visible for P3HTs polymerized with LiCl as an additive. The irregular couplings are more pronounced for the higher molecular weight samples.

SEC curves of P3HT 7 before and after separation with preparative SEC

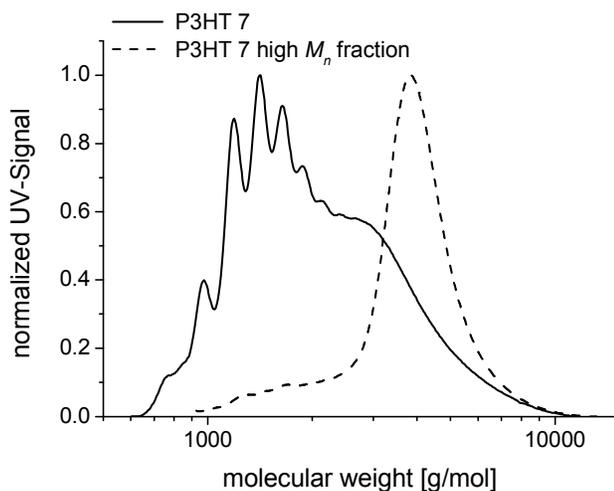


Figure SI-6: SEC curves of P3HT 7 and the high molecular weight fraction of P3HT 7, containing the coupled chains. The high molecular weight fraction was separated using preparative SEC.

References

- (1) Van Hecke, G. R.; Horrocks, W. *Inorg. Chem.* **1966**, *5*, 1968-1974.
- (2) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890-891.
- (3) Sze, S. M.; Ng, K. K. In *Physics of semiconductor devices*, Eds.; Wiley-Interscience: Hoboken, NJ, 2007.