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End-Group Telechelic Oligo- and Polythiophenes by "Click" Reactions: Synthesis and Analysis via LC-ESI-TOF MS

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ABSTRACT: End-group-modified poly(3-hexylthiophenes) (P3HT) with complex hydrogen-bonding moieties have been prepared starting from telechelic alkyne-functionalized P3HT via a copper(I) catalyzed azide/alkyne "click" reaction. The final polymers are projected to arrange into pseudoblock copolymers consisting of alternating donor/acceptor polymers for application in solar cell materials. Starting from a bromine-telechelic P3HT (M_n = 2000 g/mol; M_w/M_n = 1.2) prepared via the McCullough method followed by additional bromination reaction yielding telechelic P3HTs with (80% Br/Br; 20% H/Br) end groups, the respective α,ω-(trimethylsilyl)ethynyl-P3HTs were prepared via Sonogashira coupling reactions. Analysis of the end groups of the alkynyl-telechelic P3HT species was achieved by use of LC-ESI-TOF methods for the first time, proving the formation of ∼59% (ethynyl/ethynyl) and ∼40% (ethynyl/H) species within the α,ω-(trimethylsilyl)ethynyl-P3HTs, with only minor amounts (∼1%) of the respective (H/H)-modified species. Additionally, MALDI methods were used for a qualitative assessment. Subsequent azide/alkyne "click" reaction with either 1-(6-azidohexyl)thymine or 5-((4-azidobenzoyl)amino)-*N*,*N*′-(6-(octanoylamino)pyridin-2-yl)isophthalamide using CuI, $CuBr(PPh_3)_3$, or $CuI \cdot P(OEt)_3$ as catalyst yielded the final products with attached hydrogen bonds as judged by LC-ESI-TOF methods. The described method opens an access toward supramolecular P3HT polymers with hydrogen-bonding moieties.

Introduction

The performance of polymeric organic semiconductors has been studied intensely via the concept of the bulk-heterojunction solar cells,[1,2] often relying on supramolecular ordering concepts of oligomeric and polymeric building blocks.[3−10] Mostly poly(3-hexylthiophene)s (P3HT) or *p*-phenylenevinylene(s) have been used due to their favorable optoelectronic properties, good solubility, and solution processability. As these polymers are also envisioned as a replacement for silicon-based organic field effect transistors (OFETs), a wide range of structural variations has been studied, many of them addressing the molecular ordering of P3HT polymers in the solid state.[11] Therefore, synthetic approaches toward defined side-chain and end-group-functionalized regioregular P3HTs have been studied extensively,[12−33] most of them on the basis of the Grignard metathesis method (GRIM).[34−36] Being based on a Kumada-type coupling reaction,[15] this chain-growth polycondensation reaction yields P3HT polymers with (Br/H) end groups, if the conventional initiation via, for example, 2-bromo-5-chloromagnesio-3-hexylthiophene together with 2-bromo-3-hexyl-5-iodothiophene as monomer and $Ni(dppp)Cl_2$ (dppp = propane-1,3-diylbis(diphenylphosphine) as catalyst are used. GRIM polymerization by direct addition of functionalized Grignard reagents (R′MgX) or initiation with functionalized nickel−aryl complexes can yield end-group-functionalized P3HT polymers as either monocapped (R′) or dicapped macromolecules (R′/R′), often as a mixture with unfunctionalized, fully hydrogenated (H/H) polymers, or the respective starting polymers containing (Br/H or Br/Br) end groups. Mechanistically, these mixtures are generated by incomplete coupling reactions, or via chain transfer and subsequent Br/Mg exchange.[15]

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One of the first successful end-group functionalizations of P3HT was reported by Janssen et al.[31] transforming the bromine end groups of P3HT into 5-(trimethylsilyl)-2-thienyl end groups by adding Grignard reagents and a fresh amount of the $Ni(dppp)Cl_2$ catalyst to the polymerization reaction of P3HT. Another, similar method by Liu et al.[30] furnished the respective OH-substituted P3HT polymers by reaction with THP-protected-thienyl−zinc compounds. Subsequently, many authors[12,15−17,21,23,24,26,30,31] have extended this method using a wide variety of different Grignard reagents for quenching the GRIM polymerization, proving the (often mixed) end groups by ^{1}H NMR and MALDI-TOF MS. If alkynyl end groups[12,26] are introduced, subsequent azide/alkyne "click" reactions can be used to obtain triazole end-group-funtionalized polymers in a mixture with nonfunctionalized (Br/H; H/H) polymers.[12,13,16] Additionally, P3HT-containing block copolymers can be prepared, for example, yielding P3HT-PS, P3HT-PMMA, or P3HT-PLA block copolymers.[18,19,21,24] The direct use of nickel-based initiators[12,33] (R′-$Ni(PPh_3)_2Br$) yielded (siloxyphenyl)- or TMS-alkynyl-phenyl-capped P3HTs as a mixture of several isomeric compounds, either with the desired (R′/H; R′/Br) end groups or with capped species with the end groups of the respective starting materials (Br/Br; Br/H; H/H).[12]

The present publication aims at the synthesis of functionalized P3HTs with hydrogen-bonding moieties to study ordered supramolecular P3HT polymers for solar cell applications (Scheme 1). Our synthetic concept is based on a GRIM polymerization with successive end-group functionalization via azide/alkyne "click" chemistry and Sonogashira reaction, thus allowing us to achieve an indirect functionalization of the respective P3HTs with a multitude of hydrogen-bonding moieties in a modular fashion. An important issue concerns the subsequent characterization and

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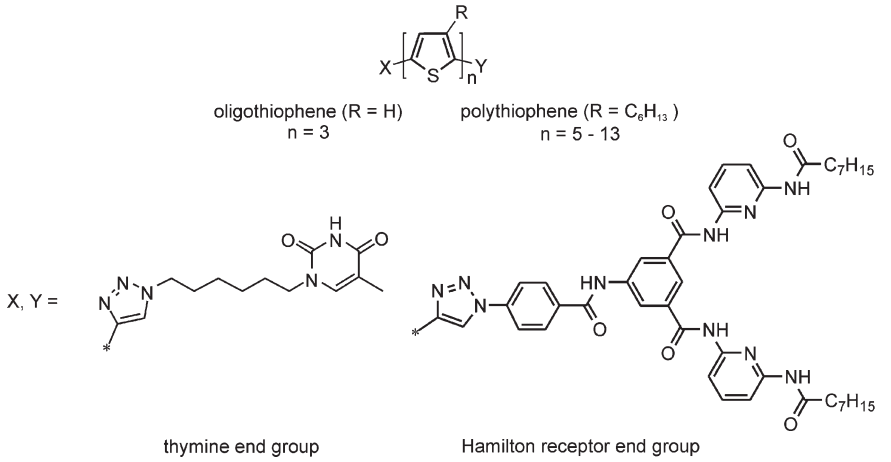
Scheme 1. Structures of Oligo- and Polythiophenes Obtained after Azide/Alkyne "Click" Reaction



quantification of the individually functionalized P3HT polymers by LC-ESI-TOF methods and additional mass spectrometric methods, such as MALDI mass spectrometry. Especially LC-ESI-TOF methods are intensively investigated as, surprisingly, this method has not been used for the analysis of P3HTs up to now.

Experimental Section

Materials. Tetrahydrofuran (THF) was predried over KOH and freshly distilled over Na and benzophenone. Triethylamine was predried by refluxing over KOH and finally freshly distilled over CaH_2. All reagents like *tert*-butylmagnesium chloride (2 M in ether), (trimethylsilyl)acetylene, tetrakis(acetonitrile)copper(I) hexafluorophosphate, copper(I) iodide, bromotris(triphenylphosphine)copper(I), tetra-*n*-butylammonium fluoride (1 M in THF), [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2), and bis(triphenylphosphino)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) were purchased from Sigma Aldrich and used without further purification. The copper catalyst $Cu^{I}I \cdot P(OEt)_3$ was synthesized according to the literature,[37] also 5,5′-bis((trimethylsilyl)-ethynyl)-2,2′:5′,2″-terthiophene (**5**) and 5,5″-diethynyl-2,2′:5′,2″-terthiophene (**6**) were synthesized on the basis of the literature.[38−40] The synthesis of 1-(6-azidohexyl)thymine (**7a**) and 5-((4-azidobenzoyl)amino)-*N*,*N*′-(6-(octanoylamino)pyridin-2-yl)isophthalamide (**7b**) was done according to the literature.[41−44] Tetrahydrofuran (THF), methanol, and acetonitrile with HPLC grade were purchased from Sigma Aldrich. The MALDI-TOF matrices, dithranol, *trans*-3-indoleacrylic acid (IAA), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), and the salt sodium trifluoroacetate (NaTFA), were purchased from Sigma Aldrich. Terthiophene used as the MALDI matrix was synthesized according to the literature.[40]

Measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Gemini 2000 FT-NMR spectrometer. For data interpretation of spectra MestRecC 4.7.0.0 was used. All chemical shifts (δ) are given in parts per million (ppm) relative to Me_4Si (TMS); coupling constants (J) are given in Hertz. All NMR samples were dissolved in $CDCl_3$ or DMSO-d_6, unless otherwise stated. Number-average molecular weights (M_n) and molecular weight distribution were measured by a Viscotek GPCmax VE2001 gel-permeation chromatography (GPC) unit with THF as eluent in a flow rate of 1 mL/min and an injection volume of 100 μL using a refractive index detector (VE 3580 RI, Viscotek) and a column set H_{HR}-HGuard+GMH_{HR}-N (Viscotek, mixed bed). An external calibration was made with polystyrene standard (1050−115 000 g/mol).

The LC-ESI-TOF (electrospray-ionization time-of-flight) measurements were performed with a microTOF II focus (Bruker Daltonics) equipped with an ESI source and combined with an Elite LaChrom HPLC by Hitachi/VWR setup with a diode array detector and a Nova Pak C18 column by Waters (60 Å, 4 μm, dimension 3.9 × 150 mm), which are temperate at 25 °C. The HPLC run for 1-(3-hexylthymine)-4-(5-(5-(1-(1-(3-hexylthymine)-1*H*-1,2,3-triazol-4-yl)thiophen-2-yl)thiophen-2-yl)thiophen-2-yl)-1*H*-1,2,3-triazole (**1a**) was performed with a MeOH−MeCN gradient of 25:75 to 99:1 in 30 min and detected at a wavelength of 200 nm. The sample was prepared as follows 1 mg/1 mL in MeCN:MeOH (1:1), afterward 5 μL of this sample solution was injected for one measurement. The chromatographic separation of all P3HTs was done with a MeCN−THF gradient of 90:10 to 20:80 in 70 min and detected at 400 nm using a sample concentration of 5 mg/1 mL in THF and an injection volume of 5 or 10 μL. The MS measurement was supported by a postcolumn injection of MeOH (300 μL/h). Afterward the LC−MS data were analyzed using DataAnalysis 4.0. The device specific mass accuracy of these recorded spectra is 10 ppm. For a rough quantification we sum up the MS trace area of a single species and divided it through the sum of whole analyzed MS trace area (100%) to yield a percentage. If we detected more than one species, we calculated the ratio between them, through a sum up of the intensities of the isotopic pattern of one single polymer species. The MALDI-TOF MS measurements were obtained on an autoflex smartbeam III by Bruker Daltonics. The instrument is equipped with a pulsed N_2 laser (337 nm, 0 ns pulse) and a time-delayed extracted ion source. MALDI spectra were recorded using the positive-ion linear (LP) and the reflector (RP) modus. The accelerating voltage was 20 kV, and the low mass gate was 400.0 m/z. For the calibration of the MALDI spectra PEG 2000 standard (polymer source Inc.) was used with DCTB and LiTFA in the ratio 100:10:1. Polymer samples were prepared by combining the matrix and the analyte in a 100:10 ratio. For the polymer with bromine end groups terthiophene was used as matrix; furthermore dithranol after the Sonogashira reaction and DCTB after "click" reaction were applied. The cationization salt solution of 20 mg/mL AgTFA in THF was added to some samples in a 100:1 ratio of matrix: salt.

Microwave irradiation supported reactions were performed on a Discover LabMate by CEM Mikrowellen. For these reactions 10 mL vials with an IntelliVent snap-on cap sytem were used.

Synthesis. *Poly(3-hexylthiophene)* (***9***)[23]. In a well dried three-necked flask 2,5-dibromo-3-hexylthiophene (**8**) (326 mg, 1 mmol) was dissolved in 5 mL of freshly distilled dry THF, and the mixture was stirred under an atmosphere of argon. *tert*-Butylmagnesium chloride (0.5 mL, 1 mmol) was added via a syringe, and the mixture was stirred for 2 h at room temperature. Subsequently, a suspension of Ni(dppp)Cl_2 (45.2 mg, 0.083 mmol) in 1 mL of dry THF was added in one portion. The mixture was stirred for 10 min at room temperature, and 400 μL of a 1 M Br_2/THF solution was added under an atmosphere of

argon. The reaction mixture was stirred for an additional 5 min and then poured to 100 mL of methanol to precipitate the polymer. After centrifugation, the polymer was dried under high vacuum (yield = 105 mg, 32%). ^{1}H NMR ($CDCl_3$, *J* (Hz), 400 MHz): δ_H 6.95 (m, 1H), 2.75 (m, 2H), 1.59 (m, 2H), 1.32 (m, 6H), 0.88 (m, 3H). GPC: M_n = 2000 g/mol, M_w/M_n = 1.20.

α,ω-(*Trimethylsilyl*)*ethynyl-P3HT* (***10***). Poly(3-hexylthiophene) (**9**) (30 mg, 0.015 mmol), $PdCl_2(PPh_3)_3$ (5.2 mg, 7.45×10^{-3} mmol), CuI (1.4 mg, 7.45×10^{-3} mmol), and (trimethylsilyl)-acetylene (41 μL, 0.3 mmol) were dissolved in 4 mL of dry triethylamine, and the solution was sealed in a 10 mL vial with a IntelliVent snap-on cap. The reaction mixture was stirred at 90 °C for 2.5 h in a cavity resonator (15 W). After cooling to room temperature the mixture was poured in 150 mL of chloroform. The organic phase was washed with 50 mL of NH_4Cl solution and 50 mL of brine. After drying over Na_2SO_4, the solvent was evaporated to dryness. The product was dried under high vacuum (yield = 32 mg, 95%). ^{1}H NMR ($CDCl_3$, *J* (Hz), 400 MHz): δ_H 6.96 (s, 12H), 2.79 (m, 24H), 1.60 (m, 24H), 1.32 (m, 72H), 0.90 (m, 36H), 0.25 (s, 9H), 0,06 (s, 18H). GPC: M_n = 2200 g/mol, M_w/M_n = 1.09.

Semitelechelic Thymine-Capped P3HT ***2*** *via "Click" Reaction*. α,ω-(Trimethylsilyl)ethynyl-P3HT **10** (17 mg, 11.2×10^{-3}mmol) was dissolved in 3 mL of dry THF in a 10 mL vial with a IntelliVent snap-on cap and degassed by argon. Tetra-*n*-butylammonium fluoride (34 μL, 0.034 mmol) was added and stirred at room temperature for 10 min. Subsequently 1-(6-azidohexyl)thymine (7 mg, 0.028 mmol) **7a**,[45] copper(I) iodide (10.4 mg, 11.2×10^{-3}mmol), diisopropylethylamine (5 μL), and 0.1 mL of 2-propanol/H_2O (1:1) were added to this solution and stirred at 120 °C for 1.5 h in cavity resonator (300 W). The reaction mixture was poured in 50 mL of chloroform and washed with 30 mL of NH_4Cl solution and 30 mL of brine. The organic phase was dried over Na_2SO_4, and the solvent was evaporated to dryness. Finally, the product was dried under high vacuum (yield = 29.3 mg, 92%). ^{1}H NMR ($CDCl_3$, *J* (Hz), 400 MHz): δ_H 6.96 (s, 22H), 2.79 (m, 44H), 1.60 (m, 44H), 1.32 (m, 132H), 0.90 (m, 66H). GPC: M_n = 3100 g/mol, M_w/M_n = 1.33.

Semitelechelic Hamilton-Capped P3HT ***3*** *via "Click" Reaction*. α,ω-(Trimethylsilyl)ethynyl-P3HT (**10**) (18 mg, 8.2×10^{-3}mmol) was dissolved in 3 mL of dry THF in a 10 mL vial with a IntelliVent snap-on cap, and the solution was degassed by argon. Tetra-*n*-butylammonium fluoride (25 μL, 0.025 mmol) was added, and the mixture was stirred at room temperature for 10 min. Subsequently, 5-((4-azidobenzoyl)amino)-*N*,*N*′-(6-(octanoylamino)pyridin-2-yl)isophthalamide (15.6 mg, 0.021 mmol) (**7b**),[41,42,44] bromotris(triphenylphosphine)copper(I) (7.6 mg, 8.2×10^{-3}mmol), diisopropylethylamine (5 μL), and 0.1 mL of 2-propanol/H_2O (1:1) were added to this solution, and the resulting mixture was stirred at 90 °C for 1.5 h in a cavity resonator (100 W). The reaction mixture was poured to 50 mL of chloroform and washed with 30 mL of NH_4Cl solution and with 30 mL of brine. The organic phase was dried over Na_2SO_4 and the solvent was evaporated to dryness. Finally, the product was dissolved in a small amount THF and precipitated in methanol, the precipitate was dried under high vacuum (yield = 14 mg, 62%). ^{1}H NMR ($CDCl_3$, *J* (Hz), 400 MHz): δ_H 6.96 (s, 21H), 2.79 (m, 42H), 1.60 (m, 42H), 1.32 (m, 126H), 0.90 (m, 63H). GPC: M_n = 3300 g/mol, M_w/M_n = 1.17.

1-(3-Hexylthymine)-4-(5-(5-(1-(1-(3-hexylthymine)-1H-1,2,3-triazol-4-yl)thiophen-2-yl)thiophen-2-yl)thiophen-2-yl)-1H-1,2,3-triazole (***1a***). 5,5″-Diethynyl-2,2′:5′,2″-terthiophene (30 mg, 0.101 mmol) (**6**), 1-(6-azidohexyl)thymine (56 mg, 0.222 mmol) (**7a**),[45] tetrakis-(acetonitrile)copper(I) hexafluorophosphate (3.7 mg, 0.01 mmol), and diisopropylethylamine (40 μL) were dissolved in 2 mL of acetonitrile under an inert gas atmosphere. The reaction mixture was degassed, and additionally a freeze−thaw cycle was done three times to remove oxygen. The suspension was stirred for 16 h at 50 °C. Afterwards the solvent was evaporated and the residue was poured into chloroform and washed with 50 mL of NH_4Cl solution and with 50 mL of brine. The organic phase was dried over Na_2SO_4, and the solvent was evaporated to dryness. The product was dried under high vacuum (yield = 69 mg, 89%). ^{1}H NMR (DMSO-d_6, *J* (Hz), 400 MHz): δ = 11.1 (s, 2H, −NH thymine), 8.5 (s, 2H, =CH− triazole), 7.4 (s, 2H, arom. H thiophene), 7.3 (m, 6H, 4H arom.H thiophene + 2H CH= thymine), 4.3 (t, 4H, ^3J(H,H) = 6.64, CH_2− triazol), 3.3 (t, 4H, ^3J(H,H) = 7.06, CH_2− thymine), 1.8 (m, 4H, $-CH_2-$), 1.7 (s, 6H, $-CH_3$ thymine), 1.5 (m, 4H, $-CH_2-$), 1.3 (m, 8H, $-CH_2-$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.8, 150.5, 140.9, 140.8, 134.8, 134.4, 132.1, 124.7, 124.6, 124.5, 120.5, 108.1, 49.4, 46.9, 29.3, 28.2, 25.4, 25.1, 11.8.

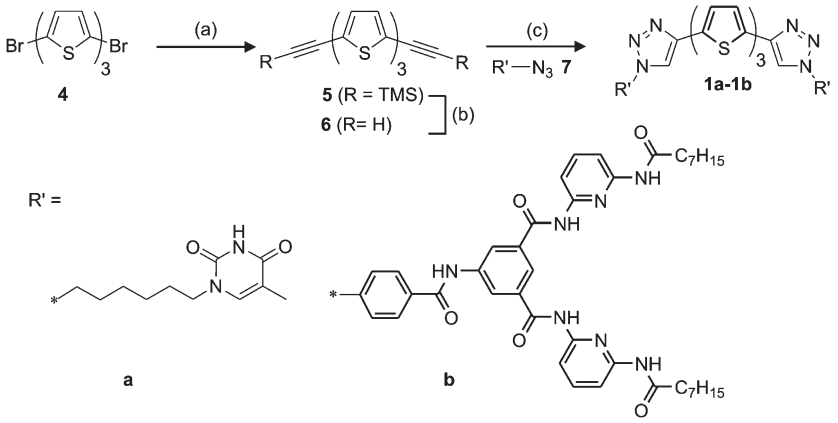
Hamilton-Receptor Capped Terthiophene (***1b***). 5,5′-Bis((trimethylsilyl)ethynyl)-2,2′:5′,2″-terthiophene (20 mg, 0.045 mmol) (**5**) was dissolved in 2 mL of dry THF in a 10 mL vial with a IntelliVent snap-on cap, and the solution was degassed by argon. Tetra-*n*-butylammonium fluoride (91 μL, 0.091 mmol) was added, and the mixture was stirred at room temperature under an argon atmosphere for 30 min. Subsequently, 5-((4-azidobenzoyl)amino)-*N*,*N*′-(6-(octanoylamino)pyridin-2-yl)isophthalamide (69 mg, 0.091 mmol) (**7b**),[41,42,44] bromotris(triphenylphosphine)copper(I) (7.6 mg, 8.2×10^{-3} mmol), diisopropylethylamine (40 μL), and 0.1 mL of 2-propanol/H_2O (1:1) were added to this solution, and the resulting mixture was stirred at 90 °C for 20 min in a cavity resonator (100 W). The reaction mixture was poured into chloroform and washed with 50 mL of NH_4Cl solution and with 50 mL of brine. The crude product was purified by column chromatography ($CHCl_3$/MeOH, 10:0.3). The product was dried on high vacuum (yield = 20 mg, 24%). ^{1}H NMR (DMSO-d_6, *J* (Hz), 400 MHz): δ = 10.8 (s, 2H, −NH), 10.42 (s, 4H, −NH), 10.34 (s, 4H, −NH), 9.41 (s, 2H, =CH− triazole), 8.20 (m, 4H, arom. H thiophene), 8.04 (s, 2H, arom. H thiophene), 8.31 (m, 6H, arom. H), 8.59 (m, 8H, arom. H), 7.56 (m, 12H, arom. H), 2.4 (m, 4H, $-CH_2$), 1.58 (m, 4H, $-CH_2-$), 1.17 (m, 18H, $-CH_2-$), 0.85 (m, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.7, 165.6, 151.04, 150.5, 140.5, 135.2, 133.6, 132.7, 132.5, 132.5, 131.9, 131.9, 130.1, 129.9, 129.2, 129.1, 36.6, 31.6, 29.0, 28.9, 25.4, 22.5, 14.4.

Results and Discussion

Our current approach toward functionalized P3HT polymers with pendant hydrogen bonds is based on (a) the synthesis of bromine-capped P3HT via the GRIM method and (b) the subsequent transformation into alkynyl-capped P3HT via Sonogashira-type reactions followed by (c) the azide/alkyne "click" reaction[46−51] to attach the respective hydrogen-bonding moieties. An important aspect of this work also concerns the exact analysis of the expected polymer mixtures by LC-ESI-TOF and also MALDI methods, which are generated by the inherent side reactions during the GRIM polymerization. As LC methods allow a rough quantification of individual oligomeric and polymeric species, this method was favored over the often used MALDI methods, which especially in the case of polar end groups lead to highly large errors in (semi)quantification of individual polymeric compounds.

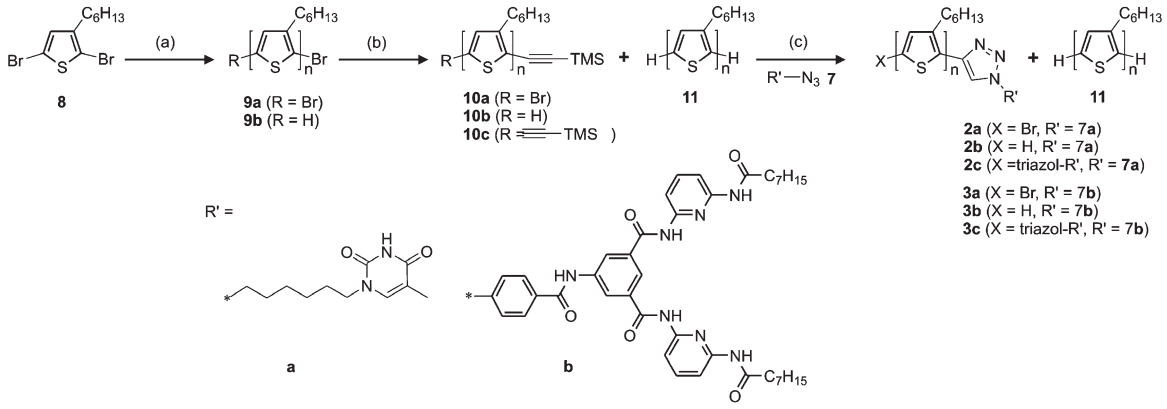
Model Reactions on Oligo(thiophene)s. As a starting point, the synthetic approach was probed on the unsubstituted terthiophene **4** to check the quality of the synthetic pathway and, additionally, get a reference compound for further spectroscopic and chromatographic investigations. Thus (see Scheme 2) we synthesized terthiophene as a central building unit via Kumada cross coupling reaction starting from the mono- and bivalent bromine thiophene. To introduce alkynyl end groups, we use the efficient Pd-catalyzed Sonogashira reaction based on the bromine-capped terthiophene **4**[39] to yield the bicapped (trimethylsilyl)ethynyl terthiophene **5** in 63%. As the deprotected compound **6** proved unstable in air and under light (formation of a brown insoluble precipitate), no further workup procedures of the alkynyl-bicapped terthiophene **6** were done, and we directly proceeded with the functionalization via a copper-catalyzed

Scheme 2. Functionalization of Bivalent Bromine Terthiophene (4) via Sonogashira and Subsequent "Click" Reaction[a]



[a] (a) (Trimethylsilyl)acetylene, $Pd(PPh_3)_2Cl_2$, Cu^II, diisopropylamine, 75 °C, 15 h (yield 63%). (b) K_2CO_3, MeOH, RT, 20 h (yield 92%). (c) $Cu^IPF_6(CH_3CN)_4$, R′−N_3 (**7**), diisopropylethylamine, CH_3CN, 50 °C, 16 h (yield: **1a** = 89% **1b** = 24%).

Scheme 3. Polymerization of 2,5-Dibromo-3-hexylthiophene (8) via GRIM Reaction and the Postfunctionalization via Sonogashira and Subsequent "Click" Reaction[a]



[a] (a) *tert*-Butylmagnesium chloride, THF, $Ni(dppp)Cl_2$ (yield = 32%; GPC M_n = 2000 g/mol, M_w/M_n = 1.20). (b) (Trimethylsilyl)acetylene, $Pd(PPh_3)_2Cl_2$, Cu^II, triethylamine, 90 °C, microwave 15 W (yield = 95%; GPC M_n = 2200 g/mol, M_w/M_n = 1.09). (c) TBAF, THF, RT, 10 min, Cu(I)-cat, R′−N_3 (**7**), diisopropylethylamine, THF, 120/90 °C, 300/100 W, 0.5−1.5 h (yield: **2** = 92%, **3** = 62%).

1,3-dipolar cycloaddition reaction to generate the bicapped terthiophene **1a** in a yield of 89%. The purity of the product was established by NMR spectroscopy and LC-ESI-TOF mass spectrometry (see Supporting Information, Figures S3 and S4). In a similar manner, other hydrogen-bonding moieties such as those depicted in Scheme 2 were attached to the terthiophene unit, yielding the respective functionalized terthiophene **1b** in yields of up to 24%.

Polymer Synthesis and Analysis via Mass Spectrometry. The cross coupling of 3-substituted thiophene monomers via organomagnesium[52] or organozinc compounds[53] yields regioregular poly(3-hexylthiophene) (HT-P3HT) in over 98% efficiency, as described via GRIM polymerization by McCullough and co-workers.[54] Thus our synthetic approach is similar to the one developed for the terthiophene **4**, relying on a series of Sonogashira reactions followed by the attachment of the hydrogen-bonding moieties via the azide/alkyne "click" reaction. We therefore started from 2,5-dibromo-3-hexylthiophene (**8**) obtaining regioregular poly(3-hexylthiophene) **9** (see Scheme 3). To achieve a more defined end-group pattern, conventional GRIM polymerization was conducted with/without a quenching reaction using Br_2/THF solution to favor the introduction of bromine end groups (H/Br; Br/Br) into the polymer at the end-group positions. As the analysis of the respective polymeric mixture (M_n = 2020 g/mol; M_w/M_n = 1.2) cannot be achieved by NMR spectroscopy, both MALDI-mass spectrometry and ESI-TOF methods were applied, as reported previously.[55] According to ESI-TOF and MALDI-TOF mass spectrometry (see Figure 1) a mixture of Br/Br-capped **9a** and Br/H capped poly(3-hexylthiophene) **9b** were generated. As both methods did not allow a direct quantification of the individual species in the direct measurement modes, LC-ESI-TOF methods were probed before further synthetic steps were undertaken.

The LC-ESI-TOF measurements of the poly(3-hexylthiophene) (**9**) were probed using conditions reported before by Langeveld-Voss et. al.[31] who used LC methods in junction with MALDI-TOF analysis of 5-(trimethylsilyl)-2-thienyl end-capped P3HTs. However, the measurements needed an additional optimization of the ESI-TOF measurements because of the difficult ionization of poly(3-hexylthiophene) with increasing chain length. As a first step to probe the optimal molecular weight for ionization via ESI, we therefore prepared P3HTs (**9**) with different molecular weights ranging from 4×10^3 to 1×10^4 g/mol (see Supporting Information, Table S1, Figures S5−S8) and measured them via ESI-TOF MS using direct injection in the presence of silver acetate or methanol to achieve an optimal ionization. The experiments showed that polymers with higher molecular weights ($(6-9) \times 10^3$ g/mol) are not desorbed well despite additional postcolumn injection of silver solution and

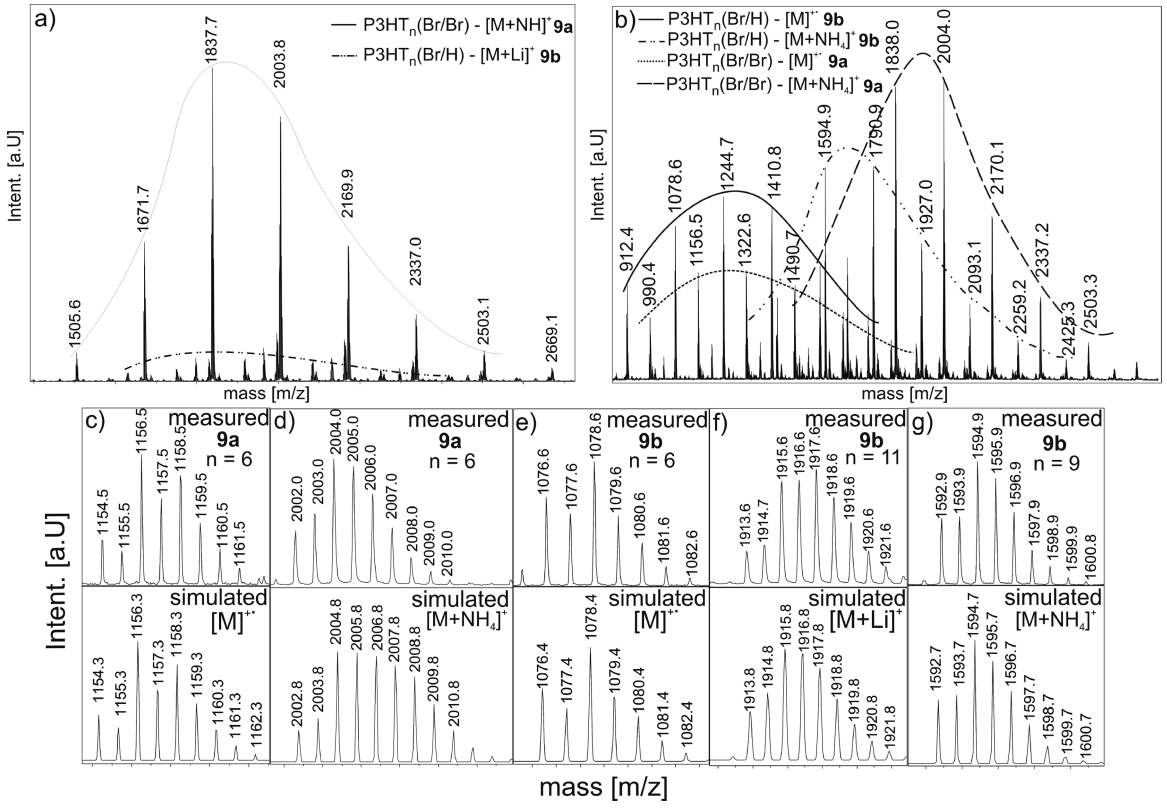


Figure 1. (a) ESI-TOF mass spectra (direct injection) and (b) MALDI-TOF mass spectra of the poly(3-hexylthiophenes) **9**, demonstrating the respective Br/Br (**9a**) and Br/H species (**9b**). (c) Isotopic pattern of P3HT$_6$(Br/Br)-**9a** (M = $C_{60}H_{84}S_6Br_2$, M_{calc} = 1154.33 g/mol) as $[M]^{+\bullet}$ adduct. (d) Isotopic pattern of P3HT$_{11}$(Br/Br)-**9a** (M = $C_{60}H_{84}S_6Br_2$, M_{calc} = 1154.33 g/mol) as $[M + NH_4]^+$ adduct. (e) Isotopic pattern of P3HT$_6$(Br/H)-**9b** (M = $C_{60}H_{85}S_6Br$, M_{calc} = 1076.42 g/mol) as $[M]^{+\bullet}$ adduct. (f) Isotopic pattern of P3HT$_{11}$(Br/H)-**9b** (M = $C_{90}H_{127}S_9Br$, M_{calc} = 1574.66 g/mol) as $[M + Li]^+$ adduct. (g) Isotopic pattern of P3HT$_9$(Br/H)-**9b** (M = $C_{90}H_{127}S_9Br$, M_{calc} = 1574.66 g/mol) as $[M + NH_4]^+$ adduct.

methanol as solvent. Thus polymer series with defined end-group structures of H/H, H/Br, and Br/Br could be identified with a molecular weight of < 4000 g/mol, showing a maximum of desorption in the mass range of 1800 m/z. Therefore, P3HT with a molecular weight of ~2000 g/mol displayed a satisfying ionization and also excellent HPLC separation for an optimal analysis of the end-group structure. Thus the directly prepared polymers were purified by repeated precipitations into methanol being then subjected to GPC measurements (M_n = 2000 g/mol; M_w/M_n = 1.15−1.20) and LC-ESI-TOF or MALDI-TOF mass spectrometry.

The LC measurements of **9** (see Figure 2) yielded an excellent separation of the low-molecular weight species (n = 5−18), also revealing species with different end-groups (n = 5−13) when a gradient of THF and acetonitrile was used. However, at chain lengths above n = 13, no separation of the individual end-group-modified species could be achieved. Thus each separated peak represents a poly(3-hexylthiophene) (P3HT$_n$) with a specific repeating unit (n) and an end-group structure either (Br/H) or (Br/Br), which could be proven by analysis of the respective ESI-TOF mass spectra and the subsequent comparison of measured and simulated isotopic pattern (see Figure 2b/2c). To achieve an idea about the amounts of the individual species **9a** and **9b**, a rough quantification via integration of the respective peak areas in the MS trace was achieved. This results in a composition of ~80% Br/Br **9a** and 20% Br/H **9b** as end groups, if Br_2/THF (0.4 equiv, 1 M solution) was used at the end of the GRIM reaction. In contrast, a conventional GRIM reaction without the final addition of Br_2/THF after the polymerization reaction yielded a polymer with ~10% H/H, 40% monovalent (Br/H), and 50% bivalent (Br/Br) end-group species.

Additionally, we analyzed polymers **9** with MALDI-TOF mass spectrometry to compare the two different techniques (desorption and ionization) according to an ideal analysis of the end-group functionalization on P3HT. The MALDI spectra in Figure 1b show four different main series, which could be identified as P3HT with Br/Br and Br/H end groups as radical cation and NH_4^+ adduct. It should be mentioned that many authors[23,26,55] have investigated their end-group compositions on P3HT often via MALDI-TOF measurements and reported about quantification values that were not explained and verified. Normally, MALDI measurements cannot be quantified directly as selective ionization may take place leading to strong deviation of the peak intensities from the actually present amounts. Therefore, in recent years a method for a (semi)quantitative relationship between different end-group polymer species and their desorption has been developed by us[56] and others,[57−59] which is based on the addition of a defined polymer as internal standard with similar or equal molecular properties to one of the polymer species in the analyzed mixture. We examined a mixture of P3HT-**9** (H/Br, Br/Br) and pure P3HT-**11** (H/H as internal standard) against desorption of the different end-group species to yield a correction factor based on the individual sensitivity of end-group species (see Supporting Information, Tables S2−S4).

According to the semiquantification methods we calculated the total signal intensity I_t from the sum of intensities of one isotopic pattern (one polymer end-group species) multiplied with their repeating unit (eq 1).

$$I_t = \sum I_S \cdot n_{unit} \quad (1)$$

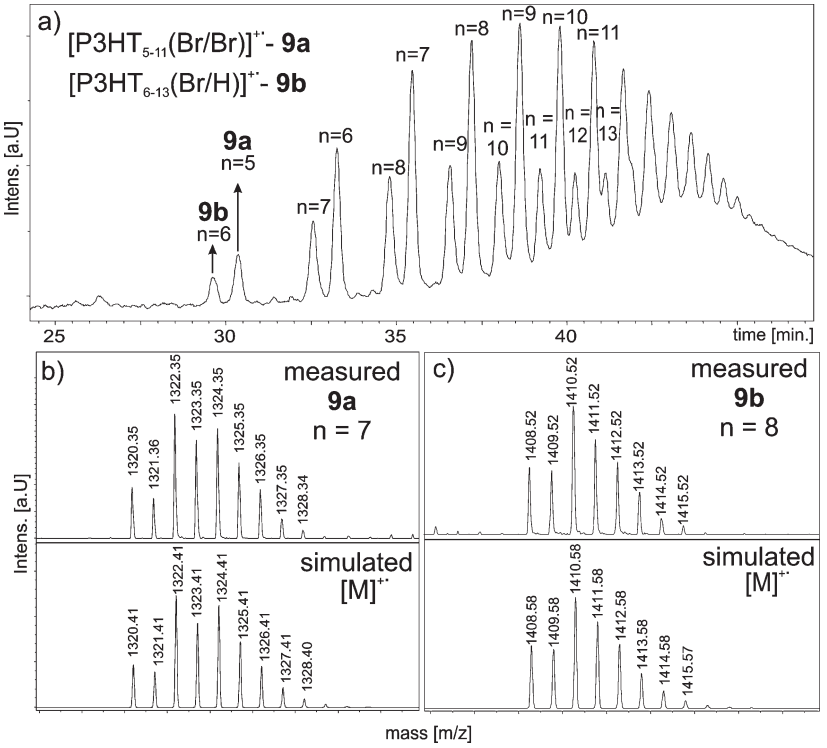


Figure 2. (a) HPLC chromatogram of P3HT-**9** at 400 nm with different fractions. Two fractions were picked out and simulated. (b) Isotopic pattern of $P3HT_7(Br/Br)$-**9a** ($M = C_{70}H_{98}S_7Br_2$, $M_{calc} = 1320.41$ g/mol) as $[M]^{+\bullet}$ adduct. (c) Isotopic pattern of $P3HT_8(Br/H)$-**9b** ($M = C_{80}H_{113}S_8Br_1$, $M_{calc} = 1408.58$ g/mol) as $[M]^{+\bullet}$ adduct.

where ΣI_S is the summed up intensity of a single isotopic pattern, n_{unit} is the number of repeating unit, and I_t is the total signal intensity of polymer with one specific end group. A plot of these signal intensities versus weight ratio of the polymer mixture with the internal standard results in two different correction factors (see Supporting Information, Figures S10 and S11). The first analysis of the MALDI spectra results in an end-group composition of 4% H/H, 53% H/Br, and 43% Br/Br end-group species without an intensity correction. Therefore, we corrected the ratio of H/H to H/Br with the factor 7.4 to yield 77.0% of H/Br species, also the ratio between H/H to Br/Br was corrected with a factor of 2.6 to get 22.2% of Br/Br species. The intensity correction yielded a new end-group composition of 0.8% H/H, 77.0% H/Br, and 22.2% Br/Br polymer species. It now shows a significantly different end-group distribution in the polymer backbone in comparison to the ESI-TOF measurements (20% H/Br, 80% Br/Br). Thus obviously polymers with H/Br end group are overestimated in the MALDI methods due to their preferred desorption.

Sonogashira Reactions. As now the different species of the poly(3-hexylthiophenes) **9a** and **9b** were analyzed, successive Sonogashira reactions were probed for the attachment of the terminal acetylene moiety (Eth) by reaction with TMS−acetylene. We tested the reaction condition on the model compound terthiophene using triethylamine as solvent and base and Cu(I) iodide and $PdCl_2(PPh_3)_3$ as the catalytic system.[38] Reaction conditions probed included reactions without cocatalyst $Cu^{I}I$ to avoid Glaser-type homocoupling reactions of the alkynes,[60] lower reaction temperature,[61] or the use of microwave irradiation.[62] Table 1 shows the efficiency of the Pd/Cu(I)-catalyzed Sonogashira reaction on end-functionalized P3HT (Br/Br and Br/H end groups). When the reaction was probed with high temperature (75 °C) for 3 days an incomplete reaction (entry 1) was observed, showing a large amount of unreacted starting materials. To increase the conversion, we chose microwave radiation, with different irradiation powers; in a second step, reaction time and different bases were probed.

Table 1. Sonogashira Reaction of P3HT (9) Synthesized via GRIM Polymerization with an Expected Molecular Weight of 2000 g/mol (GPC: M_n = 2020 g/mol, M_w/M_n = 1.2)[a]

	reaction conditions		mol %[b]					
entry	microwave power (W)	reaction time (min)	**10a**	**10b**	**10c**	**9a**	**9b**	**11**
1[d]	0	3 days	0.2	22.2		1.1[c]	20.5[c]	56
2	15	30	29	10		8[c]	41[c]	12
3	15	150		40	59			1
4	25	30	14.4	40	44		1.2[c]	
5	35	30		43	49			9
6	35	150		47	43			10
7	100	30		52	40			8
8[e]	100	30		43	44			12
9	100	360						100

[a] ESI-TOF MS: end-group distribution Br/Br = 80%, H/Br = 20%. [b] End-group distribution determined via ESI-TOF MS. [c] Incomplete reaction determined via ESI-TOF MS. [d] Reaction carried out in diisopropylamine at 75 °C for 3 days. [e] Solvent mixture of diethylamine and DMF in a ratio of 2: 1.

Again, the efficiency of the Sonogashira reaction onto P3HT (**9**) was investigated by LC-ESI-TOF MS analysis under the different reaction conditions using microwave irradiation (Figure 3). Thus the individual species with ethynyl moieties (Eth/H; H/H) with increasing chain length (n = 8−12) could be separated via the used LC method. Three different polymer end-group species could be identified in a series of two different HPLC peaks (see Figure 3). At low retention time (27−32 min) an almost complete separation is observed for the polymer species $P3HT_n$(Eth/H) **10b** and $P3HT_n$(H/H) **11**, which at higher retention times (35−40 min) merge into one single peak in the LC. Additionally,

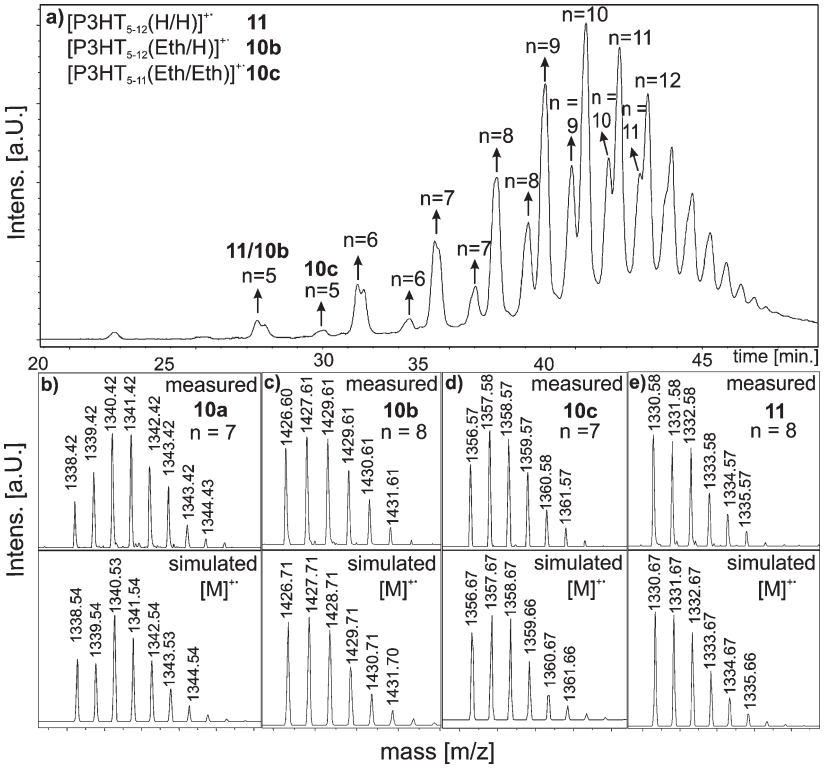


Figure 3. (a) HPLC chromatogram of P3HT-**10** (entry 3 in Table 1) at 400 nm with different fractions, two fractions were picked out and simulated. (b) Isotopic pattern of P3HT$_7$(Eth/Br)-**10b** (M = $C_{75}H_{107}S_7SiBr$, M_{calc} = 1338.54 g/mol) as $[M]^{+\bullet}$ adduct. (c) Isotopic pattern of P3HT$_8$(Eth/H)-**10b** (M = $C_{85}H_{122}S_8Si$, M_{calc} = 1426.71 g/mol) as $[M]^{+\bullet}$ adduct. (d) Isotopic pattern of P3HT$_7$(Eth/Eth)-**10c** (M = $C_{80}H_{116}S_7Si_2$, M_{calc} = 1356.57 g/mol) as $[M]^{+\bullet}$ adduct. (e) Isotopic pattern of P3HT$_8$(H/H)-**11** (M = $C_{80}H_{114}S_8$, M_{calc} = 1330.58 g/mol) as $[M]^{+\bullet}$ adduct.

a polymer with the end group P3HT$_n$(Eth/Eth) **10c** is separated at low retention times, which subsequently merges with the two other two peaks at higher retention times (43−50 min). Therefore, all species with chain lengths $n < 12$ could be separated by LC. Table 1 shows the quantitative data obtained by integration of the respective LC or mass peaks. In the case of overlapping LC peaks, the corresponding mass traces were analyzed quantitatively by taking the appropriate fraction under the LC peak, corresponding to the fraction of the respective species in the mass analysis. With increasing microwave radiation starting with 15, 25, up to 100 W (see Table 1; entries 2, 4, and 6) and equal reaction time, the amount of bivalent (Eth/Eth) **9c** and also monovalent (H/Eth) **10b** end-capped P3HT increased significantly. At longer reaction time of 150 min using a constant microwave power of 15 W (Table 1, entry 3) we recognized an increasing amount of bivalent P3HT (Eth/Eth) species **10c**. In the case of 35 W and 2.5 h the amount of monovalent (Br/Eth) (**10a**) decreased and that of the monovalent (H/Eth) species (**10b**) increased. To prove the limits of the Sonogashira reaction via microwave irradiation, we chose a high power (100 W) and a long reaction time (360 min), which indicated a complete formation of P3HT$_n$(H,H) **11**. We assumed that the Pd catalyst in the Sonogashira reaction together with the microwave irradiation induced the generation of protonated species (H/H).[63,64]

Analysis of P3HT-10 via LC-ESI-TOF. The best results were obtained with a reduced microwave power of 15 W and a reaction time of approximately 2.5 h, resulting in a ratio of 59% bivalent **10c** and 40% monovalent **10b** polymer (entry 3). Additionally, we could identify 1% of the polymer **11** (P3HT-H/H) in the mixture. Influence of base or solvent is negligible according to experiments shown in entries 7 and 8, probing the exchange of triethylamine against a mixture of diethylamine and DMF. Further investigation via MALDI-TOF MS (Figure 4, entry 3) showed similar species as in the ESI-TOF measurements ionized as the respective radical cation. Preferably radical cations of P3HT have been formed during the ESI-TOF but also MALDI-TOF analysis and can be explained due to their high affinity to donate electrons. Similar to our previous (semi-)quantification (Supporting Information, Tables S4, S5, Figures S12, S13) of the MALDI spectra, a distribution of the end groups in a ratio of 38% Eth/Eth **10c**, 50% Eth/H **10b**, and 12% H/H **11** species was observed. These different end-group species were corrected with a factor of 79.2 for polymers with Eth/Eth and with 18.9 for polymers with Eth/H end groups, yielding a new ratio of 69.7% Eth/Eth **10c**, 30.0% Eth/H **10b**, and 0.3% H/H **11**, which again shows a deviation from the values obtained via LC-ESI-TOF measurements.

Azide/Alkyne "Click" Reactions. In recent years the azide/alkyne "click" reaction was intensively investigated as a tool for the synthesis of block copolymers and their end-group functionalization reactions.[65−67] As a last step, therefore, the synthesized alkyne-modified P3HTs **10** were subjected to azide/alkyne "click" reactions to attach the hydrogen-bonding moieties via the respective azides **7a**,**b**. Results for the "click" reaction of **10** with the thymine (**7a**) and "Hamilton-receptor" (**7b**) functionalized azides are shown in Table 2, using the quantification of the complex reaction mixture by LC-ESI-TOF methods.

Table 2 summarizes the results of the azide/alkyne "click" experiments with the azide compounds (**7a**,**b**) under various reaction conditions. The products of each reaction were analyzed by LC-ESI-TOF mass spectrometry, yielding information on the product distribution in the mixture. The first reactions were conducted with azide compound **7a** on the alkyne-modified P3HT (**10**) with different copper(I)

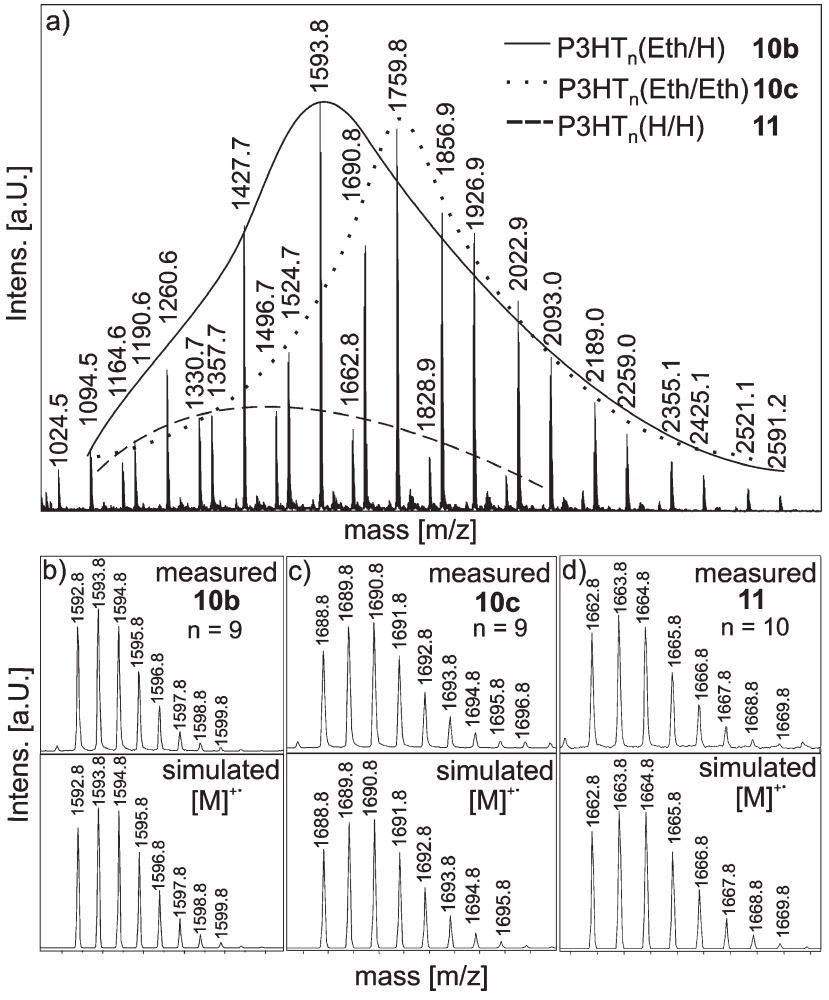


Figure 4. (a) MALDI-TOF MS spectra of P3HT-**10** (entry 3 in Table1) in the linear positive modus with three different series. (b) Isotopic pattern of P3HT$_9$(Eth/H)-**10b** (M = $C_{95}H_{136}S_9Si$, M_{calc} = 1592.78 g/mol) as $[M]^{+\bullet}$ adduct. (c) Isotopic pattern of P3HT$_9$(Eth/Eth)-**10c** (M = $C_{100}H_{144}S_9Si_2$, M_{calc} = 1688.83 g/mol) as $[M]^{+\bullet}$ adduct. (d) Isotopic pattern of P3HT$_{10}$(H/H)-**11** (M = $C_{100}H_{142}S_{10}$, M_{calc} = 1662.83 g/mol) as $[M]^{+\bullet}$ adduct.

Table 2. Azide/Alkyne "Click" Reaction of Acetylene-Functionalized P3HT 10 (GPC: M_n = 2200 g/mol, M_w/M_n = 1.1)[a]

		reaction conditions				mol %[c]				
entry	R′N$_3$	Cu(I) species	microwave power (W)	temp (°C)	time (min)	monovalent	bivalent	**11**	**10b**[b]	yield[d] (%)
1	**7a**	$CuBr(PPh_3)_3$	300	120	90	**2b** (42%)	**2c** (5%)	51	2	81
2	**7a**	CuI	300	120	90	**2b** (18%)	**2c** (82%)	0		92
3	**7a**	CuI·P(OEt)$_3$	300	120	60	**2b** (64%)	**2c** (0%)	36		87
4	**7b**	$CuBr(PPh_3)_3$	100	90	30	**3b** (92%)	**3c** (0%)	8		e
6	**7b**	$CuBr(PPh_3)_3$	100	90	60	**3b** (92%)	**3c** (0%)	8		e
7	**7b**	$CuBr(PPh_3)_3$	100	90	90	**3b** (84%)	**3c** (0%)	16		62
8	**7b**	CuI	100	90	90	**3b** (2.2%)	**3c** (6.3%)	92		55
9	**7b**	CuI·P(OEt)$_3$	100	90	60	**3b** (9%)	**3c** (0%)	91		76

[a] ESI-TOF MS: end-group distribution Eth/Eth (**10c**) ~59%, Eth/H (**10b**) ~40%, H/H (**11**) ~1%) with the azides **7a**, **7b** under microwave irradiation. [b] Incomplete reaction because of incomplete deprotection of TMS group, determined via ESI-TOF MS. [c] End-group distribution determined via ESI-TOF MS. [d] Isolated yield. [e] Sample yield not determined.

catalysts using microwave irradiation. It should be noted that the "click" reaction did not proceed without the use of microwave irradiation. The best results for the "click" reaction were achieved with copper(I) iodide generating mono- and bis-telechelic thymine-functionalized polymer **2** in a ratio of **2b** = 18% and **2c** = 82% (Table 2, entry 2). In comparison to the reaction with $CuBr(PPh_3)_3$ (entry 1) no starting material and no P3HT(H/H) **11** was observed. The "click" reaction with the Hamilton receptor azide **7b** in the presence of $CuBr(PPh_3)_3$ surprisingly results exclusively in the formation of the monotelechelic P3HT-**3b** in amounts of ~84%. In contrast, the use of copper(I) iodide catalyst (entry 8) leads the formation of mono- and bis-telechelic P3HT-**3** (**3b**/**3c** = 1: 3) with a surprisingly a large fraction of (H/H)-telechlic P3HT **11** as side product. We assume that the mismatch of the product distribution (**3b**/**3c** = 84/0) together with the formation of **11** in a significant amount hints at a reversible Sonogashira reaction forming the respective hydrogenated species discussed before.

Figure 5 displays HPLC chromatograms of P3HT **2** with the observed and simulated isotopic patterns of the identified species. The LC separation of P3HT-**2** shows a series of peaks starting at low retention time (22−45 min), where a mixture of P3HT (H/Thy) **2b**, P3HT (Thy/Thy) **2c**, and

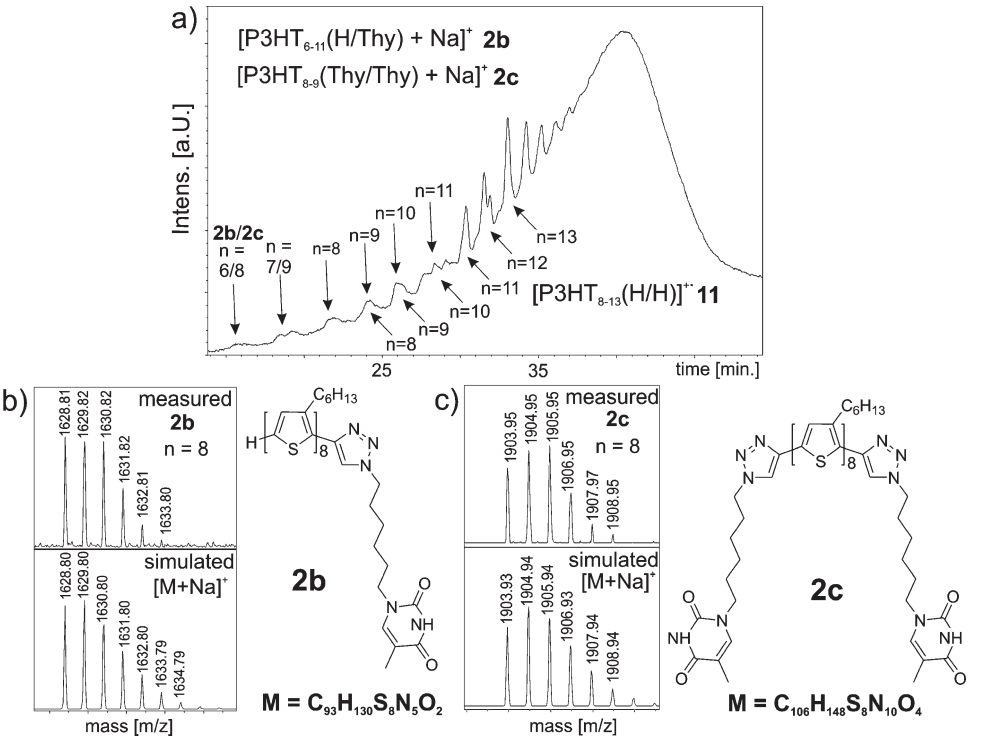


Figure 5. (a) HPLC chromatogram of P3HT-**2** (entry 1 in Table 2) at 400 nm with different fractions. (b) Measured and simulated isotopic pattern of P3HT$_8$(H/Thy)-**2b** (M = $C_{93}H_{130}S_8N_5O_2$, M_{calc} = 1605.81 g/mol) as $[M + Na]^+$ adduct. (c) Measured and simulated isotopic pattern of P3HT$_8$(Thy/Thy)-**2c** (M = $C_{106}H_{148}S_8N_{10}O_4$, M_{calc} = 1880.94 g/mol) as $[M + Na]^+$ adduct.

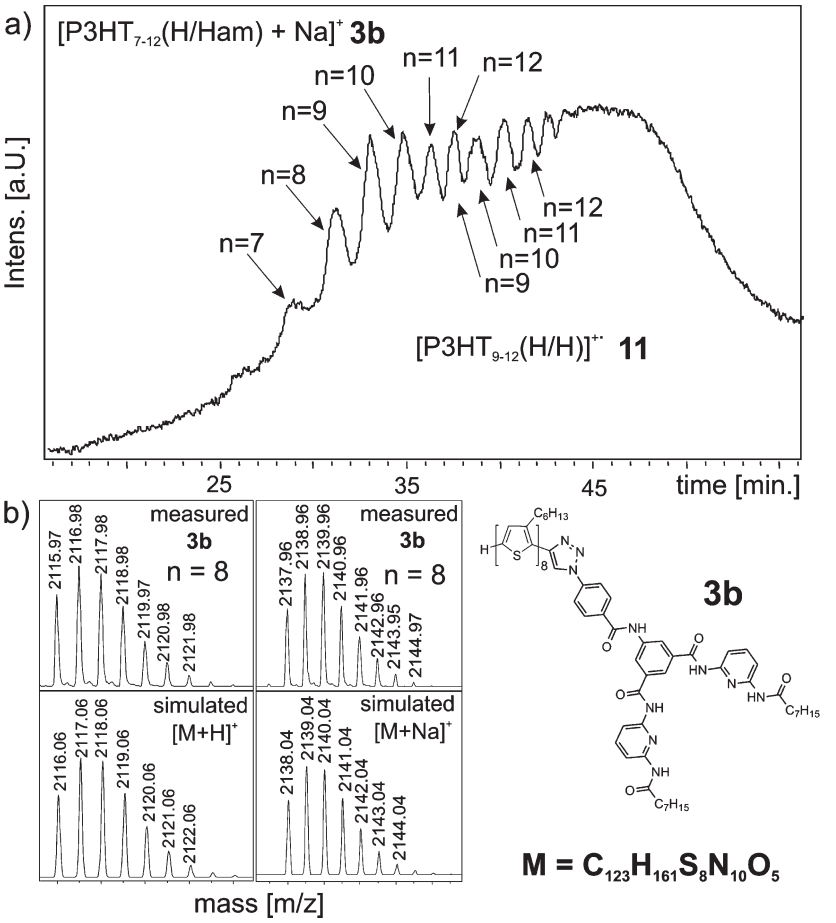


Figure 6. (a) HPLC chromatogram of P3HT-**3** (entry 4 in Table 2) at 400 nm with different fractions. (b) Measured and simulated isotopic pattern of P3HT$_8$(H/Ham)-**3b** (M = $C_{123}H_{161}S_8N_{10}O_5$, M_{calc} = 2115.05 g/mol) as $[M + H]^+$ and $[M + Na]^+$ adduct.

P3HT (H/H) **11** could be identified and simulated as the respective sodium adducts. In contrast to the alkyne-telechelic P3HTs (**10**), which were detected as radical cations by ESI-TOF mass spectrometry, the P3HTs **2** and **3** modified with H-bonding moieties were identified as sodium adducts that can be explained by the preferred complexation via the H-bonding interactions.

The chromatographic separation of the Hamilton receptor end-capped P3HT **3b**, and the measured and simulated mass peaks, are displayed in Figure 6. Two different end-group species, P3HT-**3b** (H/Ham) and P3HT-**11** (H/H), could be separated starting with the more polar clicked P3HT. The first P3HT-H/Ham species could be detected with a repeating unit of 7 and ending with 12 where an overlap with the second polymer species of H/H was observed at a retention time of 37 min. The final P3HTs **2** and **3** were additionally investigated via MALDI-TOF MS, revealing that P3HT (H/H) (**11**) is desorbed preferentially in comparison to the "click" products **2** and **3** (see Supporting Information, Figures S14 and S15).

Depending on the H-bonding moiety we therefore could synthesize preferred mono- or telechelic P3HT. In both cases of the azide compound **7a** and **7b** a mono- or telechelic P3HT could be generated exclusively in the presence of $CuBr(PPh_3)_3$; in contrast, copper(I)iodide leads to the favored telechelic P3HT. It should be noted that LC-ESI-TOF methods for the first time allowed a separation and identification of the individual end-group-modified poly(thiophene) species, which is distinctly different from the respective MALDI analysis. Whereas MALDI qualitatively yields the same results, LC-ESI-TOF methods are better suited for the separation and quantitative results of the end-group telechelic species.

Conclusion

We have described a synthetic strategy toward poly(3-hexylthiophenes) (P3HTs) with hydrogen-bonding moieties at their chain end, which is based on a combination of a Sonogashira reaction with a subsequent azide/alkyne "click" reaction to attach the hydrogen bonds in a modular fashion. For the first time, a detailed account of the quantitative composition of the individual end-group-modified P3HTs is given via coupled analytical techniques using LC-ESI-TOF. As the initial synthesis of the P3HT polymers according to McCullough yielded a mixture of different end-group-modified species (H/H; H/Br; Br/Br), LC-ESI-TOF mass spectrometry was used to quantify the individual species in addition to MALDI mass spectrometry. As proven by comparison of these two methods, MALDI significantly overestimates the H/Br- (**9b**) and H/H-telechelic species (**11**). Addition of bromine at the end of the McCullough reaction leads to a reproducible mixture of Br/Br and H/Br species in a ratio of ~80% Br/Br (**9a**) to 20% H/Br (**9b**), as judged by LC-ESI-TOF methods. The subsequent Sonogashira reaction furnished the mono- and bivalent alkyne-substituted P3HTs **10** (Eth/Br **10a**; Eth/H **10b**; Eth/Eth **10c**) by use of microwave irradiation. Again, LC-ESI-TOF analysis allowed a detailed quantification of the individual telechelic species (Eth/Eth = 59% (**10c**), Eth/H = 40% (**10b**), H/H = 1% (**11**)), which were then subjected to the azide/alkyne "click" reaction with the azides **7a**,**b**. In most cases, quantitative reactions were observed using Cu(I) species and microwave irradiation to yield the finally substituted P3HTs **2** and **3** in good yields. Thus LC-ESI-TOF MS is the advantageous method for the analysis of P3HT chemistry, allowing the full characterization and quantification of all present polymeric species. The presented methodology opens access to the end-group-modified P3HTs, which will be probed further in their optoelectronic properties with respect to their supramolecular structure.

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Supporting Information Available: Detailed information for the synthesis of the azide compound **7b** and the copper catalyst $Cu^{I}I \cdot P(OEt)_3$ and their NMR data, as well as NMR data of bifunctionalized terthiophene (**4**, **5**, and **1a**); HPLC-ESI-TOF and MALDI-TOF MS spectra for thymine-functionalized terthiophene **1a** with the simulation of the isotopic pattern; ESI-TOF MS spectra (direct infusion) of P3HT with different molecular weights (9700, 8300, 6000, and 4700 g/mol); assignment of ESI- and MALDI-TOF MS peaks of P3HT with different end-group species according to the represented figures, MALDI-TOF spectra of P3HT **3a** and **2a** with IAA/NaTFA and different matrices; plots for desorption sensitivity analysis of MALDI signal intensity ratio versus weight ratio for P3HT-**9**/P3HT **11** and P3HT-**10**/P3HT **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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