End Group-Functionalization and Synthesis of Block-Copolythiophenes by Modified Nickel Initiators

Alfons Smeets,[†] Pieter Willot,[†] Julien De Winter,[‡] Pascal Gerbaux,[‡] Thierry Verbiest,[†] and Guy Koeckelberghs[†,*]

[†]Laboratory of Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

[‡]Mass Spectrometry Research Group, Interdisciplinary Center for Mass Spectrometry, University of Mons-UMONS, 20 Place du Parc, B-7000 Mons, Belgium

S *Supporting Information*

ABSTRACT: Polythiophenes with alcohol, tosylate, azide, ethynylene, carboxylic acid, and amine end groups were prepared by a combination of functionalized nickel initiators and postpolymerization reactions. The azide and ethynylene polymers were subsequently used in a click reaction to produce a conjugated block copolymer. Finally, a conjugated triblock-copolymer was synthesized by means of a chain growth polymerization initiated by a binuclear nickel initiator.
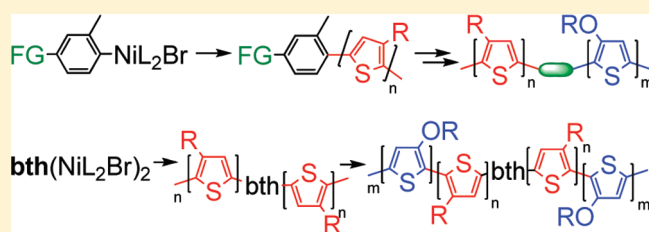
■ INTRODUCTION

Conjugated polymers (CPs) remain intensively studied materials because they hold promise as active layers in applications in the field of molecular electronics.[1] A major break-through was achieved by the groups of McCullough[2,3] and Yokozawa,[4,5] who demonstrated that the Ni(dppp)Cl₂-initiated (dppp =1,3-bisdiphenylphosphinopropane) polymerization of poly(3-hexylthiophene) (P3HT) proceeds via a controlled chain-growth mechanism. This allows the synthesis of well-defined polythiophenes with predicted molar mass and narrow polydispersities. Moreover, the controlled nature of the polymerization can also be exploited to end-cap the polymer chains, introducing functional groups, which can, after some transformation, act as initiators for a controlled radical polymerization of a second block. In this way, block copolymers composed of a P3HT block and a nonconjugated block (e.g., PMMA, PS, ...) can be prepared.[6−8] Alternatively, the living nature can be used to prepare all-conjugated block copolymers by successive addition of the respective monomers. In this way, the synthesis of block copolymers composed of two different P3AT blocks,[9−14] a P3AT and a poly(3-alkoxythiophene) (P3AOT) block,[15,16] a poly(selenophene) block,[17] or a poly(fluorene) block[18] and a poly(pyrrole)-*block*-poly(phenylene)[19] have been achieved.

End-capping of polymer chains requires a living nature of the polymerization. This is indeed the case for P3ATs and it has also been found for some other conjugated polymers (to a certain extent) using either Ni- or Pd-catalysts.[20−23] Nevertheless, some other CPs polymerize via an albeit chain-growth, but not-living, mechanism. However, if the mechanism of the Ni(dppp)Cl₂-initiated polymerization is examined into more detail, it becomes clear that a chloro organonickel(dppp) species can be considered as the actual initiator. More specifically, an arylmagnesium

moiety performs a nucleophilic attack on Ni(dppp)Cl₂, forming the chloro organonickel(dppp) initiator, which then reacts with more monomer, starting the propagation cycle. As a consequence, a functional group can also conveniently be introduced in the beginning of each polymer chain by initiating the polymerization from such organonickel species equipped with the desired functional group. Several methodologies have been reported for the synthesis of such molecules and their use as initiators for the P3HT polymerization. Luscombe and co-workers prepared aryl—Ni complexes from (in situ prepared) Ni(PPh₃)₄ or Ni(cod)₂ and the corresponding aryl bromides or chlorides.[24−26] Kiriy reacted aryl bromides with either Ni(PPh₃)₄ or diethyl(bipyridyl)-nickel, followed by a ligand exchange with dppp.[27,28] A Ni-initiator capable of initiating a NMP was also prepared through this methodology.[29] We prepared Ni-initiators bearing a (protected) alcohol or acetylenic group by reacting Ni(PPh₃)₄ with the appropriate aryl bromide and used them to polymerize P3HT, P3OATs, poly(3-alkylsulfanylthiophene)s and poly(phenylene)s.[30]

In this manuscript, we first expand the latter protocol by synthesizing a broad variety of functional Ni initiators, offering the possibility to prepare conjugated polymers equipped with alcohol, tosylate, azide, amine, ethynyl and carboxylic acid functional groups. Next, the click reaction was used to couple two different conjugated polymers (*in casu* P3AT and P3AOT) resulting in an all-conjugated block copolymer with a nonconjugated spacer. Finally, we prepared a bifunctional Ni-initiator and used it to initiate a P3HT polymerization. Moreover, the living nature of

this polymerization could be exploited for the synthesis of a P3AOT-*block*-P3HT-*block*-P3AOT triblock copolymer.

■ EXPERIMENTAL SECTION

Reagents and Instrumentation. All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck, Wako, ABCR, and Alfa Aesar. Reagent grade solvents were dried by distillation over a suitable drying agent. Bromo-[2-methyl-4-(trimethylsilylethynylene)phenyl]bis-(triphenylphosphine)nickel[30] (**1**) and 2-magnesiochloro-4-hexyl-5-bromothiophene[4] was prepared according to literature procedures. Before each polymerization, a small aliquot of 2-magnesiochloro-4-hexyl-5-bromothiophene was quenched with D_2O and analyzed by ^{1}H NMR to verify its conversion. Gel Permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran as eluent toward polystyrene standards. Mass spectra were recorded using an Agilent HP5989. [1]H nuclear magnetic resonance (^{1}H NMR) measurements were carried out with a Bruker Avance 300 MHz, 400 MHz and 600 MHz. ^{31}P NMR measurements were carried out with a Bruker Avance 400 MHz. MALDI–ToF mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10000. The matrix, trans-2-[3-(4-*tert*-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as 20 mg/mL solution in chloroform. The matrix solution (1 μL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in chloroform to obtain 1 mg/mL solutions. Then, 1 μL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air-dried. IR spectra were recorded using a Bruker Alpha-p apparatus in ATR mode.

Synthesis of the Bifunctional Initiator. *Synthesis of 2-Bromo-3-methylthiophene (**16**).* N-Bromosuccinimide (50.0 mmol, 8.88 g) was added portion wise to a solution of 3-methylthiophene (**15**) (50.0 mmol, 4.91 g) in CHCl$_3$ (20 mL) and AcOH (20 mL), which had been cooled to 0 °C, shielded from light and was equipped with a CaCl$_2$ drying tube. The reaction was then allowed to reach room temperature overnight, after which aqueous NaHSO$_3$ and NaHCO$_3$ were added. The mixture was then extracted with hexane, the organic layer was dried over MgSO$_4$ and the solvent removed in vacuo. The crude product was then vacuum distilled (66 °C, 16 mmHg), and the pure product was isolated as a light yellow oil.

Yield =7.40 g (83%).

^{1}H NMR (CDCl$_3$): 7.16 (d, 1 H, 5.5 Hz), 6.77 (d, 1 H, 5.5 Hz), 2.20 (s, 3 H).

*Synthesis of 5,5′-Dibromo-4,4′-dimethyl-2,2′-bithiophene (**17**).* A solution of **16** (20.0 mmol, 3.54 g) in dry DMSO (40 mL) was purged with argon and added to a solution of PdCl$_2$(PhCN)$_2$ (0.600 mmol, 0.230 g), AgNO$_3$ (40.0 mmol, 6.79 g) and KF (40.0 mmol, 2.32 g) in dry DMSO (40 mL). The mixture was allowed to react for 3 h at 60 °C, after which hexane was added. The resulting precipitate was then removed by filtration and subsequently washed with hexane and diethyl ether. The organic layer was then washed with a NaCl solution, dried over MgSO$_4$ and the solvent was removed in vacuo. Finally, the crude product was purified by column chromatography (SiO$_2$, eluent: hexane) and isolated as a white solid.

Yield: 2.02 g (57%).

^{1}H NMR (CDCl$_3$): δ = 6.76 (s, 2 H), 2.17 (s, 6 H).

*Synthesis of **18**.* A solution of **17** (2.00 mmol, 0.704 g) in dry toluene (50 mL) was added under argon atmosphere to Ni(PPh$_3$)$_4$ (5.00 mmol, 5.54 g). The reaction was allowed to proceed overnight, after which toluene (50 mL) was added and the solution was filtered. The

supernatant was concentrated in vacuo and the product precipitated in MeOH, yielding a yellow-brown powder.

Yield: 0.125 g (4%).

^{1}H NMR (CDCl$_3$): δ = 7.61 (m, 24 H), 7.25 (m, 36 H), 5.62 (s, 2 H), 1.47 (s, 6 H).

Synthesis of Block Copolymer Using the Click Reaction. *Synthesis of P3HT-2-P3AOT.* An argon purged solution of PMDTA (5.60 μmol, 0.97 mg) in dry THF (5 mL) was added to a suspension of CuBr (4.51 μmol, 0.650 mg) and dry THF (5 mL). A solution of **P3HT-2-N$_3$** (68.7 μmol, 11.4 mg) and **P3AOT-E** (126 μmol, 30.0 mg) in dry THF (50 mL) was added to this solution and the reaction mixture was stirred overnight under an argon atmosphere. Then, chloroform and an aqueous solution of NH$_3$ were added and the mixture was extracted. The organic layer was dried over Na$_2$SO$_4$ and concentrated to a volume of approximately 15 mL, precipitated in methanol and filtered off. The polymer was further purified by means of Soxhlet extraction with pentane, hexane, and heptane and finally with chloroform. The chloroform solution was precipitated in MeOH, filtered off, and dried in vacuo.

Yield = 18.9 mg (48%).

Synthesis of Triblock Copolymer. An argon-purged mixture of **18** (0.0486 mmol, 0.0740 g) and dppp (0.107 mmol, 0.0440 g) in dry THF (6.5 mL) was stirred for 30 min at room temperature. In the next step, 2-magnesiochloro-4-hexyl-5-bromothiophene (0.800 mmol) in dry THF (5.5 mL) was added to the initiator solution and stirred for 1 h at room temperature. Next, 3.8 mL of the mixture was quenched with HCl, precipitated in MeOH, filtered off, and dried in vacuo. Washing with acetone yielded **P3HT-bth-P3HT** as a dark purple solid. To the remaining solution (8.2 mL), 2-bromomagnesio-5-bromo-3-(3,7-(*S*)-dimethyloctyloxy)thiophene (1.65 mmol) (prepared as for **P3AOT-TMS**) in dry THF (12 mL) was added and the mixture was allowed to react overnight. The polymer was then precipitated in MeOH, further purified by means of Soxhlet extraction with pentane, hexane, heptane and finally with THF. The THF solution was precipitated in MeOH, filtered off and dried in vacuo, yielding **P3AOT-P3HT-P3AOT** as a black solid.

Yield (**P3HT-bth-P3HT**) = 26.5 mg (64%).

Yield (**P3AOT-P3HT-P3AOT**) = 185 mg (32% based on P3AOT).

■ RESULTS AND DISCUSSION

Initiator Design. In a previous communication,[30] we established a protocol for the synthesis of arylnickel complexes and their subsequent application as functional initiators for the synthesis of conjugated polymers. This allowed us to insert end groups into CPs even if their polymerization is not controlled. We decided to expand upon this protocol by inserting a wider variety of functional groups, which could then be employed in postpolymerization reactions. The end groups in question should allow straightforward coupling of the CP to the desirable substrates, i.e., other polymers or nanoparticles. Two candidates which immediately come to mind are azide and ethynylene functionalities, as they can be employed in so-called CuAAC click chemistry, which is robust and can be achieved using mild conditions,[31,32] fulfilling the requirement stated earlier. Two other functional groups we deemed worth pursuing are amine and carboxylic functionalities, because they could be useful for coupling CPs with nanoparticles[33] or surfaces.[34] As for the choice of the CPs, we decided to use poly(3-hexylthiophene) (P3HT) as main CP, because the polymerization of P3HT with functionalized nickel initiators yields polymers with a high degree of functionalization.[30] As second polymer we decided to use poly-(3-(3,7-(*S*)-dimethyloctyloxy)thiophene (P3AOT). Although the polymerization of P3AOT is less well-behaved and its

Scheme 1. Synthesis of the Ni Initiators[a]
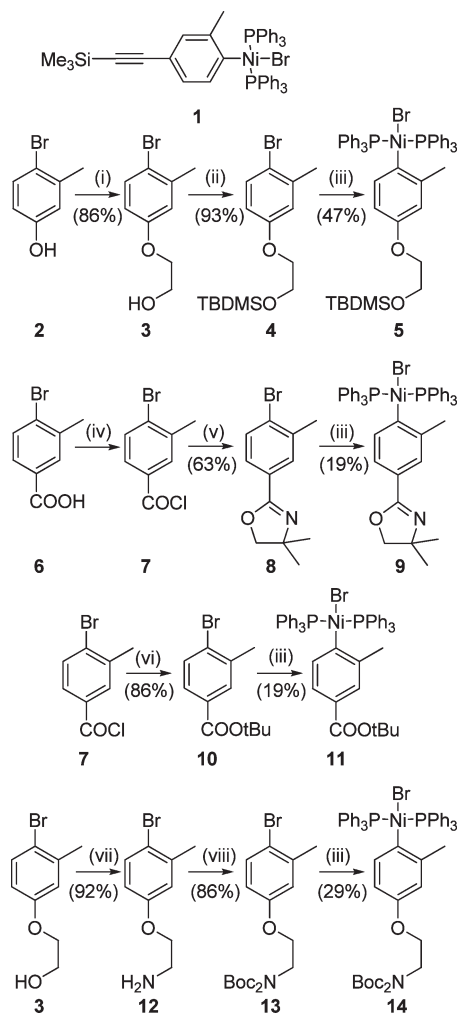
[a] Key: (i) ethylene carbonate, K$_2$CO$_3$; (ii) TBDMSCl, imidazole; (iii) Ni(PPh$_3$)$_4$; (iv) oxalyl chloride, DMF; (v) 2-amino-2-methyl-1-propanol, SOCl$_2$; (vi) KOtBu; (vii) (1) DIAD, phthalimide, (2) PPh$_3$, N$_2$H$_2$; (viii) Boc$_2$O, DMAP.

functionalization usually incomplete,[30,35] it is still a worthwhile choice because of its substantially different physicochemical properties compared to P3HT, which should allow for easy discrimination of both CPs using standard spectroscopic techniques. For the reasons mentioned above, we decided to synthesize P3HT with azide, amine, and carboxylic end groups, while a P3AOT would be synthesized with an ethynylene end group.

In order to synthesize both CPs with the desired end groups, the corresponding nickel initiators (Scheme 1) were synthesized from Ni(PPh$_3$)$_4$ and the appropriate aryl bromide. Although all four functional end groups should not pose any problems in this respect, they are unfortunately incompatible with the polymerization conditions of both P3HT and P3AOT, because both polymerizations proceed through the nickel-catalyzed coupling of an organomagnesium (or organozinc) monomer. The end groups in question thus had to be either protected or formed after polymerization from a precursor moiety. To ethynylene, amine and carboxylic functional groups, the former applies, as well established methods for protection (against either

organomagnesium or organozinc compounds) are available. The azide functionality, however, has to be formed through post-polymerization reactions of a precursor end group, as no direct method of protection is available. As precursor end group, we selected an alcohol functionality, because of its easy protection, deprotection and synthetic versatility.

The synthesis of the protected acetylene-functionalized initiator, bromo-[2-methyl-4-[(trimethylsilyl)ethynyl]phenyl]bis-(triphenylphosphine)nickel(II) (1) has been described previously.[30] For the (protected) alcohol-functionalized initiator (5), 4-bromo-3-methylphenol (2) was alkylated with ethylene carbonate in DMF using K$_2$CO$_3$ as base, forming 3. Subsequently, 3 was protected using TBDMSCl and imidazole in DMF, yielding 1-bromo-2-methyl-4-[2-($tert$-butyldimethylsilyloxy)ethyloxy]benzene (4). Reaction of 4 with Ni(PPh$_3$)$_4$ resulted in the formation of bromo[2-methyl-4-[2-($tert$-butyldimethylsilyloxy)ethyloxy]phenyl]bis(triphenylphosphine)nickel(II) (5). In order to introduce carboxyl groups in the polymers, we first selected an oxazoline moiety as a protecting group compatible with the organomagnesium monomer. The corresponding nickel initiator could be prepared by converting 4-bromo-3-methylbenzoic acid (6) to its acid chloride (7) by means of oxalyl chloride, which was reacted with 2-amino-2-methyl-1-propanol and SOCl$_2$, yielding 2-(4-bromo-3-methyl-phenyl)-4,5-dihydro-4,4-dimethyloxazole (8). Analogous to the synthesis of previous initiators, 8 was then reacted with Ni-(PPh$_3$)$_4$, forming the nickel initiator 9. However, after polymerization, it turned out that the carboxylic acid could not be deprotected without degradation of the polymer. Indeed, treatment with KOH in THF did not result in any reaction, while treatment with aqueous HCl (either in dioxane or chloroform) or MeI and subsequently NaOH resulted in degradation reactions. Because of our inability to convert the oxazoline end group back to the carboxylic acid, we were forced to consider a different protecting group. We decided to protect the carboxylic acid by esterificating it with $tert$-butanol.
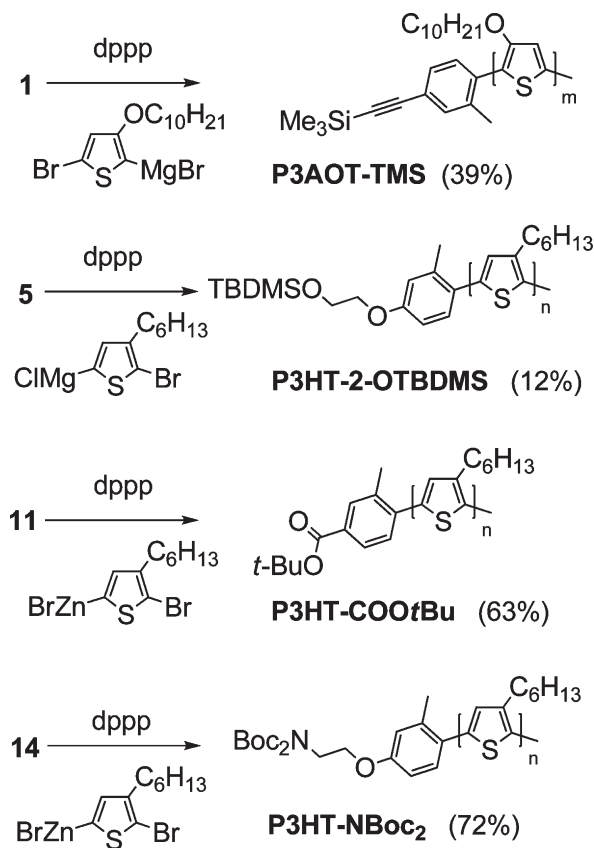
In order to synthesize the COOtBu functionalized initiator, 7 was reacted with KOtBu, yielding $tert$-butyl(4-bromo-3-methyl)-benzoate (10). Reaction of 10 with Ni(PPh$_3$)$_4$ yielded the COOtBu-functionalized initiator (11).

The introduction of an amine group into the polymers required the synthesis of a nickel initiator with an amine functionality, which also needs to be protected against the organomagnesium monomer. At first we decided to employ STABASE protection (STABASE = 1,1,4,4-tetramethyldisilyl azacyclopentane) for the amine. However, we were unable to isolate the necessary STABASE-protected precursor for the nickel initiator as it spontaneously decomposed back to the free amine during purification. We therefore had to select an alternative and switched to Boc protection instead. First, we synthesized 2-(4-bromo-3-methylphenyloxy)ethylamine (12) by performing a Mitsunobu reaction of 3 with phthalimide, subsequent hydrazinolysis of the phthalimide intermediate yielded the primary amine 12 after work-up. The amine 12 was then protected using Boc$_2$O after which ^{1}H NMR and MS analysis indicated that the amine had been bis-protected to form 13. Finally, reaction of 13 with Ni(PPh$_3$)$_4$ yielded the corresponding nickel initiator 14.

Synthesis of the Polymers. The polymers were prepared by a Ni(dppp)-mediated polymerization of metalated thiophenes, as depicted in Scheme 2. In the case of P3AOT, the actual monomer, 2-bromomagnesio-5-bromo-3-(3,7-(S)-dimethyloctyloxy)thiophene, was prepared in situ from MgBr$_2$ and 2-lithio-5-bromo-3-(3,7-(S)-dimethyloctyloxy)thiophene, which was in

Scheme 2. Synthesis of the Polymers

Figure 1. ^{31}P NMR spectrum of **5** (6.70 μmol) after 30 min of ligand exchange with dppp (13.3 μmol) in THF (0.5 mL).

turn prepared from 2-bromo-3-(3,7-(S)-dimethyloctyloxy)thiophene and LDA.[35] The monomer in the P3HT polymerization is 2-magnesiochloro-4-hexyl-5-bromothiophene which was prepared from 2-bromo-5-iodo-3-hexylthiophene and iPrMgCl. The COOtBu and Boc$_2$N moieties are not compatible with organomagnesium reagents and thus polymerization conditions which use organomagnesium monomers cannot be employed. Fortunately, the synthesis of P3HT can also be accomplished by an organozinc monomer[3,36] using the same catalyst and conditions, only transmetalation of the organomagnesium monomer with ZnBr$_2$ is required. Because the Ni-catalyzed polymerization of P3HT is controlled when dppp is used as ligand,[25,37] ligand exchange was first performed in situ before the monomers were added, thus forming the actual initiator. In order to verify whether the ligand exchange indeed takes place (quantitatively), we monitored this reaction in a separate experiment by ^{31}P NMR spectroscopy for all initiators. After 30 min, the sole species detected in all cases except for **1** were liberated PPh$_3$, excess dppp (2 equiv were used) and the end-product (Figure 1). The apparent broadness of the peaks can be attributed to the fact that it is actually a (less resolved) doublet. No starting product, nor degradation compounds (e.g., Ni(dppp)$_2$) were found (see Supporting Information, Figures S23−S26). For all P3HTs, [M$_0$]/[In] = 15.

Thus, the synthesis of the ethynylene-functionalized P3AOT was accomplished by first performing ligand exchange on **1** with dppp, after which this mixture was used to initiate the polymerization of 2-bromomagnesio-5-bromo-3-(3,7-(S)-dimethyloctyloxy)thiophene, yielding **P3AOT-TMS**. MALDI−ToF analysis (see Figure S37, Supporting Information) of **P3AOT-TMS**
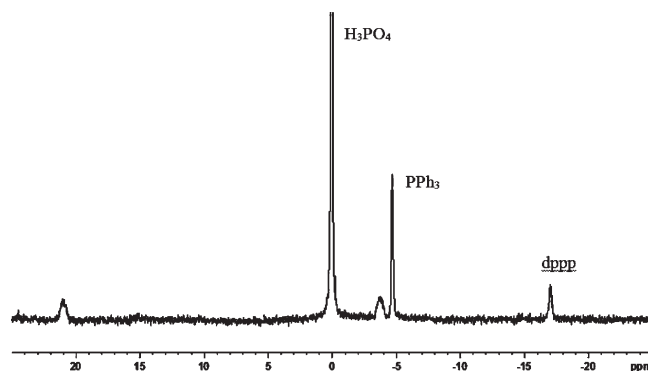
revealed that the main end groups are Br/TMS, with some minor H/Br content. This is the expected result, as the polymerization of poly(3-alkoxythiophenes) is not controlled,[35] yielding polymer chains in which chain end degradation of the polymer-Ni complex occurred. Signals corresponding to the loss of a C$_{10}$H$_{21}$$^\bullet$ radical are also detected in the mass spectrum and were previously ascribed to an aromatic β-cleavage from the ionized polymer chain.[38]

In order to prepare P3HT with an alcohol functionality, **5** was first reacted with dppp, after which a solution of 2-magnesiochloro-4-hexyl-5-bromothiophene was added, resulting in the formation of **P3HT-2-OTBDMS**. The presence of the ethylOTBDMS moiety was confirmed by ^{1}H NMR, with the ethyl protons giving rise to two triplets, respectively at 4.19 and 3.61 ppm. Also, MALDI−ToF analysis indicates that the majority of the P3HT is OTBDMS/H terminated with some remainder H/H terminated P3HT (see Figure S38, Supporting Information). H/H-terminated polymers require Ni(dppp)X$_2$ (X = Cl or Br) as initiator. Since the ^{31}P NMR spectra indicate the absence of such species at the moment the monomer is introduced, such Nicomplex must be formed when the monomer is added. The presence of nonfunctionalized P3HT is not necessarily detrimental, as it will simply not react during postpolymerization reactions (coupling reactions, block copolymer formation, ...) and can thereafter be removed by fractionation.

For the polymerization of the carboxyl-functionalized P3HT, 2-magnesiochloro-4-hexyl-5-bromothiophene was first transmetalated with ZnBr$_2$ to 2-bromozincio-4-hexyl-5-bromothiophene. Then, **11** was allowed to undergo ligand exchange with dppp and used to initiate the polymerization of the 2-bromozincio-4-hexyl-5-bromothiophene, resulting in the formation of **P3HT-COOtBu**. The MALDI−ToF analysis (see Figure S39, Supporting Information) confirmed that the polymerization reaction is quantitatively initiated by **11**. Decomposition reactions, i.e. losses of isobutene (56 u) from the ionized oligomers, were also detected and are characteristic of the COOtBu moiety. Surprisingly, the dominant ion series did not correspond to the tBu/H end groups, but to tBu/C$_4$H$_7$O end groups. This composition was unambiguously demonstrated by an accurate mass measurement performed on ionized C$_4$H$_7$O−(3HT)$_{15}$−COOtBu (measured mass, 2753.3833; u/calculated mass, 2753.3812 u/0.8 ppm error). This suggests that a reaction with THF occurs. McNeil and coworkers also observed such reaction in the PPP polymerization.[39] In order to find out whether this reaction occurs at the stage of the monomer formation or during the actual polymerization, a

Table 1. $\overline{M}_n$ and PDI for the Homopolymers Determined by GPC Calibrated toward Polystyrene Standards in THF

polymer	$\overline{M}_n$ (kg/mol)	PDI
P3HT-2-OTBDMS	1.9	1.3
P3AOT-TMS	8.1	1.6
P3HT-COOtBu	7.1	1.2
P3HT-NBoc$_2$	7.3	1.2

^{1}H NMR spectrum was recorded of the zincated compound, quenched with D$_2$O (see Supporting Information, Figure S27). No signs of reaction with THF were observed, demonstrating that this reaction takes place during the polymerization, terminating the polymerization. The ^{1}H NMR spectrum of the polymer, however, does not contain signals matching the THF end group, while those corresponding to the initiator moiety are clearly present.

Finally, the amine-functionalized P3HT was also synthesized using 2-bromozincio-4-hexyl-5-bromothiophene, which was added to a solution of **14**, after the latter underwent ligand exchange with dppp, forming **P3HT-NBoc$_2$**. The ^{1}H NMR spectrum of **P3HT-NBoc$_2$**, contains two methyl signals from the *o*-methyl moiety, indicating partial deprotection during polymerization or work-up. This could also be confirmed by recording the MALDI mass spectrum of the **P3HT-NBoc$_2$** sample (see Figure S40, Supporting Information). Indeed, this spectrum features signals corresponding to both the bis-protected polymer chains and the monoprotected molecules, respectively **P3HT-NBoc$_2$** and **P3HT-NHBoc**. Nevertheless, since isobutene losses are detected in the MALDI spectrum, we cannot rule out that the ions corresponding to **P3HT-NHBoc** can also be generated by decompositions upon MALDI analysis of **P3HT-NBoc$_2$** molecules into **P3HT-NHBoc** molecules. In addition, as already observed when analyzing the **P3HT-COOtBu** sample, polymer ions bearing a C$_4$H$_7$O residue as end group dominate the MALDI mass spectrum.

The molar masses and polydispersities (Table 1) were determined by GPC calibrated toward polystyrene standards. The DP of the P3HTs was also determined by ^{1}H NMR integration. For **P3HT-2-OTBDMS**, it was found to be equal to 10, which correlates well with the GPC result. For **P3HT-COOtBu** (26) and **P3HT-NBoc$_2$** (27) significantly higher than expected molar masses were found, which suggests an inefficient initiation by the respective Ni-initiators. The polydispersity, however, remains low. GPC, on the other hand, gives higher values. It should be noted that GPC tends to overestimate the molecular weight of P3HTs and that this error increases with higher molar mass.[40] This effect is also observed for P3AOTs which can be explained by the more rigid conformation of P3AOTs in THF, which explains the relatively high value for **P3AOT-TMS**. Its higher polydispersity can be attributed to the fact that the polymerization is not controlled.

Postpolymerization Transformations. The next step was the transformation of the prepared polymers to those with the initially desired functional group, either through deprotection or conversion to another functionality (Scheme 3). For **P3HT-2-OTBDMS**, in addition to the deprotection reaction, conversion to the azide was required. Deprotection was achieved by reaction with TBAF, which furnished the alcohol-functionalized polymer **P3HT-2-OH**. Next, the alcohol functionality in **P3HT-2-OH** had to be converted into an azide. We wondered whether it was

Scheme 3. Post-Polymerization Deprotection of P3HT-2-OTBDMS and conversion to P3HT-2-N$_3$
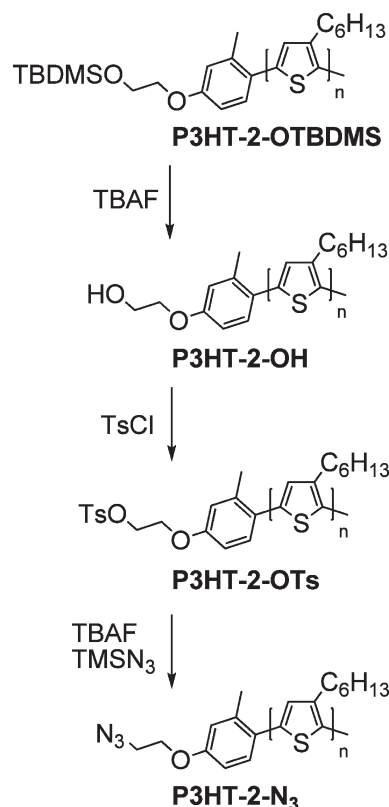
possible to achieve direct conversion of the alcohol to the azide, in order to limit the number of postpolymerization reactions, as the removal of remaining reactants from the resulting polymer is not always straightforward and can be detrimental for the final yield. Subsequent literature study revealed that diphenylphosphorylazide (DPPA) is able to achieve quantitative conversion of alcohols to azides in small molecule synthesis, using mild conditions.[41] We found that, when reacting **P3HT-2-OH** with DPPA in the presence of DBU, a substantial shift in ppm value for the ethyl protons is observed, as expected. However, the IR spectrum of the resulting P3HT did not contain the expected azide peak around 2100 cm^{-1}. Careful examination of the aromatic region of the ^{1}H NMR spectrum showed that the reaction stopped at the stage of the diphenyl phosphonate. We were therefore forced to shift our approach to a two-step conversion, first converting **P3HT-2-OH** with *p*-toluenesulfonyl chloride and NaOH to the tosylate **P3HT-O-Ts**, which was isolated and thereafter converted to the azide functionalized polymer (**P3HT-2-N$_3$**) by reaction with tetrabutylammonium azide. Although the pathway through the tosylate requires an additional step, there is also a benefit related with it, because the tosylate moiety in itself is an interesting functionality as it can serve as a springboard for many other functional groups besides the azide.

Analysis of **P3HT-2-N$_3$** by IR spectroscopy (absorption at 2103 cm^{-1}, see Figure S50, Supporting Information) and MALDI–ToF confirmed the successful insertion of the azide. In the MALDI mass spectrum, presented in Figure S41, Supporting Information, signals corresponding to ionized P3HT end-capped with a hydrogen atom and the azide-containing group were clearly identified. In addition, a characteristic nitrogen loss was
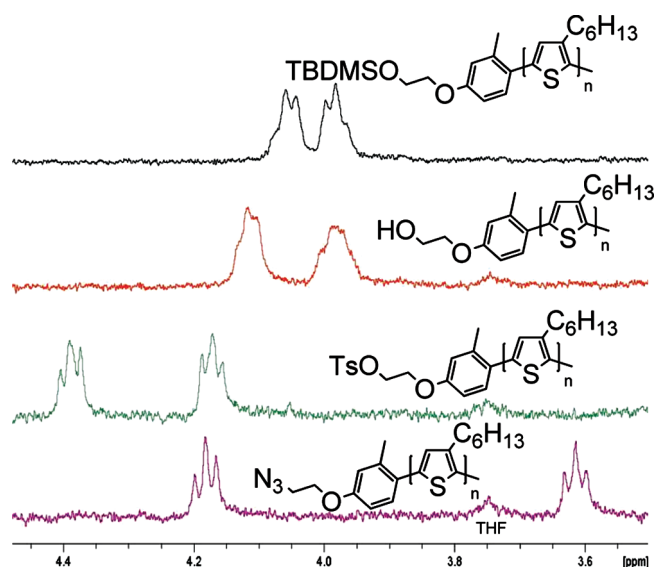
Figure 2. Chemical shift of the ethyl protons in function of the end group in the postpolymerization reactions of **P3HT-2-OTBDMS**.
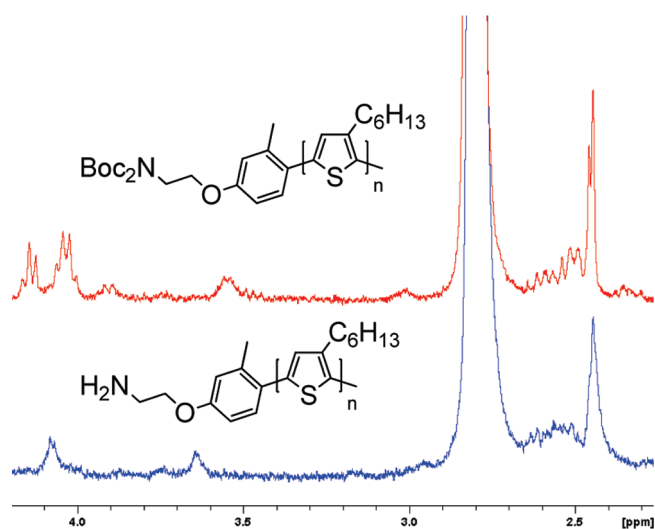
Figure 3. Chemical shift of the ethyl protons in the deprotection of **P3HT-NBoc₂**.

observed and definitively confirmed the presence of the azide moiety. The presence of P3HT polymer chains with H/H as the end groups was also highlighted by the MALDI measurement, which is due to the fact that they were already present for **P3HT-2-OTBDMS** and are not affected by the postpolymerization reactions. As a final confirmation, the different conversion steps of **P3HT-2-OTBDMS** to **P3HT-2-N₃** can all be monitored by observing the chemical shifts of the ethyl protons, as illustrated in Figure 2.

In the case of **P3AOT-TMS**, the TMS moiety was removed using TBAF, yielding the ethynylene functionalized polymer **P3AOT-E**. Again deprotection was confirmed both by ¹H NMR and MALDI—ToF (see Figure S42, Supporting Information). As already observed when analyzing the protected molecules (**P3AOT-TMS**), the MALDI process also leads to the loss of a $C_{10}H_{21}^{\bullet}$ radical from the ionized **P3AOT-E** polymers.

The deprotection of **P3HT-NBoc₂** proved to be unexpectedly difficult, as treatment with an excess of trifluoroacetic acid only achieved partial deprotection to the monoprotected amine. Substituting TFA for *p*-toluenesulfonic acid and performing the reaction under reflux conditions for 48 h, finally, yielded **P3HT-NH₂**, as indicated by the shift of the ethyl protons in the ¹H NMR spectrum (Figure 3). This was also confirmed by the MALDI—ToF analysis (see Figure S43, Supporting Information).

Finally, **P3HT-COO*t*Bu** was deprotected to **P3HT-COOH**. Initial attempts employing KOH were not successful. Fortunately, the use of NBu₄OH readily resulted in a clean and quantitative deprotection (Scheme 4), as shown by the MALDI—ToF spectra (see Figure S44, Supporting Information) and IR spectroscopy, which show a shift from 1713 cm⁻¹ (ester carbonyl) to 1684 cm⁻¹ (carboxylic acid carbonyl) (see Figures S47—S50, Supporting Information).

Block Copolymer Formation. The successful synthesis of **P3AOT-E** and **P3HT-2-N₃** provided us with two polymeric substrates suitable for application in CuAAC click-chemistry (Scheme 5). As both polymers are only soluble in either chloroform or THF, the standard CuSO₄-ascorbic acid protocol could not be used. Instead we used a combination of CuBr and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA) in THF,[42] with a slight excess of **P3HT-2-N₃** to perform the click reaction, resulting in the formation of **P3HT-2-P3AOT**.

In order to remove unreacted homopolymers, the crude **P3HT-2-P3AOT** was successively fractionated with pentane, hexane, heptane and chloroform, with the **P3HT-2-P3AOT** being dissolved in the latter fraction. GPC analysis of this fraction (Figure 4) showed a shift to higher molar mass compared to both **P3AOT-E** and **P3HT-2-N₃**, confirming the formation of block copolymer while excluding the possibility of a blend of the two homopolymers. ¹H NMR analysis clearly shows the α-methylene signals for the P3AOT (4.21 ppm) and the P3HT (2.78 ppm) block. From the integration of these signals it can also be deduced that the ratio P3AOT:P3HT is 4:1.

Bifunctional Ni-Initiator. Recent research[43] suggests that during the polymerization of P3HT using a Ni-catalyst, ring walking of the Ni-center allows the polymerization to proceed from both chain ends. However, when two significantly different monomers are polymerized, propagation can be expected to occur only at one side, since the complexation of the Ni-moiety is more favored for one system than to the other one and the Ni-catalysts cannot cross this barrier. We therefore decided to investigate whether it would be possible to grow P3HT simultaneously from both chain ends, using two nickel atoms propagating at the same time in opposite directions. The experimental verification of this hypothesis could be achieved by initiating the polymerization of P3HT with an initiator carrying two nickel atoms. In order to mimic the properties of a P3HT chain, we decided to use a bithiophene moiety, with methyl substituents ortho to the nickel moiety for stability reasons. Therefore, 5,5′-dibromo-4,4′-dimethyl-2,2′-bithiophene (**17**) was prepared through palladium coupling of 2-bromo-3-methylthiophene[44] (**16**), which was in turn prepared by bromination of 3-methyl-thiophene (**15**). Subsequently, **17** was allowed to react with 2 equiv of Ni(PPh₃)₄, resulting in the formation of the bifunctional nickel initiator **18** (Scheme 6). Although **18** was successfully isolated, it showed extremely rapid decomposition in solution, which severely complicated its analysis and explains its low yield. However, when combined with dppp, the stability was sufficient to allow initiation of the polymerization.

Scheme 4. Post-Polymerization Deprotection of the Polymers
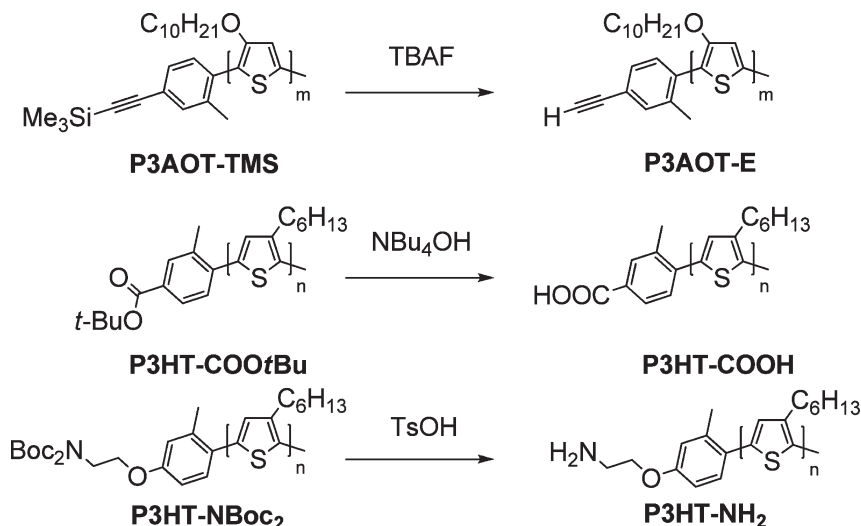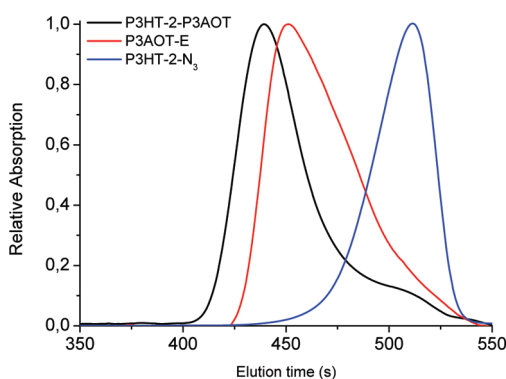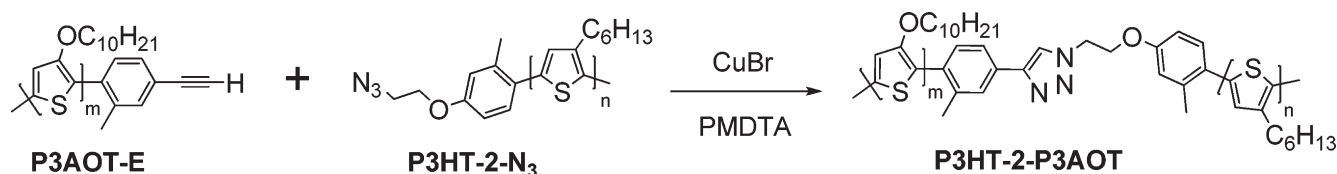

Scheme 5. Block Copolymer Formation

Figure 4. GPC elution profile for **P3HT-2-P3AOT** compared with its constituting homopolymers.

When 2-magnesiochloro-4-hexyl-5-bromothiophene was added to a solution of **17** which had first undergone ligand exchange with dppp, polymerization did occur, as expected. ^{1}H NMR of the H$^+$-terminated **P3HT-bth-P3HT** shows that polymerization did indeed proceed on both sides, as only one singlet at 2.42 ppm is visible for both 4,4′-methyls and there is a clear shift from **17** (Figure 5). Also, the presence of only one triplet at 2.62 ppm, arising from the α-methylenes from hydrogen terminated P3HT chains,[27] indicates that the polymerization is controlled. The fact that there is no distinct triplet for the α-methylenes of P3HT next to the bithiophene moiety is probably due to the high similarity of the bithiophene to the P3HT backbone. MAL-DI−ToF spectroscopy reveals that indeed only H/H terminated

chains are present (Supporting Information, Figure S45). GPC-analysis of **P3HT-bth-P3HT** results in an $\overline{M}_n$ of 3.8 kg/mol and a PDI of 1.6.

If one takes into consideration that (a) the polymerization does indeed proceed on both sides and (b) the polymerization of P3HT is controlled when employing dppp-ligated nickel catalysts, it should be possible to prepare a diblock-copolymer by extending the P3HT block on **P3HT-bth-P3HT** by addition of a second monomer. Therefore, after the polymerization of **P3HT-bth-P3HT**, one batch was quenched with acid, while 2-bromo-magnesio-5-bromo-3-(3,7-(S)-dimethyloctyloxy)thiophene was added to the other batch and the polymerization was allowed to proceed further. If the conditions mentioned above are met, the latter should result in the formation of a diblock-copolymer of P3HT and P3AOT on both sides of the bithiophene moiety, in the form of **P3AOT-P3HT-bth-P3HT-P3AOT**. Essentially, this can be regarded as a **P3AOT-P3HT-P3AOT** triblock-copolymer, and to the best of our knowledge, it is the first time that such a structure, comprised of entirely conjugated blocks, has been prepared by a chain-growth polycondensation. In the ^{1}H NMR spectrum, the α-methylene protons of the P3AOT-block (4.22 ppm) and P3HT-block (2.80 ppm) have a ratio of 3.5:1. By comparing the integration of these with the singlet of the bithiophene methyls at 2.42 ppm, it can be concluded that the P3HT-block contains 7 units and the P3AOT-block 24 on each side. The disappearance of the triplet at 2.62 ppm upon addition of the second monomer, clearly demonstrates a successful initiation of the P3AOT-blocks on both sides of the **P3HT-bth-P3HT**.

Scheme 6. Synthesis of the Bifunctional Nickel Initiator and Subsequent Polymerization[a]
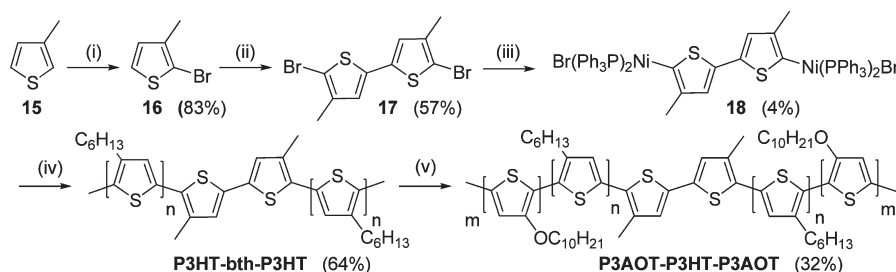
[a] (i) NBS; (ii) PdCl$_2$(PhCN)$_2$, AgNO$_3$, KF; (iii) Ni(PPh$_3$)$_4$; (iv) (1) dppp, (2) 2-magnesiochloro-4-hexyl-5-bromothiophene; (v) 2-bromomagnesio-5-bromo-3-(3,7-(S)-dimethyloctyloxy)thiophene or H$_3$O$^+$.

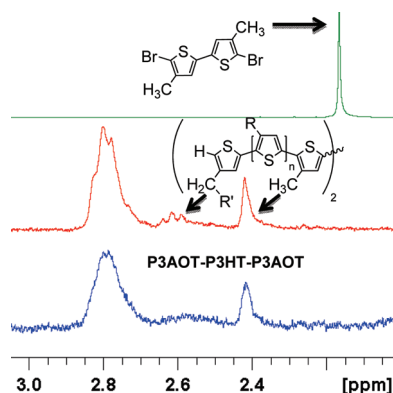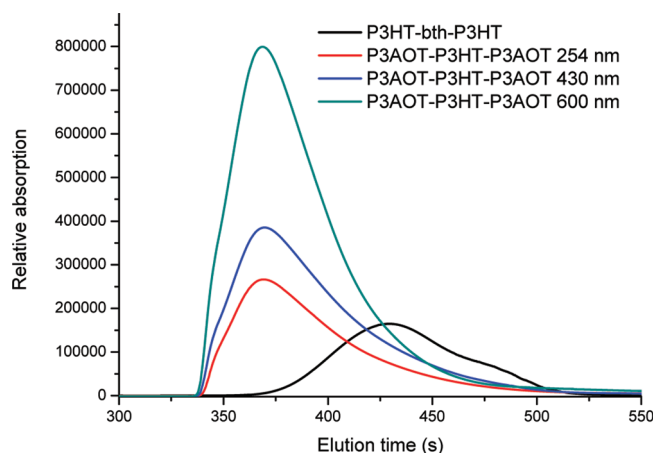**Figure 5.** ^{1}H NMR comparison of **17** and block copolymers.

Figure 6. GPC elution profile of **P3HT-bth-P3HT** compared with P3AOT-*b*-P3HT-*b*-P3AOT.

GPC-analysis shows a clear shift to shorter elution times (and thus higher molecular weight) for **P3AOT-P3HT-P3AOT** compared to **P3HT-bth-P3HT**. In order to demonstrate that the product did not simply consist of a mixture of homopolymers, we also measured GPC elution times at 430 and 600 nm, wich correspond to the respective absorption maxima of P3HT and P3AOT. The fact that these traces (Figure 6) all show the same elution time for **P3AOT-P3HT-P3AOT** proves the formation of a block copolymer and excludes the possibility of blends.

■ CONCLUSION

In conclusion, we have succeeded in preparing several poly-thiophenes with ethynylene, alcohol, tosylate, azide, amine, and carboxylic acid functionalities. We also demonstrated that these end groups can be transformed in a straightforward manner and can be used for the synthesis of a conjugated block copolymer with two electronically different blocks. For the first time, a bifunc-tional nickel initiator was synthesized and used to prepare a triblock-copolymer consisting of fully conjugated blocks.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental procedures and ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, IR, and MALDI—ToF spectra of selected compounds and/or polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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

■ ACKNOWLEDGMENT

■ REFERENCES

(1) Krebs, F. C.; Senkovskyy, V.; Kiriy, A. *IEEE J. Sel. Topics Quant. Electronics* **2010**, *16*, 1821–1826.

(2) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.

(3) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.

(4) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.

(5) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.

(6) Iovu, M. C.; Jeffries-EL, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582–8586.

(7) Iovu, M. C.; Craley, C. R.; Jeffries-EL, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Macromolecules* **2007**, *40*, 4733–4735.

(8) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329–332.

(9) Yokozawa, T.; Adachi, I.; Miyakoshi, R.; Yokoyama, A. *High Perform. Polym.* **2007**, *19*, 684–699.

(10) Wu, P.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317–2320.

(11) Ouhib, F.; Khoukh, A.; Ledeuil, J.; Martinez, J.; Desbières, J.; Dagron-Lartigau, C. *Macromolecules* **2008**, *41*, 9736–9743.

(12) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289–5294.

(13) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812–7813.

(14) Zhang, Y.; Tajima, K.; Hashimoto, K. *Macromolecules* **2009**, *42*, 7008–7015.

(15) Van den Bergh, K.; Huybrechts, J.; Verbiest, T.; Koeckelberghs, G. *Chem.—Eur. J.* **2008**, *14*, 9122–9125.

(16) Van den Bergh, K.; Cosemans, I.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2010**, *43*, 3794–3800.

(17) Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S. *J. Am. Chem. Soc.* **2010**, *132*, 8546–8547.

(18) Javier, A. E.; Varshney, S. R.; McCullough, R. D. *Macromolecules* **2010**, *43*, 3233–3237.

(19) Yokoyama, A.; Rato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.

(20) Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. *Macromolecules* **2008**, *41*, 8944–8947.

(21) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 753–765.

(22) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695–2698.

(23) Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. *Macromolecules* **2010**, *43*, 7095–7100.

(24) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894–12895.

(25) Doubina, N.; Stoddard, M.; Bronstein, H. A.; Jen, A. K.-Y.; Luscombe, C. K. *Macromol. Chem. Phys.* **2009**, *210*, 1966–1972.

(26) Doubina, N.; Ho, A.; Jen, A. K.-Y.; Luscombe, C. K. *Macromolecules* **2009**, *42*, 7670–7677.

(27) Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626–6632.

(28) Senkovskyy, V.; Tkachov, R.; Beryozkina, T.; Komber, H.; Oertel, U.; Horecha, M.; Bocharova, V.; Stamm, M.; Gevorgyan, S. A.; Krebs, F. C.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 16445–16453.

(29) Kaul, E.; Senkovskyy, V.; Tkachov, R.; Bocharova, V.; Komber, H.; Stamm, M.; Kiriy, A. *Macromolecules* **2010**, *43*, 77–81.

(30) Smeets, A.; Van den Bergh, K.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2009**, *42*, 7638–7641.

(31) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952–3015.

(32) Sharpless, K. B.; Finn, M. G.; Kolb, H. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

(33) Liu, J.; Tanaka, T.; Sivula, K.; Alivisatos, A. P.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6550–6551.

(34) Lohwasser, R.; Bandara, J.; Thelakkat, M. *J. Mater. Chem.* **2009**, *19*, 4126–4130.

(35) Van den Bergh, K.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromol. Chem. Phys.* **2010**, *212*, 328–335.

(36) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233–244.

(37) Doubina, A.; Paniagua, S. A.; Soldatova, A. V.; K. Y. Jen, A.; Marder, S. R.; Luscombe, C. K. *Macromolecules* **2011**, *44*, 512–520.

(38) De Winter, J.; Deshayes, G.; Boon, F.; Coulembier, O.; Dubois, P.; Gerbaux, P. *J. Mass. Spectrom.* **2011**, *46*, 237–246.

(39) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573–16579.

(40) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777–5785.

(41) Thompson, A. S.; Humphrey, G. R.; DeMarco, A. M.; Mathre, D. J.; Grabowski, E. J. J. *J. Org. Chem.* **1993**, *58*, 5886–5888.

(42) Urien, M.; Erothu, H.; Cloutet, E.; Hiorns, R. C.; Vignau, L.; Cramail, H. *Macromolecules* **2008**, *41*, 7033–7040.

(43) Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A. *J. Am. Chem. Soc.* **2010**, *132*, 7803–7810.

(44) Takahashi, M.; Masui, K.; Sekiguchi, H.; Kobayashi, N.; Mori, A.; Funahashi, M.; Tamaoki, N. *J. Am. Chem. Soc.* **2006**, *128*, 10930–10933.