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Synthesis of a Bifunctional Initiator for Controlled Kumada Catalyst-Transfer Polycondensation/Nitroxide-Mediated Polymerization and Preparation of Poly(3-hexylthiophene)−Polystyrene Block Copolymer Therefrom

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ABSTRACT: Herein, we present a new approach to synthesize rod−coil block copolymers via consecutive Kumada catalyst-transfer polycondensation (KCTP) and nitroxide-mediated free radical polymerization (NMP) performed from a bifunctional initiator, TIPNO−Ph−Ni(dppp)−Br (TIPNO = 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide; dppp = propane-1,3-diylbis(diphenylphosphane). The utility of the method was exemplified in a preparation of a model block copolymer, poly(3-hexylthiophene)-*block*-polystyrene (P3HT-*b*-PS) with a relatively narrow molecular weight distribution of 1.33. Synthesis of the bifunctional initiator was accomplished by a reaction of diethylbipyridylnickel with a readily accessible precursor, TIPNO−Ph−Br, followed by in situ replacement of the bipyridyl ligand onto bidentate phosphorus one.

Introduction

Poly(3-hexylthiophene) (P3HT) is one of the most promising conjugated polymers for solar cells[1] and field-effect transistors. P3HT is an excellent model for the establishment of structure−property and structure−function relationships.[2] Remarkably, the chemistry of P3HT is also unique: P3HT was the first conjugated polymer prepared via a "quasi-living" polymerization, in particular, through a Ni-catalyzed Kumada catalyst-transfer polycondensation (KCTP).[3] Later on, this reaction type was applied for the preparation of many other conjugated polymers.[4] An important advantage of the chain-growth KCTP compared with step-growth polycondensation schemes is that the former gives access to narrowly distributed polymers with well-defined end functionalities suitable for the preparation of block copolymers.[5] Block copolymers self-assemble into various nanostructures and thus are very attractive targets for many optoelectronic applications, where precise control over nanoscale organization is crucial.[1]

Under conventional KCTP conditions, the polymerization into P3HT proceeds via the one-by-one addition of 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) monomer molecules to an initiator formed from the same monomer and Ni(dppp)Cl_2 (dppp = propane-1,3-diylbis(diphenylphosphane)) or similar catalyst precursors.[4] After the polymerization, "living" ends of the resulting polymer can be capped with properly functionalized Grignard compounds that after some transformations can act as initiators for polymerization of a second block.[5] Although this strategy was already applied in the synthesis of many block copolymers, a multistep and complex nature of postpolymerization transformations is an important drawback. In addition, any undesired chain terminations during the preparation of the first block lead to incomplete chain-end functionalization and, as a result, to a contamination of diblock copolymers with homopolymers. Starting bromothiophene groups are not completely inert in the presence of Ni catalysts and Grignard reagents and can unintentionally be involved in block copolymerization, thus contaminating the desired AB diblock copolymers with ABA triblock copolymers.

We were interested at the development of a complementary way to P3HT-based block copolymers via the preparation of P3HT having specific starting rather than end functional groups that can further act as initiators (or their precursors) for growing of the second block. According to our strategy, these starting groups must be introduced at the very beginning of the KCTP via a transfer of functionality from specially designed Ni initiators. Obviously, the "classical" McCullough/Yokozawa protocol[3,4] is not suitable here because the starting groups of the resulting P3HT in this case originate from the monomer. Recently, we have introduced an alternative approach to initiate KCTP using externally added Ar−$(PPh_3)_2$−X initiators that were prepared from Ni$(PPh_3)_4$ and aryl halides.[6] An advantage of this approach is that it allows initiation of the polymerization from predesigned functions positioned at desired locations, such as from surface-immobilized aryl halides leading to P3HT brushes. The first proof-of-example of the externally initiated KCTP utilized relatively poorly performing Ni$(PPh_3)_4$-based initiators. Recently, the Luscombe group adapted this approach for external initiating of KCTP using model Ni initiators supported by bidentate phosphorouse ligands (dppp, or dppe, $Ph_2P(CH_2)_2PPh_2$).[7]

Very recently, we developed an efficient alternative route to a library of Ar−Ni(L_2)−X initiators supported by state-of-the-art bidentate phosphorouse ligands that are capable of initiating KCTP from particles on a controlled way.[8] The transformation involves a two-step reaction of aryl halides, Ar−X, with diethylbipyridylnickel, Et_2Ni(bipy), followed by an addition of dppp or dppe to exchange bipy on one of the phosphorus ligands. An attractive feature of this approach is that the transformation proceeds cleanly, even with para-substituted Ar−X without observable homocoupling side reactions, in contrast with Ni$(PPh_3)_4$-based schemes, which necessarily required the utilization of ortho-substituted Ar−X for stabilization of the intermediate complexes.[8] Going along the lines of Kiriy[6,8] and Luscombe[7]

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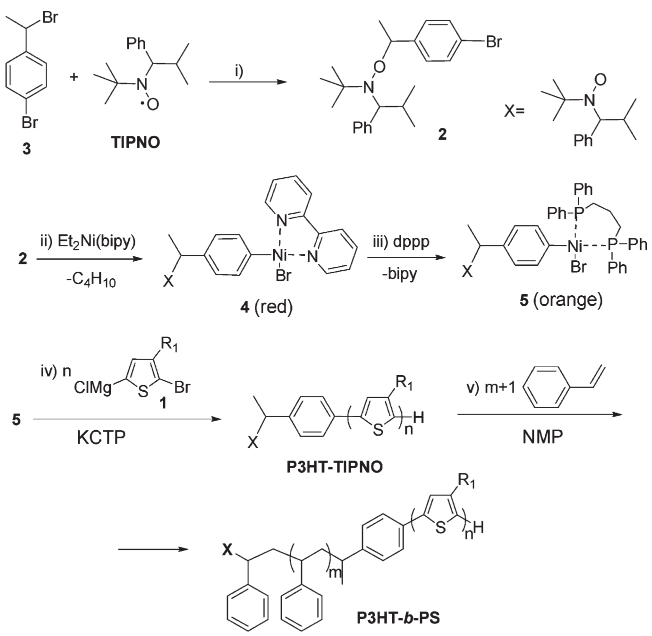
Scheme 1. Preparation of Bifunctional Initiator for Kumada Catalyst-Transfer Polycondensation and Nitroxide-Mediated Free Radical Polymerization and Synthesis of Poly(3-hexylthiophene)-*block*-polystyrene Block Copolymer[a]



[a] Key: (i) CuBr, pentamethyldiethylenetriamine, toluene, 50 °C, 1 h; (ii) Et_2Ni(bipy), toluene; (iii) diphenylphosphinopropane, toluene, RT, 30 min; (iv) 2-bromo-5-chloromagnesio-3-hexylthiophene, THF, RT, 15 min; (v) styrene, acetanhydride, 125 °C, 6 h.

groups, and having in mind the preparation of P3HT-based block copolymers as a future task, Koeckelberghs et al. have reported the incorporation of starting functional groups into P3HT utilizing specially designed Ni initiators.[9] Although the incorporated starting and end groups of P3HT were, in principle, transformable into functions able to act as initiators for subsequent polymerization of the second block, the preparation of the block copolymers by this approach was not demonstrated. Furthermore, the necessity in postpolymerization transformations of P3HT end groups for the preparation of P3HT-based macroinitiators was not eliminated in that work.[9]

In the present article, we report a facile synthesis of a bifunctional initiator that allows straightforward and convenient preparation of a model P3HT-based rod−coil copolymer, poly(3-hexylthiophene)-*block*-polystyrene (P3HT-*b*-PS), via a consecutive conduction of KCTP and NMP (nitroxide-mediated free radical polymerization) without any chemical manipulations with P3HT end groups.

Results and Discussion

2,2,5-Trimethyl-(1′-*p*-bromphenylethoxy)-4-phenyl-3-azahexane, **2**, was synthesized from 1-(4-bromophenyl)ethylbromide (**3**) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) in a single step according to previously described procedures[9] (Scheme 1). To prepare Ni catalyst, Et_2Ni(bipy) (bipy = 4,4′-bipyridine) was added dropwise to alkoxyamine **2** dissolved in dry degassed toluene under argon. The reaction involves some induction period (30−60 min) during which the reaction mixture needs to be warmed up to 40 °C. The transformation of **2** to **4** can be monitored by a color change of the reaction mixture from green, inherent to Et_2Ni(bipy), to red, typical for **4**. The preparation of bifunctional initiator **5** was accomplished by the addition of an excess of dppp (dppp = $Ph_2P(CH_2)_3PPh_2$); a successful replacement of the bipy ligand onto dppp is accompanied by a color change from red to yellow-brown.

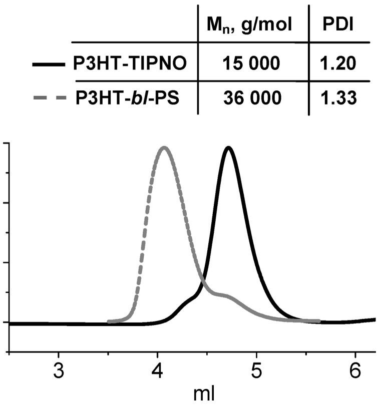


Figure 1. Gel permission chromatography traces (eluent: tetrahydrofuran) of P3HT−TIPNO macroinitiator and of poly(3-hexylthiophene)-*block*-polystyrene (P3HT: poly(3-hexylthiophene), TIPNO: 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide).

Polymerization of **1** was carried out under usual KCTP conditions by the addition of **5** to **1** and stirring for 15 min, followed by quenching with 5 N HCl. The number-average molecular weight (M_n) and polydispersity (PDI) of the resulting polymer were 15 000 g/mol and 1.2, respectively, as determined by gel permeation chromatography (GPC) against polystyrene (PS) standards (Figure 1).

The presence of a small shoulder on the GPC trace of P3HT (Figure 1, black line) may indicate an undesired dimerization of P3HT upon the quenching of KCTP,[3c] leading to P3HT terminated with TIPNO groups from both sides. Subsequent polymerization of PS from the bisfunctional macroinitiator would lead to PS−P3HT−PS triblock copolymer; however, its fraction in the resulting product should be rather small.

Although a detailed ^1H NMR signal assignment for the TIPNO end group of P3HT−TIPNO is somewhat prohibited by a relatively high molecular weight of the product and signals overlap, characteristic signals of the starting group originating from the initiator **5** are clearly seen (H_a, H_b; Figure 2; Figure S1b of the Supporting Information). The opposite end of the P3HT chain is nearly completely H-terminated. The signal at 6.82 ppm is a ^{13}C sattelite of the thiophene ring signal H_c and no indication of Br-termination, as confirmed by the absence of the α-CH_2 signal of this end group at 2.58 ppm.[3,4,6] Comparison of the signal integrals of H_b and H_d, which are representative of starting and end groups, allows us to estimate that at least 70% of P3HT chains bear a TIPNO starting group.[10] A polymerization degree of ~50 ($M_{nNMR} \approx 8600$ g/mol) was calculated from the intensities of H_d and the thiophene ring signal H_c. Other important observations are that the alkoxyamine moiety of the initiator does not suppress the performance of the KTCP and that the alkoxyamine group is robust enough under the KTCP conditions. It is also noteworthy that the introduction of a quite complex para-substituted functional group was achieved in a high yield highlighting a clear advantage of the developed Et_2Ni(bipy)-based route of the activation compared with the $Ni(PPh_3)_4$-based one (for which para-substituents in Ar−X deteriorate the oxidative addition reaction).[7,9]

In the next step, a model block copolymer, P3HT-*b*-PS, was prepared using P3HT−TIPNO as the macroinitiator under standard NMP conditions. For analytic purposes, after the polymerization, the P3HT-*b*-PS sample was subjected to extraction in Soxhlet apparatus with ethylacetate, which is a solvent for PS homopolymer and nonsolvent for P3HT−TIPNO. If PS homopolymer would be formed upon the polymerization as a side product, then it must be completely removed upon the extraction. However, no materials were extracted in this experiment,

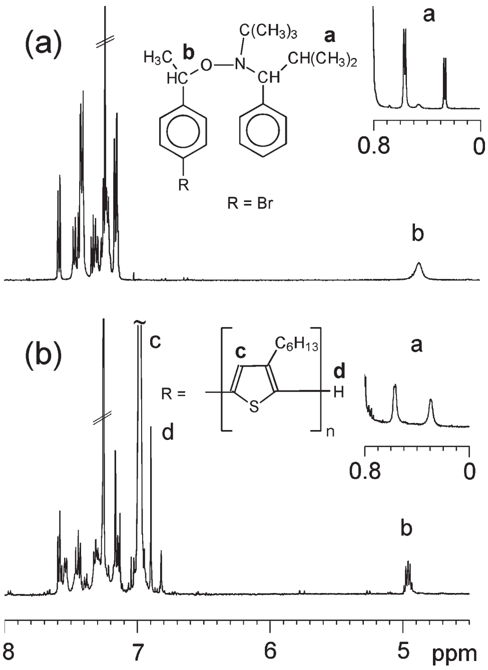


Figure 2. ^{1}H NMR spectra (solvent: $CDCl_3$) (a) of precursor of bifunctional initiator **2** and (b) of the macroinitiator P3HT−TIPNO (P3HT: poly(3-hexylthiophene); TIPNO: 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide).

reflecting the absence of free PS in the sample and the absence of an initiating TIPNO compound not bonded to P3HT. ^{1}H NMR reveals that PS is present in the sample with a styrene to 3HT monomer ratio of ~5 to 1, confirming that the product is indeed P3HT-*b*-PS block copolymer (Figure S1c, Supporting Information). With about 50 3HT units per initiator molecule, this ratio gives an averaged polymerization degree of ~250 for the PS block ($M_n \approx 26\,000$ g/mol). Taking into account $M_{nNMR} \approx 8600$ g/mol for the P3HT block, the total M_n of the block copolymer should be of ~35 000 g/mol, which is in a good agreement with $M_{nGPC} = 36\,000$ g/mol. Whereas PS calibration is less appropriated for P3HT homopolymer, the large PS block seems to result in a GPC behavior of the block copolymer, allowing PS calibration. The observed overall insolubility of P3HT-*b*-PS block copolymer in ethylacetate is, obviously, provided by sufficiently large P3HT block, for which ethylacetate is a nonsolvent. GPC also confirms successful preparation of P3HT-*b*-PS with a relatively narrow molecular weight distribution of 1.33. A lower molar mass shoulder on the GPC trace (Figure 1, gray line) reflects the presence of some amount of P3HT homopolymer, which, however, can be quantitatively eliminated by selective extraction of the block copolymer with CH_2Cl_2. One possible explanation for the presence of P3HT homopolymer in the final product would be contamination of the macromonomer by P3HT without initiating TIPNO group.[12] The latter would form as a result of insufficient purity of the bifunctional initiator **5** in the particular experiment. The degree of end-functionalization of P3HT with the TIPNO was further increased when (1) the precursor **2** was used in a slight excess relative to $Et_2Ni(bipy)$ and (2) the formed bifunctional initiator was purified prior KCTP by its precipitation after the addition of hexane and subsequent cooling of the reaction mixture down to −40 °C. Alternatively, the presence of P3HT homopolymer in the final product can be explained by the limited solubility of the macroinitiator in styrene upon the polymerization of the second block. Indeed, a deposit of insoluble macroinitiator onto walls of the reaction vessel was observed during the polymerization of styrene.

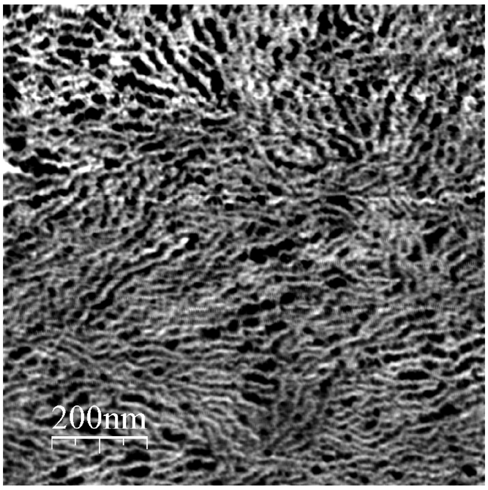


Figure 3. AFM phase image of 20 nm thick film of poly(3-hexylthiophene)-*block*-polystyrene deposited on Si wafer by spin-coating.

Surface morphology of the block copolymer film was visualized with tapping mode atomic force microscopy (AFM, Figure 3). Nanofibrillar structure is observed in 20 nm thick film of P3HT-*b*-PS spincoated from chloroform solution on silicon wafer. This type of morphology is typical for P3HT-based block copolymers[5] that further confirms successful preparation of P3HT-*b*-PS. Although the nanofibrillar structures are also formed in P3HT homopolymer films, a control experiment demonstrated that such structures are not forming in P3HT/PS physical blends.

It would be useful to compare the performance of our method to P3HT-based block copolymers and the performance of the approach developed by the McCullough group.[5] From the comparison, it becomes clear that both methods provide block copolymers of approximately the same quality with PDI in the 1.3 to 1.5 range, which is dependent mostly on the method chosen for the growing of the second block. However, a clear advantage of our method is that it completely eliminates multistep manipulations with the polymer's end groups. The existence of the alternative (complementary) methods to the same materials is always useful because the enrichment of a synthetic toolbox adds flexibility to the design and synthesis of new useful materials. For example, an obvious and useful extension of the ideas presented in this article implies a preparation of more complex initiators that contain, besides the two initiator groups, anchoring moieties having specific affinity to certain surfaces (e.g., thiols to gold). Application of such immobilizable bisfunctional initiator in a "double-grafting from" polymerization approach would be an interesting new route in the preparation of mixed polymer brushes, and this is currently underway in our lab.

Conclusions

In conclusion, we have proposed a new and straightforward route to rod−coil block copolymers via a consecutive KCTP and nitroxide-mediated free radical polymerization (NMP) performed from the bifunctional initiator **5**. The utility of the method was exemplified in the preparation of a model block copolymer, P3HT-*b*-PS, with a relatively narrow molecular weight distribution of 1.33. The synthesis of the later initiator was accomplished by a treatment of a readily available alkoxyamine **2** having TIPNO and bromophenyl moieties with $Et_2Ni(bipy)$, followed by in situ replacement of bipy ligand onto bidentate phosphorus ones (dppp). A distinct difference of our method from previously reported ones is that TIPNO residue is incorporated into P3HT as the starting group via the transfer from the Ni initiator (but not in a postpolymerization step, as reported earlier).[5] Therefore, possible chain terminations during the KCTP do not deteriorate the useful functionality of P3HT. The next advantage is that any chemical manipulations with polymer end groups are avoided. Because of a versatility of KCTP and NMP techniques, we believe that the presented approach may be used in the synthesis of a great number of rod−coil block copolymers for specific optoelectronic applications.

Experimental Part

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.13 MHz for ^{1}H using $CDCl_3$ as solvent. The spectra were referenced on the solvent peak (δ (^{1}H) = 7.26).

GPC. GPC measurements were carried out on Agilent 1100 Series (Agilent) normal-temperature size exclusion chromatograph, equipped with refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, U.K.), chloroform as eluent, and flow rate of 1 mL/min. Number-average molecular weights (M_n) and polydispersity indexes (PDIs) of obtained polymers were determined on the basis of calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

AFM. The multimode atomic force microscope (AFM) (Digital Instruments, Santa Barbara) was operated with amplitude feedback and in a "light" tapping mode configuration. The amplitude set point was set to the maximum possible value. Silicon tips with a spring constant of 0.3 N m^{-1} and a resonance frequency of 250−300 kHz were used.

Materials. 2-Bromo-3-hexylthiophene, hydrobromic acid (48% water solution), CuBr (anhydrous), pentamethyldiethylenetriamine (PMDTA), *tert*-butylmagnesium chloride (^{t}BuMgCl, 2.0 M solution in tetrahydrofuran, THF), dppp, *N*-bromosuccinimide (NBS), chloroform, dichloromethane, hexane, diethyl ether, and anhydrous $MgSO_4$ were purchased from Aldrich and used as received. 2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)[11] and diethyldipyridylnickel ($NiEt_2bpy$)[13] were synthesized as described elsewhere.

Bifunctional Catalyst (5). Bifunctional initiator **5** was prepared according to a two-step protocol recently developed in our group that includes the reaction of arylhalides with Et_2Ni(bipy), followed by the addition of an excess of the dppp ligand.[8] A few drops of Et_2Ni(bipy) solution in dry degassed toluene (0.136 g, 0.5 mmol in 5 mL of toluene) under an argon atmosphere were added to 0.248 g (0.6 mmol) of **2** dissolved in toluene (5 mL), and the mixture was warmed up to 35−40 °C until the disappearance of the green color inherent to Et_2Ni(bipy). After the induction period that typically takes about 30 min, the reaction mixture was cooled to room temperature, and the remaining quantity of Et_2Ni(bipy) solution was added dropwise; from this point, new added portions of Et_2Ni(bipy) discolor immediately, and a deep-red color develops instead that indicates the formation of **4**. Afterward, 0.272 g (0.66 mmol) of diphenylphosphinopropane in 5 mL toluene is added in one portion, and the solution is stirred for 30 min, during which the color of the reaction mixture changes from red to yellow-brown. This solution either can be used for further experiments without purification or **5** can be purified. In the latter case, 10 mL of hexane was added to the reaction mixture and was cooled to −40 °C for 1 h. A precipitated oil was separated from the solution by decantation and used for further experiments.

Macroinitiator P3HT-TIPNO. The monomer **1** was prepared as follows: 2-bromo-3-hexyl-5-iodothiophene 3.724 g (10 mmol) was placed in a round-bottomed flask equipped with a magnet stirrer bar, and the atmosphere was replaced with argon. Dry THF (60 mL) and *tert*-butylmagnesium chloride (2 M solution, 5 mL, 10 mmol) were added via a syringe, and the mixture was stirred at room temperature for 1 h. To prepare P3HT-TIPNO, 2.5 mL of freshly prepared solution of **5** in toluene (0.1 mmol) was added in one portion to solution of monomer **1** (10 mmol). The mixture was stirred for 15 min at room temperature and then quenched by 5 M hydrochloric acid. Reaction mixture was poured in water and extracted with $CHCl_3$. Combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Finally, MeOH was added to the residue, and the insoluble material was collected by filtration and washed with MeOH, acetone, and hexane to give pure P3HT-TIPNO as a purple solid (1.16 g, 70%). The ^{1}H NMR spectrum of the macroinitiator is given in Figure S1b of the Supporting Information, and it fully collaborates with the postulated structure.

Poly(3-hexylthiophene)-*block*-polystyrene Block Copolymer. A glass pressure vessel was charged with P3HT-TIPNO (0.33 g, 0.2 mmol), styrene (60 mL, 0.56 mol), and acetanhydride (0.252 g, 0.2 mmol), and then the mixture was degassed via three freeze−pump−thaw cycles. The reaction mixture was heated to 125 °C in a thermostated oil bath for 6 h. After the reaction was complete, the mixture was allowed to cool to room temperature, and the polymer was recovered by precipitation in methanol. The ^{1}H NMR spectrum of the block copolymer is given in Figure S1c of the Supporting Information, and it fully collaborates with the postulated structure.

Acknowledgment. Financial support was provided by Leibniz IPF Dresden and the Deutsche Forschungsgemeinschaft (KI-1094/3-1).

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Unfortunately, MALDI-TOF end-group analysis does not provide reliable results in our case because of decomposition of the TIPNO group during the measurements. At the same time, the end-group analysis based on ^{1}H NMR estimates approximately the degree of end-fictionalization so that the result obtained in our work does not necessarily reflect a worse performance of our approach compared with other methods (e.g., listed in ref 5). A detailed analysis of literature (e.g., ref 9) shows that there might be a significant discrepancy between MALDI-TOF and ^{1}H NMR end-group analysis data with the former method overestimating the degree of end-functionalization.

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(12) Because P3HT homopolymer with DP > 50 and P3HT-*b*-PS have very different solubility behavior, they can be quantitatively separated from each other by Soxhlet extraction using selective solvents (i.e., CH_2Cl_2 for P3HT-*b*-PS).

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