Protocols for Efficient Postpolymerization Functionalization of Regioregular Polythiophenes

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Thiophene-based conjugated polymers are receiving widespread attention as active materials in electronic devices such as sensors, field-effect transistors, and photovoltaic devices.[1−9] Functionalized poly(thiophene)s are often obtained by appending the desired functionality onto the monomer and polymerizing the resulting monomer via chemical oxidation, electrochemical oxidation, or iterative Pd(0)-catalyzed coupling.[10−16] These methods result in regiorandom polymers or low molecular weight polymers or both. Nonetheless, since Grignard metathesis (GRIM) polymerization conditions are incompatible with some functionalities, these methods are preferred over GRIM polymerization, which has emerged as a rapid and powerful method to synthesize regioregular thiophene-based polymers with molecular weight control, narrow molecular weight distribution, and superior electronic properties.[17−30] At the present time, the only method available to obtain side-chain-functionalized poly(3-substituted thiophene)s using GRIM is to use 2,5-dibromo-3-(ω-bromoalkyl)thiophene as the monomer.[31−34] Surprisingly, it has been reported that the ω-bromo group survives the Ni(0) catalyst and Grignard reagents in GRIM polymerization and has been used for further functionalization by nucleophilic substitution.

For efficient postpolymerization functionalization of regioregular poly(thiophene)s, it is important that the functional group that is being modified should be tolerant to Grignard reagents and Ni(0)-based catalysts. Moreover, the postpolymerization functionalization reaction should be of high fidelity and high yield, and the reaction conditions should be mild. In recent years, the Cu(I)-mediated Huisgen 1,3-dipolar cycloaddition reaction popularly known as "click chemistry" has been used for postpolymerization functionalization of polymers.[35−40] This reaction satisfies our aforementioned requirements. Herein, we provide an optimized protocol for the postpolymerization functionalization of regioregular poly(3-substituted thiophene)s using the Huisgen cycloaddition.

The synthesis of the thiophene monomers is outlined in Scheme 1, starting from commercially available thiophene-3-methanol (**1**). Stirring alcohol **1** in a biphasic mixture of CH_2Cl_2 and concentrated HCl easily converted the starting material to **2**; this compound degrades over time and therefore should be prepared and used immediately. The protected terminal alkyne was installed by the reaction of **2** with lithiated 1-triisopropyl-1-propyne (1-TIPS-1-propyne);[41] compound **3** was obtained in 86% yield.

Among the procedures that exist for the controlled bromination of 3-alkylthiophenes, we found that using 1 or 2 equiv of NBS in HOAc/$CHCl_3$ reproducibly afforded the desired mono- or dibrominated products, respectively. Treatment of **3** with an equimolar amount of NBS produced **4** in 82% yield, whereas 2 equiv of NBS gave compound **5** in 81% yield.

In order to generate monomers for the synthesis of alternating copolymers, we designed bithiophene monomer **8** and chose Suzuki coupling reactions to assemble these bithiophenes.[42−44] To achieve a head-to-tail coupling between **4** and a 3-alkylthiophene, a 4-alkylthiophene-2-boronic acid or ester such as **6** was needed. Reacting 3-hexylthiophene with LDA (generated in situ) followed by the addition of trimethylborate and hydrolysis gave us the appropriately substituted thiopheneboronic acid, which was converted, without purification, to the neopentyl glycol ester (**6**). Palladium-catalyzed coupling of **4** and **6** yielded bithiophene **7**. Dibromination of **7** resulted in compound **8** in 93% yield.

Scheme 2 illustrates the syntheses of poly(3-TIPS-butynylthiophene-*alt*-3-hexylthiophene) (P3TBT-*alt*-P3HT, **9**) and poly(3-TIPS-butynylthiophene-*block*-3-hexylthiophene) (P3TBT-*block*-P3HT, **10**). The polymer bearing alternating protected butynyl and hexyl side chains was synthesized via GRIM polymerization of dibromobithiophene **8**.[21] Initial experiments with this polymerization, which were conducted at ambient temperature, afforded very little of the desired polymer, regardless of the amount of catalyst used (see Supporting Information). However, the polymerization of **8** at 70 °C reproducibly afforded good yields of the desired product having M_n near 15 300 g/mol and PDI ranging from 1.28 to 1.35, as estimated from GPC (THF elution, polystyrene standards). Analysis of the product by ^{1}H NMR confirmed that the TIPS group survived exposure to Grignard reagent. The absorption spectrum of a dilute $CHCl_3$ solution of the polymer (c = ca. 1 mg/100 mL in $CHCl_3$) had a λ_{max} of 449 nm, while a film of **9** drop-cast from $CHCl_3$ solution had λ_{max} of 538 nm with optical band gap ∼1.9 eV.

The McCullough polymerization method is reported to be a quasi-living polymerization method that produces primarily head-to-tail linkages.[45] Taking these advantages into account, we reasoned that a block-type copolymer, such as **10**, could be synthesized from TIPS-protected 2,5-dibromo-3-but-3-ynylthiophene (**5**) and 2,5-dibromo-3-hexylthiophene via a stepwise polymerization procedure (Scheme 2). Indeed, polymerizing the Grignard generated from **5** for 30 min prior to adding Grignard generated from 2,5-dibromo-3-hexylthiophene yielded P3TBT-*block*-P3HT (**10**). In separate control experiments, we produced a homopolymer of **5** (P3TBT) and a random (statistical) copolymer from an equimolar mixture of monomer **5** and 2,5-dibromo-3-hexylthiophene (see Supporting Information). Analysis of the random and block copolymers by ^{1}H NMR confirmed a nearly 1:1 ratio of butynyl- and hexyl-bearing thiophene units in each copolymer. Comparison of the ^{13}C NMR spectra of the copolymers, relative to that of the homopolymer of **5**, provided evidence of the block and random nature of the copolymers.[21] The molecular weight (M_n) of P3TBT-*block*-P3HT was estimated by GPC to be 17 200 g/mol with a PDI of 1.19. The absorption spectrum of a dilute $CHCl_3$ solution of the block copolymer (c = ca. 1 mg/100 mL in $CHCl_3$) had a λ_{max} of 444 nm, while a film of **10** drop-cast from $CHCl_3$ solution had λ_{max} of 516 nm with optical band gap ∼1.9 eV.

We optimized the conditions for postpolymerization functionalization via cycloaddition reaction using ethynyl-terminated P3HT[46] (**11**, Scheme 3) and azide bearing a naphthalimide moiety (**12**). In the series of reactions summarized in Table 1,

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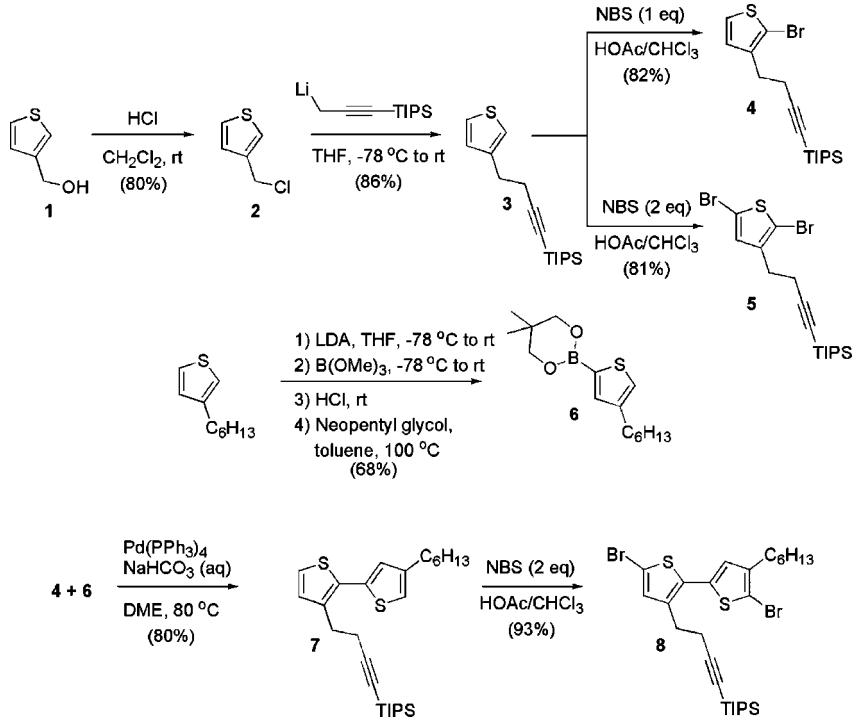
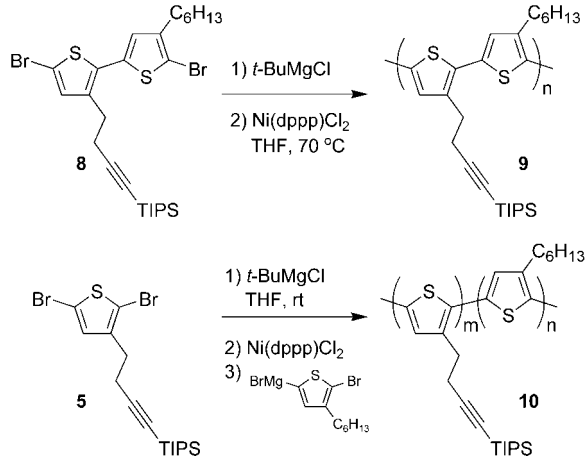
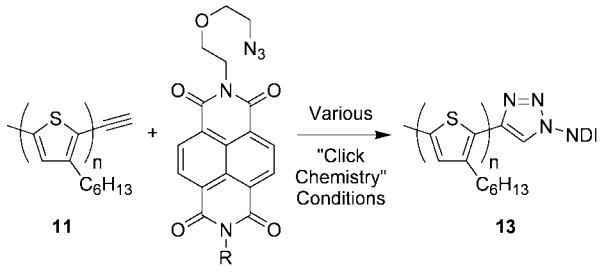
Scheme 1. Synthesis of Thiophene Monomers with Triisopropylsilyl (TIPS)-Protected Alkynyl Side Chains



Scheme 2. Synthesis of Polythiophenes with TIPS-Protected Alkynyl Side Chains



Scheme 3. Huisgen 1,3-Dipolar Cycloaddition Conditions Applied to Ethynyl-Terminated P3HT



we screened several cycloaddition conditions, purified the resultant polymer via Soxhlet extraction, and determined the production distribution via ^{1}H NMR of the isolated products. The peaks for triazole, NDI, and flexible linker protons were identified using a small-molecule model compound (see Supporting Information). The most commonly used catalyst, $CuSO_4 \cdot 5H_2O$ and sodium ascorbate in THF/H_2O,[47] worked to some degree, with 40% of end groups converted to the triazole moiety. We reasoned that since the polymer was not very soluble in the aqueous medium, the end groups were not adequately exposed to the reaction medium. Support for this hypothesis lies in the fact that fully solubilized P3HTs form bright orange solutions. However, the addition of even small amounts of water to polymer **11** dissolved in THF immediately produced purple suspensions. The optimal conditions were CuI and Hünig's base [$(i\text{-pr})_2$NEt] in THF at 50 °C. No reaction was observed when CuI was used without Hünig's base in THF, regardless of reaction temperature.

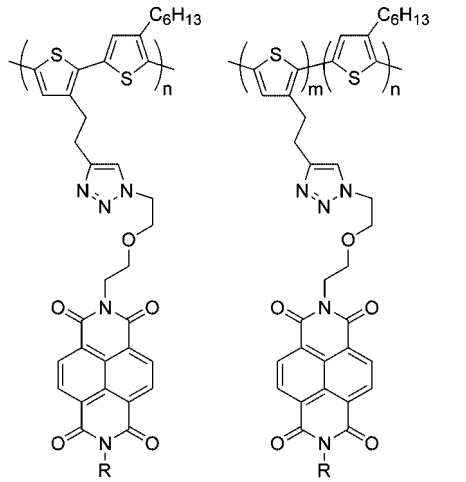
Table 1. Effect of Reaction Conditions on End-Group Functionalization of Ethynyl-Terminated P3HT[a]

entry	catalyst	solvent	*T*	*t*	**13**:**11**[b]
1	CuI, $(i\text{-pr})_2$NEt	THF	rt	24 h	1.00:0.20
2	CuI	toluene	rt	24 h	0.00:1.00
3	CuI	toluene	60 °C	24 h	0.00:1.00
4	$CuSO_4 \cdot 5H_2O$ NaAscorbate	THF/H_2O	50 °C	24 h	0.65:1.00
5	CuI, $(i\text{-pr})_2$NEt	toluene	50 °C	24 h	1.00:0.05
6	CuI, $(i\text{-pr})_2$NEt	THF	50 °C	4 days	1.00:0.00

[a] Reaction illustrated in Scheme 3: polymer **11** (50 mg), NDI-azide **12a** (37 mg), copper catalyst (0.016 mmol), solvent (10 mL), sodium ascorbate (if used, 0.08 mmol), $(i\text{-pr})_2$NEt (if used, 1 mL). [b] Based on integration of ^{1}H NMR peaks corresponding to triazole-*H* (product, δ 7.63 ppm) and terminal alkyne-*H* (starting material, δ 3.52 ppm).

Next, we applied these conditions to the synthesis of polymers **14** and **15**. The triisopropyl silyl groups in polymers **9** and **10** were deprotected with TBAF and reacted with fluorocarbon NDI-azide (**12b**). Our previous experience with oligothiophene-NDI dyads indicated that yields of the "click chemistry" step did not depend on whether the alkyne was extensively purified following treatment with TBAF. Therefore, after removal of the TIPS protecting groups, the resulting polymer solutions were

washed well with water, but not subjected to Soxhlet extraction. Following concentration in vacuo, the material was subjected to cycloaddition conditions at 50 °C in order to ensure adequate solubility of the polymer in the reaction medium. Initially, all such reactions were homogeneous orange solutions. As the reactions proceeded, they turned deep red-purple—a color indicative of all of the side-chain-functionalized polymers in this work. Soxhlet purification of the final products with MeOH, EtOAc, and $CHCl_3$ afforded recovery of unreacted azide in the MeOH extract and good yields of the desired polymers in the $CHCl_3$ extract. For example, four separate trials of this procedure, starting from 50 mg of **9**, resulted in an average isolated yield of 66 mg (57%) of **14b**. The procedure worked effectively for both P3TBT-*alt*-P3HT and P3TBT-*block*-P3HT starting materials. Polymers **14a** and **15a** bearing aliphatic hydrocarbon NDI side chains (C_6H_{13}) were synthesized in an analogous fashion (see Supporting Information). As a control reaction, we attempted the GRIM polymerization of the monomer, which we had obtained by the attachment of **12a** to molecule **5** through deprotection followed by cycloaddition reaction. The solution turned intense red immediately upon the addition of the *t*-buMgCl, and no polymer was obtained at the end of the reaction.



14a: R = $(CH_2)_5CH_3$ **15a:** R = $(CH_2)_5CH_3$
14b: R = $CH_2(CF_2)_6CF_3$ **15b:** R = $CH_2(CF_2)_6CF_3$

NMR spectra of these products were best acquired at 110 °C in 1,1,2,2-tetrachloroethane-d_2 (TCE) due to their limited solubility at room temperature in solvents such as THF and $CHCl_3$. The absence of the peak attributable to the C−H of terminal alkyne at $\delta \sim 3.5$ ppm and the concomitant appearance of the singlet peak at $\delta \sim 7.6$ ppm attributable to the proton on the triazole moiety (see Supporting Information) in the ^{1}H NMR spectra of the isolated functionalized polymer indicated that the attachment of NDI via the triazole linker was complete. The appearance of a single peak for the triazole moiety indicates the formation of only one of the two possible regioisomers. It is well-established that copper-catalyzed 1,3-dipolar cycloadditions are regioselective, affording the 1,4-regioisomer of the triazole.[48] In addition to the diagnostic peaks of the triazole, for NDI bearing fluorocarbon side chains, the lone $-CH_2-$ in the fluorocarbon side chain appeared as a triplet near δ 5.0 ppm with a distinctively large coupling constant ($^3J_{H-F} \approx 15$ Hz). The polydispersity index (PDI) of polymer **15a**, obtained from GPC traces in THF was 1.21. In comparison, polymer **10** had a PDI of 1.17 (see Supporting Information). We attribute this slight increase in the PDI to the limited solubility and possible aggregation of the polymer in THF. Also, the molecular weight of polymer **15a** obtained from GPC using polystyrene standards was less than the molecular weight of polymer **10**. We speculate that the attachment of NDI changes the solution structure and the hydrodynamic radius of the polymer.

In conclusion, we have reported a synthetic protocol for the postpolymerization of poly(3-substituted thiophene)s obtained from GRIM polymerization using Huisgen 1,3-dipolar cycloaddition chemistry. Our protocol can be readily used for side-chain functionalization or end-group functionalization. We are currently pursuing the photophysical properties and thin-film morphologies of these polymers.

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Supporting Information Available: Experimental procedures for the synthesis and purification of all materials, including the model triazole and hydrocarbon-NDI compounds; NMR and GPC data; UV−vis spectra of **9**, **10**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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