3130 *Macromolecules* **2001,** *34,* 3130−3132

A Novel and Versatile Methodology for Functionalization of Conjugated Polymers. Transformation of Poly(3-bromo-4-hexylthiophene) via Palladium-Catalyzed Coupling Chemistry

Yuning Li, George Vamvounis, Jianfei Yu, and Steven Holdcroft*

Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby BC V5A 1S6, Canada

Received February 20, 2001

Poly(thiophene)s have been an interdisciplinary subject of study over the past two decades[1−5] largely because of their novelty, characteristic electrical and optical properties, and potential application in electronic devices such as organic field-effect transistors (FETs),[2] chemosensors,[3] electrochemical capacitors,[4] and light-emitting displays (LEDs).[5] Their processability, molecular organization, and electronic and optical properties can be controlled through derivatization of the thienyl ring. However, the scientific demand for poly(thiophene)s that possess more complex structural motifs is offset by synthetic limitations. For example, preparation of poly(thiophene)s with functional side chains requires tedious procedures involving the synthesis of monomers. All but a few functional groups are intolerant of the harsh polymerization conditions, with the result that many potential functional poly(thiophene)s simply cannot be prepared.

An alternate approach to obtaining derivatized polymers is post-functionalization of precursor polymers,[6,7] which has been applied extensively to conventional non-π-conjugated polymers. Such methodology applied to poly(thiophene)s would considerably simplify the procedures for acquiring complex structures and greatly diversify the functional groups available. With this goal in mind, we recently reported that the 4-hydrogen of poly(3-hexylthiophene) (**P3HT**) is susceptible to electrophilic substitution and can be quantitatively replaced with a halogen or nitro group under mild conditions (Scheme 1).[8] We speculated that these 3,4-disubstituted poly(thiophene)s should be capable of further substitution with other functional groups. In this report, we demonstrate that Suzuki, Stille, and Heck coupling chemistry[9−12] involving poly(3-bromo-4-hexylthiophene) (**1a**) and appropriate reagents can be used to prepare poly(thiophene)s possessing aryl, vinyl, and alkynyl side chain groups.

Suzuki coupling of phenylboronic acid with **1a** was conducted in THF at 80 °C in the presence of Na_2CO_3 and 2% equiv of $Pd(PPh_3)_4$ (Scheme 1) for 48 h. The product **2a** clearly showed the emergence of aromatic protons at 7.27 and 7.15 ppm in the ^1H NMR spectrum (Figure 1). All protons of the hexyl group shifted upfield compared to those of **1a**, for example, α-methylene protons shifted from 2.72 to 2.26 ppm. (The minor peak at 2.88 ppm for **1a** is ascribed to the α-methylene group in terminal units.[8]) From the integrals of the aromatic and $-CH_3$ protons, the substitution of Br by phenyl was estimated to be >99%, a value consistent with elemental analysis (Br < 0.3%). Other *para*- or *meta*-substituted phenylboronic acids, 1-naphthylboronic acid, and 2-thiopheneboronic acid also reacted quantitatively with **1a** (Scheme 1), indicating that these reactions are tolerant to other functional groups. It is noteworthy that more bulky *ortho*-substituted reagents, 2-methylphenylboronic acid and 2-methoxyphenylboronic acid, also reacted quantitatively with **1a** to give products **2c** and **2e**, even though these reactions would seem unlikely due to congestion.

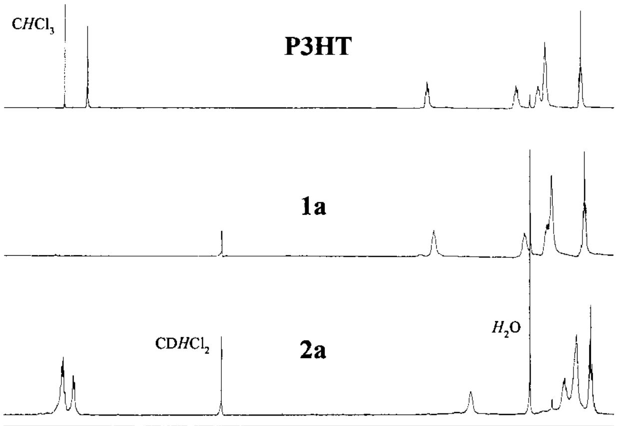


Figure 1. The 400 MHz ^1H NMR spectra of **P3HT** (in $CDCl_3$) **1a** and **2a** (in CD_2Cl_2).

Several tributyltin compounds were used for the Stille-type coupling with **1a** as illustrated in Scheme 1. Reactions of 2-thiophene- and 2-furantributyltin with **1a** at 100 °C in toluene gave products **3b** and **3c** with complete substitution of Br (>99%) within 24 h. NMR and IR data indicate that the structure of thienyl-substituted product **3a** is identical to **2k** prepared by Suzuki coupling. The furyl-substituted product **3c** becomes insoluble after exposure to air most likely due to cross-linking caused by the photooxidation of the furyl group.[13] Reaction of vinyl- and phenylethynyltributyltin with **1a** afforded substituted products **2c** (91%) and **2d** (>99%) that possess a double and triple bond, respectively, directly attached to the polymer backbone. Phenyltributyltin was reluctant to react with **1a**, and only 42% of the Br groups in **1a** were replaced by phenyl even after 120 h (**3a**). This result is in agreement with the known poor reactivity of stannylbenzenes under Stille coupling conditions.[14]

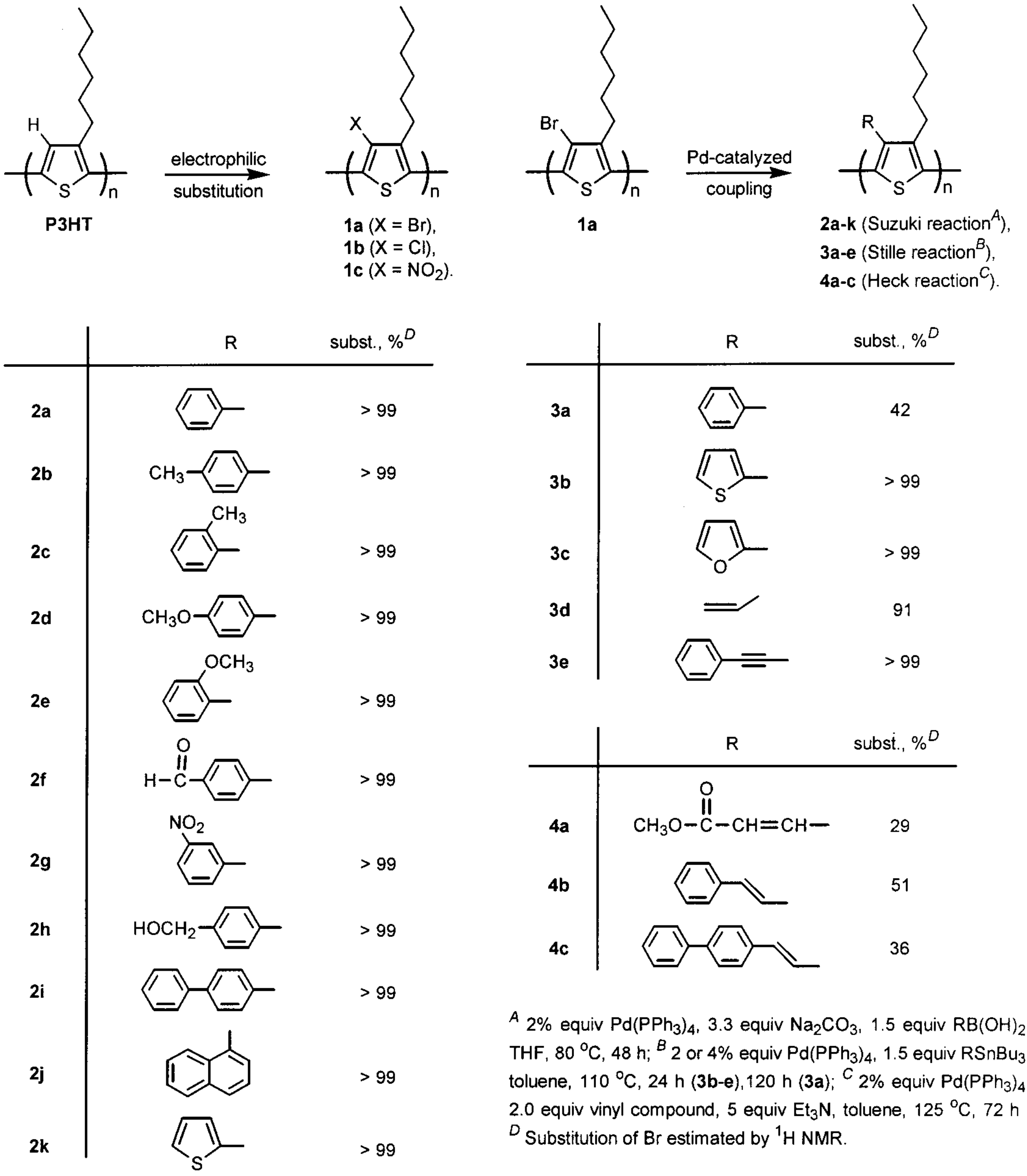
Heck reactions of **1a** were investigated using methyl acrylate, styrene, and 4-vinylbiphenyl. Under the reaction conditions employed (see Scheme 1), only 29−51% of the Br groups in **1a** were substituted (**4a**−**c**). Further investigation to improve the degree of substitution is in progress.

UV−vis spectra in THF solution showed an increase in the absorption maximum (λ_{max}: 355−403 nm) for aryl- (phenyl, naphthyl, thienyl, and furyl) and phenylethynyl-substituted polymers, compared to the starting polymer **1a** (λ_{max}: 339 nm). This suggests that the side chains exert an electronic influence on the main chain conjugation. However, a slight decrease in λ_{max} (316−338 nm) was observed for the vinyl-substituted products (**3d**, **4a**−**c**) for reasons yet unknown.

In conclusion, these results demonstrate that **P3HT** can be efficiently functionalized by bromination and subsequent palladium-catalyzed cross-coupling reactions. This study establishes a convenient pathway for

10.1021/ma010293w CCC: $20.00

Scheme 1



^{A} 2% equiv $Pd(PPh_3)_4$, 3.3 equiv Na_2CO_3, 1.5 equiv $RB(OH)_2$, THF, 80 °C, 48 h; ^{B} 2 or 4% equiv $Pd(PPh_3)_4$, 1.5 equiv $RSnBu_3$, toluene, 110 °C, 24 h (**3b-e**),120 h (**3a**); ^{C} 2% equiv $Pd(PPh_3)_4$, 2.0 equiv vinyl compound, 5 equiv Et_3N, toluene, 125 °C, 72 h ; ^{D} Substitution of Br estimated by ^1H NMR.

the construction of novel poly(thiophene)s possessing more complex structures from simple, and commercially available, poly(3-alkylthiophene) precursors. A detailed study on the electronic and optical properties of these new 3,4-disubstituted poly(thiophene)s is in progress.

Acknowledgment. This study was supported by the Natural Science and Engineering Research Council of Canada (NSERC). G.V. thanks NSERC and Xerox Research Center of Canada for scholarship support.

Supporting Information Available: Detailed synthesis and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) See review articles and references therein: (a) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183. (b) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. (c) McCullough, R. D.; Ewbank, P. C. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 225.

(2) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365. (b) Horowitz, G. *J. Mater. Chem.* **1999**, *9*, 2021. (c) Katz, H. E.; Dodabalapur, Bao, Z. In *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weiheim, 1998. (d) Bao, Z. *Adv. Mater.* **2000**, *12*, 227.

(3) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.

(4) Ferraris, J. P.; Eissa, M. M.; Brotherston, I. S.; Loveday, D. C. *Chem. Mater.* **1998**, *10*, 3528.

(5) Braun, D.; Gustafson, G.; McBranch, Heeger, A. J. *J. Appl. Phys.* **1992**, *72*, 564. (b) Greenham, N. C.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H. *Synth. Met.* **1993**, *55*–*57*, 4134. (c) Berggren, M.; Inganäs, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrõm, O. *Nature* **1994**, *372*, 444.

(6) Selected publications on reactions of polymers: (a) *Chemical Reactions of Polymers*; Fettes. E., Ed.; Interscience: New York, 1964. (b) *NATO Advanced Study Institutes Series C: Mathematical and Physical Sciences, Vol. 4: Reactions on Polymers;* Moore, J. A., Ed.; Reidel: Boston, 1973. (c) *Chemical Reactions of Natural and Synthetic Polymers*; Lazár, M., Bleha, T., Rychlý, J., Eds.; Kemp, T. J., Translation Ed.; Ellis Horwood: Chichester, 1989. (d) *Macromolecular Reactions*; Platé, N. A., Litmanovich, A. D., Noah, O. V., Eds.; John Wiley & Sons: Chichester, 1995.

(7) References on the post-functionalization of conjugated polymers: (a) Guiseppi-Elie, A.; Wnek, G. E. *J. Polym. Sci., Part*

A: *Polym. Chem.* **1985**, *23*, 2601. (b) Vork, F. T. A.; Ubbink, M. T.; Janssen, L. J. J.; Barendrecht, E. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 215. (c) Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800. (d) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665. (e) Harada, H.; Fuchigami, T.; Nonaka, T. *J. Electroanal. Chem.* **1991**, *303*, 139. (f) Qi, Z.; Rees, N. G.; Pickup, P. *Chem. Mater.* **1996**, *8*, 701. (g) Berman, B.; Hanks, T. W. *Macromolecules* **2000**, *33*, 8035.

(8) Li, Y.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2001**, *34*, 141.

(9) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; John Wiley-VCH: Weinheim, 1998.

(10) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(11) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Mitchell, T. N. *Synthesis* **1992**, 803.

(12) Heck, R. F. *Org. React.* **1981**, *27*, 345. (b) Meijere, A. de; Meyer, F. E. *Angew. Chem., Int. Engl.* **1994**, *33*, 2379. (c) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(13) Saadeh, H.; Goodson, T., III; Yu, L. *Macromolecules* **1997**, *30*, 4608.

(14) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

MA010293W