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Facile Functionalization of Poly(3-alkylthiophene)s via Electrophilic Substitution

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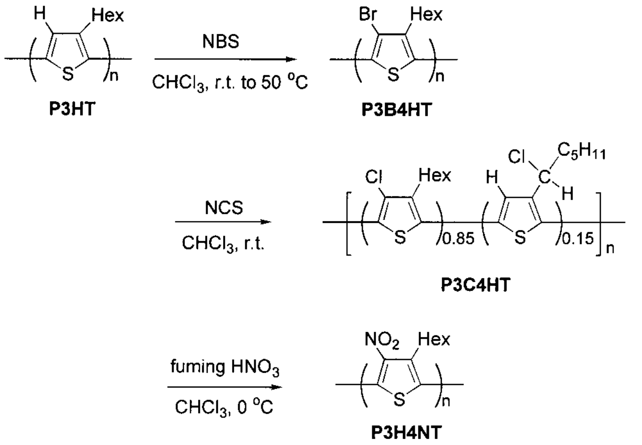
Poly(thiophene)s have become the subject of extensive study. These materials are viewed as potentially useful components in field-effect transistors, optical and electronic sensors, light-emitting devices, nonlinear optical materials, etc.[1,2] Substitution at the 3- and/or 4-position of the thiophene ring not only confers processability to poly(thiophene)s but can also be used to modify their electrooptical properties through electronic and steric interactions. However, it is difficult to prepare poly(thiophene)s with a comprehensive list of functional groups due to either an intolerance of the functional group to the rather harsh polymerization conditions, the inhibition of monomer polymerization by the functional group, or the tedious nature of the synthetic procedures.[3,4]

Post-functionalization of conjugated polymers, e.g., polyacetylene,[5] polyaniline,[6] polypyrole,[7,8b] and poly(thiophene)s,[8] as a method to modify the properties of these polymers has drawn much attention in recent years.[9] The *nucleophilic* substitution of the overoxidized poly(thiophene)s with Cl, Br, or methoxy groups in the 4-position using an electrochemical method has been investigated to functionalize poly(thiophene)s.[8] On the basis of electronic effects alone, however, the 4-position of the thiophene ring in poly(3-alkylthiophene)s (P3ATs) should be more susceptible to *electrophilic* substitution due to the high electron density on the backbone that originates from the extended π-system and the electron-donating effect of the 3-alkyl side chain. The replacement of the 4-position of P3ATs by functional groups via electrophilic substitution, and further derivatization of the functional groups, should provide a useful strategy to tailor the structure and the band gap of the polymers and therefore control their electrooptical properties. This may also yield new and structurally well-defined 3,4-disubstituted poly(thiophene)s that cannot be prepared by a conventional approach. However, this hypothesis fails to take into account the steric hindrance of the substituents on adjacent thienyls that would inhibit substitution. In this paper, we address the question as to whether substitution of P3ATs at the 4-position is possible. We herein report preliminary results of direct electrophilic substitution of poly(3-hexylthiophene) (**P3HT**) to form halogenated and nitrated products.

Scheme 1



As illustrated in Scheme 1, when regioregular **P3HT** was treated with *N*-bromosuccinimide (NBS), a yellow solid was obtained in 99% yield after work-up. The ^{1}H NMR spectrum of this product shows the disappearance of the aromatic hydrogens of **P3HT** (at 6.99 ppm) and a slight shift of the α-methylene hydrogen peak of the hexyl group from 2.80 to 2.71 ppm (Figure 1). A minor peak at 2.85 ppm is ascribed to the α-methylene group in terminal units. The disappearance of signals for the aromatic carbons of **P3HT**, the appearance of four new

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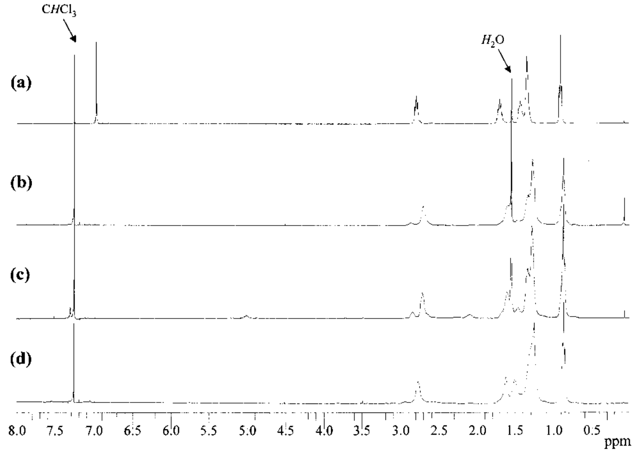

Figure 1. 400 MHz ^{1}H NMR spectra of (a) **P3HT**, (b) **P3B4HT**, (c) **P3C4HT**, and (d) **P3H4NT**.

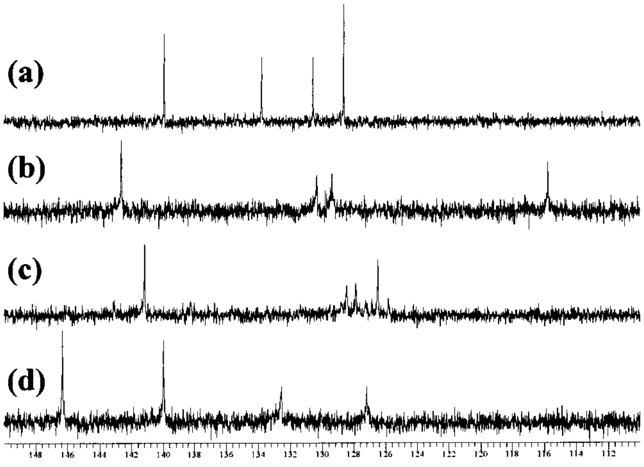

Figure 2. Aromatic regions of 100 MHz ^{13}C NMR spectra of (a) **P3HT**, (b) **P3B4HT**, (c) **P3C4HT**, and (d) **P3H4NT**.

peaks in the aromatic region (at 142.66, 130.38, 129.41, and 115.81 ppm) in the ^{13}C NMR spectrum (Figure 2), IR spectroscopy, and elemental analysis (see Experimental Section) indicate the product to be poly(3-bromo-4-hexylthiophene) (**P3B4HT**). Similarly, using *N*-chlorosuccinimide (NCS) instead of NBS produced the chlorinated product poly(3-chloro-4-hexylthiophene) (**P3C4HT**) in 98% yield based on 100% substitution. No aromatic hydrogens corresponding to **P3HT** remained in the product, but a small peak at 7.31 ppm was observed in the ^{1}H NMR spectrum (Figure 1). Two minor peaks at 5.02 and 2.10 ppm (and two minor peaks at 56.83 and 39.95 ppm in ^{13}C NMR spectrum) were assigned to α-methylene and *β*-methylene hydrogens of the side chain, respectively, using DEPT and ^{1}H−^{13}C COSY. It is thus concluded that ~85% of the aromatic hydrogens of **P3HT** are substituted with chlorine, while 15% of α-methylene hydrogens of the hexyl group are chlorinated, presumably through a free radical mechanism.[10] It is postulated that chlorination of the α-methylene hydrogen sterically prevents further substitution of the aromatic hydrogen on the same thiophene ring as shown in Scheme 1. **P3HT** was also reacted with *N*-iodosuccinimide under similar conditions to produce the iodinated derivative. The 4-hydrogen of **P3HT** disappeared after stirring for 24 h at 50 °C in a mixture of chloroform and acetic acid (95/5 v/v). However, the product was unstable upon work-up, due to the weak C−I bond, and decomposed to form an intractable solid.

Nitration of **P3HT** was conducted in the presence of fuming nitric acid (93% yield). After 2 h, no aromatic hydrogens were observed on the ^{1}H NMR spectrum of the product (Figure 1). ^{13}C NMR signals associated with aromatic carbons of **P3HT** disappeared, and four peaks in the aromatic region at 146.35, 139.97, 132.55, and 127.21 ppm were observed for the product (Figure 2). IR and elemental analysis confirmed the product to be poly(3-hexyl-4-nitrothiophene) (**P3H4NT**).

GPC-determined molecular weights for **P3B4HT** (M_n = 12 900 g/mol) and **P3C4HT** (M_n = 12 700 g/mol) are larger than the original polymer **P3HT** (M_n = 11 000 g/mol), indicating an increased radius of gyration of the derivatives. M_n for **P3H4NT** is however lower (8150 g/mol), for reasons that are not yet understood. The absorption and emission spectra of these polymers in THF solution are reported below. The absorption spectrum of **P3B4HT** exhibits a λ_{max} of 339 nm. This is much lower than that of **P3HT** (λ_{max} = 448 nm), indicating a shorter effective conjugation length. The bulky bromine atom has a repulsive effect on the sulfur atom of the neighboring thiophene ring that forces the polymer chain to be less coplanar. λ_{max} for **P3C4HT** (357 nm) was slightly less blue-shifted as a result of the smaller size of the chlorine atom compared to bromine. Emission spectra of **P3B4HT** and **P3C4HT** possessed a λ_{max} of 504 and 516 nm, respectively. The larger Stokes shift for **P3B4HT** (165 nm) and **P3C4HT** (159 nm) compared to **P3HT** ($\lambda_{em,max}$ 570 nm, Stokes shift 122 nm) reflects a more interannular twisted structure in the ground state.[11] The absorption spectrum of **P3H4NT** exhibits a λ_{max} of 338 nm, also indicating a highly sterically encumbered backbone. λ_{max} for fluorescence was 556 nm, which is surprisingly long given the absorption spectrum. The reason for this unusually large Stokes shift (218 nm) might be attributed to a difference in interaction between the planar nitro group and the thienyl ring in the ground and excited state. Detailed studies on electrooptical properties of these polymers are in progress.

In summary, we report a synthetically facile method to functionalize commercially available P3ATs by simple substitution at the 4-position with bromo, chloro, or nitro groups. Other electrophilic substitutions, e.g., sulfonation, acylation, alkylation, etc., are presently being investigated together with further derivatization of these polymers in order to achieve materials with a wide range of architecture and functionality from a single parent polymer. For instance, the 3-bromine in **P3B4H** could be readily substituted with phenyl, furan, thiophene, vinyl, and acetylene derivatives via Suzuki[12] or Stille[13] coupling reactions to further create a variety of novel 3,4-disubstituted poly(thiophene)s possessing a two- or three-dimensional conjugation system. These derivatized poly(thiophene)s may show some novel electrooptical properties and overcome the disadvantages of conventional poly(thiophene)s in some applications, e.g., their rather low quantum yield of luminescence when used as components in light-emitting diodes (LEDs).

Experimental Section. a. Measurements. The 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra were obtained in CDCl$_3$ on a 400 MHz Bruker AMX400 spectrometer; the chemical shifts are reported in ppm, referenced to CHCl$_3$ (δ 7.26) in ^{1}H NMR and CDCl$_3$ (δ 77.0) in ^{13}C NMR, respectively. IR spectra were recorded on a Bomen Michelson MB series spectrophotometer. UV−vis absorption spectra were obtained on a Cary 3E

(Varian) spectrophotometer. Fluorescence measurements were carried out on a PTI QuantumMaster model QM-1 spectrometer. Gel permeation chromatography (GPC) analysis of polymers was conducted on Waters model 510 HPLC equipped with μ-Styragel columns using tetrahydrofuran as an eluant with polystyrene as standards. Elemental analyses were performed by Canadian Microanalytical Service Ltd.

b. Materials. *N*-Bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), *N*-iodosuccinimide (NIS), and fuming nitric acid (>90%) were purchased from Aldrich and used as received. Chloroform was dried over CaH_2 and distilled prior to use. Regioregular poly(3-hexylthiophene) (**P3HT**) was prepared according to the method reported by McCullough et al.[14] ($M_n = 11\,000$, $M_w/M_n = 1.51$; head-to-tail diad content >95%).

Poly(3-bromo-4-hexylthiophene) (P3B4HT). To a flask containing **P3HT** (0.30 g, 1.81 mmol) in chloroform (20 mL) was added NBS (0.387 g, 2.17 mmol). The solution was stirred at room temperature for 15 h and heated at 50 °C for 2 h. The reaction mixture was then poured into a saturated $NaHCO_3$ solution (50 mL). The organic layer was washed with water five times and dried over $MgSO_4$. Precipitation into methanol gave a yellow solid (0.440 g, yield: 99% based on 100% substitution). GPC: $M_n = 12\,900$, $M_w/M_n = 1.53$. ^{1}H NMR: δ 2.71 (br, α-methylene), 1.60 (br), 1.33 (br), 1.28 (br), 0.87 (br, CH_3). ^{13}C NMR: 142.66, 130.38, 129.41, 115.81, 31.37, 30.40, 29.69, 29.44, 29.05, 22.56, 14.11. IR (KBr): 2954−2856, 1729, 1458, 1377, 1172, 1100, 817, 759 cm^{-1}. Elemental analysis: Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 50.07; H, 5.26; Br, 30.76; S, 12.92.

Poly(3-chloro-4-hexylthiophene) (P3C4HT). The reaction of **P3HT** (50 mg, 0.3 mmol) with NCS (48 mg, 0.36 mmol) was conducted in $CHCl_3$ (5 mL) at room temperature for 4 h. An orange-yellow solid (59 mg, yield: 98% based on 100% substitution) was obtained after work-up as described above. GPC: $M_n = 12\,650$, $M_w/M_n = 1.58$. ^{1}H NMR: δ 7.31 (minor), 5.02 (t, minor), 2.85 (minor), 2.72 (br, α-methylene), 2.10 (br, minor), 1.61 (br), 1.34 (br), 1.28 (br), 0.87 (t, CH_3). ^{13}C NMR: 143.07 (minor), 141.14, 138.22 (minor), 128.44, 127.90, 127.25 (minor), 126.49, 125.83 (minor), 56.83 (minor), 39.95 (minor), 31.40, 29.18, 29.04, 28.51, 22.54, 14.02. IR: 2955−2857, 1465, 1377, 1203, 756 cm^{-1}. Elemental analysis: Calcd for $C_{10}H_{13}ClS$: C, 59.84; H, 6.53; Cl, 17.66; S, 15.97. Found: C, 59.87; H, 6.63; Cl, 16.72; S, 15.92.

Poly(3-hexyl-4-nitrothiophene) (P3H4NT). To a **P3HT** solution (50 mg, 0.3 mmol in 5 mL of $CHCl_3$) in an ice water bath was added fuming HNO_3 (90%) (0.10 g, 1.5 mmol) dropwise, and the mixture was stirred for 2 h at 0 °C. A similar work-up procedure as described above afforded an orange-red solid (59 mg, yield: 93% based on 100% substitution). GPC: $M_n = 8150$, $M_w/M_n = 3.29$. ^{1}H NMR: δ 2.71 (br, α-methylene), 1.61 (br), 1.50 (br), 1.25, 0.87 (t, CH_3). ^{13}C NMR: 146.35, 139.97, 132.55, 127.21, 31.13, 30.20, 29.80, 29.06, 28.25, 22.37, 13.96. IR: 2955−2858, 1688, 1645, 1542, 1526, 1458, 1380, 1339, 782, 758 cm^{-1}. Elemental analysis: Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; O, 15.14; S, 15.18. Found: C, 57.27; H, 6.29; N, 5.62; O, 15.50; S, 14.77.

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