

The First Regioregular Head-to-Tail Poly(3-hexylthiophene-2,5-diyl) and a Regiorandom Isopolymer: Ni vs Pd Catalysis of 2(5)-Bromo-5(2)-(bromozincio)-3-hexylthiophene Polymerization

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Recent research on poly(alkylthiophenes) (PAT) has concentrated on the regularity and structure of the polymer chain of PAT.¹ The 3-alkyl substituent in a thiophene ring can be incorporated into a polymer chain with two different regioregularities: head-to-tail (HT) and head-to-head (HH) (see Figure 1a). Head-to-head linkages can cause defects in the polymer chain.^{1a,b,2d} The highest regioregularity reported to date for HT-PAT is 91% (usually 50–60% HT regioregularity).^{1a,2,5} We report herein a new and facile synthesis which leads to the first completely head-to-tail regioregular poly(3-hexylthiophene-2,5-diyl) (HT-PHT) and an alternative synthesis which yields an unusual regiorandom PHT with almost equal distribution of different linkages in the polymer chain. Both polymers have been characterized by NMR, IR, elemental analysis, GPC (gel-permeation chromatography), and UV-vis.

Highly reactive zinc³ was found to react chemoselectively with 2,5-dibromothiophene to yield quantitatively 2-(bromozincio)-5-bromothiophene. Significantly no bis(bromozincio)thiophene is formed. This organozinc intermediate is polymerized upon the addition of a catalytic amount of Pd(PPh₃)₄ (≤0.2 mol %) to give a quantitative yield of poly(thiophene-2,5-diyl).⁴ Addition of active zinc to 2,5-dibromo-3-hexylthiophene⁶ (1:1:1, 1 h, room temperature) in THF under argon gives a quantitative yield of the monoorganozinc thiophene with 90% regioselectivity (9:1, 2-bromo-5-(bromozincio)-3-hexylthiophene (2):2-(bromozincio)-5-bromo-3-hexylthiophene (3)). To this mixture (9:1, 2:3) was added Pd(PPh₃)₄ (0.2 mol %). Upon 4 h of refluxing at 67 °C, a quantitative polymerization to yield PHT (4) with a totally regiorandom structure in the polymer chain was obtained. Surprisingly, when the same organozinc intermediate mixture was polymerized with Ni(DPPE)Cl₂ (0.2 mol %) under identical conditions, a regioregular HT-PHT (5) was obtained, also in quantitative yield. The degree of regioregularity is a function of

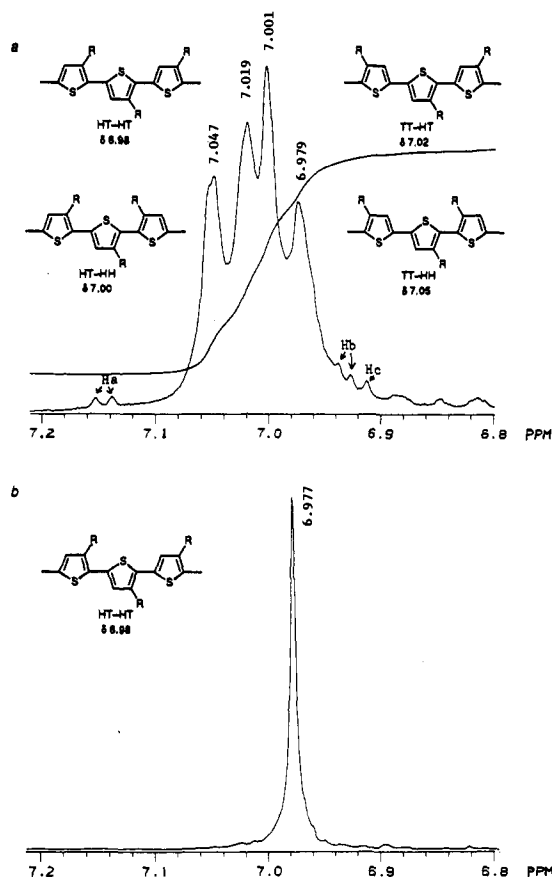


Figure 1. ¹H NMR spectra of (a) regiorandom (1:1:1:1, HT-HT:HT-HH:TT-HT:TT-HH) PHT and (b) regioregular (98.5 ± 1.5% of HT linkage) PHT. The literature assignments (below structures) are consistent with our assignments (above peaks). The structures in a and b show the different types of linkages. R = hexyl.

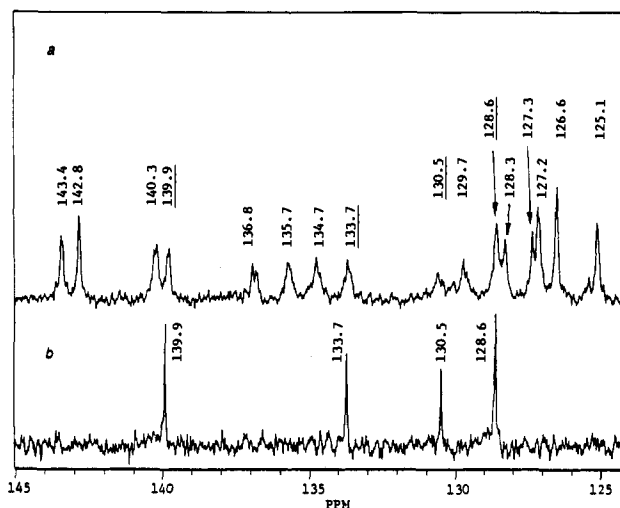


Figure 2. ¹³C NMR spectra of (a) regiorandom PHT (1:1:1:1, HT-HT:HT-HH:TT-HT:TT-HH) and (b) regioregular PHT (98.5 ± 1.5% of HT linkage). The literature assignments (refs 1b and 8b) are consistent with our assignments.

Table 1. Chemical Shift (ppm)

	C3	C4	C2	C5	H4
HT-HT	139.9	133.7	130.5	128.6	6.98
HT-HH	140.3	134.7	129.7	127.3	7.00
TT-HT	142.8	135.7	128.3	126.6	7.02
TT-HH	143.4	136.8	127.2	125.1	7.05

both the metal (Ni vs Pd) and the ligands on the metal. Use of Ni(PPh₃)₄ leads to much reduced regioregularity (65:35, HT:HH)

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compared to Ni(DPPE)Cl₂. However, Pd(DPPE)Cl₂ (70:30, HT:HH) was not nearly as effective as Ni(DPPE)Cl₂. The smaller ionic radius of Ni²⁺ vs Pd²⁺ along with the higher steric demands for DPPE indicate that the degree of stereoregularity is controlled by steric congestion of the reductive elimination step. This is further supported by the fact that **3** is apparently isomerized into **2** (by a series of transmetalation–reductive elimination followed by oxidative addition) faster than it is polymerized.

The ¹H and ¹³C NMR spectra of PHT provide sensitive probes of the substitution pattern in the polymer backbone. In a mixture of the four possible triad regioisomers (Figure 1a structures), all of the vinyl carbon atoms (16 peaks are theoretically possible) and all of the vinyl protons (4 total) can be resolved.^{1a,b,7} This is clearly demonstrated in the ¹H and ¹³C NMR spectra of **4** (Figures 1a and 2a). The observed spectra are consistent with a totally random (1:1:1:1, HT-HT:HT-HH:TT-HT:TT-HH linkages based on NMR integration) mixture of the four triad structures depicted.

In contrast, only one sharp band for the vinyl proton, which denotes the HT-HT structure, and four sharp bands for the vinyl carbon atoms (one band for each carbon), which also denotes the HT-HT structure, are observed in the ¹H and ¹³C NMR spectra of **5** (Figures 1b and 2b). The resolution and signal:noise ratio characterize **5** as pure HT-PHT (98.5 ± 1.5%). The two doublet peaks (7.15, 6.93 ppm) and one singlet peak at 6.91 ppm (Figure 1a) are assigned as the terminal ring protons Ha, Hb, and Hc of PHT.⁸

The molecular weights were determined by GPC (relative to polystyrene standard). Random PHT has $M_w = 2.44 \times 10^4$ and $M_n = 5.65 \times 10^3$, corresponding to a polydispersity index of 4.32. HT-PHT does not completely dissolve in THF at the same concentration; the soluble part has $M_w = 1.50 \times 10^4$. UV–vis data shows that HT-PHT has the longest wavelength of maximum absorption either in solution (CHCl₃, 456 nm) or in the solid state (film, 560 and 610 nm) when compared with the values of other PHT.^{1a,b,2b,9} This indicates that HT-PHT has the greatest effective conjugation length in the polymer chain, apparently due to complete head-to-tail regularity.¹⁰ Random PHT has maximum absorption with the relatively shorter wavelengths of 427 (CHCl₃) and 438 nm (film). The physical properties for the two polymers are quite different.¹¹

Neither regioregular HT-PHT, such as **5**, nor equally random PHT, such as **4**, has previously been reported.^{1a,b,2c} We expect the regioregular HT-PHT to have a large improvement not only in electrical conductivity but also in magnetic, nonlinear optical properties and other physical properties, and we are currently pursuing such characterizations. Likewise we are examining aspects of this polymerization which may explain the difference in control of regiochemistry observed in Ni and Pd catalysis.

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Supplementary Material Available: Synthetic procedures for **4** and **5**, ¹H and ¹³C NMR spectra, and tables of IR, GC, and elemental analysis data (9 pages). Ordering information is given on any current masthead page.

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(11) The solubility of random PHT in chloroform is at least 3 times greater than that of regioregular HT-PHT apparently due to the reduced crystallinity of the polymer chain. More interestingly, a film of the regular HT-PHT is gold-yellow in color, with a metallic luster and a strong fluorescence; the random polymer only forms a red-brown transparent film.

Generation and Reactivity of the First Mononuclear Early Metal Phosphinidene Complex, Cp*₂Zr=P(C₆H₂Me₃-2,4,6)

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The wide-ranging applications of metal carbenes (M=C) in organometallic chemistry¹ have spawned interest in transition metal complexes containing metal–heteroatom double bonds. While many metal–oxo and –sulfido systems are generally robust, recent work has shown that early metal systems containing metal–imido (M=NR),^{2–4} –oxo (M=O),^{5–8} and –sulfido (M=S)⁸ have a rich chemistry. Development of related early metal phosphinidene (M=PR) chemistry faces several obstacles. Firstly, synthetic routes to known phosphinidene complexes typically involve either use of metal complex anions or thermal degradation of coordinated phosphinidene precursors.⁹ Neither of these methods is amenable to early metals. A second problem is the propensity of phosphinidene moieties to bridge two or more metal centers. Thus, while V¹⁰ and Zr¹¹ phosphinidene-bridged complexes have been characterized, related mononuclear systems are unknown.¹² Herein, we describe the preparation of the primary phosphide complex Cp*₂Zr(PH(C₆H₂Me₃))₂ (**1**). This species is a synthon for a transient mononuclear Zr=PR moiety which reacts intramolecularly with sp³ C–H bonds, with P–H bonds or MeCN affording phosphametalloacycles.

The reaction of Cp*₂ZrCl₂ with 2 equiv of LiPH(C₆H₂Me₃) in benzene at 25 °C gave the wine-red diphosphido species **1**^{13,14} in 90% isolated yield. In the solid state the pseudotetrahedral zirconium center resides on a crystallographically imposed 2-fold

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(13) In all cases, C₆H₂Me₃ refers to the 2,4,6-trimethylphenyl substituent. NMR data (all recorded in C₆D₆ at 25 °C, δ (ppm) relative to TMS and 85% H₃PO₄ for ¹H and ³¹P data, respectively): **1**: ³¹P{¹H} NMR δ 39.0; ¹H NMR δ 6.91 (s, 4 H), 4.43 (d of m, 2 H, |J_{P-H}| = 268 Hz, |J_{P-H}| = 50 Hz), 2.73 (br s, 6 H), 2.60 (br s, 6 H), 2.26 (s, 6 H), 1.72 (s, 30 H). **2**: ³¹P{¹H} NMR δ -42.6; ¹H NMR δ 6.86 (s, 1 H), 6.73 (s, 1 H), 3.54 (d, 1 H, |J_{P-H}| = 180 Hz), 2.75 (s, 3 H), 2.26 (s, 3 H), 1.99 (d, 3 H, |J_{P-H}| = 4.5 Hz), 1.89 (s, 30 H). **3**: ³¹P{¹H} NMR δ 134.9; ¹H NMR δ 6.93 (s, 2 H), 6.73 (s, 2 H), 3.33 (s, 6 H), 2.29 (s, 6 H), 1.78 (s, 30 H), 1.24 (s, 6 H). **4**: ³¹P{¹H} NMR δ 0.2; ¹H NMR δ 6.89 (s, 2 H), 2.15 (s, 3 H), 1.99 (d, 3 H, |J_{P-H}| = 4.5 Hz), 1.89 (s, 30 H), 1.87 (br s, 6 H). **5**: ³¹P{¹H} NMR δ -71.9; ¹H NMR δ 6.88 (s, 1 H), 6.58 (s, 1 H), 5.36 (d, 1 H, |J_{P-H}| = 225 Hz), 2.29 (s, 3 H), 2.19 (s, 3 H), 2.08 (d, 3 H, |J_{P-H}| = 3.6 Hz), 1.76 (s, 15 H), 1.54 (s, 15 H), 1.26 (s, 2 H). **6**: ³¹P{¹H} NMR δ -30.1; ¹H NMR δ 6.80 (s, 4 H), 6.49 (s, 4 H), 3.03 (s, 6 H), 2.40 (s, 6 H), 2.07 (t, 6 H, |J_{P-H}| = 1.5 Hz), 1.99 (s, 30 H), 1.94 (s, 6 H). Satisfactory combustion analyses have been obtained for **1–6**.