A New Poly(3-alkylthiophene) Synthesis via Pd-Catalyzed Coupling of Thienyl Mercuric Chlorides

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A new coupling reaction based on the Pd-catalyzed reductive coupling of thienyl mercuric chlorides is described. A variety of substituted thiophenes react with $HgCl_2$ to produce thienyl mercuric chlorides. The degree of substitution can be controlled by the choice of temperature, solvent, and reaction time, and the resulting chloromercuri thiophenes or bis(chloromercuri)-thiophenes are stable to air and water. Heating the thienyl mercuric chlorides in pyridine solvent with Cu powder and $PdCl_2$ catalyst gave good yields of the coupled thiophenes. Poly(alkyl)thiophenes, poly(alkyl thienylacetate esters), and copolymers of alkylthiophenes with unsubstituted thiophene were formed in good yields. Molecular weights, M_w, were in the range 5300−83000. This coupling reaction was demonstrated to be compatible with the presence of an electrophilic substituent that is attacked by more nucleophilic intermediates, e.g., thienyllithium or thienyl Grignard reagents. Thus, this synthesis should be compatible with substituents known to be unreactive toward arylmercuric chlorides or arylpalladium compounds and is therefore complementary to the organometallic coupling schemes currently in use.

Introduction

Poly(alkylthiophenes)s, **PAT**s, have shown considerable promise for materials applications due to processibility and stability in both neutral and doped forms. The most widely studied monomers are the 3-alkylthiophenes, which give polymers soluble in common organic solvents (THF, $CHCl_3$, CH_2Cl_2, toluene) when the alkyl side chain, $R \geqslant Bu$. In general, syntheses of **PAT**s can be divided into two methods: oxidative coupling and organometallic coupling. Various features of these synthetic methods are discussed below.

Oxidative Coupling. Anodic electropolymerization of thiophenes can produce films of doped, high molecular weight ($n = 230$) polymer directly.[1] To obtain neutral polymer, chemical (e.g., N_2H_4) or electrochemical reduction must be employed. As the polymer grows, its oxidation potential drops, favoring chain growth,[2] but the selectivity for coupling at the α-position also decreases with increasing chain length, resulting in conjugation breaking $\alpha-\beta'$ couplings and/or cross-linking. A further complication arises due to the potentials required to oxidize the monomer: the growing polymer chains may be over oxidized and sulfur may be extracted from the ring.[3,4]

Monomers with strong electron-withdrawing groups (CO_2H, CHO, CN, NO_2) do not electropolymerize due to the high potentals required.[2] Electron-donating groups (SR, OR) overstabilize the radical cations, allowing them to diffuse away from the anode.[5] A wide variety of functional groups are tolerated, however, if they are electronically insulated from the thiophene ring by saturated carbon spacers: amides,[6] esters,[7] alkenes,[8] oligoethers,[9] viologen and ferrocene,[10] fluorine,[11] sulfonate esters,[12] bipyridyl,[13] benzoquinone,[14] and tetrathiafulvalene[15] are some examples.

Chemical oxidation of thiophene monomers with anhydrous $FeCl_3$ in chloroform produces doped polymers directly as insoluble powders.[16] Other oxidants, e.g., $Cu(ClO_4)_2$,[17] $AlCl_3$,[18] $MoCl_5$,[17] $RuCl_3$,[19] and AsF_3,[20] have been employed to a lesser extent. The undoped poly-

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mers are obtained by Soxhlet extraction (MeOH) or washing with aqueous N_2H_4.

Despite the ease of preparation, polymers produced by oxidative coupling are not so well-defined and usually contain impurities. Residual iron[18b,21] has been shown to catalyze the photodegradation of the polymer by O_2.[22] Chloride substitution has also been observed for hydroxyalkyl and alkyl ester side chains.[23] Additionally, 3-substituted thiophenes may undergo cross-linking by reaction at the 4-carbon.[24]

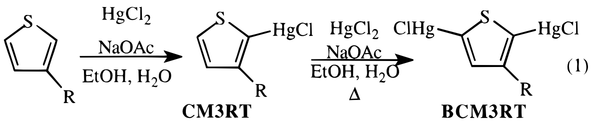
Recently, regioregular poly(3-R-thiophene)s (R = alkoxy, aryl) polymers have been obtained by the oxidative coupling route. The regiocontrol is provided by selective stabilization by the substituent of the positive charge of the radical cation at the end of the growing chain.[25,26]

Organometallic Coupling. To ensure all $\alpha-\alpha'$ linkages, monomers have been activated in the α-positions with different metals. A hybrid synthesis that gives polymers with fewer $\alpha-\beta'$ links involves the electrodesilylation of Me_3Si-capped monomers.[27,28] However, most organometallic syntheses have their origins in the 2,5-dihalothiophenes from which thienyllithium, -magnesium, -zinc, and -nickel intermediates can be generated. Thienyllithium monomers, prepared by lithium−halogen exchange[29] or deprotonation of the α-hydrogens,[30] have been coupled using $CuCl_2$. Transmetalation to bis(organostannyl)thiophenes has allowed the copolymerization with aryl iodides using the Stille reaction.[31] The coupling of thienyl Grignard reagents was reported by two research groups in 1980 using $M(acac)_n$ ($M = Ni^{2+}, Fe^{3+}, Co^{2+}$)[32] and $Ni(bipy)Cl_2$[33] as catalysts. Molecular weights were low and elemental analyses were poor, due to the insolubility of the materials. Soluble, stable polymers having alkyl side chains at the 3-position (**PAT**s) were announced a few years later.[34]

Using low temperatures and selective metalation, McCullough et al. recently prepared regioregular **PAT**s.[35] Another regioregular synthesis was discovered by coupling zinciobromothiophenes, formed from highly activated zinc and 2,5-dibromo-3-alkylthiophenes, with $Ni(dppe)Cl_2$.[36] The regioregularity was found to be critically dependent on catalyst: $Pd(PPh_3)_4$ gave completely random coupling. Increased crystallinity results from the combination of regular structure and more planar chains as a result of reduced torsion between adjacent rings (less steric crowding).[36] Increased crystallinity leads to closer interplanar spacing and higher conductivities.[37]

Yamamoto et al.[38] developed a coupling reaction based on the dehalogenation of aryl dihalides with Ni^0 complexes. The mechanism was shown to involve oxidative addition of the aryl halide to the Ni° species, followed by the rate-determining disproportionation to $NiAr_2$, and reductive elimination of the coupled product.[39] Ni^0, generated in situ from Zn and Ni^{2+}, has been used to dimerize chloroarenes having formyl, acyl, and nitrile substituents, and the synthesis of **PAT**s from 2,5-dichlorothiophene was reported.[40] Low molecular weight poly(methyl thienylcarboxylate) was made recently by this method.[41]

The mercuration of thiophene has been known for many years. Volhard demonstrated in 1892 that thiophene was mercurated by mercuric chloride in aqueous media under mild conditions (eq 1, R = H).[42] The substitution occurs exclusively α to the sulfur. Under more forcing conditions, both α-carbons are metalated.



$$2\,\mathrm{ArHgCl} + \mathrm{xs\ Cu} \xrightarrow[\text{pyr},\ 115^\circ\mathrm{C}]{\mathrm{PdCl_2}} \mathrm{Ar{-}Ar} + \mathrm{Hg} + \mathrm{CuCl} \qquad (2)$$

The demercuration of alkenyl- and arylmercurials produces 1,3-dienes and biaryls, often in high yield. Koton et al.[43] studied the effect of transition-metal powders on the production of biphenyl at elevated temperatures. Pd and Pt were found to have the highest acitivity. Several workers, attempting to couple ferrocene mercurials to biferrocenyl by this method,

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produced oligomers as side products.[44,45] Mercury elimination from ferrocenylmercury "polymers" was also reported to generate insoluble poly(ferrocenylene).[45]

This paper reports the development of a new chemical synthesis for polythiophenes based on the Pd-catalyzed coupling reaction of arylmercuric halides (eq 2), that

$$2\,\mathrm{ArHgCl} + \mathrm{xs\ Cu} \xrightarrow[\substack{\text{pyr}\\ 115\ ^\circ\mathrm{C}}]{\mathrm{PdCl_2}} \mathrm{Ar{-}Ar} + \mathrm{Hg} + \mathrm{CuCl} \qquad (2)$$

ensures α-α′ links while allowing the presence of electrophilic functional groups.[46] Though there have been many reports of coupling of arylmercurials with homogeneous catalysts, *no* polymers have been so produced.[47] A coupling based on chloromercuration was chosen because it is complementary to the chemical coupling reactions that involve strongly basic or nucleophilic reactants, e.g., organolithium or Grignard reagents. The latter attack electrophilic groups, e.g., esters, carbonyls, nitriles, etc., whereas these groups are inert toward organomercury derivatives. Furthermore, a wide variety of aryl and heteroaryl mercuric halides may be prepared readily, and they are often stable to air and water.[48] We have also modified this coupling reaction to insert carbon monoxide, thus giving a new class of poly(thienyl ketone)s.[46,49]

Experimental Section

General Considerations. All polymerization reactions were performed under nitrogen on a Schlenk line. Pyridine was freshly distilled from CaO under nitrogen before use. Reagents were purchased and used as received unless specified otherwise: thiophene, 3-methylthiophene (Aldrich); ethyl 3-thienylacetate (**ETA**), 3-bromothiophene (Lancaster); $PdCl_2$, $Ni(dppp)Cl_2$ (Strem).

^1H and ^{13}C NMR spectra were collected on a Brüker AM-500, AM-360, AM-300, or AM-200 and referenced to the residual proton solvent resonance. IR spectra were collected on a Nicolet DX-5B and were corrected for background and solvent absorbtion. UV–vis spectra were collected on a Shimadzu 3101PC with baseline correction. Fluorescence spectra were collected on a Shimadzu RF-5000 spectrofluorophotometer. GC-MS analyses were obtained on a capillary column interfaced with a Finnigan mass spectrometer. Mass spectra were collected on a VG 70-250-S high resolution spectrometer. Scanning electron micrographs (SEM) were imaged on a Hitachi S-570 using graphitized powder samples. Energy-dispersive analysis of X-rays (EDAX) was taken with a Kevex 8000 instrument. Elemental analyses were performed by Galbraith Laboratories or the University of Michigan Microanalysis Laboratory.

Molecular weights were determined by gel permeation chromatography (GPC) at 23 °C using a Waters 6000A solvent delivery system and Model 440 detector at 254 nm. A series of three μ-Styragel columns of pore sizes 500, 10^3, and 10^4 Å were utilized and calibrated with narrow molecular weight polystyrene standards.

Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer 7 apparatus. Cyclic voltammetry (CV) was performed with a Princeton Applied Research Model 173 galvanostat/potentiostat. Electrical conductivities of thin films were measured by the four-point probe technique,[50] whereas two-point probe measurements were made on insoluble powders that were pressed into pellets. Film thicknesses were determined by profilometry on a Sloan Dektak II.

Monomer Syntheses. Preparation of 3-Alkylthiophenes. The monomers, 3-butylthiophene and 3-octylthiophene, were prepared by a published procedure (Ni-catalyzed coupling of the alkyl Grignard with 3-bromothiophene).[51] **R = Oct, 3OT:** yield 71%. GC-MS (EI, 70 eV; *m/z*) 196, $[M]^+$; 111, $[M - C_6H_{13}]^+$; 97, $[M - C_7H_{15}]^+$. ^1H NMR ($CDCl_3$) δ 7.19 (dd, 1H, H5, J = 4.9, 2.9 Hz); 6.90 (dd, 1H, H4, J = 4.9, 1.2 Hz); 6.88 (dd, 1H, H3, J = 2.9, 1.2 Hz); 2.60 (t, 2H, H_α); 1.61 (p, 2H, H_β); 1.27 (m, 10H, $(CH_2)_5$); 0.88 (t, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 143.2; 128.2; 125.0; 119.7; 31.9; 30.6; 30.3; 29.7; 29.5; 29.4; 22.7; 14.1.

Preparation of Hexyl 3-Thienylacetate (HTA). Ethyl 3-thienylacetate (15.0 mL, 0.100 mol), hexyl alcohol (30 mL, 0.239 mol), toluene (30 mL), and sulfuric acid (3 drops) were added to a 100 mL three-neck flask. A still head, condenser, receiving flask, and N_2 bubbler were connected, and the system was flushed with nitrogen. The pot was heated in an oil bath (120 °C) while a slow purge of N_2 from a small needle was swept through the system. Liquid began to condense after an hour (vapor temperature 70 °C). After 4 h, GCMS revealed the presence of product and the absence of starting material. The toluene was removed under vacuum at 50 °C and the mixture of product and hexyl alcohol was distilled using a short-path condenser under reduced pressure (2 mmHg). The third fraction, collected at 125–132 °C, was the product; yield 20.5 g, 91%. Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02. Found: C, 63.52; H, 8.06. GC-MS (EI, 70 eV; *m/z*) 226, $[M]^+$; 142, $[M - C_4H_4S]^+$; 97, $[M - C_7H_{13}O_2]^+$. Bp 130–132 °C at 2 mmHg. Density 1.04 g/mL (18 °C). IR (neat, cm^{-1}) $\nu_{C=O}$ 1737. ^1H NMR ($CDCl_3$) δ 7.27 (dd, 1H, H5, J = 4.9, 3.1 Hz); 7.14 (dd, 1H, H2, J = 3.1, 1.2 Hz); 7.04 (dd, 1H, H4, J = 4.9, 1.2 Hz); 4.09 (t, 2H, H8); 3.64 (s, 2H, H6); 1.61 (p, 2H, H9); 1.28 (m, 6H, H10–H12); 0.88 (m, 3H, H13). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.0, C=O; 133.9, C3; 128.5, ring; 125.5, ring; 122.7, ring; 65.0, C8; 36.0, C6; 31.4, C9; 28.6, C10; 25.5, C11; 22.4, C12; 13.8, C13.

Preparation of 2,5-Bis(chloromercuri)-3-alkylthiophene (BCM3RT). R = H, BCMT: Thiophene was mercurated according to the method of Volhard.[42] The white solid was dried in air, then under vacuum; yield 81%. ^1H NMR (pyridine-d_5) δ 7.72 (s, 1H, ring). $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ 134.3. Anal. Calcd for $C_4H_2Cl_2Hg_2S$: C, 8.67; H, 0.36. Found: C, 8.66; H, 0.35. MS (EI, 70 eV; *m/z*) 554, $[M]^+$; 519, $[M - Cl]^+$; 272, $[HgCl_2]^+$; 237, $[HgCl]^+$; 202, $[Hg]^+$. **R = Me, BCM3MT:** Prepared as for **BCMT** from 3-methylthiophene;[42] yield 86%. IR (KBr; cm^{-1}) 3057 (w), 2918 (m), 1447 (m), 1379 (m), 1189 (m), 845 (s), 474 (vs), 419 (s). ^1H NMR (pyridine-d_5) δ 7.50 (s, 1H, ring); 2.44 (s, 3H, CH_3). Anal. Calcd for $C_5H_4Cl_2Hg_2S$: C, 10.57; H, 0.71. Found: C, 10.70; H, 0.56. MS (EI, 70 eV; *m/z*) 568, $[M]^+$; 533, $[M - Cl]^+$; 333, $[M - HgCl]^+$; 272, $[HgCl_2]^+$; 237, $[HgCl]^+$; 202, $[Hg]^+$. **R = Bu, BCM3BT:** Prepared as for **BCMT** from **3BT** with a longer reflux time (3 h); yield 90%. IR (KBr; cm^{-1}) 3057 (vw), 2951 (m), 2927 (m), 2866 (m), 1463 (m), 938 (w), 865 (m), 481 (m). ^1H NMR (pyridine-d_5) δ 7.52 (s, 1H, ring); 2.87 (t, 2H, H_α); 1.66 (p, 2H, H_β); 1.23 (sextet, 2H, H_γ); 0.76 (t, 3H, H_δ). $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ 150.6, 148.5, 136.2; 34.3 (C_α); 34.0 (C_β); 22.6 (C_γ); 14.1 (C_δ). Anal. Calcd for $C_8H_{10}Cl_2Hg_2S$: C, 15.74; H, 1.65. Found: C, 14.72; H, 1.36. MS (EI, 70 eV; *m/z*) 610, $[M]^+$. **R = Oct, BCM3OT:** Prepared by stirring **3OT** (5.00 g, 25.4 mmol), mercuric chloride (15.570 g, 57.3 mmol), and sodium acetate (11.472 g, 0.14 mol) in EtOH (225 mL) at 45 °C for 9 h. The solution was filtered warm, and the precipitate was washed with hot EtOH and water; yield 9.85 g, 58%. IR (KBr; cm^{-1}) 3058, 2953, 2946, 2924, 2851, 1465, 867, 725. ^1H NMR (pyridine-d_5) δ 7.19 (s, 1H, ring); 2.92 (t,

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2H, H_α); 1.74 (m, 2H, H_β); 1.18 (m, 10H); 0.81 (t, 3H, Me). Anal. Calcd for $C_{12}H_{18}Cl_2Hg_2S$: C, 21.62; H, 2.72. Found: C, 21.78; H, 2.63.

Preparation of Ethyl 3-(2,5-Bis(chloromercuri)thienyl)acetate (BCMETA). A solution of mercuric chloride (500 mL), sodium acetate (100 mL, 33%), ethanol (100 mL), and **ETA** (5.69 g, 33.4 mmol) were stirred in a 1 L three-neck flask (2 h). The cloudy solution was then refluxed (1 h). The suspension was cooled to room temperature, filtered through a Fritte, washed with water, and air-dried; crude yield 21.5 g. Traces of the more soluble monomercurated byproduct were removed from the crude material by twice suspending it in hot ethanol (250 mL) and filtering the hot suspension. The collected solid was dried in vacuo; yield 21.2 g, 99%. IR (KBr; cm^{-1}) $\nu_{C=O}$ 1712(s). Anal. Calcd for $C_8H_8Cl_2Hg_2O_2S$: C, 15.01; H, 1.26. Found: C, 14.87; H, 1.07. MS (EI, 70 eV; *m/z*) 640, $[M]^+$; 567, $[M - C_3H_5O_2]^+$; 272, $[HgCl_2]^+$; 237, $[HgCl]^+$; 202, $[Hg]^+$. ^1H NMR (pyridine-d_5) δ 7.74 (s, 1H, H4); 4.03 (q, 2H, H8); 4.00 (s, 2H, H6); 1.05 (t, 3H, H9).

Preparation of Hexyl 3-(2,5-Bis(chloromercuri)thienyl)acetate (BCMHTA). **HTA** (2.0 mL, 9.16 mmol) was added to a solution of mercuric chloride (100 mL, saturated), sodium acetate (25 mL, 33%), and ethanol (200 mL) which had been clarified by the addition of 2 mL of acetic acid. The mixture was stirred (2 weeks), and the white precipitate was filtered through a Fritte, washed with water and ethanol, and air-dried. The solid was suspended in hot ethanol and filtered. The vacuum-dried product yield was 3.17 g, 50%. Anal. Calcd for $C_{12}H_{16}Cl_2Hg_2O_2S$: C, 20.69; H, 2.32. Found: C, 19.89; H, 2.20. MS (DCI-EI, 70 eV; *m/z*) 696, $[M]^+$; 567, $[M - C_7H_{13}O_2]^+$; 272, $[HgCl_2]^+$; 237, $[HgCl]^+$; 202, $[Hg]^+$. IR (KBr; cm^{-1}) 3059 (vw), $C-H_\beta$; 1718 (s), C=O. ^1H NMR (pyridine-d_5) δ 7.76 (s, 1H, H4); 4.05 (t, 2H, H8); 4.04 (s, 2H, H6); 1.49 (p, 2H, H9); 1.10 (m, 6H, H10−H12); 0.77 (m, 3H, H13). $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ 172.0, C=O; 140.0, C3; 136.9, C4; 65.1, C8; 39.3, C6; 31.6, C9; 28.9, C10; 25.8, C11; 22.8, C12; 14.2, C13.

Preparation of 2-(Chloromercuri)-3-alkylthiophene (CM3RT). (a) R = H, **CMT:** Prepared according to the method of Steinkopf;[52] yield 69%. Anal. Calcd for C_4H_3ClHg: C, 15.05; H, 0.95. Found: C, 14.92; H, 0.93. IR (KBr; cm^{-1}) 3095 (w), 3073 (vw), 3063 (vw), 1392 (m), 1213 (m), 843 (m), 710 (s), 466 (m). ^1H NMR (acetone-d_6) δ 7.76 (dd, 1H, H5, J = 4.9, 0.9 Hz); 7.34 (dd, 1H, H4, J = 3.4, 4.9 Hz); 7.26 (dd, 1H, H3, J = 3.4, 0.9 Hz); plus ^{199}Hg couplings. $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 145.9; 135.3; 129.9; 127.4. (b) R = Me, **CM3MT:** Prepared according to the method of Steinkopf;[52] yield 67%. IR (KBr; cm^{-1}) 3093 (w), 3061 (w), 2914 (m), 1519 (m), 1441 (m), 1380 (m), 877 (m), 826 (m), 721 (s), 590 (m), 468 (m). ^1H NMR (acetone-d_6) δ 7.54 (d, 1H, H5, J = 4.8Hz); 7.14 (d, 1H, H4, J = 4.8 Hz); 2.37 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 143.5; 130.7; 130.1; 18.5.

Preparation of Ethyl 2-(Chloromercuri)-3-thienylacetate (CMETA). A solution of mercuric chloride (400 mL, saturated), sodium acetate (100 mL, 33%), ethanol (250 mL), and ethyl 3-thienylacetate (5.0 mL, 33.4 mmol) was stirred at room temperature (5 days). The white solid precipitate was collected in a Fritte, washed with water, and air-dried. The solid was suspended in hot ethanol (250 mL) and filtered through a Fritte. Cooling the filtrate to 0 °C yielded white needles of **CMETA**. The crystals were filtered, washed with water, and air-dried. Addition of water to the mother liquor yielded a second crop upon cooling to 0 °C; Total crude yield 4.73 g. The ethanol-insoluble material was the 2,5-dimercurated compound.

The crude **CMETA** was dissolved in acetone, filtered through Celite (2 cm) in a Fritte, and cooled (0 °C) to yield white needles. A second crop was obtained by addition of water and cooling to 0 °C; total yield 4.28 g, 32%. Anal. Calcd for $C_8H_9ClHgO_2S$: C, 23.71; H, 2.24. Found: C, 23.49; H, 2.04. MS (EI, 70 eV; *m/z*) 406, $[M]^+$; 333, $[M - C_3H_5O_2]^+$; 298, $[M - Cl - C_3H_5O_2]^+$. IR (KBr; cm^{-1}) ν_{CO} 1715(s). ^1H NMR (acetone-d_6) δ 7.63 (d, 1H, H5, $^4J_{H-Hg}$ = 73 Hz, $^3J_{H4-H5}$ = 4.9 Hz); 7.28 (d, 1H, H4, $^4J_{H-Hg}$ = 40 Hz, $^3J_{H4-H5}$ = 4.9 Hz); 4.13 (q, 2H, H8, $^3J_{H8-H9}$ = 7.1 Hz), 3.80 (s, 2H, H6, $^4J_{H-Hg}$ = 17 Hz); 1.24 (t, 3H, H9, $^3J_{H8-H9}$ = 7.1 Hz). $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 172.4, C=O; 140.4, C3; 130.5, C4/5; 130.1, C4/5; 61.5, CH_2CH_3; 38.1, CH_2; 14.4, CH_3.

Analysis of Arylmercurials. An adaptation of a mercury−carbon bond cleavage reaction[53] was used to selectively replace an HgX group with a chlorine atom to give volatile derivatives that could be analyzed by GCMS. To a small Erlenmeyer flask (25 mL) with stir bar, 0.1 g of mercurial and 0.1 g anhydrous $CuCl_2$ were added. Dry CH_3CN (5−10 mL) was added, and the flask connected to an N_2 bubbler. The cloudy brown solution became clear dark brown as it was refluxed (30 min). The solution was pipetted into a test tube, diluted with 10 mL of ether, and shaken with NH_4OH (15%, 2 × 10 mL). The ether layer was dried over Na_2SO_4 and a GC-MS analysis of the solution was run. With this procedure, the chloro derivatives reliably reflected the original mercurial substitution pattern, and the method proved effective for all the thiophene mercurials tested. However, for more electron rich systems (e.g., 1,4-bis(alkoxy)phenyl), some chlorine substitution for H in addition to the desired Cl/HgX exchanges have been observed.

Polymer Syntheses. Preparation of Poly(3-butylthiophene) (P3BT). **BCM3BT** (10 g, 16.38 mmol), Cu powder (4.17 g, 65.5 mmol), and $PdCl_2$ (0.200 g, 1.13 mmol; 7 mol %) were added to a 250 mL Schlenk flask which was then evacuated and backfilled with nitrogen three times. Pyridine (200 mL) was transferred via cannula into the flask, and the mixture was refluxed under nitrogen (15 h). The solution became green and then golden orange. The hot solution of product was filtered through Celite (3 cm) in a Fritte, trapping the excess Cu and the formed Hg. The Celite was washed with THF (100 mL). To help remove Cu^+, NH_4OH (15%, 500 mL) was added and the mixture was shaken in a separatory funnel with benzene (400 mL). The benzene layer was collected and shaken with more NH_4OH (15%, 2 × 250 mL), HCl (3 M, 4 × 250 mL), $NaHCO_3$ (saturated, 250 mL), and brine (250 mL). The benzene was removed in vacuo.

The residue was dissolved in THF (100 mL) and added to MeOH (1 L) with stirring. The fluffy orange precipitate was collected on a Fritte, washed with MeOH until the washings were colorless, and dried in vacuo. In a Soxhlet extractor, the solid was washed with acetone until the washings were colorless (24 h). Chloroform was used to wash the polymer from the thimble, and the solution was filtered through Celite to remove a fine black precipitate. The solvent was removed in vacuo. The residue was redissolved in THF (30 mL) and dripped into MeOH (800 mL) forming a flaky, orange precipitate. The solid was collected on a Fritte, washed with MeOH, and dried in vacuo with heating briefly to 130 °C, giving a dark orange-red solid; yield 1.86 g, 78%. ^1H NMR ($CDCl_3$) δ 7.06, 7.03, 7.01, 6.98 (1H, ring); 2.79, 2.58 (2H, H_α); 1.68, 1.61 (2H, H_β); 1.45, 1.37 (2H, H_γ); 0.97, 0.90 (3H, H_δ).

A second run yielded 1.43 g of P3BT (63%) after drying. Anal. Calcd for $(C_8H_{10}S)_n$: C, 69.51; H, 7.29; S, 23.20. Found: C, 69.34; H, 7.24; S, 24.04; Cl, 0.047%; Hg, <0.08%; Cu, <0.004%. UV ($CHCl_3$) λ_{max} = 434 nm, ϵ = 8270 L/mol cm. UV(film) λ_{max} = 445 nm. Fluorescence ($CHCl_3$) em max = 550 nm. GPC (THF, 1 mL/min; UV) M_n = 10828, M_w = 26912; PDI = 2.48. Conductivity (I_2-doped film) 0.59 S/cm.

Preparation of Poly(3-octylthiophene) (P3OT). Prepared as for **P3BT** using **BCM3OT**; yield 90%. GPC (THF, 1 mL/min; UV) M_n=3270, M_w = 8500; PDI = 2.6 . ^1H NMR ($CDCl_3$) δ 7.06, 7.02, 7.00, 6.97 (1H, ring); 2.77, 2.58 (2H, H_α); 1.68 (2H, H_β); 1.28 (10H); 0.88 (3H, Me). UV ($CHCl_3$) λ_{max} = 421 nm, ϵ = 6160 L/mol cm. UV (film) λ_{max} = 445 nm. Fluorescence ($CHCl_3$) em max = 557 nm. Conductivity (I_2-doped film) 0.011 S/cm.

Preparation of Poly(ethyl 3-thienylacetate) (PETA). **BCMETA** (5.0 g, 7.81 mmol), Cu powder (2.16 g, 34.0 mmol), and $PdCl_2$ (0.13 g, 0.73 mmol) were placed in a 200 mL Schlenk flask which was evacuated and backfilled with nitrogen three

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(52) Steinkopf, W.; Bauermeister, M. *Ann. Chem.* **1914**, *403*, 50−72.

(53) Nefedov, V. A. *J. Gen. Chem. USSR* **1969**, *39*, 630.

times. Pyridine (150 mL) was transferred into the flask via cannula and the mixture was refluxed under nitrogen (18 h). The mixture became golden brown. The cooled solution was filtered through a Fritte filled with Celite (3 cm) and washed with CH_2Cl_2 until the filtrate was colorless. The combined filtrate was shaken with brine (250 mL) and NH_4OH (10%, 2 × 250 mL), causing the organic layer to turn light tan. The solution was shaken with HCl (10%, 3 × 250 mL), causing the organic layer to return to darker brown. The solution was shaken with $NaHCO_3$ (saturated, 250 mL) and brine (250 mL). The solvent was removed in vacuo.

The residue was dissolved in THF (25 mL) and dripped into MeOH (1 L) causing an orange precipitate to form. The solid was collected on a Fritte and washed with MeOH. The orange solid was air-dried. The polymer was reprecipitated by dissolving it in a warm (60 °C) mixture of *N*-methylpyrrolidinone (NMP) and $CHCl_3$ (1:1, 150 mL), removing most of the $CHCl_3$ in vacuo, and dripping the solution into MeOH (800 mL) and H_2O (200 mL). The red precipitate was collected on a Fritte, washed with MeOH, and dried in a vacuum oven overnight (75 °C); yield 0.73 g, 56%. IR (KBr; cm^{-1}) $\nu_{C=O}$ 1734(s). GPC (THF, 1 mL/min; UV) $M_n = 7014$, $M_w = 20016$; PDI = 2.85. Anal. Calcd for $(C_8H_8O_2S)_n$: C, 57.12; H, 4.79; S, 19.06; Cl, 0; Hg, 0; Cu, 0. Found: C, 56.48; H, 4.39; S, 18.54; Cl, 0.15; Hg, 0.19; Cu, 0.041. ^1H NMR ($CDCl_3$) δ 7.20, 7.18, 7.12, 7.08 (1H, ring); 4.18 (m, 2H, α-CH_2); 3.78, 3.61 (m, 2H, CH_2CH_3); 1.28 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.2; 61.1; 35.2; 14.2. Conductivity ([NO](BF_4) doped powder) 10^{-8} S/cm.

Preparation of Poly(hexyl 3-thienylacetate) (PHTA). **BCMHTA** (2.905 g, 4.17 mmol), Cu powder (1.60 g, 25.2 mmol), and $PdCl_2$ (0.089 g, 0.502 mmol; 12 mol %) were placed in a 250 mL Schlenk flask and evacuated/backfilled with nitrogen three times. Pyridine (100 mL) was transferred via cannula into the flask, and the mixture was refluxed under nitrogen (18 h). The solution became green and then golden brown. The cooled solution of product was filtered through a pad of Celite (4 cm) that was wet with CH_2Cl_2 in a Fritte, trapping the excess Cu and the formed Hg. The Celite was washed with CH_2Cl_2 until the filtrate was colorless. The solution was shaken with NH_4OH (15%, 3 × 250 mL) in a separatory funnel, causing the solution to become light tan and opaque. The organic layer was collected and shaken with HCl (3 M, 3 × 250 mL), which caused the solution to clear and return to a darker brown. After drying with brine and Na_2SO_4, the solvent was removed in vacuo. The dark brown residue was dissolved in a minimum amount of warm THF (15 mL) and dripped into MeOH (500 mL). The dark red precipitate was stirred (2 h) and filtered through a Fritte, washed with MeOH, and vacuum-dried overnight. Reprecipitation by a similar procedure yielded 0.59 g (63%) of the dark, elastic material. Anal. Calcd for $(C_{12}H_{16}O_2S)_n$: C, 64.25; H, 7.19; N, 0. Found: C, 60.97; H, 6.86; N, 0.54. GPC (THF, 1 mL/min; UV): $M_n = 18\ 240$, $M_w = 83091$; PDI = 4.56. ^1H NMR ($CDCl_3$) δ 7.17 (br, 1H, ring); 4.12 (br, 2H, CH_2); 3.78, 3.6 (br, 2H, α-CH_2); 1.28 (br, 6H, $(CH_2)_3$); 0.86 (br, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 65.3; 31.4; 28.5; 25.5; 22.5; 14.0. UV ($CHCl_3$) $\lambda_{max} = 389$ nm, $\epsilon = 4700$ L/mol cm.

Preparation of Poly(3-octylthiophene-*co*-thiophene) (P3OT/T). The polymerization of **BCM3OT** was run as for **P3BOT** with varying amounts of **BCMT**. The copolymers were metallic-green solids which formed red solutions. IR (film, cm^{-1}) 3065, 2952, 2924, 2854, 1497, 1462, 1258, 822, 794. ^1H NMR ($CDCl_3$) δ 7.06 (s), 7.01 (s), 6.97 (s), 6.93 (s), 6.90 (s) ring; 2.77, 2.58 (br, 2H); 1.67 (br s, 2H); 1.29 (s, 10H); 0.89 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.90, 30.52, 29.56, 29.44, 29.28, 22.69, 14.12. Further properties of these copolymers are shown in Tables 1 and 2.

Preparation of Poly(3-butylthiophene-*co*-3-methylthiophene) (P3BT/3MT). Prepared as for **P3BT** with **BCM3MT** (1.057 g, 1.86 mmol), **BCM3BT** (4.072 g, 6.67 mmol), Cu (2.562 g, 40.3 mmol), and $PdCl_2$ (0.193 g, 1.1 mmol) in refluxing pyridine (200 mL, 15 h). After the usual workup, the copolymer was precipitated in MeOH from a THF solution and dried in vacuo; yield 1.00 g, 91%. GPC (THF, 1 mL/min; UV) $M_n = 1730$, $M_w = 5290$; PDI = 3.06. ^1H NMR ($CDCl_3$) δ 7.03 (s), 6.98 (s), 6.90 (s) ring; 2.78, 2.62 (br, α-CH_2); 2.43, 2.25 (m, Me); 1.67 (br, 2H); 1.43 (br, 2H); 0.95 (m, 3H). Conductivity (I_2-doped film) 0.08 S/cm.

Poly(3-butylthiophene-*co*-ethyl 3-thienylacetate) (P3BT/ ETA). Prepared as for **P3BT** with **BCMETA** (1.075 g, 1.55 mmol), **BCM3BT** (2.038 g, 3.34 mmol), Cu powder (1.33 g, 20.9 mmol), and $PdCl_2$ (0.192 g, 1.08 mmol) in refluxing pyridine (150 mL, 18 h). After the usual workup, the orange-red copolymer was precipitated in MeOH from a THF solution and dried in vacuo; yield 0.60 g, 60%. Anal. Calcd for $C_{24}H_{28}S_3O_2$: C, 64.83; H, 6.35. Found: C, 64.72; H, 6.22. IR (film, cm^{-1}) 3060, 2956, 2929, 2858, 1736, 1260, 1032. GPC (THF, 1 mL/min; UV) $M_n = 3300$, $M_w = 24\ 000$; PDI = 7.4. ^1H NMR ($CDCl_3$) δ 7.11 (s), 7.06 (s), 7.03 (s), 7.01 (s), 6.98 (s) ring; 4.21 (m, CH_2CH_3 from ester); 3.79, 3.61 (m, α-CH_2 from ester); 2.79, 2.57 (br, α-CH_2 from Bu); 1.67, 1.60, 1.43, 1.29, 0.93 (br). UV ($CHCl_3$) $\lambda_{max}(\epsilon) = 421$ nm (6580 L/mol cm). Conductivity ([NO][BF_4]-doped powder) 2×10^{-6} S/cm.

Model Coupling Reactions. Coupling of CMT and CM3MT with Cu. Equimolar amounts of **CMT** (2.00 g, 6.3 mmol) and **CM3MT** (2.08 g, 6.3 mmol) were dissolved in pyridine mixed with Cu powder (3.17 g, 50.2 mmol) and $PdCl_2$ (0.07 g, 0.40 mmol). The coupling reaction was run, and the product analyzed by GC-MS, revealing a statistical distribution of T-T, 3MeT-T, and 3MeT-3MeT dimers.

Results and Discussion

Mercuration Reactions. Thiophene and 3-alkylthiophenes were conveniently mercurated by adaptations of Volhard's original method (eq 1).[42] The degree of substitution was controlled by limiting the solubility of intermediates with the choice of temperature and solvent mixture. Good yields of 2-(chloromercuri)-3-alkylthiophenes (**CM3RT**; R = H, Me, CH_2CO_2Et), useful for model reactions, were obtained at room temperature. Over the course of several days, the white products precipitated from solution. The crude products were suspended in hot solvent (benzene or acetone) and the insoluble dimercurials removed by filtration. Cooling the filtrate gave the pure product as white plates.

Good yields of 2,5-bis(chloromercuri)-3-alkylthiophenes (**BCM3RT**; R = H, Me, Bu, Oct, CH_2CO_2Et, CH_2CO_2-Hex) were obtained when intermediate **CM3RT** were kept in solution by heat or additional ethanol. The mercuration of **3OT** was run in neat EtOH at 50 °C because **3OT** is immiscible with an aqueous solvent mixture. The **BCM3RT** were purified by extracting the residual **CM3RT**, leaving pure bis(mercurial) as fairly insoluble white powders that dissolve sparingly only in pyridine, nitrobenzene, or nitromethane. Care was taken to prevent polymercuration as the insolubility of trimercurials closely mimics that of **BCM3RT**.

Characterization. For **BCM3RT**, IR spectroscopy (KBr) confirmed the exclusive 2,5-substitution. The α-CH stretches ($\approx$3095 cm^{-1}) present in **CMRT** are absent. Only β-CH stretches ($\approx$3060 cm^{-1}) are seen. ^1H and ^{13}C NMR of **CM3RT** proved helpful for characterization, although signals due to carbon atoms bearing a chloromercury group were seldom observed. Coupling of ^1H and ^{13}C to ^{199}Hg ($S = {}^1/_2$, 16.9% abundant) was seen ($^3J_{H-Hg} \approx 120$ Hz, $^4J_{H-Hg} \approx 20-80$ Hz, $^3J_{C-Hg} \approx 35$ Hz).[54] **BCM3RT**, however, undergoes partial disproportionation in pyridine, our solvent of choice for the NMR spectra (eq 3).[55] Consequently, the NMR spectra

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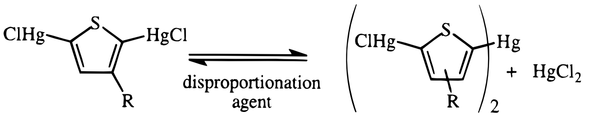
(54) Bulman, M. J. *Tetahedron* **1969**, *25*, 1433−1439.

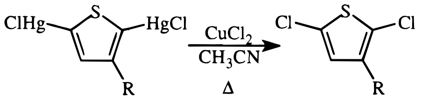
(55) Makarova, L. G. In *Organometallic Reactions*; Becker, E. I., Tsutsui, M., Eds.; Wiley-Interscience: New York, 1971; Vol. 2, pp 335−423.

show resonances for the disproportionation products in addition to those expected for **BCM3RT**.



(3)

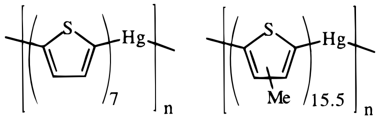
Mercuration Assay Reaction. A method was sought that would cleanly replace chloromercury groups with a halogen to give a volatile, stable compound that could be easily analyzed by GCMS. Aqueous triiodide nicely produced aryl iodides,[42] but they are somewhat reactive and not very volatile. Bromine was too reactive and cleaved C−H bonds as well as the C−Hg bonds, thereby overestimating the extent of mercurial substitution. The method of choice proved to be chloride substitution with anhydrous cupric chloride in hot, dry acetonitrile (eq 4).[53] No substitution of chlorine for hydrogen was observed; and the number of chlorine atoms was clearly evident from the $^{35}Cl/^{37}Cl$ isotope distribution pattern of the parent ion in the GCMS spectrum. Isomers could be distinguished by the fragmentation pattern. The 2,5-dichloro-3-alkylthiophenes all showed a parent ion, and the base peak appeared at $m/z = 165$ as a result of fragmentation and ring expansion.[56] The isomeric 2,4-dichloro-3-alkylthiophenes also showed the parent ion, but in this case the base peak was due to loss of all but *two* methylene units of the alkyl side chain ($m/z = 179$). The 2,4-bis(chloromercuri)-3-alkylthiophenes were removed by extraction along with the monomercurials.



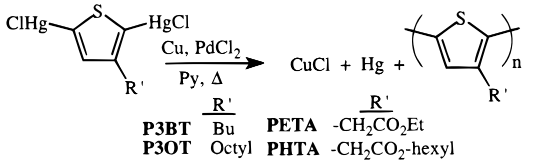
(4)

Homopolymers. The insolubility of the chloromercury monomers in most solvents restricted the choice of the polymerization solvent to pyridine. The monomers, **BCMT** and **BCM3MT**, gave insoluble red powders (**PT** and **P3MT**, respectively) upon catalytic demercuration. The IR spectra of these polymers showed no peaks due to C_α−H stretches at ∼3100 cm^{-1}; instead the C_β−H vibrations at ∼3060 and 780−830 cm^{-1} were evident.[30,57] Elemental analysis revealed the presence of significant amounts of mercury (**PT**, 24.51% and **P3MT**, 11.25%). Scanning electron microscopy (SEM) and energy-dispersive analysis of X-rays (EDAX) showed polymer particles of 3−6 μm size, which were uniformly contaminated with mercury. The mercury was most likely included in the polymer chain, resulting from precipitation of the polymer molecule before all of the mercury was extruded by the palladium (see below). Chloromercury end groups are excluded based on several data: (i) Very little chlorine was seen in elemental analyses. (ii) Heating of a **PT** sample in a mass spectrometer did not result in peaks normally associated with chloromercurithiophenes ($m/z = 272$, $[HgCl_2]^+$; 237, $[HgCl]^+$). Only peaks due to Hg^+ were observed. (iii) The amount of residual mercury is inversely proportional with the solubility of the monomer. The more soluble polymer, **P3MT**, was more fully demercurated because it stayed in solution longer. (iv) TGA of **PT** and **P3MT** under nitrogen showed mass loss of 22% and 9%, respectively, between 200 and 400 °C, the temperature range in which thermal demercuration of bis(aryl)-mercurials occurs. Note that the TGA weight loss corresponds to the percent Hg found in the elemental analysis. Hence, the insoluble **PT** and **P3MT** prepared here are formulated as shown below.

The soluble polymers, poly(3-butylthiophene) (**P3BT**), poly(3-octylthiophene) (**P3OT**), poly(ethyl 3-thienylacetate) (**PETA**), and poly(hexyl 3-thienylacetate) (**PHTA**) (eq 5) contained only traces of mercury (elemental analysis) and showed no significant weight loss to 400 °C under N_2. These polymers were isolated by extraction of copper halides by complexation with aqueous ammonia followed by aqueous acid extraction. The polymers were precipitated at least twice into MeOH to form orange-red (R = alkyl) or red-brown (R = ester) solids. The IR spectra confirm the α−α′ links between the rings. Characteristic vibrational modes for β-H are seen for each polymer (3060, 780−830 cm^{-1}),[57] and the ester-containing polymers show carbonyl stretches very similar to the monomers, around 1736 cm^{-1}.



PT **P3MT**



(5)

All the PATs synthesized from the mercurial coupling reaction contained about 65% HT diads as revealed by integration of the aromatic proton signals at δ 6.98−7.05 ppm and the peaks due to the α-methylene protons of the alkyl side chains (δ 2.8 for HT and 2.5 ppm for HH diads).[58] No crystallinity was observed by X-ray diffraction.

The molecular weight distributions (MWD) were determined by GPC analysis in THF vs polystyrene standards. Polystyrene has been shown to be an appropriate standard for MW determination of poly(thiophenes).[59,60] The MWD of **P3BT**, **P3OT**, **PETA**, and **PHTA**, determined on polymers that had been twice fractionated by precipitation, are similar to those obtained by other chemical methods (Table 1). The MWD was monomodal for the polymers with alkyl side chains. However, the MWD of the poly(thiophenes) with ester side chains were bimodal with high MW tails. **PETA** and **PHTA** were found to be susceptible to cross-linking to varying degrees: hot **PETA** solutions gelled quite rapidly in air, but **PETA** mostly dissolved in

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Table 1. MWD for Poly(3-alkylthiophene)s Determined by GPC.

polymer	yield (%)	M_n	M_w	PDI
P3BT	60−80	12500	44100	3.5
P3OT	80	3300	8500	2.6
PETA	55−83	7000	20000	2.9
PHTA	80	18200	83000	4.6
P3OT/T(80/20)	34	NA	NA	
P3OT/T(60/40)	60	8000	25700	3.1
P3OT/T(50/50)	49	3240	11000	3.4
P3BT/3MT	91	1700	5300	3.0
P3BT/ETA	40−80	3300	24000	7.4

Table 2. Properties of the Poly(3-octylthiophene-*co*-thiophene)s

3OT/T ratio	UV−vis, nm ($CHCl_3$) λ_{max} (ϵ)	UV−vis, nm (film) λ_{max}	fluorescence, nm ($CHCl_3$) λ_{max}	cond (S/cm) I_2-doped film
100/0	421	445	557	0.01
80/20	443	469	554	0.06
60/40	462 (7440)	509	560	0.15
50/50	465 (7240)	516	563	1.9

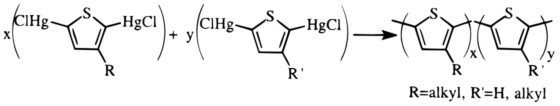
Table 3. Comparison of λ_{max} for Poly(thiophene)s in the Solid State and in Solution

polymer	λ_{max} ($CHCl_3$, nm)	λ_{max} (film, nm)	$\Delta\lambda$ (nm)	ref
100% HT **P3BT**	456	526, 560, 610	154	36
random **P3BT**	428	438	10	36
50% HH **P3HT**	389	389	0	22
65% HT **P3BT**	434	445	11	this work
P3OT	421	445	24	this work
P3OT/T 80/20	443	469	26	this work
P3OT/T 60/40	463	509	46	this work
P3OT/T 50/50	465	516	51	this work
PDBTT[a]	499	522	23	65

[a] Poly(3′,4′-dibutylterthiophene).

$CHCl_3$ after the solid had stood in air for several months. **PHTA** cross-linked readily to give dark, elastic, mostly insoluble material at the second precipitation after redissolving the solid in hot solvent.

Copolymers. One of the strengths of the present polymerization method lies in the ease of copolymerization. The composition of the copolymers was the same as the ratio of the monomers, thus indicating a low sensitivity of the coupling reaction to steric and/or electronic influences (eq 6). Except in regioregular PATs that display a high degree of crystallinity, alkyl substitution decreases the conductivity of the doped polymer as compared to that of doped poly(thiophene) itself. Hence, a soluble polymer containing as much thiophene as possible should enhance the mean conjugation length and the resulting conductivity. Copolymers of **3OT** and thiophene (**P3OT/T**; 80/20, 60/40, and 50/50) were found to be soluble while a 50/50 copolymer of thiophene and **3BT** was mostly insoluble. All of the **P3OT/T** copolymers were lustrous, green solids that formed dark red solutions in THF or $CHCl_3$. In contrast, the PAT homopolymers form red to red-orange solids. Some physical properties of the **P3OT/T** copolymers are shown in Table 2.



(6)

Oxidative coupling reactions may not copolymerize monomers having significantly different oxidation potentials. Blocky, overoxidized copolymers may result. Nucleophilic chemical coupling reactions should also give blocky copolymers for electronically different monomers due to unequal reaction rates. We prepared the copolymer of **3BT** and **ETA** (**P3BT/ETA**; 2/1) to demonstrate the insensitivity of the Hg-coupling reaction to electronic influences. To determine if the coupling reaction produced random or blocky copolymers, a model dimerization reaction of **CMT** and **CM3MT** was investigated. This coupling yielded a statistical mixture of the three possible dimers. The lack of selectivity in this coupling reaction suggested that the copolymers are random rather than blocklike. The NMR spectra of the copolymers appeared to be a superposition of the spectra of the homopolymers.

Electronic Properties. The electronic properties of PATs are, in general, influenced by molecular weight, regioregularity, and planarity. In solution, the λ_{max} for the $\pi-\pi^*$ transition (a rough measure of conjugation length) in oligomers (T_n) scales with $1/n$ up to $n \approx 10$.[57,61−64] In the solid, the larger changes in λ_{max} with respect to the solution values are due to changes in the planarity of the conjugated backbone; the solid-state packing stabilizes the more planar conformations.[64−66] In $CHCl_3$ solution, the highest λ_{max} of 100% H−T polymers is higher than regiorandom polymers which in turn is higher than in polymers with alternating HH−TT links (50% HH).[22,36] Apparently, increasing HT content causes less twisting between rings in solution and an increased conjugation length. Regioregular HT polymers also show the largest shifts on going from solution to solid due to side-chain crystallization that promotes $\pi-\pi$ stacking and a high degree of planarity of the conjugated backbone. Table 3 shows the absorption maxima in solution and in the solid state for several poly(thiophenes).

Increasing the content of unsubstituted thiophene in the **P3OT/T** copolymers has the effect of increasing the λ_{max} in solution as shown by the shift from 421 nm in **P3OT** to 465 nm for the **P3OT/T** 50/50 copolymer. **PDBTT**, a regular polymer with every third thiophene ring substituted at the 3,4-position with butyl groups, has the longest conjugation length in solution of all the polymers listed. This is a consequence of the fact that two-thirds of the rings are unsubstituted allowing more planar conformations in solution. However, **PDBTT** shows only a modest shift in λ_{max} on going to the solid state, demonstrating that these polymers do not adopt significantly more planar conformations in the solid. On the other hand, the regioregular HT polymer has only a modest conjugation length in solution but exhibits a large red shift in the solid state. Here, crystallization

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of the side chains promotes alignment of the chain backbone and increased main-chain planarity.

In contrast to the absorption spectra of PATs that are the weighted average of the absorptions of the various chain lengths present, the fluorescence spectra of the **P3OT/T** copolymers are consistent with emission from the lowest energy, longest conjugation length segment of the polymer chain. This observation is interpreted to mean that the mobile exciton can traverse the conjugated chain until it is pinned at the lowest energy, longest conjugation length segment from which it emits. **PAT**s usually emit at 550−560 nm, and the emission λ_{max} for the 80/20, 60/40, and 50/50 **P3OT** copolymers are found at 554, 560, and 563 nm, respectively, a change of only 9 nm. In contrast, the absorption λ_{max} changes by 22 nm in solution and 47 nm in the solid as the concentration of unsubstituted thiophene rings is increased in this series. Apparently, the lifetime of the exciton is sufficiently long that it can reach regions of comparable conjugation length in these **P3OT/T** copolymers. The **PDBTT** emits at 620 nm[65] and thus appears to have some segments that are extensively conjugated (planar) in solution as well as in the solid.

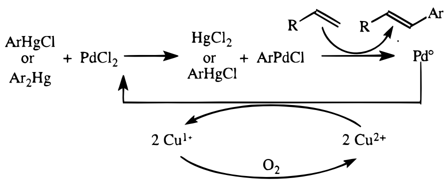
Electrical Conductivity. Electrical conductivity (σ) can be expressed in terms of two variables: carrier concentration and carrier mobility. For even lightly doped **PT**, the concentration of carriers is significant,[67] so that σ is limited by the carrier mobility. Values for carrier mobility (μ_{FET}), determined in **P3HT** field-effect transistors, have been found to be low ($10^{-4}-10^{-7}$ cm^2/Vs), an effect of the barriers to interchain hopping of the carrier.[68] Thus, reducing the barriers to interchain hopping should increase σ. Garnier et al. showed that μ_{FET} was significantly increased (to 10^{-2} cm^2/Vs) by intermolecular stacking of T_6 oligomers.[69] The electrical conductivity was found to be highly anisotropic, favoring the stacking direction by a factor of 120. Regioregularity and its associated planarity also exert a large influence on σ: **HT P3BT** (I_2 doped) gave $\sigma_{ave} = 1350$ S/cm.[35,36]

Because the mobility is limited by interchain hopping, conductivity is not directly related to the bandgap, which, in conjugated polymers, is primarily a *molecular* property, i.e., the HOMO−LUMO gap. Thus, poly(3′,4′-dibutylterthiophene) has a very low bandgap ($\lambda_{max} = 522$ nm) with conductivities in the range 1−5 S/cm,[65] but HH-**P3HT** with a larger bandgap ($\lambda_{max} = 389$ nm) had essentially identical conductivity (ca. 4 S/cm).[21] Four-point probe conductivities of the polymers prepared in this work ranged from 10^{-2} to 2 S/cm after doping with I_2. The highest conductivity (2 S/cm) was shown by the 50/50 **P3OT/T** copolymer, an increase of 10^2 over the conductivity of **P3OT**. The higher conductivity is attributed to higher carrier mobility associated with decreased interchain contact distances in the more planar 50/50 **P3OT/T** copolymer.

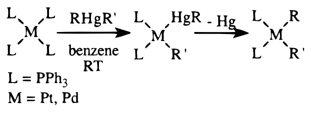
As noted by a referee, the sudden, order-of-magnitude increase in conductivity (σ) between the 60/40 and 50/50 **P3OT/T** copolymers is unexpected on the basis of the molecular properties. The sudden increase in σ is most likely due to the onset of a percolation threshold involving planar, π-stacked polymer chain segments. These observations also suggest that correlations of λ_{max} (or its inverse) or σ with M_n are either fortuitous or meaningless since, in a polymer with even modest MW, the conjugation length or carrier mobility is more dependent on local or correlated segmental order than on overall molecular weight. If this view is correct, then sample processing, morphology, and film quality are at least as important as molecular structure, MW, etc.

Coupling Mechanism. Much can be gleaned from the literature concerning the mechanism of the Pd-catalyzed coupling reaction as applied to organomercurials. Hein[70] discovered copper to be a fast symmetrizing agent for ArHgCl in the presence of pyridine (eq 3). The copper reduces mercuric chloride to elemental mercury, driving the reaction to the right. Furthermore, Ar_2Hg reacts with $Pd(OAc)_2$ faster than ArHgCl.[71] Therefore, the polymerization reaction must involve RHgCl *and* a significant amount of R_2Hg. This conclusion is buttressed by the fact that appreciable amounts of Hg were found in the chains of the less soluble polymers, **PT** and **P3MT** (see above).

In his seminal work on arylations with palladium, Heck[72] generated an arylpalladium species in situ by the transmetalation of $PdCl_2$ and arylmercurials. With an oxidant present (Cu^{2+}) in air, the reaction became catalytic in both palladium and copper (eq 7). Although $PdCl_2$ was added as the polymerization catalyst, the active species was more likely a Pd^0 species. Additional evidence for Pd^0 as the active catalyst is found in the work of Sokolov et al.[73] Both ArHgCl and Ph_2Hg were found to oxidatively add to $M(PPh_3)_n$ (M = Pt, Pd; n = 3, 4) with the elimination of elemental mercury under mild conditions (eq 8). The intermediate bis(aryl)palladium compounds reductively eliminate biaryls upon heating and regenerate the active catalyst.[74,75]



(7)



(8)

We found that the reaction of 2-(chloromercuri)thiophene with $Pd(PPh_3)_4$ gave good conversion to bithiophene. A small amount of terthienyl was also

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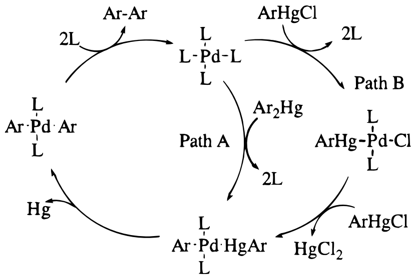
Scheme 1



observed, indicating that activation of α-hydrogens by Pd^0 occurred. Metalation of thiophene by Pd has been observed previously.[76] A proposed catalytic cycle consisting of the individual reactions just discussed is shown in Scheme 1. Paths A and B reflect the Ar_2Hg and ArHgCl present in the mixture due to the disproportionation of the ArHgCl.

Role of the Metal. As the mechanism proposed in Scheme 1 does not list copper, what role does it play? Is copper merely a reductant for mercuric chloride produced by disproportionation or transmetalation? To test this hypothesis, several other metals capable of reducing Hg^{2+} were tested. Iron, zinc, and aluminum were all rejected since their chlorides are too acidic. It was found that nickel powder effected the coupling of **CMT** and the Ni^{2+} that formed took the role of the $PdCl_2$ catalyst. Tin was also found to be active for coupling **BCMETA** in the presence of $PdCl_2$, yielding **PETA** identical with that produced using Cu. On the basis of the observed reactivity, copper is presumed to act only as a mild reducing agent.

Conclusions

A new poly(thiophene) synthesis, based on the Pd-catalyzed, reductive coupling of thienyl mercuric chlorides, has been developed. The coupling reaction reported here should be generally applicable to the wide variety of stable organomercurials that are easily obtained from the chloromercuration reaction of arenes and heteroarenes. A mechanism that incorporates demonstrated reactions of ArHgCl is proposed. The organomercurial coupling reaction was demonstrated to be compatible with functional groups that are attacked by strongly nucleophilic organometallic reagents, e.g., RLi or RMgX, that are commonly employed in other reductive thiophene coupling reactions. Compatibility with other electrophilic functional groups that are known to be inert toward arylmercurials and arylpalladium reagents is also expected.

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