Synthesis of Poly(3-alkylthienylene ketone)s by the Pd-Catalyzed Copolymerization of Carbon Monoxide with Thienyl Mercuric Chlorides

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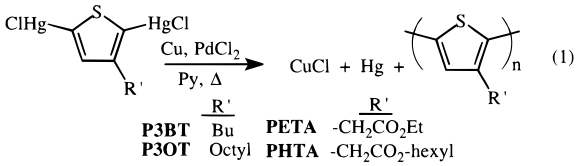
Poly(thienylene ketone)s are formed by the copolymerization of bis(chloromercuri)-thiophenes with carbon monoxide. The reaction is carried out in hot pyridine with a Pd catalyst under 500 psi of CO. The polymers, poly(3-methylthienylene ketone), poly(3-butylthienylene ketone), and poly(3-(carboethoxymethyl)thienylene ketone), with molecular weights, M_n, ranging from 1600 to 2700, were produced. The polymers have UV−vis absorption maxima near 360 nm, assigned to $\pi-\pi^*$ transitions, and are reduced irreversibly near −1.0 V vs SCE.

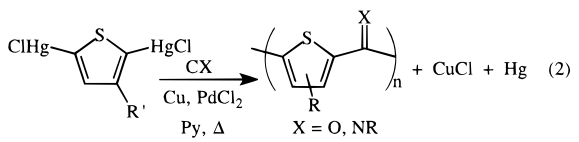
Introduction

We have recently reported the adaptation of the Pd-catalyzed coupling of organomercuric chlorides to the synthesis of poly(3-alkylthiophene)s (**PAT**s) and poly-(3-(carboalkoxymethyl)thiophene)s (**PATA**s, eq 1).[1,2]



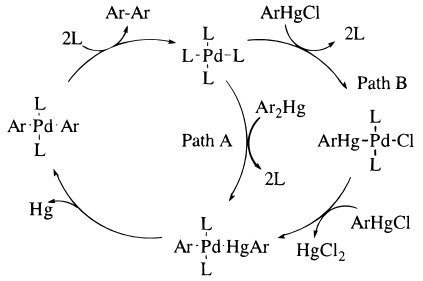
This chemical coupling reaction ensures α,α′ links between the thiophene rings and is compatible with the presence of functional groups on the pendant side chain that are attacked by strongly nucleophilic reagents, e.g., thienyllithium or Grignard reagents. The mechanism that was proposed (Scheme 1) for the coupling reaction involves the intermediacy of thienylpalladium compounds. Such species are well-known to possess a rich chemistry associated with the insertion of small molecules, e.g., CO, isonitriles, or alkenes, into the Pd−C bond (Scheme 2).[3]

With the thienyl−Pd species generated from 2,5-bis-(chloromercuri)thiophenes, regular insertion of CO or RNC could lead to a new class of thiophene copolymers, the poly(3-alkylthienylene ketone)s or poly(3-alkylthienylene imine)s (eq 2). Copolymerization of ethylene

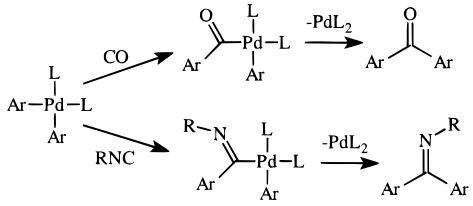


with carbon monoxide has been known since the early 1950s,[4] but this reaction has received a considerable amount of renewed interest.[5−11] Living polymerization of alkyl isocyanides catalyzed by Pd complexes is also known.[12] Poly(thienylene ketone)s or poly(thienylene imine)s are of interest due to their potential for n-doping and for the host of possibilities for further derivitization through the ketone or imine functionalities.

Scheme 1



Scheme 2



The metal complex-catalyzed insertion of CO into the Hg−C bond of organomercurials to give diaryl ketones has some precedence. Seyferth used catalytic amounts

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Table 1. Optimization of Conditions for the CO Insertion Reaction

run	reductant	added PPh_3	CO (psig)	time (h) @ temp (°C)	product distribution
1	Ni	no	30	3@80	50% T_2 50% T_2CO some oligomer
2	Cu	no	30	2.5@100	70% T_2CO 30% T_2
3	Cu	no	30	1@22, 2@80, 4@110	70% T_2Hg 25% T_2CO, 5% T_2
4	Cu	yes	30	2.5@22, 15@120	90% T_2CO, 5% T_3COH, 5% T_2
5	Cu	no	340	2@100	50% T_2Hg, 50% T_2CO, trace T_2
6	Cu	yes	500	4@100	>95% T_2CO, trace T_2,trace T_2Hg

of $Co_2(CO)_8$ and CO at atmospheric pressure under UV irradiation in THF and obtained diaryl ketones.[13] Hirota et al. obtained good yields of aryl ketones with $Ni(CO)_4$ as a stoichiometric reagent.[14] The reaction was found to be heavily solvent dependent, however, and only traces of product were formed with pyridine as solvent. Good yields of dithienyl ketone were produced from chloromercurithiophene (**CMT**) under very high CO pressures with a Rh(I) catalyst.[15] However, THF solvent was required, making this method unsuitable for copolymerization of CO with 3-alkylbis(2,5-chloromercuri)thiophenes (**BCM3RT**) which have appreciable solubility only in pyridine and are nearly insoluble in THF. Carbonylation of **CMT** with Li_2PdCl_4 in MeOH gave a mixture of products, and a 12% yield of a poly(furanyl ketone) was claimed when 2,5-bis(chloromercuri)furan was carbonylated.[16]

This paper reports the copolymerization of thienylmercuric chlorides with CO and attempted copolymerizations of these reagents with isonitriles. Some of these results have been communicated.[1]

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). The chloromercurithiophenes 2-chloromercurithiophene (**CMT**), bis(2,5-chloromercuri)-3-methylthiophene (**BCM3MT**), bis(2,5-chloromercuri)-3-butylthiophene (**BCM3BT**), and bis(2,5-chloromercuri)-3-(carboethoxymethyl)-thiophene (**BCMETA**) were synthesized as described previously.[1] Dithienyl ketone,[17] bis(2-thienyl)methane,[18] bis(5-(2-thenoyl)-2-thienyl)methane,[19] and bis(5-(2-thenoyl)-2-thienyl) ketone[19] were synthesized by published procedures.

^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 absorption. 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. 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.

Coupling of CMT with Ni under CO. A 100 mL Fischer-Porter tube loaded with **CMT** (1.00 g, 3.13 mmol) and Ni powder (0.262 g, 4.46 mmol) was evacuated and backfilled with CO three times. Pyridine (30 mL) was transferred via cannula into the tube, and the mixture was pressurized with CO (30 psig). The solution was stirred and heated (80 °C, 3 h), causing the solution to become blue-green. The heating was increased (110 °C) and the solution stirred overnight (15 h), resulting in a cherry red solution. The cooled mixture was filtered through Celite (3 cm) in a Fritte and washed with CH_2Cl_2. After the filtrate was washed with HCl (3 M; 2 × 250 mL) and a 1:1 mixture of saturated NaCl and $NaHCO_3$ (250 mL), the solution was dried (Na_2SO_4), filtered, and reduced to a red oil on a rotary evaporator. ^1H NMR ($CDCl_3$) showed about a 1:1 mixture of 2,2′-bithiophene and 2,2′-dithienyl ketone plus some peaks possibly due to oligomers.

Coupling of CMT with Cu under CO. Coupling reactions of **CMT** under an atmosphere of carbon monoxide were conducted under different conditions to optimize the CO insertion reaction (formation of dithienyl ketone). The reactions were conducted in a 500 mL Fischer-Porter vessel for moderate CO pressures (30 psig CO) or in a 150 mL Parr reactor for >300 psig CO. Variables included the amount of added triphenylphosphine, temperature, and CO pressure. The solid reagents were placed in the reaction vessel, which was subsequently evacuated/backfilled with CO three times (the Parr reactor was pressurized and purged three times). Pyridine (30−50 mL) was added, and the mixture was heated to the desired temperature (25−110 °C). Upon completion of the reaction, the cooled solution was filtered through Celite (3 cm) in a Fritte and washed with CH_2Cl_2 until the filtrate was colorless. The filtrate was shaken with NH_4OH (15%; 2 × 200 mL), HCl (3 M; 2 × 200 mL), and saturated NaCl (250 mL), in sequence. The solvent was removed in vacuo, and the residue analyzed by NMR and GC-MS. The observed products were dithienyl (T_2, trace−30%), dithienyl ketone (T_2CO, 50−95%), dithienyl mercury (T_2Hg, trace−70%), and trithienylmethanol (T_3COH, 0−5%). Low temperature and low CO pressure favored the formation of T_2Hg, whereas high temperature, high CO pressure, and added Ph_3P favored the formation of T_2CO. Under optimum conditions (added Ph_3P, 500 psi of CO, 100 °C), T_2CO was formed in essentially quantitative yield with only traces of T_2 and T_2Hg detectable. These results are summarized in Table 1.

Coupling of Ethyl 3-(2-Chloromercurithienyl)acetate (CMETA) under CO. A 150 mL Parr reactor was loaded with **CMETA** (1.002 g, 2.47 mmol), Cu powder (0.322 g, 5.07 mmol), $PdCl_2$ (0.042 g, 0.24 mmol), and triphenylphosphine. The reactor was pressurized and purged with nitrogen three times. Dry pyridine (30 mL) was transferred to the reactor via cannula. After pressurization with CO (400 psig), the reactor was heated (100 °C, 8 h) with stirring. The cooled mixture was filtered through Celite (3 cm) in a Fritte and washed with

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CH_2Cl_2. The filtrate was shaken with NH_4OH (15%), HCl (3 M), and saturated NaCl solution. After drying over Na_2SO_4, the solvent was removed in vacuo to give an oily residue. ^1H NMR ($CDCl_3$) showed 74% ethyl thienyl acetate (**ETA**) monomer with 26% dimer ketone with no uncarbonylated dimer. **ETA** was shown to result from the acid hydrolysis of unreacted mercurial (RHgCl) by suspending a small portion of **CMETA** in CH_2Cl_2 and subjecting it to the same workup as product above. GC-MS analysis of the resulting solution showed the presence of **ETA**.

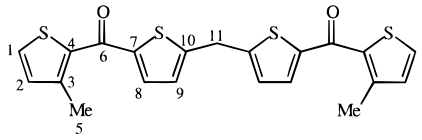
CO Insertion Copolymerizations. Preparation of Poly-(3-methylthienylene ketone) (P3MTK). A 150 mL Parr reactor was loaded with **BCM3MT** (4.998 g, 8.80 mmol), Cu powder (2.502 g, 39.37 mmol), $PdCl_2$ (99 mg, 0.56 mmol), and triphenylphosphine (0.148 g, 0.56 mmol). The reactor was pressurized (400 psig) and purged with CO three times. Pyridine (40 mL) was transferred to the reactor via cannula. After pressurization with CO (400 psig), the reactor was heated (100 °C, 17 h) with stirring. The cooled mixture was filtered through Celite (3 cm) in a Fritte and washed with CH_2Cl_2 until the filtrate was colorless. The filtrate was shaken with NH_4OH, HCl (3 M), and brine. After drying over Na_2SO_4, the solvent was removed in vacuo to give an orange oil. The residue was not completely soluble in THF, so it was dissolved in 10 mL of warm NMP. Precipitation in MeOH (250 mL) gave an orange powder that was collected on a Fritte, washed with MeOH, and dried under vacuum overnight to yield 0.691 g, 63% of poly(3-methylthienylene ketone) (**P3MTK**). Anal. Calcd for C_6H_4OS: C, 58.04; H, 3.25; S, 25.82. Found: C, 58.41; H, 3.51; S, 28.75; Cl, 0.11; Hg, <0.08. IR (KBr, cm^{-1}) $\nu_{C=O}$ 1622 (m). ^1H NMR ($CDCl_3$) δ 7.76 (m, 1H, ring); 2.6, 2.3 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 181.7, 179.8, *C*=O; many aromatic carbons 146−128; many Me 16.9−15.4. GPC (UV; THF, 1 mL/min) showed M_n = 1120, M_w = 2710, PDI = 2.42.

A second sample was prepared as above, yield 48%. Anal. Calcd for C_6H_4OS: C, 58.04; H, 3.25. Found: C, 58.41; H, 3.51; N, <0.5%; Cl, 0.11%; Hg, <0.08%; Cu, <0.020%. GPC (UV; THF, 1 mL/min) showed M_n = 1600, M_w = 3000, PDI = 1.9. UV ($CHCl_3$) λ_{max} (ϵ) 361 nm (7100 L/mol cm); 302 nm (5580 L/mol cm). Fluorescence ($CHCl_3$) em max = 540 nm.

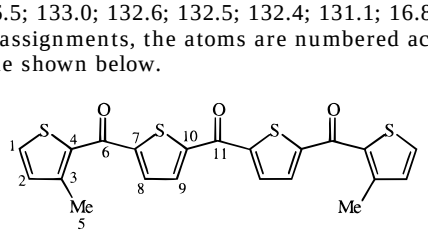
Preparation of Poly(3-butylthienylene ketone) (P3BTK). The reaction was conducted as described above using **BCM3BT** (5.009 g, 8.21 mmol), Cu powder (2.255 g, 35.48 mmol), $PdCl_2$ (0.117 g, 0.66 mmol), and triphenylphosphine (0.153 g, 0.58 mmol) in a 150 mL Parr reactor. The polymer solution was worked up as for **P3MTK**. Precipitation of a THF solution in MeOH (250 mL) yielded a dark powder which was collected on a Fritte, washed with MeOH, and dried under vacuum overnight to yield 0.639 g, 47% of poly(3-butylthienylene ketone) (**P3BTK**). IR (film, cm^{-1}) $\nu_{C=O}$ 1623 (s). Anal. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.03; N, 0. Found: C, 64.57; H, 6.17; N, 0.75. ^1H NMR ($CDCl_3$) δ 7.7−7.8 (several singlets, 1H, ring); 2.94 (m, α-CH_2), 65%; 2.66 (m, α-CH_2), 35%; 1.66 (m, 2H, β-CH_2); 1.39 (m, 2H, γ-CH_2); 0.93 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR shows the presence of many aromatic carbons. GPC (UV; THF, 1 mL/min) showed M_n = 1947, M_w = 5160, PDI = 2.65. UV ($CHCl_3$) λ_{max} (ϵ L/mol cm) 360 nm (6600); 300 nm (5170). Fluorescence ($CHCl_3$) em max = 534 nm.

Preparation of Poly(3-(carboethoxymethyl)thienylene ketone) (PETAK). The conditions and procedure were as described for the preparation of **P3MTK** using **BCMETA** (5.00 g, 7.80 mmol), Cu powder (2.00 g, 31.5 mmol), $PdCl_2$ (150 mg, 0.85 mmol), and triphenylphosphine (0.200 g, 0.76 mmol). The reaction mixture was worked up as for **P3MTK**. The oily brown residue was dissolved in THF (10 mL) and slowly dripped into MeOH (250 mL). A powdery brown precipitate was collected on a Fritte, washed with MeOH, and dried under vacuum overnight to yield 0.41 g, 27% of poly(3-(ethylacetato)-thienylene ketone) (**PETAK**). IR (film, cm^{-1}) $\nu_{C=O}$ 1734 (s), 1621 (m). ^1H NMR ($CDCl_3$) δ 7.91 (m); 4.19 (s, 2H, α-CH_2); 4.06, 3.86, 3.69 (m, CH_2CH_3); 1.27 (m, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.3; 61.2; 35.7; 14.1. GPC (UV; THF, 1 mL/min) showed M_n = 2725, M_w = 10 820, PDI = 3.97. Anal. Calcd for $C_9H_8O_3S$: C, 55.09; H, 4.11; N, 0. Found: C, 52.79; H, 3.91; N, 0.36. UV ($CHCl_3$) λ_{max} (ϵ) 353 nm (5820); 300 nm (4780). Fluorescence ($CHCl_3$) em max = 520 nm. A second trial yielded a polymer having M_n = 2291, M_w = 24 202, PDI = 10.56.

Model Thienyl Ketone Oligomers. Preparation of Bis-(5-(3-methyl-2-thenoyl)-2-thienyl)methane. Dithienyl methane (5.68 g; 31.5 mmol), 3-methyl-2-thiophene carboxylic acid (10.07 g; 70.8 mmol), and poly(phosphoric acid) (250 g) were stirred with a mechanical stirrer in a 500 mL three-neck flask (3 h, 60 °C). The brown viscous liquid was poured into ice water (600 mL) and broken up with a glass rod. The solid was extracted into CH_2Cl_2 (500 mL) and shaken with saturated $NaHCO_3$ and NaCl. The solution was dried over Na_2SO_4, and the solvent removed under vacuum to give a brown oil that would not crystallize upon cooling. Some of the oil could be dissolved in hot EtOH. Cooling of the mixture (−20 °C) gave off-white crystals which could be decanted from the solidified oil. The process was repeated with the remaining oil. Yield after two such crystallizations: 4.7 g, 35%. Anal. Calcd for $C_{21}H_{16}O_2S_4$: C, 58.85; H, 3.76. Found: C, 58.66; H, 3.99. IR (KBr, cm^{-1}) $\nu_{C=O}$ 1599. UV($CHCl_3$, nm) λ_{max} = 323, 277 (sh). HRMS (DCI) predicted *m*/*z*, 428.0033; observed 428.0021. ^1H NMR ($CDCl_3$) δ 7.74 (d, 2H, H8; J = 3.8 Hz); 7.46 (d, 2H, H1; J = 4.9 Hz); 7.01 (d, 2H, H2; J = 4.9 Hz); 6.96 (d, 2H, H9; J = 3.8 Hz); 4.41 (s, 2H, CH_2); 2.55 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 179.9, C6; 150.4; 146.0; 144.3; 133.8; 132.7; 132.1; 129.7; 126.8; 31.2, C11; 16.4, C5. For the NMR assignments, the atoms are numbered according to the scheme shown below.



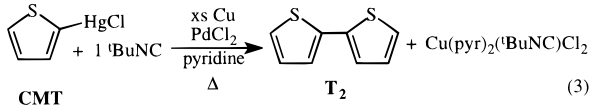
Preparation of Bis(5-(3-methyl-2-thenoyl)-2-thienyl) Ketone. A solution of the above-described dione (1.0 g) in DME (50 mL) was stirred with an ethanolic solution of KOH (200 mL). The solution became turquoise immediately. Air was passed through the solution, the color faded to dark brown, and a cream colored precipitate was observed. The solid was collected by filtration and rinsed with EtOH and Et_2O. Drying in vacuo yielded 0.582 g, 56%. The product was soluble in THF and $CHCl_3$. Anal. Calcd for $C_{21}H_{14}O_3S_4$: C, 57.00; H, 3.19. Found: C, 56.28; H, 3.29. IR (KBr, cm^{-1}) $\nu_{C=O}$ 1616 (s), 1599 (m). UV ($CHCl_3$, nm) λ_{max} = 344. HRMS (DCI): predicted *m*/*z*, 441.9826; observed 441.9810. ^1H NMR ($CDCl_3$) δ 7.92 (AB d, 4H, H8 and H9; J = 4.1 Hz, $\Delta\delta$ = 5.7 Hz); 7.56 (d, 2H, H1; J = 4.9 Hz); 7.07 (d, 2H, H2; J = 4.9 Hz); 2.62 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 179.6, C6; 178.6, C11; 150.8; 147.8; 146.5; 133.0; 132.6; 132.5; 132.4; 131.1; 16.8, C5. For the NMR assignments, the atoms are numbered according to the scheme shown below.



Results and Discussion

Model Studies. As shown in our previous papers,[1,2] the $PdCl_2$-catalyzed reaction of chloromercurithiophenes with Cu powder in refluxing pyridine gave good yields of poly(alkylthiophene)s. The low solubility of the bis-(chloromercuri)thiophenes requires the use of hot pyridine as solvent for the coupling reaction. To determine the course of the coupling reaction in the presence of CO and isonitriles, the coupling of **CMT** to give dimers was investigated. The isonitriles, ^{t}BuNC and cyclohexyl isonitrile (^{c}HexNC), did not insert cleanly. With only 1 equiv of ^{t}BuNC, no insertion reactions were observed. As the hot reaction mixture cooled to room temperature,

light yellow crystals precipitated. This solid was identified as $Cu(pyr)_3(CN^tBu)Cl_2$ by NMR and elemental analysis. GC-MS analysis of the mother liquor after workup revealed only bithiophene. Had any of the expected imine been formed, acid hydrolysis would have produced dithienyl ketone, but none was observed in the NMR or GC-MS spectra. Apparently, all the available isonitrile was complexed by the copper salts, and the reaction proceeded as shown in eq 3.

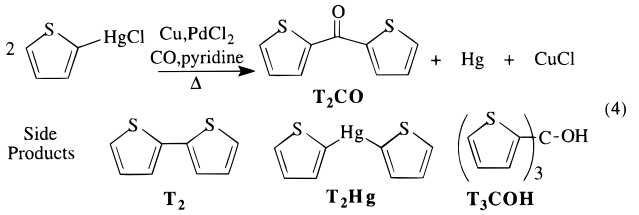


(3)

When an excess of ^{c}HexNC was employed, oligomerization of the isonitrile was observed. The NMR spectra showed the absence of ^{c}HexNC in the final reaction mixture, and the $^{13}C\{^1H\}$ NMR spectrum showed a multitude of resonances assigned to cyclohexyl ring carbon atoms. No bithiophene was observed by GC-MS or ^1H NMR analyses. This side reaction was not surprising since Ni^{2+} has been used to prepare poly(iminomethylene)s from isonitriles under mild conditions.[20]

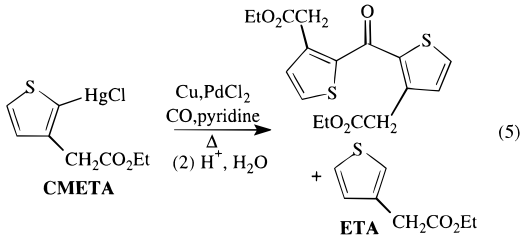
Table 1 shows the product distribution when the coupling reaction was performed in the presence of CO under several sets of conditions. The Cu/PdCl2 coupling system was superior to Ni as a single-source reductant/catalyst as shown by comparing runs 1 and 2. In run 3, the reaction mixture was stirred at 22 °C for 1 h, then at 80 °C for 2 h, and finally at 110 °C for 4 h. The product distribution at the end of this heating sequence, shown in Table 1, contained a large amount of dithienyl mercury, T_2Hg. In run 2, the reaction mixture was heated rapidly to 100 °C and held at that temperature for the duration of the run. In this instance, the thienylmercuric chloride was completely consumed, and no T_2Hg remained in the reaction mixture.

The role of the Cu in these coupling reactions appears to be that of a mild reductant that drives the disproportionation of THgCl into T_2Hg by reducing the coproduct, $HgCl_2$, to elemental mercury.[1] The Pd catalyst then converts T_2Hg to Hg and coupled products, T_2 or T_2CO. Thus, the presence of a large amount of T_2Hg in run 3 suggested that the Pd catalyst was being deactivated. Run 4 shows the effect of adding triphenylphosphine, Ph_3P, to the reaction mixture to keep the Pd(0) in a soluble form. In the presence of Ph_3P, complete conversion of the THgCl was observed, and the yield of the CO insertion product, T_2CO, increased. However, there was still a 5% yield of bithiophene, T_2, and a 5% yield of trithienylmethanol, T_3COH. The alcohol product is the result of the addition of an active thienyl organometallic (T-PdL_n or T-CuL_x) across the carbonyl C═O bond in T_2CO. In a polymerization reaction, the alcohol-forming reaction is a source of undesirable cross-links. Increasing the CO pressure to 500 psig (run 6) suppressed the formation of T_3COH and also increased the yield of T_2CO at the expense of T_2, i.e., nearly every coupling occurred with the desired CO insertion. Run 5 shows that the beneficial effect of Ph_3P is maintained even under high CO pressure. The coupling reaction under CO is summarized in eq 4.



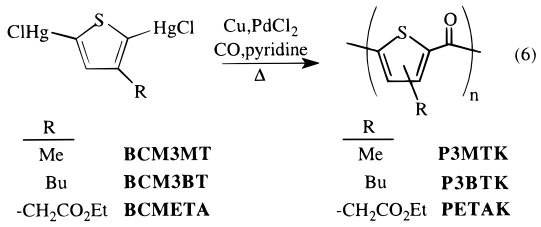
(4)

The coupling of **CMETA** in the presence of CO proceeded much more slowly. After 8 h, only 42% had reacted to give dimer ketone. During the acidic workup, the chloromercury group was cleaved to leave **ETA** as the only other thiophenic product (eq 5).



(5)

Copolymerization of Bis(chloromercurials) and CO. Under the experimental conditions optimized with the model dimerization reactions, the copolymerization of CO with the bis(chloromercurials), **BCM3MT**, **BCM3BT**, and **BCMETA**, was performed to give the polymers, **P3MTK**, **P3BTK**, and **PETAK**, respectively (eq 6).



(6)

P3MTK was obtained as a bright orange powder having good solubility in CH_2Cl_2. **P3BTK** and **PETAK** were orange-brown powders with good solubility as well. The yields and molecular weights were low (Table 2). This may be caused by low conversion due to catalyst deactivation and/or passivation. Since the reaction rate is slower than for coupling in the absence of CO, amalgamation of the Pd with the Hg produced in the coupling reaction may remove the catalyst from solution.

To assist in the characterization of the poly(alkylthienyl ketone)s, model thienyl ketone oligomers were synthesized. Dithienyl methane was acylated and oxidized (Scheme 3) to obtain the trione $\mathbf{T_4(CO)_3}$ according to the method of Meth-Cohn.[21] The trione with R = H was extremely insoluble. Acylation and oxidation of dithienyl methane with R = Me gave soluble trione, $\mathbf{T'_4(CO)_3}$.

Spectroscopic Characterization of Poly(alkylthienyl ketone)s. IR spectroscopy indicated the presence of carbonyls in the same range as observed in the model oligomers (1600−1620 cm^{-1}), and only C−H_β stretching modes were observed (Table 3) as expected

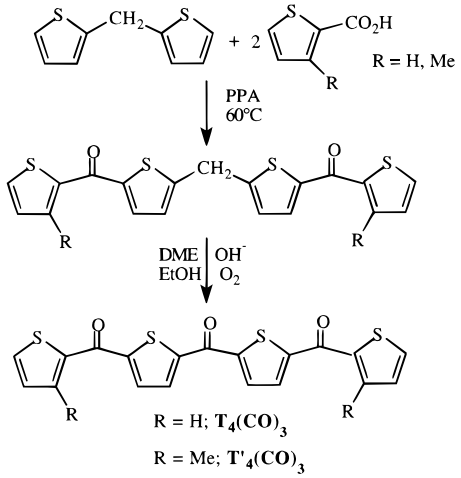
(20) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30−35.

(21) (a) Ahmed, M.; Meth-Cohn, O. *J. Chem. Soc., Chem. Commun.* **1968**, 82−83. (b) Ahmed, M.; Meth-Cohn, O. *J. Chem. Soc. C* **1971**, 2104−2111.

Table 2. Poly(thienylene ketone) Molecular Weight Data

polymer	yield (%)	Mn	Mw	PDI
P3MTK	50	1600	3000	1.9
P3BTK	50	1900	5200	2.7
PETAK	30	2700	10800	4.0

Scheme 3

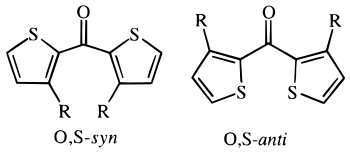


if only α,α′ coupling occurred. ^{1}H NMR analysis revealed a significant downfield shift of the thienyl ring proton resonances from δ 6.9−7.0 ppm in **PAT**s to ≈7.8 ppm in the **PATK**s. Very weak signals in the 7.0−7.5 ppm region may be due to end groups or to thienyl rings that have no attached carbonyl group as a result of a "mistake" in the insertion polymerization reaction. Several carbonyl resonances were seen at ≈180 ppm in the ^{13}C{^{1}H} NMR spectra, but the signal-to-noise ratio was poor and all the resonances associated with quaternary carbon atoms were not observed.

The thermal stability of the **PATK**s was investigated by TGA. Each polymer showed an onset of decomposition between 300 and 375 °C under nitrogen. Char yields at 800 °C were in the range 40−50%, which is somewhat lower than those observed for **PAT**s (50−70%). The lower values are attributed to loss of CO in the **PATK**s.

Electronic Spectra. The addition of trifluoroacetic acid (**TFA**) to a chloroform solution of the model oligomer, **T′$_4$(CO)$_3$**, causes λ_{max} to shift to a slightly larger value, to 346 from 343 nm. This behavior is similar to that of **T$_2$CO** for which the electronic transitions responsible for the UV−vis spectra have been assigned as $\pi-\pi^*$ instead of $n-\pi^*$.[22] The latter type of transition typically experiences a shift to shorter wavelengths as the lone pair of the carbonyl oxygen atom is lowered in energy by protonation or hydrogen bonding.[22] However, in thienyl ketones there exists the possibility that some of the transitions are from $n-\pi^*$ involving the "lone pair" on the sulfur atom. The sulfur atom in thiophenes is notoriously nonbasic[23] and may not interact with **TFA**, especially in the presence of the more basic carbonyl groups.

In fact, our extended Hückel MO (EHMO) calculations suggest that the energy levels of the S-atom lone pairs and the π-MOs of thienyl ketones are strongly coupled to the degree of twist about the C−C bond joining the thiophene ring and the carbonyl group. The lowest energy conformation of **T$_2$CO** has been assigned as O,S-*syn* with OCCS dihedral angles of about 25°.[24] This O,S-*syn* conformation is stabilized by electrostatic attractions between the positive charges on the S atoms and the negative charge on the O atom.[24] Repulsions between the 3,3′-hydrogen atoms ("R" in the structure below) causes the twist about the bonds to the carbonyl



group and the resultant non-planar structure. In this conformation, the HOMO is calculated to be a delocalized π-MO and the "lone-pair" orbitals centered on the S atom are only 0.1 eV lower in energy than the HOMO. In the less favorable O,S-*anti* conformation, lone pair−lone pair repulsion raises the energy of the antisymmetric lone-pair combination 0.22 eV above the π-level so that the S centered lone pairs becomes the HOMO. In both cases the LUMO is calculated to be a π^* MO mostly localized on the carbonyl group. Thus, the lowest energy transition in the O,S-*syn* conformation should be $\pi-\pi^*$ in character, but $n(S)-\pi^*$ in the O,S-*anti* conformation. At some intermediate twist angles, these transitions should have comparable energies. In any event, the $\pi-\pi^*$ transitions are expected to be much more intense than the $n(S)-\pi^*$, so the latter may be buried under the former and contribute to the observed shoulders and/or asymmetry of the $\pi-\pi^*$ absorption.

The UV−vis spectrum of the PATK polymers are similar to those of the model oligomers. **P3MTK** has distinct peaks at 312 and 367 nm and a prominent shoulder at 426 nm. The spectrum of **P3BTK** has two peaks at 302 and 360 nm with a less-pronounced shoulder (Figure 1). The energy differences between the peaks (3000−5000 cm^{-1}) are too large to be attributed to vibronic coupling. Therefore, we attribute the observed peaks to $\pi-\pi^*$ transitions arising from different conformations of the polymer chain backbone. Indeed, our EHMO calculations suggest shifts on the order of 50 nm between the $\pi-\pi^*$ transition energies of the lowest energy O,S-*syn* and the next lowest energy O,S-*anti* conformations.[25]

The model ketones showed no fluorescence upon excitation at the absorption λ_{max}. This is consistent with the fluorescence quenching properties of carbonyl groups due to rapid intersystem crossing. The **PATK**s, however, gave some fluorescence (em max 520−540 nm) possibly emanating from a small number of rings missing a carbonyl group.

Electrochemistry. The electrochemistry of the PATKs and the model oligomers was investigated by cyclic voltammetry (CV) under N_2 atmosphere in THF solution with 0.1 M Bu_4NBF_4 as supporting electrolyte.

(22) Becker, R. S.; Favaro, G.; Poggi, G.; Romani, A. *J. Phys. Chem.* **1995,** *99*, 1410.
(23) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 260.
(24) Benassi, R.; Folli, U.; Iarossi, D.; Schenetti, L.; Taddei, F.; Musatti, A.; Nardelli, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1741.
(25) EHMO calculations, performed with Personal CAChe suite of programs, are not expeced to give accurate values for the electronic transition energies, but the method is capable of reproducing trends in energy changes that result from rotations about bonds.

Table 3. Spectroscopic Data for Thienylene Ketone Oligomers and Polymers

sample	ν(C−H$_\beta$) (cm^{-1})	ν(C=O) (cm^{-1})	δ(*C*−O) (ppm) (^{13}C NMR)	λ_{max} (nm)	$E_{p/2}$ (V vs SCE)
T$_2$CO	3099	1616		271, 311	−1.65
T$_4$CO		1599			
T′$_4$CO		1616, 1599	180, 179	300 (sh), 344	−0.96, −1.41, −2.24
P3MTK	3084	1622 (br)	182, 180	312, 367, 426	−1.01
P3BTK	3087	1623 (br)		302, 360	−0.89
PETAK	3093	1621 (br), 1734 (br)	170	300, 353	−0.96

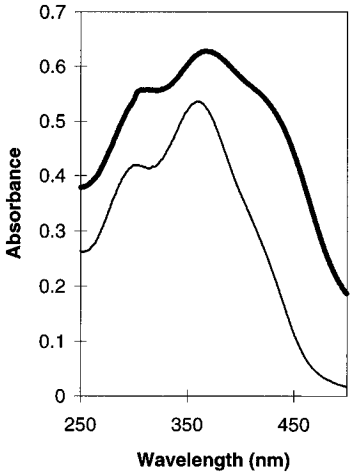


Figure 1. UV−vis spectra of **P3MTK** (top) and **P3BTK** (bottom).

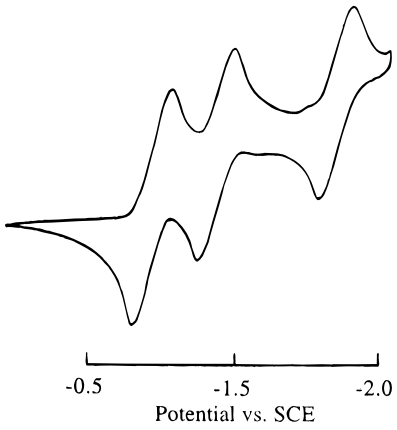


Figure 2. Cyclic voltammetry curve for **T′$_4$(CO)$_3$** (sweep rate = 50 mV/s).

Scan rates were varied from 50 to 500 mV/s. The potentials, measured against a Ag wire electrode, were referenced by the addition of ferrocene on the last scan and calibrated to the reported E_p of benzophenone in THF (−2.06 V vs SCE).[26] The measured potentials are collected in Table 3.

Benzophenone and dithienyl ketone each gave one, cleanly reversible reduction at all the sweep rates studied. **T′$_4$(CO)$_3$**, however, showed three highly reversible peaks at −0.96, −1.41, and −2.24 V, corresponding to the sequential reduction of each of the three carbonyl groups (Figure 2). The lower first reduction potential of **T′$_4$(CO)$_3$** as compared to **T$_2$CO** is consistent with the carbonyl group of the former being in a more delocalized π-system, and the differences in the potentials of the successive reductions of **T′$_4$(CO)$_3$** are consistent with substantial interaction between the sequentially added electrons. The polymeric thienyl

(26) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley: New York, 1980; p 701.

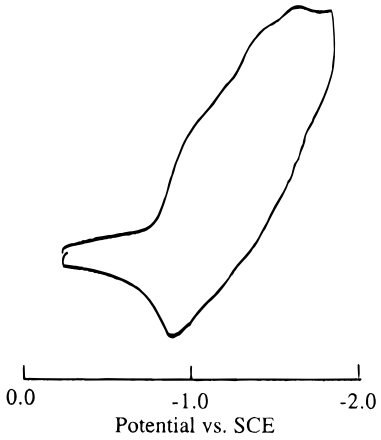
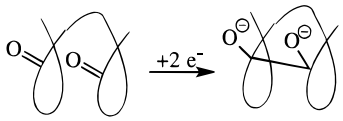


Figure 3. Cyclic voltammetry curve for **P3BTK** (sweep rate = 50 mV/s).

Scheme 4



ketones, on the other hand, showed what appears to be a series of unresolved reduction peaks that commence near the first reduction potential of **T′$_4$(CO)$_3$**, followed by only a weak oxidation signal on the return anodic sweep. The E_p values of the polymers suggest that their carbonyl groups are associated with a conjugated π-system that is similar in effective conjugation length to that in the **T′$_4$(CO)$_3$** model oligomer. The close series of unresolved reduction peaks may be explained by the reductions of carbonyl groups that are not in good conjugation due to twisting of the polymer chain backbone. The lack of electrochemical reversibility in the polymer reductions suggests that there exists a chemical reaction pathway following the electrochemical reduction that is available to the polymers but not to the oligomer, **T′$_4$(CO)$_3$**. We suggest that this "follow-on" reaction is the *intramolecular* dimerization of the ketyl radicals that are formed upon reduction of the carbonyl groups. The favored conformations of the thienyl ketones will result in a spiral structure if extended to a polymeric chain. Such a structure will bring the carbonyl groups that are spaced one helical turn apart into near proximity, allowing for their dimerization into geminal diolate anions (Scheme 4). If this dimerization occurs rapidly with respect to the CV sweep rate, the reduction is irreversible. Thus, even though the PATKs are reducible at a relatively low potential, the lack of reversibility will severely limit their application as n-dopable polymers.

Conclusions. The Pd-catalyzed coupling of thienyl mercuric halides may be adapted to the copolymerization of carbon monoxide to form poly(3-alkylthienyl ketone)s, **PATK**s. This reaction should be generally

applicable to the formation of poly(aryl ketone)s or poly(heteroaryl ketone)s. The lack of electrochemical reversibility limits their use as n-dopable conducting polymers or as electron storage polymers in battery applications. However, such polymers might be useful as selectively permeable membranes in gas-separation technology. The photochemistry and photophysics of these poly(aryl ketone)s could also be of interest in connection with photoinduced charge generation and transport.

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