Novel Poly(3-alkylthiophene) and Poly(3-alkylthienyl ketone) Syntheses via Organomercurials

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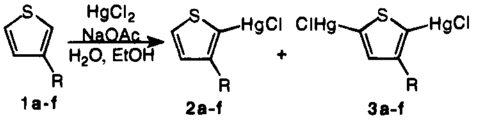
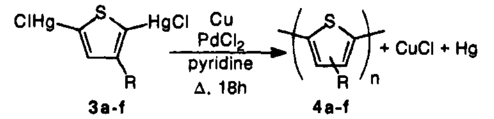
Of the current chemical syntheses of poly(3-alkylthiophene)s (PATs), few methods *exclusively* produce α-α′ linkages for monomers containing reactive functional groups such as carbonyls. Organolithium,[1] -magnesium,[2] -zinc,[3] and tin[4] syntheses, as well as nickel(0) dehalogenative coupling,[5] have been developed to ensure the 2,5-linkages necessary for conjugation along the backbone; however, most methods cannot tolerate electrophilic functional groups. Chemical oxidation using $FeCl_3$[6] may result in conjugation-breaking α-*β*′ links,[7] chloride substitution,[8] or iron impurities which enhance oxidative degradation.[9] We report herein a gentle new PAT synthesis based on the coupling of 2,5-bis(chloromercurio)-3-alkylthiophenes and the alternating copolymerization with carbon monoxide to produce poly(3-alkylthienyl ketone)s (PATKs), a new class of polythiophene copolymers. These syntheses represent the first use of organomercurials for making soluble, well-characterized polyarylenes and polyarylene ketones. Our method also easily produces random copolymers of 3-alkylthiophenes with varying amounts of thiophene or with monomers having different oxidation potentials. All polymers have been characterized by NMR, IR, gel-permeation chromatography (GPC), elemental analysis, dc conductivity, and UV−vis.

The facile mercuration of 3-alkylthiophenes (**1**) with mercuric chloride to produce 2-(chloromercurio)-3-alkylthiophenes (**2**) and 2,5-bis(chloromercurio)-3-alkylthiophenes (**3**) has been known for many years (eq. 1).[10] The high yield synthesis[11] of



(1)

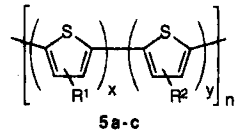
2,2′-bithiophene through coupling of **2a** with copper powder and a catalytic amount of palladium chloride in refluxing pyridine suggested a new polymerization based on mercurials. Soluble homopolymers **4c−f**[12] were synthesized in good yield (65−80%) from the difunctional monomers **3** (eq 2).



(2)

		M_w	M_n	PDI
4a R = H	**4c** R = $CH_2(CH_2)_2CH_3$	10500	26200	2.5
4b R = CH_3	**4d** R = $CH_2(CH_2)_6CH_3$	3300	8500	2.6
	4e R = $CH_2CO_2CH_2CH_3$	7000	20000	2.9
	4f R = $CH_2CO_2(CH_2)_5CH_3$	18200	83000	4.6

The reaction of 2,5-bis(chloromercurio)-3-alkylthiophenes with different substituents, R, produced random copolymers **5**, in which the proportion of the different alkyl groups in the copolymers matched the ratio of their respective monomers in the reaction mixture. Model reactions of **2a** with 2-(chloromercurio)-3-alkylthiophenes gave nearly random 1:2:1 mixtures of di-, mono-, and unsubstituted bithiophene, demonstrating that the coupling reaction shows very little steric discrimination. Random copolymers **5e** of 3-butylthiophene with ethyl 3-thienylacetate were also formed, suggesting that the organomercurial coupling reaction is relatively insensitive to electron-withdrawing or -donating effects of the side chains.



5a-c

$R^1(x), R^2(y)$ =	M_w	M_n	PDI
a $CH_2(CH_2)_6CH_3$ (0.80), H (0.20)			
b $CH_2(CH_2)_6CH_3$ (0.60), H (0.40)	8000	25700	3.1
c $CH_2(CH_2)_6CH_3$ (0.50), H (0.50)	3240	11000	3.4
d $CH_2(CH_2)_2CH_3$ (0.78), CH_3 (0.22)	1700	5300	3.0
e $CH_2(CH_2)_2CH_3$ (0.67), $CH_2CO_2CH_2CH_3$ (0.33)	3300	24000	7.4

The soluble polymers did not retain copper, mercury, or chlorine in the chains or as endgroups.[13] Hydrogen endgroups most likely result from acid hydrolysis during the workup. Molecular weights and polydispersities are indicated in the graphics.[14] Polymers **4e**, **4f**, and **5e** appear to be unstable with respect to air oxidation in solution. Some cross-linking, indicated by the formation of some insoluble gel, occurred during redissolution of **4e** and **5e** and upon heating a solution of **4f** in air. The MW depends strongly on the purity of the starting bis(mercurial); small amounts of the mono(mercurial) act as chain terminators. ^1H NMR indicated 65% head−tail regioregularity, resulting in little crystallinity in solvent-cast films.[15] UV−vis analysis showed the expected $\pi-\pi^*$ transitions in the 390−460 nm region. Copolymers **5b** and **5c** had much higher λ_{max} values in $CHCl_3$ solution (463 and 465 nm, respectively) or as thin films (509 and 516 nm, respectively) than that of the homopolymer **4d** ($CHCl_3$, 421 nm; film, 441 nm). This results from increased conjugation length due to the incorporation of sterically unhindered thiophene into the backbone[16] and more planarity in the solid state. ^1H NMR revealed a decreased signal for the octyl side chain α-CH_2 due to head−head couplings of octylthiophenes, as expected for

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(1) Berlin, A.; Pagani, G. A.; Sannicolo, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1663−1664.

(2) (a) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608−11609. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912.

(3) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087−10088.

(4) (a) Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, *5*, 2−3. (b) Marsela, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214−12215. (c) Galarini, R.; Musco, A.; Pontellini, R.; Bolognesi, A.; Destri, S.; Catallani, M.; Mascherpa, M.; Zhuo, G. *J. Chem. Soc., Chem. Commun.* **1991**, 364−365.

(5) Yamamoto, T.; Morita, A.; Mayazaki, Y.; Maruyama, T.; Wakayama, Z. Z.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214.

(6) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.

(7) Chen, S. A.; Tsai, C. C. *Macromolecules* **1993**, *26*, 2234−2239.

(8) Della Casa, C.; Salatelli, E.; Andreani, F.; Costa Bizzarri, P. *Makromol. Chem., Macromol. Symp.* **1992**, *59*, 233−246.

(9) Abdou, M. S. A.; Holdcroft, S. *Macromolecules* **1993**, *26*, 2954−2962.

(10) Steinkopf, W.; Killingstad, A. *Ann. Chem.* **1937**, *532*, 288.

(11) Kretchmer, R. A.; Glowinski, R. *J. Org. Chem.* **1976**, *41*, 2661−2662.

(12) Polymers **4a** and **4b** were insoluble brick-red powders that contained one Hg atom per 5−6 thiophene rings, as deduced from elemental analysis, TGA, SEM-EDAX, and mass spectral analysis.

(13) Elemental analysis gave, for **4c**, <0.05% Cl, <0.08% Hg, and <0.004% Cu; for **4e**, 0.15% Cl, 0.19% Hg, and 0.041% Cu.

(14) Molecular weights were determined by GPC in THF at 1 mL/min by UV detection using polystyrene standards for calibration.

(15) The lack of X-ray diffraction lines showed the polymers to be amorphous.

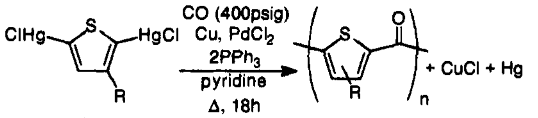
(16) (a) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901−1907. (b) Inganäs, O. *Trends Polym. Sci.* **1994**, *2*, 189−196.

0002-7863/95/1517-3887$09.00/0

random inclusion of thiophene along the backbone. Four-point probe electrical conductivities[17] of I$_2$-doped thin films of the copolymers **5a**–**c** also increased with increasing thiophene content from 6×10^{-2} to 1.9 S/cm. The increasing conductivity of the polymers with higher thiophene content is also consistent with longer conjugation lengths in the solid state.

Since the reaction of organomercurials with CO under palladium catalysis can yield symmetrical ketones,[18] we examined the model reaction of **2a** with CO in a high-pressure reactor under the copper coupling conditions. GC/MS and NMR showed >99% conversion to the CO insertion product, di(2-thienyl) ketone. Reaction of **2a** with alkyl isocyanides did not yield the desired imines.

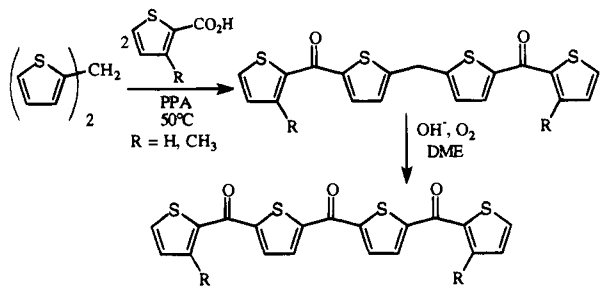
Coupling of **3** under CO (400 psig) in a high-pressure reactor produced soluble poly(3-alkylthienyl ketone)s (PATK, **6**) in moderate yields (~50%) (eq 3). Poly(heteroarylene ketone)s were a previously unknown class of materials. Only passing mention was made of an ill-characterized "polymer" (aryl = furan)[19] formed in low yield (7%) during carbonylation of 2,5-bis(chloromercurio)furan in methanol. NMR, IR (thin film; $\nu_{C=O}$ = 1621–1623 cm^{-1}), elemental analysis, and UV–vis spectroscopy (CHCl$_3$; λ_{max} (ϵ) = ~360 nm (~6000), ~300 nm (~5000)) data are all consistent with complete insertion of carbonyls groups between the rings.[20] The spectroscopic properties of the polymers **6** are very similar to those of the model tetramers (**7**) (for **7b**, $\nu_{C=O}$ = 1616, 1599 cm^{-1}; λ_{max} = 344 nm, 300 nm) produced by the acylation of di(2-thienyl)methane[21] with 3-alkyl-2-thiophenecarboxylic acid (alkyl = H, Me) in polyphosphoric acid, followed by oxidation (Scheme 1).[22]



3b,c,e (3)

	M_w	M_n	PDI
6b	1600	3000	1.9
6c	1950	5260	2.7
6e	2700	10800	4.0

Scheme 1



7 a: R = H; b: R = CH$_3$

PATKs are expected to show enhanced electrical conductivity upon n-doping, due to the formation of radical anions along the backbone. Cyclic voltammetry (in THF) revealed the onset of reduction in the expected range (~−1.0 V vs SCE), compared to −0.96 V for **7b**. Studies are currently underway to explore the electrical properties of this new class of polythiophene.

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Supplementary Material Available: Representative synthetic procedures and physical properties of **3e**, **4e**, **4c**, and **6c** (2 pages). This material is containedin many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[17] Spin-coated polymer films (2000–8000 Å thickness) were solution-doped with I$_2$ in hexane, rinsed with fresh hexane, and taken into a drybox for measurement. The conductivity was calculated using the average of five resistivity measurements.

[18] Narayana, C.; Periasamy, M. *Synthesis* **1985**, *3*, 253–268 and references therein.

[19] Izumi, T.; Iino, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1973**, 46, 2251–2252.

[20] NMR: The aromatic proton resonances of the PATKs are shifted downfield ~1 ppm relative to the PATs. No peaks were observed in the PAT regions, thus indicating complete CO insertion within the sensitivity of the NMR method. Anal. Found (Calcd) for **6b**, C$_6$H$_4$OS: C, 58.41 (58.04); H, 3.51 (3.25).

[21] Gol'dfarb, Y. L.; Danyushevskii, Y. L. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1956**, 1361–1369.

[22] (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.