J|A|C|S
COMMUNICATIONS

Transition-Metal-Free Synthesis of Alternating Thiophene−Perfluoroarene Copolymers

Yongfeng Wang and Mark D. Watson*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received September 2, 2005; Revised Manuscript Received January 8, 2006; E-mail: mdwatson@uky.edu

Thiophene-containing polymers, copolymers, and small molecules are heavily pursued as organic electronic materials.[1] Thiophenes are covalently entrained at their 2,5-positions within these materials most commonly by transition-metal-catalyzed coupling[2] or (electro)chemical oxidative polymerization. The limited means by which conjugated polymers can be purified may leave behind residues from catalysts and reactive functionalities, as well as intrinsic chemical defects arising from side reactions. If all other factors were equal, selection of synthetic methodology could be reduced to choosing which associated trace defects/impurities minimally impact targeted properties.

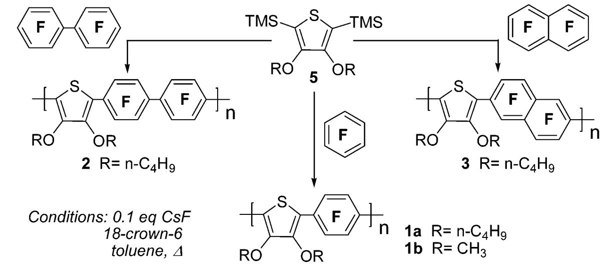
Regioselective fluoride-displacement reactions[3] undergone by perfluorinated π-systems (πF) provide unique opportunities to prepare conjugated polymers with minimal reagents/catalysts. Reactions between chalcogenide nucleophiles and πF's have been exploited to make alternating copolymers,[4] but few carbon−carbon bond-forming polymerizations are reported. Notable examples are oligomers and polymers obtained via reaction of πF's with metalated ferrocenes[5a] or indene,[5b] and small molecules from lithiated thiophenes.[1i] We prepared poly(phenylene ethynylene)s[5c] and thiophene copolymers from πF's and bis-lithiated diethynylbenzenes or thiophenes, but metalated monomers which are environmentally stable would be preferred.

We present preliminary investigations into exploiting the known[6] fluoride activation of silicon−carbon bonds toward electrophiles to prepare π−πF copolymers. Here, the electrophiles are perfluoroarenes and the silyl-functionalized, masked nucleophiles are 2,5-bis(trimethylsilyl)thiophenes. These studies are further motivated by the possibility to control supramolecular behavior via π−πF interactions and manipulation of (opto)electronic properties[7] at the molecular level by incorporation of highly electronegative fluorides.

The synthetic pathway and representative polymers are illustrated in Scheme 1. Facile purification of the monomers and resulting polymers makes this an attractive alternative to Stille coupling. In addition, πF's are substantially less expensive than their counterparts carrying additional functionality needed for transition-metal-catalyzed couplings. Copolymerization with various πF's is initiated here with catalytic fluoride ion, which is regenerated with each C−C bond formed. In principle, the only constituents of the reaction mixture should be target polymer, solvent, fluorotrimethylsilane (bp = 16 °C), and the water-extractable initiator system.

^{1}H, ^{13}C, and ^{19}F NMR spectra for **1a** and **2** indicate high chemical purity, in accordance with the structures in Scheme 1 (see Supporting Information for full spectra). Polymer **2** is defect-free within detection limits. The absence of detectable defects for polymer **2** indicates that perfluorobiphenyl is reactive only at the 4,4′-positions under these conditions. Small signals in the ^{19}F spectrum of **1a** indicate ortho/meta linkages or branching with estimated concentration ≤1/53 repeat units (1 defect/106 rings).

Scheme 1. Synthesis of Alternating Thiophene−πF Copolymers.



Polymer	Yield (%)	M_n (kDa) [PDI]^a	P_n GPC	P_n NMR	λ_{max}^{b} abs (nm)	T_g^{c} (°C)
1a	85%	28 [2.7]	75	37	334	57
1b	86%	insoluble	-	-	-	86
2	quant	17 [3.9]	33	17	325	96
3	quant	13 [3.4]	28	14	360	93

^{a} GPC vs polystyrene standards, toluene. ^{b} 10^{-5} M THF. ^{c} Differential scanning calorimetry (midpoint). Reaction conditions not optimized.

Similar to small-molecule products resulting from reaction of other nucleophiles with perfluoronaphthalene,[3] polymer **3** is significantly less regiopure. ^{19}F NMR shows three major signals corresponding to the symmetry depicted in Scheme 1, along with seven smaller signals arising from end-groups. There are three additional small signals, most likely from 2,7-substitution about naphthalene (∼7% based on relative integrals). NMR indicates that the end-groups are almost exclusively monosubstituted πF residues for polymers **1**−**3**. These polymers are therefore telechelic macromonomers, which might be end-functionalized via fluoride displacement by other nucleophiles.

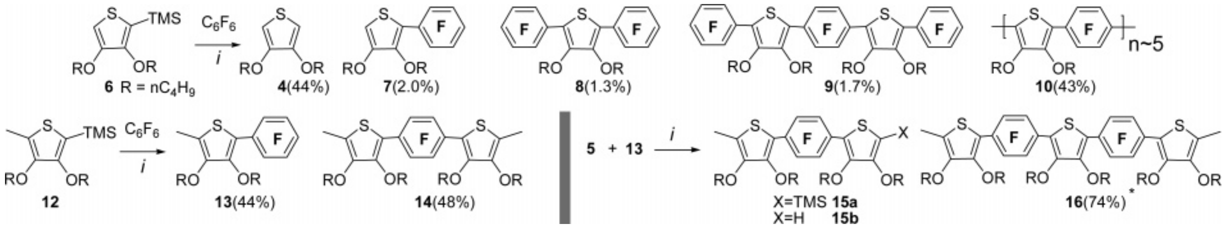
The end-groups are defined because the πF monomer was added in excess. This stoichiometric imbalance should have led to lower than observed degrees of polymerization according to the Carothers equation [$P_n = (1 + r)/(1 - r)$, where r is the ratio of limiting to excess monomer]. For polymer **1a**, the employed 20% molar excess of C_6F_6 should provide $P_n \approx 11$ ($M_n \approx 4$ kDa). The difference between measured (28 kDa) and predicted M_n far exceeds the typical 2-fold overestimation by gel permeation chromatography for semirigid polymers. Further, exact stoichiometry led to swollen but insoluble gels. This indicates that the average functionality of C_6F_6 under these conditions is >2, i.e., on average, slightly more than two reactive C−F bonds per molecule. This should lead to higher than predicted P_n, branching, and gelation, the last of which can be suppressed via stoichiometric imbalance.

In any case, the Carothers equation assumes equal reactivity of all functional groups, and therefore it cannot apply here. Most substituents activate the para position of pentafluorobenzenes toward further substitution.[3] The first and second attacks on C_6F_6 should occur with different rates.

The 2- and 5-positions of the thiophenes should also have variable reactivity in this scheme. These polymerizations must proceed through anionic intermediate(s), i.e., pentacoordinate silicate

10.1021/ja056074y CCC: $33.50 © 2006 American Chemical Society

Scheme 2. Model Reactions To Elucidate Reactivity[a]



[a] Conditions: (i) 0.1 equiv of CsF, 0.2 equiv of 18-C-6, toluene, 80 °C. (%) = isolated yields. *Based on **13**.

anions,[6b] whether or not desilylation to a formal carbanion intermediate precedes C−C bond formation. Therefore, reactivity at the 5-position should change significantly after an *electron-donating* TMS group at the 2-position is replaced by an *electron-withdrawing* πF group.

The model studies in Scheme 2 delineate functional group reactivity during the polymerizations. The well-defined nature of this chemistry is also supported by the mass balance for each model reaction, which is excellent, given that the products were isolated by chromatography. Compound **6** provided details beyond those involved in the related polymerization. Nearly 50% conversion to oligomers **8**−**10** requires that the thiophenes gain a second nucleophilic site. A reasonable scenario is proton transfer to fluoride-activated **6** from **7** (C_6F_5 lowers pK_a), also accounting for approximately eqimolar production of **4**. Fluoride is lost in this step but can be regenerated when the new anion of **7** reacts with other πF's to form the higher oligomers. The low P_n of the oligomers results from gross imbalance in stoichiometry between C_6F_6 and *bifunctional* thiophenes.

To avoid proton-transfer chemistry, the 5-position was blocked with a methyl group (**12**). The ratio of isolated **13** and **14** indicates that the first and second attacks on C_6F_6 proceed with essentially the same rate. On the other hand, the high isolated yield of **16** upon reaction of equimolar amounts of **5** with **13** shows that conversion of the second TMS group of **5** is markedly more rapid than that of the first. For that reason, ∼43% of **5** was recovered, separately, as unreacted starting material and monodesilylated product **6**. Since the amount of desilylation was approximated by the amount of CsF employed (∼10%) and desilylation is minimal during the related polymerizations, **6** was likely formed during workup. The remaining **5** and **13** were converted to an inseparable mixture of **15a**,**b**, thereby accounting for nearly complete mass balance.

These reactions contrast the reported behavior of silyl thiophenes during fluoride-activated palladium-catalyzed Hiyama coupling,[8] during which the thienyl groups are expelled from the catalytic cycle following proteodesilylation. We have, however, found that stoichiometric CsF and a palladium catalyst can indeed lead to moderately successful Hiyama coupling between silyl thiophenes and iodobenzene (∼40% conversion, not shown). The fluoride source may be crucial.

In regard to physical properties of the polymers **1**−**3**, steric repulsion between pendant alkoxy groups and fluorides should cause significant twisting along the backbone, leading to amorphous polymers. Accordingly, differential scanning calorimetry revealed only second-order transitions, and no birefringence was seen from thin films between cross-polars. Higher glass transition temperatures (T_g) for related amorphous materials seems to improve LED performance.[9] Substituting perfluorinated biphenyl (**2**) or naphthalene (**3**) for benzene as well as shorter methoxy (**1b**) for butoxy side chains increases the T_g by 30−40 °C in all cases. Unlike deeply colored thiophene (co)polymers, which may attain ground-state main-chain coplanarity, **1**−**3** are colorless solids and emit in the UV/visible blue region. The λ_{max} values for absorption/emission correlate well with the polymer structures: replacement of benzene by biphenyl led to a moderate blue shift, while naphthalene led to a significant red shift (∼30−40 nm, see Supporting Information).

All reaction conditions reported here are not optimized. Optimization is underway to reduce the required reaction temperatures via alternate solvents and fluoride sources. Lower temperatures should lead to even higher selectivity during bond formation. Our findings with other silyl-functionalized π-systems suggest that this pathway will find a broad scope similar to the related Hiyama coupling reaction.

Acknowledgment. This work was supported by the University of Kentucky Research Foundation.

Supporting Information Available: Experimental procedures; spectroscopic and analytical data; complete ref 1i. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355−62. (b) Hong, X. M.; Tyson, J. C.; Collard, D. M. *Macromolecules* **2000**, *33*, 3502−04. (c) Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084−85. (d) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324−33. (e) Welsh, D. M.; Kloeppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, *35*, 6517−25. (f) Caras-Quintero, D.; Baeuerle, P. *Chem. Commun.* **2004**, 926−27. (g) Zhang, W.; Moore, J. S. *Macromolecules* **2004**, *37*, 3973−75. (h) Zhang, W.; Moore, J. S. *Macromolecules* **2004**, *37*, 3973−75. (i) Crouch, D. J.; et al. *Chem. Mater.* **2005**, *17*, 6567−78.

(2) Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11−34.

(3) For a thorough review: Brooke, G. M. *J. Fluorine Chem.* **1997**, *86*, 1−76.

(4) (a) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230−31. (b) Kim, J.-P.; Lee, W.-Y.; Kang, J.-W.; Kwon, S.-K.; Kim, J.-J.; Lee, J.-S. *Macromolecules* **2001**, *34*, 7817−21. (c) Kimura, K.; Tabuchi, Y.; Nishichi, A.; Yamashita, Y.; Okumura, Y.; Sakaguchi, Y. *Polym. J.* **2001**, *33*, 290−96. (d) Kimura, K.; Tabuchi, Y.; Yamashita, Y.; Cassidy, P. E.; Fitch, J. W., III; Okumura, Y. *Polym. Adv. Technol.* **2000**, *11*, 757−65.

(5) (a) Deck, P. A.; Lane, M. J.; Montgomery, J. L.; Slebodnick, C.; Fronczek, F. R. *Organometallics* **2000**, *19*, 1013−24. (b) Deck, P. A.; Maiorana, C. R. *Macromolecules* **2001**, *34*, 9−13. (c) (d) Beckner, K. L.; Bullock, J. E.; Parkin, S.; Watson, M. D., in preparation.

(6) (a) Omotowa, B. A.; Shreeve, J. N. M. *Organometallics* **2000**, *19*, 2664−70. (b) Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757−86.

(7) (a) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900−03. (b) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138−40. (c) Winkler, B.; Meghdadi, F.; Tasch, S.; Mullner, R.; Resel, R.; Saf, R.; Leising, G.; Stelzer, F. *Opt. Mater.* **1998**, *9*, 159−62.

(8) (a) Denmark, S. E.; Ober, M. H. *Aldrichim. Acta* **2003**, *36*, 75−85. (b) Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58−61.

(9) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556−73.

JA056074Y