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New fluorinated thiophenes and their electrochemical properties

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The current intense interest in the search for new electrically conducting materials, which have applications as charge storage devices, electrochromic displays, non-linear optical devices, and sensors has led us to the synthesis and electrochemical study of a variety of substituted thiophenes. Our expectation was to selectively influence the oxidation potential of the thiophene ring by means of the electron-donating or -withdrawing power of the substituent in the 3-position.

Previously, we reported the synthesis and oxidative polymerization of 3-trimethylsilyl-, 3-germyl- and 3-trimethylgermylthiophenes [1]. As anticipated, the oxidation potentials of the 3-substituted thiophene monomers were low; however, the polymeric films were found to contain greatly reduced amounts of the Group 14 element based on the original composition of the parent monomeric thiophene. A recent claim that the electrochemical oxidation of 3-trimethylsilylthiophene in nitrobenzene produced poly(3-trimethylsilylthiophene) [2] prompted us to review our earlier work. Our polymerization experiments were repeated under the conditions employed by the authors [2] and our earlier results were verified; the polymers contained very small amounts of silicon as measured by energy dispersive X-ray analysis. In contrast to the authors [2] findings that electropolymerization of 3-trimethylsilylthiophene did not occur in acetonitrile, it was found that electropolymerization occurred readily with the formation of a film containing higher amounts of silicon (S/Si about 5:1), provided that the initial concentration of monomer was high enough (at least 30 mM).

Our studies have been extended to the preparation of thiophenes bearing polyfluoro and perfluoroalkyl groups such as 3-fluoromethyl-, 3-difluoromethyl- and trifluoromethylthiophene [3,4]; however, conductive films of good quality could only be produced from 3-difluoromethylthiophene [4]. Oxidized poly(3-difluoromethylthiophene) has an oxidation potential high enough to oxidize reduced poly(3-methylthiophene) and, thus, can serve as the cathode in a cell in which poly(3-methylthiophene) serves as the anode.

Recent work has focused on the preparation of monomers with fluorine-containing imide groups which have the potential to be self-doped polaron/bipolaron conductors in the oxidized state and ion conductors in the reduced state. Using a synthetic method reported by Murakami and Hikichi [5], we have prepared and characterized the new compound *N*-heptafluorobutyrylthiophene which undergoes electro-oxidative polymerization to produce a free-standing conductive film. A study of the composition and electrochemical properties of this material is under way.

References

[1] S.K. Ritter and R.E. Noftle, *Chem. Mater., 4* (1992) 872. 3-Trimethylsilylthiophene reported previously by: D. Häbich and F. Effenberger, *Synthesis,* (1979) 841; H. Frolich and W. Kalt, *J. Org. Chem., 55* (1990) 2993; Poly(3-trimethylsilyl- and 3-trimethylgermyl-thiophene) previously reported by transition-metal-induced polymerization of bis-Grignard compounds derived from the 3-substituted 2,5-dibromothiophenes: A. Czerwinski, D.D. Cunningham, A. Amer, J.R. Schrader, C. van Pham, H.B. Mark, Jr. and S. Pons, *J. Electrochem. Soc., 134* (1987) 1158.

[2] D. Abedimpe, P. Kathirgamanathan and P. Shepherd, *J. Electroanal. Chem., 346* (1993) 447.

[3] W. Büchner, R. Garreau, J. Roncali and M. Lemaire, *J. Fluorine Chem., 59* (1992) 301.

[4] S.K. Ritter, R.E. Noftle and A.E. Ward, *Chem. Mater., 5* (1993) 752.

[5] M. Murakami and M. Hikichi, Japan Patent 6912895, June 10, 1969.

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