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New Studies of Polyfuran and Polymers of 3-Substituted Furan Rings

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Polyfuran, polypyrrole, and polythiophene are conjugated planar aromatic polymers that have shown a great deal of promise as conductive polymers (Lee and Kertesz, 1988; Colon and Kwiatkowski, 1990; Sabbatini and Zambonin, 1992; Hong and Marynick, 1992; Christensen et al., 1994). Very little research on polyfuran (Fig. 1) has been reported in the literature, compared to that on polypyrrole and polythiophene. The synthesis of polyfuran by electrochemical means was reported in 1990 (Nessakh et al., 1990). However, the electrochemical formation of polyfuran requires an applied potential of greater than 3 volts. This potential was found to be too oxidizing for the resulting polymer, which decomposes oxidatively. Later, it was found that electrochemical polymerization of the tetramer, terfuran, could be accomplished at a lower potential, ~ 0.75 volt (Hernandez et al., 1993). Unlike polypyrrole and polythiophene, very little has been reported in the literature about chemical preparations of polyfuran (Baker et al., 1994; Robitaille and Leclerc, 1994; Murao, 1990). Out of these three polymers, polyfuran appears to be the most chemically unstable with respect to ring opening by nucleophilic reagents, especially in the oxidized, doped state. A potential method of ring opening would be nucleophilic attack on the α -carbons by water.

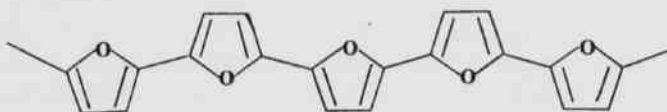


Fig. 1. Polyfuran in "head to tail" arrangement.

In this note we report the chemical synthesis of polyfuran starting from the monomer. Initially chemical polymerization of furan was attempted using a number of oxidizing agents. Several experiments using O_2 and a Ni catalyst, ferric chloride, and potassium ferricyanide resulted in only aliphatic products. An oxidizing agent which has proven more successful is pyridinium chlorochromate (PCC). Several polymers of furan have been synthesized with PCC under a variety of conditions. While these polymers were proven to be primarily aromatic (as shown by 1H NMR),

some still had evidence of ring opening (as shown in the IR spectra by OH stretch at $3200 - 3500\text{ cm}^{-1}$). The conditions which provided the least amount of ring opening (less than 5% aliphatic) are described as follows. Inhibitor free furan (60 mL) was added to 40 mL of a 0.29 M PCC solution in dry tetrahydrofuran (THF). The mixture was stirred at room temperature for 12 hours, resulting in a black, tar-like precipitant. Excess furan and THF were evaporated under reduced pressure. To remove the PCC from the product, the precipitant was repeatedly dissolved in dimethyl sulfoxide (DMSO), reprecipitated by the addition of THF and then decanted. This reprecipitation process was repeated until essentially all the PCC was recovered from the decanted THF (a minimum of four times). The product was then washed three times with THF and dried under vacuum. (Average yield = 4.2 ± 0.5 grams).

The product was characterized by UV, IR, NMR, and ESR spectroscopy. The UV-visible spectra of the polyfuran product exhibits a broad absorption band with a maximum of 469 nm. This broad absorption band, from 430 nm to 540 nm (2.9 eV - 2.3 eV) corresponds to a $\pi \rightarrow \pi^*$ transition. The infrared spectra of the polyfuran product has some bands that are characteristics of the monomer ($1585, 1530, 1383, 1200, 1160, 1060, 890, \text{ and } 730\text{ cm}^{-1}$). Additional bands shown in the IR of the polymer at 1165, 1090, and 1030 were attributed to C-H bending and stretching, and a band at 640 cm^{-1} was attributed to aromatic C-H out of plane bending. One band at 789 cm^{-1} can probably be attributed to the head to tail coupling (Fig. 1) of the carbon backbone. These data are consistent with IR data reported on polyfuran produced by electrochemical means (Hernandez et al., 1993). The room temperature ESR spectra of the polyfuran product exhibits a Gaussian signal ($\Delta H_{pp} = 0.8G$) with a spin concentration of 8.6×10^{19} spins/mole. The species responsible for the ESR signal is most likely unpaired electrons in the conjugated π system, which may come from defects in the polymer.

The chemical instability of polyfuran created problems during attempts to derivatize the polyfuran for cross-linking. Derivatization attempts using chlorosulfonic acid (as used in procedures for derivatization of polypyrrole and polythiophene) proved to be extremely unsuccessful. In each attempt, the polymer was broken down into small, ether soluble fragments. Similar depolymerization problems with

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functionalizing furan based polymers has been reported in the literature (Viswanathan et al., 1993). Therefore, we concentrated on derivatizing the monomer prior to polymerization.

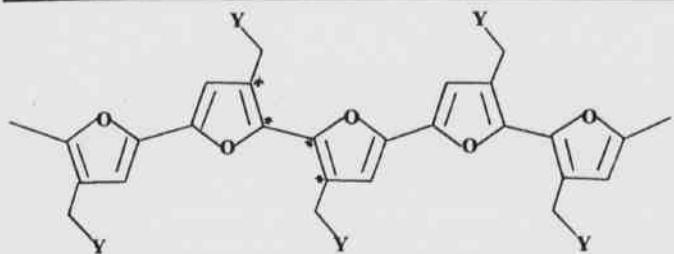


Fig. 2. Y = -OH, =O, -O-C(=O)-CH₃, -SH

Our most recent work has focused on an effort to determine an appropriate 3-substituted furan monomer which could be polymerized into a conjugated polymer that would maintain the co-planarity of the furan rings. A molecular modeling study, using a PCMODEL program (Serena Software), was conducted of polymers produced from several monomers (furan, 3-furan methanol, 3-furan methanol acetate, and 3-furan mercaptomethanol - Fig. 2). Structures of 4 to 20 monomeric units were examined to determine the most stable configuration and degree of co-planarity. The structures were energy minimized via molecular mechanics, and dihedral rotation (around the four atoms indicated in bold on Fig. 2) vs energy plots were produced. For each of the monomers the head to tail arrangement with the 3-substituent group pointed in opposite directions (as shown in Fig. 2) represented the lowest energy structure. Chains of polyfuran in head to head arrangements of six or more monomers acquire significant energy increases in the torsional angle from the curvature. Modeling of longer chains of polyfuran (30 to 50 monomers) shows that the torsional strain is relieved somewhat when an occasional monomer inverts from the head to tail arrangement during minimization. Modeling studies of polymers of 3-furan methanol showed a dramatic loss in coplanarity in chains containing 4 to 10 monomers. The twisting of the molecule, due to hydrogen bonding of the hydroxy groups, greatly disrupts the planarity of the pi system. While dimers of 3-furan methanol show coplanarity, tetramers have about a 30° rotation from planarity. The torsional angle increases with increasing polymer size. The models of 3-furan methanol acetate show very little planarity; however, models of 3-furan mercaptomethanol show very good coplanarity of the rings even in tetramers or larg-

er. The dihedral rotation plots (atoms indicated in Fig. 2) of 3-furan mercaptomethanol show extremely low energy minima (< 64.5) at 180°. The hydrogen bonding of 3-furan mercaptomethanol is much less extensive than that seen in 3-furan methanol; therefore, coplanarity is much more conserved. Synthesis of the monomer, chemical polymerization of studies of the unprotected monomer, as well as molecular modeling studies of 3-furan mercaptomethanol with a sulfhydryl protecting group (Bodanszky and Bodansky, 1989) recommend either a S-ethylcarbonyl or a S-acetamidomethyl protecting group) will be forthcoming.

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