POLYFURAN AND CO-POLYMERS: A CHEMICAL SYNTHESIS

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*The use of conductive polymers as a substitute for metallic conductors and semi-
conductors has attracted much attention in the literature. In particular, aromatic
heterocyclic polymers constitute an important class because they possess chemical
and electrical stability. The properties of these polymers are promising for their
many technological uses such as antistatic coatings, solar cells, electronic devises,
and so on. Polyfuran is among the least common heterocyclic polymers. Polyfuran
has been reported to be much less stable that either polypyrrole or polythiophene.
The chemical synthesis of polyfuran using a mild oxidizing agent, pyridinium*

chlorochromate is described. Also, the preparation of ten co-polymers of polyfuran with one to five percent pyrrole or thiophene is reported. The polymers are characterized by ^{1}H NMR, IR, and ESR spectroscopy, and the electrical conductivity of the synthetic polyfuran and ten co-polymers is provided.

INTRODUCTION

In recent years, electronically conducting polymers have attracted a great deal of attention from scientific and technological groups. Conducting polymers have many applications in fields such as gas sensors, rechargeable batteries, electronic and optical devices, and corrosion inhibitors of metal substances [1−9]. Many coastal cities in the U.S. and around the world spend enormous resources maintaining bridges and high-rise structures because of corrosion of the metal surfaces. Recently, conductive polymers have been shown to be very good corrosion inhibitors to metal substrates [3]. For much of the past decade polyaniline has generated tremendous interest as a corrosion inhibitor [7−8]. Although uncertain of the exact mechanism of corrosion inhibition, it is widely believed that redox forms of polyaniline help stabilize a thin oxide layer on the surface of iron. Polypyrrole has also received attention due to its ability to inhibit corrosion of metal surfaces [7,9]. Unlike polyaniline, polypyrrole can be prepared even at neutral pH, which can be an advantage [10].

Polymers of heterocyclic aromatic compounds, such as polypyrrole, polythiophene, polyaniline, and poly(p-phenylene) have also been of particular interest due to their small band gap (1.4−3.2 eV), and doping capability, which greatly varies the conductivity and so makes them useful in microelectronics and sensors [11−12]. The electrical conductivity of these polymers, both neutral and doped, has been greatly studied and seems to depend on the degree of disorder in the solid state, including the disorder caused by the dopant [8,12−13].

Polyfuran (Scheme 1) is an aromatic heterocyclic polymer that has attracted much less attention than polypyrrole, polyaniline, and polythiophene [8,14−16]. Polyfuran is among the least common and ill-defined polymers. However, as a five-membered heterocycle polyfuran should have electrical and optical properties similar to polypyrrole and polythiophene, with variations due to the differing electronegativity of the heteroatoms [12]. In 1997, ours was the first reported chemical synthesis of polyfuran from the monomer using a mild oxidizing agent, pyridinium chlorochromate [17]. Polyfuran has been shown to be much less stable than polypyrrole with respect to
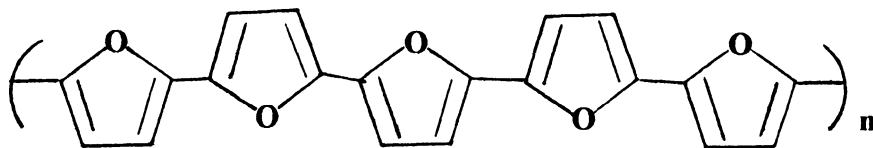
SCHEME 1: Structure of linear polyfuran

ring opening by nucleophilic reagents (Scheme 2), especially in the oxidized, doped state [18]. However, molecular modeling, via HyperChem, indicated that polyfuran can be greatly stabilized either by introducing small amounts (5% or less) of pyrrole or thiophene units throughout the polymer. The authors have therefore synthesized polyfuran and ten co-polymers (polyfuran with 1, 2, 3, 4, and 5% pyrrole, and polyfuran with 1, 2, 3, 4, and 5% thiophene). The ^{1}H NMR and IR spectra of these 10 new co-polymers show them to be almost completely aromatic, with little or no ring opening. Recently co-polymerization techniques to form primarily polypyrrole and poly-aniline composites have been used to create stable materials with a wide variety of properties [3,7,19].

Conductive polymers have been synthesized by a variety of techniques, including chemical, electrochemical, and photochemical polymerization [8]. Synthesis by chemical polymerization is by far the most useful method for preparing large amounts of the polymer. However, most of the preparations of aromatic polymers described in the literature utilize electrochemical polymerization processes. Due to the use of electrodes in electrochemical polymerization processes only small amounts of the polymer can be generated. The authors' preparation of polyfuran, as well as co-polymers of polyfuran with one to five percent pyrrole or thiophene, involves chemical polymerization by oxidative coupling. The mild oxidizing agent used in this synthesis of polyfuran is pyridinium chlorochromate (PCC). The chlorochromate anion (CrO_3Cl^-) could also serve as a doping material for these polymers. Chemical polymerization techniques, such as ours, are not often utilized in the preparation of co-polymer composites.
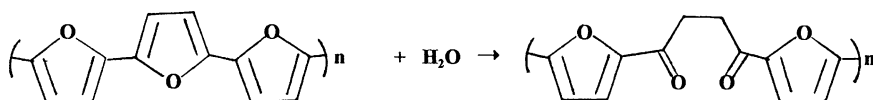
SCHEME 2: Opening of furan ring by water during polymerization

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Company Inc. The tetrahydrofuran (THF) solvent was refluxed and then distilled over sodium just prior to use. The furan, pyrrole, and thiophene were also freshly distilled and inhibitor free.

The synthesis of polyfuran was achieved by the following method. In an oven-dried flask inhibitor free furan (100 mL) was added to 40 mL of a 0.29 M PCC solution in dry, freshly distilled tetrahydrofuran (THF). The mixture was refluxed for 2 h and then stirred at room temperature for 12 h, resulting in a black, tar-like precipitate. Excess furan and THF were evaporated under reduced pressure. To remove the PCC from the product, the precipitate was repeatedly dissolved in 50 mL dimethyl sulfoxide (DMSO), re-precipitated by the addition of 200 mL THF. The slurry was stirred for 5 min and then the precipitated polymer was allowed to settle to the bottom of the flask. The mother liquors were then decanted. This re-precipitation 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 (200 mL) and dried under vacuum (Average yield = 4.2 + 0.5 grams).

A similar approach was taken for the preparation of co-polymers of furan and pyrrole, or thiophene. For the co-polymers of furan with pyrrole, one to five percent inhibitor free pyrrole was added, along with the furan, to a 0.29 M PCC solution in freshly distilled THF. For the co-polymers of furan with thiophene, one to five percent inhibitor free thiophene was added instead. The mixture was refluxed for 2 h and then stirred at room temperature for 12 h, resulting in a brown to black solid. Excess furan and THF were evaporated under reduced pressure. To remove the PCC from the product, the precipitate was repeatedly dissolved in 35 mL dimethyl sulfoxide (DMSO), re-precipitated by the addition of 200 mL THF. The slurry was stirred for 5 min and then the precipitated polymer was allowed to settle to the bottom of the flask. The mother liquors were then decanted. This re-precipitation process was repeated until essentially all the PCC was recovered from the decanted THF (a minimum of five times). The product was then washed three times with THF (200 mL) and dried under vacuum. (Average yield = 5.1 + 0.5 grams).

The ^{1}H NMR spectra were collected on a Bruker 200 MHz AC 200 Superconducting spectrometer. The spectral data was processed with NTNMR software produced by TeleMag. The NMR samples of the polymers were solutions utilizing deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent with tetramethylsilane (TMS) as an internal

standard. The FTIR spectroscopy was performed on a Bio-Rad FTS-40 FTIR spectrophotometer with the samples prepared as KBr pellets. Electron Spin Resonance (ESR) spectra were recorded on a Varian E-4 spectrometer. Direct current electrical conductivity was measured of each co-polymer as a pressed pellet of the dry polymer powder by a method described by Lyding et al. [20]. The molecular modeling was conducted by a Molecular Mechanics (MM+) computational method using HyperChem 6 software by Hypercube. Bond dipoles with no cut offs were selected as electrostatic options. Geometry optimization of polymers containing 12 to 2000 monomer units was achieved by the Polak-Ribiere method of conjugate gradient, with a terminal condition RMS gradient of 0.1 kcal/Å mole.

RESULTS AND DISCUSSION

Molecular Modeling

Molecular modeling of polyfuran showed that the head to tail (staggered) form of polyfuran is more stable than the head to head form. Chains of polyfuran in a head to tail arrangement (10−2000 monomers) maintain a planar conjugated arrangement with very little torsional strain. This arrangement should also allow a monomer chain to cross-link to two parallel chains without a great deformation of the basic chain structure. Initially, modeling was conducted to determine an appropriate 3-substituted furan monomer, which could be polymerized into a conjugated polymer that maintains the coplanarity of the furan rings. That modeling study showed that a 3-chloromethyl substituted polyfuran would remain the most coplanar and still provide a site for cross-linking. However, because a large amount of ring opening resulted when the authors attempted to synthesize the 3-chloromethyl substituted polyfuran a new approach was taken. The new approach involved the molecular modeling of co-polymers of polyfuran with 1 to 5% pyrrole or 1 to 5% thiophene units. Molecular modeling studies showed that co-polymers of furan with 1 or 2% pyrrole were more stable with great coplanarity along the aromatic pi system (Figure 1). Molecular modeling studies have also been conducted of the co-polymers with cross-linking from the 3-position on the pyrrole (or thiophene) units. The cross-links consisted of

FIGURE 1 Co-polymer of polyfuran with 2% pyrrole.
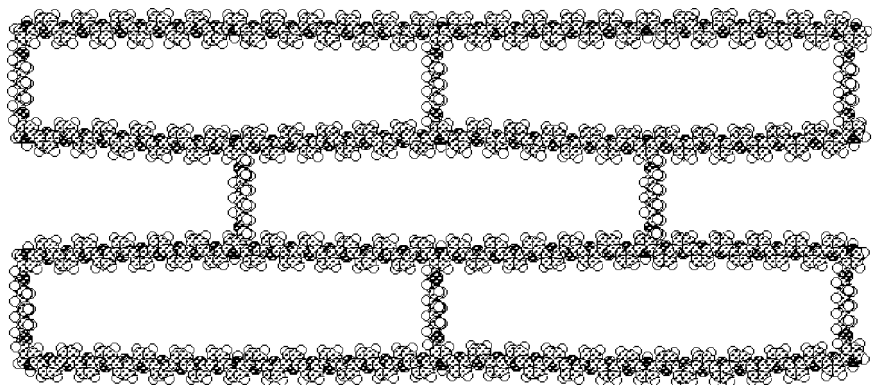
FIGURE 2 Co-polymer of polyfuran with 2% pyrrole: Cross-linked.

$-CH_2O-(CH_2)_n-OCH_2-$ connected from the 3-position of pyrrole or thiophene units in the polyfuran co-polymers.

Initial model studies of pyrrole-furan co-polymers show that cross-linking is easier when even numbers of furans (at least 10 units in head to tail arrangement) are placed between 2 pyrrole units. These model studies of the pyrrole-furan co-polymers also showed that cross-links of $-CH_2O-(CH_2)_n-OCH_2-$ (where $n = 7$ or 9) allows coplanarity even when large multi-chain lattices are constructed (Figure 2). This arrangement of stacked aromatic rings may allow for two-dimensional conductivity.

In the case of the thiophene-furan co-polymers the model studies indicate that co-polymers with 1 or 2% thiophene, and cross-links of $-CH_2O-(CH_2)_n-OCH_2-$, (where $n = 5$ or 7), continue to maintain a planar pi electron ring system. Co-polymers of 4 or 5% thiophene with similar cross-links, however, showed some twisting into a helical pattern.

Synthesis

Polyfuran, like polypyrrole and polythiophene, is a conjugated planar aromatic polymer (Scheme 1) that shows a great deal of promise as a conductive polymer. Very little research on polyfuran has been reported in the literature, compared to that of polypyrrole and poly-thiophene. The synthesis of polyfuran was first reported in 1984 but only by electrochemical means [14]. However, the electrochemical formation of polyfuran required an applied potential of >3 volts. This potential was found to be too oxidizing for the resulting polymer, which decomposed oxidatively. In 1990, Zotti et al. found polyfuran could be formed with a somewhat lower voltage using a Ni(bipy)$_3^{2+}$

catalyst and an electrochemical technique [15]. In 1993, Glenis et al. found that polyfuran could be made by electrochemical polymerization of the tetramer, at a lower potential of 0.75 volts [16]. Glenis et al. used a variety of dopant anions (i.e., $CF_3SO_3^-$, BF_4^-, ClO_4^-, and PF_6^-) in their preparations of polyfuran. They found that the polymer color and structure (according to the IR spectra) to be greatly influenced by the nature of the dopant anion. In 1997, the present authors reported the chemical synthesis of polyfuran from the monomer using a mild oxidizing agent, pyridinium chlorochromate [17]. During synthesis, polyfuran is believed to be much less stable that polypyrrole with respect to ring opening by nucleophilic reagents, such as water (as shown in Scheme 2). Therefore, the authors took great care to utilize anhydrous conditions. A similar approach was utilized in the preparation of the co-polymers of furan with 1 to 5% pyrrole, and furan with 1 to 5% thiophene. The pyridinium chlorochromate serves as a extremely mild oxidizing agent, and the chlorochromate anion (CrO_3Cl^-) can also serve as a dopant. However, in each case essentially all the pyridinium chlorochromate was recovered from the product by repeatedly dissolving the polymer in a small amount of dimethyl sulfoxide (DMSO) and then precipitating it with the addition of cold tetrahydrofuran (THF). The polymer is then decanted. Because pyridinium chlorochromate is very soluble in THF as well as DMSO, it can be recovered from the mother liquors. The furan co-polymer products vary in color from brown to shiny black, depending on the amount of pyrrole or thiophene added. ^{1}H NMR spectra were used to detect ring opening, by comparing aromatic hydrogen signals to aliphatic hydrogen signals.

^{1}H NMR Spectra

The ^{1}H NMR spectra of all the synthetic co-polymers show significant peak broadening typically seen in polymer spectra. The ^{1}H NMR spectra of polyfuran, prepared using PCC, display primarily aromatic signals (δ 7.420, 7.740, 8.066, 8.581). However, about 3 to 7% ring opening was detected through aliphatic signals (in addition to DMSO-d_6 solvent signals). When one to five percent thiophene is combined in the polyfuran polymer the aromatic portion of the spectra increases in complexity (with signals at δ 7.132, 7.412, 7.787, 8.336, 8.594, 8.865). However, the amount of ring opening was decreased to 3 to 5% as observed through relative intensities of aliphatic signals. When one to five percent pyrrole was used in preparation of the polyfuran the aromatic portion of the ^{1}H NMR spectra is further complicated (signals at δ 7.094, 7.421, 7.549, 7.787, 8.023, 8.322, 8.510, 8.589,

8.861, 9.116), however only 0 to 2% aliphatic signals were observed. This indicates that the introduction of small amounts of pyrrole or thiophene into the polyfuran matrix helps to prevent ring opening and loss of aromaticity during the polymerization process.

IR Spectra

The infrared spectra of polyfuran (Figure 3) has some bands that are characteristic of the monomer (1585, 1535, 1438, 1200, 1160, 1060, 940, and 730 cm^{-1}). Additional bands shown in the IR of polyfuran at 1165, 1090, and 1030 cm^{-1} were attributed to C-H bending and stretching, and additional bands at 953, 790, and 630 cm^{-1} were contributed to aromatic C-H out of plane bending. These bands are consistent with IR spectra reported of polyfuran prepared by electro-chemical means [15,16]. Some ring opening was suggested by a band at 1740 cm^{-1} in the IR spectra of polyfuran. This band was reduced significantly and disappeared completely in several of the IR spectra of co-polymers of furan with 1 to 5% pyrrole (Figure 4) or 1 to 5% thio-phene (Figure 5). Figures 2–5 shows sample IR spectra of polyfuran
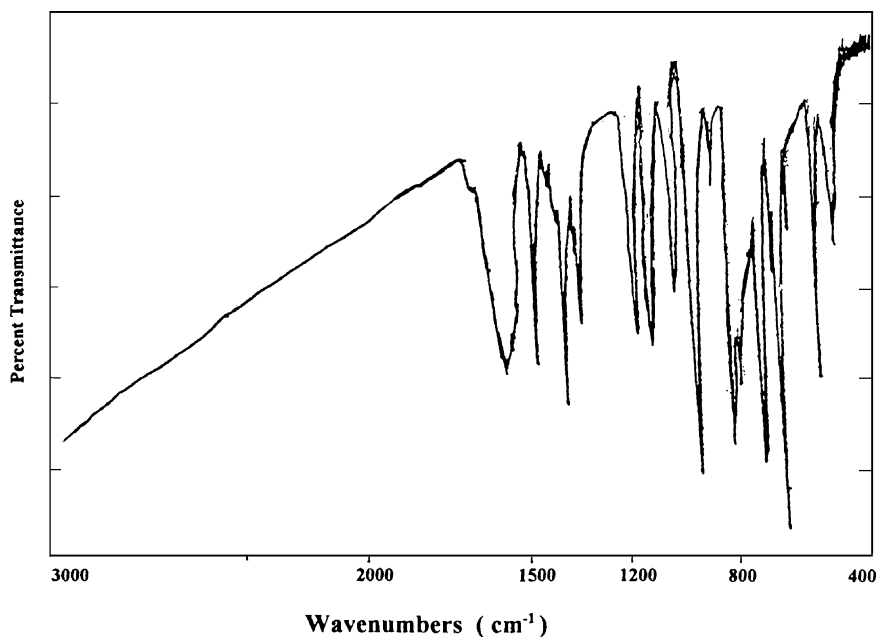
FIGURE 3 Infrared transmission spectra of polyfuran from powder pressed in KBr.
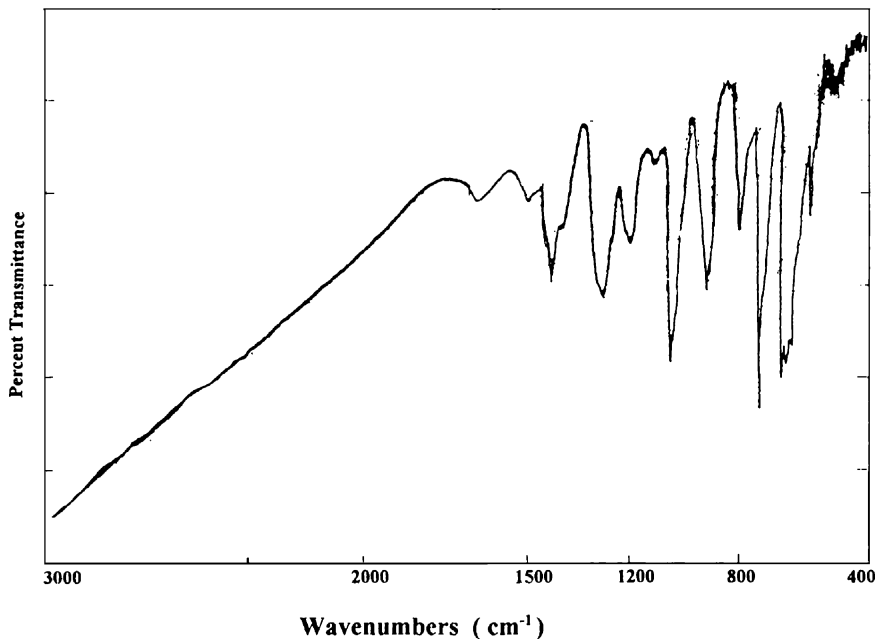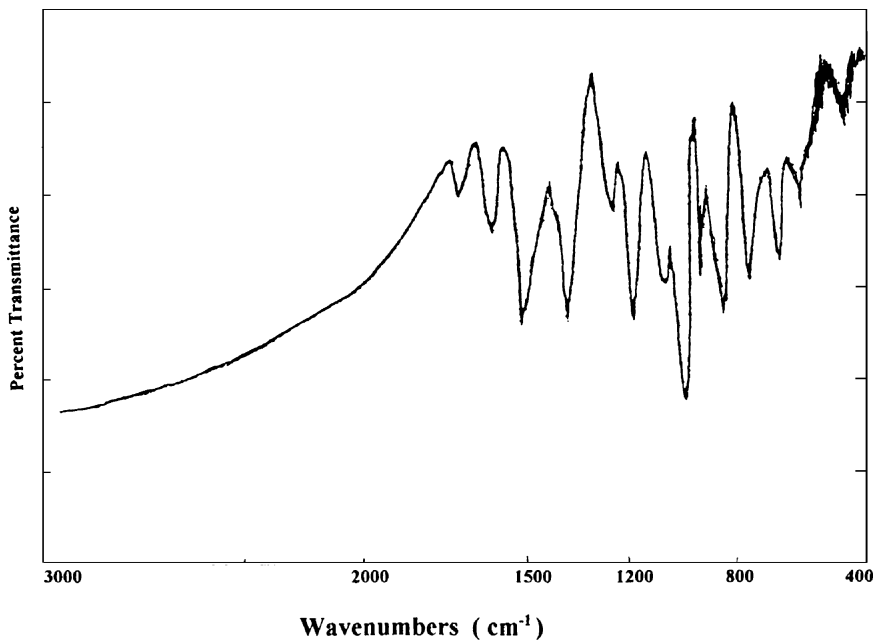
FIGURE 4 Infrared transmission spectra of polyfuran with 2% pyrrole from powder pressed in KBr.

(PF), polyfuran with 2% thiophene (PF-T2), and polyfuran with 2% pyrrole (PF-P2).

ESR Spectra

Polyfuran and the co-polymers of polyfuran containing either 1 to 5% pyrrole or 1 to 5% thiophene were examined by electron resonance spectroscopy (ESR). The room temperature ESR spectra of polyfuran (PF) exhibits a Guassian signal ($\Delta H_{pp} = 0.79\,\text{G}$) with a spin concentration of 8.2×10^{19} spins/mole. In the polyfuran co-polymers produced with 1 to 5% thiophene (PF-T1 through PF-T5), the ΔH_{pp} line width decreases to $0.71\,\text{G}$ as the amount of thiophene increases. A similar observation is made in the co-polymers produced with 1 to 5% pyrrole (PF-P1 through PF-P5) in that the ΔH_{pp} line width decreases to $0.69\,\text{G}$. Polyfuran and the co-polymers all have g values ranging from 2.0011 to 2.0015, which indicates that unpaired electrons of the conjugated carbon backbone structure are most likely responsible for the ESR signals. No g-value anisotropy is observed in any of the co-polymers.

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FIGURE 5 Infrared transmission spectra of polyfuran with 2% thiophene from powder pressed in KBr.

TABLE 1 Electrical Conductivity of Pressed Pellets of Polyfuran and Copolymers at 298 K

Material	Conductivity, S/cm
Polyfuran	1.3×10^{-6}
PF-T1	7.8×10^{-5}
PF-T2	2.1×10^{-4}
PF-T3	6.8×10^{-4}
PF-T4	7.3×10^{-4}
PF-T5	9.5×10^{-4}
PF-P1	7.3×10^{-4}
PF-P2	1.5×10^{-3}
PF-P3	9.2×10^{-3}
PF-P4	8.6×10^{-3}
PF-P5	3.2×10^{-2}

PF-T1 . . . PF-T5 = polyfuran with 1% thiophene . . . polyfuran with 5% thiophene. PF-P1 . . . PF-P5 = polyfuran with 1% pyrrole . . . polyfuran with 5% pyrrole.

Electrical Conductivity

The electrical conductivity at 25°C for polyfuran prepared through chemical polymerization using pyridinium chlorochromate is 1.3×10^{-6} S/cm. The electrical conductivity of the furan-thiophene co-polymers (PF-T1 through PF-T5) ranged from 7.8×10^{-5} to 9.5×10^{-4} S/cm, as shown in Table 1. Higher electrical conductivity was observed in the furan-pyrrole co-polymers (7.3×10^{-4} to 3.2×10^{-2} S/cm). In general the electrical conductivity of the co-polymers is directly proportional to the amount of thiophene or pyrrole introduced into the polymer matrix. The apparent increase in conductivity is attributed to an increase in the stability of the polymer and a higher degree of backbone conjugation. This is supported by the spectral data of the co-polymers.

CONCLUSIONS

Very little research on polyfuran has been reported in the literature, compared to that of polypyrrole and polythiophene. Although, polyfuran is predicted to be a good conductive polymer, polyfuran is much less stable than polypyrrole and polythiophene with respect to ring opening by nucleophilic reagents, especially in the oxidized, doped state. This article has demonstrated that polyfuran can be produced in reasonable yield through chemical polymerization and has also shown that excessive ring opening can be avoided through the use of anhydrous conditions during the polymerization process. Also, the quality of the polymer is improved, and ring opening minimized, by the introduction of small amounts of thiophene or pyrrole into the polymer matrix. The absence of g-value anisotropy in the ESR and the correlation between the increase in electrical conductivity with polymer stability may indicate that the charge transport occurs primarily along the conjugation of the carbon backbone.

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