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Rose M. McConnell

University of Arkansas at Monticello

Walter E. Godwin

University of Arkansas at Monticello

Susan E. Baker

University of Arkansas at Monticello

Kenya Powell

University of Arkansas at Monticello

Martha Baskett

University of Arkansas at Monticello

See next page for additional authors

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Co-polymers of Furan with Pyrrole or Thiophene: A Synthetic Study

Authors

Rose M. McConnell, Walter E. Godwin, Susan E. Baker, Kenya Powell, Martha Baskett, Amy Morara, and Xiadong Ma

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Rose M. McConnell*, Walter E. Godwin, Susan E. Baker,
Kenya Powell, Martha Baskett, and Amy Morara
School of Mathematical & Natural Sciences
University of Arkansas at Monticello
Monticello, AR 71656

Xiadong Ma
College of Science
and Engineering Technology
University of Arkansas at Little Rock,
Little Rock, AR 72204

*Corresponding Author

Abstract

The use of conductive polymers as a substitute for metallic conductors and semiconductors has attracted much attention in the literature. In particular, aromatic heterocyclic polymers constitute an important class since they possess chemical and electrical stability in both the oxidized (doped) and neutral (undoped) state. Doping a polymer allows one to vary its electrical, mechanical, optical, and thermal properties. The properties of these polymers are promising for their many technological uses such as antistatic coatings, solar cells, and electronic devices. Polyfuran is among the least common heterocyclic polymers. Polyfuran has been reported to be much less stable than either polypyrrole or polythiophene. The preparation of co-polymers of polyfuran with two percent pyrrole or thiophene is reported. The polymers are characterized by ^1H NMR, IR, and ESR spectroscopy, and the electrical conductivity of the doped and un-doped synthetic polyfuran and co-polymers is provided.

Introduction

Electronically conducting polymers have attracted a great deal of attention from scientific and technological groups. There are many applications for conducting polymers in fields such as gas sensors (Nigorikawa et al., 1995), rechargeable batteries (Choi et al., 2001), electronic and optical devices (Nguyen and Potje-Kamloth, 1999), and corrosion inhibitors of metal substances (Rajagopalan and Iron, 2001). In the U.S. many cities 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 (Mikalo et al., 2001). For the past ten years polyaniline has generated tremendous interest as a corrosion inhibitor (Kumar and Sharma, 1998). Many investigators believe that redox forms of polyaniline

help stabilize a thin oxide layer on the surface of iron (Dalas et al., 2000). Polypyrrole has also received attention due to its ability to inhibit corrosion of metal surfaces (Su and Iron, 2000; Ivanov et al., 2001). Unlike polyaniline, polypyrrole can be prepared even at neutral pH, which can be an advantage (Kang and Geckeler, 2000).

Polymers constructed of heterocyclic aromatic compounds, such as polypyrrole, polythiophene, polyaniline, have also been of particular interest due to their small band gap (1.4 - 3.2 eV) and doping capability. Doping a polymer with a small amount of a metal salt can greatly vary the conductivity of the polymer and so makes it useful in microelectronics and sensors (Kumar and Sharma, 1998). The electrical conductivity of these polymers, both neutral and doped, seems to depend on the degree of disorder in the solid state, including the disorder caused by the dopant (Mikalo et al., 2001; Ivanov et al., 2001).

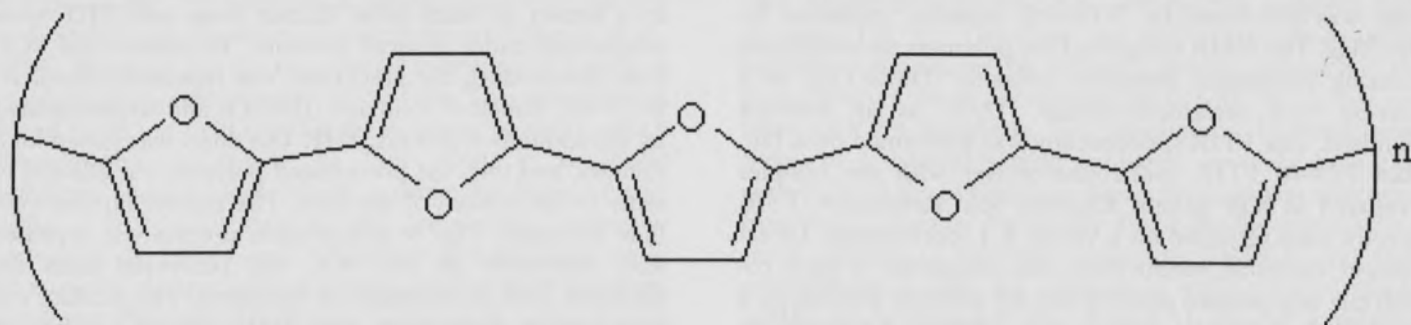


Fig. 1. Polyfuran in the more stable head to tail configuration.

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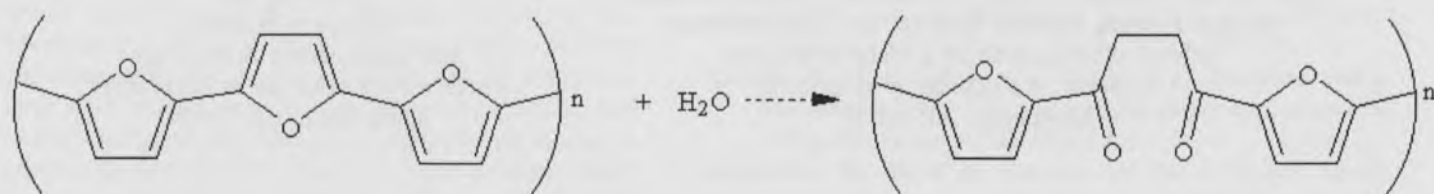


Fig. 2. Ring opening of polyfuran by nucleophilic attack of water.

Polyfuran (Fig. 1) is an aromatic heterocyclic polymer that is fairly uncommon and ill-defined. 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 (Ivanov et al., 2001). In 1997, ours was the first reported chemical synthesis of polyfuran from the monomer using a mild oxidizing agent, pyridinium chlorochromate (McConnell et al., 1997). Polyfuran has been shown to be much less stable than polypyrrole with respect to ring opening by nucleophilic reagents (Fig. 1) especially in the oxidized, doped state (Distefano et al., 1991). However, molecular modeling, via HyperChem, indicated that polyfuran can be greatly stabilized either by introducing small amounts of pyrrole or thiophene units throughout the polymer. Co-polymerization techniques to form primarily polypyrrole and polyaniline composites have been used to create stable materials with a wide variety of properties (Aubert et al., 1999; Dalas et al., 2000; Rajagopalan and Iron, 2001). We have therefore synthesized polyfuran and co-polymers (polyfuran with 2% pyrrole and polyfuran with 2% thiophene) in both the doped and un-doped states. The ^1H NMR and IR spectra of these polymers show them to be almost completely aromatic with little or no ring opening.

Materials and Methods

The ^1H NMR spectra were collected on a Bruker 200 MHz AC 200 superconducting spectrometer. The spectral data was processed by 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. (1988). All chemicals were purchased from Aldrich Chemical Company Inc. The tetrahydrofuran (THF) solvent was refluxed and 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) with or without doping agent (0.1 mg silver *p*-toluene sulfonate). The mixture was refluxed for 2 hours and then 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 50 mL dimethyl sulfoxide (DMSO) and re-precipitated by the addition of 200 mL THF. The slurry was stirred for 5 minutes, 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, two percent inhibitor free pyrrole was added, along with the furan, to the 0.29M PCC solution in freshly distilled THF. For the co-polymers of furan with thiophene, two percent inhibitor free thiophene was added instead. The mixture was refluxed for 2 hours and then stirred at room temperature for 12 hours, resulting in a brown to black solid. Excess furan and THF were evaporated under reduced pressure. To remove the PCC from the product, the precipitant was repeatedly dissolved in 35 mL dimethyl sulfoxide (DMSO) and re-precipitated by the addition of 200 mL THF. The slurry was stirred for 5 minutes, 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).

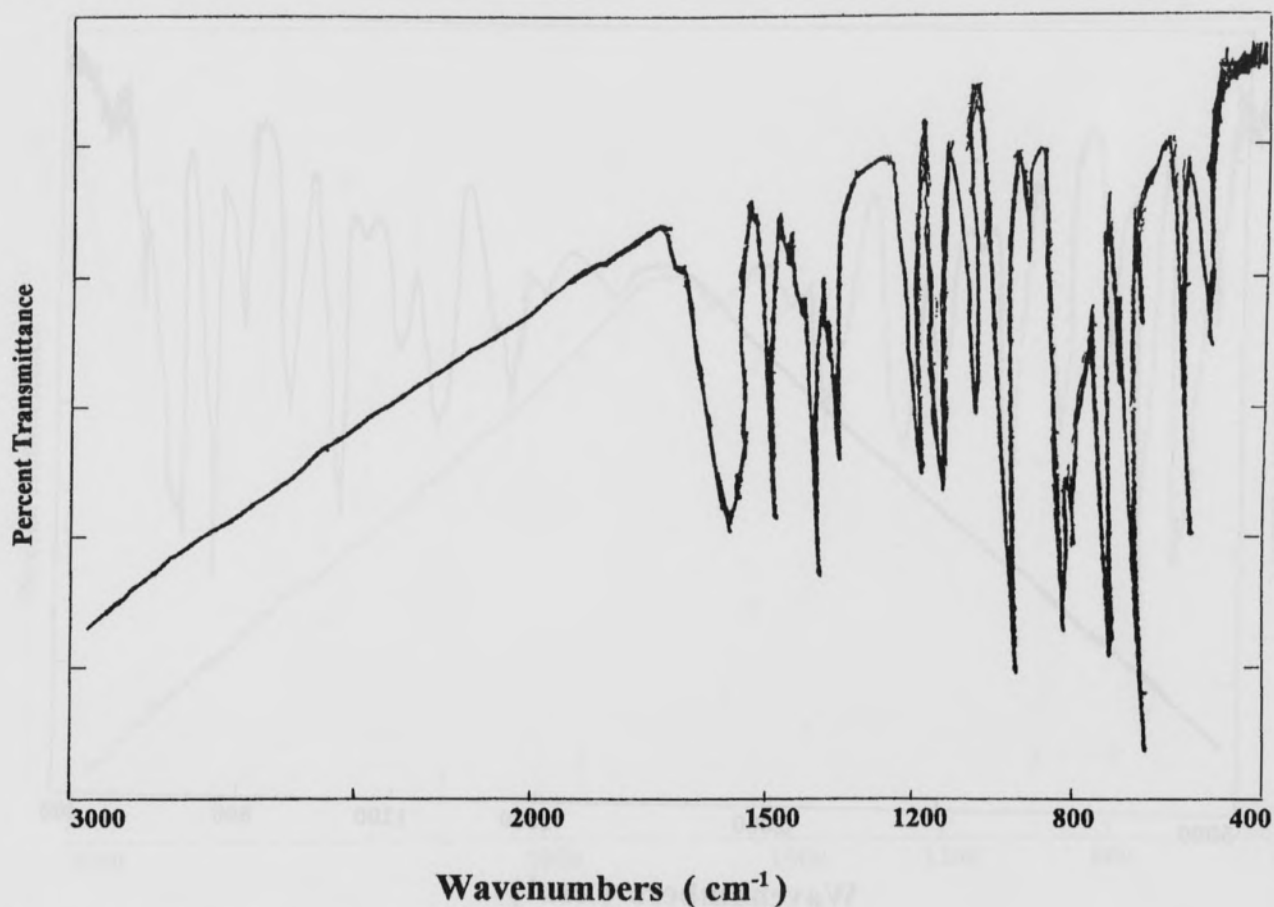


Fig. 3. Infrared transmission spectra of polyfuran from powder pressed in KBr.

Results and Discussion

Synthesis.--Polyfuran, like polypyrrole and polythiophene, is a conjugated planar aromatic polymer (Fig. 1). Little research on polyfuran has been reported in the literature compared to that of polypyrrole and polythiophene. The synthesis of polyfuran was first reported in 1984 but only by electrochemical means (Ohsawa et al., 1984). 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 $\text{Ni}(\text{bipy})_3^{2+}$ catalyst and an electro-reduction technique. 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. Glenis et al. (1993) 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, we reported the chemical synthesis of polyfuran from the monomer using a mild oxidizing agent, pyridinium chlorochromate (McConnell et al., 1997). During synthesis, polyfuran is believed to be much less stable than polypyrrole with respect to ring opening by nucleophilic reagents, such as water (Fig. 2). Therefore, we took great care to utilize anhydrous conditions. We utilized a similar approach in the preparation of the co-polymers of furan with 2% pyrrole and furan with 2% thiophene. The pyridinium chlorochromate serves as an extremely mild oxidizing agent. 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). In some cases the dopant, 1 mL of a solution containing 0.1mg/mL silver p-toluene sulfonate in DMSO, is added along with the oxidizing agent. The furan co-

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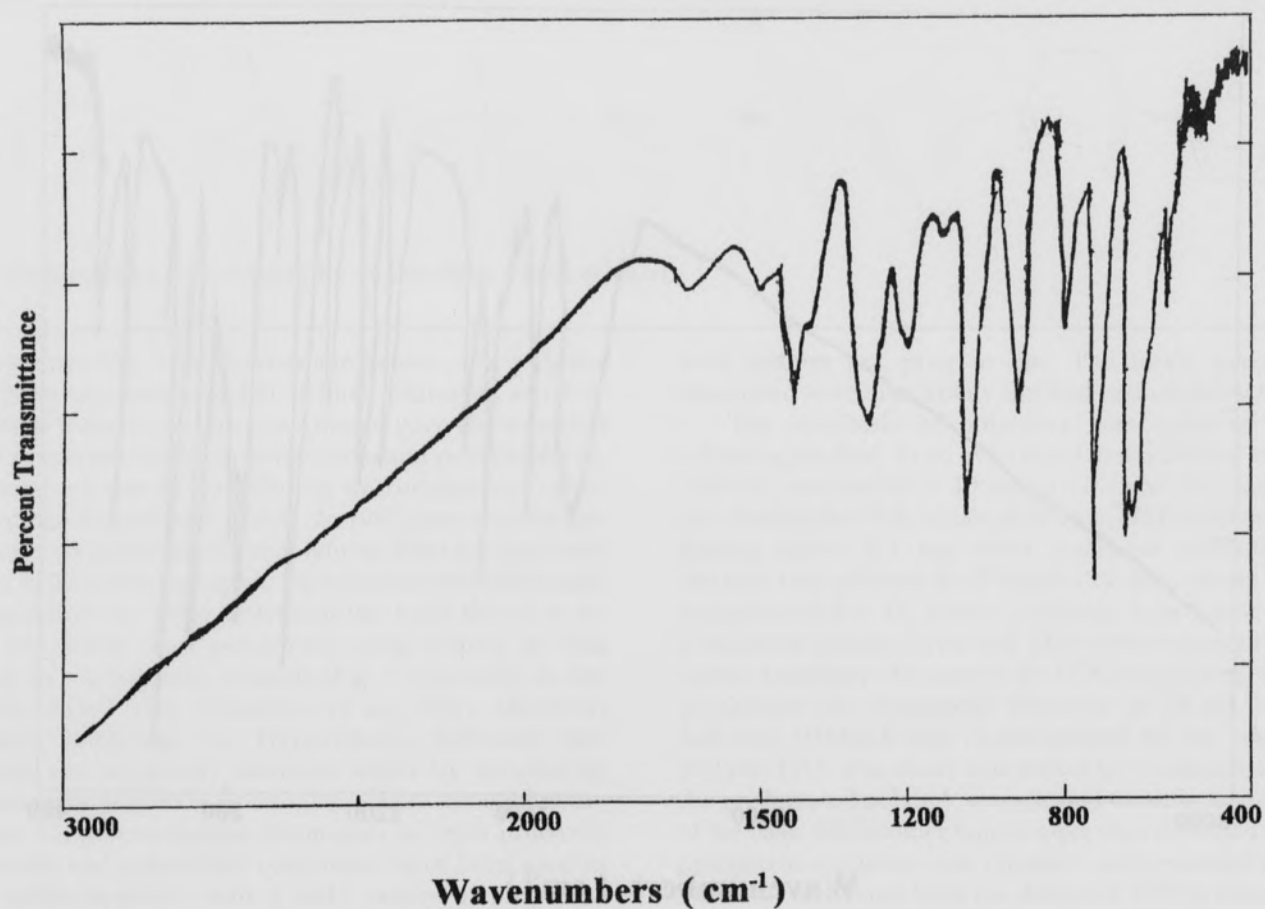


Fig. 4. Infrared transmission spectra of polyfuran with 2% pyrrole.

polymer products vary in color from brown to shiny black, depending on the dopant and pyrrole or thiophene added. ^1H NMR spectra were used to detect ring opening by comparing aromatic hydrogen signals to aliphatic hydrogen signals.

^1H NMR Spectra.--The ^1H NMR spectra of all the synthetic co-polymers show significant peak broadening typically seen in polymer spectra. The ^1H NMR spectra of polyfuran, prepared using PCC, display primarily aromatic signals (δ 7.420, 7.740, 8.066, 8.581). However, about 5% ring opening was detected through aliphatic signals (in addition to DMSO- d_6 solvent signals). When two 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 % as observed through relative intensities of aliphatic signals. When two percent pyrrole was used in preparation of the polyfuran the aromatic portion of the ^1H 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, the observation of about 1% aliphatic signals in the ^1H NMR also indicated that only a trace amount of ring opening occurred during the reaction. This demonstrates 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 (Fig. 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 electrochemical means (Zotti et al., 1990; Glenis et al., 1993). Some ring opening was suggested by a band at 1740 cm^{-1} in the IR spectra of polyfuran. This

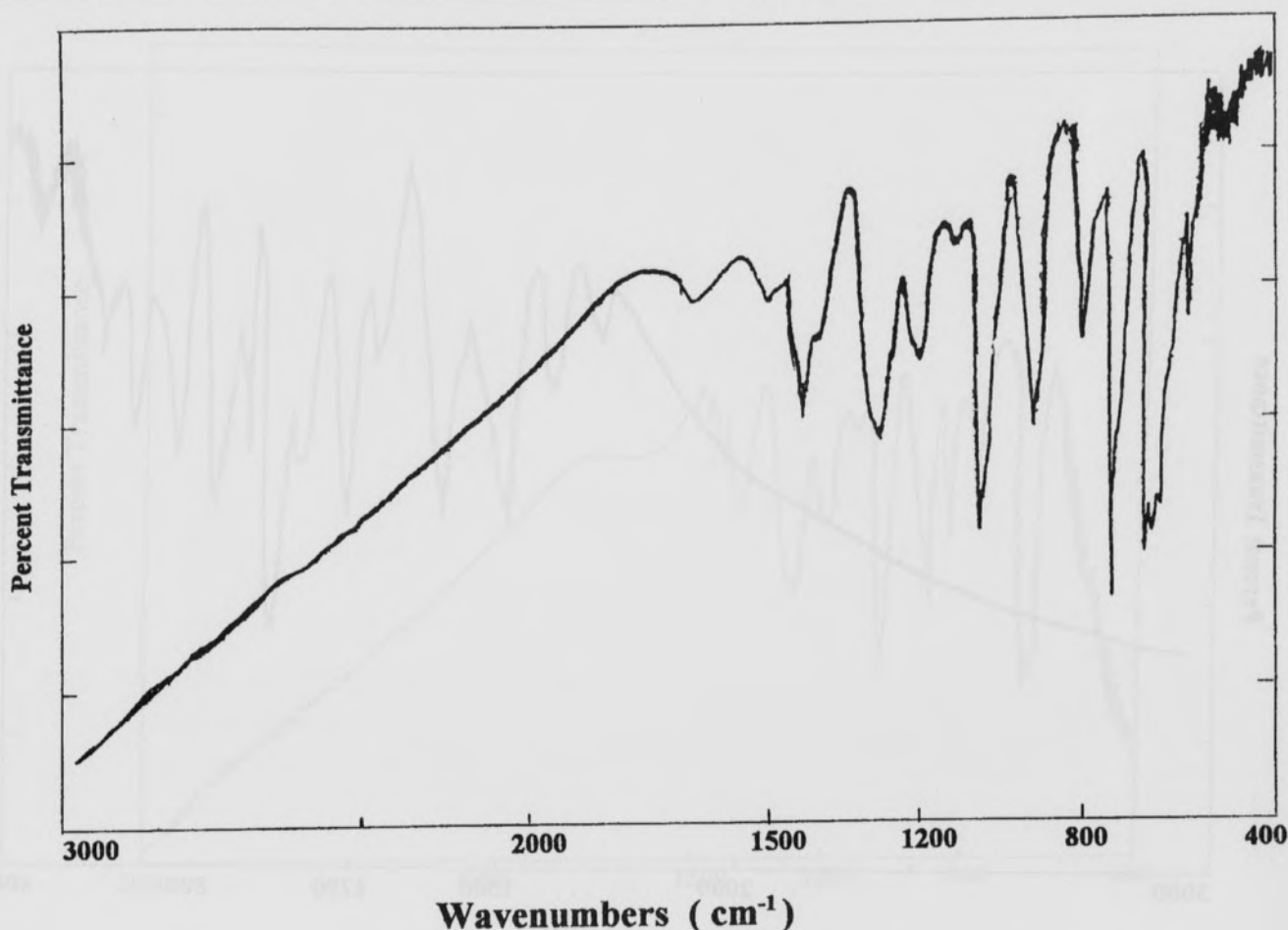


Fig. 5. Infrared transmission spectra of polyfuran with 2% thiophene.

band was reduced significantly and disappeared completely in several of the IR spectra of co-polymers of furan with 2% pyrrole (Fig. 4) or 2% thiophene (Fig. 5). Figure 6 shows sample IR spectra of polyfuran (PF) doped with silver p-toluene sulfonate. The band at 1740 cm^{-1} (attributed to ring opening) has been significantly reduced. This is also the case in the IR spectra (Figs. 7 and 8) of doped polyfuran with 2% thiophene (PF-T2) and doped polyfuran with 2% pyrrole (PF-P2).

ESR Spectra.--Polyfuran and the co-polymers of polyfuran, both the neutral and doped forms, containing either 2% pyrrole or 2% thiophene were examined by electron resonance spectroscopy (ESR). The room temperature ESR spectra of polyfuran (PF) exhibits a Gaussian signal ($\Delta H_{pp} = 0.79\text{G}$) with a spin concentration of 8.2×10^{19} spins/mole. In the polyfuran doped with silver p-toluene sulfonate, the Gaussian signal ($\Delta H^1 = 0.68\text{G}$) was significantly reduced. In the polyfuran co-polymers

produced with 2% thiophene (PF-T2), the H^1 line width was 0.75G in the un-doped polymer and 0.70G in the doped polymer. A similar observation is made in the co-polymers produced with 2% pyrrole (PF-P2) in that the H^1 line width was 0.71G in the undoped version and 0.65G in the doped co-polymer. Polyfuran and the co-polymers all have g values ranging from 2.0011 to 2.0014 which indicates that unpaired electrons of the conjugated carbon backbone structures are most likely responsible for the ESR signals. No g -value anisotropy is observed in any of the co-polymers.

Electrical Conductivity.--The electrical conductivity at 25°C for polyfuran prepared through chemical polymerization using pyridinium chlorochromate is $1.3 \times 10^{-6}\text{ S/cm}$ for the neutral polymer and $1.2 \times 10^{-3}\text{ S/cm}$ for polyfuran doped with silver p-toluene sulfonate. The electrical conductivity of the furan-thiophene co-polymer (PF-T2) was $2.1 \times 10^{-4}\text{ S/cm}$ in the undoped form (Table 1) and $1.1 \times 10^{-2}\text{ S/cm}$ in the doped form. This increase in

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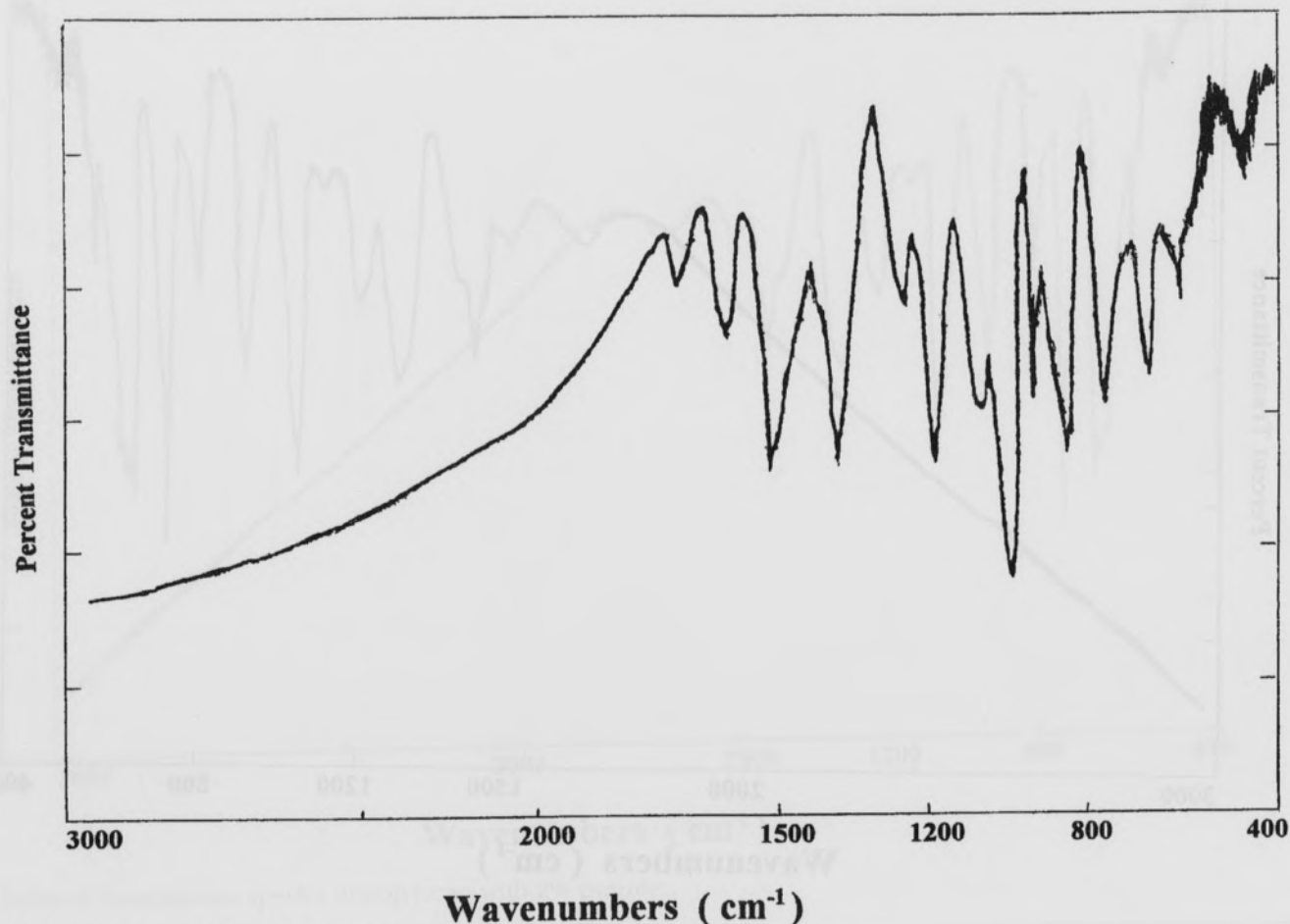


Fig. 6. IR spectra of polyfuran doped with silver p-toulene sulfonate.

electrical conductivity was also observed in the doped furan-pyrrole co-polymer (from 1.5×10^{-2} S/cm for the undoped polymer to 3.5×10^{-2} S/cm for the doped co-polymer). In general the electrical conductivity is higher for the co-polymers and is further increased when the dopant is 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

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. We have demonstrated that not only can polyfuran be produced in good quantity through chemical

polymerization, but 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. Under these conditions the use of silver p-toulene sulfonate as a dopant does not decrease the stability of the co-polymers. 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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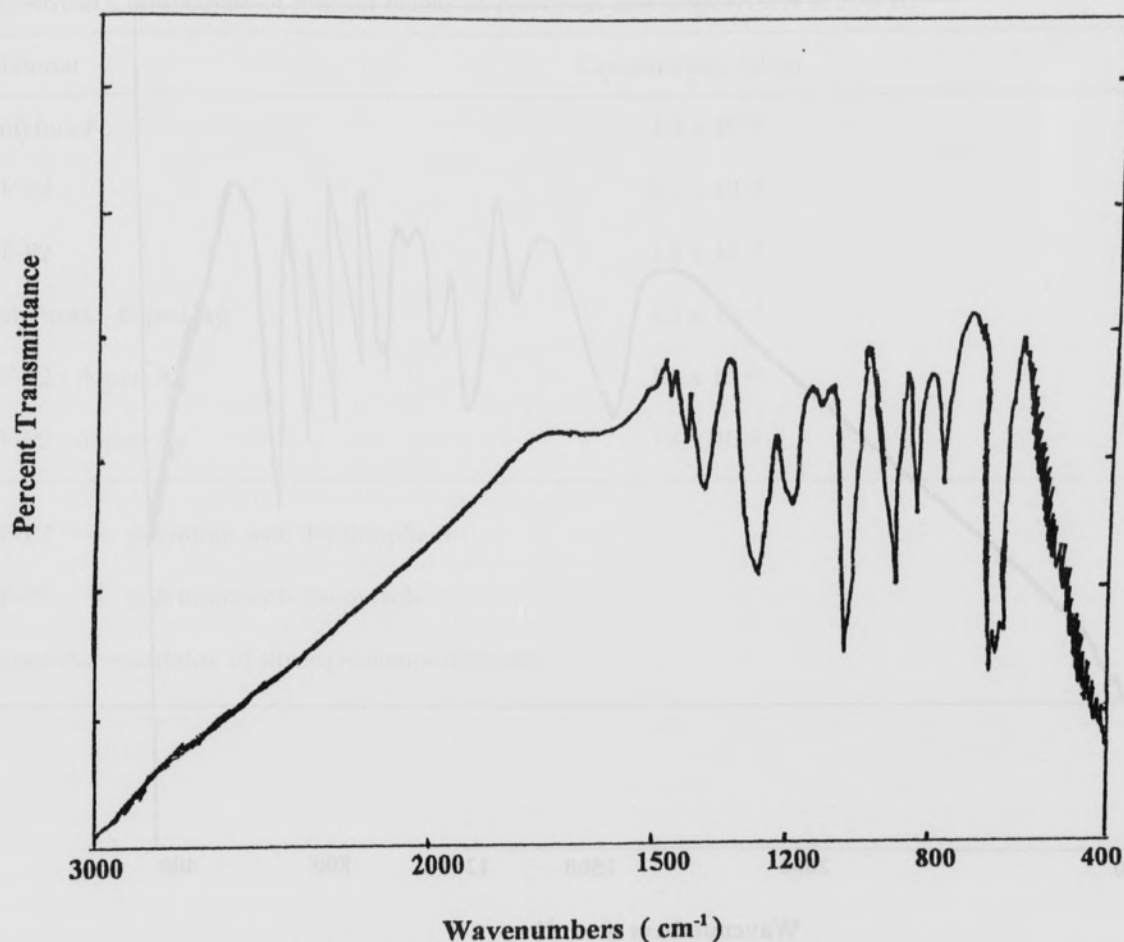


Fig. 7. IR spectra of polyfuran-2% thiophene doped with silver p-toluene sulfonate.

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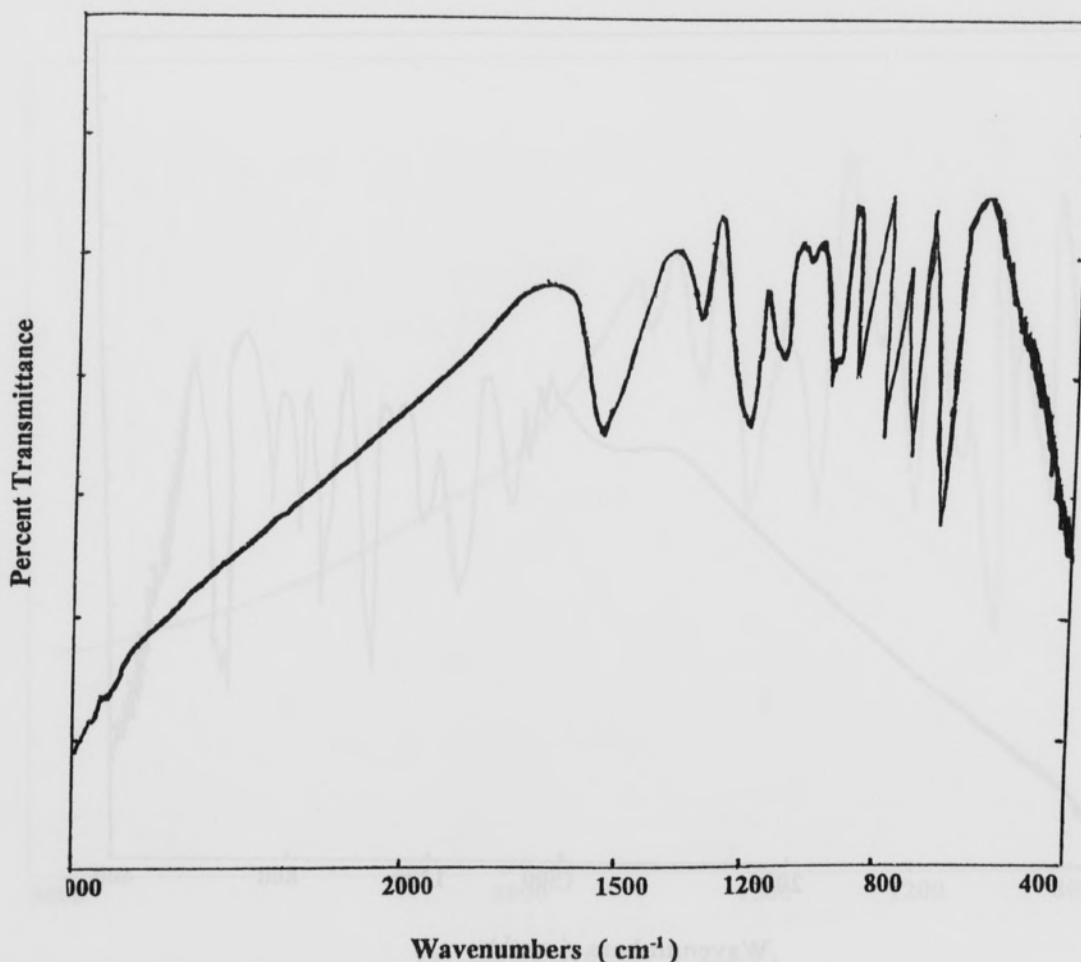


Fig. 8. IR spectra of polyfuran-2% pyrrole doped with silver p-toluene sulfonate.

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

Material	Conductivity, S/cm
Polyfuran	1.3×10^{-6}
PF-T2	2.1×10^{-4}
PF-P2	1.5×10^{-3}
Polyfuran - doped-Ag	1.2×10^{-3}
PF-T2 - doped-Ag	1.1×10^{-2}
PF-P2 - doped-Ag	3.4×10^{-2}

PF-T2 = polyfuran with 2% thiophene

PF-P2 = polyfuran with 2% pyrrole

doped-Ag = addition of silver p-toluene sulfonate