Organometallics **1997,** *16,* 4857−4860 4857

Soluble Organoiron Derivatives of Polypyrrole

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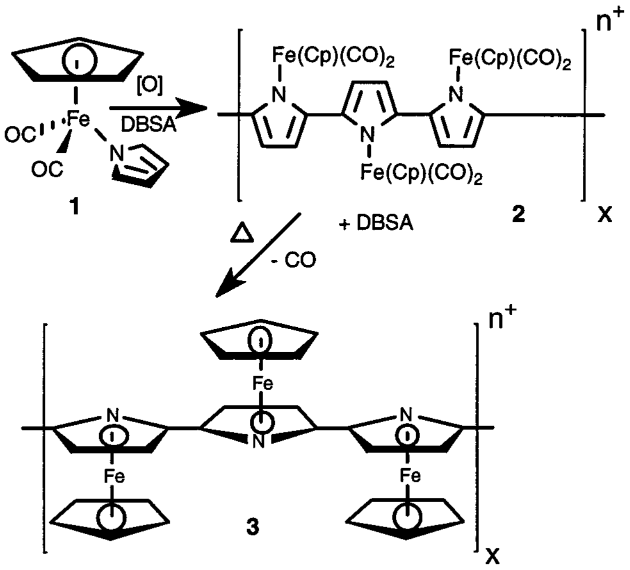
Received March 27, 1997[⊗]

Treatment of Fe(η^5-C_5H_5)(η^1-NC_4H_4)$(CO)_2$ (**1**) with $N(Bu)_4S_2O_8$ in the presence of dodecylbenzenesulfonic acid leads to the formation of a soluble, electrically conducting polymer (**2**). Solutions of **2** lose CO upon heating to give a new polymer, **3**, which is postulated to contain primarily azaferrocene units in the backbone.

Polypyrrole and other conducting polymers have been developed to the point where they are being used in commercial products,[1] but the search for derivatives possessing enhanced physical, electronic, optical, and chemical properties continues. A strategy which offers particular promise in this regard is to incorporate organometallic functionalities into the polymer matrix.[2] We are interested in creating conducting polymers in which a transition metal complex is incorporated directly into the conjugated polymer backbone. One such system is dicarbonyl(η^5-cyclopentadienyl)(η^1-pyrrolyl)-iron(II), **1**,[3] referred to as Fp-pyr for the remainder of the paper. Oxidation of this complex leads to a pyrrolyl-based radical cation, which polymerizes to a highly conducting material similar to polypyrrole.[4] Both chemical polymerization[4a] and electrochemical copolymerization[4b] of **1** with pyrrole or thiophene leads to polycationic polymer films or powders which have exceedingly poor solubility in all solvents. The lack of solubility in these materials, like that of polypyrrole, seriously limits their characterization, processability, and ultimately their practical utilization. In this paper, we describe a synthetic route to a modestly soluble form of poly(Fp-pyr) and examine some of its properties.

Recently, Lee, Kim, and Kim reported[5] that the aqueous polymerization of pyrrole could be effected by ammonium persulfate in the presence of dodecylbenzenesulfonic acid (DBSA). The resulting oligomeric material was then dissolved in organic solvents with the addition of excess DBSA, which acts both as a counterion and as a surfactant. This procedure is not suitable for **1** because it is insoluble in water as well as mildly moisture sensitive. Compound **1** is, however, soluble in benzyl alcohol, and oxidative polymerization can be achieved using tetrabutylammonium persulfate (TBAPS) as the oxidant.[6] The product of this reaction, **2**, is a deep red (almost black), homogeneous powder, Scheme 1. Upon addition of a 2-fold (by mass) excess of DBSA, **2** is modestly soluble in various organic solvents, particularly aromatics and small halocarbons.

Scheme 1



Elemental analysis and ^{1}H NMR spectroscopy of **2** gave ambiguous results. In each case, the large amount of DBSA present obscured the data from the polymer. In addition, the polymer is paramagnetic (below). The IR spectrum showed strong absorbances in the metal carbonyl region consistent with the Fp moiety remaining intact. The symmetric and asymmetric stretches are found at 2046 and 1996 cm^{-1}, respectively, as compared to 2033 and 1983 cm^{-1} for the parent complex **1**. This blue shift would be expected from an oxidation of the

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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[6] Dicarbonyl(η^5-cyclopentadienyl)(η^1-pyrrolyl)iron(II), **1** (0.80 g, 3.29 mmol) and docecylbenzenesulfonic acid (0.50 mL, 1.65 mmol) were dissolved in 15 mL of benzyl alcohol. The resulting solution was chilled to 10 °C. Tetrabutylammonium persulfate (0.50 g, 0.66 mmol) was dissolved in 10 mL of benzyl alcohol and then added dropwise to the solution of **1**. After 15 h, the solution was warmed to room temperature, diluted with 200 mL of methanol, and filtered to give 0.35 g of **2** in the form of a black powder. IR (cm^{-1}): 2046, 1996. XPS (eV): 724.4 [Fe(2p$_{3/2}$)], 711.0 [Fe(2p$_{1/2}$)], 401.6 [N(1s), 20%], 399.8 [N(1s), 80%].

S0276-7333(97)00257-4 CCC: $14.00

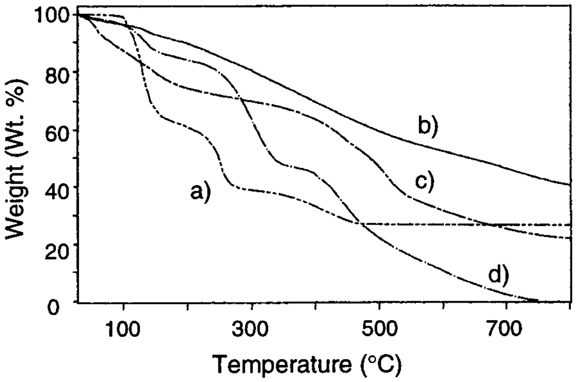

Figure 1. Thermograms of (a) Fp-pyr, (b) poly(Fp-pyr) from the $FeCl_3$-catalyzed reaction, (c) polymer **2**, and (d) polymer **3**.

metal center and is comparable to that observed previously for the products of other chemical polymerizations of Fp-pyr.[4a]

Fp-pyr has been shown to lose 2 equiv of CO in refluxing benzene to give azaferrocene.[3b] The reverse reaction can be accomplished by simply bubbling CO through a room temperature solution of azaferrocene. This reversible generation and protection of two coordination sites has the potential to be of use for the construction of molecular sensors and catalysts. Unlike the solution reaction, solid state thermolysis of Fp-pyr results in loss of the pyrrolyl moiety before loss of CO, leading to the formation of $[FeCp(CO)_2]_2$. Figure 1 (curves b and c) shows the thermograms of poly(Fp-pyr), prepared from the $FeCl_3$-catalyzed polymerization, and polymer **2**.[7] Both materials are far more thermally robust than Fp-pyr, which is consistent with a polymeric structure. Polymer **2** shows much more sharply defined mass losses than our previous polymers and it loses 25% of its mass in a thermal event occurring below 200 °C (onset 43 °C).

We have found that ring-slip reactions can take place in polymer matrices if the matrix is sufficiently flexible.[8] To investigate the possibility that the DBSA-swollen polymer would also allow a low-temperature ring slip, a sample of **2** was heated at 150 °C until 25% of the total mass was lost and then examined by IR spectroscopy. The CO stretches were found to be slightly shifted to shorter wavelengths, but not noticeably diminished in intensity. While the ring-slip reaction had clearly not taken place, there was also no indication that $[FeCp(CO)_2]_2$ had been formed from Fe–pyrrolyl bond thermolysis. This first mass loss appears to consist entirely of evaporation of DBSA and entrapped solvent. The organometallic moiety remains largely intact until the second major thermal event (onset 404 °C), during which there is a general degradation of the entire polymer.

If **2** is heated to reflux in either 1,2-dichloroethane or toluene, a new material, **3**, is formed.[9] After 4 h of heating, the intensities of the CO stretches were reduced by >80%, but even after 12 h, they could still be easily observed. Again, there was no evidence of the formation of $[FeCp(CO)_2]_2$.[10] The thermogram of **3** (Figure 1, curve d) showed a low-temperature mass loss (onset 111 °C) of 14% of the total mass due to evaporation of excess DBSA. A second mass loss (onset 269 °C) resulted in a sharp loss of an additional 39% of the total mass, and a third loss (onset 403 °C) resulted in the loss of the remaining mass. Unlike the polymers of Fp-pyr, there was no residual mass of iron above 700 °C. The lower thermal stability of **3** is due to either weaker pyrrolyl–pyrrolyl linkages or a more facile rearrangement of the monomers to ferrocene, which then sublimes from the sample.[11]

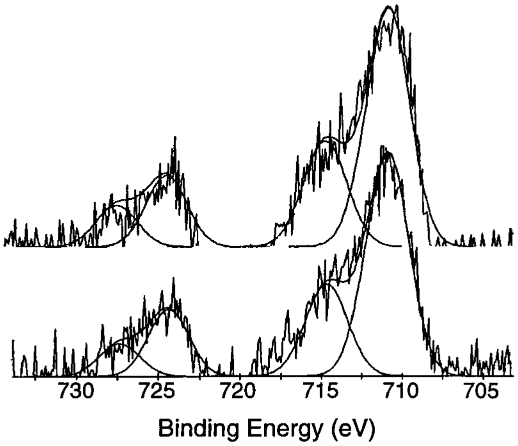

Figure 2. XPS spectra of the $Fe(2p_{1/2})$ and $Fe(2p_{3/2})$ region for polymers **2** (bottom) and **3** (top).

Films of **2** and **3** were prepared by spin casting the samples onto appropriate substrates for further analysis. Samples were cast onto aluminum foil for examination by X-ray photoelectron spectroscopy or onto glass plates for conductivity studies and field emission microscopy (FEM). In each case, high-quality films could be cast which adhered strongly to the substrates.

The binding energies[12,13] of the iron nuclei were virtually identical for **2** and **3** (Figure 2) and a full 3 eV larger than those reported for ferrocene or $[FeCp(CO)_2]_2$.[14] Figure 2 also shows that the iron centers in each compound display prominent shake-up lines, com-

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[7] Thermal gravimetric analyses were performed on a Perkin-Elmer TGA 7 analyzer. All samples had a mass of approximately 10 mg. All calculations were performed on data represented as percent loss of starting mass. Fp-pyr and polymer films were heated at a constant rate of 5 °C/min from 25 to 1000 °C. Mass loss and onset calculations were performed by standard methods.

[8] We have recently examined the ring-slip reaction of $Re(\eta^1\text{-}C_{13}H_9)(CO)_5$ in inert polymer matrices, See: Mejdrich, A.; Hanks, T. W. *Synth. React. Inorg. Met.-Org. Chem.*, submitted for publication.

[9] Polymer **2** (0.25 g) and dodecylbenzenesulfonic acid (0.50 mL, 0.82 mmol) were added to 15 mL of 1,2-dichloroethane. The solution was heated at reflux for 8 h, and the solvent was removed by rotary evaporation to give an amorphous black solid (**3**). IR (cm^{-1}): 2047, 1996 (both very weak). XPS: 724.3 [$Fe(2p_{3/2})$], 710.9 [$Fe(2p_{1/2})$], 401.7 [N(1s), 52%], 399.8 [N(1s), 48%].

[10] An examination of the metal–ligand stretching region in the far-IR did not provide unambiguous evidence of a ring-slip process.

[11] Attempts were made to convert **3** back into **2** by bubbling CO through methylene chloride solutions of the polymer for 4 h. No change was observed by IR spectroscopy. Exposing the solution of compound **3** to 3 atm of CO for 48 h with agitation also had no effect.

[12] All XPS spectra were measured on a Physical Electronics Industries, Inc., XPS 5400 spectrometer, utilizing Mg Kα radiation. Since the bulk of the carbon in the samples was due to DBSA, the C(1s) signal was used as an internal standard and set to 284.6 eV to eliminate errors due to charging.[13d] Due to the good conductivity of the samples, charging was not a major problem in any case. Errors are conservatively estimated at ±0.3 eV.

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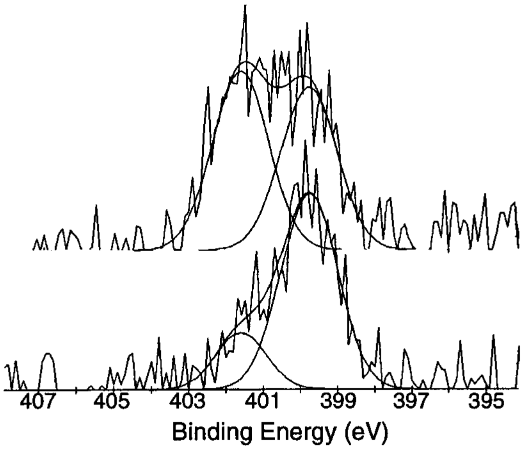

Figure 3. XPS spectra of the N(1s) region for polymers **2** (bottom) and **3** (top).

monly associated with paramagnetic states.[13] Together, these spectral features indicate that the iron centers are best characterized as being in the +3 oxidation state in each polymer.

The XPS spectra of the N(1s) region are quite different for **2** and **3** (Figure 3). Compound **2** contains predominately one type of nitrogen with a binding energy of 399.8 eV. In polymer **3**, a similar signal is observed, but the majority of the nitrogens have a binding energy of 401.6 eV, clearly indicating that the loss of CO from the sample is accompanied by a change in the environment of the nitrogen atoms. We attribute the latter signal to monomers which have slipped to an azaferrocene configuration. The relative intensities of the two types of nitrogen are not what would be expected based upon the IR data, which indicates >90% conversion to the azaferrocene form in polymer **3**. The discrepancy is under investigation but may be due to limitation of XPS analysis to the surface of the material rather than the bulk solid.[14]

The cyclic voltammogram[15] (CV) of **2** in acetonitrile showed a single reversible oxidation/reduction wave at 65 mV vs Ag/AgNO$_3$ when the potential was swept between −500 and +1000 mV. As expected, the polymer is more easily oxidized than the monomer.[4a] Under the same conditions, the CV of polymer **3** is more complex. There are two distinct oxidation waves, a smaller one at $E_{pa} = +199$ mV and a larger one at $E_{pa} = +342$ mV. There is only a single somewhat broad reduction wave at $E_{pc} = -86$ mV. On repeated scans, the current flow decreases slowly, indicating fouling of the electrode. These results suggest that in the reduced (nonconducting) form of the polymer there are two nonequivalent, localized domains within the polymer in unequal amounts. The minor-domain oxidation occurs within 20 mV of that seen in polymer **2**. In the oxidized, conducting form of the polymer, the electron-accepting orbitals are delocalized. Thus, there are no longer separate domains to be reduced.

When poly(Fp-pyr) is prepared by phosphomolybdic acid oxidation, the resulting films were found to crumble easily into powders.[4] FEM studies show that the material produced by this process is highly granular, with particle sizes in the 0.1−0.7 μm range (Figure 4 (top)). Films of **2** and **3** are significantly smoother. Polymer **2** produces good quality films (Figure 4 (middle)) which show only small voids and bubbles, while the films produced from **3** (Figure 4 (bottom)) show only occasional bubbles and small ridges due to the casting process. The major difference between the films of **2** and **3** are due to the greater homogeneity of the solutions of **3**, which result from the extended refluxing. Interestingly, the improved physical properties of the films produced by the DBSA/TBAPS method discussed

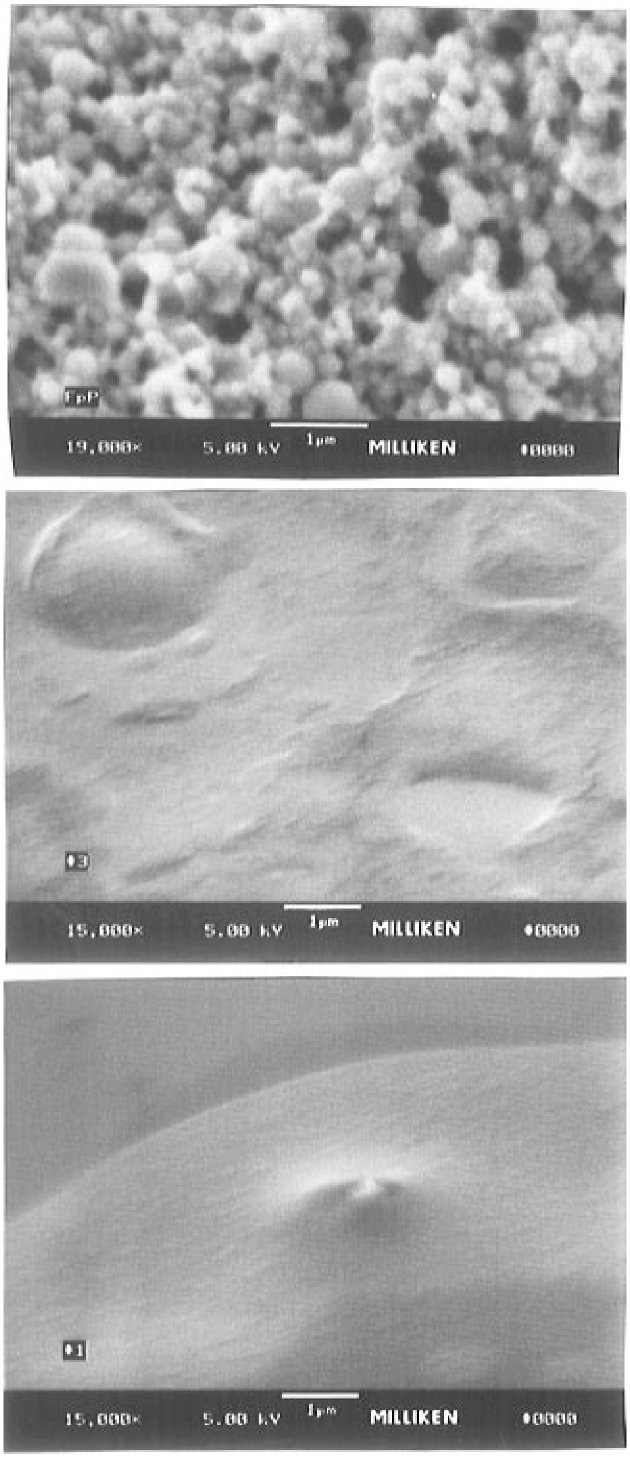

Figure 4. FEM images of poly(Fp-pyr) (top) prepared by FeCl$_3$-catalyzed polymerization, polymer **2** (middle), and polymer **3** (bottom).

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[15] Electrochemical experiments were performed on a BAS 100B electrochemical analyzer. Experiments were performed in a three electrode cell using a gold disk microelectrode as the working electrode, a platinum wire auxiliary electrode, and a Ag/AgNO$_3$ reference electrode. All experiments were performed in acetonitrile and under nitrogen using N(Bu)$_4$BF$_4$ as the supporting electrolyte.

in this report do not result in improved electrical properties. The electrical conductivities of the films shown in Figure 4 are 2.5 × 10^{-1}, 7.0 × 10^{-3}, and 1.5 × 10^{-4} S/cm, respectively. The lower conductivity of the materials reported here are probably a function of the shorter average chain length expected by this route as well as the DBSA counterion. Similar decreases in conductivity are seen with polypyrrole prepared under related conditions.[5]

In summary, a soluble derivative of poly(Fp-pyr) has been prepared. The ability to dissolve this material allows us to cast high-quality films and to perform a ring-slip reaction to give polyazaferrocene. Studies are in progress to take advantage of the improved solubility in order to better characterize the polymers and to explore their reaction chemistry.

Acknowledgment. This work was supported by the ACS-PRF. We thank Michael Sullivan, Milliken Research Corp., for assistance with the FEM images and Dr. Paul Deck, Virginia Polytechnic Institute and State University, for assistance with XPS data collection.

OM970257E