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then cooled to 200 °C without releasing the pressure before the sample was taken out of the press and plunged into cold water. The copper foil was carefully peeled away from the film. If necessary, removal of the foil was facilitated by soaking the film adhering to the copper foil in concentrated ammonium hydroxide for 30 min. All films were thoroughly washed with water and air-dried prior to testing.

Neat Resin Disk Melt Processing. A steel die with brass punches of a diameter of 0.790 in. was used to make the neat resin disks. A 200-mg powder sample of the polymer (with or without catalyst) was placed in the die and then melt-processed in a hydraulic press at 2000 psi for 2 h between two platens heated at 330 °C (625 °F) for catalyzed cures or at 375 °C (707 °F) for uncatalyzed/thermal cures. The die was cooled to <200 °C (392 °F) under pressure before it was taken out of the press and disassembled to obtain the neat resin disk.

Prepreg Preparation. Chloroform solutions of **7a–c** were brush-coated onto both sides of a piece of Celion-3000 graphite cloth of specific dimension/weight such that the prepreg would result in a 30% resin content. The cloth was solidly restrained on all four edges to prevent shrinkage. After it had air-dried overnight, the prepreg was cut into pieces with dimensions of 0.99 in. × 2.70 in.

Composite Preparation. The prepreg was staged as a 6-ply layup in a $\sim$1 in. × 27 in. steel mold for 1 h at 121 °C (250 °F) and then melt-processed at 375 °C (707 °F) under 1500 psi for 2 h. The steel mold was cooled to <200 °C (392 °F) under pressure before it was taken out of the press and then disassembled to obtain the graphite-cloth-reinforced composite.

Interlaminar Shear Strength (ILSS). The interlaminar (or short beam) shear strength was determined as per ASTM D2344-76 by applying a load to a short (span/depth = 5/1) composite specimen supported lengthwise in a variable-span vise. The specimen was pushed against a pin until failure. The pressure at failure was measured by an Instron and used to calculate the ILLL. (Because the specimen is short, failure occurs between plies. Thus, the ILSS affords a measure of the resin's ability to transfer the load from one ply to the next in a composite.)

Flex Strength and Flex Modulus. An analysis similar to the above was performed except longer (2 in.) specimens were used and tested as per ASTM D790-1. (Because the specimen is considerably longer, failure occurs perpendicular to the longest axis of the specimen and requires breakage of the fibers. As a result, flex strength and flex modulus are fiber-dependent properties and quantify the extent to which the composite retains the high strength imparted by the fiber reinforcement. Flex strength is an indication of the composite's ultimate strength, while flex modulus is an indication of the composite's initial stiffness.)

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References and Notes

(1) Droske, J. P.; Stille, J. K.; Alston, W. B. *Macromolecules* **1984**, *17*, 14.
(2) Sutherlin, D.; Stille, J. K. *Macromolecules*, preceding paper in this issue.
(3) Friedman, L.; Rabideau, P. W. *J. Org. Chem.* **1968**, *33*, 451.
(4) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krueger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224.
(5) Vymetal, J.; Ambroz, M. *Chem. Prum.* **1977**, *27*, 116.
(6) Droske, J. P.; Stille, J. K. *Macromolecules* **1984**, *17*, 1.
(7) Luijten, J. G. A.; van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 295.

Metal Poly(benzodithiolenes)

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ABSTRACT: The title polymers were prepared by several different approaches employing benzene-1,2,4,5-tetrathiol and transition-metal salts. The two best-characterized solids were an iron and a cobalt salt, the subjects of this publication. Preliminary results on pressed-pellet conductivities (on the order $0.2{-}10^{-5}$ S/cm), magnetic susceptibility, and Mössbauer spectroscopy are presented.

Introduction

The metal dithiolenes are a unique and large family of transition- and main-group-metal complexes.[1] They have been of interest because they are easily formed (particularly the maleonitrilodithiolato (mnt) complexes), they are room temperature and atmosphere stable, and they exhibit a number of stable oxidation states containing open-shell molecular orbitals. It is this last property that has been the main reason for interest in these coordination complexes by solid-state scientists. Open-shell molecules are essential for achieving highly conducting systems, and they offer the potential of achieving organic and organometallic ferromagnets. As early as 1972, attempts were made to develop organic metals based on dithiolenes.[2] The most recent success has been with hydrated lithium dithiolene salts.[3] There has also been a report on polymers containing metal dithiolenes.[4]

The metal dithiolenes of the nickel triad (Ni, Pd, Pt) as well as those of Co, Cu, Zn, and Cd are square planar. Presumably, in solution, the apical coordination sites are solvated in coordinating solvents and open in noncoordinating solvents. In most cases in the solid state, the axial coordination sites are occupied by sulfur atoms of neighboring molecules. One important exception is the structure of the conducting mixed-valent mnt salts of Underhill,[3] where flat metal complexes form a zigzag stack reminiscent of the structure of most organic superconductors.[5]

In this paper we describe the preparation of new polymers that use the ligand benzene-1,2,4,5-tetrathiol[6] (1) in conjunction with divalent transition metals as backbone (see Scheme I). The rationale for the development of these polymers rests on several principles:

(a) The possibility of mixed valence (through doping) and electron delocalization will produce conducting polymers.

(b) A high density of unpaired spins (up to one per each metal atom) will be possible, leading to the formation of paramagnetic polymers. Ferromagnetic and/or antifer-

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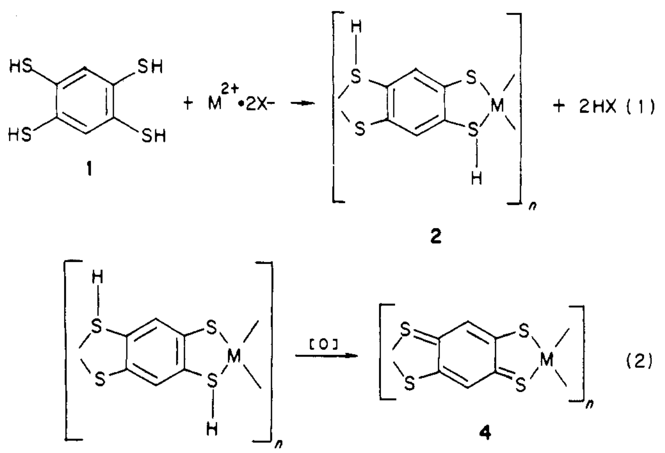
Scheme I



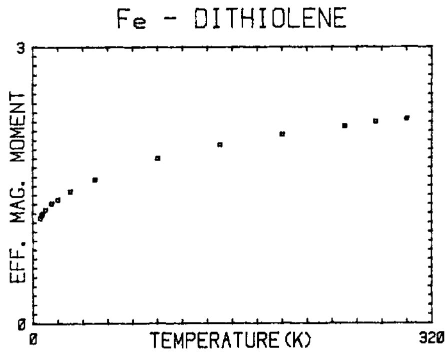


Figure 1. Effective magnetic moment in Bohr magnetons as a function of absolute temperature for iron poly(benzodithiolene) hydrate.

romagnetic polymers can be expected, provided the interaction between metal atoms (via the ligands) is large enough.

(c) The multiple valence states available to the transition-metal atoms suggest possible areas of specific chemical or electrochemical interest including electrodes for fuel cells, etc.

(d) Mixed-metal polymers can be prepared and will therefore have an *imposed* mixed valence and thereby a potential for electrical conductivity and for catalysis.

It should be noted that the tetrathiol ligand described here is related to the previously investigated dihydroxybenzoquinone[7] ligand. Transition-metal polymer and oligomer systems of this tetraoxo analog have been extensively investigated.[8-10] Until now, investigations of the oxygen-sensitive tetrathio ligand have been prevented because of difficulties in its preparation and isolation.[6]

Results and Discussion

In Scheme I, we drew the structure of the final polymer as a result of ligand oxidation. In fact, a combination of ligand and metal centered oxidation states are expected in these systems. Again in the scheme, intermediate **2** is usually avoided by incorporation of a weak base to remove the byproduct HX and two protons from **2**. The expected product is then a polyanion (two negative charges per site). However, as will be shown below when **1** is used as ligand in water, no base is necessary to obtain polymers of type **4** containing approximately one water of hydration per metal atom.

Compound **1** was prepared by a modification of a literature procedure.[6b] For the polymerization, several conditions were explored; of these, the use of ethylene glycol, ethanol, or water were the most successful. Trialkylamines, sodium carbonate, and no added base (in water) were examined.

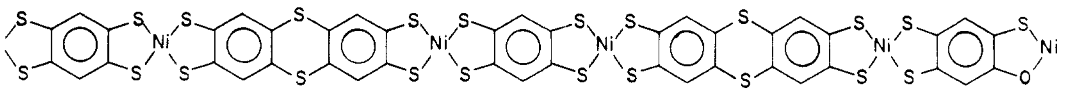
In the initial experiments, polar aprotic solvents in conjunction with long-chain tertiary amines were employed because we reasoned that the long-chain alkylammonium cations would keep the growing polymer chain in solution. However, observation of the reaction course and results of elemental analyses indicated that there was no advantage to the use of the above conditions; i.e., there was immediate precipitation (no slow chain growth), and large C and H percentages due to the long chains of the amines obscured the elemental analyses results.

After a large amount of experimentation, the best results were obtained with neutral aqueous conditions. Under these circumstances, $CoCl_2$ gave a crystalline compound, but other transition-metal salts gave amorphous (on the basis of Cu Kα radiation, X-ray powder patterns), black powders. The elemental analysis of the Co "polymer" is perfect for $L_{11}Co_2$ (L = **1**) implying an intriguing structure, probably a disulfide containing macrocycle encapsulating two cobalt atoms.

Of the materials prepared, the iron polymer appeared from initial characterization (elemental analysis and Mössbauer analysis) to be the most interesting. Consequently, we decided to focus the research on solids derived from this ion. These iron-based polymers had a room-temperature compaction conductivity of 0.2 S/cm and were paramagnetic. The value of μ_{eff} at 300 K was found to be 2.23 μ_B, which is a typical value for low-spin Fe^{III} in a ^2T ground state.[11] The excess over the spin-only value of 1.73 μ_B is very probably due to TIP (temperature-independent paramagnetism) from second-order Zeeman splitting[12] and from conduction electrons.[13] The temperature dependence of μ_{eff} is peculiar (Figure 1), suggesting a positive spin-orbit coupling constant. Since this is unlikely, we are probably seeing the same behavior observed in other iron dithiolenes; i.e., spin–spin coupling to give a net $S' = 0$ ground state.[14] The iron dithiolenes are known to dimerize in the solid state and to possess magnetic moments that decrease anomalously with temperature.[1] The bis mnt complex of iron(III) exhibits a μ_{eff} temperature dependence similar to that observed with our polymer.[15] However, in our case, the magnetic moment decreases much less precipitously than in the mnt case. At 6 K it is still significant (1.15 μ_B), when it should be nearly 0. The inference from this result would be that a large portion of the sample (44%)[16] is not in the usual dithiolene dimer form.

Mössbauer spectroscopy (300 K) revealed three sets of doublets with QS of 0.65, 1.88, and 2.79 mm/s in a ratio of 1:5:2 and isomer shifts of 0.35, 0.25, and 0.20 mm/s, respectively. The isomer shifts (relative to α-Fe^0) suggested that all the iron was in the Fe^{3+} oxidation state, in agreement with the magnetic susceptibility results. At 10 K the Mössbauer spectrum shows no magnetic ordering, in apparent contradiction to the presumption of an $S' = 0$ ground state for at least a portion of the sample (vide infra).

Buckley et al.[17] have suggested this to be possible for the $S' = 0$ state. This proposition has been verified in the case of a bis(quinoxaline-2,3-dithiol) adduct of Fe(III).[14] The different isomer shifts and quadrupole splittings must result from iron in three different environments. The quadrupole splittings fall into the three typical areas of iron–sulfur compounds.[18] The splitting of 2.79 mm/s is in the region seen for iron–sulfur compounds in a strong square pyramidal crystal field; the dithiolene dimers[1,19] and halo bis(dithiocarbamates)[20] are relevant examples. The splitting of 1.88 mm/s is most characteristic of iron tris complexes of bidentate dithio ligands.[1,19,21] The 0.65 mm/s



A

splitting implies a low field gradient at iron, characteristic of a relatively symmetric environment. The central member of a trimer system of three iron bis(dithiolenes) would be octahedrally coordinated by six sulfur atoms and would be in good agreement with Fe(III) in the octahedral site of the mineral greigite (Fe_3S_4; QS = 0.40 mm/s).[22] The relative proportion of sites could be better modeled by assigning the 1.88 splitting to a nonaxially coordinated iron bis(dithiolene) site and the 0.65 splitting to a terminal iron dithiolene coordinated with one to two hydroxides and two to three water molecules. The rationale for the first assignment is that the reduction in asymmetry on going from a dimer (QS = 2.79) to an uncoordinated monomer may be sufficient to reduce the quadrupole splitting to 1.88. The assignment of the 0.65 is tenuous, but if it is right, we can deduce a number-average molecular weight of at least eleven iron atoms and ten tetradentate ligands in a chain:

$$L_2Fe(S_2C_6H_2S_2Fe')_2(S_2C_6H_2S_2Fe'')_5\text{-}(S_2C_6H_2S_2Fe')_2S_2C_6H_2S_2FeL_2$$

In this oligomeric chain, Fe, Fe′, and Fe″ refer to iron atoms in different coordination environments, in good agreement with elemental analyses results (see Experimental Section).

Susceptibility results indicate that 44% of all irons are nondimeric, while Mössbauer results suggest this fraction to be 75% (6/8). If the Debye temperature for each iron site is different, the recoil-free fractions and the consequent relative peak areas will vary with temperature.[23] The resulting room-temperature site proportions derived from Mössbauer analysis may not be accurate. Low-temperature Mössbauer spectra have indicated a variance in relative proportions; however, the data were of insufficient quality. The discrepancy between the magnetic susceptibility and the Mössbauer results makes the structural conclusions reached above only tentative.

The effective magnetic moment for the crystalline cobalt compound is 2.69 μ_B (per Co atom) at 300 K and 1.70 μ_B at 6 K. The ground state must consequently be ^2E_g, whereas the room-temperature susceptibility value indicates that at higher temperatures an admixture of the ^4T state takes place. This is not unusual since crossovers between spin states are known in Co compounds.[24]

The nickel compound exhibits a room temperature μ_{eff} of 3.5 μ_B that decreases to 2.01 μ_B at 6 K. This is entirely analogous to the Fe polymer.

Just as in the case of the Co polymer, the ratio of ligand to metal is larger than 1. Unlike the cobalt case where the ratio of carbon to sulfur is exactly 1.5:1 in the Ni polymer, this ratio is 1.77:1, compatible with an *average* possible structure depicted as A.

This structure is in good accord with results of elemental analysis (see Experimental Section). It is possible that nickel catalyzed the nucleophilic substitution leading to the postulated thianthrenes. Experiments to establish the existence of the thianthrene tetrathiols are in progress.

Summary

We have prepared a new family of coordination polymers starting with the tetrathiol 1 and transition-metal ions. With the exception of a cobalt salt, which exists in the form of blue-black microcrystals, these polymers are deeply colored powders that are insoluble in all solvents. They are all paramagnetic conductors at room temperature with conductivities ranging from 0.2 to 10^{-4} S/cm (see Table I). The iron polymers contain iron in a single oxidation state of 3+ but in three different chemical environments as determined through Mössbauer spectroscopy.

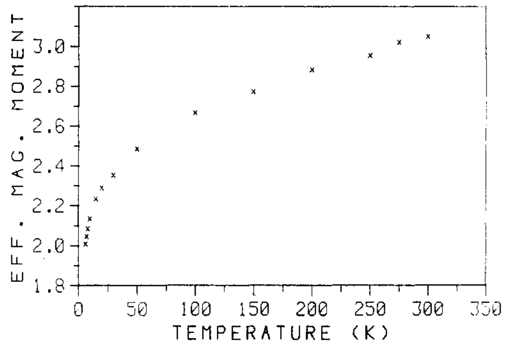


Figure 2. Effective magnetic moment in Bohr magnetons as a function of absolute temperature for nickel poly(benzodithiolene) hydrate.

Table I
Summary of Properties

polymer[a]	conductivity[b]	magnetism
$(FeBT)_n(H_2O)_m$	0.2	paramagnetic Fe^{III}
$(NiBT)_n(H_2O)_m$	2×10^{-3}	paramagnetic Ni^{II}
Co_2BT_{11}	2×10^{-3}	paramagnetic Co^{II}
$(CuBT)_n$	2×10^{-5}	

[a] BT = 1,2,4,5-tetrakis(thiobenzene). [b] S/cm, compressed pellet. [c] Crystalline, probably not a polymer.

Experimental Section

Susceptibility results were obtained with a SQUID susceptometer belonging to a regional facility at the Department of Chemistry, University of Southern California, under the direction of Prof. C. Reed. Iron-57 spectra were obtained with a Co-57/Pt source in a constant-acceleration Mössbauer spectrometer. The absorbers were made of polymer powder pressed into thin, flat disks.

A typical procedure is described here for the preparation of iron poly(benzodithiolene) but is general for most transition metals. The polymers were all black, air stable, and insoluble in all solvents.

A suspension of 246.3 mg of $FeCl_2$ in 9 mL of thoroughly degassed water was added via syringe to a refluxing suspension of 400 mg of tetrathiol 1 in 25 mL of degassed water. The mixture turned dark rapidly, eventually turning black. The whole was allowed to reflux for 48 h, cooled rapidly, filtered through a medium frit Schlenk filter, washed with water, acetone, and water, and dried at 95 °C under vacuum for 12 h: IR (KBr) 2910 (vw), 1490 (w), 1450 (w), 1410 (w), 1390 (m), 1380 (s), 1375 (m), 1065 (m), 1055 (m), 1025 (w), 695 (m), 630 (m).

Anal. Calcd for $C_{75}H_{25}Fe_{14}S_{50}\cdot 11H_2O$: C, 25.67; H, 1.34; Fe, 22.31; S, 45.64. Found: C, 25.74; H, 1.31; Fe, 22.02; S, 44.21.

Under the same conditions, black microcrystals of a cobalt complex were isolated. The material had a conductivity of 10^{-3} S/cm, but its elemental analysis revealed that it contained no waters of hydration and that there were only two cobalt atoms for every eleven ligand molecules: IR (KBr) 2910 (vw), 2560 (vw), 1725 (vw) 1540 (m), 1490 (vw), 1445 (w), 1415 (s), 1300 (m), 1245 (w), 1110 (w), 1050 (m), 1015 (vw), 930 (vw), 860 (m), 750 (w), 690 (s).

Anal. Calcd for $C_{66}H_{40}Co_2S_{44}$: C, 33.56; H, 1.71; Co, 4.99; S, 59.73. Found: C, 33.05; H, 1.93; Co, 4.94; S, 59.56.

The above conditions afforded a black Ni polymer from $NiCl_2$: IR (KBr) 3020 (vw), 2910 (w), 2840 (vw), 1495 (m), 1485 (w), 1455 (m), 1445 (m), 1300 (w), 1050 (w), 1020 (w), 850 (vw), 750 (m), 690 (s).

Anal. Calcd for $C_{48}H_{16}Cl_{0.4}Ni_5OS_{27}\cdot 7.33H_2O$: C, 30.13; H, 1.60; Cl, 0.74; Ni, 15.35; O, 6.97; S, 45.19. Found: C, 30.30; H, 1.70; Cl, 0.75; Ni, 15.41; S, 44.79.

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References and Notes

(1) McCleverty, J. A. *Progr. Inorg. Chem.* **1968**, *10*, 49. Eisenberg, R. *Ibid.* **1970**, *12*, 295.
(2) Wudl, F.; Ho, C. H.; Nagel, A. *J. Chem. Soc., Chem. Commun.* **1973**, 923.
(3) Underhill, A. E.; Ahmad, M. *J. Chem. Soc., Chem. Commun.* **1981**, 67.
(4) Rivera, N. M.; Engler, E. M. *J. Chem. Soc., Chem. Commun.* **1979**, 184.
(5) Bechgaard, K.; Jerome, D. *Sci. Am.* **1982**, *247*, 52.
(6) (a) Dirk, C. W.; Cox, S. D.; Wellman, D. E.; Wudl, F. *J. Org. Chem.* **1985**, *50*, 2395. (b) Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Org. Chem.* **1980**, *45*, 4376.
(7) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 498.
(8) Pierpoint, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 2367.
(9) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 2738.
(10) Bottei, R. S.; Green, D. L. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1469.
(11) Figgis, B. N.; Lewis, J. *Progr. Inorg. Chem.* **1964**, *6*, 37.
(12) Mabbs, F. E.; Machin, D. J. "Magnetism and Transition Metal Complexes"; Chapman & Hall: New York, 1973.
(13) Kittel, C. "Introduction to Solid State Physics", 5th ed.; Wiley: New York, 1976.
(14) Dalziel, J. A. W.; Donaldson, J. D.; Mehta, B. D.; Tricker, M. J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3811.
(15) Simpson, G. D.; Carlisle, G. O. *Inorg. Chim. Acta* **1973**, *7*, 378.
(16) $(1.15)^2/(1.73)^2$.
(17) (a) Buckley, A. N.; Herbert, I. R.; Rumbold, B. D.; Wilson, G. V. H. *J. Phys. Chem. Solids* **1970**, *31*, 1423. (b) Buckley, A. N.; Herbert, I. R.; Rumbold, B. D.; Wilson, G. V. H. *J. Chem. Soc. A* **1971**, 2298.
(18) Rubinson, K. A.; Palmer, G. *J. Am. Chem. Soc.* **1972**, *94*, 8375.
(19) Birchall, T.; Greenwood, N. N. *J. Chem. Soc. A* **1969**, 286.
(20) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301.
(21) Martin, R. L.; Roos, I. A. G. *Aust. J. Chem.* **1971**, *24*, 2231.
(22) Vaughan, D. J.; Ridout, M. S. *J. Inorg. Nucl. Chem.* **1971**, *33*, 741.
(23) Gonser, U., Ed. "Mössbauer Spectroscopy: Topics in Applied Physics"; Springer-Verlag: New York, 1975; Vol. 5.
(24) (a) Martin, R. L.; White, A. H. *Transition Met. Chem. (N. Y.)* **1968**, *4*, 113. (b) Barefield, E. K.; Busch, D. H.; Nelson, S. M. *Chem. Soc. Q. Rev.* **1968**, *22*, 457.

Poly[ferricenium-1,2(1,3:1,1′)-diylmethylene tetrachloroferrate(III)], a Hydrophilic Polysalt for Biomedical Applications[†]

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ABSTRACT: The oxidation of poly(ferrocenylenemethylene) (1) ($\bar{M}_n$ = 2400) by a variety of oxidants in benzene medium affords polysalts possessing ferricenium-1,2(1,3:1,1′)-diylmethylene recurring units. Molecular iodine as the oxidant gives the DMF-soluble polyiodide **2a**, possessing approximately 10% unoxidized units, and *p*-benzoquinone-mediated oxidation in the presence of picric acid or trichloroacetic acid leads to the formation of similar polysalts **2b,c** with (solvated) picrate or trichloroacetate anions. Excess anhydrous $FeCl_3$ gives a crude (hydrated) poly(tetrachloroferrate) **2d** of limited purity. With ferricenium tetrachloroferrate(III) as the oxidant, pure poly(tetrachloroferrate) **2e** is obtained. Samples showing incomplete oxidation of the ferrocene units can be fully oxidized by reprecipitation from acetonitrile solution in the presence of ferricenium tetrachloroferrate. IR and Mössbauer spectroscopic data are presented in support of the assigned structures. Freshly prepared poly(tetrachloroferrates) **2d** and **2e** dissolve readily in water, thus demonstrating the feasibility of converting inherently hydrophobic ferrocene polymers into biomedically useful, hydrophilic poly(ferricenium) compounds.

Introduction

Certain water-soluble ferricenium salts, specifically those with tetrachloroferrate, (μ-oxo)bis(trichloroferrate), picrate, and trichloroacetate anion structures, were recently found[2] to show powerful antineoplastic, i.e., cancerostatic, activity toward Ehrlich ascites murine tumor, the increase in life span ranging from 350 to 490% (against untreated controls). Both ferrocene proper and a (water-insoluble) ferricenium molybdate displayed no activity toward the Ehrlich ascites tumor line, nor was such activity observed with (water-soluble) simple alkyl- and aralkylammonium tetrachloroferrates.

The promising results with water-soluble nonpolymeric ferricenium salts has prompted an extended program in our group aimed at the synthesis of stable, hydrophilic macromolecular ferricenium compounds for biomedical applications. While for the medicinal use of macromolecular drugs a biodegradable backbone structure is generally given preference for reasons of more efficacious elimination of the "spent" macromolecule from the biological system, we chose the nondegradable chain structure 1 of a poly(ferrocenylenemethylene)[3,4] ($\bar{M}_n$ = 2400) as a model for our preliminary studies of the oxidizability of ferrocene-containing polymers. Specifically, we set out to demonstrate the practicability of converting this strongly hydrophobic macromolecule into a hydrophilic polysalt and so pave the way for the development of biocompatible poly(ferricenium) compounds. In the following, we report on the oxidation of 1 in the organic phase and the isolation and characterization of polysalts comprising tetrachloroferrate(III) anion units.

Results and Discussion

The literature provides several examples of solid polymers possessing ferricenium cation sites either as backbone

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[†] Metallocene Polymers 43. For part 42, see ref 1.

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