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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# 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, ($\mu$-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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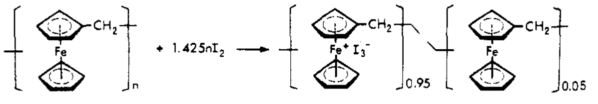
constituents[5] or as side groups or side-group constituents.[5a,6] Only in exceptional cases, however, were the polymers reported to display some degree of solubility in organic media. For example, partial solubility in *N,N*-dimethylformamide was reported[6a] for the 2,3-dichloro-5,6-dicyanobenzoquinone salts of poly(ferricenylmethyl acrylate) and poly(ferricenylmethyl methacrylate), and poly(ferricenylene tetrafluoroborate) was found[5b] to be initially soluble in acetonitrile. Of the many known simple ferricenium ($Fc^+$) salts,[7] the tetrachloroferrate(III), $Fc^+FeCl_4^-$, stands out on account of its excellent water solubility and hydrolytic stability.[8] It is also known[9] that certain polyammonium salts possessing $FeCl_4^-$ anions dissolve readily in aqueous media, and so does a cationic titanocene complex having a $FeCl_4^-$ counterion.[10] The tetrachloroferrate ion therefore suggested itself as a particularly promising anion species and was selected for the present investigation. Other hydrophilic counterions chosen on the strength of the good water solubility of the respective ferricenium salts[11] include the trichloroacetate (complexed with free trichloroacetic acid) and the picrate (2,4,6-trinitrophenoxide) ions. The media selected for oxidation of 1 were benzene and toluene, in both of which the polymer possesses excellent solubility.

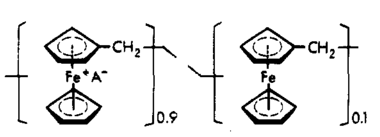
The oxidizability of 1 was first examined in a preliminary experiment in which the polymer, dissolved in benzene, was treated at room temperature with slightly more than the stoichiometric quantity (1.5 molar equiv) of iodine. This halogen is known to oxidize ferrocene readily, giving ferricenium triiodide as the most stable product salt.[7,12] The reaction, proceeding as shown in eq 1, afforded in 94% yield a black poly(ferricenium) salt, for which elemental analysis and $^{57}Fe$ Mössbauer spectroscopy (vide infra) suggested structure **2a** with approximately 95% completed oxidation. The polysalt, not unexpectedly, possessed no water solubility but dissolved readily in *N,N*-dimethylformamide or dimethyl sulfoxide; it could be recovered from such solutions by precipitation with ether, although this treatment caused a significant reduction in the content of oxidized repeat units, even if performed in an argon atmosphere. The IR spectrum (KBr pellet) of **2a** featured the CH deformation band at 848 $cm^{-1}$ due to $\nu_{19}$ of the ferricenium system as the most intense absorption, while a weak shoulder near 820 $cm^{-1}$ ($\nu_9$ of ferrocene) and a faint band at 490 $cm^{-1}$ ($\nu_{11}$, $\nu_{21}$ of ferrocene) both indicated the presence of unoxidized units. Use of a large excess (2–3 molar equiv) of the halogen in this oxidation reaction produced only insignificant further increases in the degree of oxidation.



(1)

1 **2a**

Having thus demonstrated the feasibility of oxidizing 1 in an organic medium, we proceeded to explore the utility of both picric acid and trichloroacetic acid as the anion sources. To this end, benzene or toluene solutions of 1 were treated with *p*-benzoquinone (1 equiv) as the oxidant, followed by the addition of either picric acid (2 equiv) or trichloroacetic acid (3 equiv). From the respective solutions, polysalts soon precipitated as black solids in nearly quantitative yields. The Mössbauer spectra indicated the degree of oxidation achieved in both polymers to approximate 90%, and this percentage was not appreciably altered by varying the reaction stoichiometries toward higher concentrations of acids or oxidant. Elemental analytical results were in fair agreement with compositions **2b** and **2c**, respectively. However, run-to-run reproducibility was poor, and other polysalt products were found to incorporate rather variable proportions (0.5–0.9) of solvating acid molecules. IR spectroscopy proved to be of little value for assessment of the degree of oxidation attained because of significant anion absorption in the critical 850-$cm^{-1}$ region. To our disappointment, both types of polysalt, in stark contrast to their monomeric ferricenium counterparts,[7] proved entirely insoluble in water, although they were partially (**2c**) or completely (**2b**) soluble in dipolar aprotic media. These two polysalts were, therefore, not further investigated.

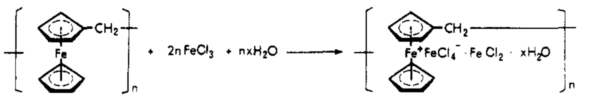


**2b**, $A^- = C_6H_2N_3O_7^- \cdot 0.75C_6H_3N_3O_7$

**2c**, $A^- = CCl_3COO^- \cdot 0.7CCl_3COOH$

Our attention now turned to the tetrachloroferrate(III) as the counterion. Two different preparative approaches toward the desired tetrachloroferrate polysalt were explored. In the first, utilizing the time-proven ferrocene oxidation reaction with ferric salt,[8] 1 was treated in benzene solution with 2 molar equiv of anhydrous iron(III) chloride. The crude polysalt, precipitated in 90–95% yield, was shown spectroscopically to possess a backbone made up entirely of cationic ferricenylenemethylene units. The IR spectrum displayed the characteristic ferricenium deformation band $\nu_{19}$ as a strong and sharp singlet at 853 $cm^{-1}$, whereas the two ferrocene bands due to $\nu_9$ ($\sim$820 $cm^{-1}$) and $\nu_{11}$, $\nu_{21}$ ($\sim$490 $cm^{-1}$) were absent. The 295 K $^{57}Fe$ Mössbauer spectrum displayed only the expected[8c] broad composite resonance in the $\delta$ range 0.2–0.5 mm $s^{-1}$ made up of the ferricenium singlet and superimposed low-spin ferric iron signals of both symmetric and distorted chloroferrate anion units (in addition to ill-defined, weak high-spin ferrous iron doublets[13] of hydrated $FeCl_2$; vide infra), whereas the ferrocene doublet[14] ($\delta$ = 0.45 mm $s^{-1}$, $\Delta eq$ = 2.34 mm $s^{-1}$), conspicuous as a weak "impurity" signal in the spectra of **2a–c**, was undetectable.

The counterion, as would be expected on the basis of the ferrocene behavior[8c] in this oxidation process, substantially represented a $FeCl_4^-$ unit associated with hydrated[15] $FeCl_2$ (**2d**) in accordance with eq 2 ($x$ = 1.5–2),

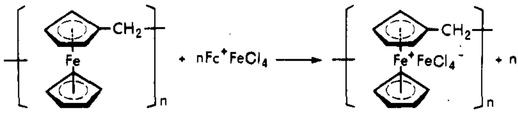


(2)

1 **2d**

with traces of $FeCl_3OH^-$ possibly[8c] included. In accord with the presence of coordinated water, the IR spectrum revealed intense absorption at 3400 and 1615 $cm^{-1}$. A brief (ca. 30-s exposure) washing treatment with absolute ethanol, as recommended[8a] for the purification of crude $Fc^+FeCl_4^-$, removed part of the contaminating $FeCl_2$ along with coordinated water. At the same time, however, this caused a partial (5–10%) reduction in the content of ferricenium units in the backbone. More thorough washing (2–3-min exposure) with the carbinol caused essentially complete removal of the admixed ferrous salt and major elimination of water, as indicated by the elemental analytical results; on the other hand, some 15% of $Fc^+$ units were reduced under these conditions. The observed partial reduction of cationic sites in the crude polysalt in contact with ethanol is not unexpected in view of the reported[16] propensity of $Fc^+$ for reduction by $Fe^{2+}$ ion in ethanolic solution. Both **2d** and the miscellaneous ethanol-washed product polymers were found to be readily and completely soluble in water, forming a dark greenish-blue solution. Remarkably, however, the solubility began to decrease after several months of storage, and a year later the materials had for the major pat become insoluble, possibly as a result of (thermodynamically favored) gradually decreasing intersegmental spacing and, thus, increasing electrostatic cation–anion attraction.

It was obvious from the findings discussed in the foregoing that pure poly(tetrachloroferrate) of the type $(1^{n+})(FeCl_4^-)_n$, with all repeat units in the cationic state, could not be obtained by the method used. Further work was focused, therefore, on the second preparative approach, involving the electron-transfer reaction between 1 and a suitable $Fc^+$ acceptor compound. The (electron-donating) methylene bridge in 1 is expected markedly to reduce the redox potential of the substituted ferrocene complex in the recurring unit relative to unsubstituted ferrocene,[17] suggesting electron transfer from 1 to an unsubstituted $Fc^+$ salt to be a thermodynamically feasible process. In order to provide a preformed $FeCl_4^-$ anion, ferricenium tetrachloroferrate(III) was chosen as the acceptor salt. The compound, when shaken with a solution of a stoichiometric quantity of 1 in benzene or toluene, indeed readily converted to ferrocene, which accumulated in the solvent while the oxidized polymer precipitated out. No traces of 1 were detected in the residue of ferrocene remaining after solvent removal from the organic phase. The degree of oxidation in the precipitated polysalts generally approached or attained 100% (eq 3, Fc = ferrocene), and averaged elemental analytical results agreed substantially with composition **2e**. Small quantities of oxidant occasionally admixed could be removed by anhydrous and anaerobic reprecipitation of the crude polymer from acetonitrile. The IR spectrum of **2e** showed $\nu_{19}$ of the ferricenium system as a strong band at 853 $cm^{-1}$. Other ferricenium bands appeared at 3100 wm ($\nu_8$, $\nu_{17}$), 1410 m ($\nu_{20}$), 1107 vw ($\nu_{10}$), and 1007 wm ($\nu_{18}$) $cm^{-1}$, and the (antisym) Fe–Cl stretching band ($\nu_3$) of the tetrachloroferrate anion complex emerged as an intense signal at 379 $cm^{-1}$ (weak shoulder at 350 $cm^{-1}$).[8c] The 295 K Mössbauer spectrum featured a two-component resonance with singlet maxima at $\delta$ = 0.23 (high-spin Fe(III) in $FeCl_4^-$) and 0.45 mm $s^{-1}$ (ferricenium iron). Polysalt **2e** dissolved readily in water, formic acid, and DMF; it was largely soluble in acetonitrile. After several months of storage a similar reduction in water solubility became noticeable as observed with **2d** and its ethanol-washed counterparts.



1 2e (3)

Occasionally, the poly(tetrachloroferrates) precipitating in these reactions possessed small (5–10%) populations of nonoxidized repeat units. The reduced degree of oxidation in such polymers was indicated by the emergence of a faint Mössbauer signal due to the neutral ferrocene complex (vide supra), as well as by the appearance of a low-intensity shoulder near 815 $cm^{-1}$ ($\nu_9$ of ferrocene) and weak absorption at 490 $cm^{-1}$ ($\nu_{11}$, $\nu_{21}$ of ferrocene) in the IR spectra. It was found to be possible, however, to achieve complete oxidation in these polysalts by careful anaerobic reprecipitation from acetonitrile solution in the presence of a little $Fc^+FeCl_4^-$.

The findings of this study clearly demonstrate the practicability of transforming an inherently hydrophobic ferrocene polymer into a highly hydrophilic polysalt with the aid of the tetrachloroferrate(III) counterion. It is intended to widen the synthetic scope of the electron-transfer reaction involving ferrocene-containing macromolecules and a ferricenium tetrachloroferrate with the aim of preparing other water-soluble ferricenium polymers for biomedical investigations.

## Experimental Section

**Reagents and Analyses.** Trichloroacetic acid and *p*-benzoquinone (Fluka AG) were purified by sublimation (70–80 °C (0.1 torr)). Picric acid and anhydrous iron(III) chloride (Merck AG) were both used as received. Ferrocene (Strem Chemicals) was recrystallized from hexane. All solvents were dried over molecular sieves 4A and were thoroughly deoxygenated. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, Robertson Laboratory, Florham Park, NJ, and the Analytical Laboratory of this department; all determinations were made in triplicate or more frequently if required (necessitated by considerable scattering of data: C, ±0.7%; H, ±0.2%; Cl, ±1.5%; Fe, ±0.8%), and findings were averaged. $^{57}Fe$ Mössbauer spectra were recorded at 295 K. Isomer shifts $\delta$ were referenced against $\alpha$-iron foil at room temperature; degrees of oxidation in polysalts **2** were assessed from area ratios of ferricenium ($\delta \simeq 0.46$ mm $s^{-1}$, $\Delta eq \simeq 0$ mm $s^{-1}$) to ferrocene ($\delta \simeq 0.45$ mm $s^{-1}$, $\Delta eq \simeq 2.35$ mm $s^{-1}$) signals.

**Poly(ferrocenylenemethylene) (1).** This condensation polymer was prepared by the $ZnCl_2/HCl$-catalyzed polymerization of ((dimethylamino)methyl)ferrocene under the conditions of experiment 4 of the described procedure.[3] The crude polymer 1, isolated in 59% yield (in addition to 12% of oligomeric 1), was stepwise reprecipitated from $N_2$-saturated benzene solution by excess hexane in such a fashion as to afford a minor first fraction (15%) and a major second fraction (39%). The latter was used for the present study; it was dried for 24 h at 80 °C (0.5 torr). The tan product dissolved smoothly in aromatic hydrocarbons and chloroform, $\bar{M}_n$ = 2400 (by vapor pressure osmometry at 30 °C in benzene; *c* = 0.3 g/(100 mL); Anal. Calcd for $(C_{11}H_{10}Fe)_n$ (H end group[3] neglected): Fe, 28.20. Found: Fe, 27.91.

**Poly(ferriceniummethylene) Polysalts 2. Poly(triiodide) 2a.** A solution was prepared from 1 (396 mg, 2 mmol, recurring unit) in dry benzene (4 mL) saturated with $N_2$ as a precautionary measure. To the filtered and vigorously shaken solution was added iodine (840 mg, 3.3 mmol) dissolved in the same medium (9 mL). The black mixture was stored overnight at room temperature in a stoppered flask protected from light, and the blackish precipitate of **2a** was collected by filtration, washed thoroughly with benzene, and dried for 24 h at 40 °C (0.5 torr); yield, 1.05 g (94%). Anal. Calcd for $(C_{11}H_{10}FeI_{2.85})_n$ (**2a**): C, 23.60; H, 1.80; Fe, 9.98; I, 64.62. Found: C, 23.25; H, 1.72; Fe, 9.66; I, 64.87. The polymer was insoluble in water but dissolved completely in $N_2$-saturated DMF or $Me_2SO$ to become yellow-brown. It was recovered from such solutions as a less oxidized polysalt by precipitation with excess ether and thorough washing with the precipitant. Anal. Calcd for $(C_{11}H_{10}FeI_{1.95})_n$ (polysalt with 65% oxidation): Fe, 12.54; I, 55.55. Found: Fe, 12.23; I, 55.31. Precipitation was similarly accomplished with excess water.

**Polypicrate 2b.** *p*-Benzoquinone (540 mg, 5 mmol) was added to the rapidly stirred solution of 1 (0.99 g, 5 mmol, recurring unit) and picric acid (2.29 g, 10 mmol) in toluene (10 mL) under $N_2$. The mixture was shaken in a stoppered flask for 2 h at room temperature. The precipitated black polysalt **2b** was filtered off, washed well with benzene, and dried for 24 h at 60 °C (0.1 torr); yield, 2.71 g (97%). Anal. Calcd for $(C_{20.45}H_{13.83}FeN_{4.73}O_{11.03})_n$ (**2b**): C, 44.01; H, 2.50; Fe, 10.01; N, 11.87. Found: C, 39.87; H, 2.76; Fe, 10.49; N, 11.56. The polypicrate was insoluble in water but dissolved readily in DMF and $Me_2SO$.

**Poly(trichloroacetate) 2c.** A toluene solution of 1 was oxidized as described for **2b** except that trichloroacetic acid (15 mmol) was substituted for the picric acid. The black polysalt **2c**, obtained in 95% yield by the same workup procedure, was insoluble in water and largely so in DMF or $Me_2SO$. Anal. Calcd for $(C_{14.06}H_{10.63}Cl_{4.59}FeO_{3.06})_n$ (**2c**): C, 37.77; H, 2.40; Cl, 36.39; Fe, 12.49 Found: C, 37.44; H, 2.71; Cl, 36.20; Fe, 12.02.

A poly(trichloroacetate) of similar composition precipitated after 16 days at room temperature from an $O_2$-saturated toluene solution of 1 and trichloroacetic acid (7-fold molar equiv) in the absence of *p*-benzoquinone. The black polysalt, collected in 89% yield, exhibited the same solubility behavior as observed for **2c**.

**Poly(tetrachloroferrate) 2d.** The suspension (and partial solution) of anhydrous $FeCl_3$ (1.63 g, 10 mmol) in ether (7 mL) was added to the stirred and prefiltered solution of **1** (0.99 g, 5 mmol) in benzene (10 mL), whereupon a black precipitate settled out. The mixture was shaken in a stoppered flask for 6 h at ambient temperature. The precipitate was filtered off, washed with benzene and ether, and dried for 48 h at 50 °C (0.5 torr); yield, 2.54 g (91%). Anal. Calcd for $(C_{11}H_{14}Cl_6Fe_3O_2)_n$ (**2d**, $x = 2$): C, 23.66; H, 2.53; Cl, 38.09; Fe, 30.00. Found: C, 23.19; H, 2.73; Cl, 36.54; Fe, 29.72. The freshly prepared polysalt was completely soluble in water (dark greenish-blue) and DMF (brownish-blue) and partly dissolved in acetonitrile; however, the solubility decreased steadily on prolonged storage, and after 1 year the material was substantially insoluble in water and acetonitrile although still almost completely soluble in DMF.

In an oxidation reaction performed as above, the crude polysalt **2d** was immediately, without drying, digested with absolute ethanol (2 mL) for about 30 s, and the mixture was rapidly filtered by suction through fritted glass. The residual polymer was washed with ether and dried for 8 h at 100 °C (0.1 torr); yield, 1.97 g (86%). Anal. Calcd for $(C_{11}H_{12}Cl_{4.6}Fe_{2.4}O)_n$ $[(C_{11}H_{10}Fe\cdot 0.9FeCl_4\cdot 0.5FeCl_2\cdot H_2O)_n]$: C, 28.89; H, 2.65; Cl, 35.66; Fe, 29.31. Found: C, 28.85; H, 2.80; Cl, 34.51; Fe, 30.99. An analogous experiment in which the ethanol (2 × 2 mL) washing period totaled 3 min, the brownish-black polysalt, precipitated in 85% yield, possessed an elemental composition essentially consistent with $(C_{11}H_{10}Fe\cdot 0.85FeCl_4\cdot 0.5H_2O)_n$. Anal. Calcd for $(C_{11}H_{11}Cl_{3.4}Fe_{1.85}O_{0.5})_n$: C, 35.22; H, 2.96; Cl, 32.14; Fe, 27.55. Found: C, 34.77; H, 3.01; Cl, 31.90; Fe, 28.02. The various ethanol-washed polysalts showed solubility properties similar to those of **2d**.

**Poly(tetrachloroferrate) 2e.** The filtered solution of **1** (0.99 g, 5 mmol) in benzene (25 mL) was reduced to ca. half its original volume by rotary evaporation (50 °C bath temperature). To this azeotropically dehydrated solution was added predried (100 °C (0.1 torr)) solid ferricenium tetrachloroferrate(III)[8c] (1.92 g, 5 mmol). The mixture was saturated with $N_2$ and shaken for 6 h at ambient temperature. The blackish precipitate was collected by filtration, washed thoroughly with benzene and ether under anhydrous conditions, and dried overnight at 100 °C (0.1 torr); yield, 2.0 g (101%, indicating admixture by oxidant). Anal. Calcd for $(C_{11}H_{10}Cl_4Fe_2)_n$ (**2e**): C, 33.39; H, 2.55; Cl, 35.84; Fe, 28.23. Found: C, 32.98; H, 2.67; Cl, 35.37; Fe, 28.71. Solvent was removed under reduced pressure from the combined filtrate and washings; the orange crystalline residue (0.46 g) was pure ferrocene (IR). A sample of the crude **2e** was reprecipitated from acetonitrile solution (ca. 60% soluble) by excess ether/hexane (1:1) in the absence of moisture and oxygen; the collected greenish-black and somewhat sticky product, washed thoroughly (until powdery) with the ether/hexane mixture under $N_2$ and dried as before, gave similar analytical results as found for the crude polymer. Samples of incompletely oxidized polysalt were reprecipitated by the same method, yet with predried ferricenium tetrachloroferrate (5–10% by weight of crude polymer) added to, and dissolved in, the acetonitrile solution. The precipitated polymer generally possessed composition **2e** at this stage; occasionally, however, a repeat reprecipitation of the freshly precipirated (still completely acetonitrile soluble) polysalt was required for completion of the oxidation process.

Polymer **2e** dissolves readily in water, formic acid, DMF and $Me_2SO$, forming greenish-blue (water, formic acid) or greenish (DMF, $Me_2SO$) solutions; aqueous solutions are reasonably stable for some 24 h, whereas DMF and $Me_2SO$ solutions, even when thoroughly deoxygenated, degrade almost immediately, this being accompanied by a color change to yellow-brown.

Several oxidation experiments were performed as described in the foregoing except that fractions of **1** with different chain lengths ($\bar{M}_n = 1270$ and 4300) were used. There were no differences in composition or spectroscopic and solubility behavior of the resulting polysalts.

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