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Synthesis of Polyesters Containing Tetrathiafulvalene Groups in the Backbone

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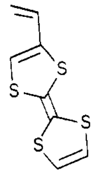
ABSTRACT: New polyesters, incorporating the tetrathiafulvalene (THF) moiety within the polymer backbone, were prepared by polycondensation of 2,6(7)-bis(*p*-hydroxyphenyl)tetrathiafulvalene with either sebacyl chloride or terephthalyl chloride using solution techniques. The effects of various bases, solvents, and reaction temperatures were studied, but the molecular weights were rather low in all cases. The polymers were highly soluble in CF_3COOH, soluble in dipolar aprotic solvents (i.e., HMPA, Me_2SO, DMF) on heating, slightly soluble in THF and acetone, and largely insoluble in other common solvents. TGA and DTA studies indicated the polyesters were stable to about 270 °C and an exotherm (in air) occurred at 280 °C followed by rapid weight loss. Attempts to prepare tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyanoquinone (DDQ) complexes were unsuccessful. Bromine complexes were prepared.

Studies of highly conducting organic charge-transfer (CT) complexes have attracted enormous recent interest with the development of pseudo-one-dimensional "organic metals".[1] In particular, molecular CT complexes of either tetrathiafulvalenes (TTF)[2-4] or tetraselenafulvalenes (TSeF)[5,6] with tetracyanoquinodimethane (TCNQ) have been most intensively investigated owing to their quasi-metallic conductivity. The preparations of TTF and TSeF derivatives have been reviewed[7] and new synthetic procedures for preparing unsymmetrical TTF derivatives continue to appear regularly.[8-12] However, there exists a clear need for such conductors with improved material properties and three-dimensional conductivity. One approach to this problem is to prepare multidimensional networks[2f] or polymers.

Many reports of semiconducting organic polymers have appeared.[13] One approach has been to make anion–radical TCNQ salts of polymeric cations.[14,15] Conductivities as high as $\sim 10^{-2}$ ohm^{-1} cm^{-1} were obtained for TCNQ complexes of poly(3-vinylbis(fulvalenediiron)),[16,17] while TCNQ, DDQ, and I_3^- complexes of poly(vinylferrocene), poly(ferrocenylene), and poly(ethynylferrocene) had conductivities below 10^{-5} ohm^{-1} cm^{-1}.[17,18] Polymers containing TTF units, however, have been much less studied owing, in part, to the relative logistics encountered in monomer synthesis.

Among the first TTF-containing polymers were those prepared via a polycoupling process by Okawara et al.[19] Only two reports of condensation polymers containing TTF exist; polyurethanes[20] and polyamides[21] were synthesized and both failed to form CT complexes with TCNQ and DDQ. Three vinyl monomers of TTF have now been made. Vinyltetrathiafulvalene, **1**, gave low molecular weight polymers on standing or exposure to UV or azo initiators.[22] (*p*-Vinylphenyl)tetrathiafulvalene, **2**, resisted anionic and radical initiation but thermally polymerized in bulk. Its polymer was insoluble and did not give TCNQ complexes, although bromine complexes were reported.[23] Finally, acrylate **3** was prepared and both homo- and copolymerized. Its polymers gave evidence of TCNQ complexation.[24]



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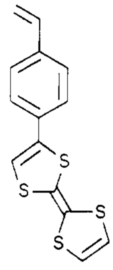

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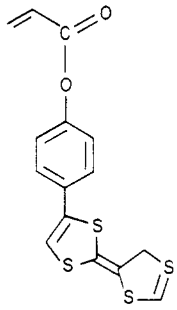

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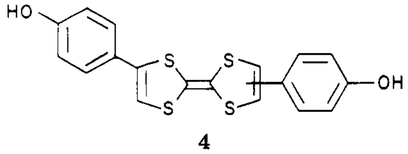
We now report the polycondensation of 2,6(7)-bis(*p*-hydroxyphenyl)tetrathiafulvalene, **4**,[25] with diacid chlorides.



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Experimental Section

Materials. Solvents and Nitrogen bases. 1,2-Dichloroethane was purified by washing sequentially with diluted aqueous acid, water, diluted aqueous base, and water followed by drying (anhydrous Na_2SO_4) and distillation from calcium hydride.

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N,N-Dimethylacetamide (DMAc) and hexamethylphosphortriamide (HMPA) were distilled under nitrogen from phosphorus pentaoxide. Tetramethylene sulfone (TMS) was purified by warming over potassium permanganate, filtration, and distillation from phosphorus pentaoxide under vaccum. Chloroform was purified by aqueous washing, drying, and distillation from calcium hydride. Toluene and *p*-xylene were distillated from calcium hydride under nitrogen. Nitrobenzene was purified by aqueous washing, drying (CaH), and distillation from phosphorus pentaoxide at 1 atm. Triethylamine and *N*-ethylmorpholine were distilled from phosphorus pentaoxide under nitrogen while pyridine, 2-picoline, 2,6-lutidine, and isoquinoline were distilled from barium oxide under nitrogen.

Monomers. Sebacyl chloride (Eastman Kodak) was distilled at reduced pressure under nitrogen. Terephthaloyl chloride (Aldrich Chem. Co.) was recrystallized from *n*-hexane. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene was prepared according to our previously published eight-step synthesis[25] starting with the 4-hydroxyacetophenone in 29% overall yield. However, monomer 4 was found to be unstable in the air and this required a modification of the last step as described below.

To a suspension of 2,6(7)-bis(*p*-acetoxyphenyl)tetrathiafulvalene (0.47 g, 1.0 mmol) in methanol (20 mL) hydrazine hydrate (3 mL) was added. The reaction was stirred at room temperature, while the color changed from orange to blood red. After 12 h, deoxygenated water was added and a red precipitate was filtered under nitrogen. Recrystallization from nitrogenated preboiling methanol gave golden air-sensitive crystals (which were stored in an inert atmosphere) melting at 207–208 °C: IR (KBr) 1600, 1548, 1502, 1455, 1382, 1248, 1172, 919, 825, 760 cm^{-1}; NMR (Me$_2$SO-d_6) δ 6.74–7.43 (multiplet, aromatic, 8 H), 6.95 (s, 2, ring H), 3.42 (s, OH, 2 H). Anal. Calcd for $C_{18}H_{12}S_4O_2$: C, 55.66; H, 3.09; S, 33.02. Found: C, 55.56; H, 3.10; S, 32.87.

Polymerization. 1. Low-Temperature Solution Polymerizations. Two methods were used as given below.

Method A. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3885 g, 1.0 mmol) was placed in a dried, 50-mL flask equipped with a magnetic stirrer and pressure-equalizing dropping funnel which was fitted with a drying tube filled with calcium chloride. Purified *N,N*-dimethylacetamide (1 mL) and purified pyridine (0.1584 g, 2 mmol) were added with a pipet to the flask and the mixture was cooled (ice bath) with stirring. Sebacyl chloride (0.2391 g, 1 mmol), in 1 mL of purified 1,2-dichloroethane, was added dropwise to the cooled diol solution and the mixture was stirred at room temperature for 12 h. The polymer was precipitated by adding the reaction solution to 100 mL of water, collected by suction filtration, and washed thoroughly with water. After drying the wet polymer over phosphorus pentaoxide at 80 °C (0.2 torr) for 48 h, 0.50 g (90%) of polymer was obtained. The inherent viscosity in CF$_3$COOH was 0.14 measured at a concentration of 0.5 g/dL at 30 °C.

Method B. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3885 g, 1 mmol) was placed in a dried 50-mL flask equipped with a magnetic stirring bar. *N,N*-Dimethylacetamide (DMAc) (1 mL) and triethylamine (0.2024 g, 2 mmol) were added with stirring. A solution of sebacyl chloride (0.2391 g, 1 mmol), dissolved in 1 mL of purified *N,N*-dimethylactamide (DMAc), was added all at once to the stirred diol suspension without cooling. After addition, the polymerization mixture was stirred at 20–25 °C for 12 h. Then water (100 mL) was added. The resulting polymer was filtered and washed thoroughly with water, and the brown solid product was dried over phosphorus pentaoxide at 80 °C (0.2 torr) for 48 h giving 0.54 g (98%). The inherent viscosity in CF$_3$COOH was 0.16 measured at a concentration of 0.5 g/dL at 30 °C.

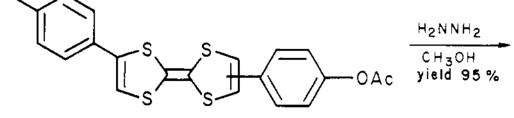
2. Typical Higher Temperature Solution Polymerization. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3885 g, 1 mmol) was placed in a dried, 50-mL flask equipped with a magnetic stirrer and condenser. *p*-Xylene (1 mL) and pyridine (0.1584 g, 2 mmol) were added and the flask was heated under nitrogen. Sebacyl chloride (0.2391 1 mmol), dissolved in 1 mL of *p*-xylene, was added all at once to the boiling diol suspension with vigorous stirring. The reaction was stirred at reflux for 12 h. The polymer was obtained by precipitation from cold water (100 mL), filtration, water washing, and drying in vacuo (80 °C, 0.2 torr) over phosphorus pentaoxide for 48 h. The resulting orange solid (0.26 g, 99% yield) had η_{inh} = 0.24 in CF$_3$COOH.

Synthesis of Bromine Complexes. Two preparative methods were used. Small samples of polyester **5** (entree 2, Table IV) and **6** (entree 4, Table II) were weighed into a watch glass. The samples were subjected to excess bromine vapor (in a closed beaker in the presence of air) for 10 min. The polymers turned black and appeared to soften, somewhat, during the treatment. Analysis of the bromine complex of **5** gave C, 47.09; H, 3.81; Br, 20.71. This corresponds to the emperical formula $[C_{28}H_{26}O_4S_4Br_{1.99}]_n$ most closely based on the carbon analysis where theory requires C, 47.09; H, 3.64; Br, 22.30. Analysis of the bromine complex of **6** gave C, 48.98; H, 2.42; Br, 14.47. This corresponds to the empirical formula $[C_{26}H_{14}O_4S_4Br_{1.49}]_n$ based on the carbon analysis where theory required C, 48.98; H, 2.22; Br, 18.65.

The second method involved heating small amounts of a polyester suspension in a 50% CCl$_4$ solution of bromine at 80 °C for 10 min. In this method a substantially larger amount of bromine was incorporated. The resulting polymers were filtered, washed repeatedly with CCl$_4$, and dried 24 h in vacuo. The bromine complex of **5** obtained in this way analyzed for C, 33.32; H, 2.70; Br, 41.36. This corresponds to the formula $[C_{28}H_{26}O_4S_4Br_{3.13}]_n$ based on the carbon analysis where theory requires C, 33.32; H, 2.58; Br, 45.01. Analysis of the bromine complex of **6** prepared in the same way gave C, 40.36; H, 1.87; Br, 26.69. This corresponds to $[C_{26}H_{14}O_4S_4Br_{3.19}]_n$ based on the carbon analysis where theory requires C, 40.36; H, 1.83; Br, 32.96.

Results and Discussion

Preparation of Polyesters. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene, **4**, is unstable in air, quickly turning from an orange color to dark brown. Therefore, its preparation from 2,6(7)-bis(*p*-acetoxyphenyl)tetrathiafulvalene (eq 1)[25] and recrystallization from methanol should be carried out under nitrogen and in nitrogenated solvents. After recrystallization from methanol, a series of solution polycondensations were carried out at various conditions with sebacyl chloride or terephthaloyl chloride as shown in eq 2. Two general methods were employed.



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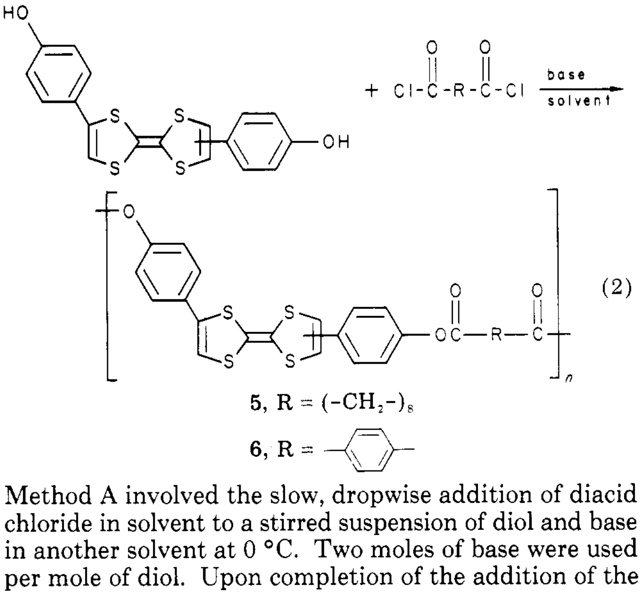


(2)

5, R = (-CH$_2$-)$_8$

6, R =

Method A involved the slow, dropwise addition of diacid chloride in solvent to a stirred suspension of diol and base in another solvent at 0 °C. Two moles of base were used per mole of diol. Upon completion of the addition of the diacid solution, the polymerization solution was stirred for 12 h at 20–25 °C before the polymer was isolated. Method B involved preparing two solutions of equal volume. One solution contained the diol, 2 equiv of base, and solvent. The other solution contained the diacid chloride and solvent. The diacid chloride solution was added all at once

Table I
Solution Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with Sebacyl Chloride at Lower (0-25 °C) Temperatures[a]

solvent[b]	base	polymer yield, %	polymer η_{inh}[c]
DMAc[d]/1,2-dichloroethane	pyridine	90	0.14
DMAc[d]/1,2-dichloroethane	triethylamine	92	0.12
DMAc[d]	pyridine	81	0.12
DMAc[d]	triethylamine	98	0.16
1,2-dichloroethane	triethylamine	89	0.14
TMS[d]	pyridine	96	0.16
TMS[d]	triethylamine	98	0.17
TMS[d]/1,2-dichloroethane	triethylamine	99	0.17
HMPA[d]	pyridine	95	0.12
HMPA[d]	triethylamine	95	0.13
HMPA[d]/1,2-dichloroethane	triethylamine	96	0.14
chloroform	triethylamine	97	0.18

[a] All polycondensations were carried out using 1 mmol of each monomer and 2 mmol of base in 2 mL of solvent at 20-25 °C for 12 h. [b] Method A was employed in reactions using mixed solvents. Method B was used whereever a single solvent was used. [c] Measured at a concentration of 0.5 g/dL in CF_3COOH at 30 °C. [d] DMAc = dimethylacetamide, TMS = tetramethylene sulfone, HMPA = hexamethylphosphortriamide.

Table II
Solution Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with Terephthaloyl Chloride at Lower (0-25 °C) Temperatures[a]

solvent	base	polymer yield, %	polymer η_{inh}
$CHCl_3$	pyridine	96	0.16
$CHCl_3$	triethylamine	98	0.25
TMS[b]	pyridine	96	0.17
TMS[b]	triethylamine	98	0.28
DMAc[b]	triethylamine	98	0.25

[a] All polycondensations were conducted by method B and employed 1 mmol of each monomer and 2 mmol of base in 2 mL of solvent at 20-25 °C for 12 h. [b] TMS = tetramethylene sulfone, DMAc = dimethylacetamide.

Table III
Effect of the pK_a of Added Base on Polymer Molecular Weight in Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with Sebacyl Chloride Using Method A in Chloroform

base	pK_a	polymer yield, %	polymer η_{inh}
triethylamine	10.75	97	0.18
N-ethylmorpholine	7.67	96	0.14
2,6-lutidine	6.60	99	0.20
2-picoline	5.94	98	0.16
pyridine	5.22	90	0.14
isoquinoline	4.81	98	0.12

Table IV
Higher Temperature Solution Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with Sebacyl and Terephthaloyl Chlorides[a]

polymer	solvent	base	yield, %	η_{inh}
5	*p*-xylene	pyridine	100	0.24
5	*p*-xylene	triethylamine	98	0.22
6	*p*-xylene	triethylamine	99	0.11
6	*p*-xylene	pyridine	94	0.07
6	toluene	triethylamine	90	0.16
6	toluene	pyridine	90	0.15

[a] Each polycondensation was carried out at reflux for 12 h using 1 mmol of each monomer and 2 mmol of base in 2 mL of solvent.

to the diol solution with stirring but without cooling. These reactions were stirred for 12 h at 20–25 °C. The polymer was then collected. Method A was used in cases where dual solvents were employed while method B was followed in single solvent reactions. Representative low-temperature solution polycondensations and polymer viscosities are given in Table I for **5** (sebacyl polymers) and Table II for **6** (terephthaloyl polymers).

Although the polymers were isolated in excellent yields, the molecular weights remained low over the entire series. In order to determine the influence of base strength in these polymerizations, amines with a wide range of pK_a values were tested. As shown in Table III, there is no correlation between base strength and the resulting polymer's viscosity despite a change in base strength over a range of six powers of ten.

Although the polycondensation proceeds readily at room temperature in solvents such as *N,N*-dimethylacetamide (DMAc), 1,2-dichloroethane, tetramethylene sulfone (TMS), hexamethylphosphortriamide (HMPA), and chloroform, only low molecular weight polyesters were obtained. The use of higher temperatures was considered. Thus, additions of diacid chloride to hot diol solutions, in the presence of base, followed by heating at reflux for 12 h was tried. These results are summarized in Table IV. Indeed, the molecular weights of **5** did show an increase. However, polycondensations using terephthaloyl chloride at higher temperatures gave **6** with lower molecular weights than were obtained at lower temperature.

The incremental addition method was employed to see if the molecular weights could be increased. Thus, individual polycondensations were carried out with terephthaloyl chloride:**4** ratios of 98/100, 99/100, 1/1, and 101/100 in tetramethylene sulfone according to method A. The resulting polymers exhibited inherent viscosities of 0.10, 0.16, 0.28, and 0.14, respectively. This demonstrates that the molecular weights were relatively low for reasons other than poorly matched M_1/M_2 ratios.

Characterization. Polyesters **5** and **6** gave elemental analyses in excellent agreement with theory. For example, for polymer **5** (entree 1, Table IV) Calcd: C, 60.60; H, 4.69; S, 23.08; Found: C, 60.38; H, 4.75; S, 22.96. For polymer **6** (entree 2, Table II) Calcd: C, 60.21; H, 2.73; S, 24.73; Found: C, 60.87; H, 2.85; S, 24.95. The IR spectra were also in accord with structures **5** and **6**. Ester carbonyl absorption occurred at 1740–1730 cm^{-1} and each spectra exhibited bands at 830, 770, and 720 cm^{-1} which are characteristic of disubstituted TTF unit.[26]

Polymers **5** and **6** were completely soluble in CF_3COOH at room temperature and soluble in HMPA, Me_2SO, and DMF on heating. They were only partially soluble in THF and acetone and insoluble in chloroform, methylene chloride, tetrachloroethane, dioxane, diethyl ether, benzene, toluene, and hexane. We were not able to obtain representative gel permeation chromatographic molecular weight determinations since **5** and **6** were only partially soluble in THF.

The glass transition temperature (T_g) of polyester **5** was observed at 140 °C by differential scanning calorimetry (DSC) at a heating rate of 20 °C min^{-1}. This may be compared to the report that homopolymers of **2** do not soften even at 300 °C.[23] In contrast to **5**, the T_g of polyester

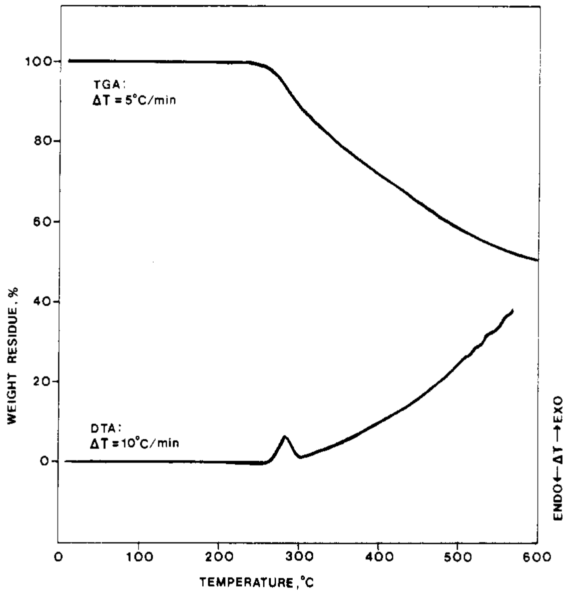


Figure 1. DTA and TGA curves of polyester 5.

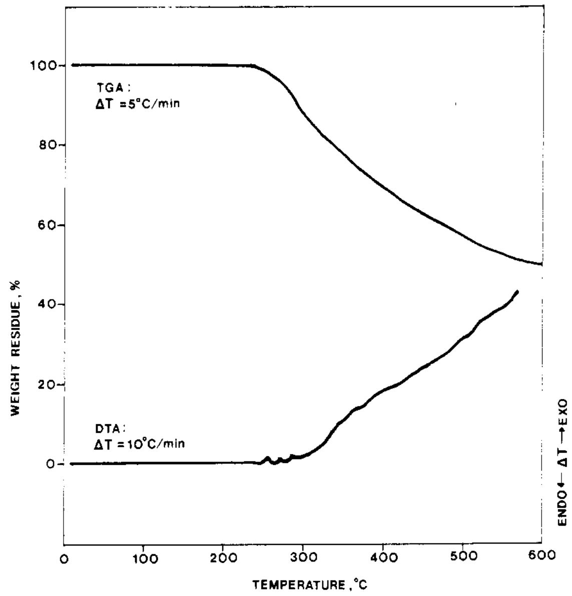


Figure 2. DTA and TGA curves of polyester 6.

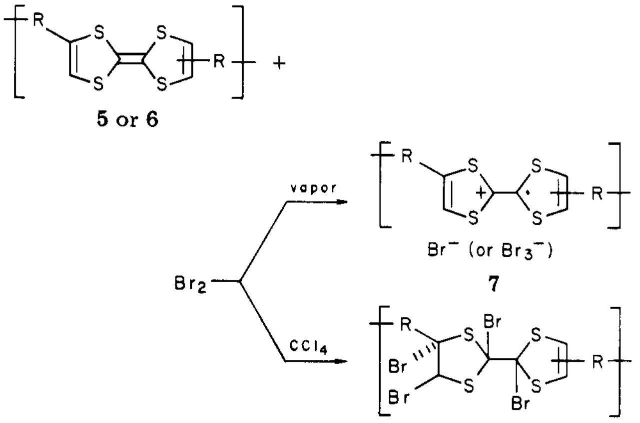
6 could not be detected, presumably because it is expected to be very high. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out at 5 and 10 °C min^{-1}, respectively, on both 5 and 6. Typical thermograms are shown for each polyester in Figures 1 and 2. The DTA curves of 5 exhibited a strong exotherm at about 280 °C in air which correlated well with TGA studies showing that the initial loss of weight occurred at about this temperature. The decomposition temperature for 10% weight loss was ~290 °C for both 5 and 6 in nitrogen.

The origin of the 280 °C exotherm was found to be due to a reaction of the TTF nucleus. Pure tetrathiafulvalene was studied as a model compound. No thermal decomposition of TTF occurs at its melting point (118–119 °C). However, at temperatures above 250 °C it decomposes with gas evolution both in air and under nitrogen. After TTF is raised only briefly to 280 °C and cooled, it has totally decomposed, according to the IR spectra of the residue. When polyester 5 was heated in sealed tubes at 280 °C (in air or under nitrogen), the IR bands at 770 and 750 cm^{-1}, characteristic of the disubstituted TTF nucleus, disappear over a period of ~5 min. Thus, the TTF nucleus is thermally degraded. The ester carbonyl bands at 1740 cm^{-1} remain undiminished.

Attempts to Form TCNQ and DDQ Complexes. Both polyesters 5 and 6 were refluxed to acetonitrile under nitrogen for 24 h with equimolar amounts of either TCNQ or DDQ. The product was washed with copious amounts of acetonitrile. The IR spectra of the resulting product were identical with those of 5 or 6 and showed no evidence of the presence of TCNQ or DDQ. Since polyesters 5 and 6 were both soluble in HMPA, hot HMPA solutions of 5 or 6 were reacted with an equivalent of TCNQ (or DDQ). After being refluxed for 10–20 min, the solutions were cooled, HMPA was removed in vacuo, and the residue was washed with methanol and dried. Only pure polyester was recovered.

The UV–visible spectra of polyesters 5 and 6 were obtained independently in HMPA, as were the spectra of TCNA and DDQ. Then HMPA solutions of the polyesters were mixed with TCNA or DDQ. No evidence of CT complexation was obtained. Both polyesters exhibited strong absorptions at 420 nm, while TCNQ in HMPA has two strong bands at 420 and 500 nm, and DDQ absorbs at 405 nm in HMPA. Mixing HMPA solutions of the polyesters with those of TCNQ (or DDQ) gave spectra consistent with those obtained by simply adding their individual spectra. No low-energy CT bands were observed.

Bromine Complexes. Both polyesters 5 and 6 were converted to bromine complexes by exposure to bromine vapor in air at room temperature. By this treatment, 5



5 or 6

7

8

was converted to a solid analyzing (see experimental) for $[C_{28}H_{26}O_4S_4Br_{1.99}]_n$ while 6 gave a solid corresponding to $[C_{26}H_{14}O_4S_4Br_{1.49}]_n$. The infrared spectra of polymers 5 and 6 exhibited absorptions at ~1600 cm^{-1} which we attribute to carbon–carbon double bond absorptions from the TTF moiety. Upon treatment with bromine vapor, the intensity of these bands remained undiminished suggesting the complex has a structure such as 7.

The ESR spectra were obtained for the Br_3^- complexes of polymers 5 and 6. Welcome[19] had previously reported *g* value of 2.00789 G for the tetrathiafulvalene radical cation in TTF-containing polymers which had been oxidized to Br_3^- salts. Using solid samples, the Br_3^- salt of 5 exhibited a $g = 2.0075$ G while the Br_3^- salt of 6 gave a $g = 2.0076$ G. This provides further evidence for the structure shown in 7.

Polyesters 5 and 6 were also treated with CCl_4 solutions of bromine to give complexes analyzing for $[C_{28}H_{26}O_4S_4Br_{3.13}]_n$ and $[C_{26}H_{14}O_4S_4Br_{3.19}]_n$, respectively. In order to see if bromine addition to the double bonds in the TTF nucleus had occurred, the IR spectra were recorded. The absorption at ~1600 cm^{-1} found in 5 and

6 was greatly diminished suggesting bromine addition to TTF double bonds as implied by structure **8**. Also, carbonyl absorption was found at lower frequencies, 1680–1700 cm^{-1}, suggesting further structural changes in the solid.

Attempts to prepare higher molecular weight condensation polymers from monomer **4** are currently in progress.

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