

Synthesis and Polymerization of p-(2-Tetrathiafulvalenyl)phenyl Methacrylate

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A new vinyl monomer of tetrathiafulvalene (TTF), p-(2-tetrathiafulvalenyl)phenyl methacrylate (**3**), was prepared, and its homopolymerization was accomplished by a thermal, bulk technique. The poly[p-(2-tetrathiafulvalenyl)phenyl methacrylate] was largely insoluble in common organic solvents. The copolymer of **3** and methyl methacrylate was made by solution polymerization. The copolymer was soluble in halogenated hydrocarbons, halobenzene, toluene, acetone, and THF and was insoluble in water, methanol, ether, and hexane. TGA and DTA studies indicated the polymers were stable to about 250 °C, and an exotherm (in air) occurred at 255 °C for the homopolymer, followed by rapid weight loss. The copolymer formed a 2:1 complex with DDQ. Bromine complexes were prepared.

Introduction

The development of pseudo-one-dimensional "organic metals"¹ has attracted recent interest in studies of highly conducting organic charge-transfer (CT) complexes. In particular, molecular CT complexes of tetrathiafulvalenes (TTF)²⁻⁴ and tetraselenafulvalenes (TSeF)^{5,6} with tetracyanoquinodimethane (TCNQ) have been most intensively investigated owing to their quasi-metallic conductivity. The preparations of TTF and TSeF have been reviewed,⁷ and new synthetic procedures for preparing unsymmetrical TTF derivatives continue to appear.⁸⁻¹² However, there exists a clear need for such conductors with improved material properties. Three-dimensional conductivity is also desired for some applications. One approach to this problem of achieving higher dimensionality in conducting compounds is to take known systems with high one-dimensional conductivity and attach more than one donor or acceptor unit to the same molecule. Thus, a network of a multidimensional nature might be achieved.^{2f} The preparation of polymeric CT complexes could be a route

to achieving improved material properties provided that conductivity remains a property of the resulting polymer. For this reason, we have undertaken the preparation of polymers containing TTF and their conversion to CT complexes.

The first polymers containing TTF moieties were prepared via a polycoupling process by Okawara et al.¹³ Four reports of condensation polymers containing TTF exist.¹⁴⁻¹⁷ Polyurethanes,^{14,17} polyamides,¹⁵ polyesters,¹⁶ and polysulfonates¹⁷ were synthesized, and all failed to form charge-transfer complexes with either TCNQ or dichlorodicyanoquinone. However, Br₃⁻ complexes were obtained.^{16,17} Two vinyl monomers of TTF have been made. Vinyltetrathiafulvalene (**1**) gave low molecular weight polymers on standing, on exposure to UV radiation or azo initiators, or on addition of TCNQ.¹⁸ (p-Vinylphenyl)tetrathiafulvalene (**2**) resisted anionic and radical initiation but thermally polymerized in bulk.¹⁹ Its polymer was insoluble and did not give TCNQ complexes, although bromine complexes were reported.¹⁹

We now report the preparation of p-(2-tetrathiafulvalenyl)phenyl methacrylate (**3**) and its homo- and copolymerization.

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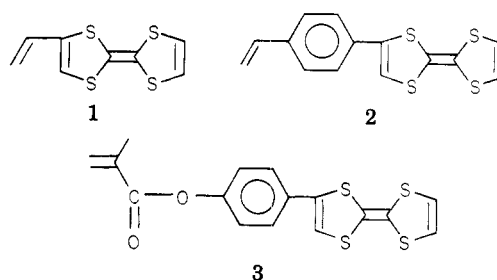
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Results and Discussion

The methods used for preparation of substituted TTF molecules have mostly involved symmetrical molecules. Thus, two molecules of a suitable precursor were coupled in the presence of a coupling agent⁷ (see eq 1). Mixed

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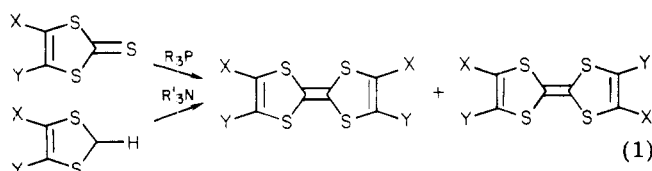
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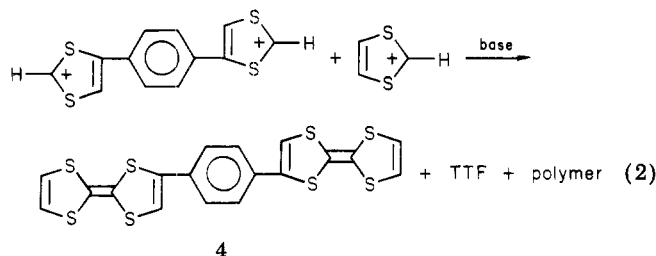
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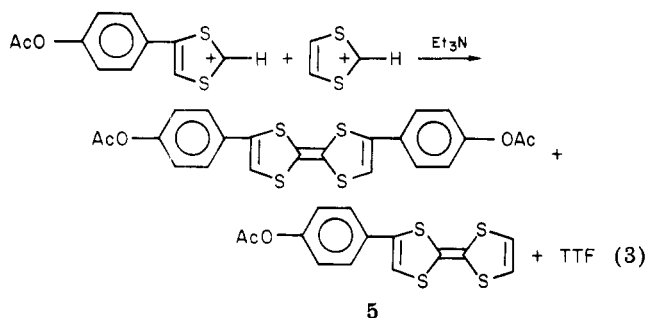


coupling reactions have been used to prepare unsymmetrical TTF derivatives.⁷ The first monophenyl-substituted TTF was *p*-phenylenebis(tetrathiafulvalene) (4).^{2f} That



preparation was achieved by mixed coupling of two different dithiolium cations and the subsequent physical separation of the products formed. Recently, the low-temperature lithiation of TTF has been demonstrated to be an efficient route to monosubstituted TTF derivatives.^{2h}

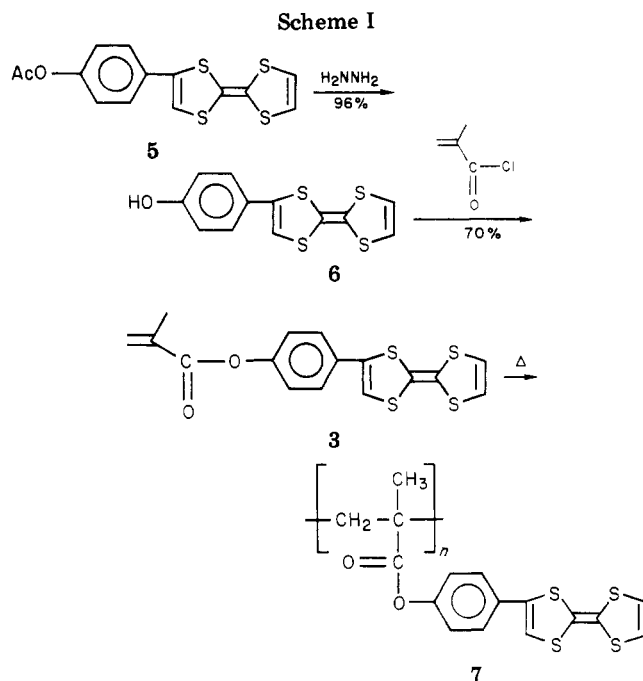
For synthesis of 3, we employed a mixed coupling reaction. Thus, (*p*-acetoxyphenyl)tetrathiafulvalene (5) was generated by coupling an equimolar ratio of 4-(*p*-acetoxyphenyl)-1,3-dithiolium²⁰ and 1,3-dithiolium salts²¹ in the presence of triethylamine (eq 3). Unsymmetrical 5



was then separated from the symmetrical coupling products by means of their solubility differences in acetonitrile. Crude 5 (80% yield, based on a theoretical 33% yield of each product) was purified by recrystallization to give a brownish orange solid melting at 125–127 °C. Its NMR spectrum consisted of a multiplet for the aromatic hydrogens at δ 7.10–7.60 (4 H), two singlets in the ratio of 1:2 for the olefinic hydrogens at δ 6.54 (1 H) and 6.42 (2 H), and a singlet at δ 2.37 (3 H) for the methyl protons. Its IR spectrum has a strong ester carbonyl absorption at 1740 cm^{-1} .

The synthesis of *p*-(2-tetrathiafulvalenyl)phenyl methacrylate (3) from (*p*-acetoxyphenyl)tetrathiafulvalene (5) and the polymerization of 3 are outlined in Scheme I.

Hydrolysis of 5 to 6 proceeded in excellent yield (96%) upon stirring the ester with hydrazine in methanol at room temperature for 4 h followed by pouring the mixture into water. Filtration gave a yellow product, which melted at 122–124 °C. The NMR spectrum of 6 showed a multiplet for the aromatic hydrogens at δ 6.78–7.47 (4 H), two singlets for the olefinic hydrogens at δ 6.97 (1 H) and 6.79 (2 H), and a singlet at δ 3.65 for the hydroxyl proton.



Compound 3 was then prepared in 70% yield by reacting (*p*-hydroxyphenyl)tetrathiafulvalene (6) with methacryloyl chloride and triethylamine in HMPA. Recrystallization from methanol gave yellow crystals melting at 85–86 °C. Its NMR spectrum exhibited a multiplet for the aromatic hydrogens at δ 7.09–7.58 (4 H), two singlets in the ratio of 1:2 for the TTF ring hydrogens at δ 7.16 (1 H) and 6.70 (2 H), a doublet for the vinyl hydrogens at δ 6.04 (2 H, $J = 23$ Hz), and a singlet for the methyl protons at δ 2.0 (3 H). The IR spectrum showed olefinic C–H stretching at 3060 cm^{-1} , ester carbonyl absorption at 1730 cm^{-1} , multiple bands at 1130–1220 cm^{-1} due to C–O stretching of the α,β -unsaturated ester, and TTF bands at 760, 780, and 800 cm^{-1} .

Attempted radical-initiated homopolymerizations (using AIBN or benzoyl peroxide) and anionic homopolymerizations (using BuLi or $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$) of 3 were unsuccessful. Monomer 3 was recovered unchanged. The resistance to polymerization is presumably due to an inhibitory effect of the TTF moiety. Indeed, TTF is known to inhibit the polymerization of styrene under conditions where styrene underwent normal, rapid polymerization.¹⁹

Successful homopolymerization of 3 was effected in a sealed tube in vacuo upon heating at 120 °C for 48 h. A shiny, hard, black, brittle polymer formed in quantitative yield. Elemental analysis agreed with a polymer that had retained the integrity of the *p*-(2-tetrathiafulvalenyl)phenyl methacrylate unit ($\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_4$). The infrared spectrum of the polymer also confirmed the existence of the TTF unit by virtue of the presence of bands at 750, 770, and 800 cm^{-1} . The $\nu_{\text{C}=\text{C}}$ band, found at 1636 cm^{-1} in the monomer, disappeared, indicating that polymerization occurred. The observed thermal polymerization of 3, when this monomer would not polymerize with radical or anionic initiation, suggests that initiator species may react with the TTF nucleus. It is known that strong bases can abstract a proton from TTF.^{12b} Thus, this would prevent anionic initiation. It is possible that radicals formed during AIBN decomposition may either abstract a hydrogen atom from TTF or add to a TTF double bond, thereby preventing normal initiation. However, no direct evidence exists yet to bear out these ideas.

The polymer appeared to be virtually insoluble in water, alcohols, halogenated hydrocarbons, halobenzenes, toluene,

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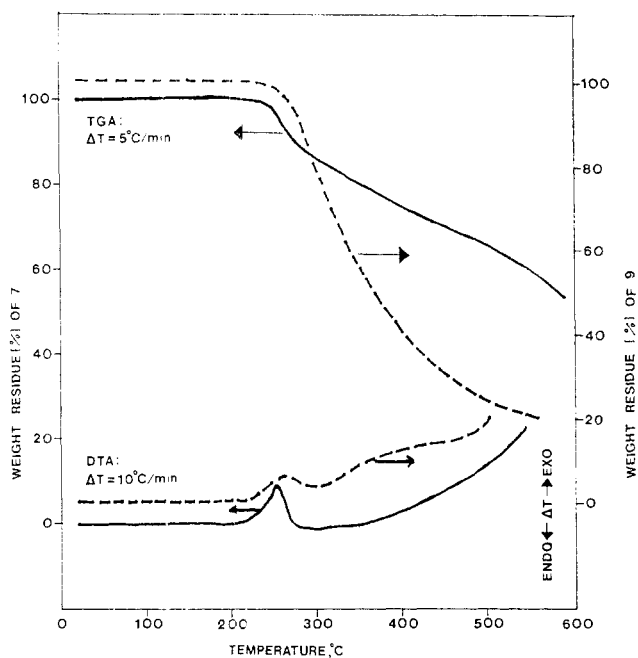
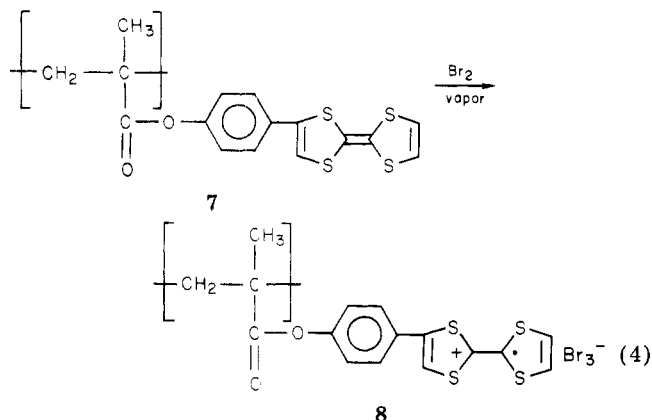


Figure 1. DTA and TGA curves of poly[*p*-(2-tetrathiafulvalenyl)phenyl methacrylate] (7) and its methyl methacrylate copolymer (9).

acetone, THF, and other common solvents. The only solvents able to dissolve the polymer were strong acids. The inherent viscosity in H₂SO₄ was 0.09, measured at a concentration of 0.5 g/dL at 30 °C. A gel-permeation chromatographic molecular weight determination was not obtained due to this solubility limitation.

The thermal stability of polymer 7 was studied by thermogravimetric analysis (TGA) under nitrogen and by differential thermal analysis (DTA) in air. The heating rates employed were 5 °C min⁻¹ for TGA and 10 °C min⁻¹ for DTA. Thermograms for the polymer are shown in Figure 1. The DTA curve exhibits a strong exotherm at 255 °C in air which correlated well with the initial weight loss observed by TGA about this temperature. The decomposition temperature for 10% weight loss was 270 °C in nitrogen.

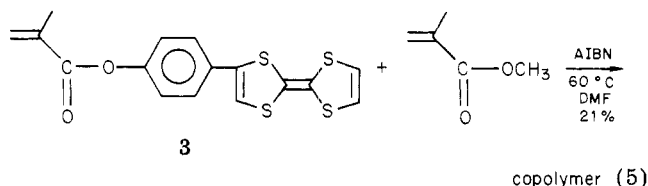
The homopolymer was converted to its bromine complex by exposure to bromine vapor in a nitrogen atmosphere at room temperature (eq 4). The complex analyzed for



[C₁₆H₁₂O₂S₄Br_{0.43}]_n. The infrared spectrum of the starting polymer was similar to that of its bromine complex which suggested that a TTF⁺Br₃⁻ complex (i.e., 8) had formed. By increasing the exposure time to bromine or by grinding the polymer to a finer powder, one can continuously increase the percentage of the TTF units oxidized in 8. The reaction of bromine vapor with tetrathiafulvalene com-

pounds is known to give TTF⁺Br₃⁻ salts on the basis of the studies of Welcome,¹³ Wudl,¹⁹ and Pittman.^{16,17} A combination of analyses, spectral studies (including ESR), and work with the model parent compound (TTF) confirmed this point.^{13,16,17,19}

Since the homopolymer was insoluble, a copolymerization of 3 with methyl methacrylate (MMA) was carried out. Radical initiation of a 14.1/1 MMA/3 solution, using AIBN at 60 °C in DMF, gave a soluble copolymer in 21% yield (eq 5).

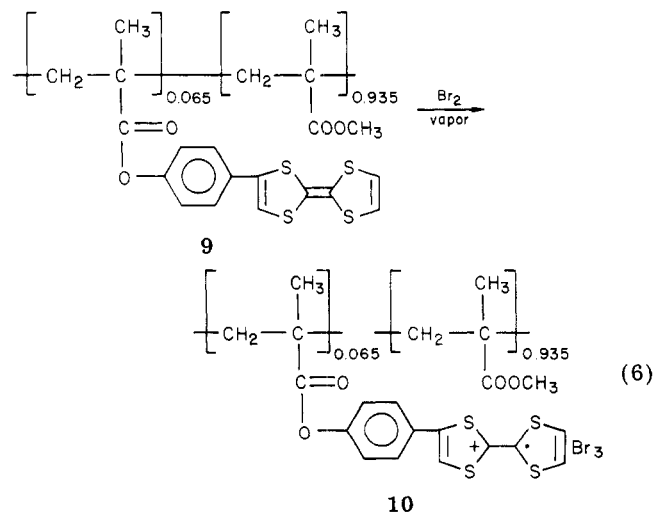


Sulfur analysis corresponded to a copolymer containing 6.5% of monomer 3 and 93.5% of MMA. The infrared spectrum of the copolymer indicated the existence of the TTF unit by the absorption bands at 745, 770, and 790 cm⁻¹. Strong aliphatic absorption bands at 2950 and 2990 cm⁻¹ were observed, confirming that copolymerization had indeed occurred. These were much weaker in the homopolymer.

The copolymer was soluble in halogenated hydrocarbons, halobenzenes, toluene, acetone, and THF and was insoluble in water, methanol, ether, and hexane. The inherent viscosity of the copolymer in acetone was 0.10, measured at a concentration of 0.5 g/dL at 30 °C. Gel-permeation chromatography experiments showed that the molecular weight (*M_n*) of the copolymer was about 10000 (compared to polystyrene standard samples).

Thermal behavior of the copolymer was evaluated by means of TGA at 5 °C min⁻¹ under nitrogen and DTA at 10 °C min⁻¹ in a pinhole sealed cell system. Thermograms for the copolymer are shown in Figure 1. The decomposition temperature for 10% weight loss was about 285 °C in nitrogen.

The bromine complex was also made which corresponded to [(C₁₆H₁₂O₂S₄)_{0.065}(C₅H₈O₂)_{0.935}Br_{0.21}]_n according to bromine analysis. The similarity in infrared spectra between the starting copolymer and its bromine complex suggests that a TTF⁺Br₃⁻ complex (e.g., 10) has formed.



A study of the ability of this TTF-containing copolymer to form salts or charge-transfer complexes with TCNQ and DDQ was made. Hot acetone solutions of TCNQ or DDQ were added to a hot acetone solution of the copolymer. A dark gray color was obtained by mixing a DDQ solution

with the copolymer solution, but no color change occurred when TCNQ was used. The mixtures were cooled, acetone was removed, and the residue was washed with methanol and dried. The pure, yellow copolymer was recovered from the TCNQ solution. However, a gray solid was obtained from the DDQ mixture. Elemental analysis found the polymer was a complex with 2:1 ratio of TTF:DDQ.

The UV-visible spectra of the copolymer **9** were obtained in Me_2SO , as were the spectra of TCNQ and DDQ. Me_2SO solutions of the copolymer were then mixed with TCNQ or DDQ. The copolymer exhibited a strong absorption at 430 nm in Me_2SO , while TCNQ in Me_2SO absorbed strongly at 435 nm and DDQ had a strong band at 410 nm. Mixing a Me_2SO solution of the copolymer with a solution of TCNQ gave spectra consistent with those obtained by simply adding their individual spectra. No evidence of charge-transfer complexation was obtained. In the case of DDQ, however, a low energy band was observed at 450 nm by mixing its Me_2SO solution with solution of the copolymer. This suggests that CT complexation or ionization indeed occurred.

Experimental Section

Melting points were uncorrected. Infrared spectra were obtained as potassium bromide disks with a Beckman IR-33. Nuclear magnetic resonance spectra were obtained by using a Perkin-Elmer Hitachi Model R-20B spectrometer. 4-(*p*-Acetoxyphenyl)-1,3-dithiolium perchlorate²⁰ and 1,3-dithiolium perchlorate²¹ were prepared according to the previous reports.

(*p*-Acetoxyphenyl)tetrathiafulvalene (5). A solution containing 4-(*p*-acetoxyphenyl)-1,3-dithiolium perchlorate (1.66 g, 4.84 mmol) and 1,3-dithiolium perchlorate (0.98 g, 4.84 mmol) in 40 mL of CH_3CN was cooled to 0 °C and treated with excess triethylamine (3 mL). After the mixture was stirred for 1 h, water was added to precipitate the products. A brown solid formed. It was collected, washed with water, and dried. The solid (1.32 g) was stirred in 200 mL of cold CH_3CN for 4 h and then filtered. The insoluble orange solid was 2,6(7)-bis(*p*-acetoxyphenyl)-tetrathiafulvalene²⁰ (0.53 g, 70% yield, based on the theoretical 33% yield of each product). The filtrate was evaporated to dryness, and the residue was dissolved in hot CH_3CN (10 mL), filtered, and allowed to cool. The crude product was then collected by filtration (0.44 g, 80%) and purified by recrystallization from CH_3CN to give the brownish orange, pure material which melted at 125–127 °C: IR (KBr) 3060, 1740, 1600, 1500, 1363, 1200, 1160, 1010, 905, 837, 795, 775, 756 cm^{-1} ; NMR (CDCl_3) δ 7.35 (m, 4 H), 6.54 (s, 1 H), 6.42 (s, 2 H), 2.37 (s, 3 H). Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}_4$: C, 49.70; H, 2.96. Found: C, 49.66; H, 3.00.

(*p*-Hydroxyphenyl)tetrathiafulvalene (6). To a suspension of 0.34 g (1.0 mmol) of **5** in 20 mL of methanol was added 2 mL of hydrazine hydrate. The reaction mixture was stirred at room temperature while the solution became homogeneous. After 4 h, water was added to precipitate the product which was collected by filtration and dried (0.28 g, 96%). Recrystallization from ethanol/ H_2O gave pure, yellow, crystalline material which melted at 122–124 °C: IR (KBr) 3300, 1600, 1500, 1450, 1250, 1170, 825, 794, 775, 755 cm^{-1} ; NMR ($\text{Me}_2\text{SO}-d_6$) δ 7.13 (m, 4 H), 6.97 (s, 1 H), 6.79 (s, 2 H), 3.65 (s, 1 H). Anal. Calcd for $\text{C}_{12}\text{H}_8\text{OS}_4$: C, 48.63; H, 2.70. Found: C, 48.58; H, 2.88.

***p*-(2-Tetrathiafulvalenyl)phenyl Methacrylate (3).** To a solution of 1.4 g (4.73 mmol) of **6** and 1.4 mL (10.0 mmol) of triethylamine in 20 mL of HMPA was added 0.48 mL (4.90 mmol) of methacryloyl chloride dropwise with stirring at 0 °C. The reaction was warmed to 25 °C and stirring continued for 20 h. The reaction mixture was then poured into water (250 mL) and extracted with ether. The combined ether layers (300 mL) were washed three times with 300-mL portions of saturated aqueous NaHCO_3 , and twice with 300-mL portions of distilled water. After the combined ether layers were dried (MgSO_4) and filtered and the ether was evaporated, the crude methacrylate was isolated (1.2 g, 70%). It was purified by recrystallization from methanol to give a yellow solid: mp 85–86 °C; IR (KBr) 3060, 1730, 1636, 1608, 1500, 1320, 1220, 1170, 1130, 800, 780, 760 cm^{-1} ; NMR

($\text{Me}_2\text{SO}-d_6$) δ 7.34 (m, 4 H), 7.16 (s, 1 H), 6.70 (s, 2 H), 6.04 (d, 2 H), 2.0 (s, 3 H). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_4$: C, 52.75; H, 3.30; S, 35.16. Found: C, 52.61; H, 3.34; S, 34.98.

Polymerization of *p*-[2-Tetrathiafulvalenyl]phenyl Methacrylate. A Pyrex ampule containing 100 mg of *p*-(2-tetrathiafulvalenyl)phenyl methacrylate was sealed in vacuo and heated at 120 °C for 48 h. The ampule was cooled to room temperature and then opened. The black, brittle solid was removed by scraping it out with a stainless steel spatula. The infrared spectrum (KBr) was as follows: 1730, 1600, 1500, 1366, 1270, 1200, 1163, 1117, 800, 770, 750 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_4$: C, 52.75; H, 3.30; S, 35.16. Found: C, 52.70; H, 3.36; S, 35.06.

The polymer was insoluble in halogenated aliphatics, halobenzenes, THF, and other common organic solvents. The inherent viscosity in H_2SO_4 was 0.09 measured at a concentration of 0.5 g/dL at 30 °C.

Radical polymerization of *p*-(2-tetrathiafulvalenyl)phenyl methacrylate was attempted with AIBN or benzoyl peroxide as the initiator in dried and degassed cyclohexanone or THF. The reaction mixture was sealed in vacuo and heated at 65 °C for 48 h. No polymer was formed, and starting material was recovered unchanged.

Anionic polymerization with butyllithium or benzylmagnesium bromide as the initiator in dried and degassed THF was also attempted. Again, no polymer was formed.

Copolymerization of *p*-(2-Tetrathiafulvalenyl)phenyl Methacrylate and Methyl Methacrylate. In an ampule, a solution of *p*-(2-tetrathiafulvalenyl)phenyl methacrylate (0.31 g, 0.85 mmol), methyl methacrylate (1.2 g, 12 mmol), and AIBN (4.3 mg, 0.026 mmol) in 4 mL of dimethylformamide was flushed with nitrogen and then degassed thoroughly. The ampule was sealed in vacuo and heated at 65 °C for 72 h. After this period, the ampule was heated an additional 24 h at 100 °C. After cooling, the ampule was broken open. The reaction mixture was poured slowly into 100 mL of methanol to precipitate the product which was filtered, washed thoroughly with methanol, and dried in vacuo: yield 0.31 g (21%); IR (KBr) 2990, 2950, 1730, 1470, 1450, 1430, 1265, 1240, 1190, 1145, 980, 835, 790, 770, 745 cm^{-1} . Elemental analysis gave C 58.16, H 6.70, S 7.12 which corresponds to $[(\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_4)_{0.065}(\text{C}_5\text{H}_8\text{O}_2)_{0.935}]_n$ on the basis of the sulfur analysis where theory requires C, 58.53; H, 7.09.

Synthesis of Bromine Complex. Small samples of polymer **7** and **9** were subjected to bromine vapor (in a closed beaker under a nitrogen atmosphere) for 5 min. The polymers became dark during the treatment. Analysis of the bromine complex of polymer **7** gave C 49.34, H 3.51, Br 8.80 which corresponds to $[(\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_4\text{Br}_{0.46})_n]$ most closely on the basis of the carbon analysis where theory requires C 49.34, H 3.09, Br 7.48. Analysis of the bromine complex of copolymer **9** gave C, 51.58; H, 6.10; S, 6.23; Br 13.83; this corresponds to $[(\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_4)_{0.065}(\text{C}_5\text{H}_8\text{O}_2)_{0.935}\text{Br}_{2.21}]_n$ on the basis of the sulfur analysis, where theory requires C, 51.21; H, 6.20; S, 6.23; Br, 12.51. When the sample of polymer **7** was ground to a very fine powder and subjected to excess bromine vapor, the ratio of $\text{Br}_3^-/\text{TTF}^+$ units increased to 1:1.

Charge-Transfer Complex of Copolymer **9 with TCNQ and DDQ.** To a hot solution of copolymer **9** (23.4 mg, 0.2 mmol) in 10 mL of acetone was added a hot solution of TCNQ (40.8 mg, 0.2 mmol) or DDQ (45.4 mg, 0.2 mmol) in 10 mL of acetone. The mixtures were slowly cooled to room temperature, the acetone was removed, and the residue was washed with methanol and dried. Copolymer **9** was recovered from the TCNQ mixture. A gray solid was obtained from the DDQ mixture. Analysis of the gray material gave C, 57.41; H, 6.78; S, 6.77; N, 0.62; this corresponds to a complex with a 2:1 ratio of TTF in **9** to DDQ where theory requires C, 57.58; H, 6.67; S, 6.68; N, 0.73.

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Registry No. **3**, 71195-37-4; **5**, 71195-38-5; **6**, 71195-39-6; **7**, 71195-53-4; **9**, 71195-54-5; 4-(*p*-acetoxyphenyl)-1,3-dithiolium perchlorate, 71195-41-0; 1,3-dithiolium perchlorate, 3706-77-2; 2,6(7)-bis(*p*-acetoxyphenyl)tetrathiafulvalene, 59269-75-9; methacryloyl chloride, 920-46-7.