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Syntheses of Poly(urethanes) and Poly(sulfonates) Containing Tetrathiafulvalene Nuclei in the Backbone

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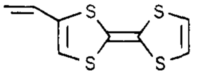
ABSTRACT: Two types of polymers, poly(urethanes) and poly(sulfonates), incorporating the tetrathiafulvalene (TTF) moiety within the polymer backbone were prepared by polycondensation of 2,6(7)-bis(*p*-hydroxyphenyl)tetrathiafulvalene with diisocyanates and disulfonyl chlorides using solution techniques. The effects of various solvents, bases, and reaction temperature were studied in the poly(sulfonate) syntheses, but the molecular weights were rather low in all cases. Poly(urethanes), however, were obtained with moderate molecular weights by a high-temperature polycondensation method. Both classes of polymers were soluble in CF_3COOH, soluble in dipolar aprotic solvents (i.e., DMF, Me_2SO, HMPA) on heating, slightly soluble in THF and acetone, and largely insoluble in acetonitrile, benzene, hexane, and other common solvents. TGA and DTA studies indicated the polymers were stable to about 260 °C. Exotherms at 260–280 °C (DTA in air) correlated with the sharp initial 10% weight losses observed by TGA (under nitrogen). These observations resulted from decomposition of TTF groups and of urethane groups in the poly(urethanes). Attempts to prepare tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyanoquinone (DDQ) complexes were unsuccessful. Bromine salts were prepared.

Interest in donor molecules, such as tetrathiafulvalenes (TTF)[1-3] or tetraselenafulvalenes (TSeF),[4,5] that form electrically conducting, metallic-like, organic, charge-transfer salts[6] has expanded recently with attempts to incorporate such donor molecules into polymeric frameworks. The first polymers containing TTF moieties were prepared via a polycoupling process by Okawara et al.[7] Three reports of condensation polymers containing TTF exist. Poly(urethanes),[8] poly(amides),[9] and poly(esters)[10] were synthesized and all failed to form charge-transfer (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 on exposure to UV, azo initiators, or addition of TCNQ.[11] (*p*-Vinylphenyl)tetrathiafulvalene (2) resisted anionic and radical initiation but thermally polymerized in bulk.[12] Its polymer was insoluble and did not give TCNQ complexes, although bromine complexes were reported.[12] Finally, methacrylate (3) was prepared and polymerized.[13]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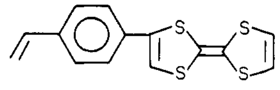
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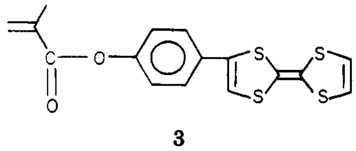
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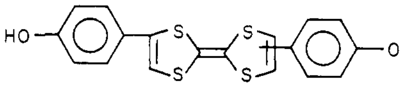
We now report the polycondensation of 2,6(7)-bis(*p*-hydroxyphenyl)tetrathiafulvalene (4)[14] with diisocyanates and disulfonyl chlorides.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Experimental Section

Materials. Solvents and Nitrogen Bases. Ethyl acetate, chlorobenzene, and 4-methyl-2-pentanone were purified by distillation from calcium hydride. Methylene chloride and 1,2-dichloroethane were purified by washing them sequentially with dilute aqueous acid, water, dilute aqueous base, and water followed by drying (anhydrous Na_2SO_4) and distillation from calcium hydride. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (Me_2SO), *N*-methyl-2-pyrrolidinone (NMP), and hexamethylphosphortriamide (HMPA) were distilled under vacuum from phosphorus pentaoxide. Tetramethylene sulfone (TMS) was purified by warming over potassium permanganate, filtering, and distilling from phosphorus pentaoxide under vacuum. Chloroform was purified by aqueous washing, drying (anhydrous Na_2SO_4), and distilling from calcium hydride. Toluene and *p*-xylene were distilled from calcium hydride under nitrogen. Nitrobenzene was purified by aqueous washing, drying (anhydrous $CaCl_2$), and distilling from

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Table I
Solution Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with Methylenebis(*p*-phenyl isocyanate)[a]

solvent	temp, °C	polymer yield, %	polymer η_{inh}[b]
p-xylene	138	96	0.34
4-methyl-2-pentanone/Me_2SO[c]	115	96	0.18
ethyl acetate	77	85	0.19
TMS[c]	150	92	0.18
DMF[c]	150	95	0.19
Me_2SO[c]	150	95	0.12
HMPA[c]	150	95	0.13

[a] All polycondensations were carried out using 1 mmol of each monomer in 2 mL of solvent for 2 h by Method A. [b] Measured at a concentration of 0.5 g/dL in CF_3COOH at 30 °C. [c] Me_2SO = dimethyl sulfoxide, TMS = tetramethylene sulfone, DMF = *N,N*-dimethylformamide, HMPA = hexamethylphosphortriamide.

Table II
Solution Polycondensation of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with Hexamethylene Diisocyanate[a]

solvent	temp, °C	polymer yield, %	polymer η_{inh}
p-xylene	138	97	0.34
4-methyl-2-pentanone/Me_2SO	115	92	0.15
chlorobenzene	132	90	0.18
1,2-dichloroethane	84	90	0.14
toluene	111	90	0.20
4-methyl-2-pentanone	115	96	0.27
DMAc[b]	150	96	0.18
NMP[b]	150	90	0.17
nitrobenzene	150	96	0.24

[a] All polycondensations were carried out using 1 mmol of each monomer in 2 mL of solvent for 2 h according to Method B. [b] DMAc = *N,N*-dimethylacetamide, NMP = *N*-methyl-2-pyrrolidinone.

Table III
Solution Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with *m*-Benzenebis(sulfonyl chloride) and 4,4′-Oxybis(phenylsulfonyl chloride)[a]

polymer	solvent	temp, °C	polymer yield, %	polymer η_{inh}
7	chloroform	20–25	91	0.08
7	methylene chloride	41	91	0.06
7	chloroform	61	90	0.06
7	toluene	111	91	0.06
7	*p*-xylene	138	92	0.13
8	chloroform	20–25	90	0.06
8	*p*-xylene	138	90	0.08

[a] All polycondensations were carried out using 1 mmol of each monomer and 2 mmol of triethylamine in 2 mL of solvent for 2 h.

phosphorus pentaoxide. 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. Methylenebis(*p*-phenyl isocyanate) (Eastman Kodak) and hexamethylene diisocyanate (Aldrich Chem. Co.) were purified by vacuum distillation. *m*-Benzenebis(sulfonyl chloride) (Eastman Kodak) was purified by dissolving it in benzene and crystallizing it from hexane, mp 61–62 °C (lit. mp 62–62.5 °C[15]). 4,4′-Oxybis(phenylsulfonyl chloride) was purified by recrystallization from hexane, mp 128–129 °C (lit. mp 128–129 °C[16]). Diol 4 was recrystallized from nitrogenated preboiled methanol[10] to give golden crystals, mp 207–208 °C (lit. 207–208 °C[10]).

Polymerization. 1. Poly(urethanes). Two methods were employed as given below.

Method A. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3884 g, 1 mmol) and *p*-xylene (2 mL) were placed in a dried, 50-mL flask equipped with a magnetic stirrer and condenser. Methylenebis(*p*-phenyl isocyanate) (0.2503 g, 1 mmol) was added, all at once, to the boiling diol suspension with vigorous stirring. The reaction mixture was stirred at reflux for 2 h. The polymer was isolated by precipitation from hexane, filtration, and drying in vacuo (80 °C (0.2 torr)) for 48 h. The resulting orange solid (0.61 g, 96% yield) had η_{inh} = 0.34 in CF_3COOH measured at a concentration of 0.5 g/dL at 30 °C.

Method B. A dried, 50-mL, three-necked flask, equipped with a stirrer, nitrogen inlet, and reflux condenser fitted with calcium chloride drying tube, was flushed out with nitrogen. Then 2,6(7)-bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3884 g, 1 mmol) and *p*-xylene (1 mL) were added. The nitrogen inlet was replaced by a dropping funnel, and the solution was heated to reflux. Then hexamethylene diisocyanate (0.1682 g, 1 mmol) in 1 mL of *p*-xylene was added dropwise to the boiling diol solution followed by stirring at reflux for 2 h. The polymer was precipitated into hexane and collected by suction filtration. After 48 h of drying at 80 °C (0.2 torr), 0.54 g (97%) of yellow polymer was obtained. Its inherent viscosity in CF_3COOH was 0.34 measured at a concentration of 0.5 g/dL at 30 °C.

2. Poly(sulfonates). Typical example procedures are given below.

Low-Temperature Solution Polymerization. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3884 g, 1 mmol) was placed in a dried flask (50 mL) equipped with a magnetic stirring bar. Chloroform (2 mL) and pyridine (0.1584 g, 2 mmol) were added with stirring. *m*-Benzenebis(sulfonyl chloride) (0.2751 g, 1 mmol) was then added all at once to the stirred diol suspension followed by stirring at 20–25 °C for 2 h. Then hexane (100 mL) was added. The resulting polymer was filtered, washed thoroughly with water, and dried over phosphorus pentaoxide at 80 °C (0.2 torr) for 48 h. A brown solid was obtained (0.56 g, 95% yield) with an inherent viscosity in CF_3COOH of 0.12 measured at 0.5 g/dL at 30 °C.

High-Temperature Solution Polymerization. 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (0.3884 g, 1 mmol) was placed in a dried flask (50 mL) equipped with a magnetic stirrer and reflux condenser. *p*-Xylene (2 mL) and triethylamine (0.2024 g, 2 mmol) were added, and the flask was heated to reflux under nitrogen. *m*-Benzenebis(sulfonyl chloride) (0.2751 g, 1 mmol) was added, all at once, to the refluxing diol suspension with stirring. After an additional 2 h at reflux, the polymer was obtained by precipitation from hexane, filtration, water washing, and drying in vacuo (80 °C (0.2 torr)) over phosphorus pentaoxide for 48 h. The resulting brown solid (0.56 g, 95%) had η_{inh} = 0.13 in CF_3COOH.

Synthesis of Bromine Complexes. Small samples of poly(urethane), 5 (entree 1, Table I) and 6 (entree 1, Table II), and poly(sulfonate), 7 (entree 1, Table III) and 8 (entree 6, Table III), were subjected to excess bromine vapor (in a closed beaker under the nitrogen atmosphere) for 10 min. The polymers turned black and appeared to soften, somewhat, during the treatment. Analysis of the bromine complex of poly(urethane) 5 gave C, 42.81; H, 2.72; N, 2.63; Br, 27.12, which corresponds to $[C_{33}H_{22}O_4S_4N_2Br_{3.59}]_n$ most closely, based on the carbon analysis where theory required C, 42.81; H, 2.40; N, 3.03; Br, 31.01. Analysis of the bromine complex of poly(urethane) 6 gave C, 39.20; H, 3.47; N, 3.73; Br, 26.67, corresponding to $[C_{26}H_{24}O_4S_4N_2Br_{3.00}]_n$ based on the carbon analysis where theory requires C, 39.20; H, 3.05; N, 3.51; Br, 30.13. Analysis of the bromine complex of poly(sulfonate) 7 gave C, 33.80; H, 2.10; Br, 26.98. This corresponds to $[C_{24}H_{14}O_6S_6Br_{3.28}]_n$ based on the carbon analysis where theory requires C, 33.80; H, 1.66; Br, 30.72. Analysis of the bromine complex of poly(sulfonate) 8 gave C, 38.16; H, 2.50; Br, 23.75, which corresponds to $[C_{30}H_{18}O_7S_6Br_{3.27}]_n$ based on the carbon analysis where theory requires C, 38.16; H, 1.92; Br, 27.69. Based on Br analysis, the amount of Br per repeating unit is lower in each case.

Table IV
Effect of the pK_a of Added Base on Polymer Molecular Weight in Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with *m*-Benzenebis(sulfonyl chloride) at Room Temperature[a]

base	pK_a	polymer yield, %	polymer η_{inh}
triethylamine	10.75	91	0.08
N-ethylmorpholine	7.67	92	0.07
2,6-lutidine	6.60	92	0.08
2-picoline	5.94	92	0.11
pyridine	5.22	95	0.12
isoquinoline	4.81	92	0.10

[a] All polycondensations were conducted by using 1 mmol of each monomer and 2 mmol of base in 2 mL of chloroform at 20-25 °C for 2 h.

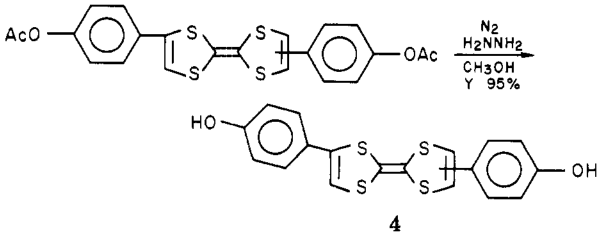
Table V
Effect of the pK_a of Added Base on Polymer Molecular Weight in Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with *m*-Benzenebis(sulfonyl chloride) at Higher Temperature[a]

base	pK_a	polymer yield, %	polymer η_{inh}
triethylamine	10.75	92	0.13
N-ethylmorpholine	7.67	95	0.17
2,6-lutidine	6.60	92	0.13
2-picoline	5.94	92	0.12
pyridine	5.22	90	0.05
isoquinoline	4.81	95	0.16

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

Results and Discussion

Preparation of Poly(urethanes). 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)[14] and recrystallization from methanol should be carried out under nitrogen and in nitrogenated solvents. After **4** was recrystallized from methanol, high-temperature solution polycondensations were carried out with either methylenebis(*p*-phenyl isocyanate) or hexamethylene diisocyanate as shown in eq 2.



(1)

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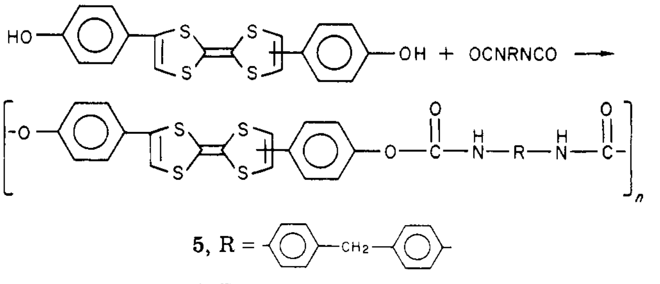


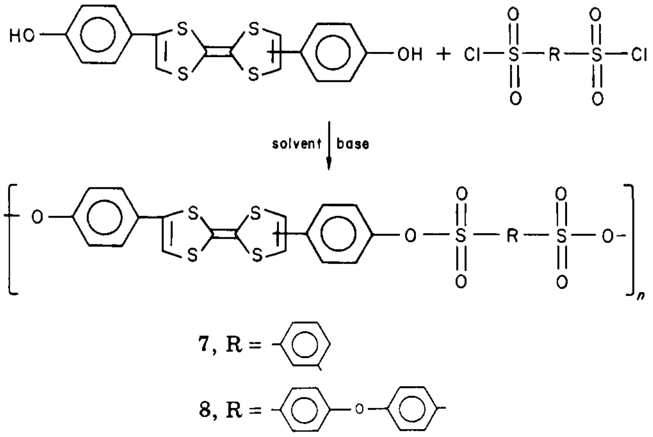
(2)

Two general methods were employed. Method A involved the addition of a molar equivalent of diisocyanate, all at once, to a stirred refluxing suspension of diol **4** in solvent. The polymerization solution was stirred at reflux for 2 h before the polymer was collected. Method B involved the slow, dropwise addition of diisocyanate solution to a refluxing suspension of diol **4** with vigorous stirring, followed by heating at reflux for 2 h. The polymer was then isolated. Method A was used when methylenebis(*p*-phenyl isocyanate) was employed. Representative high-temperature solution polycondensations and polymer viscosities are given in Table I for **5** and Table II for **6**.

The poly(urethanes) were isolated in good yields, but only moderate molecular weights were achieved. *p*-Xylene was found to be the best solvent for preparation of both polymers **5** and **6**. Dipolar aprotic solvents (e.g., Me_2SO, HMPA) gave relatively low molecular weight polymers.

The incremental addition method was used to see if the molecular weights could be increased. Thus, individual polycondensations were carried out with methylenebis(*p*-phenyl isocyanate):**4** ratios of 98/100, 99/100, 1/1, 101/100, 102/100 in *p*-xylene according to method A. The resulting polymers exhibited inherent viscosities of 0.13, 0.20, 0.34, 0.24, and 0.17, respectively. This demonstrates that the molecular weights were inherently rather low for reasons other than poorly matched M_1/M_2 ratios.

Preparation of Poly(sulfonates). A series of solution polycondensations was carried out, at various conditions, between diol **4** and *m*-benzenebis(sulfonyl chloride) as shown in eq 3. Two polymerization procedures were used.



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Room-temperature solution polymerization involved the addition of disulfonyl chloride to a stirred suspension of diol and base in chloroform. Two moles of base were used per mole of diol **4**. The reaction was stirred for 2 h at 20–25 °C before the polymer was isolated. Higher temperature solution polymerizations involved the addition of disulfonyl chloride to the refluxing diol suspension with vigorous stirring in a variety of solvents. The polymerization mixture was then stirred at reflux for 2 h. The polymer was then collected. Representative polycondensations and polymer viscosities are shown in Table III where triethylamine was the base employed.

The molecular weights were low using either of the two methods, although the polymer yields were high. Attempts to obtain higher molecular weights focused on varying the pK_a of the base. Previous studies have shown that the molecular weights obtained in poly(sulfonate)[17] and poly(sulfonamide)[18] syntheses can be quite sensitive to the pK_a of the base employed. Thus, a series of different bases were used in both high- and low-temperature systems, and the results are summarized in Tables IV and V. Unfortunately, there was no correlation between base strength and the resulting polymers' viscosities despite a variation of base strength over a range of six powers of ten.

Table VI
Solution Polycondensations of 2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene with *m*-Benzenebis(sulfonyl chloride) in Dipolar Aprotic Solvents[a]

	polymer	
solvent[b]	yield, %	η_{inh}
DMF	85	0.12
DMAc	82	0.10
Me_2SO	70	0.07
HMPA	70	0.08
NMP	80	0.09
TMS	84	0.10

[a] All polycondensations were carried out using 1 mmol of each monomer and 2 mmol of triethylamine in 2 mL of solvent at 150 °C for 2 h. [b] DMF = *N,N*-dimethyl formamide, DMAc = *N,N*-dimethylacetamide, Me_2SO = dimethyl sulfoxide, HMPA = hexamethylphosphortriamide, NMP = *N*-methyl-2-pyrrolidinone, TMS = tetramethylene sulfone.

Although the polycondensation proceeds readily at room temperature in solvents such as chloroform, toluene, and *p*-xylene, only low molecular weight poly(sulfonates) were obtained. The use of dipolar aprotic solvents was considered. Thus, reactions of the disulfonyl chlorides with diol 4 in dipolar aprotic solvents, in the presence of triethylamine at 150 °C, were tried. These results are summarized in Table VI. No increase in molecular weight was found in these polycondensations.

The incremental addition method[19] was also tried to see if the molecular weights could be increased. Individual polycondensations were performed with *m*-benzenebis(sulfonyl chloride):4 ratios of 98/100, 99/100, 1/1, 101/100, and 102/100, using the high-temperature solution method in *p*-xylene. The inherent viscosities of the resulting polymers were found to be 0.06, 0.13, 0.13, 0.11, and 0.08, respectively. This demonstrated that the low molecular weights observed in Tables III–VI were not due to poorly matched monomer ratios.

Characterization. The elemental analysis of both poly(urethanes) 5 and 6 and poly(sulfonates) 7 and 8 were in excellent agreement with their calculated values. Anal. Calcd, for example, for poly(urethane) 5 (entry 1, Table I): C, 62.05; H, 3.48; S, 20.08; N, 4.39. Found: C, 61.86; H, 3.54; S, 19.95; N, 4.43. Calcd for poly(urethane) 6 (entry 1, Table II): C, 56.10; H, 4.36; S, 23.04; N, 5.03. Found: C, 55.85; H, 4.43; S, 22.94; N, 5.11. Calcd for poly(sulfonate) 7 (entree 1, Table III): C, 48.79; H, 2.39. Found: C, 48.60; H, 2.60. Calcd for poly(sulfonate) 8 (entree 6, Table III): C, 52.76; H, 2.66. Found: C, 52.59; H, 3.04. The polymer's spectra were also in accord with the structure. Carbonyl stretching vibrations of poly(urethanes) 5 and 6 occurred at 1710 cm^{-1}, and each spectrum exhibited strong bands at 1490 and 1200 cm^{-1} attributed to N–H bending and C–O stretching, respectively. The IR spectra of poly(sulfonates) 7 and 8 exhibited strong absorptions at 1380–1360 and 1180–1150 cm^{-1} due to S=O stretching vibrations. Bands at 770 and 720 cm, characteristic of disubstituted TTF, were observed.

Both poly(urethanes) and poly(sulfonates) were completely soluble in CF_3COOH at room temperature and in DMF, Me_2SO, and HMPA on heating. They were only partially soluble in THF and acetone and insoluble in acetonitrile, diethyl ether, dioxane, hexane, chloroform, methylene chloride, 1,2-dichloroethane, benzene, and toluene. Gel permeation chromatographic molecular weight determinations were not obtained due to these solubility limitations.

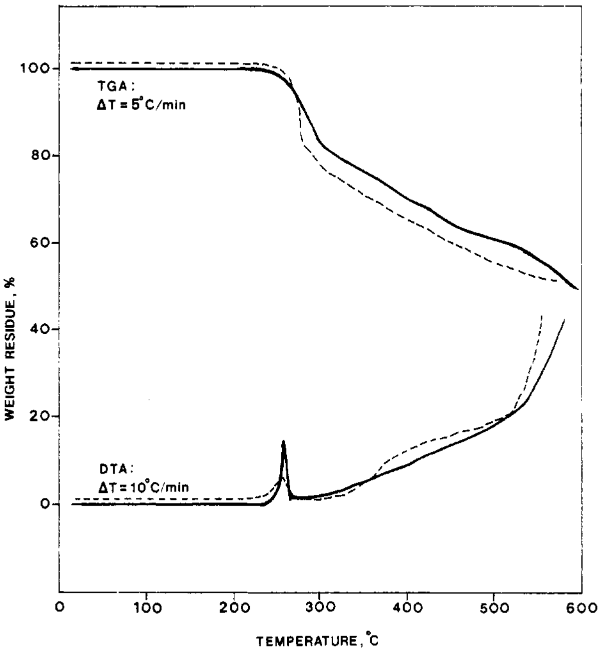


Figure 1. DTA and TGA curves of poly(urethane) 5 (—) and 6 (- - -).

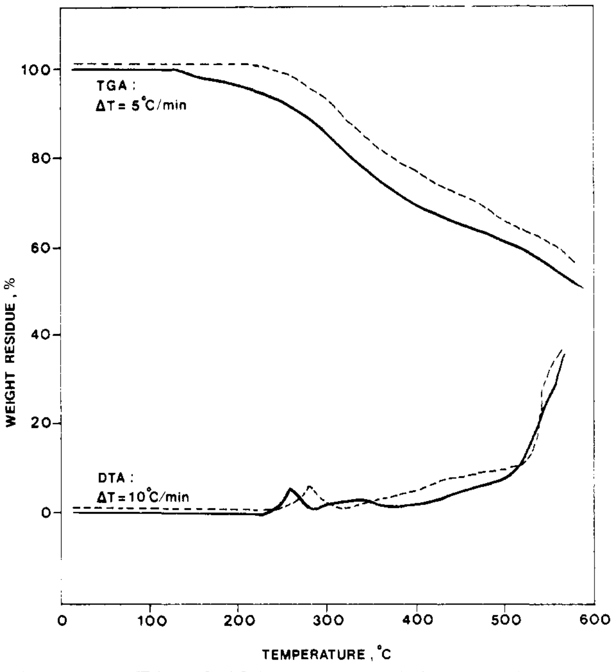
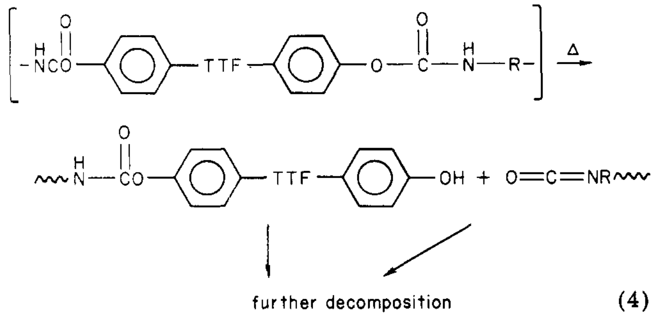


Figure 2. DTA and TGA curves of poly(sulfonate) 7 (—) and 8 (- - -).

The thermal stabilities of poly(urethanes) 5 and 6 and poly(sulfonates) 7 and 8 were 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 poly(urethanes) 5 and 6 are shown in Figure 1 while those of poly(sulfonates) 7 and 8 appear in Figure 2. The poly(urethanes) exhibit a sharp exotherm at ~260–270 °C (TGA). The poly(sulfonates) exhibit a similar behavior. These exotherms occur at about the same temperatures that initial weight losses are seen in the TGA studies. Thus, 10% weight losses were observed at ~285 and ~275 °C for poly(urethanes) 5 and 6, respectively, and 280 and 300 °C for poly(sulfonates) 7 and 8, respectively. The similarity of the results for the aryl and alkyl polymers (both urethanes and sulfonates) suggests that it is the TTF moieties which are decomposing. Furthermore, we previously demonstrated that TTF-containing poly(esters) decompose in the 270–290 °C temperature range,[10] and that TTF, itself, decomposes with gas evolution, in air or in nitrogen, at temperatures above 250 °C.[10]

To confirm this conclusion, the IR spectra of polymers **5**–**8** were studied after being heated to 280 °C for 15 min. Bands characteristic of the TTF unit, such as those at 770 and 720 cm^{-1}, were not present. For poly(sulfonates) **7** and **8** a gradual decrease in all the intense bands occurs at 300 °C. However, for the poly(urethanes) **5** and **6** all the polymers IR bands disappear rapidly when heated at 260 °C (within 4 min). Not only do TTF moieties decompose, but rapid depolymerization occurs here as phenol moieties split from the urethane linkages.



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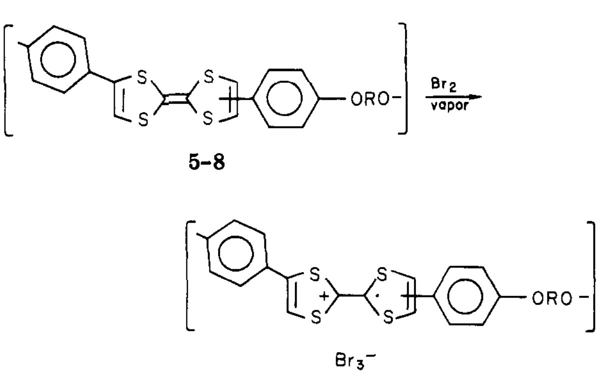
Attempts to Form TCNQ and DDQ Complexes. The method employed by Okawara[7] to prepare TCNQ complexes of insoluble TTF polymers was tried first. Both poly(urethanes) **5** and **6** were refluxed as suspensions in acetonitrile with equimolar amounts of either TCNQ or DDQ under nitrogen for 24 h. The product was washed thoroughly with acetonitrile. The IR spectrum of the resulting product was identical with that of **5** or **6** and showed no evidence of the presence of TCNQ or DDQ. Since poly(urethanes) **5** and **6** were both soluble in Me$_2$SO on heating, hot Me$_2$SO solutions of **5** or **6** were reacted with an equivalent amount of TCNQ (or DDQ). After refluxing for 30 min, the solutions were cooled. Me$_2$SO was removed in vacuo, and the residue was washed with methanol and dried. Only pure poly(urethane) was recovered.

The UV–vis spectra of poly(urethanes) **5** and **6** were obtained independently in Me$_2$SO, as were the spectra of TCNQ and DDQ. Then Me$_2$SO solutions of the poly(urethanes) were mixed with TCNQ or DDQ. No evidence of charge-transfer complexation was obtained. Both poly(urethanes) exhibited strong absorptions at 430–440 nm in Me$_2$SO, while TCNQ in Me$_2$SO absorbed strongly also at 430–440 nm and DDQ had a strong band at 410 nm in Me$_2$SO. Mixing Me$_2$SO solutions of the poly(urethanes) with solutions of either TCNQ or DDQ gave spectra consistent with simply adding their individual spectra. No low-energy charge-transfer bands were observed. Similar attempts were made with poly(sulfonates) **7** and **8**. Again, no evidence of charge-transfer complexation was observed.

Bromine Complexes. Poly(urethanes) **5** and **6** and poly(sulfonates) **7** and **8** were allowed to react with bromine vapor in a nitrogen atmosphere to generate bromine complexes. These reactions were identical with those reported by Wudl,[12] who reported the bromine complexes of poly(*p*-styryltetrathiafulvalene). The ratio of bromine atoms per TTF unit in the polymer complex was 3.59 for **5**, 3.00 for **6**, 3.28 for **7**, and 3.27 for **8**. The infrared spectra of the starting polymers **5**–**8** were similar throughout to those of their bromine complexes which suggests that TTF$^+$–Br$_3^-$ complexes (such as **9**) have formed. If bromine had added across the double bonds in TTF groups, the TTF double bond absorption at 1600 and other bands in the 860–600-cm^{-1} region would have been diminished.



5–8

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(5)

To further confirm the structure, ESR spectra were obtained on the bromine complexes of polymers **5** and **7**. They exhibited *g* values of 2.0076 and 2.0079 G, respectively. This is in excellent agreement with results reported in the thesis of Welcome[7] for TTF$^+$–Br$_3^-$ complexes. Conductivity studies will be reported elsewhere.

It is interesting that bis(*p*-acetoxyphenyl)tetrathiafulvalene gave a 1:1 salt when reacted with DDQ in acetonitrile,[14] while the poly(urethanes) and poly(sulfonates), reported here, did not react with DDQ in dimethyl sulfoxide. The change in solvent could be the cause, but the polymers were not soluble in acetonitrile to test that point. Reaction of the bis(acetate) with TCNQ, in either acetonitrile or dimethyl sulfoxide, gave no salt or charge-complex formation. The UV spectra of such solutions gave no evidence of charge-transfer absorptions. The inability in dimethyl sulfoxide of the polymers' TTF units to be oxidized by DDQ may relate to very small changes in the local environment. Perhaps a very small equilibrium exists to the salt, but precipitation never occurs and, hence, salt formation is not "locked in". Perhaps important crystalline energy factors are involved which permit the bis(acetate) to readily be isolated as a DDQ salt, but which are not favorable in the polymer. The explanation is elusive but in character with the history of this area of chemistry.

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Poly(α-methylene-γ-butyrolactone) Synthesis, Configurational Structure, and Properties

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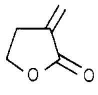
ABSTRACT: α-Methylene-γ-butyrolactone (α-MBL, I) has been shown to be a reactive vinyl monomer capable of both free-radical and anionic polymerization. High-resolution ^{13}C NMR was found to be of particular value in determining the configurational microstructure of the polymers using the quaternary carbon as the stereochemical probe. Poly(α-MBL) from free-radical initiation was found to be atactic with slight preponderance of syndiotactic placements ($P_m \simeq 0.37$) with very little dependence of the tacticity on the temperature of the polymerization. Anionic polymerization with PhMgBr in toluene and 9-fluorenyllithium in THF at −78 °C yielded polymers that on the basis of present assignments are predominantly isotactic ($P_{mm} = 0.73, 0.75$, respectively). Poly(α-MBL) from free-radical polymerization is amorphous and has a high glass transition temperature ($T_g = 195$ °C) and solvent resistance, characteristic of structural rigidity of the chain segments.

α-Methylene-γ-butyrolactone[1] (α-MBL, I) is the simplest member of a class of naturally occurring sesquiterpene lactones which have become, in recent years, the subject of considerable research interest[2] owing to their demonstrated cytotoxicity and tumor-inhibitory properties.[3] α-MBL itself, often referred to as Tulipalin A,[4] occurs in the common tulip, Tulipa Gesneriana L, as the glucoside of the corresponding γ-hydroxy acid. Since the initial report of Jones et al.[5] on the synthesis of α-MBL, other methods have been described for the synthesis of both α-MBL and related compounds containing the α-methylene-γ-lactone structural moiety of interest to medicinal chemists.[6] However, very little attention has been paid to the potential of α-MBL as a reactive, polymerizable monomer, particularly in view of the fact that the monomer possesses structural features similar to those of methyl methacrylate (II, MMA). Except for a patent by McGraw,[7] very little is known regarding the polymerization characteristics of α-MBL or the structure and properties of the polymer. α-MBL may be considered as an example of a more general class of *exo*-methylene cyclic monomers capable of polymerizing via the double bond. Methylene cycloalkanes,[8] however, are known to polymerize reluctantly by cationic initiators yielding low molecular weight polymers. 2-Methylenetetrahydrofuran[9] is another example known to polymerize cationically and was reported to yield predominantly isotactic polymer[10] in hydrocarbon solvents.



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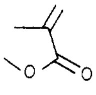

II

Since the growing chain end in the polymerization of α-MBL consists of a cyclic moiety, as in the above examples, it was of interest to determine the effect of the lactone ring on the propagation and stereochemistry of the chain. In view of the structural similarity to MMA, it was also of interest to determine whether α-MBL would polymerize by anionic initiation without ring opening. In this paper, some aspects of the free-radical and anionic polymerization characteristics of α-MBL, as well as the stereochemical configuration and other pertinent properties of the polymer, are discussed.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (Aldrich), *n*-butyllithium (1.6 M in hexane, Foote Mineral Co.), γ-butyrolactone (Matheson Coleman and Bell), diethyl oxalate (Aldrich), di-*tert*-butyl peroxide (Polysciences, Inc.), paraformaldehyde, and sodium ethoxide (Aldrich) were all of reagent grade and were used as supplied.

Tetrahydrofuran and toluene were distilled from 0.5% calcium hydride (Ventron). Fluorene (Aldrich) was recrystallized from cyclohexane and dried under vacuum just prior to use.

α-Methylene-γ-butyrolactone (α-MBL, I). I was synthesized from γ-butyrolactone (III) in an overall yield of ~60% according to the reaction scheme, shown below, reported by Ksander et al.[11] The procedure was, however, modified such that the intermediate α-ethoxalyl-γ-butyrolactone (IV) was not isolated, and instead its sodium salt was reacted directly with formaldehyde using THF as solvent.

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