

PART I BLOCK COPOLYMERS
PART II POLYMERS OF 1,3-DITHIOLES

by

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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by John Everard Leland entitled Part I Block Copolymers
Part II Polymers of 1,3-Dithioles be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

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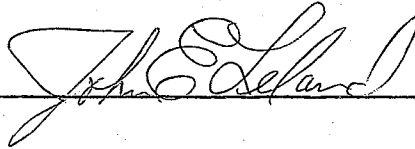
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A handwritten signature in cursive script, appearing to read "John E. Seland", is written over a horizontal line.

To Rita Kay, Michael, Mark, and Matthew

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ABSTRACT

Part I Block Copolymers

Copolymers of vinylene carbonate were prepared. These copolymers were hydrolyzed and then cleaved with periodic acid and potassium permanganate to yield polymers with carboxylic acid endgroups.

The carboxyl-terminated polymers were coupled with other difunctional polymers or monomers to form block copolymers.

Part II Polymers of 1,3-Dithioles

Both 1,3-dithiole-2-thione and 1,3-dithiole-2-one were prepared to determine whether they could be polymerized or copolymerized. Attempted polymerizations of both monomers were unsuccessful. However, 1,3-dithiole-2-one did copolymerize with methyl methacrylate using zinc chloride and azobisisobutyronitrile (AIBN).

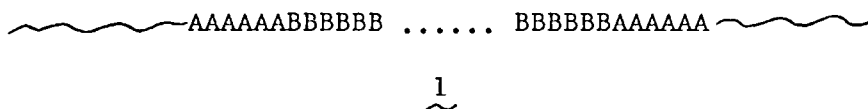
A substituted tetrathiafulvalene and a disubstituted 2-benzylidene-1,3-dithiole were prepared and condensed with difunctional compounds to prepare polymers containing the 1,3-dithiole ring system.

PART I

BLOCK COPOLYMERS

INTRODUCTION

Block copolymers are linear macromolecules with two or more different runs of monomer units bonded together as represented in 1.

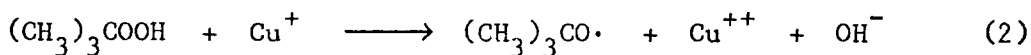
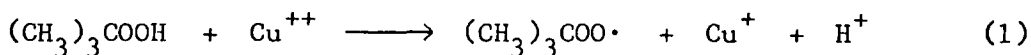


Block copolymers frequently exhibit properties quite different from random copolymers or a mixture of homopolymers. Elastomeric fibers are block copolymers consisting of alternating segments of rigid and hydrogen bonding units with rubbery units resulting in a polymer tough to be a fiber but still elastic.

A number of methods for the synthesis of block copolymers have been developed and several excellent reviews and books are available [1,2,3,4].

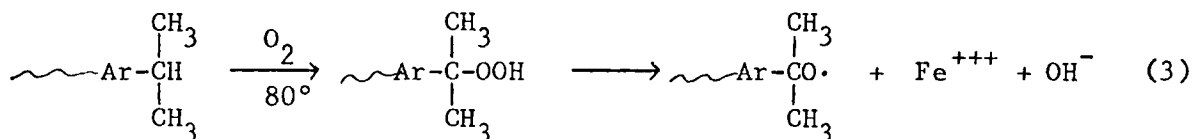
The first reported synthesis of a block copolymer was in 1941 [5], during the examination of photoinitiation of monomers in the vapor phase. A film of poly(methyl methacrylate) was deposited in an evacuated glass chamber when the monomer was exposed to ultraviolet radiation. Removal of unreacted monomer and introduction of chloroprene vapor produced polymerization as a layer on top of the film of poly(methyl methacrylate) without irradiation. Later work demonstrated the existence of trapped radicals which were capable of propagating a second monomer to give a linear block copolymer of poly(methyl methacrylate-b-chloroprene).

Block copolymers have been prepared using a homopolymer having one or two active ends which can initiate the polymerization of another monomer. An example of this method involves the introduction of peroxides as endgroups of homopolymers. Trace amounts of copper(II) and t-butyl hydroperoxide form radicals [6] (Equations 1 and 2) which can initiate polymerization of certain monomers.

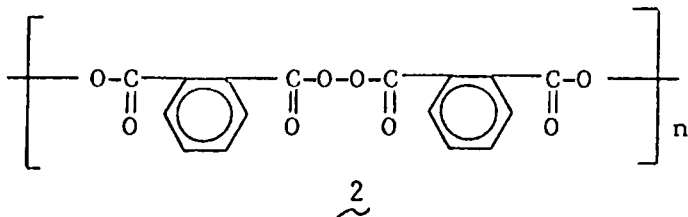


Polymers produced in this system would have t-butyl peroxide and t-butyl ether endgroups. The peroxide-terminated polymer can then initiate polymerization of a different monomer to form a block copolymer. Since only half of the endgroups were peroxides, a mixture of block copolymer and homopolymer would be produced.

Peroxide endgroups have also been prepared using initiators and/or transfer agents which contain isopropyl aryl groups [7] as in Equation 3.

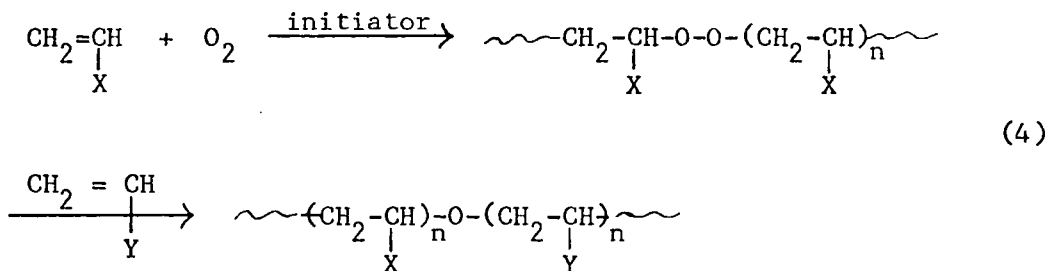


Another method of preparing polymers with radical endgroups is to use a multifunctional initiator such as polymeric phthalyl peroxide (2).



By using this initiator with styrene, a polymer was isolated which contained peroxide linkages as the endgroups and/or within the polymer itself. When heated in the presence of another monomer, the peroxide linkages decomposed to give radicals which initiate the second monomer to produce a block copolymer [8].

Oxygen copolymerizes with some vinyl monomers to form a polymer with peroxy linkages in the backbone of the polymer. Thermal decomposition of the polymer in the presence of another monomer can produce block copolymers (Equation 4) [9].



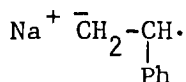
Poly(tetramethylene oxide) terminated with tolylene diisocyanate (3) was capped with t-butyl hydroxymethyl peroxide (4). The resulting prepolymer peroxide (5) was used as a free-radical initiator of methyl methacrylate which gave a block copolymer with improved impact strength [10].

These polymers (7) were irradiated in the presence of another monomer which produced block copolymers.

Block copolymers have been prepared from trapped radicals in a heterogeneous solution. Acrylonitrile-styrene, vinyl chloride-styrene, and vinyl chloride-methyl methacrylate block copolymer were prepared by trapped radicals in poly(vinyl chloride) formed in a heterogeneous system. The trapped polymer radicals were activated by addition of dimethylformamide as solvent, and block polymer was obtained by the addition of a second monomer [12].

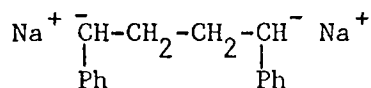
By polymerizing epoxides with hydroxide ion hydroxyl-terminated polymers are obtained which can be used to initiate the polymerization of other epoxides to form block copolymers [13].

"Living" polymers are well suited to the synthesis of block copolymers [14]. For example, styrene can be polymerized by electron transfer from a solution of sodium-naphthalene in tetrahydrofuran. Anion radicals of styrene are formed (8)



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which then couple to form dianion 9

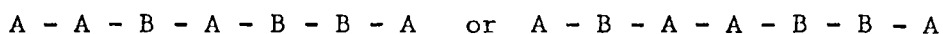
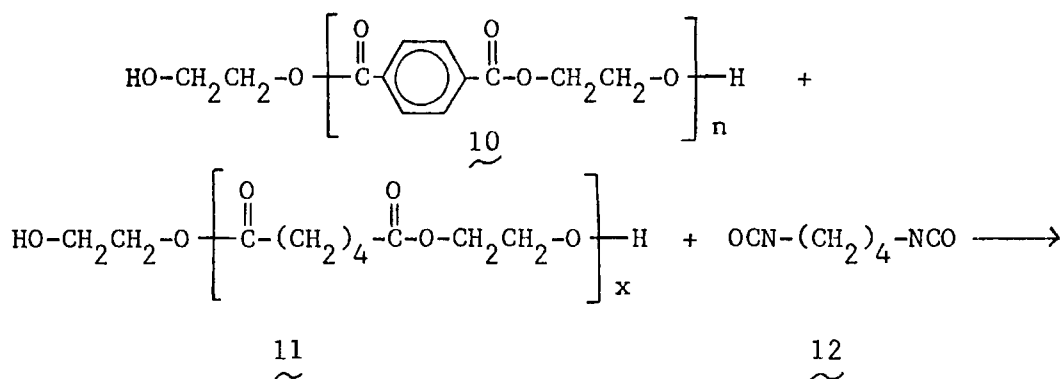


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which then adds more monomer, forming a polymeric dianion. Subsequent addition of a second monomer which can polymerize anionically produces block copolymers which still have anionic endgroups.

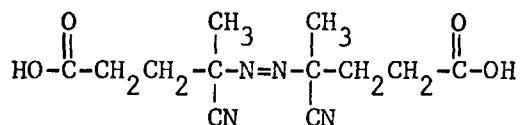
The "living" polymer technique is presently the best synthetic method to prepare block copolymers of uniform size and sequence and free of homopolymers. Experimentally, it is not a routine matter to obtain and maintain the high degree of purity needed to prevent termination reactions. In addition to difficult experimental conditions, another limiting factor is that the method is restricted to monomers that polymerize anionically.

The coupling of polymers with reactive endgroups by condensation reactions affords another method of preparing block copolymers. Polyesterurethane block copolymers have been made from polyesters with hydroxyl endgroups and diisocyanates [15]. A random block copolymer has been prepared from poly(ethylene terephthalate) (10), poly(ethylene adipate) (11), and tetramethylene diisocyanate (12)



where A denotes 10 and B denotes 11.

By using a difunction initiator that is capable of both free-radical initiation and of coupling reactions, such as 4,4'-azo(4-cyanovaleric acid) (13), polymers have been prepared with carboxyl endgroups.



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Block copolymers of the type $\left\langle \text{S-A} \right\rangle_n$ and M-S-M, where S, A, and M represent polystyrene, polyacrylonitrile, and poly(methyl methacrylate), respectively, have been prepared by this method [16]. A serious limitation to this method is that only monomers that terminate by combination of growing radicals can be used to obtain difunctional endgroups.

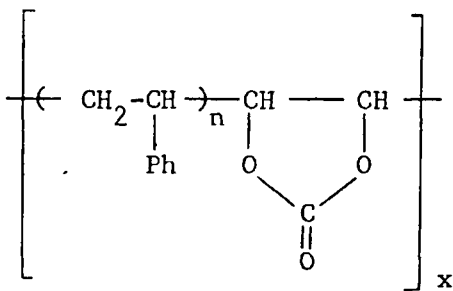
Block copolymers have found use as nonvulcanized elastomers. The styrene butadiene block copolymers are especially useful in improving the ease of fabrication of synthetic rubber [17,18] because they are not cross-linked and therefore soluble. Poly(propylene oxide-b-ethylene oxide) is effective as a surface-active agent and is used as a nonionic detergent [13]. A block copolymer of styrene and isoprene gave improved hardness, permanent set, and static compression [19,20]. Block copolymers also can be used to prevent the growth of bacteria on the surface of natural rubber by adding 10% or more block-copolymerized monomer [2]. Block copolymers have also been used to prepare materials with improved impact strength [10]. Some synthetic fibers present a serious problem in dyeing and dye retention. This difficulty can be

This method has an advantage over carboxyl-terminated polymers prepared using a difunctional initiator because one is not limited to monomers which terminate by radical combination (see above).

The carboxyl-terminated polymers were coupled with difunctional compounds and difunctional polymers to prepare block copolymers.

RESULTS AND DISCUSSION

The copolymerization of styrene and vinylene carbonate has been reported [21,22,23,24]. Because vinylene carbonate is a 1,2-disubstituted vinyl monomer, it is not very reactive in copolymerizations. Therefore copolymers of vinylene carbonate and reactive monomers such as styrene contain long blocks of polystyrene connected by vinylene carbonate (Table 1).



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The length of the styrene blocks will be controlled by the styrene-vinylene carbonate feed ratio. The initial polymerization mixture contained a 3.5/1.0 ratio of vinylene carbonate. Twice during the polymerization, additional styrene and initiator were added in order to copolymerize as much of the vinylene carbonate as possible. The ratio of the area of the ir absorption bands at 1800 cm^{-1} (due to the carbonyl stretching and phenyl deformation) and 1940 cm^{-1} (due to phenyl deformation only) was used in comparison with a calibration curve [23], made from known mixture of homopolymers, to determine the mole percent vinylene carbonate. The mole percent vinylene carbonate determined by

Table 1. Copolymerization of styrene (M_1) and vinylene carbonate (M_2).

Sample no.	M_1 (mmol)	M_2 (mol)	% Conversion	Mole % carbonate ^a	$[\eta]$ ^b	$\bar{M}_n^c \times 10^{-4}$
<u>17</u>	77	0.22	37.5	2.4 ± 1.0^d	0.84	14.4
<u>18</u>	33	0.10	70.0	2.5 ± 0.8	0.36	4.4
<u>19</u>	33	0.10	66.2	3.8 ± 0.8	-	-
<u>20</u>	75	0.23	39.0	-	0.84	14.3

a. Determined by infrared spectroscopy.

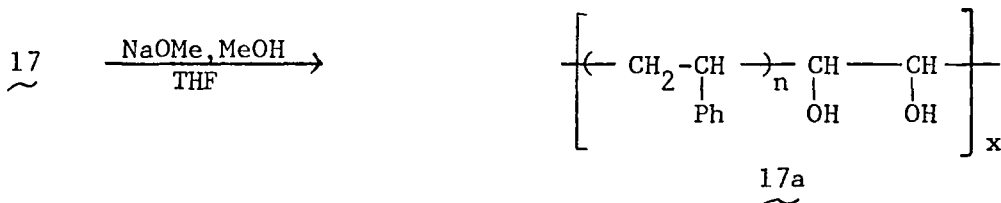
b. Determined in benzene at 30°.

c. $\bar{M}_n = 184000$ $[\eta] = 1.40$ [25].

d. Calculated from standard deviation.

ir measurements, 2.5%, does not agree with the observed decrease in molecular weight after periodate cleavage. This lack of correlation may be due to incomplete cleavage by periodic acid, incomplete hydrolysis of carbonate to glycol adjacent units of vinylene carbonate, or inaccuracy of the ir method. In the experimental section the periodate-treated polymer was once more subjected to treatment with periodate. No decrease in viscosity was observed. It seems likely, therefore, that the discrepancy is due to incomplete carbonate hydrolysis and perhaps the presence of occasional adjacent vinylene carbonate units.

Poly(vinylene carbonate) and copolymers containing vinylene carbonate have been hydrolyzed [23,24,26,27] to yield products containing vinylene glycol units. It was found that hydrolysis with sodium methoxide in tetrahydrofuran was complete in 22 hr at 50°.



Glycols are cleaved by periodic acid [28] to produce aldehydes. Copolymer 17a was cleaved by periodic acid in tetrahydrofuran in the presence of potassium permanganate to yield carboxyl-terminated polystyrene (17b) (Table 2).

Table 2. Carboxyl-terminated polystyrene by cleavage of poly(styrene-co-vinylene glycol).

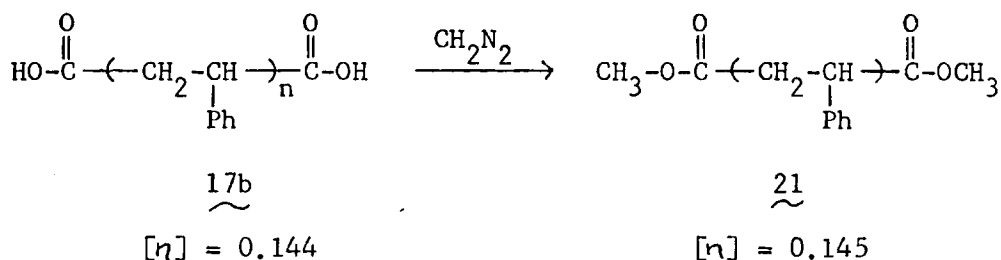
Sample no.	$[\eta]$	$\bar{M}_n^a \times 10^{-4}$	$-\text{CO}_2\text{H}/\text{chain}^b$
<u>17b</u>	0.14	1.20	1.80
<u>18b</u>	0.13	1.05	1.98
<u>19b</u>	0.13	1.05	1.82
<u>20b</u>	0.16	1.43	1.63

a. Number average molecular weight, from intrinsic viscosity [25].

b. Determined by titration.

The number of carboxyl groups per polymer chain, 1.8 to 2.0, was determined by titration with sodium methoxide and using the measured value of \bar{M}_n , number average molecular weight.

The preparation of the methyl ester of carboxyl-terminated polystyrene (21) without change in intrinsic viscosity showed that carboxyl groups of the polystyrene do not interact with one another to change the intrinsic viscosity. Titration of the methylated polystyrene showed that all carboxyl groups were methylated.



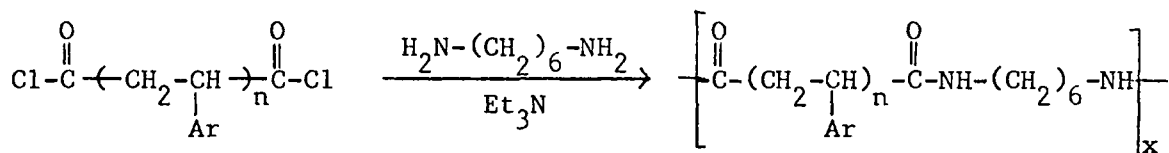
The carboxyl-terminated polystyrene and poly(4-vinyltoluene) were converted to acid chlorides by treatment with thionyl chloride or oxalyl chloride [29,30,31].

It was found that the best method of preparing the polymeric acid chlorides was to heat the carboxyl-terminated polymer at 60° for 20 hr in thionyl chloride. The excess thionyl chloride was removed by distillation at reduced pressure and the remainder by freeze-drying. This was followed by the addition of portions of dry benzene and distillation until the distillate gave no positive test for chloride with aqueous silver nitrate.

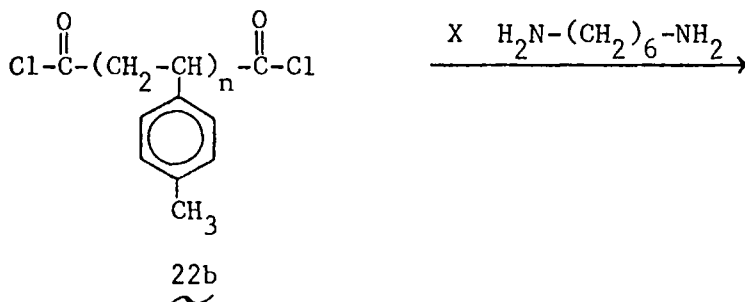
The polymeric acid chlorides were coupled with various difunctional compounds and polymers. An attempt to prepare a block

copolymer from carboxyl-terminated polystyrene with hexamethylenediamine by the interfacial method [32] resulted in no measurable coupling. This is probably due to the large amount of water and the minute quantity of diamine required resulting in hydrolysis of the acid.

Carboxyl-terminated polystyrene and poly(4-vinyltoluene) were coupled with hexamethylenediamine under a number of conditions as shown in Table 3. Significant increases in viscosity were obtained in at least three of the five examples. In Table 3, 22b refers to carboxyl-terminated poly(4-vinyltoluene).



Carboxyl-terminated poly(4-vinyltoluene) (22b) was coupled with a 20-fold excess of hexamethylenediamine in order to prepare an amine-terminated poly(4-vinyltoluene) (22c), which was coupled to an equivalent amount of polymeric acid chloride but no increase in viscosity



was observed.

Table 3. Coupling of carboxyl-terminated polymers with hexamethylenediamine.

Run no.	Diacid chloride polymer ^a	Process ^b	Polymerization solvent	Acid acceptor	Rxn time, min	Viscosity	
						Before ^c	After ^d
1	<u>18b</u>	I	1,2-dichloroethane	NaOH	8	0.130	0.133 ^e
2	<u>19b</u>	S	1,2-dichloroethane	Et ₃ N	10	0.130 ^f	0.196 ^f
3	<u>22b</u>	S	chloroform	.2-fold excess diamine	45	0.137	0.216
4	<u>22b</u>	S	chloroform	20-fold excess diamine	90	0.137	0.372
5	<u>22b</u> + run 4 ^g	S	chloroform	Et ₃ N	60	-	0.277

a. Polystyrene, 18b and 19b; poly(4-vinyltoluene), 22b.

b. I, interfacial polycondensation and S, solution polycondensation.

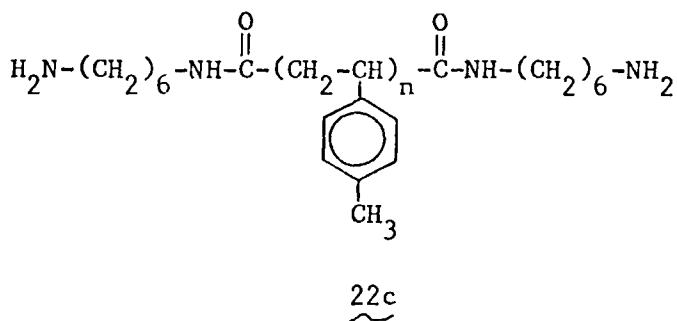
c. Inherent viscosity of carboxyl-terminated polystyrene and poly(4-vinyltoluene) before coupling.

d. Inherent viscosity (0.50 g/dl) unless otherwise noted.

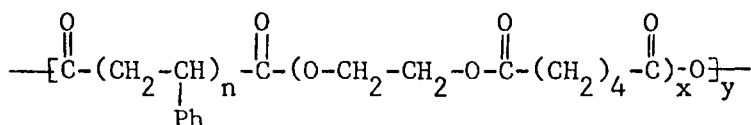
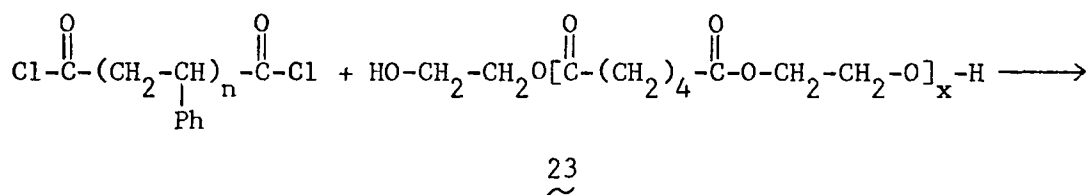
e. Conc. 0.52 g/dl.

f. Intrinsic viscosity.

f. This coupling was with product of run 4 instead of hexamethylenediamine.



Carboxyl-terminated polystyrene and poly(4-vinyltoluene) were coupled with hydroxyl-terminated poly(ethylene adipate) (23). Results are presented in Table 4. It was found that an equimolar mixture of 23 (η_{inh} 0.0604) and carboxyl-terminated polystyrene (19b) (η_{inh} 0.132) had an inherent viscosity of 0.114. The nmr spectrum showed protons from polystyrene and protons of poly(ethylene adipate) at τ 5.8 (s).



A hydroxyl-terminated poly(4-vinyltoluene) (24) was prepared by adding a threefold excess of hydroxyl-terminated poly(ethylene adipate) (23). The hydroxyl-terminated poly(4-vinyltoluene) was then coupled with a carboxyl-terminated poly(4-vinyltoluene) to give a copolymer (25) with η_{inh} 0.188 which is a 38% increase in viscosity.

Table 4. Coupling of carboxyl-terminated polymers with hydroxyl-terminated poly(ethylene adipate)* (23) by the solution polycondensation process.

Run no.	Diacid chloride polymer ^a	Polymerization solvent	Rxn time, hr	Temp.	Viscosity	
					Before ^b	After ^c
1	<u>19b</u>	1,2-dichloroethane	2	25 ^o	0.132	0.132
2	<u>19b</u>	dioxane/pyridine	12	85	0.132	0.165
3	<u>19b</u>	dioxane	20	85	0.132	0.179
4	<u>19b</u>	nitrobenzene	25	90	0.132	0.182 ^d
5	<u>22b</u>	nitrobenzene	20	92	0.137	0.182 ^e
6	<u>22b</u> + run 5 ^f	nitrobenzene	20	88	-	0.188
7	<u>22b</u> ^g	pyridine	21	88	0.137	0.163 ^h
8	<u>20b</u>	pyridine	21	88	0.161	0.180

*. The inherent viscosity of the poly(ethylene adipate) (23) was 0.0604 (0.50 g/dl).

a. Polystyrene, 19b and 20b; poly(4-vinyltoluene) 22b.

b. Inherent viscosity of carboxyl-terminated polystyrene and poly(4-vinyltoluene) (0.50 g/dl) before coupling.

c. Inherent viscosity at 0.50 g/dl unless otherwise noted.

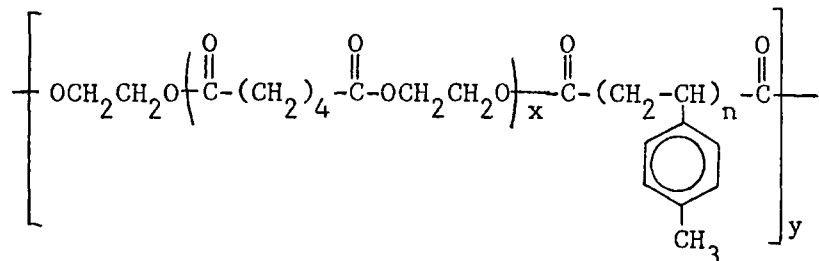
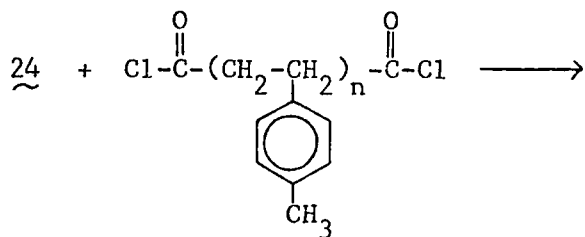
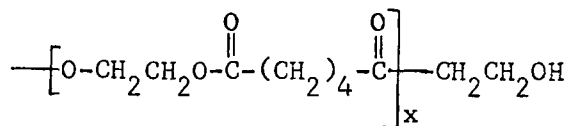
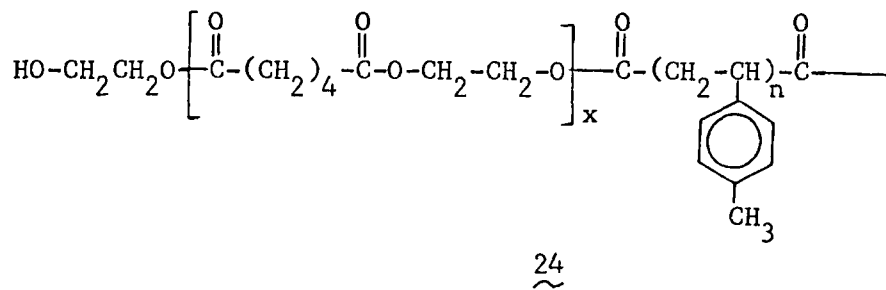
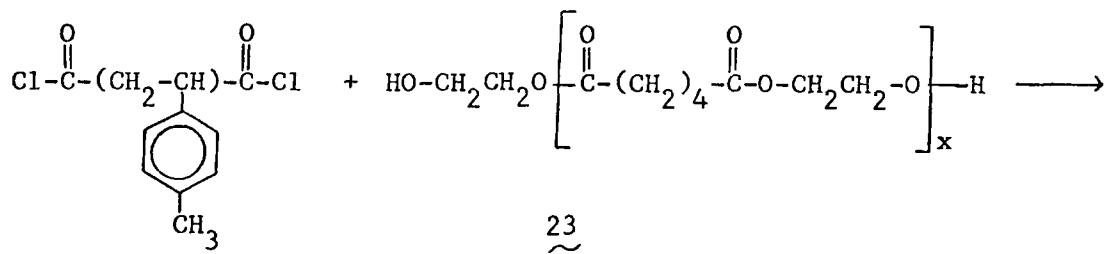
d. Conc. 0.51 g/dl.

e. Conc. 0.48 g/dl.

f. This coupling was with product of run 5 instead of poly(ethylene adipate).

g. This coupling was with hydroxyl-terminated poly(4-vinyltoluene) (inherent viscosity of 0.158).

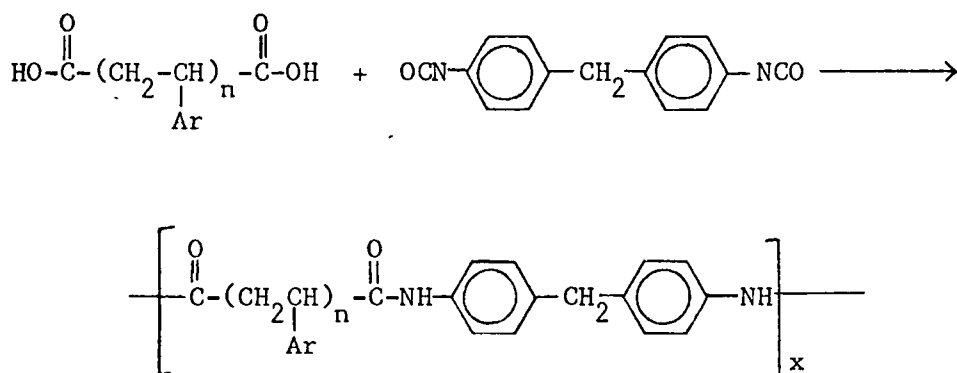
h. Conc. 0.49 g/dl.



A larger scale coupling was tried with carboxyl-terminated polystyrene (20b) and hydroxyl-terminated poly(ethylene glycol) (23) in pyridine to obtain precise stoichiometry. The inherent viscosity was 0.180 which is only a 12% increase in viscosity.

Carboxyl-terminated polystyrene and poly(4-vinyltoluene) were coupled with various difunctional compounds. Results are presented in Table 5.

The preparation of polyamides from dicarboxylic acids and diisocyanates has been reported [33].



Carboxyl-terminated poly(4-vinyltoluene) was coupled with hydroxyl-terminated poly(propylene glycol) by a solution polycondensation method. Use of the poly(propylene glycol) made it possible to integrate the aromatic protons of the poly(4-vinyltoluene) and the protons next to oxygen of the poly(propylene glycol) in the nmr. The integration showed a one-to-one block copolymer (26). Oxygen analysis also showed that 26 is a one-to-one block copolymer. The inherent viscosity was 0.240 at 0.43 g/dl for a 77% increase in viscosity.

Table 5. Coupling of carboxyl-terminated polymers with various difunctional compounds.

Run no.	Acid chloride polymer ^a	Difunctional compound	Process ^b	Rxn time, min	Temp.	Polymerization solvent	Viscosity	
							Before ^c	After ^d
1	<u>19b</u>	1,10-decanediol	M	24 24	150° 180	-	0.132	0.160
2	<u>22b</u>	1,10-decanediol	S	18	90	nitrobenzene	0.137	0.210 ^e
3	<u>22b</u>	1,10-decanediol	T	23	25	benzene	0.137	0.147
4	<u>22b</u>	methylenebis (4-phenyl-iso- cyanate)	S	1.5	170	nitrobenzene	0.137	0.177 ^f
5	<u>22b</u>	Hydroxyl-terminated poly(propylene glycol)	S	23	90	nitrobenzene	0.137	0.240 ^g

a. Polystyrene, 19b; poly(4-vinyltoluene), 22b.

b. M, melt polycondensation; S, solution polycondensation; T, trifluoroacetic anhydride esterification.

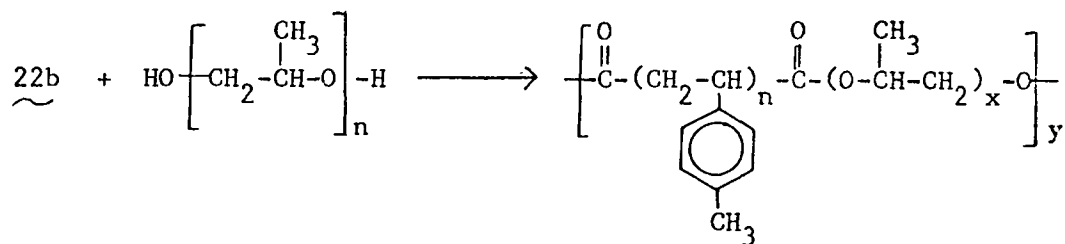
c. Inherent viscosity at 0.50 g/dl.

d. Inherent viscosity at 0.50 g/dl unless otherwise noted.

e. Conc. 0.43 g/dl.

f. Conc. 0.52 g/dl.

g. Conc. 0.46 g/dl.



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In conclusion, the synthesis and the coupling of polymers with reactive endgroups to other difunctional polymers or monomers to form block copolymers have been demonstrated. The viscosity increases ranged from zero (no measurable coupling) to nearly a threefold increase (substantial coupling). The formation of block copolymers has clearly been shown.

EXPERIMENTAL

Materials

Styrene (Matheson, Coleman, and Bell Company) and 4-vinyltoluene (Polysciences, Inc.) were washed with aqueous 5% sodium hydroxide, then with water, followed by drying over magnesium sulfate and vacuum distillation. Vinylene carbonate was prepared from ethylene carbonate (Matheson, Coleman, and Bell Company) by the method of Gross [24] and purified by distillation from sodium borohydride. Vinylene carbonate (Aldrich Chemical Company) was also used after distillation from sodium borohydride. Azobisisobutyronitrile (AIBN) (Matheson, Coleman, and Bell) was recrystallized from methanol.

Benzene (Matheson, Coleman, and Bell) used in coupling reaction was distilled twice from sodium and stored over calcium hydride and distilled under nitrogen prior to use. Tetrahydrofuran (Mallinckrodt Chemical Works) was distilled from lithium aluminum hydride. Dioxane (Mallinckrodt Chemical Works) was refluxed over sodium hydroxide under nitrogen, then distilled, and refluxed over sodium followed by distillation under nitrogen prior to use. Chloroform and 1,2-dichloroethane (Matheson, Coleman, and Bell) were shaken with sulfuric acid, washed with water, dried with sodium sulfate, and distilled from phosphorus pentoxide. Nitrobenzene (Mallinckrodt Chemical Works) was distilled from barium oxide twice, stored under calcium hydride, and distilled under reduced pressure prior to use. Pyridine (Allied Chemicals) was

purified by distillation from sodium under nitrogen. Thionyl chloride (Matheson, Coleman, and Bell) was distilled from quinoline, followed by distillation from linseed oil. Oxalyl chloride (Matheson, Coleman, and Bell) was purified by distillation. Methylene bis(4-phenyl isocyanate) (Eastman Organic Chemicals) was purified by vacuum distillation.

Hexamethylenediamine (Matheson, Coleman, and Bell) was purified by sublimation. Adipic acid (Matheson, Coleman, and Bell) was crystallized first from water, then from acetone. Poly(propylene glycol) (Union Carbide) was used without further purification. The compound 1,10-decanediol was prepared by a known procedure [34] from ethyl sebacate. Trifluoroacetic anhydride was prepared by distilling trifluoroacetic acid in the presence of excess phosphorus pentoxide.

Instrumentation

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined on a Varian model T-60 (60 MHz), a Varian model A-60 (60 MHz), or a Varian model HA-100 (100 MHz) using tetramethylsilane as an internal standard. Infrared spectra were determined using a Perkin-Elmer Infrared or Perkin-Elmer model 337 Grating Infrared Spectrophotometer and calibrated with a polystyrene film.

Elemental Analyses

Microanalysis was determined by Micro-Tech Laboratories, Inc., Skokie, Illinois, and Huffman Laboratories, Inc., Wheatridge, Colorado.

Experimental ProcedurePoly(styrene-co-vinylene Carbonate) (17)

As a typical example, styrene (8.0 g, 0.077 mol), vinylene carbonate (19.3 g, 0.225 mol), AIBN (0.010 g, 6.1 mmol), and 10 ml of benzene were degassed by freeze-thawing and heated under nitrogen at 60°. On the fourth and eighth days the flask was recharged with styrene (8.0 g) and AIBN (0.015 g, 9.15 mmol). Degassing and heating under nitrogen was done as before. After a total of fourteen days, the solution was diluted with benzene and precipitated in methanol. A white polymer 9.0 g (37.5%) was obtained. The intrinsic viscosity was 0.84 in benzene at 25°, \bar{M}_n , 144000 [25]. The ir spectrum (film) showed the carbonate carbonyl band at 1800 cm⁻¹ overlapping a band in polystyrene. Similar copolymerizations can be found in Table 1.

Poly(styrene-co-vinylene Glycol) (17a)

As a typical example, 6.5 g of poly(styrene-co-vinylene carbonate) (17) was dissolved in 200 ml of tetrahydrofuran. Sodium (1.4 g) was dissolved in 30 ml of methanol and the solution was filtered into the reaction mixture which was then stirred at 40° for 40 hr. Precipitation in methanol yielded 6.5 g (100% recovery). The inherent viscosity was 0.773 (0.5 g/100 ml of benzene at 30°). The ir spectrum (film) showed the disappearance of the carbonate carbonyl band.

Preparation of Carboxyl-terminated Polystyrene (17b)

A solution of 7.0 g of poly(styrene-co-vinylene glycol) (17a) in 300 ml of THF was treated with 4.0 g (17.5 mmol) of periodic acid in 20 ml of THF and 4.0 g (25 mmol) of potassium permanganate in 25 ml

of H_2O . After stirring at room temperature for 3 days, the reaction mixture was worked up by bubbling in sulfur dioxide to remove the manganese dioxide. The polymer was precipitated in methanol yielding 5.9 g (84% recovery) of a pink product. The color was removed by aqueous extraction of a $CHCl_3$ solution of the polymer followed by reprecipitation into methanol. This procedure was repeated twice. The yield of colorless polymer was 5.2 g (74%). Results of this series can be found in Table 2.

Anal. Calcd for C_8H_8 : C, 92.3; H, 7.7. Found: C, 91.9; H, 7.4.

Poly(4-vinyltoluene-co-vinylene
Carbonate) (22)

This was prepared in the same way as poly(styrene-co-vinylene carbonate). The percent conversion was 73.5. Intrinsic viscosity was 0.365 in toluene at 30° , \bar{M}_n , 81000 [25].

Anal. Found: C, 89.4; H, 8.4.

Poly(4-vinyltoluene-co-vinylene
Glycol) (22a)

This was prepared in a similar manner to poly(styrene-co-vinylene glycol). However it was found that a reaction time of 22 hr at 50° was sufficient for hydrolysis. The ir spectrum showed no carbonyl band due to carbonate and the product was obtained in 97% yield.

Preparation of Carboxyl-terminated
Poly(4-vinyltoluene) (22b)

This was prepared in a similar manner to carboxyl-terminated polystyrene. However the reaction was more rapid at 50° . Cleavage

and oxidation were complete in 24 hr for 68.5% recovery. The intrinsic viscosity in toluene at 30° was 0.136. The number average molecular weight, \bar{M}_n , was 21500 [35]. Titration showed 2.04 carboxyls per chain.

Anal. Calcd for C_9H_{10} : C, 91.5; H, 8.5. Found: C, 89.1; H, 8.4.

Titration of Carboxyl-terminated Polymers

The polymers were titrated with sodium methoxide solution prepared according to a known procedure [36]. The 0.1 N methanolic methanolic solution was diluted with benzene-methanol (80:20 v/v) until the concentration was approximately 10^{-2} N. The sodium methoxide was standardized against benzoic acid in benzene-methanol (80:20 v/v) solution using thymol blue (titrated to permanent blue) as indicator.

A benzene solution of the indicator which usually required 0.05 to 0.20 ml of sodium methoxide solution was standardized before and after titrations and no change in concentration was observed. Polymer samples of 0.3 to 0.5 g were used (see Table 2 for results).

Methylation of Carboxyl-terminated Polystyrene

Diazomethane was generated from N-nitroso-N-methyl urea [37, p. 165 and p. 461] and added to a solution of 0.70 g of polystyrene with carboxyl endgroups (17b) in 20 ml of benzene until the yellow color of the diazomethane persisted. The polymer solution was precipitated in methanol and 0.5 g of white polymer was collected. The intrinsic viscosity before methylation in benzene at 25° was 0.144, 0.145 under the same conditions after methylation. Titration of polymer with sodium methoxide showed no carboxyl groups present.

Treatment of Carboxyl-terminated
Polystyrene with Periodic Acid

A solution of 0.2 g of 19b in 20 ml of tetrahydrofuran and 0.3 g of periodic acid was stirred at 53° for 15 min followed by precipitation in methanol. The intrinsic viscosity in benzene at 25° was 0.13 before and after treatment with periodic acid.

Preparation of Hydroxyl-terminated
Poly(ethylene Adipate) (23)

This polymer was prepared in a similar manner to a reported procedure [33, p. 154]. Adipic acid, 15.0 g (0.103 mol), and ethylene glycol, 7.6 (0.122 mol), were heated to 140° under nitrogen. After 18 hr the temperature was raised to 200° for 5 hr. Upon cooling 16.0 g of a white, waxy solid was obtained.

Titration and Molecular Weight Determination of
Hydroxyl-terminated Poly(ethylene Adipate) (23)

Hydroxyl and carboxyl numbers were determined by a reported procedure [33, p. 154]. The hydroxyl number was 78 and the carboxyl number was 1. Calculated number average molecular weight, \bar{M}_n , was 1420. The inherent viscosity was 0.0604 (0.5 g/100 ml of benzene at 25°).

Viscosity of a 50:50 Molar Solution of
Hydroxyl-terminated Poly(ethylene Adipate)
(23) and Carboxyl-terminated Polystyrene (19b)

Carboxyl-terminated polystyrene (19b), 66.0 mg (6.28×10^{-3} mol), and 6.0 mg (6.3×10^{-3} mol) of 23 were dissolved in 15 ml of benzene. The inherent viscosity was 0.114 (0.5 g/100 ml of benzene

at 25°). The inherent viscosities of 19b and 23 were 0.132 and 0.0604, respectively (0.5 g/100 ml of benzene at 25°).

Attempt to Couple Carboxyl-terminated Polystyrene (18b) with Hexamethylenediamine by the Interfacial Method

A solution of 1.0 g of 18b, 0.1 ml of oxalyl chloride and 30 ml of 1,2-dichloroethane was heated slowly to reflux. After 2 hr approximately 10 ml of 1,2-dichloroethane was distilled. The remaining acid chloride was cooled in an ice bath and transferred to a Waring blender. Hexamethylenediamine (10.0 ml, 6.24×10^{-2} mmol) in a standardized 6.25×10^{-3} M solution and 4.75 ml (6.25×10^{-2} mmol) of sodium hydroxide solution were added. After the mixture was stirred for 8 min, it was poured into methanol giving a white precipitate 0.8 g. The inherent viscosity was 0.133 (0.52 g/100 ml of benzene at 25°). Since the inherent viscosity of 18b was 0.130 (0.50 g/100 ml of benzene at 25°), a very small amount of coupling occurred.

Coupling of Carboxyl-terminated Polystyrene (18b) with Hexamethylenediamine by the Solution Polycondensation Process in Chloroform with Triethylamine

A solution of 1.0 g of 18b, 0.03 ml of oxalyl chloride, and 15 ml of chloroform was stirred for 2 hr, then heated to reflux for an additional 2 hr. About 10 ml of solvent was removed by distillation. After cooling, the acid chloride-terminated polymer was dissolved in 15 ml of chloroform and added dropwise to 2.3 ml (6.25×10^{-2} mmol) of hexamethylenediamine in chloroform with 1 ml (12.3×10^{-2} mmol) of triethylamine in chloroform at 0° under nitrogen flow. After 45 min, the

reaction mixture was precipitated in methanol for 100% recovery. The inherent viscosity was 0.175 (0.51 g/100 ml of benzene at 25°). The inherent viscosity of 18b was 0.130 (0.50 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Polystyrene (19b)
with Hexamethylenediamine by the Solution Poly-
condensation Process in 1,2-Dichloroethane
with Triethylamine

A solution of 1.0 g of 19b, 0.3 ml of thionyl chloride, and 40 ml of 1,2-dichloroethane was stirred for 2 hr, then heated to reflux for an additional 2 hr. The excess thionyl chloride was removed by distillation. The acid chloride polymer was added dropwise during 10 min to 7.3 mg (6.25×10^{-2} mmol) of hexamethylenediamine in 10 ml of 1,2-dichloroethane at room temperature. Precipitation in methanol gave 100% recovery. The intrinsic viscosity in benzene at 25° was 0.196. The intrinsic viscosity of 19b benzene at 25° was 0.130.

Attempt to Couple Carboxyl-terminated Polystyrene
(19b) with Hydroxyl-terminated Poly(ethylene Adi-
pate) (23) by the Solution Polycondensation
Process in 1,2-Dichloroethane with Triethylamine

This method was the same as the one above except oxalyl chloride was used to make the acid chloride and hydroxyl-terminated poly-(ethylene adipate) (23) was used instead of hexamethylenediamine. The reaction time was 2 hr. The inherent viscosity was 0.132 (0.50 g/100 ml of benzene at 25°). The inherent viscosity of 19b was 0.132 (0.50 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Polystyrene (19b)
with Hydroxyl-terminated Poly(ethylene Adipate)
(23) by the Solution Polycondensation Process
in Dioxane with Pyridine

A solution of 0.302 g of 19b, 0.25 ml of thionyl chloride, 0.2 ml of pyridine, and 10 ml of dioxane was heated to 70° for 5 hr. After freeze-drying, the polymeric acid chloride was dissolved in dioxane and heated to 85° with 26.8 mg (1.89×10^{-2} mmol) of 23 in 5 ml of dioxane and 0.6 ml of pyridine for 12 hr. Precipitation in methanol gave 100% recovery. The inherent viscosity was 0.165 (0.50 g/100 ml in benzene at 25°). The inherent viscosity of 19b was 0.132 (0.50 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Polystyrene
(19b) with Hydroxyl-terminated Poly(ethylene
Adipate) (23) by the Solution Polycondensation
Process in Dioxane

The polymeric acid chloride was made in the same manner as the one above. A solution of 42.5 mg (3×10^{-2} mmol) of 23 in 10 ml of dioxane was added to the acid chloride in dioxane and was heated to 85° under nitrogen for 20 hr. The reaction mixture was precipitated in methanol. The inherent viscosity was 0.179 (0.50 g/100 ml of benzene at 25°). The inherent viscosity of 19b was 0.132 (0.50 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Polystyrene
(19b) with Hydroxyl-terminated Poly(ethylene
Adipate) (23) by the Solution Polycondensa-
tion Process in Nitrobenzene

Carboxyl-terminated polystyrene (19b) (0.300 g) was converted to the acid chloride by heating with excess thionyl chloride (0.5 ml)

in benzene at 60° for 20 hr. Most of the excess thionyl chloride was removed by distillation at reduced pressure and the remainder by freeze-drying and repeated addition and distillation of portions of dry benzene until the distillate gave no positive test for chloride with aqueous silver nitrate. A solution of 42.5 mg (3×10^{-2} mmol) of 23 in 5 ml of nitrobenzene was added to the acid chloride and heated to 90° with nitrogen flow for 25 hr. The polymer was isolated by precipitation in methanol for nearly 100% recovery. The inherent viscosity was 0.182 (0.51 g/100 ml of benzene at 25°). The inherent viscosity of 19b was 0.132 (0.51 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Polystyrene (19b) with 1,10-Decanediol by Melt

A solution of 1.0 g of 19b and 20.6 mg (1.18×10^{-4} mol) of 1,10-decanediol was heated to 150° for 24 hr under nitrogen. Vacuum from a water aspirator was applied and the mixture was heated to 180° for 24 hr. The dark brown solid was dissolved in chloroform and precipitated in methanol giving nearly 100% recovery of a tan polymer. The inherent viscosity was 0.160 (0.50 g/100 ml of benzene at 25°). The inherent viscosity of 19b was 0.132 (0.50 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Polystyrene (19b) with 1,10-Decanediol by the Solution Polycondensation Process in Nitrobenzene

A solution of 19b (0.600 g) in 5 ml of thionyl chloride was heated to 60° for 20 hr. Most of the thionyl chloride was removed by distillation and the remainder by freeze-drying and repeated addition

and distillation of portions of dry benzene until the distillate gave no positive test for chloride with aqueous silver nitrate. A solution of 11.0 mg (6.4×10^{-2} mmol) of 1,10-decanediol in 10 ml of nitrobenzene was heated to 90° for 18 hr with the acid chloride. The polymer was isolated by precipitation in methanol. The inherent viscosity was 0.210 (0.43 g/100 ml benzene at 25°). The inherent viscosity of 19b was 0.132 (0.50 g/100 ml of benzene at 25°).

Coupling of Carboxyl-terminated Poly(4-vinyltoluene)
(22b) with Methylene Bis(4-phenyl Isocyanate)

A solution of 0.300 g of 22b, 3.5 mg (1.4×10^{-2} mmol) of methylene bis(4-phenyl isocyanate), and 15 ml of nitrobenzene was heated to 170° for 1.5 hr under nitrogen. After heating to 205° for 2 hr, an additional 3.5 mg of methylene bis(4-phenyl isocyanate) was added. After 16 additional hours the reacting mixture was precipitated in methanol. The inherent viscosity was 0.177 (0.52 g/100 ml of toluene at 30°). The inherent viscosity of 22b was 0.137 (0.50 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Poly(4-vinyl-
toluene) (22b) with 1,10-Decanediol
Using Trifluoroacetic Anhydride

A solution of 0.300 g of 22b, 2.5 mg (1.44 mmol) of 1,10-decanediol, 2.7 g (1.3×10^{-2} mol) of trifluoroacetic anhydride, and 10 ml of benzene was stirred at room temperature for 23 hr. The polymer was isolated by precipitation in methanol. Inherent viscosity was 0.147 (0.50 g/100 ml of toluene at 30°). Inherent viscosity of 22b was 0.137 (0.50 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Poly(4-vinyltoluene) (22b) with Hexamethylenediamine by the Solution Polycondensation Process with Diamine as the Acid Acceptor

Carboxyl-terminated poly(4-vinyltoluene) (22b) 0.300 g was converted to the acid chloride with thionyl chloride and purified by repeated distillation and freeze-drying as before. Hexamethylenediamine (3.2 mg, 2.8×10^{-2} mmol) (twofold excess) in 10 ml of chloroform was added dropwise to the acid chloride polymer during 45 min. After stirring at room temperature for 1.5 hr, it was precipitated in methanol. The inherent viscosity was 0.216 (0.50 g/100 ml of toluene at 30°). The inherent viscosity of 22b was 0.137 (0.50 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Poly(4-vinyltoluene) (22b) with Hexamethylenediamine-terminated Poly(4-vinyltoluene) by a Solution Process

Carboxyl-terminated poly(4-vinyltoluene) (22b) was converted to the acid chloride as above. Hexamethylenediamine (32 mg, 2.8×10^{-1} mmol) (20-fold excess) in 10 ml of chloroform was added to the polymeric acid chloride during 0.75 hr. After stirring for 1.5 hr, the reaction mixture was precipitated in methanol (22c). Additional polymeric acid chloride was prepared in the same manner and an equivalent amount was added to hexamethylenediamine-terminated poly(4-vinyltoluene) (22c) in chloroform in the presence of triethylamine. After one hour the reaction mixture was precipitated in methanol (22d). The inherent viscosity of 22c and 22d was 0.372 and 0.277, respectively

(0.50 g/100 ml in toluene at 30°). The inherent viscosity of 22b was 0.137 (0.50 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Poly-(4-vinyltoluene) (22b) with Excess Hydroxyl-terminated Poly(ethylene Adipate) (23) by a Solution Process

The polymeric acid chloride was prepared in the same manner as above. Hydroxyl-terminated poly(ethylene adipate) (23) (60 mg, three-fold excess), the polymeric acid chloride, and 10 ml of nitrobenzene were heated at 92° for 20 hr under nitrogen. The polymer (24) was precipitated in methanol. The inherent viscosity was 0.182 (0.48 g/100 ml of toluene at 30°). The inherent viscosity of 22b was 0.137 (0.50 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Poly-(4-vinyltoluene) (22b) with Hydroxyl-terminated Poly(4-vinyltoluene) (24) by a Solution Process

The polymeric acid chloride (0.250 g) was prepared in the same manner as above and was added to 0.250 g of 24 in nitrobenzene at 88° for 20 hr. The reaction mixture was precipitated in methanol. The inherent viscosity was 0.188 (0.50 g/100 ml of toluene at 30°). The inherent viscosity of 24 was 0.182 (0.48 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Poly-(4-vinyltoluene) (22b) with Hydroxyl-terminated Poly(ethylene Adipate) (23) by a Solution Process in Pyridine

This experiment is the same as the one above except pyridine was the solvent instead of nitrobenzene. The inherent viscosity was

0.158 and 0.163, respectively (0.49 g/100 ml of toluene at 30°). The inherent viscosity of 22b was 0.137 (0.50 g/100 ml of toluene at 30°).

Coupling of Carboxyl-terminated Polystyrene (20b) with Hydroxyl-terminated Poly(ethylene Adipate) (23) by the Solution Process in Pyridine

The polymeric acid chloride 3.00 g was prepared as above. A solution of 310 mg (2.18×10^{-1} mmol) of 23 and 25 ml of pyridine was added to the acid chloride and heated to 88° for 21 hr. The polymer was collected by precipitation. The inherent viscosity was 0.180 (0.50 g/100 ml benzene at 30°). The inherent viscosity of 20b was 0.162 (0.50 g/100 ml of benzene at 30°).

Coupling of Carboxyl-terminated Poly(4-vinyltoluene) (22b) with Hydroxyl-terminated Poly(propylene Glycol) by the Solution Process

The polymeric acid chloride 0.600 g was prepared as above. Hydroxyl-terminated poly(propylene glycol) (150 mg, 3.65×10^{-2} mmol) in 10 ml of nitrobenzene was added to acid chloride polymer and heated to 90° for 23 hr. An attempt to precipitate the solution into absolute methanol gave a cloudy solution which was difficult to filter. However, a white polymer was obtained by precipitating into methanol-water mixture (60:40 v/v). Integration of the nmr spectrum of aromatic protons and protons from the polyether showed that the precipitate was a one-to-one block copolymer. The inherent viscosity was 0.240 (0.46 g/100 ml of toluene at 30°). The inherent viscosity of 5b was 0.137 (0.50 g/100 ml of toluene at 30°).

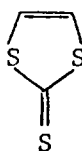
Anal. Calcd for $C_{48}H_{56}O$: C, 85.71%; H, 8.57%. Found: C, 85.7%; H, 8.6%.

PART II

POLYMERS OF 1,3-DITHIOLES

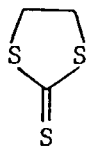
INTRODUCTION

Since 1,3-dithiole-2-thione (1) was first prepared in 1952 [38], much effort has been directed toward the preparation and study of the reactions of 1,3-dithiole derivatives and an excellent review is available [39].

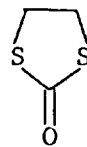


1

Both 1,3-dithiolane-2-thione (2) and 1,3-dithiolane-2-one (3) have been patented as insecticides [40]. The use of 3 as a stabilizer



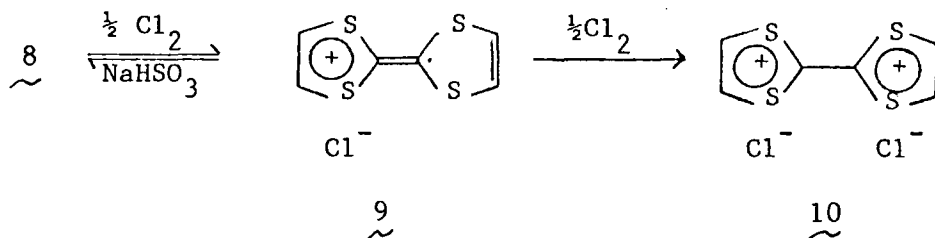
2



3

for alkoxy-substituted aromatic amines and as a flotation agent for copper ores has been patented [41,42]. Derivatives of 1,3-dithiolane have been used in protecting zinc against hydrochloric and sulfuric acids, and aluminum against hydrochloric acid [43]. A hydrazone derivative of 1,3-dithiolane has been patented as a pesticide [44].

tetrathiafulvalene (8) which is readily photo-oxidized in the presence of air to the cation-radical (9). The cation-radical (9) can be prepared efficiently by the action of chlorine gas on a carbon tetrachloride solution of 8. Excess chloride gas gives the dication (10) [47].



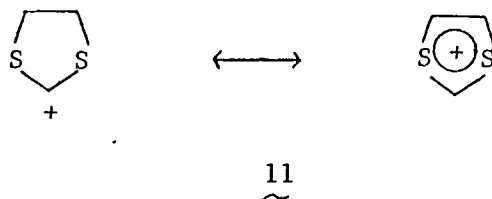
In early 1972, it was reported that the bis-1,2-dithiolium chloride was an excellent organic solid-state semiconductor [48].

Most synthetic polymers are good insulators. However, there is a need for conductive polymers with good mechanical and thermal properties, such as strength, rigidity, high softening temperature, and good corrosion resistance. If the plastic properties of polymers could be incorporated into a semiconductor, then semiconducting elastic films and coatings, filaments, and molded shapes could be made. The present method of preparing conductive polymeric films is to incorporate metallic or other conductive material into present polymers, but because of electrical resistance which generates heat and expands the material, the conductivity decreases until failure occurs. An excellent review on semiconductive polymers is available [49].

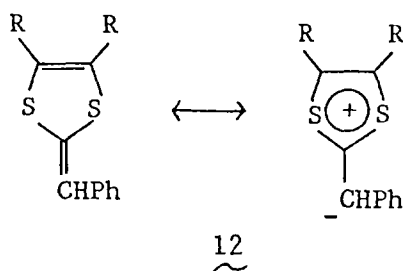
In this work we are interested in preparing polymers containing the tetrathiafulvalene (8) moiety. An excellent review of the synthesis of tetrathioethylenes can be found in the literature [50]. The

method of deprotonation of dithiocarbonium ions, described above, has been applied extensively to the preparation of tetrathiofulvalenes. However, another method of preparation will have to be used in preparing tetrathiafulvalenes with electron-withdrawing substituents. It has been reported [46] that 1,3-dithiolium salts could not be prepared from 1,3-dithiole-2-thiones with electron-withdrawing substituents.

The 1,3-dithiolium ion (11) is an unsaturated five-membered ring cation in which each sulfur atom can contribute a free pair of $3p\pi$ electrons. Therefore 11 possesses a potential "aromatic" sextet [51].



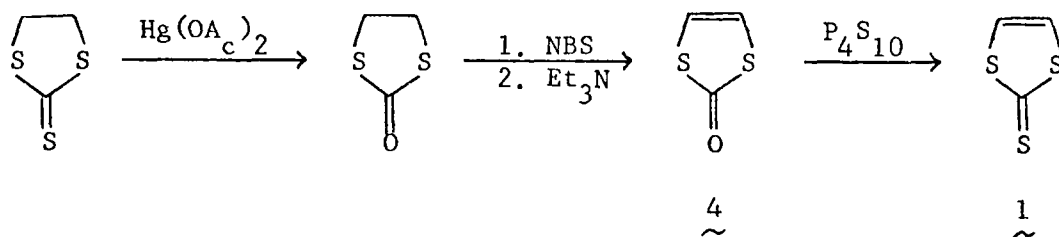
The 2-benzylidene-1,3-dithioles (12) would also possess potential "aromatic" sextet [52].



In this work, a substituted tetrathiafulvalene and a disubstituted 2-benzylidene-1,3-dithiole were prepared and condensed with difunctional compounds to prepare polymers.

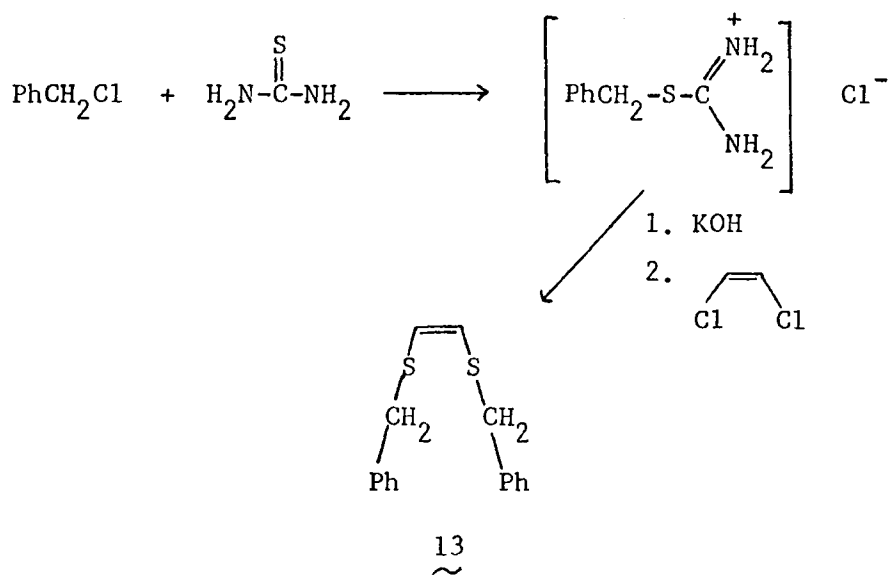
RESULTS AND DISCUSSION

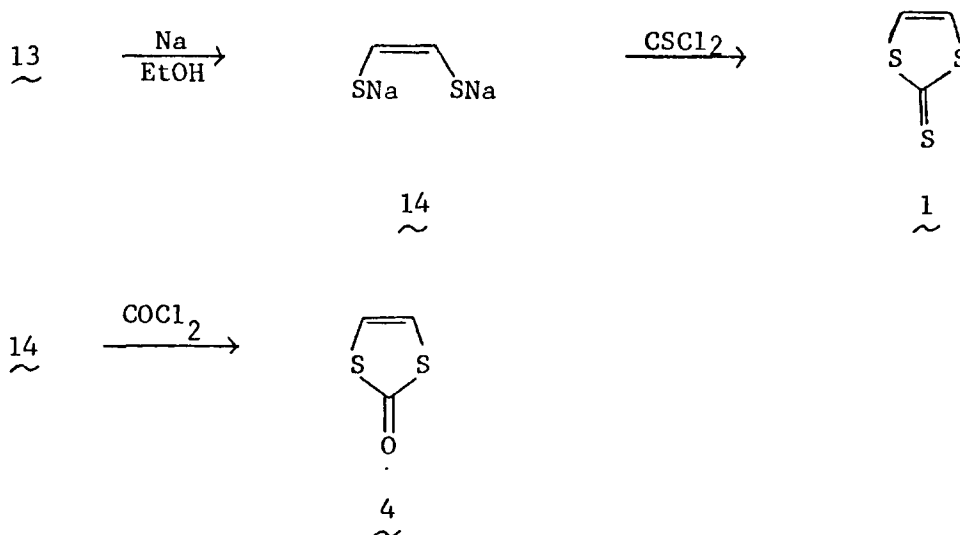
Both 1,3-dithiole-2-thione (1) and 1,3-dithiole-2-one (4) were prepared according to scheme 1 [53].



Scheme 1

However, in our hands the bromination proceeded in very low yield. A better method for the synthesis of 1 and 4 is shown in scheme 2.





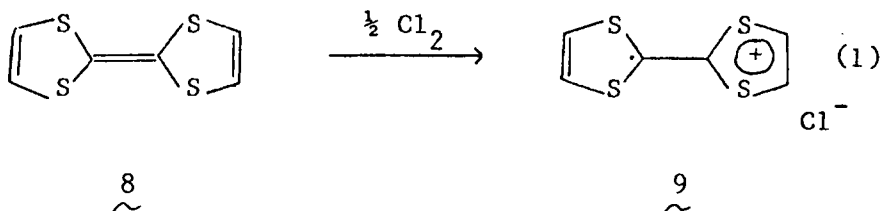
Scheme 2

The cis-dibenzyl ethylene dithioether (13) was prepared in 50% yield from benzyl chloride, thiourea, and cis-dichloroethylene, and the disodium-cis-dimercaptoethylene (14) was prepared in 97% yield from 13 according to a reported procedure [54]. Disodium-cis-dimercaptoethylene reacted with thiophosgene to give 1,3-dithiole-2-thione in 43% yield and with phosgene to give 1,3-dithiole-2-one (4) in 37% yield.

Attempted polymerizations of 1,3-dithiole-2-thione (1) using azobisisobutyronitrile (AIBN) or boron trifluoride etherate in toluene-hexane at -78° were unsuccessful. In addition an attempted copolymerization of 1,3-dithiole-2-thione with styrene using AIBN gave only polystyrene.

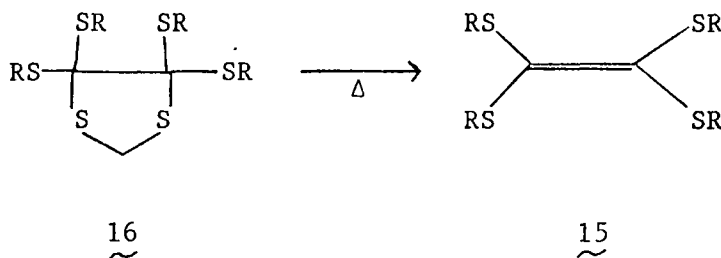
The attempted polymerization of 1,3-dithiole-2-one (4) using AIBN was unsuccessful. However, 1,3-dithiole-2-one (4) did copolymerize with methyl methacrylate using zinc chloride and AIBN. The use of Lewis acid and radical initiators in copolymerizations has been reported [55]. The copolymer contained 5 mole % of 4.

Tetrathiafulvalene (8) can be oxidized to a radical-cation (9) as shown in Equation 1. The bis-1,2-dithiolium chloride (9) was found

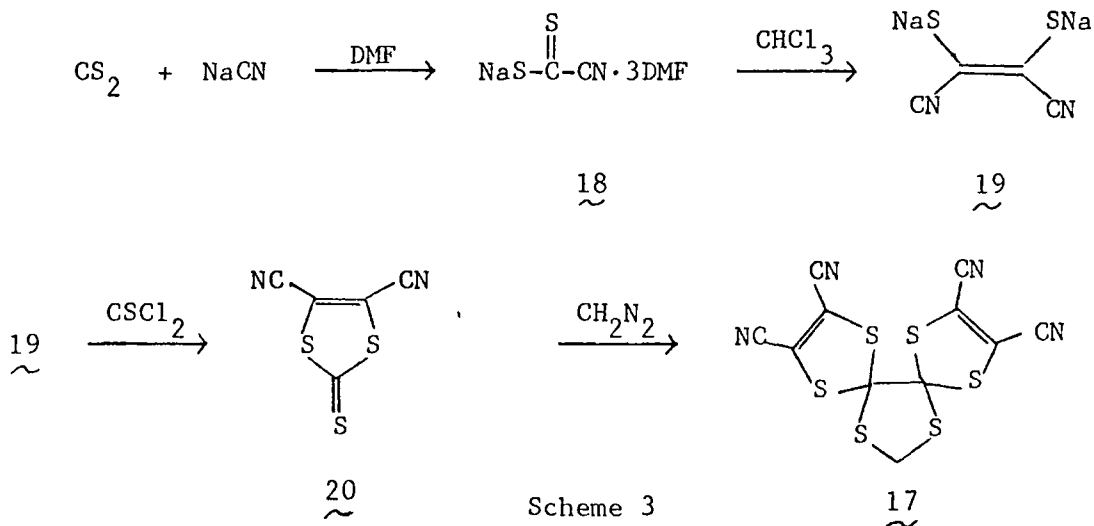


to be an excellent organic solid-state semiconductor [48], and we therefore attempted to prepare polymers containing this moiety.

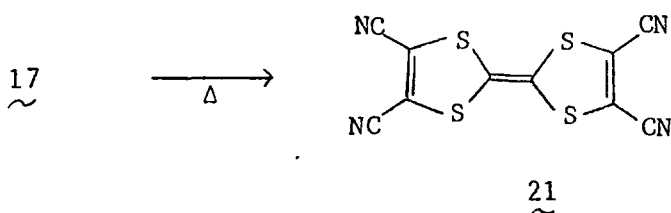
The synthesis of tetrathioethylenes (15) from orthothiooxalates (16) has been reported [50]. The preparation of 1,3-dithiolane-



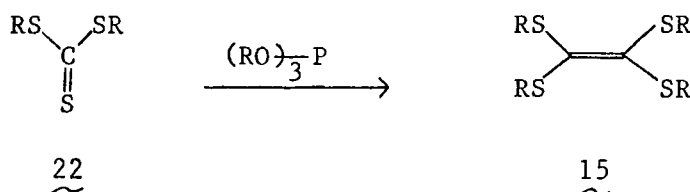
4,5-dione bis(dicyano vinylene thioketal) (17) is shown in scheme 3.



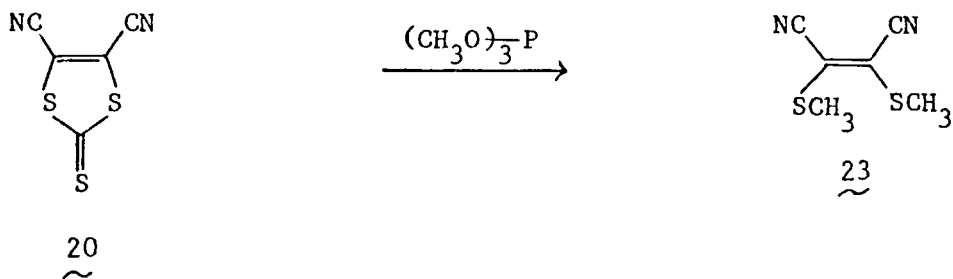
Sodium cyano dithioformate·3 dimethylformamide (18) was prepared in 96% yield from carbon disulfide and sodium cyanide. Disodium dimercaptomaleonitrile (19) was prepared in 45% yield from 18 according to reported procedures [56,57]. The compound 4,5-dicyano-1,3-dithiole-2-thione (20) was prepared in 75% yield from 19 according to Klingsberg [46]. The compound 1,3-dithiolane-4,5-dione bis(dicyano vinylene thio-ketal) (17) was prepared from 20 in 88% yield. However, the attempt to prepare 2,3,6,7-tetracyano-1,4,5,8-tetrathiafulvalene (21) by pyrolysis of 17 was unsuccessful.



The preparation of tetrathioethylenes (15) by desulfurization of trithiocarbonates (22) has been reported [58]. An attempt to desulfurize 4,5-dicyano-1,3-dithiole-2-thione (20) with trimethyl phosphite

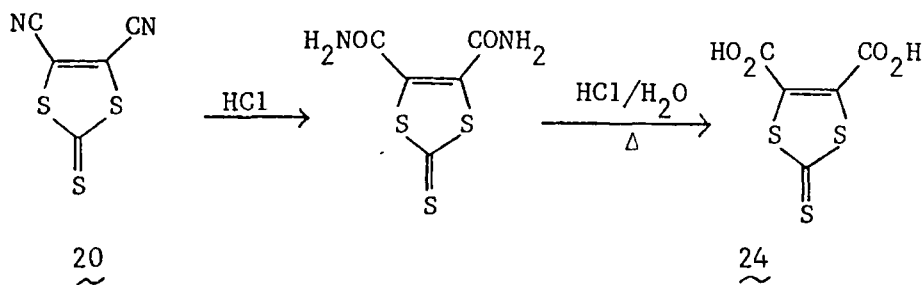


did not yield the expected tetrathioethylene but gave cis-dimethyl dimercaptomaleonitrile (23).



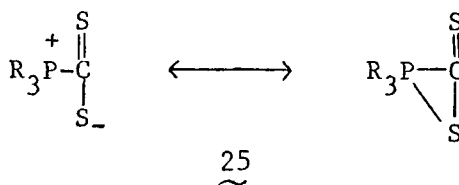
Attempts to form a Diels-Alder adduct with 4,5-dicyano-1,3-dithiole-2-thione and cyclopentadiene were unsuccessful.

The compound 1,3-dithiole-2-thione-4,5-dicarboxylic acid (24) was prepared by hydrolysis of 20 by a reported procedure [46].

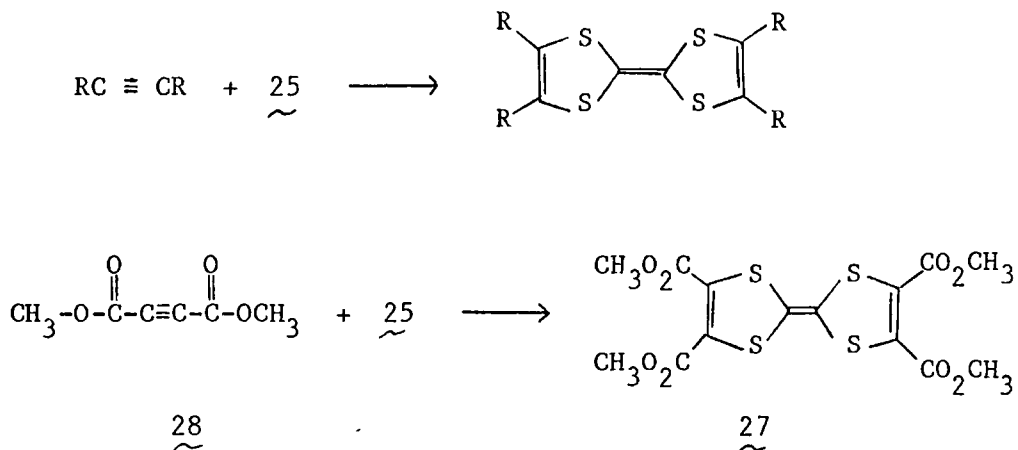


Treatment of 24 with thionyl chloride followed by an interfacial polycondensation with hexamethylenediamine gave a polymer with inherent viscosity of 0.41. The ir spectrum indicated amide formation, but showed no thiocarbonyl absorption. Analysis showed a lower per cent of sulfur than calculated for the desired polymer.

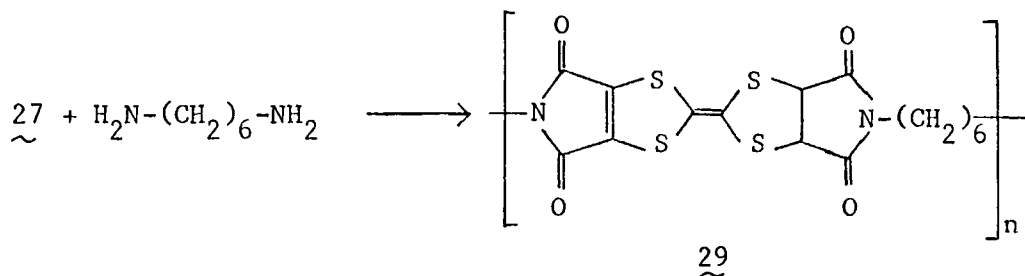
The adduct (25) of carbon disulfide and tributylphosphine reacts with acetylenes having at least one electron-withdrawing substituent to give poor yields of substituted tetrathiafulvalenes (26) [52].



The attempt to prepare 2,3,6,7-tetracarboxylic acid-1,4,5,8-tetrathiafulvalene from acetylenedicarboxylic acid was unsuccessful presumably because the carboxylic acid reacts with the ylide (25). However, 2,3,6,7-tetramethyl-1,4,5,8-tetrathiafulvalene tetracarboxylate (27) was prepared from dimethyl acetylene dicarboxylate (28) in 8% yield.



It was hoped that the treatment of 27 with hexamethylenediamine would produce a polymer (29) with tetrathiafulvalene units connected by imide linkages.



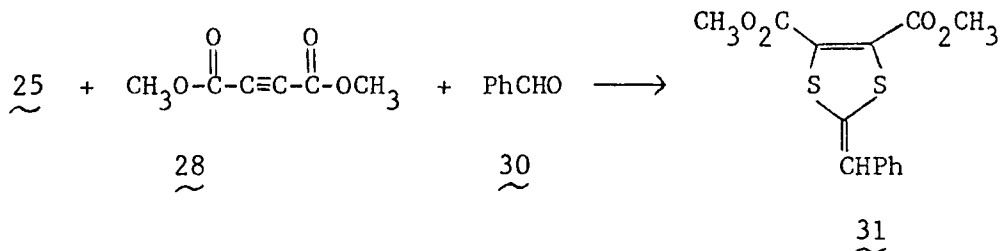
The polycondensation of (27) with hexamethylenediamine by a melt process resulted in an insoluble crosslinked polymer. When the polycondensation was carried out in dimethylformamide, a soluble polymer with inherent viscosity of 0.078 was obtained. The ir spectrum

indicated no imide formation but did show amide carbonyl. The ultraviolet spectrum did not show the expected absorptions characteristic of tetrathiafulvalenes. Also, analysis of the polymer showed a lower percent of sulfur than that calculated for the desired polymer. In addition, similar results were obtained when 27 was treated with butylamine. These results lead to the conclusion that the tetrathiafulvalene ring system is unstable to base. This conclusion is reinforced by the fact that an attempt to hydrolyze 27 with a 10% potassium hydroxide solution led to a product with a low sulfur content.

An attempt to prepare a dicarboxylated tetrathiafulvalene from ethyl propiolate, tributyl phosphine, and carbon disulfide yielded a brownish-red oil which could not be purified.

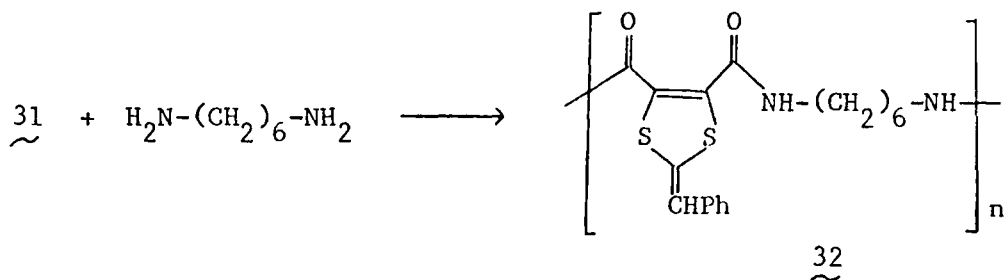
The attempt to prepare the carboxylated tetrathiafulvalene using ethyl propiolate, carbon disulfide, and trifluoroacetic acid at 100° was unsuccessful; a literature report is to the contrary [59].

The adduct (25) of carbon disulfide and tributyl phosphine reacted with dimethyl acetylene dicarboxylate (25) and benzaldehyde (30)



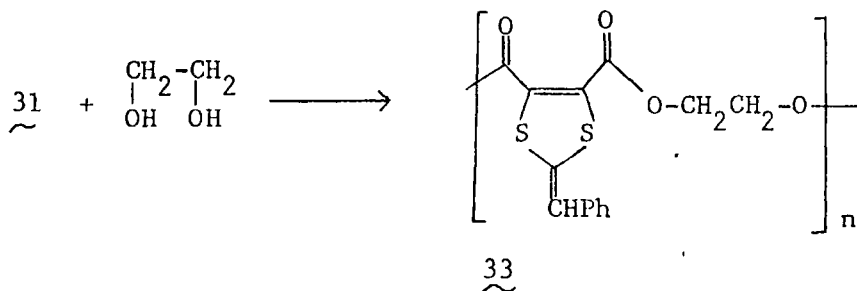
to give dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate (31) in 48% yield.

A solution polycondensation of 31 with hexamethylenediamine



gave a polymer (32) with an inherent viscosity of 0.10. The ir and nmr spectra were consistent with the polymer structure. The small discrepancy in the extinction coefficient and the analysis can be explained by the difficulty encountered in purifying the polymer. Polycondensation of 31 with hexamethylenediamine by a melt process gave a polymer that was soluble only in acidic solvents such as m-cresol and formic acid with an inherent viscosity of 1.05. Analysis of the polymer showed a low sulfur content indicating that the dithiole ring system was not preserved. The solution condensation of 31 with butylamine showed that there was no imide formation and that the dithiole ring system was preserved under the reaction conditions.

The polycondensation of 31 with ethylene glycol with



tetraisopropyl titanate and isopropoxide gave a polymer (33) with inherent viscosity of 0.015. The nmr and uv spectra were consistent with the polymer structure. By heating 33 under nitrogen to a higher temperature, the inherent viscosity was increased to 0.04.

In conclusion, monomers and polymers containing the 1,3-dithiole ring system have been prepared. Further work in the preparation of polymers with tetrathiafulvalene units is encouraged. Possibly by preparing a dicarboxylated tetrathiafulvalene, polyesters could be prepared with tetrathiafulvalene units. The results obtained in the 2-benzylidene-1,3-dithiole system are encouraging and continued effort to prepare high molecular weight polymers system should be made so that their physical properties can be determined.

EXPERIMENTAL

Materials

Sodium cyanide (Mallinckrodt Chemical Works) was dried at 100° in vacuum oven for 2 hr. Hexamethylenediamine (Matheson, Coleman, and Bell Company) was purified by sublimation. Boron trifluoride etherate (Matheson, Coleman, and Bell Company) and toluene (Matheson, Coleman, and Bell Company) were distilled from calcium hydride. Hexane (Mallinckrodt Chemical Works) was washed successively with acidic and alkaline potassium permanganate solution, washed with water, and distilled from calcium hydride. Styrene (Matheson, Coleman, and Bell Company) was washed with 5% sodium hydroxide solution, then with water, followed by drying over magnesium sulfate, and distilled under reduced pressure. Cyclopentadiene (Matheson, Coleman, and Bell Company) was purified by distillation. Dimethyl acetylene dicarboxylate (Aldrich Chemical Company) and methyl propiolate (Aldrich Chemical Company) were distilled at reduced pressure under nitrogen. Dimethylformamide (Mallinckrodt Chemical Works) was distilled from barium oxide. Zinc chloride (Mallinckrodt Chemical Works) was dried in vacuum at 240° for 20 hr. Methyl methacrylate (Matheson, Coleman, and Bell Company) was washed with 5% sodium hydroxide solution, washed with water, dried with magnesium sulfate, and distilled at reduced pressure from calcium hydride. Tetramethylene sulfone (Aldrich Chemical Company) was distilled from sodium hydroxide. Benzaldehyde (Mallinckrodt Chemical Works) was washed with 5% sodium hydroxide solution, washed with water, dried with

magnesium sulfate, and distilled at reduced pressure under nitrogen. Ethylene glycol (Matheson, Coleman, and Bell Company) was distilled from sodium. Butylamine (Matheson, Coleman, and Bell) was dried over sodium hydroxide and distilled from calcium hydride.

Diazomethane was generated from N-nitrosomethylurea by a reported procedure [37, p. 165 and p. 461]. Acetylenedicarboxylic acid was prepared by acidification of acetylene dicarboxylic acid monopotassium salt (Eastman Organic Chemicals) according to a reported procedure [60]. Ethylene trithiocarbonate was prepared from ethylene oxide by a reported procedure [61]. Ethylene trithiocarbonate (Aldrich Chemical Company) was also used without further purification. Ethylene dithiocarbonate was prepared according to reported procedure [38]. Both 4-bromo-1,3-dithiole-2-one and 1,3-dithiole-2-one were prepared in low yield according to the method of Mayer and Gebhardt [53]. The preparation of disodium dimercaptomaleonitrile [56], which was prepared from sodium cyano dithioformate.3 dimethylformamide [57], has been reported. The preparation of 4,5-dicyano-1,3-dithiole-2-thione, 1,3-dithiole-2-thione-4,5-dicarboxamide, and 1,3-dithiole-2-thione-4,5-dicarboxylic acid have all been reported [46]. Sodium isopropoxide was prepared by dissolving sodium in isopropyl alcohol and removing excess alcohol by vacuum. Disodium-cis-dimercaptoethylene was prepared from cis-dibenzyl-ethylenedithioether from a reported procedure [54]. Azobisisobutyronitrile (AIBN) (Matheson, Coleman, and Bell Company) was recrystallized from methanol.

Instrumentation

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined on a Varian model T-60 (60 MHz), a Varian model HA-100 (100 MHz) using tetramethylsilane as an internal standard. Infrared spectra were determined using a Perkin-Elmer Infracord or Perkin-Elmer model 337 Grating Infrared Spectrophotometer and calibrated with a polystyrene film. Ultraviolet and visible spectra were determined using a Cary 14 recording spectrophotometer.

Elemental Analyses

Microanalysis was determined by Micro-Tech Laboratories, Inc., Skokie, Illinois, and Huffman Laboratories, Inc., Wheatridge, Colorado.

Experimental Procedures

Preparation of 1,3-Dithiole-2-thione

A solution of 6.9 g (4.6 ml, 0.060 mol) of thiophosgene in 10 ml of benzene was added during 30 min to a suspension of 8.0 g (0.059 mol) of disodium cis-dimercaptoethylene stirred in 100 ml of benzene with ice cooling. The reaction mixture was then stirred 2 hr at room temperature, filtered, dried over sodium sulfate, and evaporated. The yield of black oil was 3.4 g (43%). Crystallization from pet ether gave yellow needles with mp 48-49° (lit [53] mp 48.5°); nmr (CDCl₃) τ 2.95 (s).

Preparation of 1,3-Dithiole-2-one

Phosgene gas was bubbled slowly into a suspension of 19.3 g (0.142 mol) of disodium cis-dimercaptoethylene stirred in 500 ml of benzene with ice cooling. After 1 hr the solution was supersaturated with phosgene, and the reaction mixture was stirred at room temperature for 1 hr. Nitrogen was then bubbled through the solution for 2 hr to remove excess phosgene. The reaction mixture was filtered and evaporated. The yield of yellow oil was 15.5 g (92.5%). Distillation from sodium borohydride gave colorless solid 6.2 g (37%) with mp 33-44° (lit [53] mp 35°); nmr (CDCl₃) τ 3.2 (s).

Attempt to Polymerize 1,3-Dithiole-2-thione Radically

A mixture of 1,3-dithiole-2-thione (0.5 g, 3.7 mmol) and AIBN (2 mg, 0.012 mmol) was degassed by freeze-thawing and heated under nitrogen at 62° for 96 hr. The reaction mixture was dissolved in chloroform, but no precipitate was obtained by addition to methanol. The nmr spectrum, τ 2.95 (s), showed that no polymer was formed.

Attempt to Polymerize 1,3-Dithiole-2-thione Cationically

A solution of 0.20 g (1.5 mmol) of 1,3-dithiole-2-thione and 10 ml of toluene-hexane (70:30 v/v) was cooled to -78° under nitrogen. Boron trifluoride etherate (9 mg) in 1 ml of toluene-hexane (70:30 v/v), previously chilled in Dry Ice-acetone, was added by syringe. After 3.5 hr an additional portion of boron trifluoride etherate was added. The reaction mixture was stirred for an additional 8 hr and evaporated.

The nmr spectrum (CDCl_3), τ 2.95 (s), of the yellow solid indicated that no polymerization occurred.

Attempt to Copolymerize 1,3-Dithiole-2-thione and Styrene

A mixture of 0.460 g (3.38 mmol) of 1,3-dithiole-2-thione, 0.720 g (6.9 mmol) of styrene, and 5 mg (0.03 mmol) of AIBN was degassed by freeze-thawing and heated to 60° for 21 hr under nitrogen. The viscous gel was diluted with chloroform and precipitated in methanol. The yield of the slightly yellow polymer was 0.5 g (70%). The color was removed by reprecipitation from chloroform into methanol. Analysis showed that the 1,3-dithiole-2-thione did not copolymerize with styrene.

Anal. Found: S, < 0.1.

Attempt to Polymerize 1,3-Dithiole-2-one Radically

A mixture of 3.0 g (25 mmol) of 1,3-dithiole-2-one and 10 mg (0.06 mmol) of AIBN was degassed by freeze-thawing and heated at 73° for 96 hr under nitrogen. The reaction mixture was diluted with chloroform, but no precipitate was obtained in methanol. The nmr spectrum, τ 3.2 (s), showed that no polymer was formed.

Copolymerization of 1,3-Dithiole-2-one and Methyl Methacrylate with Zinc Chloride

A mixture of 2.3 g (16.9 mmol) of zinc chloride, 1.70 g (16.9 mmol) of methyl methacrylate, 15 mg (0.091 mmol) of AIBN, and 20 ml of tetramethylene sulfone was stirred for 1 hr. The reaction mixture was charged with 2.0 g (16.9 mmol) of 1,3-dithiole-2-one, degassed by

freeze-thawing, and heated at 60° for 3 hr under nitrogen. Precipitation in methanol gave a colorless polymer. Analysis indicated 5 mole % of 1,3-dithiole-2-one.

Anal. Found: S, 3.0.

Preparation of 1,3-Dithiolane-4,5-dione
Bis(dicyano Vinylene Thioketal)

A slurry of 4,5-dicyano-1,3-dithiole-2-thione (15.0 g, 86 mmol) was stirred in 190 ml of ethyl ether and treated with 300 ml of freshly prepared ethereal diazomethane solution (approximately 4.5 g, 99 mmol of diazomethane) at 0°. The slurry was stirred at 0° for 2 hr and at room temperature for 22 hr. A second 300-ml portion of ethereal diazomethane solution was added and stirring continued for a further 24 hr. The reaction mixture was filtered, yielding 14.5 g (88.5%) of a yellow solid. Recrystallization from acetonitrile gave 9.2 g (63.5%) of yellow needles with mp 204-207°; ir (KBr) 2230, 1540, 1420, 1185, 1060, 890, 860, and 815 cm⁻¹; nmr (CDCl₃) τ 5.7 (s).

Anal. Calcd for C₁₁H₂N₄S₆: C, 34.50; H, 0.52; N, 14.65; S, 50.25.

Found: C, 34.64; H, 0.51; N, 14.70; S, 50.03.

Attempt to Prepare 2,3,6,7-Tetracyano-1,4,5,8-tetra-
thiafulvalene by the Pyrolysis of 1,3-Dithiolane-
4,5-dione Bis(dicyano Vinylene Thioketal)

A solution of 1,3-dithiolane-4,5-dione bis(dicyano vinylene vinylene thioketal) (0.5 g, 1.3 mmol) in 25 ml of bromobenzene was heated to reflux for 24 hr. Evaporation of the reaction mixture gave 0.5 g of a dark solid. Recrystallization from acetonitrile gave yellow

needles, mp 205-207°. The ir spectrum confirmed that it was the starting material.

Pyrolysis at higher temperatures in cis-trans decalin gave uncharacterized decomposition products.

Attempt to Prepare 2,3,6,7-Tetracyano-1,4,5,8-tetrathiafulvalene by Desulfurization of 4,5-Dicyano-1,3-dithiole-2-thione

A solution of 2.00 g (10.9 mmol) of 4,5-dicyano-1,3-dithiole-2-thione and 1.35 g (1.28 ml, 10.9 mmol) of trimethyl phosphite was heated to reflux for 1.5 hr. A 10% potassium hydroxide solution was added, and the black reaction mixture was extracted with chloroform. Evaporation of chloroform layer gave 1.0 g (63% of a dark oil). Recrystallization from methyl cyclohexane gave orange needles with mp 97-98°, nmr (CDCl₃) τ 7.35 (s); and mass spectrum 170(M⁺). Analysis confirmed the product to be cis-dimethyl dimercaptomaleonitrile (lit [62] mp 99°).

Anal. Calcd for C₆H₆N₂S₂: C, 42.3; H, 3.5; N, 16.5; S, 37.6.

Found: C, 42.5; H, 3.7; N, 16.4; S, 37.4.

Attempt to form Diels-Alder Adduct of 4,5-Dicyano-1,3-dithiole-2-thione with Cyclopentadiene

A mixture of 2.0 g (10.9 mmol) of 4,5-dicyano-1,3-dithiole-2-thione, 10 g (0.15 mol) of cyclopentadiene, and 0.25 g of copper tetrafluoroborate was stirred at 0° for 5 hr under nitrogen, then at room temperature for 14 hr. The yellow solid 2.0 g that remained was

recrystallized from ethanol giving dark yellow solid with mp 123-126°.

The nmr spectrum indicated that no Diels-Alder adduct formed.

Polycondensation of 1,3-Dithiole-2-thione-4,5-dicarboxylic Acid with Hexamethylenediamine

A solution of 0.500 g (2.25 mmol) of 1,3-dithiole-2-thione-4,5-carboxylic acid, 10 ml of thionyl chloride, and 5 ml of benzene was heated to reflux for 1.5 hr. The solvent and excess thionyl chloride were removed by vacuum distillation. The yellow solid was dissolved in 35 ml of chloroform and added to a solution (0.50 g, 4.3 mmol) of hexamethylenediamine, 90 mg (2.5 mmol) of sodium hydroxide, and 20 ml of water in a Waring blender. After stirring for 4 min a dark brown insoluble solid was removed from the reaction mixture which was insoluble in most organic solvents, but soluble in m-cresol. Precipitation in methanol gave 0.8 g (80%) of a light tan solid. The inherent viscosity was 0.41 (0.48 g/100 ml of m-cresol at 37°).

Anal. Calcd for $C_{11}H_{14}N_2O_2S_3$: N, 9.3; S, 31.7.

Found: N, 13.3; S, 16.2.

Attempt to Prepare 2,3,6,7-Tetracarboxylic Acid-1,4,5,8-tetrathiafulvalene

A similar reaction has been reported [52], but the experimental conditions were not given. A solution of 2.0 g (17.5 mmol) of acetylenedicarboxylic acid in 20 ml of ethyl ether was added during 20 min to 3.6 g (17.5 mmol) of tri-n-butylphosphine, 1.33 g (17.5 mmol) of carbon disulfide, and 10 ml of ethyl ether under nitrogen at -23°. The dark red color from the phosphine carbon disulfide complex was discharged.

The reaction mixture was filtered yielding 5.4 g of a pink solid. Crystallization from ethanol gave pale yellow crystals with mp 129-131° dec. The nmr spectrum and ir spectrum indicated the absence of a carboxylic acid. No further characterization was made.

Preparation of 2,3,6,7-Tetramethyl-
1,4,5,8-tetrathiafulvalene
Tetracarboxylate

A solution of 2.0 g (0.014 mol) of dimethyl acetylene dicarboxylate in 15 ml of ethyl ether was added during 5 min to a solution of 2.85 g (0.014 mol) of tri-n-butyl phosphine, 1.07 g (0.014 mol) of carbon disulfide, and 20 ml of ethyl ether at -23° under nitrogen. The reaction mixture was stirred at -23° for 4 hr, and then 14 hr at room temperature. The resulting dark oil was diluted with 30 ml of ethyl ether. Filtration gave 150 mg of a brown solid and crystallization of the filtrate from ethanol gave an additional 100 mg of brown solid. The yield was 250 mg (8.2%). Recrystallization from ethanol gave brownish-red crystals with mp 171-172°; nmr (CDCl₃) τ 6.2 (s); ir (KBr) 1710, 1690, 1550, 1410, 1280, 1240, 1090, 1020, 970, 910, 770, 750, and 710 cm⁻¹; $\lambda_{\text{max}}^{\text{EtOH}}$ 440 nm (ϵ 2100), 315 nm (ϵ 13,400), 280 nm (ϵ 12,500), 222 nm (ϵ 11,200).

Anal. Calcd for C₁₄H₁₂O₈S₄: C, 38.5; H, 2.8, S, 29.4.

Found: C, 38.2; H, 2.8; S, 29.6.

Attempted Preparation of Diethyl-
1,4,5,8-tetrathiafulvalene
Dicarboxylate

A solution of 5.0 g (0.05 mol) of ethyl propiolate in 12 ml of ethyl ether was added during 10 min to a solution 10.3 g (0.051 mol) of tri-n-butyl phosphine, 3.88 g (0.051 mol) of carbon disulfide, and 50 ml of ethyl ether at -23° under nitrogen. The reaction mixture was stirred at -23° for 4.5 hr, then at room temperature for 14 hr. The resulting oil was diluted with 50 ml of ethyl ether, but filtration did not produce a solid. Attempts to purify the oil failed. The mass spectrum did show a parent peak with a mass number of 348 which corresponds to the desired product.

Attempt to Prepare Diethyl-
1,4,5,8-tetrathiafulvalene
Dicarboxylate

The preparation of substituted tetrathiafulvalenes has been reported [59], but experimental conditions were not given. A solution of 4.85 g (0.0495 mol) of ethyl propiolate, 3.76 g (0.0495 mol) of carbon disulfide and 1.45 g (0.013 mol) of trifluoroacetic acid was sealed in a tube under vacuum. The reaction mixture was heated at 100° for 22 hr. The nmr spectrum (neat) τ 5.9 (quartet, 2H), τ 7.0 (s, 1H), and τ 8.8 (triplet, 3H) indicated that the compound was starting material. The same reaction was also tried with a trace of trifluoroacetic acid at 158° for 70 hr without positive results.

Preparation of Dimethyl-
2-benzylidene-1,3-dithiole-
4,5-dicarboxylate

The preparation of 2-benzylidene-1,3-dithioles has been reported [52], but the experimental procedure was not given. Dimethyl acetylene dicarboxylate (7.0 g, 0.049 mol) was added during 10 min to a solution of 10.0 g (0.049 mol) of tri-n-butyl phosphine, 3.7 g (0.049 mol) of carbon disulfide, 5.2 g (0.049 mol) of benzaldehyde, and 14 ml of ethyl ether at -23° under nitrogen. A red-orange solid 7.2 g (48%) precipitated from solution. Recrystallization from ethanol gave red-orange needles with mp $97-98^{\circ}$; ir (KBr) 1740, 1720, 1590, 1550, 1500, 1440, 1350, 1240, 1100, 1020, 1000, 930, 850, 820, 780, 760, 755, and 690 cm^{-1} ; nmr (CDCl_3) τ 2.8 (mult, 5H), τ 3.6 (s, 1H), and τ 6.2 (s, 6H); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 410 nm (ϵ 1600), 328 nm (ϵ 16,400), and 245 nm (ϵ 14,000).

Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_4\text{S}_2$: C, 54.5; H, 3.9; S, 20.8.

Found: C, 54.5; H, 4.02; S, 21.2.

Polycondensation of 2,3,6,7-Tetramethyl-
1,4,5,8-tetrathiafulvalene Tetracarboxylate
with Hexamethylenediamine by a Melt Process

A solution of 0.201 g (0.45 mmol) of 2,3,6,7-tetramethyl-1,4,5,8-tetrathiafulvalene tetracarboxylate, 0.0072 g (0.62 mmol) of hexamethylenediamine, and 4 ml of dimethylformamide was heated to 118° for 70 hr under nitrogen. The solvent was removed by vacuum leaving a dark, gummy solid which was dissolved in chloroform and precipitated into methanol giving 150 mg (75% of a dark brown solid). The ir spectrum (KBr) showed broad carbonyl bands at 1690 and 1650 cm^{-1} . The nmr

spectrum (CDCl_3) showed τ 6.2 (mult, 4H) and τ 8.5 (mult, 3H); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 300 (s) nm (ϵ 3300), 240 nm (ϵ 4000). The inherent viscosity was 0.078 (0.30 g/100 ml of chloroform at 30°).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2\text{S}_4$: N, 6.6; S, 30.2.

Found: N, 5.2; S, 20.3.

Condensation of 2,3,6,7-Tetramethyl-1,4,5,8-tetrathiafulvalene Tetracarboxylate with Butylamine

A solution of 0.200 g (0.45 mmol) of 2,3,6,7-tetramethyl-1,4,5,8-tetrathiafulvalene tetracarboxylate, 0.076 g (0.65 mmol) of butylamine, and 3 ml of dimethylformamide was heated at 118° for 70 hr under nitrogen. The solvent was removed by vacuum leaving a dark oil. The oil was dissolved in chloroform, washed with water, dried over sodium sulfate, and evaporated; ir (CCl_4) 3200 (w), 300 (s), 1730 (s), 1650 (m), 1550 (s), 1450 (s), 1260 (s), 1100 (m), and 1020 (m) cm^{-1} ; nmr (CDCl_3) τ 6.3 (mult), τ 8.5 (mult), and τ 9.1 (mult); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 295 nm (ϵ 17000), and 235 (ϵ 17000).

Hydrolysis of 2,3,6,7-Tetramethyl-1,4,5,8-tetrathiafulvalene Tetracarboxylate

A mixture of 0.100 g of 2,3,6,7-tetramethyl-1,4,5,8-tetrathiafulvalene, 2 g of potassium hydroxide, and 10 ml of water was heated to reflux for 4 hr. Acidification of the clear orange solution with hydrochloric acid gave a purple solid: nmr (d_6 -DMSO) τ 2.2 broad; ir 3200 (broad) and 1680 cm^{-1} .

Anal. Calcd for $C_{10}H_4O_8S_4$: C, 31.6; H, 1.05; S, 33.7.

Found: C, 34.9; H, 1.4; S, 12.9.

Polycondensation of Dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate with Hexamethylenediamine by a Solution Process

A solution of 1.00 g (3.25 mmol) of dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate, 0.380 g (3.25 mmol) of hexamethylenediamine, and 5 ml of dry toluene was stirred at room temperature for 4 hr under nitrogen, then heated at 75° for 16 hr. The toluene was distilled off and gave a dark brown solid: nmr ($CDCl_3$) τ 2.75 (mult, 5H), τ 3.7 (s, 1H), τ 5.9 (s, 1H), τ 5.5 (mult, 4H), and τ 8.5 (mult, 8H); ir (KBr) and 3200 and 1630 cm^{-1} ; $\lambda_{\text{max}}^{CHCl_3}$ 400 (s) nm (ϵ 1200), 328 nm (ϵ 6500), and 245 nm (ϵ 12000). The inherent viscosity was 0.10 (0.60 g/100 ml of dimethylformamide at 30°).

Anal. Calcd for $C_{18}H_{20}O_2N_2S_2$: N, 7.8; S, 17.8.

Found: N, 8.5; S, 14.2.

Polycondensation of Dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate with Hexamethylenediamine by a Melt Process

A mixture of 0.50 g (1.62 mmol) of dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate and 0.190 g (1.62 mmol) of hexamethylenediamine was heated at 200° for 24 hr under vacuum. The dark solid was insoluble in chloroform, dimethylformamide, dimethylsulfoxide, but was soluble in m-cresol: ir (KBr) 3200 , 1690 , and 1630 cm^{-1} . The inherent viscosity was 1.05 (0.21 g/100 ml of m-cresol at 30°).

Anal. Calcd for $C_{18}H_{20}O_2N_2S_2$: C, 60.0; H, 5.5; N, 7.8; S, 17.8.

Found: C, 65.1; H, 7.1, N, 9.8, S, 8.0.

Condensation of Dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate with Butylamine

A solution of 0.700 g (2.27 mmol) of dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate, 332 mg (4.54 mmol) of butylamine, and 4 ml of toluene was stirred at room temperature for 4 hr, then 75° for 16 hr under nitrogen. The toluene was distilled off leaving a dark red oil: ir (CCl_4) 3200, 1700, and 1640 cm^{-1} ; nmr ($CDCl_3$) τ 2.75 (mult, 3H), τ 3.6 (s, 0.5H), τ 5.9 (s, 0.5H), τ 6.2 (s, 1H), τ 6.6 (mult, 4H), τ 8.5 (mult, 4H), and τ 9.1 (mult, 3H); $\lambda_{max}^{CHCl_3}$ 410 (s) nm (ϵ 1300), 328 nm (ϵ 10500), and 240 (s) nm (ϵ 13000).

Polycondensation of Dimethyl-2-benzylidene-1,3-dithiole-4,5-dicarboxylate with Ethylene Glycol

A similar polycondensation has been reported [33, p. 133]. A mixture of 0.850 g (13.8 mmol) of ethylene glycol, 1.921 (6.25 mmol) of dimethyl-2-benzylidene-1,3-dithiole-4,5-carboxylate, 4 mg of isopropoxide, and 4 mg of tetraisopropyl titanate was heated at 170° for 3 hr under nitrogen, then at 195-200° for 2.5 hr. Precipitation from dimethylformamide into methanol gave a brown-orange solid: nmr ($CDCl_3$) τ 2.75 (mult, 5H), τ 3.6 (s, 1H), and τ 5.6 (s, 4H); $\lambda_{max}^{CHCl_3}$ 400 nm (ϵ 2500), 328 (ϵ 17000), and 245 nm (ϵ 12000). The inherent viscosity was 0.015 (0.50 g/100 ml of dimethylformamide at 30°).

Anal. Calcd for $C_{18}H_{20}O_2S_2$: C, 55.0; H, 3.3; S, 20.9.

Found: C, 55.5; H, 5.5; S, 23.3.

Polycondensation of Poly(ethylene-
2-benzylidene-1,3-dithiole-
4,5-dicarboxylate)

Poly(ethylene-2-benzylidene-1,3-dithiole-4,5-dicarboxylate)
(0.50 g, 1.62 mmol) from above was heated at 210° for 3 hr under nitro-
gen, then at 220 for 0.5 hr, followed by 235° for 1 hr. Precipitation
from chloroform into methanol gave a brown solid: ir 1700 cm⁻¹; nmr
(CDCl₃) τ 2.75 (s, 5H), τ 3.6 (s, 1H), and τ 5.6 (s, 4H); λ_{max}^{CHCl₃} 3400 nm
(ε 2400), 328 nm (ε 12600), and 245 nm (ε 11800). The inherent vis-
cosity was 0.04 (0.50 g/100 ml of dimethylformamide at 30°).

Anal. Calcd for C₁₄H₁₀O₄S₂: C, 55.0; H, 3.3; S, 20.9.

Found: C, 54.3; H, 3.4; S, 23.5.

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