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(2) The polymer samples were obtained from Polysciences, Inc., Warrington, Pa.
(3) The ir absorption patterns of the polymer films agree with that of 2,2′,4,4′-tetramethylglutaric anhydride in which case the 1800-cm^{-1} absorption is weaker than the 1757-cm^{-1} peak, quite different from those of pivalic anhydride. This observation does not exclude the presence of several percent of the interchain anhydride linkage. An ammonia treatment of the polymer films yielded exactly the same ir absorption spectra with those of poly(dimethacrylimide) and poly(diacrylimide), reported by G. Schröder, *Makromol. Chem.*, **96**, 227 (1966).
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(6) Another possibility for these ir absorptions could be trapped carbon monoxide in the films. However, this possibility is rejected because of the following reasons: (1) the temperature of the sodium chloride plate in the low-temperature photolysis was measured to be −100°C, which was much higher for entrapment of carbon monoxide as reported by O. L. Chapman, C. L. McIntosh, and L. L. Barber, *Chem. Commun.*, 1162 (1972); (2) if they were due to carbon monoxide, its amount trapped in the films less than 10^{-2} cm thick as studied here must have been 10^{-5} mol/cm^2, exceeding the strength of the polymer films; (3) the different wave numbers, 2125 and 2145 cm^{-1}, indicate different chemical structures; (4) after the reaction with methanol no carbon monoxide was detected.
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Synthesis of Tetrathiafulvalene-Containing Polyamides

C. U. PITTMAN, Jr.,* M. NARITA, and Y. F. LIANG

Department of Chemistry, University of Alabama, University, Alabama 35486. *Received December 8, 1975*

Molecular charge-transfer complexes of tetrathiafulvalene (TTF)[1-3] or its selenium analogue, tetraselenafulvalene (TSeF),[4] with tetracyanoquinodimethane behave electrically and optically like one-dimensional metals at room temperature. Recently, these "organic metals" were reviewed by Garito and Heeger.[5] Because of their high conductivity at room temperature[1,2] ($\sigma > 10^2$ ohm^{-1} cm^{-1} have been observed) and the fact that the complex of hexamethylenetetraselenafulvalene–tetracyanoquinodimethane remains a conductor down to 0.006 K,[6] derivatives of TTF and TSeF have attracted wide attention.

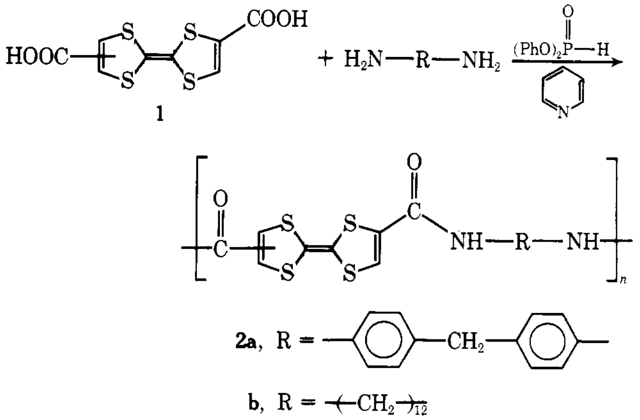
It was of interest to prepare polymers containing the TTF group in order to see (a) if TCNQ complexes could be made and (b) if such polymeric complexes were semiconductors. At the start of this work no polymers of TTF had been reported in the open literature.[7] One TTF polymer was since prepared in a polycoupling process by Okawara et al.[8] We have just reviewed, comprehensively, the preparative methods for TTF and TSeF derivatives.[9]

The high anisotropic conductivity of the TCNQ complexes of TTF has been attributed to the regular parallel stacking of TCNQ and TTF molecules in crystals of this complex.[1-3,5] It was not considered possible to maintain such regular stacking in polymeric complexes. However, even if the conductivity of polymeric complexes was five orders of magnitude less than TTF–TCNQ itself, this would give a useful semiconductor. The preparation of semiconducting polymers has been a continuing goal in our laboratory.[10,11]

Polycondensation of Tetrathiafulvalene-4,4′(5′)-dicarboxylic Acid (TTF-diacid), 1, with Diamines

The TTF-diacid, 1, and a diamine could be converted to a salt for pyrolytic polycondensation. However, it was reported that the pyridine salt of TTF-diacid, **1**, was thermally unstable at 240 °C where decarboxylation resulted in the formation of tetrathiafulvalene.[12] Thus the direct polycondensation of the diacid, **1**, with diamines was effected using diphenyl phosphite–pyridine as a dehyration reagent.[13]

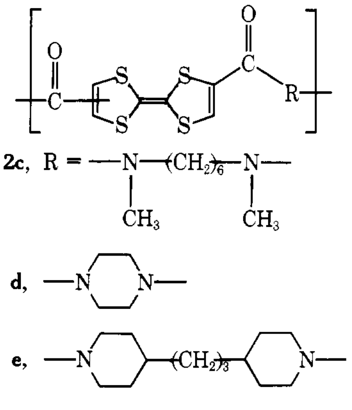
Scheme I



Successful polycondensation of diacid **1** with both aryl and alkyl diamines was readily effected in *N,N*-dimethylformamide (DMF) at 70 °C using the diphenyl phosphite–pyridine reagent. Representative polymers are shown in Scheme I. The major problem encountered was the poor solubility of the resulting polymers, **2.** Trifluoroacetic acid and hexamethylphosphortriamide (HMPA) were fairly good solvents, but other solvents were unsatisfactory.

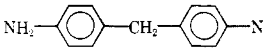
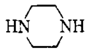
In an attempt to generate more soluble polymers, bis(secondary)amines such as *N,N′*-dimethyl-1,6-hexanediamine, 4,4′-trimethylenepiperizine, and piperazine were used. Polymerization took place to produce polymers **2c** and **2d**, but **2e** was not obtained. Instead, diacid **1** was recovered in this case. The solubility of the polymers **2c** and **2d** was still poor. The results of polycondensation reactions and the solubility of the polyamides **2** are shown in Tables I and II.

The elemental analyses of polymers **2a–d** were in good agreement with their calculated values. Ir spectra of polymers **2a** and **2b** show peaks at 1630 and 1550–1540 cm^{-1} attributed to amide I and amide II bands. Ir spectra of polymers **2c** and **2d** also showed a peak at 1650–1630 cm^{-1} due to amide groups. The spectra also contained bands at 840–820, 765–775, and 730 cm^{-1} which are characteristic of the disubstituted TTF nucleus.[8,12]



Polytransesterification has been briefly studied, but high molecular weight polymers have not yet been prepared due to thermal instability of the TTF nucleus at higher temperatures. The TTF bisanhydride, prepared from acetic anhy-

Table I
Results of Polycondensation of Tetrathiafulvalene-4,4′(5′)-dicarboxylic Acid with Diamines

Diamines	Yield, %	Polymer	η_{inh}	Anal. (Calcd), % C	H	N
	68	**2a**	0.34[a]	55.53 (55.48)	3.64 (3.10)	6.16 (6.16)
$NH_2—(CH_2)_{12}—NH_2$	43	**2b**	0.31[a]	51.25 (52.60)	6.31 (6.18)	5.78 (6.13)
$NH(CH_3)—(CH_2)_6—NHCH_3$	52	**2c**	0.30[a]	47.59 (47.97)	5.41 (5.03)	7.49 (6.99)
	35	**2d**	0.21[a,b]	43.18 (42.08)	2.70 (2.94)	8.42 (8.18)

[a] In trifluoroacetic acid. [b] Polymer was not completely soluble. [c] In DMSO.

Table II
Solubility of Polyamides of Tetrathiafulvalene[e]

Polymer	CF_3COOH	HMPA[a]	DMF[b]	DMSO[c]	pyridine	THF[d]
2a	◎	○	△	△	X	X
2b	◎	△	X	X	X	X
2c	◎	○	△	X	X	X
2d	△	X	X	X	X	X
2e	○	◎	◎	◎	◎	○

[a] HMPA: hexamethylphosphoroamide. [b] DMF: *N,N′*-dimethylformamide. [c] DMSO: dimethyl sulfoxide. [d] THF: tetrahydrofuran. [e] ◎, readily soluble; ○, soluble; △, partially soluble; X, insoluble.

dride and TTF-diacid,[14] **1**, was also unsatisfactory for use in polycondensation with diols because the carbonyl group adjacent to the methyl group was preferentially attacked and diacid **1** was recovered.[14]

The formation of TCNQ complexes of TTF-amide polymer **2a** was then attempted. To the solution of TTF-amide polymer **2a** in hexamethylphosporamide (HMPA) was added the solution of TCNQ in HMPA. The mixture was poured into acetonitrile, but the complex of **2a** with TCNQ was not obtained, and polymer **2a** was recovered. Several other such attempts on polymers **2a–d** and on model TTF-diamides were also unsuccessful. Apparently the electron withdrawing amide functions prevent complex formation. Since 2,3-dichloro-5,6-dicyanoquinone (DDQ) is a stronger oxidizing agent than TCNQ, attempts were made to form complexes of **2a** and DDQ. However, even in refluxing HMPA, DDQ and **2a** did not react to form complexes. Furthermore, the diamide formed from **1** and aniline was inert to DDQ in acetonitrile or HMPA.

Experimental Section

Polycondensation of the TTF-Diacid (1) with Diamines. To equimolar amounts of diacid **1**[15] (0.585 g, 20 mmol) and a diamine (2.0 mmol) suspended in DMF (20 ml) was added pyridine (5 ml) and diphenyl phosphite (1.404 g, 6.0 mmol). The reaction mixture was kept at 70 °C for 10 h under continuous stirring. In the case of bis(secondary)amines, the reaction was continued for 48 h. The reaction mixture gradually became homogeneous (except for polymer **2e**). The polymer was collected by pouring the reaction mixture into methanol, filtering, washing with methanol, and drying under vacuum. The polymer was purified by reprecipitation using HMPA–methanol or formic acid–methanol.

The results are summarized in Table I.

Attempts to form TCNQ or DDQ Complexes. To a hot HMPA (10 ml) solution of **2a** (0.0227 g) was added an equivalent volume of a DDQ (0.0136 g) solution in HMPA. The reaction mixture was refluxed 10 min, after which cooling and removal of solvent in vacuo gave a residue. The ir spectrum of the residue was identical with a physical mixture of **2a** and DDQ. Upon washing the residue with methanol and drying, polymer **2a** was recovered (0.0158 g). Similar reactions of **2a** with TCNQ resulted only in the recovery of **2a**.

In this work, DMF and HMPA had been distilled from molecular sieves under nitrogen after first deoxygenating via nitrogen purging. Center distillation cuts were used. Pyridine was distilled from calcium hydride under nitrogen.

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