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PHOTO- AND SEMI-CONDUCTING MATERIALS

by

Daniel Ming Chang

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 7 4

THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Daniel Ming Chang
entitled Photo- and Semi-conducting Materials

be accepted as fulfilling the dissertation requirement of the
degree of Doctor of Philosophy

J. Mulvaney 8/29/74
Dissertation Director Date

After inspection of the final copy of the dissertation, the
following members of the Final Examination Committee concur in
its approval and recommend its acceptance:*

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SIGNED:

Walter M. Chang

To My Wife and My Parents

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ABSTRACT

Photoconductive copolymers containing N-vinylcarbazole and electron acceptors such as β -hydroxyethyl 3,5-dinitrobenzoate, β -(2,4-dinitrophenoxy)propionate, and p-chloranil were synthesized. The absorption spectra of these intramolecular charge-transfer complex polymers were reported. Water soluble or dispersible copolymers containing N-vinylcarbazole were also synthesized by copolymerization of N-vinylcarbazole and water soluble monomers such as sodium N-acryloylsulfanilate, sodium p-styrenesulfonate, N,N,N-trimethyl-N-(p-vinylbenzyl)ammonium chloride (TVBA), and N,N,N-triethyl-N-[2-(methacryloxy)-ethyl]ammonium iodide.

Substituted 2-benzylidene-1,3-dithioles and their charge-transfer complexes were synthesized. The ir, nmr, uv, visible, near ir and esr spectra of these complexes were also reported. Electric resistance of the TCNQ-2-benzylidene-4,5-diphenyl-1,3-dithiole complex measured by the two-probe method was found to be between 10^{10} and 10^{11} ohm-cm. Free radical and cationic polymerizations of these 2-(p-vinylbenzylidene)-1,3-dithioles yielded only low molecular weight polymers. A polymer containing 2-(p-vinylbenzylidene)-1,3-dithiole repeating units was prepared by chemical modification of the poly(p-vinylbenzaldehyde). The polymer doped with 20% p-chloranil showed a resistance of 10^5 ohms determined on a 0.1 mil thick, 2 inch long disc by the two-probe method.

INTRODUCTION

One of the most interesting and useful problems of modern synthetic organic chemistry is to develop new materials possessing photo- or semi-conducting properties. Organic compounds or polymers containing charge-transfer complexes have been recently shown to be photo- or semi-conducting materials. Their applications¹ include electronic reproduction of images, radioelectronic materials, active media for lasers, etc.

Metals, semiconductors, and insulators can be classified by differences in resistivities (Figure 1).² The resistivity, r , is calculated by

$$r(\text{ohm-cm}) = R \frac{A}{L}$$

where R is the measured resistance (ohms), A is the cross sectional area (cm^2), and L is the length of the sample in the direction of the current flow (cm).

Conductivity, σ , is the reciprocal of resistivity. Relatively reliable resistivity data are determined on a single crystal. However, in the case of amorphous materials, measurements can be made on a compact disc.

The electric conduction mechanism is explained most satisfactorily by the band theory.³ In the solid state, there are closely spaced energy levels. The higher band is called the conduction band,

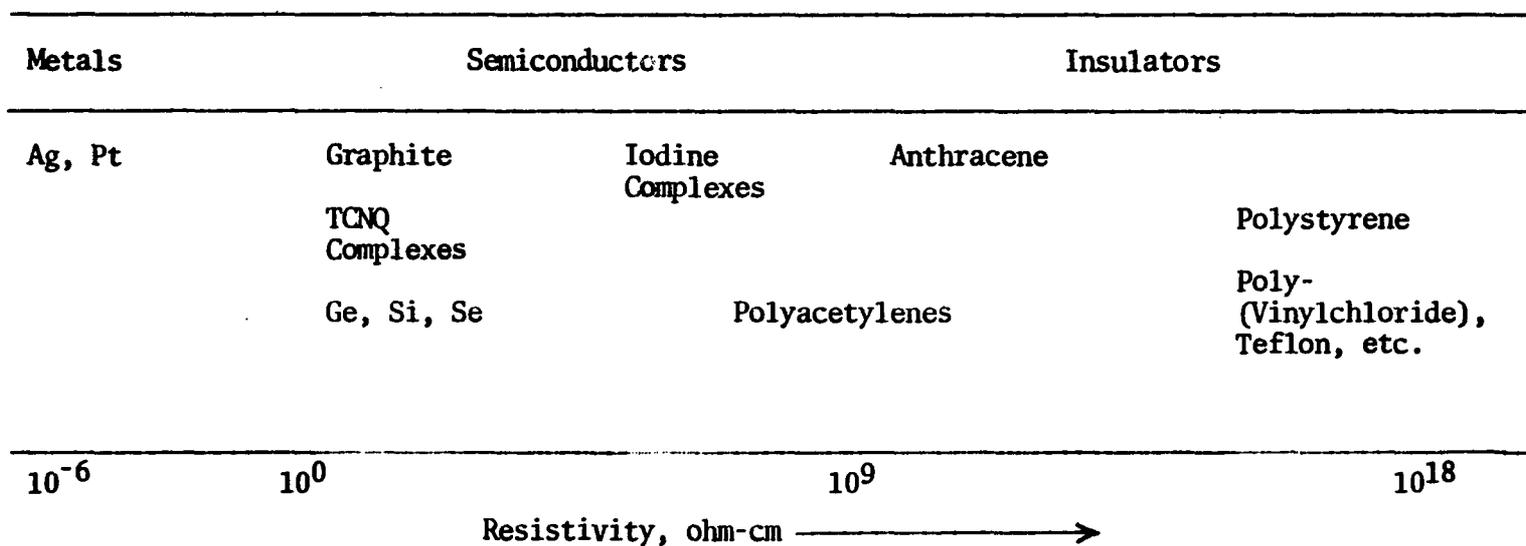


Figure 1. Resistivities of metals, semiconductors, and insulators.²

and the lower, the valence band. The energy gap between the two bands is the activation energy for conduction (Figure 2).

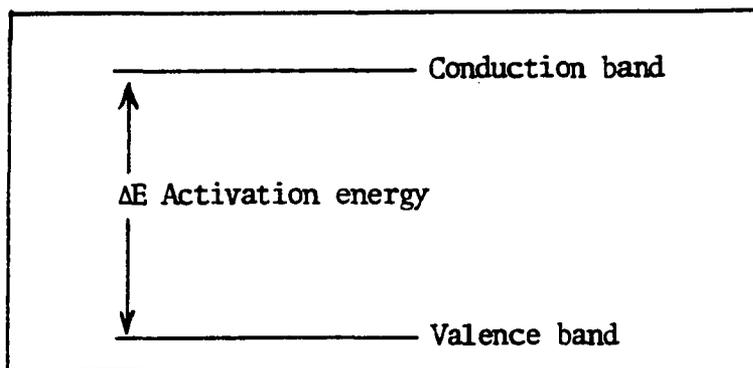


Figure 2. Energy bands in a solid.

In insulators, the valence band is full, and the energy gap is large. It is difficult for an electron to jump from the valence band to the conduction band. In metals, the conduction band is partially filled, and electrons in the conduction band can move relatively freely when an electric field is applied. In semiconductors, the valence band is full, and the conduction band is empty, but the energy gap is small enough that an electron can jump to the conduction band by absorption of energy from the electric field creating a carrier (hole or electron) for conduction. In photoconductors, the energy source for the electronic transition is the photon.

There are two methods for measuring the resistivity of an organic semiconductor as described below:

1. The two probe method--A voltage is applied to the sample and the current is measured in the external circuit (Figure 3).⁴ R_x is the sample resistance and S is a switch. The resistance can be

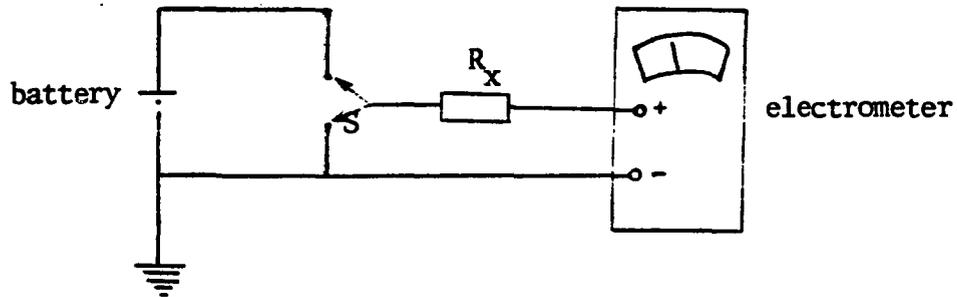


Figure 3. Electrical circuit for the two-probe method.

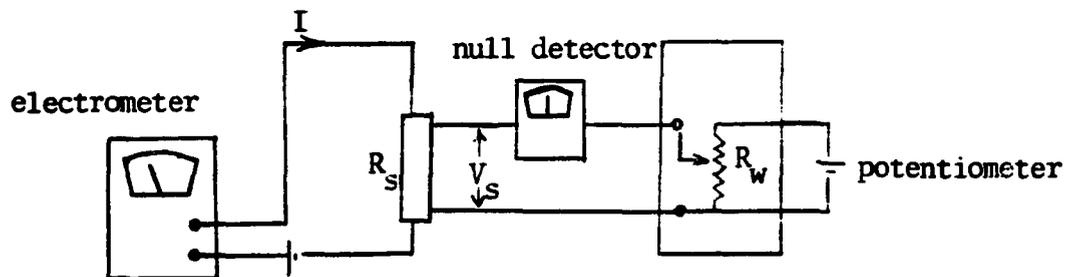


Figure 4. Electrical circuit for the four-probe method.

calculated from Ohm's law. However, the resistance measured by this simple method is the sum of the sample resistance and the contact resistance. The formation of good contacts is always difficult.

2. The four-probe method (Figure 4)⁵--Difficulties arising from the contacts can be overcome in this method. R_w is a variable resistance and R_s is the sample resistance. R_w can be changed until there is no current flowing through the null detector and V_s can be measured from the potentiometer. Since there is no current flowing through the null detector the contact resistance can be eliminated. From the current (I) and V_s , R_s can be calculated from Ohm's law.

The photoconductivities were evaluated from the current vs. time curve or the voltage vs. time curve^{6,7} (Figures 5 and 6). The RC time, the half-life ($t_{1/2}$), and the time at $V = 0$ ($t_{V=0}$) are referred to as the coating speed or photoresponse. The RC (a product of resistance and capacitance) time is the time measured from the peak current to the point on the curve where current is 0.37 or $1/e$ of the peak current at constant voltage. The half-life is the time to reach $1/2$ maximum voltage, and the time at $V = 0$, the time to reach zero voltage.

There are several types of organic semiconductors. They are classified below:⁸

1. Molecular crystals--They are usually large aromatic molecules such as anthracene ($r = 10^9$ - 10^{22} ohm-cm at room temperature depending on the purity and the method of measurement).

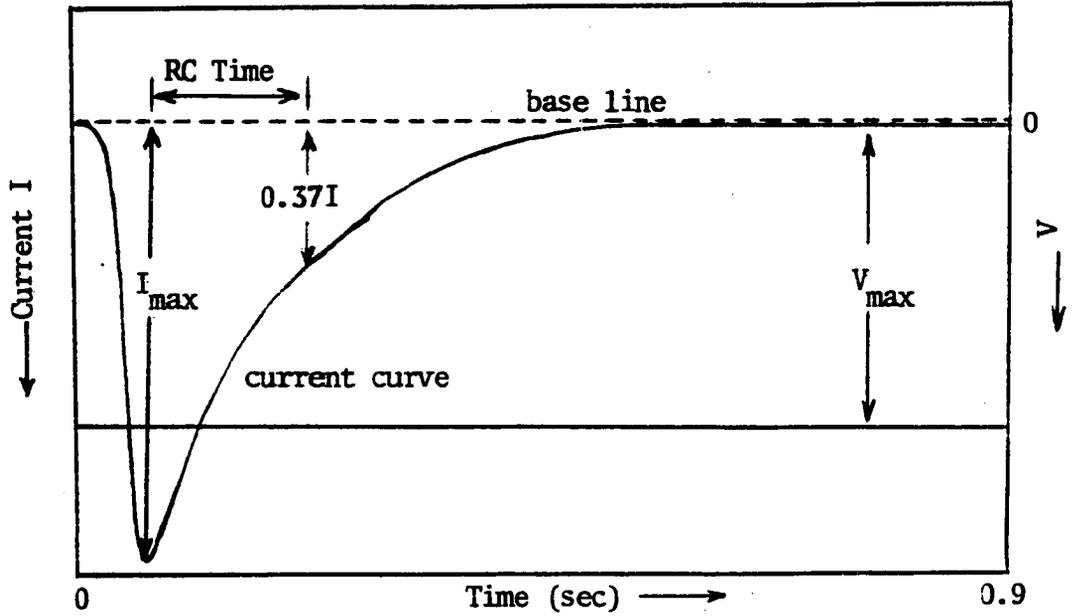


Figure 5. Current-time curve in measuring the photoconductivity.

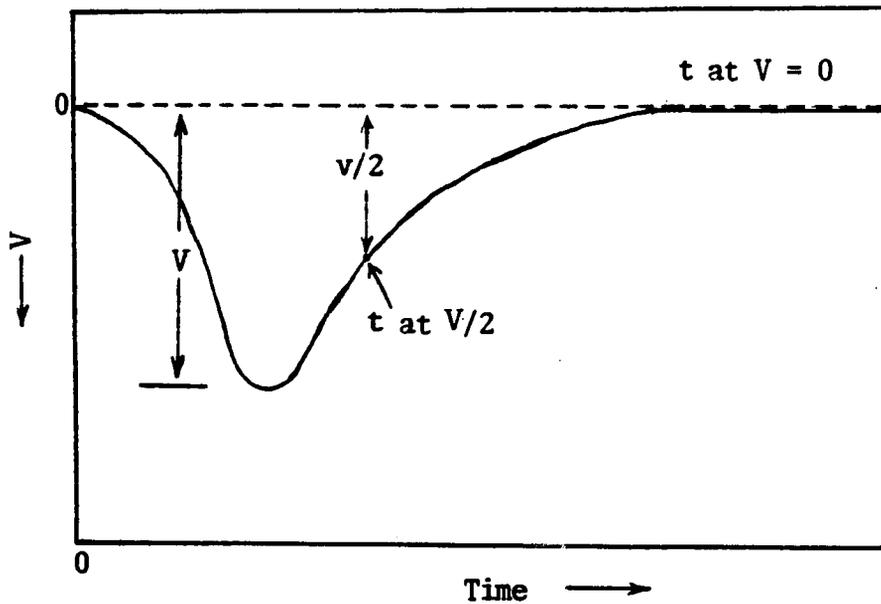


Figure 6. Voltage-time curve in measuring the photoconductivity.

2. Charge-transfer complexes--Complexes formed from an electron donor and an electron acceptor such as diaminodurene-p-chloranil ($r = 10^4$ ohm-cm at room temperature).
3. Polymers of conjugated double bond systems--such as polyacetylene ($r = 10^4$ - 10^{12} ohm-cm at room temperature).
4. Complex metal compounds--such as Cu-phthalocyanine ($r = 10^{11}$ ohm-cm at room temperature).

Of the several types of semiconductors listed above, the charge-transfer complexes are one of the best.

Dewar, cited by Foster⁹, described the charge-transfer complexes by using a simple molecular orbital description (Figure 7). For a single charge-transfer band, or for the lowest-energy charge-transfer band in π - π complexes, the electron transfer is generally referred to as transfer of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. The formation of a charge-transfer complex induces a new low energy excited state into the complex. The electronic transition from ground state to the new low energy excited state can be achieved by absorption of light at lower wavelength than the donor or the acceptor, usually in the visible or infrared region of the absorption spectrum. This broad absorption band is called a charge-transfer band (CT band). Table 1 shows absorption bands of some charge-transfer complexes. When there is only a very weak interaction between the donor and the acceptor of a charge-transfer complex, no CT band is observed. However, the intensities of the absorption bands of the two components

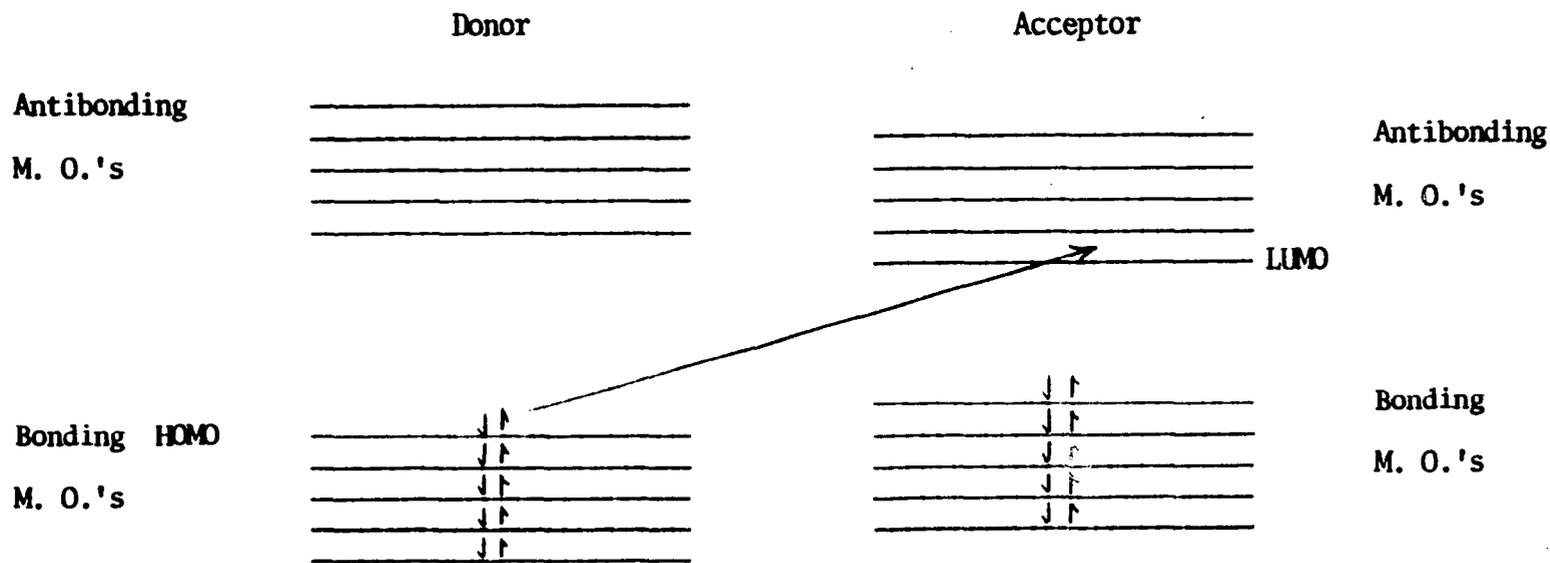


Figure 7. Lowest charge-transfer transition from HOMO of the donor to the LUMO of the acceptor.

Table 1. CT bands of some charge-transfer complexes.

Donor	Acceptor	λ_{max} (nm)	Solvent	Reference
N-ethylCbz ^a	p-chloranil	525	CH ₂ Cl ₂	10
Poly(N-vinylCbz) ^a	"	590	"	11
"	"	574	C ₆ H ₆	12
Anthracene	"	607	CHCl ₃	13
N,N-dimethylaniline	"	654	CH ₂ Cl ₂	14
Phenothiazine	"	789	CH ₃ CN	15
Thioanisole	TCNE ^b	573	CH ₂ Cl ₂	16
Cbz ^a	"	610	CHCl ₃	11
N-ethylCbz ^a	TCNQ ^c	590	CH ₂ Cl ₂	10
Poly(N-vinylCbz) ^a	"	610	"	10
10-Methylphenothiane	"	990	C ₆ H ₅ Cl	17
Et ₃ N	"	842 420	CH ₃ CN	18
10-Methylphenothiane	TNF ^d	570	C ₆ H ₅ Cl	17
Anthracene	"	541	CHCl ₃	19
Pyrene	"	520	"	19
Naphthalene	"	430	"	19

a. Cbz = Carbazole

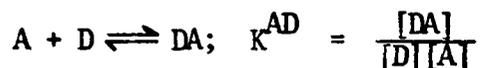
b. Tetracyanoethylene

c. Tetracyanoquinodimethane

d. 2,4,7-Trinitro-9-fluorenone

are increased. Poly(N-vinylcarbazole)-picric acid complex¹² is such a case.

In solution, a charge-transfer complex will dissociate and the following equilibrium is established:



The equilibrium constant and molar extinction coefficient can be evaluated by the Benesi-Hildebrand equation²⁰:

$$\frac{[A]_0}{A'} = \frac{1}{K^{AD} \epsilon^{AD}} \frac{1}{[D]_0} + \frac{1}{\epsilon^{AD}}$$

where ϵ^{AD} is the molar extinction coefficient of the charge-transfer complex (DA), $[D]_0$ and $[A]_0$ represent the total, free and complexed, concentration of D and A respectively, and A' is the absorbance of the CT band. The plot of $[A]_0/A'$ against $[D]_0^{-1}$ should be linear. The slope is equal to $(\epsilon^{AD} K^{AD})^{-1}$ so that K^{AD} may be evaluated, and the intercept of the straight line with the vertical axis is $(\epsilon^{AD})^{-1}$.

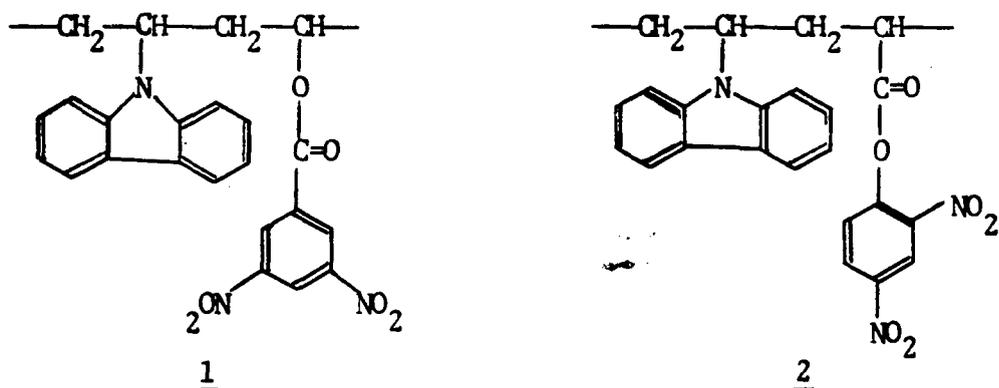
Due to the change in the electronic environment in the formation of a charge-transfer complex, peaks in the nmr spectrum may be shifted, compared to that of the two individual components. A maximum upfield shift of 7.1 cps was observed²¹ in the spectrum of the hexamethylbenzene-TCNQ complex in 1,4-dioxane. When the charge-transfer interaction becomes stronger, the upfield shift becomes less. Hanna and Ashbaugh²¹ explained that the ring current of the donor made the TCNQ protons shift upfield and alteration of the paramagnetic contribution to the acceptor

made the TCNQ protons shift downfield. The observed chemical shift is a result of the interplay of these two factors. A series of complexes may be made in which the chemical shift begins upfield, goes through zero, and ends as a downfield shift, as the DA interaction becomes stronger.

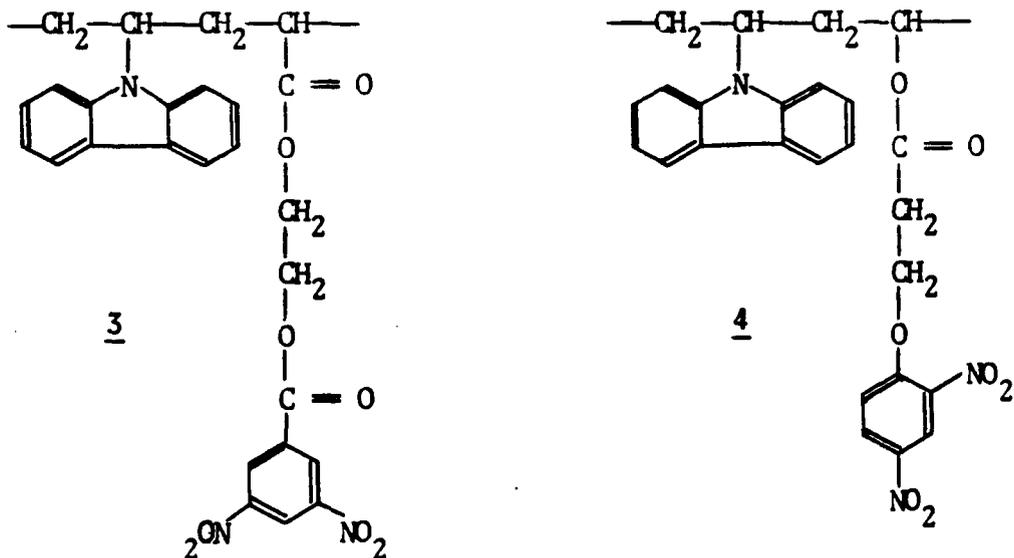
Sensitization or doping refers to the addition of a small amount of impurities to the host substance. Hoegl²² found that polymers with aromatic or heteroaromatic groups such as poly(N-vinylcarbazole) to be photoconducting. This photoconductivity could be enhanced by the addition of electron acceptors such as aromatic nitro compounds, cyano compounds, and quinones by forming a charge-transfer complex.

Poly(N-vinylcarbazole) has been used as a light-sensitive and photoconductive layer for electrophotography²³ and xerographic plates of photoconductive fibers.²⁴ However, a drawback is that the polymers are brittle (softening point 205°). The flexibility of poly(N-vinylcarbazole) might be increased by copolymerization of the N-vinylcarbazole with a "soft" monomer without affecting its photoconductivity. Photoconductivity might be enhanced by copolymerization of N-vinylcarbazole with an electron poor monomer. Acrylophenone and α -methylacrylophenone are chosen as comonomers in this work.

Copolymers 1 and 2 were synthesized previously.^{25,26}



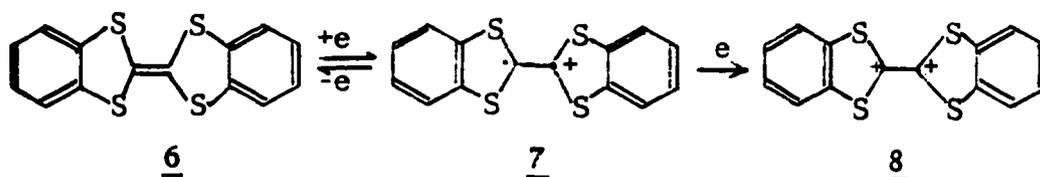
The photoconductivity of copolymer 1 (RC time 0.16-0.24 sec) is better than poly(N-vinylcarbazole) (RC time 0.3 sec, doped with 10% p-chloranil)²⁵, and copolymer 2 (no photoresponse) is a poor photoconductor.²⁶ The 3,5-dinitrobenzoate group is a better electron acceptor than the 2,4-dinitrophenoxy group. Insertion of the $-\text{CO}-\text{O}-\text{CH}_2\text{CH}_2-$ group or $-\text{O}-\text{CO}-\text{CH}_2\text{CH}_2-$ group between the polymer backbone and the electron acceptor might provide better flexibility to enhance the charge-transfer formation. In order to investigate this, copolymer 3 and 4 were synthesized.



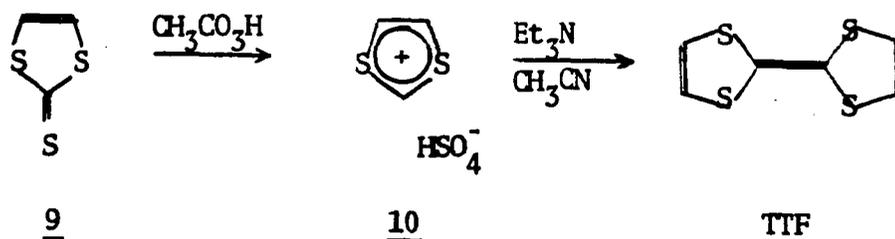
Poly(N-vinylcarbazole) doped with p-chloranil (10 wt %) showed better photoconductivity than undoped polymer (RC time 1.0 sec).²⁵ In order to compare the photoconductivity of the poly(N-vinylcarbazole) doped with p-chloranil and chemically bonded p-chloranil, copolymer 5 was also synthesized.

The development of water soluble or dispersible photoconductive materials is of particular importance because of the pollution problems presented in coating and casting by the use of organic solvents. By copolymerization of N-vinylcarbazole with water-soluble monomers such as sodium N-acryloylsulfanilate and sodium p-styrenesulfonate, water soluble or dispersible photoconductors might be prepared and this was investigated.

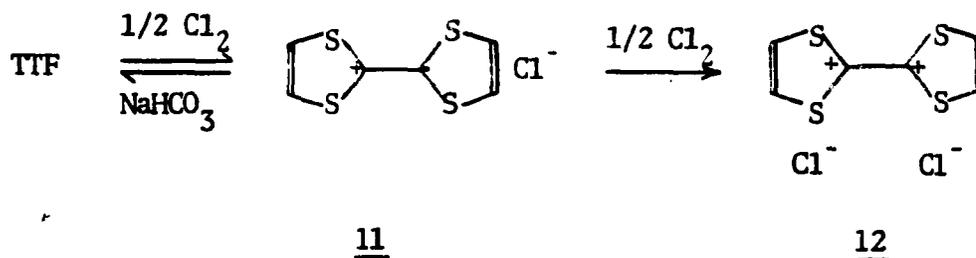
The cation-radical of a tetrathioethylene was first detected in 1969²⁷ by the reversible oxidation of 6 to the cation radical 7 which can be further oxidized to the dication 8. However, not until 1970 was a stable radical cation isolated and characterized. Klingsberg²⁸



treated 1,3-dithiole-2-thione 9 with peracetic acid to give 1,3-dithiolium hydrogen sulfate 10. Deprotonation²⁹ of 10 gave tetrathiafulvalene (TTF) in 50% yield, which was readily photo-oxidized in the presence



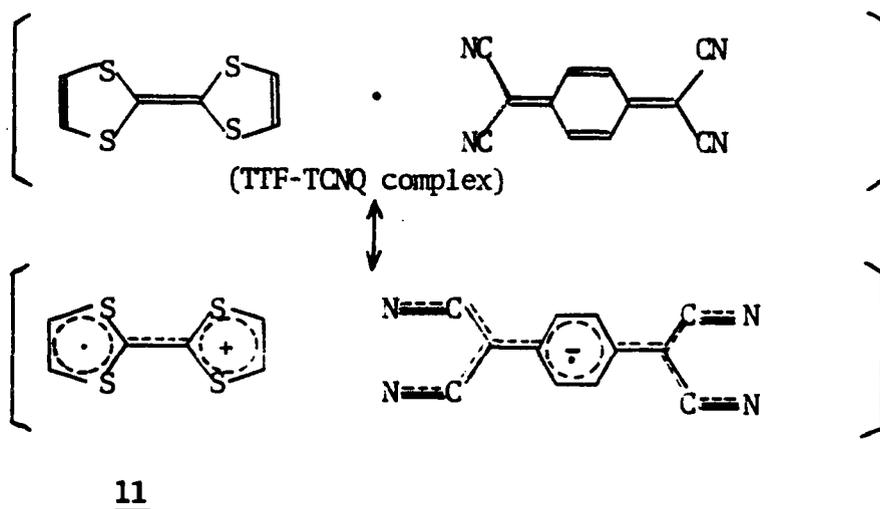
of air to the cation radical 11. 11 was also prepared by the oxidation of TTF with chlorine in carbon tetrachloride. 11 can be further



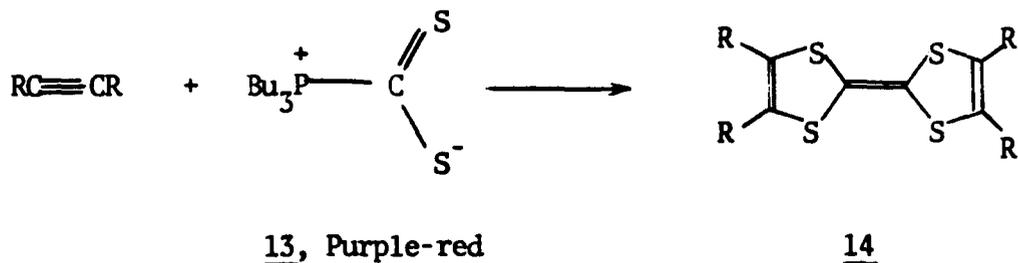
oxidized to 12 by adding an excess of chlorine. The esr spectrum of 11 in water-acetonitrile showed a quintet ($a_{\text{H}} = 1.26 \pm 0.02$, $g = 2.00838$). In 1972, Wudl, Wobschall and Hufnagel³⁰ also reported that TTF was a semiconductor at room temperature in the dark ($r = 10^{12}$ ohm-cm) and 11 was an excellent organic solid-state semiconductor at room temperature ($r = 3.7 \pm 1$ ohm-cm).

TTF-TCNQ charge-transfer complex³¹ was found to be a superconductor at 66°K ($r = 6.8 \times 10^{-5}$ ohm-cm) and a good conductor at room temperature ($r \sim 7.4 \times 10^{-3}$ ohm-cm). The "superconductivity" is a matter of some dispute. Heeger et al., cited by Metz³², found only three of

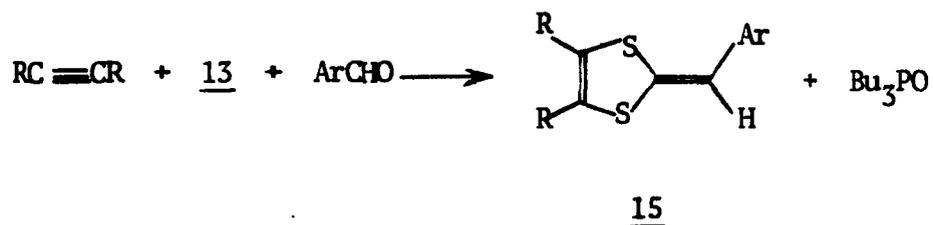
seventy crystals to be superconductive, and others have not been able to reproduce this experiment. TCNQ anion radical complexes, known as good semiconductors, contain one dimensional conducting chains of face to face stacked TCNQ groups³³. Presumably both the cation radical and the dication are stabilized by the aromatic 6π -electron structure of the heterocyclic rings.



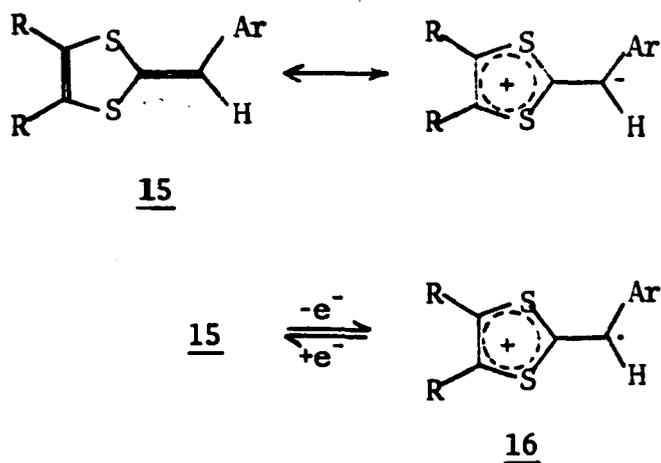
The adduct 13 of carbon disulfide and tri-*n*-butylphosphine reacted with acetylenes having at least one electron-withdrawing substituent at -30°C to give poor yields of substituted tetrathiafulvalenes 14.



However, excellent yields of 2-benzylidene-1,3-dithioles 15 were obtained in the presence of aromatic aldehydes.³⁴



Dithioles such as 15 might be oxidized reversibly to give a cation radical stabilized by the six π -electrons of the dithiole ring.



In this work monomeric and polymeric substituted 2-benzylidene-1,3-dithioles and tetrathiafulvalenes were prepared in order to evaluate them as semiconducting or photoconducting materials.

RESULTS AND DISCUSSION

Photoconductive Polymers

The flexibility of the chains of the poly(N-vinylcarbazole) can be improved by copolymerization. N-Vinylcarbazole was copolymerized in the presence of the weak electron acceptor such as methyl methacrylate without any initiator to give a high molecular weight copolymer at the early stage.³⁵ Acrylophenone and α -methylacrylophenone are weak electron acceptors. Attempts have been made to copolymerize N-vinylcarbazole with acrylophenone or α -methylacrylophenone under nitrogen at room temperature in the dark and in the absence of any added initiator with THF as the solvent even up to 20 hr failed to yield any polymer.

Acrylophenone, a very reactive monomer, can be polymerized^{36,37} or copolymerize with radical initiation with maleic anhydride³⁸ and styrene³⁹ to give polymers of intrinsic viscosities 0.2-0.5. Copolymerizations of acrylophenone (AP) and N-vinylcarbazole (VCbz) with AIBN yielded copolymers of various compositions (Table 2). Sample DC-I-15 doped (10% by wt.) with p-chloranil showed an RC time of 0.28 sec, which is comparable to that of poly(N-vinylcarbazole) (RC time 0.3 sec doped with 10% p-chloranil).

Mulvaney, Dillon and Laverty⁴⁰ reported that no polymer was obtained by radical polymerization of α -methylacrylophenone with temperatures ranging from -50 to 100°C. However some Diels-Alder dimer (head to head structure) 17 was isolated. α -Methylacrylophenone was

Table 2. Radical copolymerization of AP and VCbz.

Sample No.	AP in feed (mmol)	VCbz in feed (mmol)	Temp. (°C)	Time (hr)	THF (ml)	Conv. (wt%)	AP in copolymer (mole%) ^a	η_{inh} ^b
DC-I-19	10	1 ^c	27	17	10	15	94	0.28
DC-I-18	10	1 ^c	27	20	10	27	94	-
DC-I-14	20	20 ^d	27	25	20	23	70	-
DC-I-13	20	20 ^d	30	26	20	38	67	0.48
DC-I-16	1	10 ^c	27	5.3	10	2.2	54	-
DC-I-15 ^e	1	10 ^c	30	17	10	13	48	0.46

a. Copolymer compositions were calculated from the nitrogen analyses.

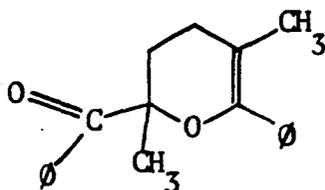
b. Viscosities were determined in benzene.

c. AIBN (azobisisobutyronitrile) 1% to monomers.

d. AIBN (0.5% to monomers).

e. Sample sent to Sherwin-Williams Company.

copolymerized with N-vinylcarbazole using AIBN to give a copolymer containing 21 mole % α -methylacrylophenone with $n_{inh} = 0.13$ at 6.6% conversion.



17 ($\emptyset = C_6H_5$)

The inherent viscosity of the acrylophenone polymerized by lithium at room temperature is about one-tenth of that of the polymer obtained from radical polymerization.^{36,39} Lithium metal initiated copolymerization of acrylophenone and N-vinylcarbazole yielded largely homopolyacrylophenone (Table 3). Because this is a heterogeneous polymerization, the results depend on the surface area of the lithium metal and reproducibility is poor.

Anionic copolymerization of methyl methacrylate and styrene gave a copolymer consisting of a block of methyl methacrylate and a block of styrene.^{41,42} The initial copolymer formed by heterogeneous propagation is largely styrene. Styrene, containing a larger cloud of π -electrons than methyl methacrylate, was preferentially adsorbed on the lithium metal surface which is slightly positive. N-Vinylcarbazole contains a larger cloud of π -electrons than styrene. However, copolymerization of acrylophenone and N-vinylcarbazole initiated by lithium

Table 3. Lithium metal initiated copolymerization of acrylophenone and N-vinylcarbazole.^a

Sample No.	Li (mmol)	Time (hr)	Conversion (% by wt)	AP in Copolymer (% by mole) ^b	η_{inh}^c
DC-I-11	1.3	1.5	32	97.74	0.067
DC-I-10	1.3	3	26	98.14	0.068
DC-I-8	1.1	5	28	96.52	0.069
DC-I-1	1.1	46	28	97.18	-
DC-I-19	1.1	100	28	81.20	-

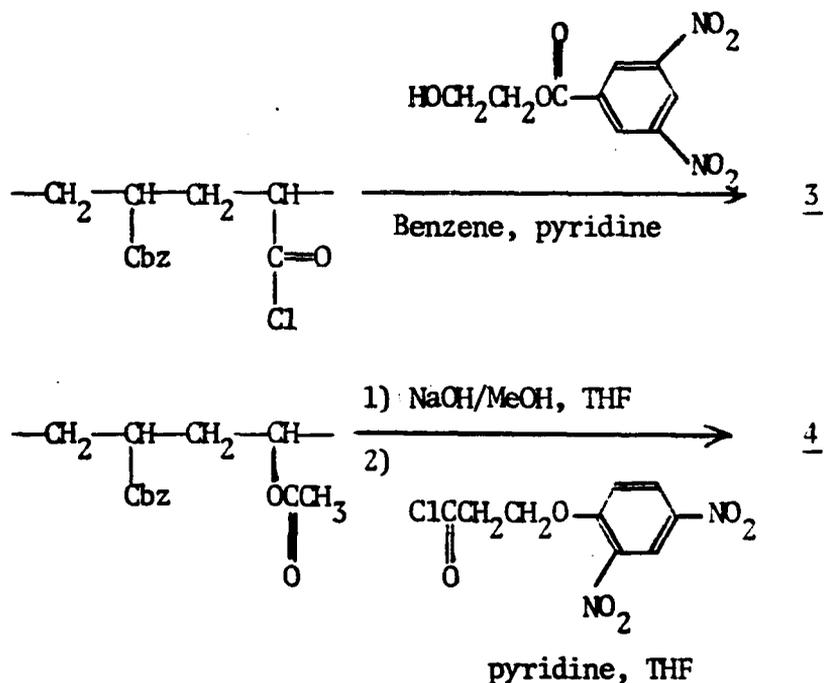
a. 10 mmol AP + 10 mmol VCbz + Li + 10 mmol THF.

b. Calculated from the nitrogen analyses.

c. Viscosities were determined in benzene.

dispersion in wax yielded homo polyacrylophenone instead of a block copolymer (Table 4).

Copolymers 3 and 4 were synthesized by the following schemes.



β -Hydroxyethyl 3,5-dinitrobenzoate (HDND) was prepared by direct esterification of 3,5-dinitrobenzoic acid in excess ethylene glycol as solvent. Copoly(N-vinylcarbazole-acryloyl chloride) was prepared by copolymerization of N-vinylcarbazole and freshly distilled acryloyl chloride in benzene with AIBN as initiator (Table 5). Copolymer 3, a yellow polymer, contained 9-13 mole % of HDNB.

It was reported that no charge-transfer band was found when equivalent amounts of picric acid and poly(N-vinylcarbazole) were mixed in sym-dichloroethane. Only an increase in absorbance at 343 nm was

Table 4. Copolymerization of AP and VCbz by lithium dispersion in wax.^a

Sample No.	THF (ml)	Time (min)	Conversion (wt %)	AP mole % in Polymer ^b
DC-I-35 ^c	10	60	35	98.9
DC-I-37	5	20	32	-
DC-I-42	5	9	10	99.31
DC-I-40	5	8	22	98.2
DC-I-41	5	3.5	0	-

a. 10 mmol AP + 10 mmol VCbz + 0.5 mmol Li-dispersion.

b. Calculated from nitrogen analyses.

c. Inherent viscosity, 0.1 in benzene.

Table 5. Synthesis of copolymer 3.^a

Sample No.	VCbz (mmol)	Acryloyl Chloride (mmol)	HDNB ^b (mmol)	Time (hr)		HDNB in Copolymer (mole%)	η_{inh} ^c
				Room Temp.	Reflux		
DC-III-78	10	5	5.1	15	1	9.8	0.13
DC-III-77 ^d	10	10	11	15	1	13.2	0.15
DC-III-82 ^{d,e}	10	15	7.8	2	1	11.3	0.15
DC-III-83 ^e	10	20	7.8	2	1	11.4	0.14

- a. Monomers + AIBN (0.1% mole) in 10 ml of dry benzene were refluxed 24 hr under nitrogen.
- b. Pyridine (3 ml) as base to trap hydrogen chloride.
- c. Viscosities were determined in THF.
- d. Samples sent to Sherwin-Williams Co.
- e. Excess acryloyl chloride was swept out with nitrogen.

observed¹². Table 6 presents the absorption spectra of copolymer 3 and poly(N-vinylcarbazole)-HDNB charge-transfer complexes.

Sample DC-III-82A showed a RC time of 0.37 sec which is comparable to that of the p-chloranil-doped poly(N-vinylcarbazole), but worse than the copolymer 1. Contrary to part of our proposal, the insertion of the $-\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-$ group between the polymer backbone and the 3,5-dinitrobenzoate might reduce the charge-transfer formation.

β -(2,4-Dinitrophenoxy)propionic acid was prepared⁴³ by reacting 2,4-dinitrophenol with β -propiolactone, and β -(2,4-dinitrophenoxy)-propionyl chloride was prepared from the acid and thionyl chloride in 81% yield. Copoly(N-vinylcarbazole-vinyl alcohol) was prepared by copolymerizing N-vinylcarbazole and vinyl acetate with AIBN in benzene or toluene at 60°C followed by hydrolysis with 1 N NaOH (in methanol) in THF as solvent (Table 7). Copolymer 4 was synthesized by reacting copoly(N-vinylcarbazole-vinyl alcohol) with β -(2,4-dinitrophenoxy)propionyl chloride (DNPP) in pyridine-benzene or pyridine-THF (Table 8).

The copolymer 4 has a sharp strong carbonyl band in the ir spectrum indicating that the reaction between β -(2,4-dinitrophenoxy)propionyl chloride and copoly(N-vinylcarbazole-vinyl alcohol) was almost complete. However, a weak nitro band at 1520 cm^{-1} in the ir, and a low nitrogen content were observed. The elimination of 2,4-dinitrophenol might have occurred by the following reaction.

Table 6. Absorption spectra of poly(N-vinylcarbazole)-HDNB complexes.

Sample	$\lambda_{\text{max}}^{\text{THF}} (\epsilon)$
HDNB	343 (2840) 370 (950)
Poly VCbz	343 (2930) ^a 400 (70) ^a
Poly VCbz + HDNB (1:1)	343 (3370) ^a 370 (215) ^a
Poly VCbz + HDNB (10:1)	343 (3180) ^a 370 (48) ^a
DC-III-77	343 (3100) ^a 370 (150) ^a
DC-III-82	343 (3005) ^a 370 (260) ^a
DC-III-78	343 (3340) ^a 370 (125) ^a

a. ϵ_{max} were calculated based on the poly VCbz concentrations.

Table 7. Preparation of copoly(VCbz-VOH).

Sample	Copoly(VCbz-VOAc) (g)	THF (ml)	VOAc (mmol)	NaOH (mmol)	Reflux (hr)	VCbz in Copolymer (mole%) ^a
RR-68 ^b	RR-64 (5)	100	18.8	25	3	47
DC-IV-34	RR-64 (0.626)	10	2.37	5	4	48
DC-IV-88 ^c	RR-103 (3.80)	100	11.5	50	2	56
RR-104	RR-87 (5.0)	100	3.32	10	3.5	81
DC-IV-32	RR-87 (5.0)	100	3.32	20	3	81

a. Copolymer compositions were estimated by assuming that hydrolyses are complete.

b. Intrinsic viscosity was 0.219, in THF.

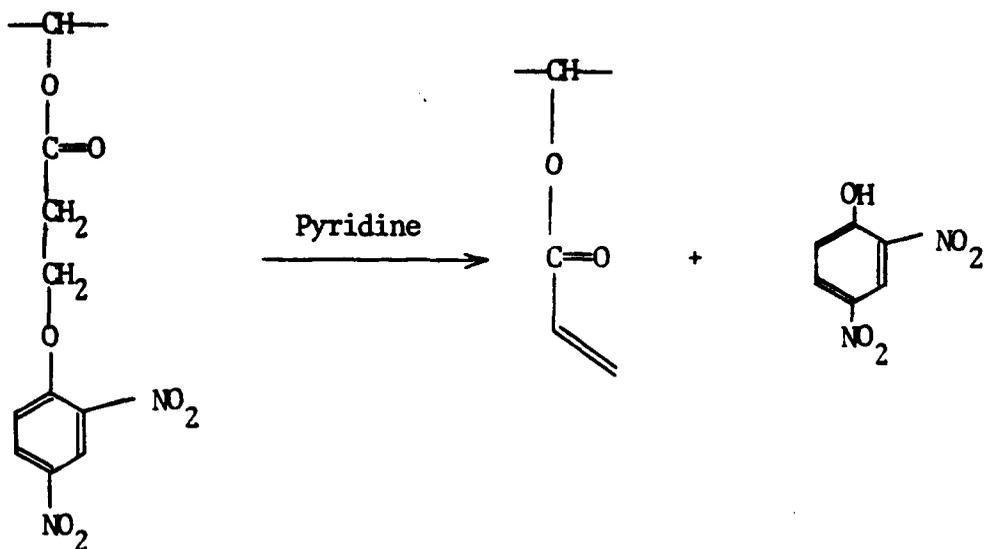
c. Inherent viscosity, 0.158 in THF.

Table 8. Preparation of copolymer 4.

Sample No.	VOH in Polymer (mmol)	Solvent (ml)	DNPP (mmol)	Solvent (ml)	Time (hr)		DNPP in Polymer (mole%)	η_{inh}
					Room Temp.	75°C		
DC-IV-27B	RR-68 (2.33)	pyridine (15)	4.0	benzene (10)	2	2	-	0.62 ^a
DC-IV-27C	RR-68 (2.02)	pyridine (10)	3.0	benzene (10)	4	0	33	0.12 ^a
DC-IV-34	RR-64 (1.59)	THF (10) pyridine (10)	1.7	THF (10)	4	1	30	0.46 ^a
DC-IV-26	RR-III-88A (1.67)	pyridine (15)	3.0	benzene (10)	2	2	26	0.21 ^a
DC-IV-28	RR-104 (0.494)	pyridine (15)	1.0	benzene (10)	4	0	12	0.21 ^a
DC-IV-32B	DC-III-32A (1.181)	THF (10) pyridine (0.3)	1.5	THF (10)	4	1	11	0.21 ^b

a. In DMSO (samples were insoluble in THF).

b. In THF.



The copolymers containing the 2,4-dinitrophenoxyl group higher than 15 mole % were insoluble in THF, but soluble in DMSO. Sample DC-IV-32B showed no photoelectric response. The 2,4-dinitrophenoxyl group is a poorer electron acceptor than the 3,5-dinitrobenzoate group.

Copolymer 5 was synthesized by the following scheme (Table 9). THF is a good solvent for the first step since it dissolved the oil in sodium hydride oil dispersion to create more surface area. After the reaction was completed, the polymer solution became cloudy. However, DMSO is a better solvent for the second step since it dissolved the polymer anion.

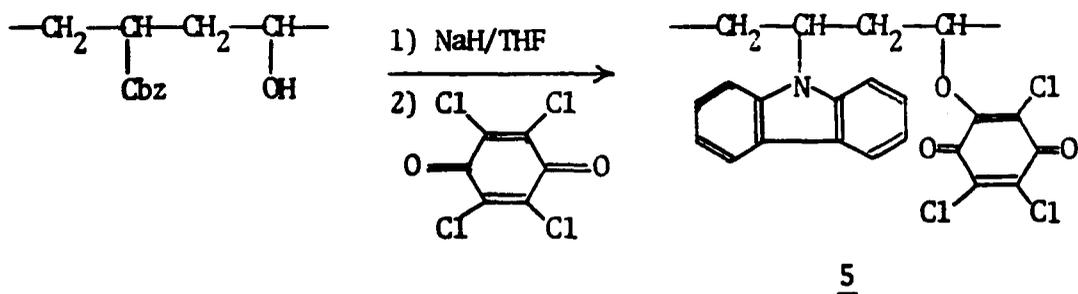


Table 9. Synthesis of copolymer 5.

Sample No.	VOH in Copolymer (mmol)	Solvent ^a (ml)	NaH (mmol)	Time ^b (hr)	p-Chloranil (mmol)	Solvent ^c (ml)	Time ^d (hr)	p-Chloranil in Copolymer ^e (mole%)	η_{inh} ^f
DC-III-90	DC-III-88A 1.77	THF (10)	2.0	0.5	2.0	THF (15)	0.6	0	-
DC-IV-1	DC-III-88A 1.77	THF (10) DMSO (10)	2.0	2	2.0	DMSO (10)	15	19	0.14
DC-IV-16	DC-III-88A 3.54	THF (10)	3.6	2	3.6	THF (10)	48	24	0.32
DC-IV-35	DC-IV-32A 2.11	THF (10) DMSO (15)	2.5	6	2.5	DMSO (15)	15	11	0.26

a. Solvent for starting copolymer.

b. Reaction time for NaH and starting copolymer.

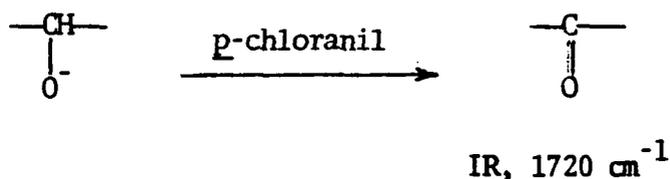
c. Solvent of p-chloranil.

d. Reaction time for p-chloranil and polymeric anion.

e. Calculated by chlorine analysis.

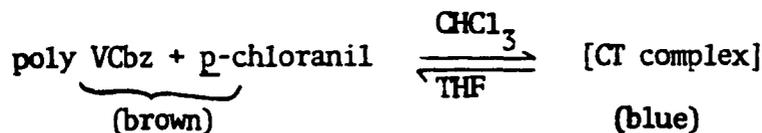
f. Viscosities in THF.

Sample DE-IV-16 (Table 9) was prepared in THF, and partial oxidation of the polymer presumably by hydride transfer to *p*-chloranil occurred as indicated by a band at 1720 cm^{-1} in the ir spectrum. However, in the presence of DMSO, no band at 1720 cm^{-1} in the infrared spectrum was observed. *p*-Chloranil shows a carbonyl band at 1680 cm^{-1} and the copolymer 5 had a band at 1680 cm^{-1} .

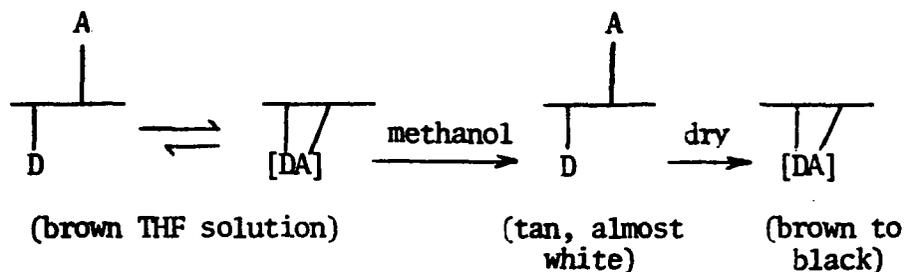


The copolymer was purified by pouring the dark brown THF solution into methanol. After drying, it changed color, from tan to nearly black. It could be assumed that more charge-transfer complex was formed in the solid state.

p-Chloranil formed a light blue charge-transfer complex with polyvinylcarbazole in chloroform. When poly(*N*-vinylcarbazole) and *p*-chloranil were mixed in THF, the polymer surface turned light blue. After all the polymer dissolved, the solution became light brown, the color of the uncomplexed *p*-chloranil. This could be explained by the following equilibrium.



The dark brown copolymer 5 can also be explained by the following processes.



p-Chloranil ($\lambda_{\text{max}}^{\text{CHCl}_3}$, 374 nm, $\log \epsilon = 2.37$ or $\epsilon = 223$) formed a dark green complex with polyvinylcarbazole in chloroform (λ_{max} , 590 nm, ϵ_{max} , 118)¹¹ and in benzene (λ_{max} , 574 nm)¹². However, the absorption spectrum of polyvinylcarbazole and p-chloranil in THF shows only a very weak band (shoulder around 550 nm). This confirms that THF is a poor solvent for charge-transfer formation. The copolymer 5 (forming charge-transfer complex by intramolecular reaction) absorbs considerably more strongly in the 590 nm region than homo polyvinylcarbazole and p-chloranil complex. The uv and visible spectra are presented in Figure 8.

Sample DC-IV-16A and DC-IV-35 showed RC times 0.65 and 0.53 sec respectively, which are worse than the value for p-chloranil-doped poly-(N-vinylcarbazole). This might be explained by the fact that the oxygen-substituted p-chloranil is a poorer electron acceptor than p-chloranil.

Water soluble photoconductive polymers might be synthesized by copolymerization of N-vinylcarbazole with the highly water soluble monomers listed below.

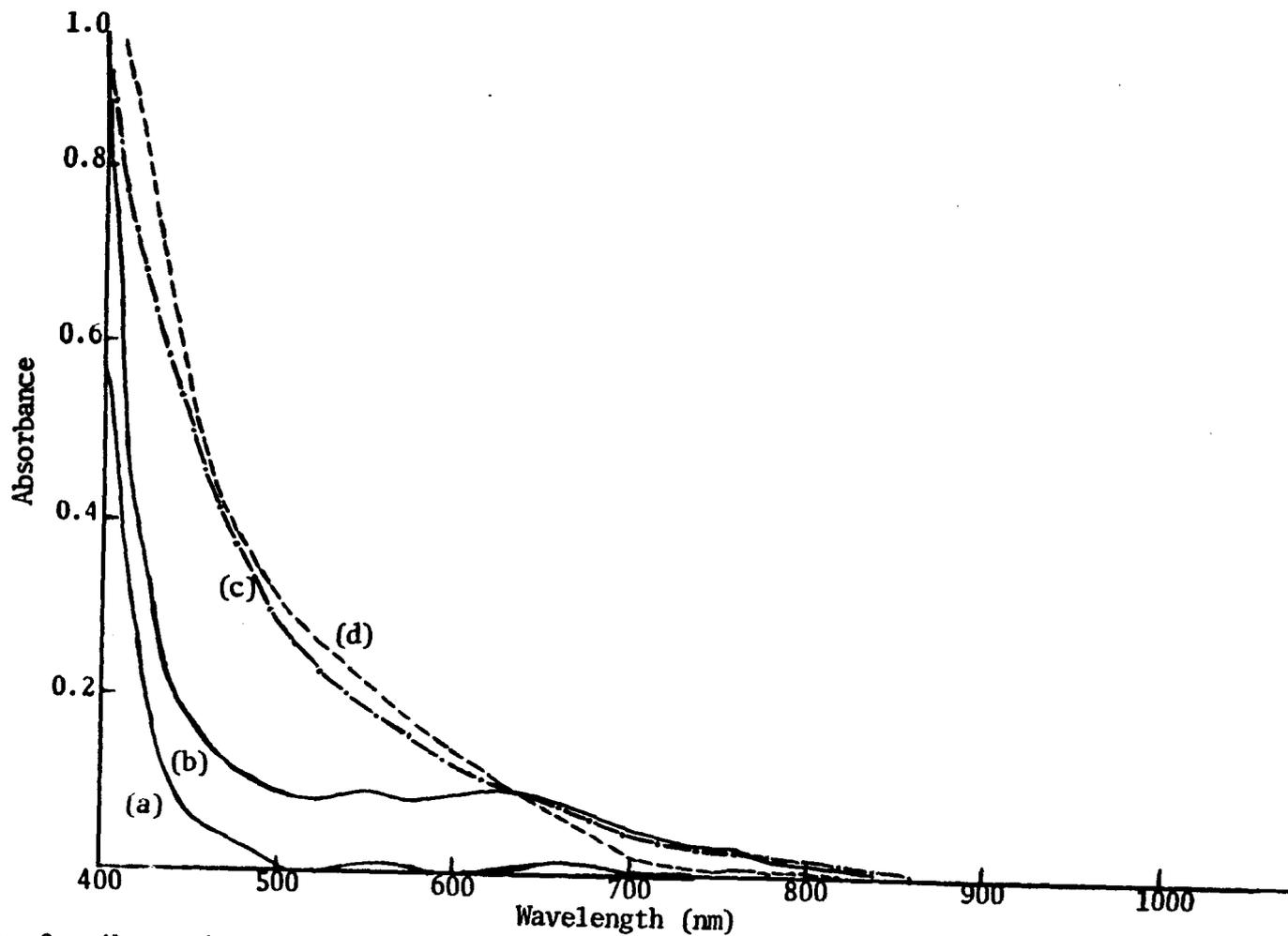
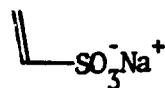
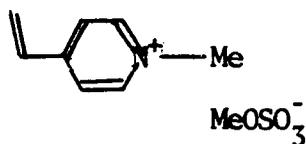
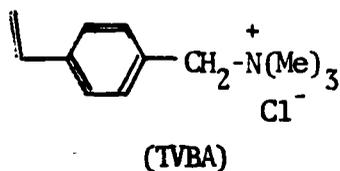
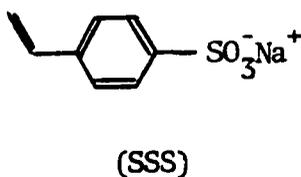
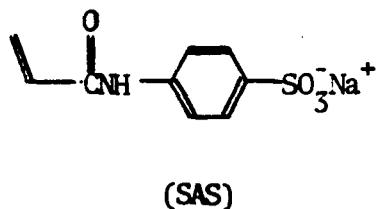
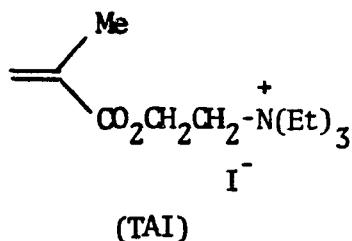


Figure 8. Absorption spectra of polyvinylcarbazole complexes.

(a) PolyVCbz (0.0197 M) plus *p*-chloranil (0.00432 M) in THF. (b) PolyVCbz (0.020 M) plus *p*-chloranil (0.00429 M) in chloroform. (c) Sample DC-IV-1 (9.5 mg) in 5 ml THF. (d) Sample DC-IV-16 (23.0 mg) in 10 ml THF.



Sodium N-acryloylsulfanilate (SAS) was prepared with slight modification, according to the patent of Wilkinson.⁴⁴ It was polymerized in DMSO using AIBN as the initiator for 46 hr at 75°C with 92% conversion. The polymer was hygroscopic and soluble in water with inherent viscosity 0.84 in DMSO. N-Vinylcarbazole was also polymerized using AIBN in the same solvent at 70°C for 24 hr with 64% conversion with inherent viscosity 0.52 in benzene. Copolymerizations of N-vinylcarbazole and SAS were run under the same conditions mentioned above.

But in this case, no polymerization occurred and N-vinylcarbazole was converted to carbazole. The decomposition mechanism is not clear.

Copolymerization of VCbz and SAS was run successfully in N,N-dimethylacetamide (DMAM) (Table 10). The reactivity of SAS is comparable to that of VCbz. Conversions, inherent viscosities and water solubilities increased with the initial feed concentration of SAS. The copolymers containing VCbz higher than 51 mole % were insoluble in water. A relatively flexible transparent film was prepared from a water solution of the sample DC-III-38.

Potassium styrenesulfonate (M_1 , $r_1 = 0.54$) had been copolymerized with styrene (M_2 , $r_2 = 0.06$) in DMF at 90°C.⁴⁵ By comparison of the reactivity ratio of styrene ($r = 5.7$) to that of VCbz ($r = 0.035$) in benzene at 75°C,⁴⁶ it is apparent that a high concentration of VCbz would be required in copolymerization with SSS. Copolymerizations of VCbz and SSS were carried out in DMAM (Table 11). Relatively low molecular weight water soluble copolymers were obtained. Copolymerization also was run in dimethyl sulfoxide (DMSO) with AIBN at 70°C for 24 hr. Only a trace of polymer was isolated. These Copoly (VCbz-SSS) containing VCbz higher than 64% were water insoluble.

N,N,N-Triethyl-N-[2-(methacryloxy)-ethyl]-ammonium iodide (TAI) was prepared according to the method of Overberger,⁴⁷ and the reactivity ratios of TAI ($r = 0.61$) and 4-vinylpyridine ($r = 0.30$) had previously been determined in acetone at 60°C.⁴⁷ TAI is less hygroscopic than choline chloride acrylate. Attempts to synthesize choline chloride acrylate by reacting choline chloride with acrylic acid, acryloyl chloride or methylacrylate failed. Copolymerizations were carried out in

Table 10. Copolymerization of VCbz and SAS.^a

Sample No.	VCbz in Feed (mmol)	SAS in Feed (mmol)	Conversion (wt %)	VCbz in Polymer ^b (mole %)	Water Soluble?	η_{inh} ^c
DC-III-42	5	6	90	35	yes	1.12
DC-III-38 ^d	5	5	85	45	yes	1.01
DC-III-41	5	4	56	43	yes	0.91
DC-III-43	5	3	70	51	yes	0.81
DC-III-39	5	2.5	68	51	slightly	0.73
DC-III-44	5	2	63	60	dispersed	0.72

a. Monomers, AIBN (0.5% mole), 10 ml DMAM was stirred at 70°C for 24 hr.

b. Copolymer compositions were calculated from sulfur analyses.

c. Viscosities in water.

d. Sample sent to Sherwin-Williams Co.

Table 11. Copolymerization of VCbz and SSS.^a

Sample No.	VCbz (mmol)	SSS (mmol)	DMAM (ml)	Conversion (wt %)	VCbz in Copolymer ^b (mole %)	Water Soluble?	η_{inh} ^c
DC-III-59	10	1	25	13	64	swelled	-
DC-III-60 ^d	20	3	50	14	63	yes	0.15
DC-III-57	10	2	25	8	-	yes	0.07
DC-III-63	10	2	25	7	21	yes	0.13
DC-III-58	10	3	25	17	52	yes	0.13

a. Monomers, AIBN (0.5 mole), DMAM were stirred at 70°C for 24 hr.

b. Copolymer compositions were calculated from nitrogen analyses.

c. Viscosities in water.

d. Sample sent to Sherwin-Williams Co.

DMAM with AIBN (Table 12). Reactivity of TAI in DMAM is comparable to that of N-vinylcarbazole. Copolymers containing VCbz higher than 42 mole % were water insoluble.

N,N,N-Trimethyl-(p-vinylbenzyl)ammonium chloride (TVBA) was prepared by treating p-vinylbenzyl chloride with trimethylamine in ether at 0°C for 24 hr in the presence of hydroquinone as an inhibitor. The monomer was a crystalline hygroscopic substance. TVBA has been copolymerized with styrene, methyl acrylate, acrylonitrile, etc., by using AIBN as the initiator.⁴⁸ In every copolymerization, TVBA was so reactive that a large excess of comonomer had to be used to get a copolymer. It was reported that the copolymer containing 70% of styrene was soluble in water.⁴⁸

Copolymerizations of VCbz and TVBA were run in DMF, methanol, and DMSO by using AIBN (0.5 mole% to monomer). In every run, either homo poly(TVBA) or no polymer was isolated along with recovery of the unreacted VCbz. However, copolymerizations were carried out successfully in DMAM (Table 13).

A copolymer of N-vinylcarbazole and methyl acrylate containing 56 mole % of N-vinylcarbazole was hydrolyzed with 1 N NaOH or KOH (in methanol) with THF as a polymer solvent. The infrared spectra of the resulting copolymer (sodium or potassium salt) revealed the absence of a carbonyl ester linkage, but bands at 1580 and 1400 cm^{-1} showed the presence of a carboxylic acid salt. The copolymer was insoluble in organic solvents and water. However, it can be dispersed in hot water.

Table 12. Copolymerization of TAI and VCbz.^a

Sample No.	VCbz (mmol)	TAI (mmol)	AIBN (% mole)	Conversion (wt %)	VCbz in Copolymer ^b (% mole)	Water Soluble?	η_{inh} ^c
DC-IV-23	5	3.16	0.5	0	-	-	-
DC-IV-22B ^d	5	3.16	2	72	-	swelled	1.68
DC-IV-24	5	5	2	81	47	dispersed	1.37
DC-IV-25B	5	7	1.5	75	-	dispersed	-
DI-IV-25D ^e	5	7	1	75	44	dispersed	-
DC-IV-30B	5	9	1	77	42	slightly soluble	2.12

a. Monomers, AIBN and DMAM (10 ml) were stirred at 75°C for 24 hr.

b. Copolymer compositions were calculated from nitrogen analyses.

c. Viscosities in DMAM.

d. Stirred at 70°C.

e. Polymerization for 17 hr.

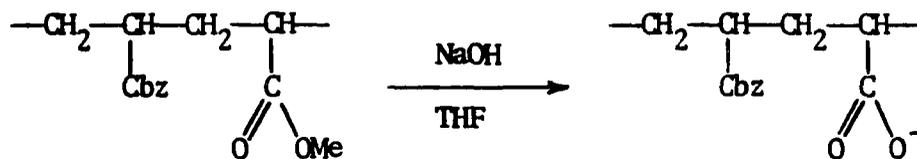
Table 13. Copolymerization of TVBA and VCbz.^a

Sample No.	VCbz (mmol)	TVBA (mmol)	Conversion (wt %)	VCbz % mole in Copolymer ^b	η_{inh}^c	Water Soluble?
DC-III-72	4	2	37	10	0.21	Yes
DC-III-93	5	2	31	40	0.36	Yes
DC-III-97	5	2	28	40	-	Yes
DC-III-95	7	2	49	-	-	insoluble

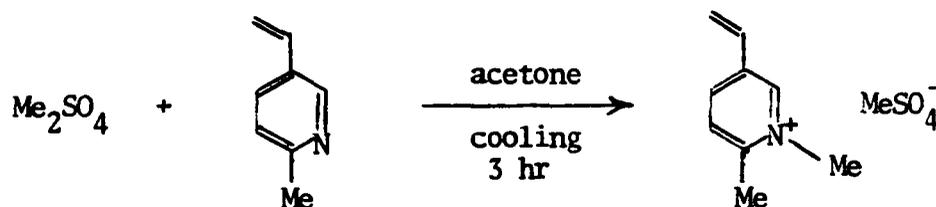
a. Monomers + AIBN (0.5 mole %) + DMAM (30 ml) were stirred at 70°C for 24 hr.

b. Calculated from chlorine analyses.

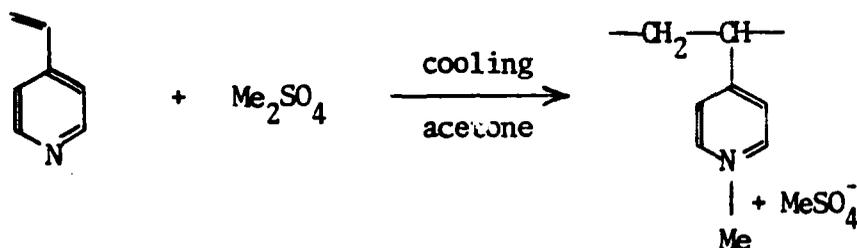
c. Viscosities were determined in distilled water.



It has been reported^{49,50} that 4-vinylpyridine reacts with alkyl halides in solution to produce high molecular weight polymers via anionic polymerization. Shyluk⁵¹ first isolated the N-methyl-2-methyl-5-vinylpyridinium methylsulfate by the following reaction:



Our attempt to isolate the corresponding 4-vinylpyridinium salt by the same method failed, and only polymer was isolated, with $n_{\text{inh}} = 1.59$ in methanol.



Attempts to copolymerize N-vinylcarbazole (M_2) (M_1 styrene $r_1 = 5.7$, $r_2 = 0.035$ in benzene at 75°C),⁴⁶ and 4-vinylpyridine (M_2) (M_1 , styrene $r_1 = 0.54$, $r_2 = 0.7$ at 60°C)⁵² in benzene, pyridine, or DMAM failed. 4-Vinylpyridine is too reactive to give a copolymer with VCbz.

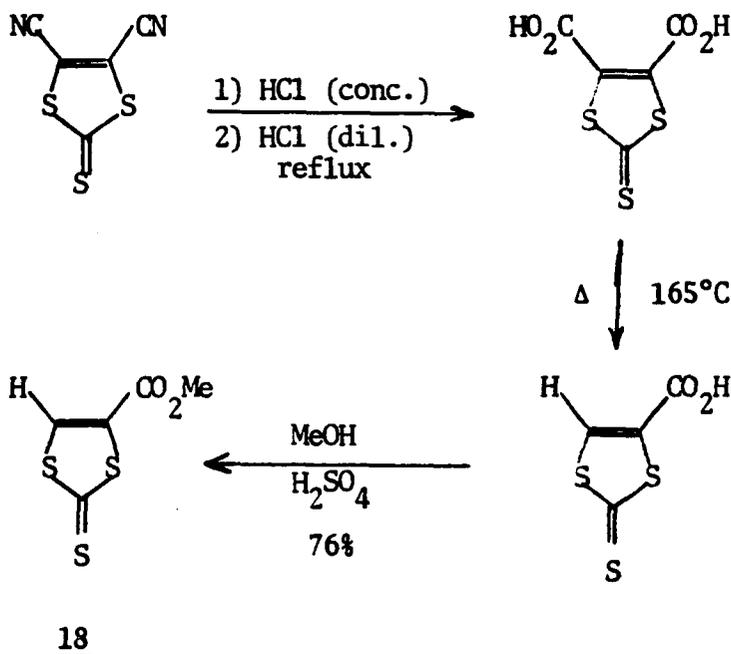
Breslow and Kutner⁵³ reported that sodium vinylsulfonate copolymerized slowly with acrylonitrile and methyl acrylate, but water soluble copolymers could not be prepared. Vinyl acetate formed a water soluble copolymer, but no more than 9% of vinyl acetate could be introduced. Attempts to copolymerize sodium vinylsulfonate and N-vinylcarbazole with AIBN in DMAM failed. Either largely homo polyvinylcarbazole or largely homo poly(sodium vinylsulfonate) was obtained. Under these copolymerization conditions, N-vinylcarbazole is more reactive than sodium vinylsulfonate.

The unsensitized water soluble polymers showed no photoresponse. There is no good water soluble sensitizer available in the present time.

In conclusion, photoconductive copolymers containing N-vinylcarbazole and electron acceptors such as β -hydroxyethyl 3,5-dinitrobenzoate, β -(2,4-dinitrophenony) propionate, and *p*-chloranil were synthesized. Generally, the absorbance in the uv and visible range for the polymeric intramolecular charge-transfer complexes are stronger than those of the corresponding polymeric intermolecular charge-transfer complexes. Water soluble polymers containing N-vinylcarbazole were also synthesized. Further work in the evaluation of good water soluble sensitizers will be necessary.

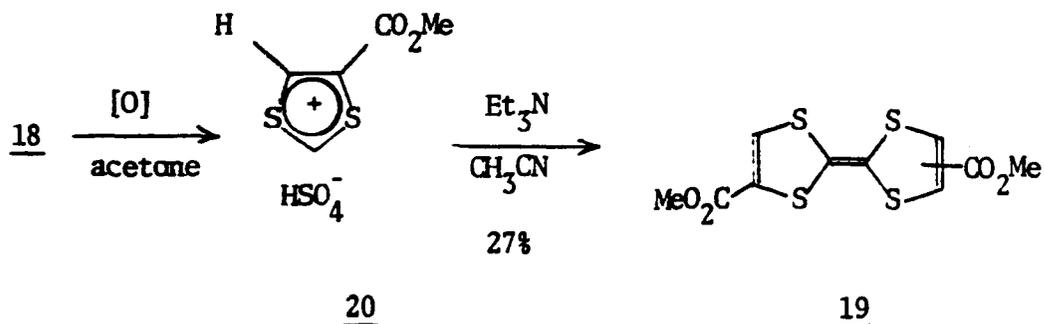
Semiconducting Materials

Methyl 1,3-dithiole-2-thione-4-carboxylate 18 was prepared according to the method of Klingsberg.²⁸



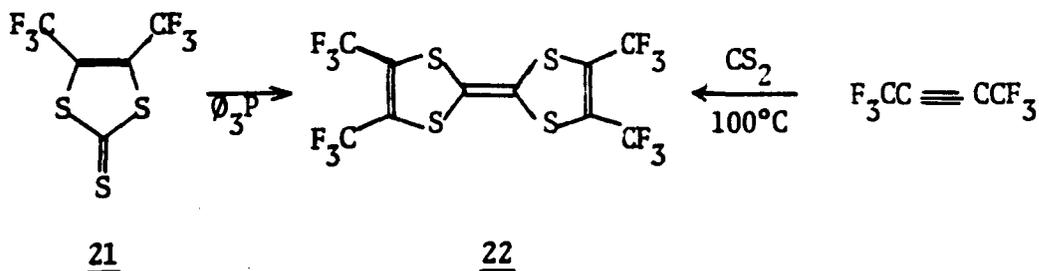
Compound 18 was obtained as yellow plates m.p. 109°C. Its ir spectrum showed thiocarbonyl band at 1053 cm⁻¹ and carbonyl ester band at 1710 cm⁻¹. The dithiole ring is highly aromatic with the C-5 proton at δ8.0 in the nmr spectrum.

Dimethyl bis-1,3-dithiole-4-carboxylate 19 was synthesized by the following scheme:



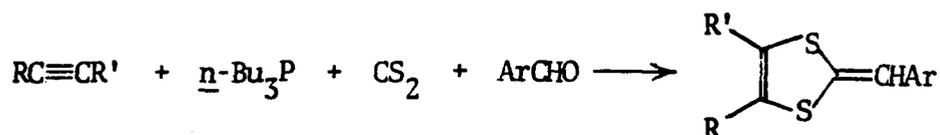
It was reported²⁸ that 1,3-dithiolium salts could not be prepared from 1,3-dithiole-2-thiones with electron-withdrawing substituents by oxidation with peracetic acid. However, 20 was synthesized in 55% yield by oxidation of 18 with *m*-chloroperbenzoic acid. Deprotonation of 20 with triethylamine in anhydrous acetonitrile gave the blood-red 19 in 5 min in 27% yield. Compound 19, sensitive to air oxidation, especially on exposure to light, became orange on storing. The bis-1,3-dithiole 19 obtained by the above scheme was a mixture of geometric isomers. The nmr spectrum showed singlets at δ 7.3 and 7.4.

Compound 22 was prepared⁵⁴ in high yield by desulfurization of 21 by triphenylphosphine or reaction of hexafluoro-2-butyne with carbon disulfide at 100°C in the presence of trifluoroacetic acid. However, attempts to synthesize 19 either by desulfurization of 18 by



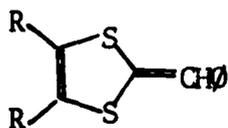
triphenylphosphine or reaction of ethyl propiolate with carbon disulfide at 100°C in a sealed tube in the presence of a catalytic amount or one equivalent of trifluoroacetic acid failed.

Hartzler³⁴ reported that 2-benzylidene-1,3-dithioles were synthesized by the following scheme:

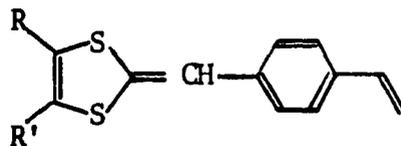


- 23 a: R=H R'=CO₂Me
Ar= 4-pyridyl
b: R=H R'=CO₂Me
Ar= 4-ClC₆H₄
c: R=H R'=CO₂Me
Ar= 4-O₂N-C₆H₄

Compounds 24 and compounds 25 were synthesized with modifications, according to the scheme of Hartzler (Table 14).



- 24 a: R=R'=CO₂Me
b: R=H R'=∅
c: R=R'=∅
d: R=H R'=CO₂Et



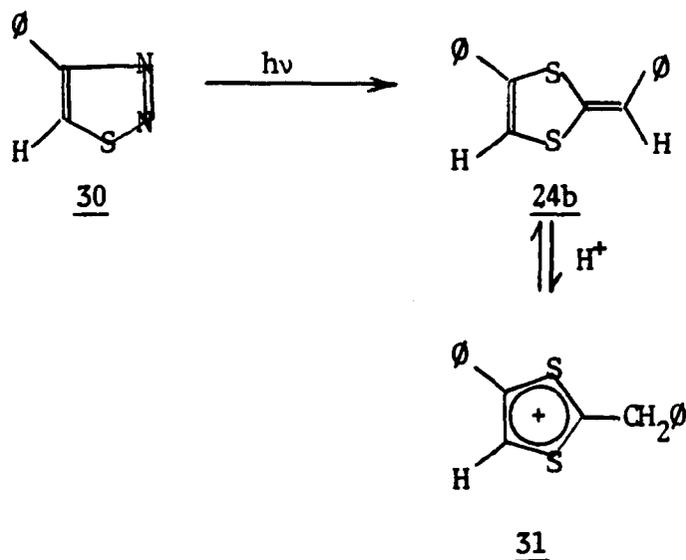
- 25 a: R=R'=CO₂Me
b: R=H R'=CO₂Et
c: R=H R'=∅

Table 14. Synthesis of compounds 24 and 25.

Compound No.	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)	Crystal Form
24a ^a	-23	0.5	45	red needles
25a	-23	0.5	57	orange-red needles
24d	-23	1	30	yellow plates
25b	-23	1	57	yellow plates
24b	25	8	10	yellow plates
25c	25	8	10	yellow plates
24c	25	a week	5	yellow crystals

a. This compound was prepared by Leland.⁵⁵

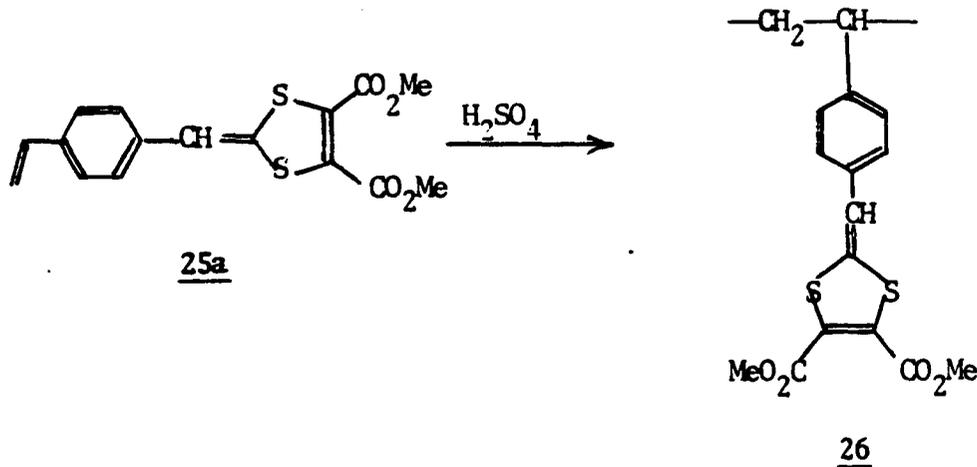
Acetylenes having at least one electron withdrawing substituent reacted readily to give a stable 1,3-dithioles in good yield.³⁴ Phenylacetylene and tolan reacted slowly to give an unstable dithiole in poor yield. Compounds 24b, 24c, and 25c became dark-red dyes on exposure to light in the air. Attempts to synthesize 24c at higher temperature (80°C) in a sealed tube failed. Compound 24b was first isolated⁵⁶ by the photolysis of aryl-substituted 1,2,3-thiadiazoles 30, and can be protonated to give 1,3-dithiolium salt 31.



p-Vinylbenzaldehyde was prepared⁵⁷ by reacting the Grignard reagent from *p*-chlorostyrene with DMF. Compound 25a, orange-red needles, was obtained in 57% yield from *p*-vinylbenzaldehyde and acetylenedicarboxylic ester. Attempts to polymerize 25a with AIBN in refluxing THF or benzene up to 48 hr failed, with recovery of the monomer. However, 25a can be copolymerized with methyl methacrylate (MMA),

α -methylacrylophenone (α -MAP), and α -chloroacrylonitrile (Cl-AN) to give one to one low molecular weight polymers with low conversion (Table 15).

Cationic polymerization of 25a by SnCl_4 in nitrobenzene-carbon tetrachloride gave an oligomer. Boron trifluoride etherate initiated polymerizations gave low molecular weight polymers ($n_{\text{inh}} = 0.06$ in benzene) in THF, benzene, or toluene. Compound 25a was stirred in concentrated sulfuric acid at room temperature for 4 hr to give a polymer with 85% conversion ($n_{\text{inh}} = 0.03$ in benzene, molecular weight 7,000 by ebullioscopic method). An attempt to polymerize 25a using $n\text{-BuLi}$ failed. An attempt to polymerize 24a with hexamethylenediamine by high temperature polycondensation reaction gave a black insoluble solid.



Polymer 26 was also synthesized by the following scheme:

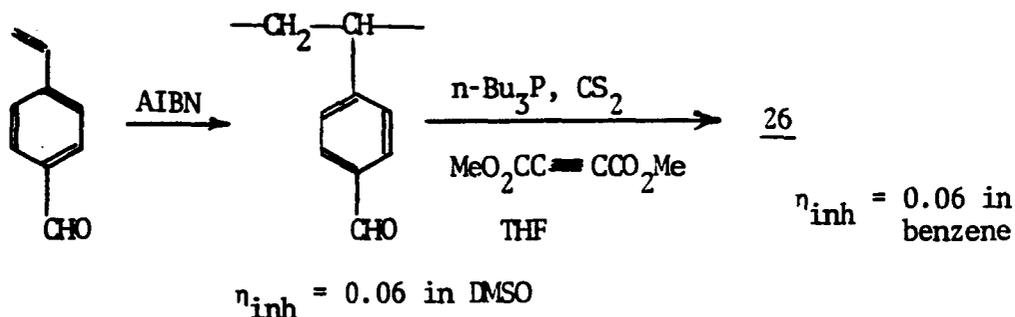
Table 15. Copolymerization^a of 25a.

Sample No.	Comonomer	Time (hr)	Conversion (wt %)	$[\eta]^b$	25a in Copolymer ^c (mole %)
DC-II-27	MMA	28	12	0.02	50
DC-II-28	α -MAP	43	10	0.01	50
DC-II-29	Cl-AN	48	23	0.01	51

a. 1 mmol 25a + 1 mmol comonomer + 5×10^{-2} mmol AIBN in 10 ml benzene at 78°C.

b. Viscosities were determined in benzene.

c. Copolymer compositions were calculated from sulfur analyses.



p-Vinylbenzaldehyde was polymerized according to the procedure of Kinoshita and Schulz⁵⁸ for 21 hr with 73% conversion. The reaction of the poly(vinylbenzaldehyde) was carried out by the same procedure as used in preparing the monomer 25a, except THF was used as the solvent. The yield was 82% from the sulfur analysis, which is higher than the yield in monomer synthesis.

Polymer 26 showed a resistance of 10^{12} ohms on a 2 inch long, 0.1 mil thick disc determined by the Sherwin-Williams Co. The resistance was dropped to 10^5 ohms after the polymer 26 was doped with 20% of p-chloranil. This doped polymer might be a potential semiconducting polymer.

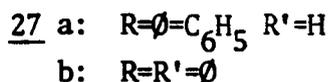
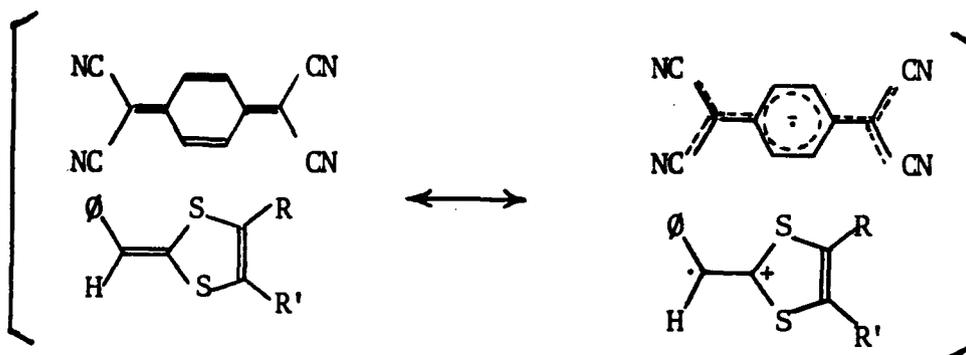
The nmr of 25b showed that the 1,3-dithiole ring is aromatic with proton C-5 at $\delta 7.3$ in CDCl_3 . Compound 25b, yellow plates, was polymerized by AIBN, SnCl_4 , and sulfuric acid to give low molecular weight polymers (Table 16).

Hot acetonitrile solutions of dithiole 24b or 24c and TCNQ were mixed and 1:1 charge transfer complexes 27a and 27b were obtained. Structure 27 showed the four TCNQ protons as an A_2B_2 pattern at $\delta 7.5$ - 7.9

Table 16. Polymerization of 25b.

Sample No.	Initiator	Time (hr)	Temp. (°C)	Conversion (wt %)	Solvent	η_{inh}^a
DC-p-51	AIBN	48	78	14	C ₆ H ₆	0.05
DC-p-53	SnCl ₄	48	0	17	CCl ₄ - ϕ NO ₂	0.03
DC-p-54	H ₂ SO ₄	2	0	70	H ₂ SO ₄	0.03

a. Viscosities in benzene.



(TCNQ protons show a singlet at δ 7.55 in dioxane) in CDCl₃ in the nmr spectrum. Hanna and Ashbaugh²¹ reported that alteration of the paramagnetic contribution to the TCNQ protons in various charge-transfer complexes shifted them downfield as the complex interaction become stronger. The benzylidene proton was also shifted from δ 6.44 to δ 5.1 by the contribution of the cation radical structure (sp^3) of the dithiole. The cyano peak in the ir spectrum was also shifted from 2225 to 2255 cm^{-1} . Complex 27 showed bands at 420, 785, and 842 nm in the visible and ir region (Figure 9) which confirmed the existence of the TCNQ anion radical.¹⁵ These dithiole-TCNQ complexes may produce semiconducting crystals.

Melby et al.¹⁸ reported that solid Li⁺ TCNQ⁻ has an electrical resistivity of 10^5 ohm-cm (in a powder compact), which is in the semiconductor range. Typical TCNQ anion radical salts showed resistivity values between 10^4 and 10^9 ohm-cm. The resistivity of 27b was measured

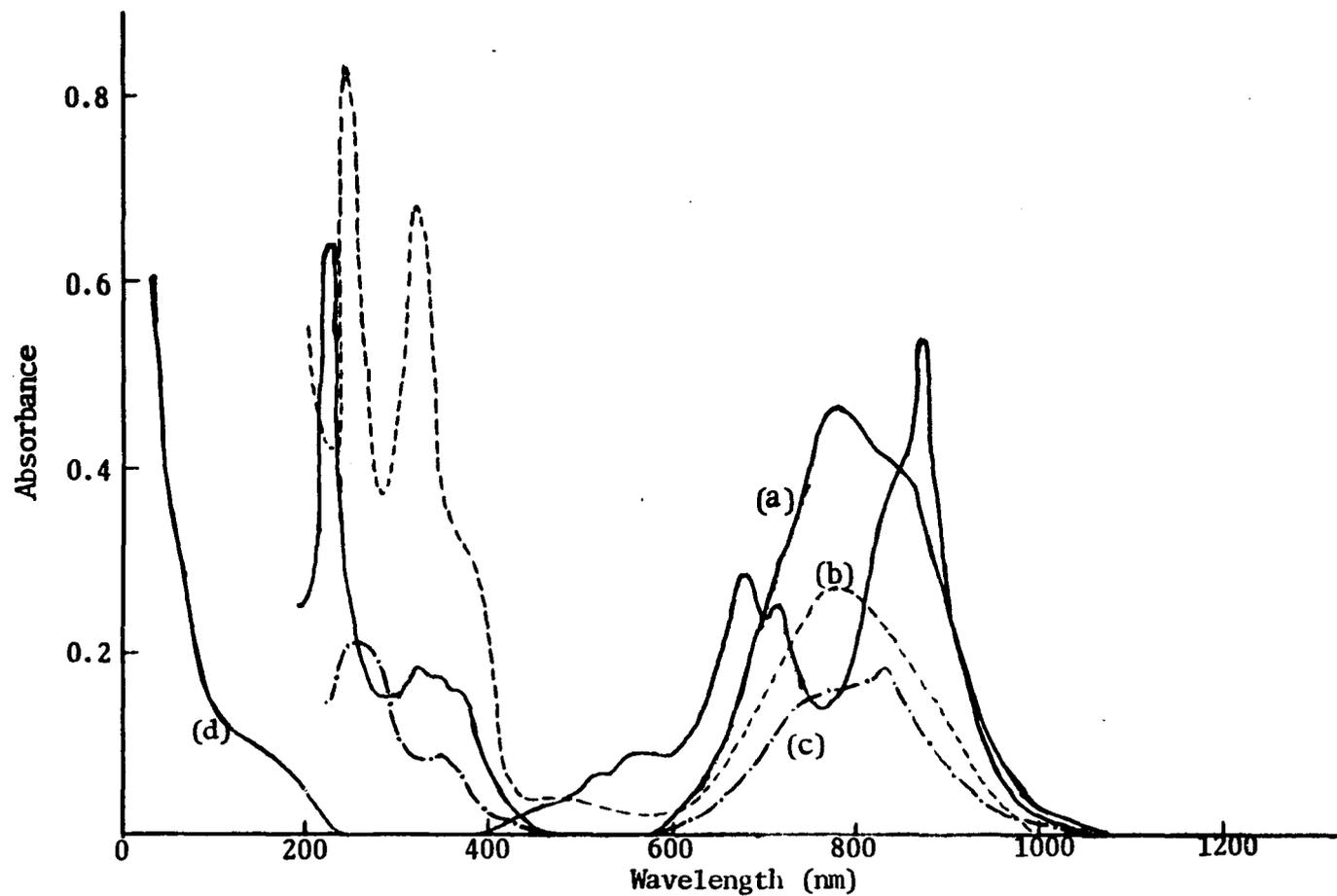
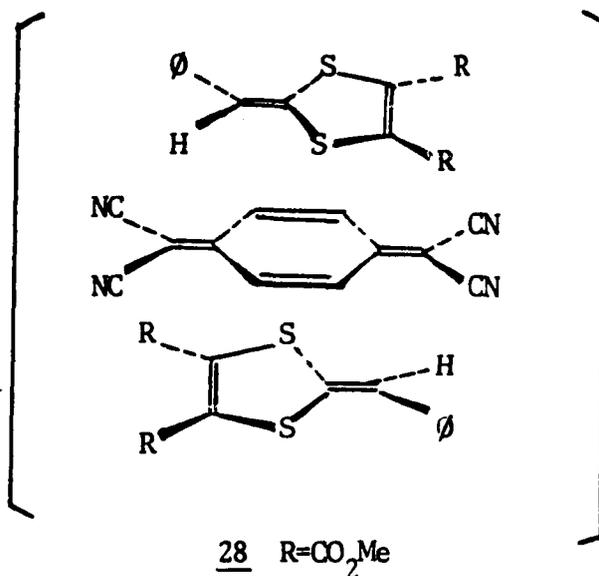


Figure 9. Absorption spectra of TCNQ charge-transfer complexes.

(a) $[27b \cdot TCNQ]$ 1.386×10^{-5} M in CH_3CN . (b) $[27b \cdot TCNQ]$ 5.72×10^{-5} M in CH_2Cl_2 . (c) $[27a \cdot TCNQ]$ 7.61×10^{-6} M in CH_3CN . (d) $[(24a)_2 \cdot TCNQ]$ 3.78×10^{-4} M in CH_3CN .

by a two probe method on a single crystal (Figure 3). Two probes were made under a microscope by using electrically conductive silver paint dispersed in toluene. Toluene dissolved a small amount of the TCNQ surface and formed a number of tiny crystals around the probes. These poor contacts did not permit a quantitative measurement. The resistivity was found to be in the order of 10^{10} - 10^{11} ohm-cm, which is higher than the typical TCNQ anion radical salts. Careful review of the published data⁸ showed that the resistivity is affected by the contacts, method of measurement, purity of the single crystal (method of purification), and the perfection of crystal structure.

Dithiole 24a reacted with TCNQ in hot acetonitrile to give a 2:1 complex 28. However, in hot THF, only starting materials were recovered. Complex 28 showed a singlet at $\delta 7.8$ (TCNQ protons) and a multiplet at $\delta 7.2$ - 7.6 (benzylidene proton and aromatic proton) in the nmr spectrum. An absorption spectrum (ir and visible) also showed the presence of TCNQ anion radical (Figure 9). However, the cyano peak at 2225 cm^{-1} in their spectrum was not observed.

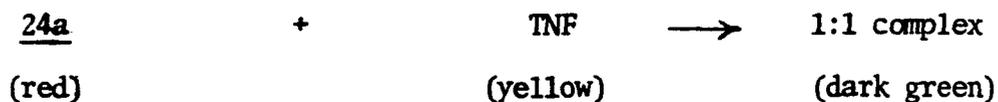


Fischer and McDowell⁵⁹ generated the TCNQ anion radical by electrolysis of TCNQ in 80% dimethoxyethane and 20% acetonitrile. The epr spectrum showed 45 lines with $a_H = 1.44$ gauss, $a_N = 1.02$ gauss, field set at 3387 gauss. The epr spectrum of $K^+ TCNQ^-$ on a single crystal showed⁶⁰ one signal at $g_{11} = 2.0024$, $g_{\perp} = 2.0031$ below 130°C. The epr spectra of the complexes 27b and 28 in acetonitrile solutions showed a singlet with $g = 2.001$, $a_H = 6.8$ gauss and $g = 2.001$, $a_H = 6.1$ gauss respectively, with field set at 3392 gauss. The rough g factors were calculated by:³

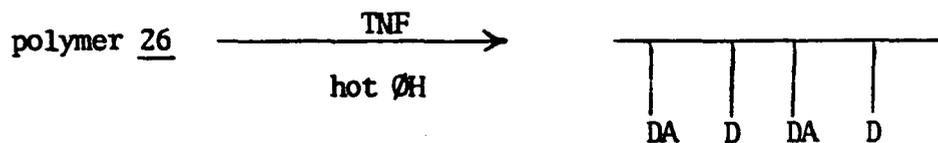
$$g = \frac{h\nu}{\beta H} = 0.7145 \frac{\nu(\text{MHz})}{H(\text{gauss})}$$

Dithiole 24a and TNF in hot absolute ethanol were mixed, and a dark green charge-transfer complex immediately precipitated out.

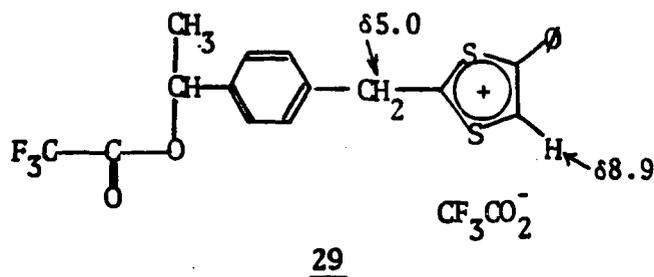
The carbonyl peak in TNF had shifted from 1735 to 1700 cm^{-1} in the ir spectrum. However, no obvious change in the nmr spectrum and no new charge-transfer band were observed. Dithiole polymer 26 polymerized by



sulfuric acid ($n_{\text{inh}} = 0.03$, molecular weight 7000 by ebullioscopic method) also formed a dark green complex polymer with TNF in hot benzene. The nmr spectrum showed that only half of the dithiole heterocycles formed a complex with TNF after precipitation into methanol. An attempt to prepare 24a-p-chloranil complex in hot acetonitrile failed, with recovering of starting materials (checked by m.p.).



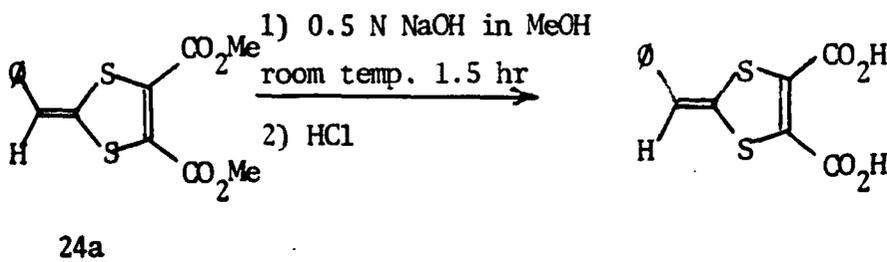
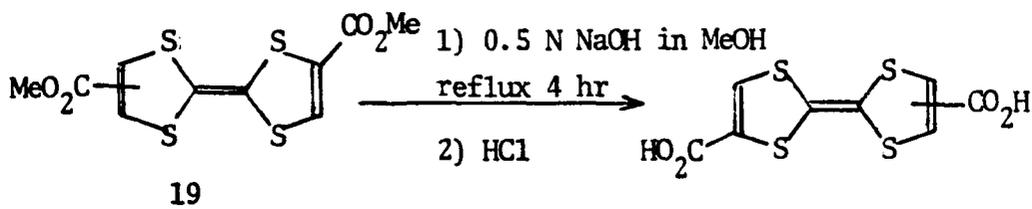
In trifluoroacetic acid, 25c was protonated to form a salt 29 as shown by nmr. An attempt to isolate 29 failed.



An attempt to make the bis-1,3-dithiole 19-TCNQ complex in hot THF failed. Compound 19 was insoluble in acetonitrile.

TTF is a semiconductor at room temperature ($r = 10^{12}$ ohm-cm) and the cation radical 11 was an excellent semiconductor at room temperature ($r = 3.7 \pm 1$ ohm-cm).³⁰ It was of interest to make a polymer containing TTF and study the electric properties. Attempts to polymerize 19 with ethylene glycol or 1,4-butanediol by high temperature polycondensation reactions failed. Only low molecular oligomer or polymer with the decomposed dithiole ring was obtained.

Compounds 19 and 24a can be hydrolyzed to the corresponding diacids by the following reactions:



The corresponding diacid chloride might be prepared, followed by interfacial polymerization with diamines.

In conclusion, substituted 2-benzylidene-1,3-dithioles and their charge-transfer complexes have been prepared. The properties of their

charge-transfer complexes were effected by the substituents on the 1,3-dithiole ring. The electric resistance of the 27b-TCNQ complex measured by the two-probe method was found to be between insulators and semiconductors. The four-probe method is highly recommended in measuring the electric resistance because of its great accuracy. However, a four probe instrument was not available. Low molecular weight polymers containing 2-benzylidene-1,3-dithioles repeating units were also prepared. This doped polymer might be a potential semiconductor. Further work in the preparation of high molecular weight polymers by low temperature condensation polymerization is encouraged.

EXPERIMENTAL

Instrumentation

Melting points were determined on a Fisher-Johns melting point or a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined on a Varian Model T-60 (60 MHz) NMR spectrometer using tetramethylsilane as a standard. Infrared spectra were determined using either a Perkin-Elmer Infracord or a Perkin-Elmer model 337 Grating Infrared Spectrometer and calibrated with a polystyrene film. Ultraviolet, visible, and near infrared absorption spectra were determined using a Cary 14 recording spectrometer. A Varian model E-3 EPR spectrometer was used to determine epr spectra. Viscosities were determined using Ubbelohde type or Cannon-Fenske viscometers. Inherent viscosities (dl/g) were determined in 0.5% solution at 30°C. A Keithly 600B current electrometer was used to determine the resistance (Figure 3). Photoconductivities were determined by George Q. Moses, Sherwin-Williams Co. using a quartz halogen light source, Tektronix oscilloscope, and a Keithly 610c current electrometer.

Elemental Analyses

Elemental analyses were determined by Huffman Laboratories, Inc., Wheatridge, Colorado.

Materials

Tetrahydrofuran (THF) (J. T. Baker Co.) was distilled from lithium aluminum hydride under nitrogen, stored over 3A molecular sieves

under nitrogen, and passed through an alumina column before use. Benzene and toluene (J. T. Baker Co.) were distilled from sodium under nitrogen and stored over 3A molecular sieves under nitrogen. Carbon tetrachloride and methylene chloride used in cationic polymerization were distilled from P_2O_5 under nitrogen. Dimethyl sulfoxide (DMSO) (J. T. Baker Co.) and DMAM (Matheson, Coleman, and Bell Co.) were distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves under nitrogen. Pyridine (Matheson, Coleman, and Bell Co.) was distilled from calcium hydride and stored over NaOH. Dioxane was distilled from lithium aluminum hydride and stored over 4A molecular sieves. Dimethylformamide (DMF) (Matheson, Coleman, and Bell Co.) was distilled from KOH and stored under nitrogen. Acetonitrile (Mallinckrodt Chemical Works) was distilled from calcium hydride under nitrogen and stored over 4A molecular sieves under nitrogen. Nitrobenzene (Matheson, Coleman, and Bell Co.) was distilled from calcium chloride and stored over 4A molecular sieves in the dark. Absolute ethyl ether (Mallinckrodt Chemical Works) was used without further purification.

Azobisisobutyronitrile (AIBN) (Matheson, Coleman, and Bell Co.) was recrystallized from methanol. Lithium wire was from Lithium Corporation of America, Inc. Lithium dispersion in wax (30% by wt) and n-butyllithium in hexane (2.4 M) were from Ventron Corporation. Boron trifluoride etherate (Matheson, Coleman, and Bell Co.) was distilled under nitrogen before use. Stannic chloride (Fisher Scientific Co.) was used without further purification.

Dimethylamine hydrochloride, *p*-chlorostyrene, tri-*n*-butylphosphine, dimethyl acetylenedicarboxylate, ethyl propiolate, phenylacetylene, diphenylacetylene, *m*-chloroperbenzoic acid, acryloyl chloride, choline chloride, *p*-chloranil, and TCNQ (Aldrich Chemical Co.) were used without further purification. Acetophenone, propiophenone, benzaldehyde, 2,4-dinitrophenol, 3,5-dinitrobenzoic acid, *N,N*-diethylaminoethanol, and trifluoroacetic acid (Matheson, Coleman, and Bell Co.) were used without further purification. Carbon disulfide (Allide Chemical) was used without further purification. Trimethylamine (anhydrous, Eastman Organic Chemicals) was used without further purification. Triethylamine (Matheson, Coleman, and Bell Co.) was distilled from NaOH. Thionyl chloride (Matheson, Coleman, and Bell Co.) was distilled from quinoline. 1,6-Hexanediamine (Matheson, Coleman, and Bell Co.) was recrystallized from acetonitrile. Methyl propiolate (Pfaltz and Bauer, Inc.), TNF (K and K Laboratories, Inc.), methyl iodide, sodium sulfanilate (Mallinckrodt Co.) were used without further purification.

N-Vinylcarbazole (Polysciences, Inc.) in methylene chloride was washed three times with 5% NaOH, 3 times with distilled water, and recrystallized twice from methanol. Methyl acrylate, α -chloroacrylonitrile, acryloyl chloride (Aldrich Chemical Co.), *p*-chloromethylstyrene (Polyscience, Inc.), and methyl methacrylate (Matheson, Coleman, and Bell Co.) were distilled before use. 4-Vinylpyridine and 2-methyl-5-vinylpyridine (Aldrich Chemical Co.) were distilled from KOH under reduced pressure. Sodium styrenesulfonate was crystallized from water-methanol. Sodium vinylsulfonate (40% aqueous solution,

Polyscience, Inc.) was diluted with 95% alcohol until turbid, and crystallized at -22°C .

Experimental Procedures

Copolymerization of Acrylophenone and N-Vinylcarbazole Without Initiator

Acrylophenone (10 mmol, 1.329 g) and 10 mmol (1.926 g) of N-vinylcarbazole were dissolved in 10 ml of dry THF (run through alumina column before use) and the solution was degassed by the freeze-thaw process, three times. Nitrogen was then put in and the solution was stirred for 20 hr at room temperature in the dark. After adding dropwise to 20 ml of methanol, no precipitate formed.

Copolymerization of α -Methylacrylophenone and N-Vinylcarbazole Without Initiator

The polymerization was done according to the above procedure. After the solution was stirred in THF at room temperature under nitrogen for 35 hr, no polymer was found.

Copolymerization of Acrylophenone and N-Vinylcarbazole by Lithium Metal

Acrylophenone (10 mmol) and 10 mmol of N-vinylcarbazole were dissolved in 10 ml of dry THF and was degassed by the freeze-thaw process, three times. In a dry box, 1.0 mmol of lithium metal (several pieces) was added and the system was sealed under nitrogen. Lithium metal was washed first with methanol then washed with THF in a dry box to obtain fresh surface. The solution was stirred at room temperature

in the dark and was then poured into 200 ml of methanol. The polymer was reprecipitated from benzene into methanol and dried in a drying pistol.

Copolymerization of Acrylophenone and N-Vinylcarbazole by AIBN at Room Temperature

After acrylophenone and N-vinylcarbazole were dissolved in THF, the solution was degassed by the freeze-thaw process, 3 times. AIBN was added and the system was sealed under nitrogen and wrapped with aluminum foil. After stirring, the solution was poured into methanol. The precipitated polymer was dried in a drying pistol.

Copolymerization of Acrylophenone and N-Vinylcarbazole by Lithium Dispersion in Wax (Lithium 30 Wt %)

Acrylophenone (10 mmol) and 10 mmol of N-vinylcarbazole were dissolved in 5 ml of dry THF and degassed by the freeze-thaw process, 3 times. In a dry box, 0.122 g (0.5 mmol lithium) of lithium dispersion was added, and the system was sealed under nitrogen. The solution was stirred at room temperature and was then poured into 200 ml of methanol. The polymer was dried in a drying pistol.

β -Hydroxyethyl 3,5-Dinitrobenzoate

3,5-Dinitrobenzoic acid (50 mmol, 10.6 g) and p-toluenesulfonic acid monohydrate (0.3 g) were slurried in 30 ml of ethylene glycol, and the mixture was stirred overnight at 105°C. After cooling, the crystalline needles were filtered, followed by recrystallization from 250 ml of methanol, giving 10.7 g of pale yellow needles; 84% yield; m.p. 138-9°C;

ir (KBr) 3250, 1725 (s), 1610, 1550 (s), 1345, 1285 cm^{-1} ; nmr (DMSO- d_6) δ 3.8 (t, 2H), 4.4 (t, 2H), 5.1 (t, 1H), 9.1 (3H); uv (THF) λ_{max} , 285 (24,000) nm.

Copolymer 3

Freshly distilled (under nitrogen) acryloyl chloride, N-vinyl-carbazole, and AIBN (0.1% to monomers) in 10 ml of dry benzene was degassed for 1 hr by passing nitrogen through, and the solution was refluxed for 24 hr under nitrogen. At the end of polymerization, β -hydroxyethyl 3,5-dinitrobenzoate in 3 ml of dry pyridine and 7 ml of dry benzene was added and the orange solution was stirred overnight and refluxed for 1 hr. The polymer solution was poured into methanol and yellow polymer was obtained. The polymers were purified by pouring the THF solution into methanol, ir (KBr) 1545 cm^{-1} , (NO_2).

β -(2,4-Dinitrophenoxy)- propionyl Chloride

2,4-Dinitrophenol (0.13 mol, 24 g), in β -propiolactone (0.18 mol, 13.2 g) was stirred at 130°C overnight, and 200 ml of methanol and 1 ml of concentrated sulfuric acid were added. The mixture was refluxed for 8 hr for esterification. The reaction mixture was poured in 1 liter of ice water and extracted three times with ether. After washing (4 times with 25 ml of 0.5 NaOH, and once with water) and drying (over sodium sulfate), the ether was evaporated to give crude methyl 3-(2,4-dinitrophenoxy)propionate. The crude ester was hydrolyzed by refluxing in a mixture of 25 ml conc. HCl and 20 ml of water for 4 hr. The product was isolated by cooling and crystallization from ether: overall

yield 4.7 g, m.p. 117°C (lit.⁴³ 118-119°C). The acid (4.5 g) was refluxed in 5 ml of distilled thionyl chloride for 3 hr and the excess thionyl chloride was distilled out. The residue was warmed with benzene (10 ml) and pet. ether (3 ml). After cooling, sitting, and filtering, 3.96 g of pale yellow crystals were obtained; ir (KBr) 1775 (C=O), 1520 (NO₂) cm⁻¹.

Copolymerization of N-Vinylcarbazole and Vinyl Acetate

N-Vinylcarbazole and vinyl acetate were stirred in degassed dry benzene or toluene under nitrogen and the polymer solution was poured into methanol. The polymer was purified by reprecipitation from benzene into methanol; ir (KBr) 1730 (C=O), 1595, 1605 (Cbz) cm⁻¹.

Copoly (N-vinylcarbazole-vinyl Alcohol)

Copoly (N-vinylcarbazole-vinyl acetate) was dissolved in THF and 1 N NaOH in methanol was added slowly to avoid precipitation. The solution was refluxed for several hr and poured into methanol; ir (KBr) 3400 cm⁻¹ (broad) and no carbonyl. The hydrolysis was almost complete.

Copolymer 4

Copoly (N-vinylcarbazole-vinyl alcohol) was dissolved in dry pyridine (distilled over calcium hydride) or THF (distilled over lithium aluminum hydride), and (2,4-dinitrophenoxy)propionyl chloride in dry benzene or THF was added dropwise. The solution was stirred for several hr at room temperature, and in some cases, refluxed for several hr. If the resulting polymer was soluble, the solution was poured into methanol

and reprecipitated from THF into methanol. If the resulting polymer was insoluble and precipitated as a lump, the clear solution was discarded and DMSO was added to dissolve the polymer. After the polymer was precipitated into acetone (no precipitate in methanol, water), the polymer was purified by pouring the DMSO solution into acetone; ir (KBr) 1730 (C=O), 1520 (NO₂) cm⁻¹.

Copolymer 5

Copoly(N-vinylcarbazole-vinyl alcohol) was dissolved in THF (or THF and DMSO), sodium hydride dispersed in oil was added, and the mixture was stirred for several hr at room temperature. p-Chloranil in THF or DMSO was added dropwise over 30 min and the dark solution was stirred at room temperature overnight or for two days. The resulting dark solution was poured into methanol (400 ml) to give a gray polymer and a purple solution. A black polymer was obtained after drying; ir (KBr) 1685 cm⁻¹ (C=O).

Sodium N-Acryloylsulfanilate

Sulfanilic acid (0.25 mole, 48 g) was neutralized with sodium hydroxide (10 g) in 100 ml of water and the solution was heated to dissolve all the salts. After sodium bicarbonate (21 g, 0.25 mole) and picric acid (1 g) were added, acryloyl chloride (0.25 mole, 23 g) was added dropwise for 2 hr at room temperature. The solution was stirred for 30 min more and cooled to 0°C and 40 g of precipitate was obtained. The precipitate was very soluble in water and purified by reprecipitating twice from the water solution into acetone. The pure monomer was obtained by crystallizing from methanol-water solution; ir (KBr) 3500

(s), 3300 (s), 1660 (s), 1640, 1610 (s), 1540 (s), 1410, 1330, 1200 (broad), 1140, 1060, 1020, 840 cm^{-1} ; nmr (DMSO-d_6), δ 7.66 (4H), 5.6-6.8 (3H), sample was hygroscopic.

Analysis: Calcd for $\text{C}_9\text{H}_8\text{NO}_4\text{SNa}$: C, 43.34; H, 3.22; N, 5.62.

Found: C, 40.84; H, 3.79; N, 5.44.

Attempt to Copolymerize VCbz and SAS in DMSO

After 20 ml of DMSO was degassed by bubbling nitrogen through for 30 minutes, VCbz (10 mmol, 1.934 g), SAS (10 mmol, 2.934 g) and AIBN (0.1 mole %, 3.3 mg) were added. The resulting solution was stirred for 24 hr at 72°C in the dark followed by pouring into 800 ml of acetone. After filtration a yellow filtrate and a brittle solid were isolated; ir (KBr), and nmr (DMSO-d_6) show that the brittle solid is starting monomer SAS. The yellow filtrate was concentrated and poured into 500 ml of water. After filtration, a white precipitate was isolated and it was purified by sublimation at 110°C. The ir (KBr) and nmr (DMSO-d_6) of the sample were identical with those of carbazole (m.p. 243-245°C).

Copolymerizations of VCbz and SAS in DMAM

DMAM (10 ml) was degassed for 30 min by bubbling nitrogen through and monomers plus AIBN (0.5% by mole to monomers) were added. The resulting solution was stirred for 24 hr at 70°C in the dark and the polymer solution was poured into 200 ml of 95% ethanol. Inherent viscosities were determined in distilled water at 30°C. Copolymer compositions were calculated from sulfur analyses.

Copolymerizations of VCbz and
SSS in DMAM

Monomers and AIBN were added to the degassed DMAM (25 ml) and the solution was stirred for 24 hr at 70°C in the dark. The resulting solutions were poured into 500 ml of acetone, and the polymers were dried in a drying pistol overnight. Inherent viscosities were determined in distilled water at 30°C.

TAI

N,N,-Diethylethanolamine (45 g, 0.384 mole), p-toluenesulfonic acid (5 g) and picric acid (5 g) in 125 g methyl methacrylate were stirred overnight at 60°C and the azeotrope was distilled out slowly at 60°C. Excess methyl methacrylate was distilled out under vacuum. 2-(N,N,-Diethylaminoethyl methacrylate was obtained (41 g, $n_d^{25} = 1.448$, lit.⁴⁷ $n_d^{24} = 1.442$) by vacuum distillation at 85°C, 10 torr (lit.⁴⁷ 80°C at 10 torr), yield 57%.

2-(N,N-Diethylaminoethyl) methacrylate (31.5 g, 0.17 mole) in ethyl iodide (132.5 g, 0.85 mole) was refluxed for 2 hr and 50 ml benzene was added to precipitate the salt. After standing overnight, the solid was filtered, washed several times with absolute ether and dissolved in 50 ml of absolute methanol. The solution was made faintly cloudy by the addition of ether and was stored in the freezer for 24 hr. The white crystals that had precipitated were filtered off and recrystallized in the same manner to yield 24 g (41%); m.p. 103-104°C (dec.; lit.⁴⁷ m.p. 103-104°C dec.); ir (KBr) 1730 (ester). 1645 (C=C) cm^{-1} .

Copolymerization of TAI and VCbz

TAI, VCbz and AIBN were dissolved in 10 ml of degassed DMAM (N,N-dimethylacetamide) and the solution was stirred 24 hr at 70°C under nitrogen. The polymer solution was poured into acetone and the polymer was purified by reprecipitation from DMSO or DMAM into acetone; ir (KBr), 1710 (ester) 1610, 1590 (Cbz) cm^{-1} .

TVBA

Trimethylamine (7 ml cooled to 0°C) was added to a chloromethylstyrene (16 g, from Polysciences, Inc.)-ether (50 ml) solution at 0°C in the presence of hydroquinone and the solution was stirred for 8 hr at 0°C and overnight at room temperature in a closed system. The precipitate (9 g) was filtered out and recrystallized twice from acetonitrile, 160°C dec. The monomer was synthesized⁴⁸ in aqueous solution, but no melting point was reported.

Analysis: Calcd for $\text{C}_{12}\text{H}_{18}\text{NCl}$: C, 68.20; H, 8.58; N, 6.61.

Found: C, 69.44; H, 8.57; N, 6.94.

Copolymerization of VCbz and TVBA in DMAM

Monomers and AIBN (0.5 mole % to monomers) were added to 30 ml of degassed DMAM and the solution was stirred for 24 hr at 70°C in the dark. The polymer solution was poured into 500 ml acetone, and the polymer dried in a drying pistol. Copolymer compositions were determined from chlorine analyses.

Hydrolysis of MA-N-Vinylcarbazole Copolymer

Copolymer (DC-III-8, 1.00 g, containing MA 0.23 g, 2.68 mmol) was dissolved in 120 ml THF and 10 ml of 1 N NaOH or 1 N KOH methanol solution (10 mmol, NaOH or KOH) was added slowly to avoid precipitation. After stirring for 14 minutes at room temperature, the solution was refluxed for 1 hr and a white precipitate formed. The mixture was filtered and a hard brittle polymer was obtained. The polymer was insoluble in water, methanol, THF, DMSO, and chloroform, but can be dispersed in hot water; ir (KBr) 1580, 1400 cm^{-1} , ($-\text{CO}_2^-$) and ester band at 1710 cm^{-1} disappeared. No nmr spectrum was run due to the solubility problem.

Attempts to Copolymerize Sodium Vinylsulfonate and N-Vinylcarbazole

DMAM (30 ml) was degassed for 2 hr by bubbling nitrogen through and monomers (in various feed ratios) and AIBN were added. The solution was stirred for 24 hr at 75°C in the dark under nitrogen. The solution was then poured into 400 ml of 95% ethanol. In each run, either largely homo polyVCbz or largely poly (sodium vinylsulfonate) was obtained.

Methyl 1,3-Dithiole-2-thione-4-carboxylate

1,3-Dithiole-2-thione-4-carboxylic acid (10 mmol, 1.78 g) was slurried in 1 ml of methanol, 0.2 ml of concentrated sulfuric acid and 5 ml of 1,2-dichloroethane, and the mixture was refluxed 18 hr. The reaction mixture was diluted with 20 ml water and the organic layer was washed with 5% sodium carbonate twice and dried over magnesium sulfate.

The solvent was distilled out and the residue was crystallized from 100 ml of n-hexane. Plates (1.457 g, m.p. 109°C) were obtained in 76% yield; ir (KBr) 1710 (ester) cm^{-1} ; nmr (CDCl_3) δ 3.9 (3H), 7.95 (1H).

Dimethyl bis-1,3-Dithiole-
4-carboxylate

After 2.21 g (11.5 mmol) of methyl 1,3-dithiole-2-thione-4-carboxylate was slurried in 40 ml of cold acetone, 9.35 g (46 mmol) of m-chloroperbenzoic acid in 20 ml of cold acetone was added slowly dropwise for 30 min. The solution was stirred 20 min more in an ice-bath. After filtration, a pale-yellow solid (1.65 g) was obtained; yield 55%; ir (KBr) 3000 (broad), 1750 (s), 1510, 1420, 1380, 1260 (broad, s), 1075 (s), 1015 (s), 890, 860 (s), 740 (s) cm^{-1} ; m.p. 65°C dec.

Triethylamine (2 ml) was added through an addition funnel under nitrogen to a slurry containing 1.65 g of the salt in 10 ml of acetonitrile (distilled over P_2O_5). As soon as the amine was added, a blood-red solid precipitated. After filtration, drying, and crystallization from methanol and THF, red crystals (0.28 g) were obtained; yield 27%; m.p. 240°C; MS m/e = 320; ir (KBr) 1695 (s), 1550 (s), 1425, 1380, 1245 (s), 1050, 730 cm^{-1} ; nmr (CDCl_3) δ 7.3 (1H, s), 7.4 (1H, s), 3.8 (6H, s); uv $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 430 (1350), 314 (9,500), 300 (9,650), 289 (9,700), 231 sh (13,800) nm.

Analysis: Calcd for $\text{C}_{10}\text{H}_8\text{S}_4\text{O}_4$: C, 37.50; H, 2.52; S, 40.05.

Found: C, 37.57; H, 2.70; S, 40.06.

Dimethyl 2-(p-Vinylbenzylidene)-
1,3-dithiole-4,5-dicarboxylate

p-Vinylbenzaldehyde (1.32 g, 0.01 mmol) was added through an addition funnel to the purple-red complex of carbon disulfide (0.76 g, 0.01 mmol) and tri-n-butylphosphine (2.02 g, 0.01 mmol) in 10 ml of absolute ether. Dimethyl acetylenedicarboxylate (0.01 mmol, 1.42 g) in 5 ml of absolute ether was then added dropwise over 10 min. At the end of addition, a red precipitate formed suddenly and the mixture was stirred 10 min more. After filtration and crystallization of the precipitate from 20 ml of hot 95% ethanol, orange-red needles (1.59 g) were obtained, yield 57%; m.p. 99.5°C; MS m/e = 334; ir (KBr) 1725 (s), 1580 (s), 1435, 1250 (s), 1100, 1030, 995, 920 cm^{-1} ; nmr (CDCl_3) δ 3.80 (s, 6H), 5.25 (q, 1H), 5.80 (q, 1H), 6.40 (s, 1H), 6.45-6.95 (q, 1H), 7.05-7.50 (q, 4H); uv $\lambda_{\text{max}}^{\text{EtOH}}$ 410 (500), 359 sh (22,700), 345 (24,000), 245 (17,500) nm.

Analysis: Calcd for $\text{C}_{16}\text{H}_{14}\text{S}_2\text{O}_4$: C, 57.50; H, 4.19; S, 19.15.

Found: C, 57.60; H, 4.23; S, 19.06.

Ethyl 2-(p-Vinylbenzylidene)-
1,3-dithiole-4-carboxylate

p-Vinylbenzaldehyde (2.64 g, 20 mmol) was added to a complex of carbon disulfide (1.52 g, 20 mmol) and tri-n-butylphosphine (4.04 g, 20 mmol) under nitrogen at -23°C in a carbon tetrachloride dry ice bath. Ethyl propiolate (1.96 g, 20 mmol) in 15 ml of absolute ether was then added through addition funnel in 10 min and the solution was stirred 10 min more at -23°C. While still cold, the reaction mixture was filtered through a sintered glass and 2.46 g of yellow crude product was obtained

(57% yield). After crystallization from 200 ml of ether at -20°C , yellow plates were obtained; m.p. $122-123^{\circ}\text{C}$; ir (KBr) 1700 (s), 1580, 1410 (w), 1300, 1210, 1070 (s), 1000, 920, 860 (s), 735 (s) cm^{-1} ; nmr (CDCl_3) δ 1.3 (t, 3H), 4.3 (q, 2H), 5.2 (q, 1H), 5.7 (q, 1H), 6.4 (s, 1H), 6.5-6.9 (q, 1H), 7.2 (5H); MS m/e = 290; uv $\lambda_{\text{max}}^{\text{EtOH}}$ 405 sh (3,500), 363 (28,900), 355 sh (28,000), 246 (18,250) nm.

Analysis: Calcd for $\text{C}_{15}\text{H}_{14}\text{S}_2\text{O}_2$: C, 62.10; H, 4.86; S, 22.08.

Found: C, 61.71; H, 4.83; S, 22.54.

Ethyl 2-Benzylidene-1,3-dithiole-4-carboxylate

The procedure is the same as above. The compound was obtained in 30% yield: m.p. $102-108^{\circ}\text{C}$ (geometrical isomers); ir (KBr) 1710, 580, 1570, 1280 (s), 1200, 1070 (s) cm^{-1} ; nmr (CDCl_3) δ 1.2 (t, 3H), 4.3 (q, 2H), 6.55 (d, 1H), 7.30 (s, 5H), 7.35 (1H); MS m/e = 264 (parent peak); uv $\lambda_{\text{max}}^{\text{EtOH}}$ 385 (3,300), 340 (s) (17,100), 326 (18,300), 228 (17,100) nm.

Analysis: Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$: C, 59.15; H, 4.59; S, 24.21.

Found: C, 59.23; H, 4.66; S, 23.97.

2-(p-Vinylbenzylidene)-4-phenyl-1,3-dithiole

p-Vinylbenzaldehyde (2.64 g, 20 mmol) was added under nitrogen at room temperature to a tri-n-butylphosphine (4.04 g)- CS_2 (excess) complex. Phenylacetylene (2.04 g, 20 mmol) in 50 ml of ether was then added through an addition funnel over 10 min and the solution was stirred 7 hr more at room temperature. After filtration and

crystallization from carbon tetrachloride, 0.261 g of yellow powder was obtained: m.p. 228°C; yield 10%; MS m/e = 294; uv $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 378 (27,200), 230 sh (15,000) nm; ir (KBr) 1575 (s), 1525, 1490, 1450, 1400, 1000, 940, 900, 860 (s), 745 (s) cm^{-1} ; nmr ($\text{CF}_3\text{CO}_2\text{H}$) δ 1.75 (d, 3H), 5.0 (s, 2H), 6.2 (q, 1H), 7.55 (s, 4H), 7.65 (s, 5H).

Analysis: Calcd for $\text{C}_{18}\text{H}_{14}\text{S}_2$: C, 73.45; H, 4.79.

Found: C, 74.30; H, 5.18.

2-Benzylidene-4-phenyl-1,3-dithiole

The procedure is the same as above. This compound was obtained in 10% yield; m.p. 204°C dec. (lit.⁵⁶ 207°C); ir (KBr) 1575 (s), 1565 (s), 1480, 1425, 1375 cm^{-1} ; nmr (CS_2) δ 6.4 (s, 1H), 6.5 (s, 1H), 7.2-7.4 (2 peaks, 10H); MS, m/e = 268 (parent peak).

Analysis: Calcd for $\text{C}_{16}\text{H}_{12}\text{S}_2$: C, 71.60; H, 4.51.

Found: C, 71.46; H, 4.56.

2-Benzylidene-4,5-diphenyl-1,3-dithiole

Benzaldehyde (4.24 g, 40 mmol) was added under nitrogen at room temperature to a tri-n-butylphosphine (8.10 g, 40 mmol)- CS_2 (excess) complex in 50 ml of absolute ether. Tolan (7.12 g, 40 mmol) in 150 ml of absolute ether was then added through an additional funnel over 1 hr and the resulting solution was stirred for a week under nitrogen at room temperature. At the end of the reaction, tri-n-butylphosphine was swept away by air, and a tolan-dithiole mixture was obtained. After crystallizing twice from methanol, the mixture was sublimed at 50°C for 2 days to get rid of the tolan. The final pure product was obtained after recrystallization from methanol, yield 5%, m.p. 124°C. The low yield is

due to the difficult purification steps; ir (KBr), 1591, 1545, 1490, 1440 cm^{-1} ; nmr (CDCl_3) δ 7.3 (s, 5H), 7.2 (s, 10H), 6.45 (s, 1H); MS m/e = 334 = base peak = parent peak; uv $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 339 (21,150), 237 (23,600) nm.

Analysis: Calcd for $\text{C}_{22}\text{H}_{16}\text{S}_2$: C, 76.80; H, 4.68.

Found: C, 76.83; H, 4.83.

An Attempt to Polymerize 25a Radically

A 25 ml 3-necked flask containing compound 25a (0.334 g, 1 mmol) and AIBN (8.2 mg, 5%) was flushed with nitrogen and dry benzene was distilled from sodium into the polymerization flask under nitrogen, the benzene solution was refluxed up to 48 hr and the monomer was recovered quantitatively (m.p. 99°C).

Cationic Polymerization of Dimethyl 2-(p-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate

Initiator preparation. 0.764 g of SnCl_4 from a new bottle was injected in a 50 ml flask flushed with nitrogen. Approximately 20 ml of carbon tetrachloride (dried over calcium chloride) was injected in and the flask was weighed again. The resulting initiator contained 2.42% of stannic chloride by weight.

Polymerization. 5×10^{-3} mole of monomer (1.670 g) was dissolved in 5.1 ml of nitrobenzene (5×10^{-2} mole) and 4.8 ml of carbon tetrachloride (5×10^{-2} mole) and the resulting solution was degassed by bubbling nitrogen through for 30 min. After the solution was cooled to

0°C in ice bath, the initiator (0.334 ml) was injected in (1% by mole to monomer). The solution was stirred for 48 hr. The polymeric solution was precipitated into hot methanol twice and 0.224 g of polymer was obtained with 13% conversion. Some sticky orange oil was also obtained at the bottom of the beaker; nmr (CDCl_3) showed broad peaks at δ 1.7, 2.4, 3.7, 5.4, 6.4, 7.0; ir (KBr) 1720 (s), 1580 (s), 1260 (s), 1095 (w), 1030 (w) cm^{-1} ; molecular weight 950 (by ebullioscopic method).

Analysis: Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4\text{S}_2$: C, 57.50; H, 4.19; S, 19.15.

Found: C, 57.35; H, 4.49; S, 19.19.

Anionic Polymerization of Dimethyl 2-(p-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate

A solution of 1 mmol of monomer in 10 ml of THF was degassed by bubbling nitrogen through for 30 min and 6.7×10^{-2} ml (5% to monomer) of n-BuLi (0.75 M in hexane) was injected in with hypodermic syringe. After being stirred for 48 hr the solution was poured into methanol and no polymer was found.

Polymerization of Dimethyl 2-(p-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate by Concentrated Sulfuric Acid

The monomer (0.500 g) was dissolved in 5 ml concentrated sulfuric acid and the solution was stirred for 4 hr at room temperature. The solution was then poured into ice water, filtered and washed with water. The polymer was precipitated twice into hot methanol to give 0.42 g of polymer with 85% conversion; nmr (CDCl_3) δ 7.1 (4H), 6.4 (1H), 3.8 (6H), 1.0-2.5 (3H, broad); ir (KBr) 1720 (s), 1580, 1420, 1240

(broad, s), 1095 (w), 1030 (w) cm^{-1} ; uv $\lambda_{\text{max}}^{\text{CHCl}_3}$ 405 (1,000), 328 (12,500), 238 (12,900) nm; molecular weight 7,000 (by ebullioscopic method); $n_{\text{inh}} = 0.03$ in benzene.

Analysis: Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4\text{S}_2$: C, 57.50; H, 4.19; S, 19.15.

Found: C, 56.79; H, 4.11; S, 19.06.

Copolymerization of Dimethyl 2-(p-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate by AIBN

Dimethyl 2-(p-vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (1.0 mmol) and comonomer (1.0 mmol) were dissolved in 10 ml of dry benzene and the solution was degassed by bubbling nitrogen through. After 0.0082 g of AIBN (2.5% by mole to monomers) was added, the resulting solution was refluxed under nitrogen. After precipitation and reprecipitation, low molecular weight alternating copolymer was obtained $n_{\text{inh}} = 0.02$ in benzene; composition was calculated from sulfur analysis.

Poly Dimethyl 2-(p-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate

p-Vinylbenzaldehyde was polymerized according to the procedure of Kinoshita and Schulz⁵⁸ for 21 hr with 73% conversion. The polymer obtained was insoluble in benzene and slightly soluble in chloroform. The chemical modification was done in THF by reacting the polymer (0.7 g) with carbon disulfide (10 mmol), tri-n-butylphosphine (10 mmol, and dimethyl acetylene-dicarboxylate (10 mmol), at -23°C ; nmr (CDCl_3) δ 1.5 (broad, 3H), 3.9 (s, 6H), 6.4 (s, 1H), 6.6-7.6 (broad, 4H); ir (KBr), 1720, 1590, 1430, 1260, 1095 (w), 1035 (w) cm^{-1} ; uv $\lambda_{\text{max}}^{\text{CHCl}_3}$ 405 (1,050), 326 (13,300), 255 sh (11, 500) nm; $n_{\text{inh}} = 0.06$ in benzene.

Analysis: Calcd for $C_{16}H_{14}O_4S_2$: C, 57.50; H, 4.19; S, 19.15.

Found: C, 57.46; H, 4.25; S, 15.73.

Cationic Polymerization of Ethyl 2-
(p-Vinylbenzylidene)-1,3-dithiole-
4-carboxylate

The initiator contained $SnCl_4$ 2.42% by weight. 2 mmol (0.580 g) of monomer was dissolved in 5 ml of dry nitrobenzene and 4.8 ml of dry CCl_4 and the solution was degassed by bubbling nitrogen through for 30 min. The orange solution was then cooled to $0^\circ C$ and some of the monomer was precipitated out. After 0.67 ml of initiator (5% to monomer) was injected in through the rubber cap under nitrogen, all the monomer dissolved immediately to give a dark-orange solution. The solution was then stirred for 48 hr at $0^\circ C$ under nitrogen. After precipitation into hot methanol, 0.10 g of polymer was obtained with 17% conversion; $\eta_{inh} = 0.03$ in benzene.

Analysis: Calcd for $C_{15}H_{14}S_2O_2$: C, 62.10; H, 4.86; S, 22.08.

Found: C, 62.19; H, 5.06; S, 22.15.

TCNQ-(2-Benzylidene-4,5-diphenyl-1,3-
dithiole) Complex

Hot, saturated acetonitrile solutions of TCNQ (0.204 g, 1 mmol) and dithiole (0.344 g, 1 mmol) were mixed and the resulting solution was concentrated by evaporation at room temperature. After it was dried, 0.30 g of yellow crystals was isolated: m.p. $165^\circ C$ with dec. (sublimation of TCNQ); ir (KBr), 3080 (TCNQ), 2250 (TCNQ) 1595 (dithiole), 1580 (dithiole), and 860 (s), (TCNQ) cm^{-1} ; nmr ($CDCl_3$) δ 7.5-7.9 (q, 4H, TCNQ), 7.4 (s, 5H), 7.2 (d, 10H); uv $\lambda_{max}^{CH_2Cl_2}$ 240, 320, 370, 465, 780,

842 nm; MS m/e = parent peak = 548 (small), base peak = 334 (dithiole), 204 (TCNQ), $p\text{-CN}$ = 522.

Analysis: Calcd for $C_{34}H_{20}N_4S_2$: C, 74.40; H, 3.68; N, 10.21.

Found: C, 74.27; H, 3.87; N, 9.98.

Dimethyl 2-Benzylidene-1,3-dithiole-4,5-dicarboxylate-TCNQ Complex 28

Dithiole (4.72 mmol, 1.455 g) in 35 ml of hot acetonitrile was added dropwise to a 100 ml hot acetonitrile solution of TCNQ (0.965 g, 4.72 mmol). The solution was concentrated and sat to crystallize the complex. The yellow crystals were recrystallized from 30 ml of acetonitrile and 0.763 g of yellow crystals was obtained, m.p. 220°C (became green); ir (KBr) 1755 (s), 1735 (s), 1590 (s), 1420; nmr ($CDCl_3$) δ 3.80 (d, 12H), 7.2-7.6 (m, 12H), 7.8 (s, 4H); uv $\lambda_{max}^{CH_3CN}$ 840, 820, 795 (sh), 760, 742, 725 (sh), 675, 663, 470 (sh), 420 (sh) nm.

Analysis: Calcd for $C_{40}H_{28}N_4S_4O_8$: C, 58.55; N, 6.83; S, 15.65; H, 3.44.

Found: C, 58.52; N, 8.50; S, 15.87; H, 3.54.

TNF-(Dimethyl 2-Benzylidene-1,3-dithiole-4,5-dicarboxylate) Complex (1:1)

Dithiole (3.308 g) and 0.315 g (1 mmol) of TNF were dissolved in hot absolute ethanol and a dark green precipitate was obtained immediately. After recrystallization, 0.514 g of dark green finely divided crystals was obtained, m.p. 145°C sharp (dithiole m.p. 100°C, TNF m.p. 175-176°C) yield 84%; ir (KBr), 1730 (s), 1700 (s), 1600, 1580, 1525 (s), 1430, 1340 (s), 1260 (broad), 1080, 1035; nmr ($CDCl_3$) δ 9.0 (d, 1H),

8.7 (d, 1H), 8.6 (d, 1H), 8.5 (d, 1H), 8.4 (d, 1H), 7.2 (d, 5H), 6.4 (d, 1H), 3.9 (s, 6H); MS m/e = base peak = parent peak 315 (TNF), and 308 (dithiole); uv $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 420 (sh) (855), 370 sh (3,400), 322 (12,200), 286 (24,800), 280 (25,100 nm. TNF:uv $\lambda_{\text{max}}^{\text{alcohol}}$ 336-348 (7,940), 280 (32,600) nm.

Analysis: Calcd $\text{C}_{27}\text{H}_{17}\text{N}_3\text{S}_2\text{O}_{11}$: C, 52.10; H, 2.75; N, 6.74; S, 10.03.

Found: C, 52.26; H, 2.87; N, 6.68; S, 10.13.

Poly[dimethyl 2-(p-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate]-TNF Complex

Dithiole polymer (84 mg polymerized by sulfuric acid $n_{\text{inh}} = 0.03$ in benzene) and 81 mg of TNF were dissolved in 1 ml of benzene and the solution was heated to boiling. The dark solution was poured into methanol and dried. 106 mg of dark green π -complex was obtained; ir (KBr) 1730 (s), 1720 (s), 1595 (s), 1440, 1375 (s), 1260 (broad), 1090, 1020 cm^{-1} ; nmr (CDCl_3) δ 8.4-9.0 (q, broad), 7.1 (broad, 4H), 6.4 (broad, 1H), 3.9 (s, 6H). Integration showed only half of the dithiole heterocycles formed complexes with TNF.

Hydrolysis of 19

Dithiole 19 (0.960 g, 3 mmol) was slurried in 0.5 N NaOH in methanol and the mixture was refluxed for 4 hr. After cooling and filtering, 0.65 g of red precipitate was isolated, ir (KBr) no ester, 1580 (CO_2^-), 1550 (C=C) cm^{-1} ; nmr (D_2O) δ 7.2 (s); 280°C dec.; yield 60%. The disodium salt (0.501 g, 1.49 mmol) was dissolved in 20 ml of distilled

water and 1 M HCl (3 ml) was added slowly with stirring the red precipitate was filtered off (0.315 g, yield 73%), 200°C dec.; ir (KBr) 3000 (broad), 1660 (C=O), 1450 (C=C) cm^{-1} ; nmr (DMSO- d_6), δ 7.65 (s, 2H), 10 (broad, 2H).

Hydrolysis of 24a

Dithiole 24a (4.82 mmol, 1.484 g) was slurried in 0.5 N NaOH in methanol (40 ml, 20 mmol NaOH) and the mixture was stirred 1.5 hr at room temperature. The yellow crystals were filtered off (1.281 g, 82% yield), 140°C dec., in (KBr), 1580 (broad, s), no ester; nmr (D_2O) δ 6.4 (s, 1H), 7.3 (d, 5H). The disodium salt was dissolved in distilled water and the solution was precipitated into 0.5 N HCl. The dark red precipitate was recrystallized from the minimum amount of ethyl ether and dark red needles were obtained; ir (KBr), 1710 (acid), 1590, 1580, 1530, 1440 cm^{-1} ; nmr ($CDCl_3$), δ 6.5 (s, 1H), 7.3 (d, 5H), \sim 13 (2H, s); dark red needles were heated to 120°C and became brown needles.

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