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SYNTHESIS OF FILM-FORMING ELECTRON-ACCEPTING POLYMERS
(U) ARIZONA UNIV TUCSON DEPT OF CHEMISTRY H K HALL
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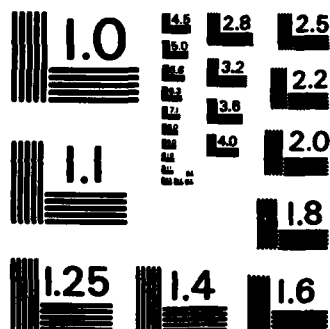
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Certain organic charge-transfer salts behave as organic or molecular metals and show conductivity. But these salts have weak interactions between the layers of donors and acceptors which make them fragile and difficult to fabricate. The objective of this research was to incorporate electron-poor sites in a polymer chain. After polymerization, these sites can be complexed with appropriate electron-donating compounds, and lead to charge-transfer complex salts that are incorporated in a strong matrix. However, the intermediates to the electron-poor polymers proved to be too difficult to synthesize.

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FINAL TECHNICAL REPORT.

Contract DAAG-29-82-K-0049

SYNTHESIS OF FILM-FORMING
ELECTRON-ACCEPTING POLYMERS.

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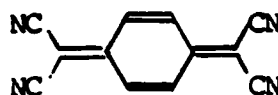
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Certain organic charge-transfer salts behave as organic or molecular metals and show conductivity. But these salts have weak interactions between the layers of donors and acceptors which make them fragile and difficult to fabricate. The objective of this research was to incorporate electron-poor sites in a polymer chain. After polymerization, these sites can be complexed with appropriate electron-donating compounds, and lead to charge-transfer complex salts that are incorporated in a strong matrix.

Dialkyl dicyanofumarate was found to be a moderately strong electron-acceptor, although not as strong as TCNQ.



R= Et, Me

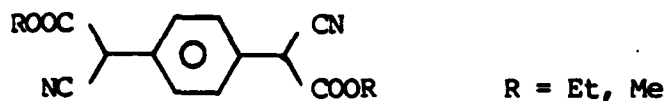


TCNQ

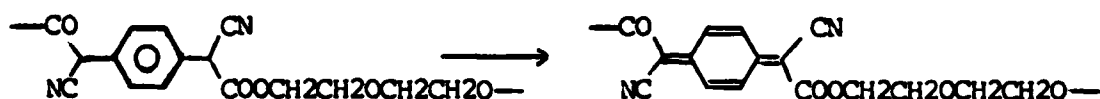
The electrode reduction potentials for a whole series of electrophilic olefins, substituted with cyano and carbomethoxy groups, were measured by cyclic voltammetry, to appraise their electron-accepting capabilities.

A tetrathiafulvalene (TTF) complex of dimethyl dicyanofumarate crystallized in a columnar array, as was proven by X-ray structure determination. However, high uniaxial conductivity has not been observed in this compound.

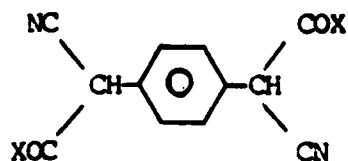
In order to prepare polymers containing TCNQ analogs in the polymer chain the following monomer was prepared:



Ester interchange polycondensation of this diester with a diol leads to the following polyester. However, the polymerization is slow and gave low molecular weight polymers. No films could be formed from the polymers we obtained. N-Chlorosuccinimide oxidation of this polymer though, leads to the new electron-accepting polymer with the desired structure.



The research then concentrated on the synthesis of more reactive intermediates for the polycondensation reaction.



a: $X = \text{OCH}_3$

b: $X = \text{OC}_6\text{H}_4\text{CH}_3$

c: $X = \text{OC}_6\text{H}_4\text{-p-NO}_2$

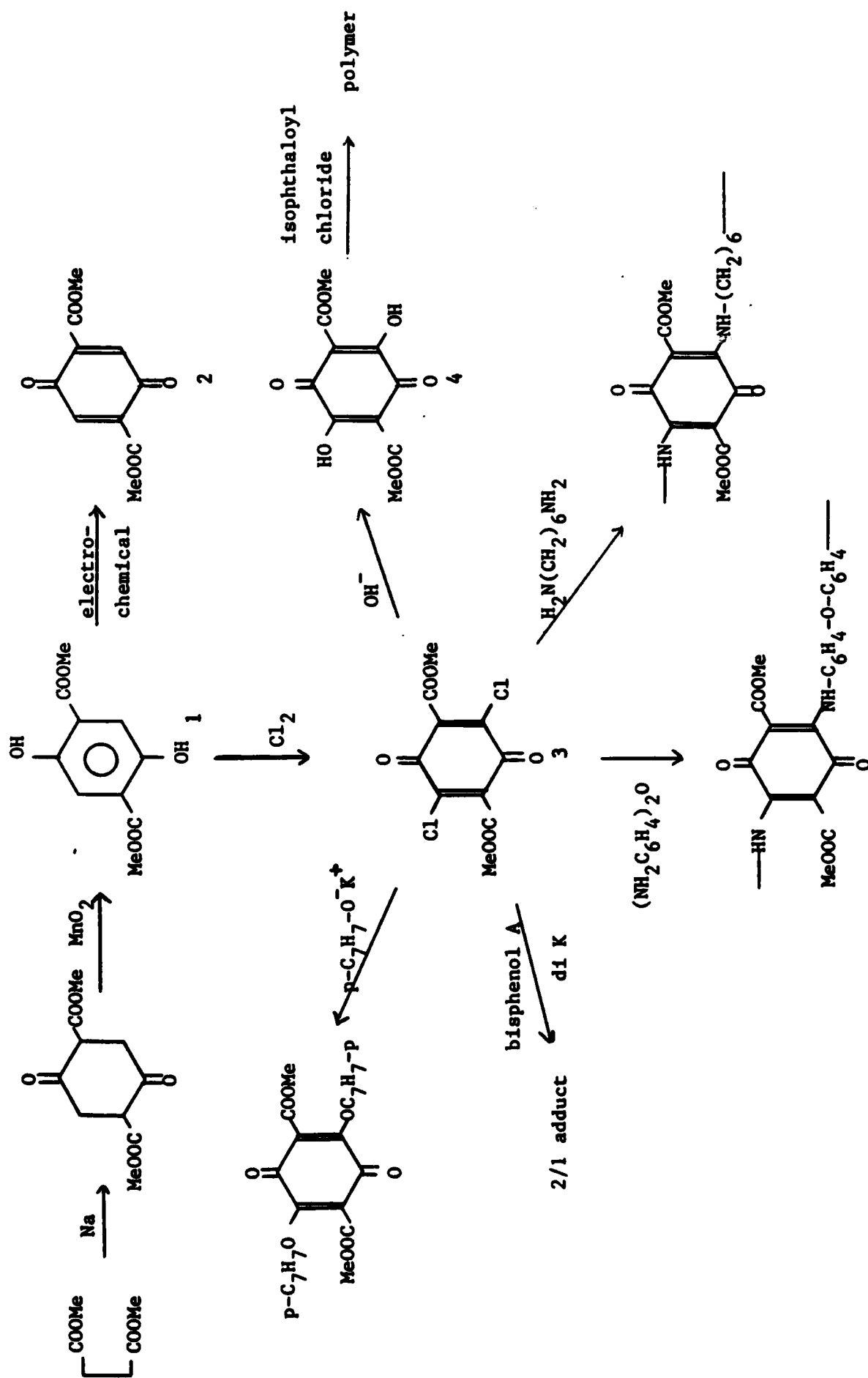
d: $X = \text{Cl}$

The dimethyl ester a with ethylene glycol gives low molecular weight, as mentioned above. Attempts to make the more reactive phenyl esters b and c from the diacid did not succeed. The diacid chloride d could not be obtained in high enough purity for polymerization. Although all these reactions were successfully performed on the monofunctional analogs of these compounds, they could not be duplicated on the bifunctional molecules. A major problem was the lability of the carbomethoxy substituent and also the high acidity of the benzylic protons.

A third route to polymers containing electrophilic sites was the incorporation of electrophilic quinone groups in the polymer chain. Dicarbomethoxy hydroquinone **1** is synthesized by oxidation of the diethyl succinate adduct. Reaction of **1** with 1,4-butanediol lead to a high-melting polyester. Oxidation of this polyester was not attempted in view of the difficulties encountered in oxidizing the monomeric hydroquinone (see below).

Chemical oxidation of **1** has not succeeded, even though the isomeric 2,3-dicarbomethoxy hydroquinone is easily oxidized by nitrogen oxides. Cyclic voltammetry in acetonitrile indicates an oxidation potential of 1.47 eV. Electrochemical oxidation in the presence of 2,6-dimethyl pyridine did succeed, and yielded a small quantity of the desired 2,5-dicarbomethoxy quinone **2**. Charge-transfer complexes with several electron-rich compounds were synthesized and the UV-spectrum measured. In analogy, complexes of the 2,3-dicarbomethoxy isomer were also investigated.

Chlorination of **1** in methanol at room temperature to form the dichloro dicarbomethoxy benzoquinone **3** proceeds in 100% yield in a few minutes. This is a much more convenient route to this compound than the



literature procedure. Reaction of 3 with p-cresol potassium salt proceeds in 30% yield. Attempted polymerization of 3 with bisphenol A di-potassium salt only yields the 2/1 adduct.

Reaction of 3 with aniline or with neopentylamine in a two-phase system proceeds in very good yield. Polymerization of 3 with hexamethylene diamine yields a dark red polymer. The polymerization also proceeds with bis-p-aminophenyl ether. Both these polymerizations were done in a phase-transfer system. Attempted polymerization with p-phenylene diamine only resulted in black insoluble material, presumably a complex between the starting materials.

Hydrolysis of 3 in very mild conditions yields the dihydroxy dicarbomethoxy benzoquinone 4 which on reaction with isophthaloyl chloride yielded a polymer.

Conclusion: The intermediates to the electron-poor polymers which we hoped to synthesize, proved to be too difficult to obtain.

Publications:

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2. Polymer Bulletin 7,173 (1982).
3. J. Cryst. Spectr. Res. 12,331 (1982).
4. J. Polym. Sci., Polym. Chem. Ed. 21,309 (1983).
5. 2,5-Dicarbomethoxy Benzoquinone (in preparation).

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