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ELECTROCHEMISTRY OF POLYMER FILMS APPLICATIONS TO
CHEMICAL ANALYSIS AND ENERGY CONVERSION(U) TENNESSEE
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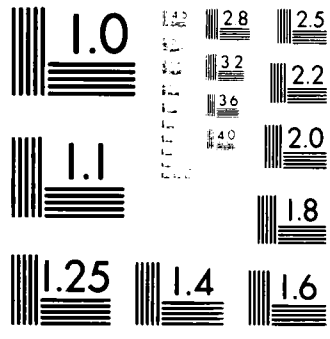
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electroactive polymers containing the widely studied electron acceptor, tetracyanoquinodimethane or TCNQ, in the polymer backbone have been synthesized. The charge transport processes through thin films of these TCNQ polymers and related materials have been thoroughly studied leading to new insight at the molecular level. Chemical reactions coupled to the electron hopping steps can profoundly influence the rate of charge transport in fixed site polymer films. Methodology and techniques have been developed and refined for the study of polymer film modified electrodes.		

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APPLICATIONS TO CHEMICAL ANALYSIS
AND ENERGY CONVERSION

Final Report

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Professor of Chemistry

Oct. 17, 1984

U. S. Army Research Office

Grant No. DAAG29-81-K-0036

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Knoxville, TN 37996

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Statement of the Problem Studied

This research involved the synthesis and characterization of electroactive polymers by electrochemical and spectroscopic methods. An understanding was sought, at the molecular level, of the charge transport process through thin films of these materials cast on uniform substrates. Voltammetric and spectroscopic methods were developed and refined for the study of polymer modified electrodes.

Summary of Most Important Results

The significant results of our work lie in three areas: polymer synthesis, development of experimental methodology in the area of polymer modified electrodes, and the advancement of our understanding of charge transport in fixed-site electroactive polymer film.

The TCNQ polymer synthesis of Roger W. Day (Ph.D. Thesis, University of Tennessee, and references 1 and 12 below) is the first report of a polymer containing neutral TCNQ units covalently attached to the polymer structure. Day's synthesis required the use of a low-temperature polyesterification of aliphatic diacid chlorides with aliphatic diols. In a systematic study the conditions necessary to achieve high molecular weight linear aliphatic polyesters were defined.

In the area of experimental methodology several results stand out. The spectroelectrochemical techniques employed in the study of the TCNQ films have original aspects. In reference 3 below we reported on the simultaneous electron spin resonance/electrochemistry of an electroactive polymer film for the first time. This technique was developed further in references 4 and 5. The derivative voltabsorptometric method was applied to a polymer film for the first time in reference 3, and again in reference 7. Other somewhat novel techniques used to study the TCNQ films were SEM (scanning electron microscopy) and SIMS (secondary ion mass spectroscopy) reported in reference 6. Simple theoretical analyses for low-temperature voltammetry and chronocoulometry of thin polymer films are presented in references 12 and 1.

Probably the most significant finding of this research is our increased understanding of charge transport in fixed-site polymer films at a molecular level provided by the detailed work on TCNQ polymer films. For these films chemical reactions that are coupled to the electron hopping steps in the bulk of the polymer film phase can profoundly influence the charge-transport process. These include dimerization and association reactions of the radical anion sites in reduced films (reference 4), ion-pair formation with counter ions in the electrolyzed films (references 2 and 7), and protonation of the reduced acceptor sites in TCNQ films (reference 9). It will be necessary to take these properties into account in applications (e.g. electrocatalytic sensors) based on polymer modified electrodes.

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11. J. Q. Chambers, G. Inzelt, "Temperature dependence of the voltammetric response of thin electroactive polymer films," to be submitted for publication.
12. R. W. Day, J. Q. Chambers, J. F. Kinstle, "Low-temperature solution polycondensation reactions. Synthesis of tetracyanoquinodimethane polymers," manuscript in preparation.

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