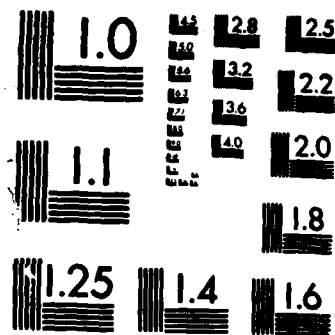


AD-A172 040 PULSED MICROWAVE CHARACTERIZATION OF CONDUCTING 1/1  
POLYMERS(U) UNIVERSITY OF SOUTHERN CALIFORNIA LOS  
ANGELES DEPT OF CHEMISTRY L R DALTON 24 FEB 86  
UNCLASSIFIED AFOSR-TR-86-0768 AFOSR-82-0184 F/G 7/4 NL





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PULSED MICROWAVE CHARACTERIZATION OF  
CONDUCTING POLYMERS

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## I. RESEARCH OBJECTIVES

The primary objective of this project was to characterize the time-independent and time-dependent properties of solitonic and polaronic species in polymers characterized by extensive  $\pi$  electron delocalization. Such species are expected to play the dominant role in defining electrical conductivity, nonlinear optical properties and physical properties in such polymers.

## II. STATUS OF THE RESEARCH AT THE END OF THE FUNDING PERIOD

### A. Polyacetylene.

All objectives have been realized for polyacetylene samples prepared by both the Durham and Shirakawa synthetic methods. In particular, the time-independent solitonic wavefunction has been defined by both electron nuclear double resonance (ENDOR) and electron spin echo envelope modulation (ESEEM) techniques. The wavefunction for the highest occupied molecular orbital (HOMO) has been completely characterized and found to be metallic in nature extending over 50-100 Å of the polyene backbone (depending on pinning potentials felt by the soliton defect). Spin densities at carbon have been directly measured and found to alternate between +0.06 and -0.02. This sign alternation has been investigated theoretically by ourselves<sup>1,2</sup> and by others<sup>3,4,5</sup> and has been shown to arise from electron coulomb interactions. For example, we have examined the effect of electron phonon interaction and electron coulomb interaction on the soliton wavefunction employing a modified Unrestricted Hartree Fock (UHF) theoretical approach and have found that an electron coulomb potential of 3 eV is necessary to rationalize the experimentally measured spin density variation<sup>1</sup>. Similar values have been obtained by other workers supporting the contention that the defect is a spin density wave (SDW) rather than a charge density wave (CDW). Investigation of trans-polyacetylene segments in cis-rich polyacetylene<sup>1,6</sup>, in trans-rich polyacetylene<sup>7</sup>, in copolymers of trans-polyacetylene and polythiophene<sup>8</sup>, and in composites with the structural polymers polyethylene, polystyrene, and polybutadiene<sup>9,10</sup> establish that the soliton wavefunction is determined by local interactions on the trans-polyacetylene chain and is little influenced by the lattice surrounding the trans-polyacetylene segments.

Both one-dimensional (1-D) and three-dimensional (3-D) soliton dynamics have been completely characterized by a variety of magnetic resonance techniques including electron spin echo-magnetic field gradient measurements, temperature

dependent ENDOR studies, and frequency and temperature dependent electron spin echo studies. One dimensional soliton dynamics are found to be phonon driven<sup>11,12</sup> while three-dimensional dynamics are found to be activated. Activation barriers are found to typically vary between 200-400K and are found to vary with crosslink concentration and with the concentration of segments incapable of supporting solitons<sup>13</sup>. Strong interchain soliton-soliton interaction is observed<sup>12</sup>, which may account for the fact that substantial electrical conductivity is observed for copolymers and composites of polyacetylene with structural polymers. In short, charge transport can take place involving electron hopping between metallic soliton regions on different chains thus reducing the importance of on-chain charge transport.

#### B. Polypyrrole, polyfuran, polythiophene, and metallophthalocyanine polymers

Polypyrrole, polyfuran, polythiophene have been synthesized by chemically and electrochemical means and have been characterized by the variety of measurement techniques discussed above and in terms of electrical conductivity. Both solitonic and polaronic species have been observed but electrical conductivity appears to involve a polaronic mechanism. One paper has been published on this work<sup>14</sup> and several others are in preparation. In like manner, metallophthalocyanine polymers have been prepared and examined<sup>15</sup>. These polymers are also been employed in copolymer preparation with ladder polymers.

#### C. Rigid rod and ladder polymers

The rigid rod polymer PBT has been obtained from the polymer laboratory at Wright Paterson and has been characterized by magnetic resonance techniques. An extensively delocalized  $\pi$  electron defect of metallic character is observed. When PBT is exposed to polyphosphoric acid (PPA) a charge transfer complex characterized by a <sup>31</sup>P doublet in the EPR spectrum is observed. Charge transfer complex formation appears to result in substantial electron localization. The ladder polymers BBL, PBL, POL, and PQL have been synthesized at USC and investigated<sup>13</sup>. The results are analogous to those obtained for PBT. Significant increases in electrical conductivity with exposure to electron donor or acceptor dopants is observed for the ladder polymers. The lack of such increases in conductivity for PBT with doping is likely due to a closely packed lattice which prevents dopant intercalation. Preliminary studies suggest that substantial nonlinear optical properties may be observed for both rigid rod and ladder polymers. Theoretically, third order susceptibilities are expected to depend strongly upon electron delocalization and ENDOR results would suggest that effects should be large for both rigid rod and ladder polymers with the largest effects observed for polymers such as PQL.

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