PHOTO-INDUCED MAGNETIC DEFECTS IN CONDUCTING POLYMERS

DISSERTATION

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*****

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Dedicated to
the memory of my father, Col. Dana B. Cromack, U.S.A.F
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CHAPTER I

Introduction

Electronically conducting polymers have attracted considerable attention in recent years, and are playing an increasingly important role in science and technology \(^1\). Conducting polymers are already in use commercially as battery electrodes and antistatic materials\(^1,2\). In addition, there have been many proposals for other applications including chemical sensors, video displays, microwave absorbers, and optical devices\(^1,3\).

Polymers generally consist of chains whose links (or repeat units) are characteristic groups of atoms. Chains may form as separate macromolecules or may be cross linked by chemical bonds forming two- or three-dimensional networks. The chains grow together to form a solid phase in which the chains can be perfectly aligned (crystalline), partially aligned, or have a completely random distribution (amorphous). The vast majority of polymers are insulators, however, conducting polymers are semiconductors with an energy gap that can be varied from 1 to 4 eV in their neutral form and are easily doped with various p- and n-dopants, increasing their conductivity by many orders of magnitude. Recent reports\(^1,4\) for polyacetylene \((CH)_2\) show that upon doping the conductivity changes from \(10^{-13} \text{ohm}^{-1}\text{cm}^{-1}\) to \(10^5 \text{ohm}^{-1}\text{cm}^{-1}\).

Because of the one-dimensional structure of polyacetylene and other polymers, the doping process is unlike that in three-dimensional semiconductors. The dopant atoms (or molecules) are positioned interstitially between chains, where they accept
or donate a charge to the backbone of the chain, becoming ionically bound to the polymer. To understand doping in three-dimensional semiconductors, one can generally ignore the changes in atomic positions upon addition of charge to the lattice, whereas in polymers these are very important effects. The addition of a charge to a chain can cause a redistribution of bonds along the chain with the resulting formation of doping-induced defect states called solitons, polarons, and bipolarons. The observed behavior in conducting polymers is intrinsic to these defects.

The investigation of these defects is hindered by the interaction of the charged dopant ions with the induced chain defects. The mutual Coulomb attraction between the dopant ion and the defect tend to pin the defect to some position along the chain. This complicates the understanding of the doping induced defects and in some cases may be a major factor in the observed behavior of the materials. However, these defects can also be produced by photo-excitation. During photo-excitation the interaction of a photon with the polymer creates electron-hole pairs which can recombine or separate to form new defect states on the polymer backbone. These new defect states are no longer pinned by dopant ions and therefore their behavior is determined by only the local molecular environment of the polymer chains.

The optical properties of these defects can be studied by photo-induced UV/Vis and IR spectroscopy. Photo-generated defects give rise to characteristic subgap electronic levels and to new infrared active vibrational transitions that make it possible to study in detail the nature of photo-induced defects in these systems. This technique does have its limitations. Quite often the results of photoinduced absorption experiments can not conclusively distinguish between the possible different types of photo-induced defects of a system. In these cases, usually the systems
Figure 1.1. Repeat units of several conducting polymers (from Reference 1.1).
possible photo-induced defects differ in one important aspect, they either have a spin associated with them or not.

It follows therefore that an understanding of the photo-induced defects in conducting polymers must be based on a detailed study of the optical and magnetic phenomena in these materials. In the case of magnetic studies; the number of defects, their molecular environments, and the interaction between defects and the polymer structure can be determined. Optically, charged defects produce new absorption lines due to electronic transitions and charge-induced infrared active vibrational modes. These optical changes give information on molecular changes induced by the defects.

An important example of a conducting polymer is polyaniline. Polyaniline is a family of compounds possessing a backbone of nitrogen atoms and \( C_6H_4 \) rings. Its possible states (Figure 1.2) vary in composition due to differences in the number of electrons on the polymer backbone; this difference is referred to as its oxidation state. A given oxidation state can exist in its base form, i.e. uncharged, or in its salt form, with excess protons bonded to the nitrogens. The oxidation state of polyaniline can be controlled to produce three stable forms of the base material; Leucoemeraldine (LEB), Emeraldine (EB), and Pernigraniline (PNB). With treatment with aqueous HCl of different pH values, the conductivity of the emeraldine form of polyaniline can increase from \( 10^{-10} \) S/cm to \( 10^0 \) S/cm. The microscopic mechanism of this 'insulator-metal' transition has been proposed as the doping induced generation of polaron defects on the polymer backbone as shown in Figure 1.3.

The emeraldine base form of polyaniline (Figure 1.3a) differs substantially from earlier studied polymers in several important aspects. First, it is not a charge conjugation symmetric system, unlike polyacetylene and polythiophene. That is,
Figure 1.2. Oxidation states of polyaniline. (a) leucoemeraldine base. (b) emeraldine base. (c) pernigraniline base.
the Fermi level and band gap are not formed in the center of the $\pi$ energy levels and the valence and conduction bands are very asymmetric. Second, both nitrogen atoms and benzene rings are in the conjugation path, forming a generalized 'A-B' polymer, which is essentially different from polythiophene and polypyrrole where sulfur or nitrogen heteroatoms play a small role in the $\pi$-band formation. Third, the emeraldine polymer can be converted from an insulating state to a 'metallic' state without changing the total number of electrons on the chains; instead, protons are added to the chains on the imine (-N=) sites as shown in Figure 1.3.

The nature of the doping induced defects in the polyaniline family have been an area of controversy for several years. Currently, these defects are believe to be mainly spin polarons, but it is possible that there is an equilibrium between spin polarons and spinless bipolarons present in these materials.

A greater understanding of the properties of polyaniline is the goal of the work described in this thesis. This work is concerned with the investigation of the nature of the doping-induced and light-induced defect states in conducting polymers with the application of Light-induced Electron Spin Resonance (LESR). In Chapter II, the theoretical background of one-dimensional systems and their defects (solitons, polarons, etc.) is reviewed, along with a discussion of the theory of electron spin resonance experiments.

The various experimental approaches used in this work will be reviewed in Chapter III. The technique of photoinduced absorption is used to identify possible photo-induced defects of a system. Static magnetic susceptibility measurements were used to investigate both the doping induced and undoped spins in these polymer systems. The molecular structure of the undoped spin defects were determined from ESR measurements. The spin, induced defect concentration, and defect interactions where probed by LESR measurements.
Figure 1.3. (a) Schematic illustration of the protonic acid doping of emeraldine base (i) to the emeraldine salt (ii).
Chapter IV describes and analyzes the results of these experiments. Static magnetic measurements revealed the presence of uncompensated spin defects in all oxidation states of the polyaniline family. Solution and solid state ESR experiment allowed the determination of the structure of these defects and lead to the proposal of the existence of neutral solitons in undoped polyanilines. LESR experiments detected the photo-production of spin defect states, gave information on the time dynamics involved in this photo-production, and demonstrated that these photo-produced defects are not independent defects, but are in fact interacting spin defects. Based on these results a model of interacting photo-induced soliton defects is proposed.

Chapter V describes and analyzes the results of experiments on the Polythiophene family of polymers. Here a small, but positive LESR signal shows that there is a photo-production of spin polarons in the polythiophene family. The comparison of the number of induced charges to the number of induced spins in this system demonstrate that the branching ratio for the production of bipolarons to polarons is a factor of 10. Also shown in these section is that the number of both polarons and bipolarons are very dependent on the excitation energy and that there is a maximum in the production rate at a photon energy of 2.05 eV.
CHAPTER II

THEORETICAL BACKGROUND

One of the most successful and elegant models describing the electronic structure of one-dimensional conducting polymers is the model proposed originally by Su, Schrieffer, and Heeger (SSH) \(^2\) for polyacetylene. Although polyaniline is different from polyacetylene in its structure, the concepts introduced in this model (such as solitons, and subsequently polarons and bipolarons) are very important in understanding polyaniline and polythiophene polymers.

SSH considered a polyacetylene chain as shown in Figure 2.1\(^2\)\(^3\). Each carbon atom has four outer electrons, three of them in \(sp^2\) orbitals forming \(\sigma\)-bonds with two neighboring carbon atoms and a hydrogen atom. These major lobes of the three \(\sigma\)-bonds are in a plane separated by 120\(^\circ\). The fourth electron is in a \(p_z\) orbital perpendicular to the plane forming a \(\pi\)-bond with one of its two neighbors\(^2\)\(^1\). A Bloch wavefunction for the chain can be constructed using a linear combination of each atom's \(p_z\) atomic wavefunction \(\Phi_n\):

\[
\Psi_k = \frac{1}{\sqrt{N}} \sum e^{i\kappa n} \Phi_n
\]

\[2.1\]

where \(\Psi_k\) is the Bloch wavefunction with wavevector \(k\) and \(\Phi_n\) is the atomic wavefunction for site \(n\). Assuming that \(^2\)\(^1\), (1) the lattice degrees of freedom can be treated classically, (2) only the electron-phonon interaction is taken into account (specifically, the electron-electron correlations are neglected), and (3) only one polyacetylene chain is considered, then we get the Hamiltonian
Figure 2.1. A schematic diagram of the mass-spring model for trans-polyacetylene (From Reference 1.3).
Figure 2.2. (a) Displacement of the nth carbon atom from its equal-bond-length position; (b) Variation of the transfer integral $t$ with near-neighbor separation (from Reference 2.1).
\[ H_{SSH} = \frac{K}{2} \sum_n (u_n - u_{n+1})^2 + \frac{M}{2} \sum_n \dot{u}_n^2 - \sum_{n,s} t_{n,n+1}(C_{n+1,s}^+ C_{n,s} + C_{n,s}^+ C_{n+1,s}) \]

where \( K \) is the spring constant of the \( \sigma \)-bonds, \( M \) is the CH mass, and \( C_{n,s}(C_{n,s}^+) \) is the annihilation (creation) operator of the \( \pi \)-electron on the \( n \)th site with spin \( s \). The nearest-neighbor transfer integral's \((t = t_0 + \alpha(u_n - u_{n+1}))\) dependence on the lattice distortion \((u_n - u_{n+1})\) is shown in Figure 2.2 b.

In the case of a uniform lattice \((u_n = 0)\) the SSH Hamiltonian can be solved exactly with the solution

\[ E(k) = E_0 - 2t_0 \cos k a \]

where \( E_0 \) is a constant which includes the site energy. The density of states per site per spin \( N(E) = \frac{dN}{dk}(\frac{dE}{dk})^{-1} \) is\(^{2,1}\)

\[ N(E) = \frac{1}{\pi \sqrt{4t_0^2 - E^2}} \]

For this case, the lattice energy is at a minimum and the \( \pi \)-band is half-filled; there is one \( \pi \)-electron for each unit cell (see Figure 2.3 a,b). Thus, in the limit of small electronic correlations, polyacetylene should be a metal. It is well known, however, that a one-dimensional metal is unstable against a periodic distortion of the lattice with a wave vector \( g = \pm 2k_F \): a Peierls distortion\(^{2,2}\). The origin of the Peierls distortion is the lowering of the total energy of the occupied electronic states near the Fermi level. For a half-filled band, \( k_F = \pi/2a \). So the distortion
Figure 2.3. (a) Energy dispersion and (b) density of states for undimerized trans-polyacetylene. Shading denotes filled states (from Reference 2.1).
Figure 2.4. (a) Energy dispersion and (b) density of states for a uniformly dimerized lattice, showing the energy gap formed (after Reference 2.1).
produces a dimerization of the lattice, i.e., the bonds alternate between double bonds and single bonds as is shown in Figure 2.2a. Although the dimerization will cost some lattice energy, the energy gained by \( \pi \)-electrons will lower the total energy. With a uniform dimerization, \( u_n = (-1)^nu_{n+1} \), the unit cell doubles in size and the original \( \pi \)-band splits into two bands with gap \( E_\delta = 2\Delta_0 = 8\alpha'|u|^2 \), as is shown in Figure 2.4. Since electrons fill up one band completely, undoped dimerized polyacetylene is an insulator.

The ground state energy versus the lattice distortion is shown in Figure 2.5. As can be seen, the ground state of the polyacetylene chain is doubly degenerate; there are two ways for the \( \pi \)-electrons to overlap with the neighbors as in Figure 2.2a. If we define the periodicity of the lattice in terms of an "order parameter" \( \Psi_n \), then the A phase can be written as \( \Psi_n = (-1)^nu_n = u_0 \) while the B phase can be written as the \( \Psi_n = (-1)^{n+1}u_n = -u_0 \). As the chain changes from phase A to phase B, a kink (called a soliton) which smoothly connects the two phases, appears on the polyacetylene chain (see Figure 2.6). A soliton can be either neutral with spin \( \frac{1}{2} \) or charged \( \pm e \) with spin 0, thus it has a reversed spin-charge relation. A soliton (the kink from phase A to B) and an anti-soliton (the kink from phase B to A) always appear in pairs on a chain of one phase, as is shown in Figure 2.7. If they are not greatly separated, two soliton wave functions can bind together to make new energy levels, forming a polaron (see Figure 2.8). A neutral polaron in polyacetylene is not stable. A polaron with charge \( \pm e \) has spin \( \frac{1}{2} \). A bipolaron has charge \( \pm 2e \) and spin 0. In polyacetylene bipolarons are unstable and separate into two charged solitons.

The above concepts, solitons, polarons and bipolarons, can be applied to the polyaniline system. The polyaniline system is in fact a family of polymers composed of benzenoid rings, quinoid rings, and nitrogen atoms. The wide range of possible
Figure 2.5. Total energy per site as a function of dimerization amplitude. Two degenerate ground states exist, at $\pm u_0$ (from Reference 2.1).
Figure 2.6. (a) Order parameter and (b) chemical bond diagram for a neutral soliton (from Reference 2.15). In actuality the soliton is spread out over $\sim 15$ carbon sites.
Figure 2.7. The order parameter of a soliton-antisoliton $(S - \bar{S})$ pair nucleated in an 'A' phase chain (from Reference 2.15).
Figure 2.8. Schematic hybridization of midgap soliton levels $S^0, \tilde{S}^+$ to form the energy levels for a polaron $P^+$ (from Reference 2.15). The energy splitting $\omega_1$ is related to the confinement length of the soliton-antisoliton pair.
forms that this family can be prepared in make the polyaniline system a much richer system than other polymers. There are three stable base forms in the polyaniline family, Figure 2.9; the most reduced, Leucoemeraldine base-LEB (a), the most oxidized, Pernigraniline base-PNB (c), and the most stable, Emeraldine base-EB (b).

Since polyaniline has two different components in a unit cell, it is an example of a generalized A-B polymer. To a first approximation the nitrogen atoms in the polyaniline system are expected to bond in a $sp^2p_z$ configuration; as a result, the polyaniline chains are drawn as zig-zags with the nitrogen positions at the vertices defining a plane, this structure has been confirmed by X-ray studies\textsuperscript{2,3}. For the amine sites, -NH-, nitrogen atoms possess a lone pair of $p_z$ electrons; while for the imine sites, -N=, nitrogen atoms possess both a lone pair of $\sigma$ electrons and one $p_z$ electron pairing with another $p_z$ electron from the quinoid rings. Since the benzenoid rings can rotate around the $\sigma$ bonds, the transfer integral between the nitrogen atoms and the carbons in the para-position of the benzene rings is not a simple function of the carbon-nitrogen bond lengths, but also is a function of the benzene ring torsion angle.\textsuperscript{2,7} It is expected that the repulsion between the hydrogen atoms on neighboring benzene rings force the rings to be twisted out of the plane of the polyaniline backbone and that this ring torsion angle plays an important role in the behavior of this class of materials.

In the emeraldine oxidation state on passing from one benzenoid unit to the next through a quinoid unit there is a bond alternation reversal (i.e. -N= to =N-) which is similar to the change from phase A to B to A in polyacetylene. Since quinoid rings have a different energy than benzenoid rings, emeraldine does not have a degenerate ground state and thus solitons are not energetically favored excitations. The elementary excitations in emeraldine are polarons and bipolarons.
Figure 2.9. Oxidation states of polyaniline: LEB-Leucoemeraldine, EB-Emeraldine, and PNB-Pernigraniline.
Figure 2.10. One possible structure of a soliton in pernigraniline base (PNB).
This is not true for all the forms of polyaniline. The idealized LEB oxidation state contains no quinoid units and therefore cannot support a bond length reversal defect such as those in emeraldine and polyacetylene, but Ginder et al.\textsuperscript{2.7} have recently have proposed the existence of a ring angle soliton in for this oxidation state. Also, in the LEB oxidation state the optical gap of the system is not the same type of gap derived in the SSH formalism, but is due to the $\pi$ to $\pi^*$ transition associated with the benzenoid rings. Dos Santos and Bredas\textsuperscript{2.4} have predicted the existence of a Peierls band gap, inherent to the single bond/double bond character of PNB, with a two-fold degenerate ground state in PNB, figure 2.10, and the existence of solitons. The PNB system is different from that found in polyacetylene in that there are two order parameters, bond length and ring angle, that influence the ground state of this system. Although ring rotations were treated implicitly by dos Santos and Bredas\textsuperscript{2.5} in their studies on PNB, the work of Ginder et al\textsuperscript{2.5} proposed the central role of the ring torsion angle degrees of freedom to the description of ring containing polymers. In Ginder's model, the nitrogen $p_z$ orbitals are coupled to the ring $\pi$ orbitals by a transfer integral that has a cosine dependence on the ring torsion angle. The conformation and energy of the system is determined by a competition between electron delocalization at full orbital overlap and the steric interaction between adjacent phenyl rings that force the rings to be non-planar. The Ginder model suggests that in ring containing polymers "the charged defect states, particularly hole polarons, are associated with localized distortions in the ground state ring torsion angles toward planar conformation"\textsuperscript{2.7}. These type of defects differ from the usual polarons in that only one new state is formed in the gap, instead of the expected two new states associated with conventual bond order polarons that form in Peierls gaps of charge conjugation symmetric polymers. These defects have much larger masses than those found in polyacetylene due to the large moments of inertia of the phenyl rings.
In summary, the concepts of the defect states introduced by the elegant SSH theory, which describes polyacetylene, can be used to describe the behavior of polyaniline and polythiophene. Polyacetylene, which has translation symmetry and a degenerate ground state, can have solitons, polarons, and bipolarons as its elementary excitations. These same types of defect states play an important role in the behavior of the polyaniline and polythiophene systems, but for the polyaniline system in particular the role of phenyl ring degrees of freedom is still an area of controversy. In order to gain further insight into the defect states of ring containing polymer systems, we undertook a study of the magnetic and light-induced magnetic properties of polythiophene and the polyaniline family of polymers.

ESR Theory

The behavior of spins in an ESR spectrometer can be described by two different methods. The first to be considered is the classical phenomenological approach of Bloch where the equation

$$\frac{dM}{dt} = \gamma H \times M.$$  \hspace{1cm} (2.5)

is used to describe the time dependence of the magnetization. This is simplified if the magnetic field ($H$) is in the $z$ direction. With the inclusion of relaxation, Equation 2.5 becomes

$$\frac{dM_z}{dt} = \omega_0 M_y - \frac{M_z}{T_2}$$ \hspace{1cm} (2.6)

$$\frac{dM_y}{dt} = -\omega_0 M_x - \frac{M_y}{T_2}$$ \hspace{1cm} (2.7)
\[ \frac{dM_x}{dt} = \frac{M_y - M_z}{T_1} \] \tag{2.8}

where \(T_1\) and \(T_2\) are referred to as the longitudinal (or spin-lattice) and transverse (or spin-spin) relaxation times respectively. Incorporating a time varying microwave magnetic field \(H_1\) that is perpendicular to \(H_z\) and solving for the imaginary part of the susceptibility \(\chi''(H)\) (the part which causes absorption of energy) leads to the following solution:

\[ \chi''(H) = \frac{\chi_0 H_1}{(1 + \gamma^2 T_2^2 \Delta H^2 + \frac{1}{4} \gamma^2 H_1^2 T_1 T_2)} \] \tag{2.9}

In most cases \(\gamma^2 H_1^2 T_1 T_2 << 1\) and usually ESR spectra are taken at constant frequency, thus Equation 2.9 becomes

\[ \chi''(H) = \frac{\chi_0 H_1}{(1 + \gamma^2 T_2^2 \Delta H^2)} \] \tag{2.10}

In other words, the microwave magnetic field \(H_1\) will exert a torque on the spin system and energy will be absorbed from the oscillating electromagnetic field. The resonant absorption will be Lorentzian in shape with a linewidth that depends on \(T_2\).

From this description of spin mechanics it can be seen that information on the number of spins and their relaxation times can be gained from studies of the resonance behavior as a function of microwave power \((H_1)\) and sample temperature. Interactions between spins are not taken into account in the Bloch approach and therefore application of this approach is limited.
The second way to formalize the results of ESR is the secular equation approach where the Hamiltonian is diagonalized to obtain the energy levels and eigenfunctions. From this approach, one obtains the positions and intensities of spectral lines. The Hamiltonian for atoms or molecules with unpaired electrons or nuclei is:

\[ \mathcal{H} = \mathcal{H}_{ei} + \mathcal{H}_{CF} + \mathcal{H}_{LS} + \mathcal{H}_{Ze} + \mathcal{H}_{HF} + \mathcal{H}_{SS} + \mathcal{H}_{Zn} + \mathcal{H}_{II} + \mathcal{H}_{Q} \]  

where \( \mathcal{H}_{ei} \) is an electronic energy, \( \mathcal{H}_{CF} \) is the crystal field interaction, \( \mathcal{H}_{LS} \) is a spin-orbit interaction, \( \mathcal{H}_{Ze} \) is a electron Zeeman interaction, \( \mathcal{H}_{HF} \) is a hyperfine interaction term, \( \mathcal{H}_{SS} \) is a electron spin-spin interaction term, \( \mathcal{H}_{Zn} \) is a nuclear Zeeman interaction, \( \mathcal{H}_{II} \) is a nuclear spin-spin interaction, and \( \mathcal{H}_{Q} \) is a nuclear quadrupole interaction. The terms of interest in ESR are:

\[ \mathcal{H}_{Ze} \equiv \text{Zeeman energy} = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) \]  

\[ \mathcal{H}_{HF} \equiv \text{hyperfine interaction} = (A_x S_x I_x + A_y S_y I_y + A_z S_z I_z) \]  

\[ \mathcal{H}_{SS} \equiv \text{spin-spin interaction} = D [S_z^2 - \frac{1}{3} S(S + 1)] + E [S_x^2 - S_y^2] \]

giving the magnetic Hamiltonian

\[ \mathcal{H}_{\text{mag}} = \mathcal{H}_{Ze} + \mathcal{H}_{HF} + \mathcal{H}_{SS} \]
In spin $\frac{1}{2}$ systems the wavefunctions are simple products of electron and nuclear spin functions where the selection of the basis set used depends on the relative size of the $\mathcal{H}_{HF}$ and $\mathcal{H}_{SS}$ interactions. In the high field limit at which most ESR is done ($\mathcal{H}_{HF} \gg \mathcal{H}_{SS}$), the secular equation can be solved exactly for the first two terms of the Hamiltonian. The $\mathcal{H}_{SS}$ term can then be included by use of perturbation theory. Neglecting $\mathcal{H}_{SS}$, the energy levels for an electron with spin $S$ in the vicinity of $j$ different atoms with nuclear spins $I$ when anisotropy in the hyperfine coupling value is neglected is\(^2\):\(^7\)

$$E = g\beta H_z M_S + \sum_{i=1}^{j} a_i M_i M_I, \quad 2.16$$

where $M_S$ is the electron spin angular momentum quantum number, $M_I$ is the nuclear spin angular momentum quantum number, and the term $a_i = K_H \rho(0)$ is the coupling constant of electron spin with nucleus $i$ and depends on the spin density $\rho(0)$ at the nucleus, the constant $K_H$ is an empirically determined proportionality constant. The selection rules for this equation are $\Delta M_I = 0$ and $\Delta M_S = \pm 1$. A photon of energy $h\nu$ can be absorbed or emitted by an electron when it jumps from one possible energy level to any other possible energy level accessible by the selection rules. Thus, there will be a resonant absorption of microwave power when the condition

$$h\nu = E(M_S, M_I) - E(M_S \pm 1, M_I) \quad 2.17$$

is met. Combining 2.16 and 2.17 and solving for $H_z$, it is seen that

$$H_z = \frac{1}{g\beta} (h\nu - \sum_{i=1}^{j} a_i M_I) \quad 2.18$$
where the second term gives information on the spins' nuclear environments. Since
the term $a_i$ is dependent on the density of spins on the atom $i$, well resolved
hyperfine splittings in ESR spectra enables one to map out the spin density, and
therefore the spin wavefunctions, in molecules that contain free radicals. In the
solid state, information on hyperfine interactions is usually lost due to motional
and/or exchange interactions that average out all nuclear interactions. This results
in either broadening or narrowing of resonance lines depending on the time scale
of the interactions at work.

Linewidth - Anderson Exchange Narrowing.

The previous section discussed the positions of resonance lines but neglected
the shape and width of resonance lines. A great deal of information can be gained
from these aspects of the resonance line structure. In magnetic resonance exper-
iments the majority of resonant lines are either Lorentzian or Gaussian in shape
and the linewidth depends on dipole-dipole, exchange, and motional interactions
in the system. The intrinsic linewidth can be considered as arising from a large
number of these type of interactions where each interaction splits the energy levels
by a small amount, Figure 2.11. This line broadening mechanism can be added
to the energy matrix calculations by adding imaginary terms into the Hamiltonian
matrices in the same way that dissipative processes are treated in electrical circuits.
Dipole-dipole interactions broaden resonance lines in proportion to $r^{-3}$, where $r$ is
the distance between spins$^{2,9}$, but the influence of the exchange interaction, which
falls off much more rapidly then the dipole term, on the resonance linewidth is
much more complicated.

Anderson$^{2,9}$ treated the case of the influence of random exchange on the ESR
linewidth by adding to the energy matrix a group of exchange matrices. In this
Figure 2.11. Broadening of spin $S=\frac{1}{2}$ Zeeman energy levels by the successive applications of small $I=\frac{1}{2}$ dipolar interactions. The lineshape of each level is shown at the right. (From Reference 2.9)
method, the energy matrix is first diagonalized in the absence of exchange, then the exchange interaction is considered by adding a term $\pm \frac{1}{2}i\hbar\omega_e$, where $\hbar\omega_e$ is the exchange energy. The solutions to this modified energy matrix equation have the form

$$E_i = \pm g\beta H \pm T_{eff} + \frac{1}{2}i\hbar\Delta\omega$$

where $T_{eff}$ is the effective hyperfine interaction constant and the term $\frac{1}{2}i\hbar\Delta\omega$ contains all linewidth contributions. There are three regions of interest for this equation.

1) For exchange rates $\hbar\omega_e < \frac{1}{2}T_{eff}$ the effective hyperfine constant decreases with increasing exchange and the linewidth increases linearly with $\omega_e$

$$\Delta\omega = (\omega_e + \Delta\omega_0).$$

2) At $\hbar\omega_e = \frac{1}{2}T_{eff}$ the hyperfine doublets collapse into singlets and the linewidth becomes

$$\Delta\omega = \Delta\omega_0 + \omega_e(1 \pm [1 - (T/2\hbar\omega_e)^2]^{\frac{1}{2}}).$$

3) For strong exchange, $\hbar\omega_e >> \frac{1}{2}T_{eff}$,

$$\Delta\omega = \Delta\omega_0 + (T^2/16\hbar^2\omega_e).$$

The change from weak exchange to strong exchange is shown graphically in Figure 2.12. Two separate resonance lines move together and merge as the exchange
Figure 2.12. Hyperfine doublet (a) in the absence of exchange, (b) with weak exchange, (c) with moderate exchange, and (d) with strong exchange. (From Reference 2.9)
Figure 2.13. Dependence of the linewidth $\Delta \omega$ on the exchange frequency $\omega_e$ for the case of zero intrinsic linewidth. Both axes are normalized relative to the true hyperfine coupling constant $T=2I_A$. (From Reference 2.9)
interaction energy approaches the hyperfine interaction energy. As the exchange energy increases further the two lines collapse into one line, and on any further increase in the exchange energy the single line narrows to the limit $\Delta \omega_0$. The linewidth as a function of the exchange energy is plotted in Figure 2.13. The linewidth increases linearly at low exchange energy then the line collapses into a narrow line and a broad undetectable line as the exchange energy becomes larger then the hyperfine energy.

**Lineshape - Method of Moments**

Information on the dipole-dipole and exchange interactions is also contained in the lineshape of the ESR signal. As mentioned above, the most common lineshapes are either Gaussian or Lorentzian or a convolution of the two. The analysis of the lineshape can be done by computer fitting, graphical methods, or the method of moments. The first two of these methods have been extensively used in the literature of ESR but are still plagued with controversy about their significance \textsuperscript{2.8,2.9}, whereas, the method of moments has a physical significance due to the theories of Van Vleck \textsuperscript{2.10}. In general, the $n$th moment of a resonance absorption is defined as

$$M_n = \frac{\Delta H_{data}}{A} \sum_{j=1}^{m} (H_j - H_0)^n y_j$$ \hspace{1cm} 2.23

where $H_0$ is the resonance center field, $H_j$ is the magnetic field at position $j$, $y_j$ is the height of the resonance absorption line at field $H_j$, $m$ is the number of data points in the spectrum, $\Delta H_{data}$ is the interval between data points, and

$$A = \Delta H_{data} \sum_{j=1}^{m} y_j$$ \hspace{1cm} 2.24
is the area under the absorption curve. In ESR experiments the moments of interest are the second and fourth with all odd moments equal to zero when the resonance is symmetric. Van Vleck\textsuperscript{2,12,2,13} showed that the second moment $M_2$ of an ESR line is

$$M_2 = -Tr[HS_x - S_x H]^2 / Tr(S_x)^2$$ \hspace{1cm} 2.25

Using standard trace and commutation relations this can be solved to find

$$M_2 = \frac{1}{3} S(S + 1) \sum_k B_{jk}^2$$ \hspace{1cm} 2.26

where $B_k \propto r_k^{-3}$, $r_k$ is the spin-spin distance from one spin to all other spin sites $k$. For a powder sample of simple cubic structure this reduces to

$$M_2 = \frac{3}{5} g^2 \beta^2 S(S + 1) \sum_k r_k^{-6}$$ \hspace{1cm} 2.27

A similar calculation for the fourth moment $M_4$ gives

$$M_4 = 3M_2^2 + AM_2 J^2$$ \hspace{1cm} 2.28

where $A$ is a constant depending on the lattice type, in particular for a simple cubic lattice structure $A = 3.3$, $M_2$ is the second moment, and $J$ is the quantum exchange interaction. Thus the use of the method of moments gives one additional independent way of finding the exchange interaction in a spin system.
CHAPTER III
EXPERIMENTAL TECHNIQUES

Sample Preparation

Samples used in this study were polymerized chemically by the process given in a previous report\(^3.1\). Briefly, a solution of \((NH_4)_2S_2O_8\) was added to a mixture of aniline and 1 M HCl at \(\sim 5^\circ C\). The precipitate was then filtered and washed with 1M HCl. Next samples were dried under vacuum and treated with NH\(_4\)OH to deprotonate them to obtain an end product of emeraldine base. Characterization studies \(^3.2\) of the net product show that it has an oxidation level that varies with preparation conditions (inert atmosphere, laboratory air, excess oxidation in solution, etc.). Samples prepared in air with excess oxidation have a higher number of quinoid units than expected for the ideal EB structure. For the ideal EB structure NMR studies have shown that even though there are an unequal number of benzenoid and quinoid units there seems to be a strong tendency to distribute amine and imine units in an alternating manner with the extra quinoid units at the end of the chains \(^3.3\).

The conversion of emeraldine base (EB) to permigraniline base (PNB) was done by Yan Sun at the University of Pennsylvania and was described previously\(^3.4\). In a typical synthesis EB was dissolved in a solution consisting of N-methylpyrrolidinone (NMP; 100mL) and glacial acetic acid (5mL). A glacial acetic acid solution (10mL) containing purified m-chloroperbenzoic acid (0.72g) was then added in 1mL portions every 10 min. A dark violet solution was observed after stirring
at room temperature for an additional 15 min. Triethylamine (10mL) was added to produce a dark purple precipitate, which was filtered on a Buchner funnel. The precipitate was stirred with acetone (60mL) for 30 min and filtered. This procedure was repeated and the precipitate was washed on the filter with acetone (200mL) followed by diethyl ether (200mL). The analytically pure, partially crystalline pernigraniline was obtained as a brownish-purple powder. A TiCl₃ volumetric titration of the oxidized repeat units gave a (1-y) value of 0.97 ± 0.02.

Leucoemeraldine was synthesized by Jim Masters at the University of Pennsylvania by a previously published method⁴. In a typical synthesis EB (2.14g) was placed into a vacuum joint fitted flask. Hydrazine monohydrate (N₂H₂) was then added in one portion to the flask. The dark blue suspension was then magnetically stirred at room temperature for ≈ 5 minutes during which time gas evolution occurred and the suspension became slightly lighter in color. At this time the freeze, pump, and thaw method was used and the suspension was stirred overnight at ≈ 45°C under static vacuum. Filtration under vacuum of the suspension yielded a light gray powder. The powder was washed 3 times with 20mL portions of methanol and then 3 times with 20 mL portions of diethyl ether. The powder was dried at room temperature for ≈ 24 hours and then under dynamic vacuum for ≈ 72 hours at 80°C. Analytically pure leucoemeraldine was obtained as a light gray-white powder.

Samples for LESR experiments were mixed with potassium bromide (KBr) in a 0.1-0.2% by weight ratio, ground, and pressed into pellets in a optical quality pellet press at 4.8 x 10⁴ psi. The resulting pellets were optically transparent. The KBr was used for two purposes: (1.) To suspend the polymer grains in a matrix such that as much surface area as possible was available for illumination. If we assume that the samples grain size is on the order of the material's optical skin
depth there is an increase in the ratio between the sample's optical surface area and sample mass of \( \approx 1000 \). (2.) To act as a thermal reservoir to reduce the sample heating on illumination, since the temperature change \( \Delta T_{S-KBr} \) with the sample embedded in KBr is determined by

\[
\Delta T_{S-KBr} = \frac{P_{\text{absorbed}}}{(MC_{KBr} + mC_{\text{sample}})}
\]

where \( P \) is the laser power absorbed by the sample, \( M \) is the mass of the KBr, \( m \) is the mass of the sample, and \( C_{KBr} \) and \( C_{\text{Sample}} \) are the specific heats of the KBR and sample respectively, assuming rapid thermal transfer between the sample and the KBr. In contrast, the temperature change \( \Delta T_S \) of the sample alone would be

\[
\Delta T_S = \frac{P_{\text{absorbed}}}{mC_{\text{sample}}}
\]

where the laser power absorbed is proportional to the sample mass and not the KBr mass. In the limit \( MC_{KBr} \gg mC_{\text{Sample}} \)

\[
\Delta T_{S-KBr} = \frac{M_{\text{Sample}}}{M_{KBr}} \Delta T_S.
\]

Since the EPR signal is proportional to \( 1/T \), embedding the sample in KBr decreases the heating induced decrease of both the dark and light-induced signal-to-noise ratio \( S/N \) by

\[
\frac{S/N_{KBr}}{S/N_{S-KBr}} = \frac{T + \frac{m}{M} \Delta T_S}{T + \Delta T_S}
\]

Even at room temperature this heating effect can easily obscure the real effect.
Photo-induced Absorption

The technique of photo-induced absorption has been instrumental in the understanding of defect states. \(^3.6 \, 3.7\) The change of the absorption upon photo-excitation is directly related to the number of photo-produced defects, and can provide information about the defect formation and decay dynamics. The production of defects depends on both the intensity \(I\) of the illumination and the probability per photon of producing a defect \((g)\). The defects can decay by two possible routes: recombination of the original electron-hole pair or by the interaction of two independent defects. The probability of recombination of electron-hole pairs depends upon the number of defects present \((n)\) and the unimolecular decay coefficient \((\gamma)\); The probability of two independent defects interacting depends upon the square of the number present \((n^2)\) and the bimolecular decay rate \((\beta)\). Combining these terms, the rate equation for defect decay can be written as

\[
\frac{dn}{dt} = gI - \gamma n - \beta n^2.
\]

This equation is easily solvable if either \(\gamma\) or \(\beta\) is zero, i.e., for pure uni- or bimolecular decay. The solutions for the steady state conditions \((\frac{dn}{dt} = 0\), i.e., the illumination time is long compared with the decay time\) are

\[
n = \frac{gI}{\gamma} \quad 3.6
\]

for uni-molecular \((\beta = 0)\) and

\[
n = \sqrt{gI/\beta} \quad 3.7
\]
for bi-molecular ($\gamma = 0$) decay.

If the excitation generation time is short compared to the decay time, the time dependent solutions are

$$n(t) = n_0 e^{-\gamma t}$$  \hspace{1cm} (3.8)

for uni-molecular ($\beta = 0$) and

$$n(t) = \frac{n_0}{1 + \beta n_0 t}$$  \hspace{1cm} (3.9)

for bi-molecular ($\gamma = 0$).

For the same two types of decay, the growth of the defects under constant illumination can be found from integrating Equation 3.5 with the results

$$n(t) = \frac{I}{\gamma}(1 - \exp(-\gamma t))$$  \hspace{1cm} (3.10)

for unimolecular decay ($\beta = 0$) and

$$n(t) = \sqrt{\frac{I}{\beta}} \tanh(\sqrt{\frac{\beta}{I} t})$$  \hspace{1cm} (3.11)

for bimolecular decay ($\gamma = 0$).

Although unimolecular and bimolecular decay are often observed in experiments, especially in crystalline materials, in disordered materials the phenomena are usually not so simple. Excitations experience a variety of different environments in disordered materials and as a result they can have a distribution of decay routes and/or lifetimes. For example, for unimolecular recombination, the observed
defect concentration $n(t)$ is a result of the summing of many exponential decays with varying amplitudes $n_i$ and time constants $\tau_i$:

$$n(t) = \Sigma_i n_i \exp \frac{-t}{\tau_i}$$  \hspace{1cm} 3.12

Two independent possible exact solutions of this equation with different weighting functions are a stretched exponential,

$$n(t) = n_0 \exp \left( \frac{t}{\tau} \right)^\alpha,$$  \hspace{1cm} 3.13

or a power law,

$$n(t) = n_0 \left( \frac{t}{\tau} \right)^{-\alpha},$$  \hspace{1cm} 3.14

where $0 \lesssim \alpha \lesssim 1$.

If two or more recombination processes are in competition, further complications can arise. Another possibility is that there may be several successive levels that an excited state must decay through. In this case it becomes necessary to solve several rate equations, one for each level, simultaneously. When there exist more than one type of excitation (i.e. polarons that can combine to form bipolarons) which can interact, the situation becomes further complicated.

For these reasons, it is critical to know the types of excitations and the types of environments these excitations are likely to encounter in the material being studied in order to properly analyze excitation time behavior.

It is the steady state solutions that are usually measured in photoinduced absorption experiments, but with the advent of fast lasers with time resolutions
of $\approx 1\text{ps}$ and Time-Resolved Fourier Transform Infrared spectroscopies with time resolutions of $\approx 100\text{ns}$ there has been a great deal of investigation of the time dynamics of the low-dimensional systems$^{3,6,3,9}$. Nonetheless, it has been difficult to decide on the basis of optical absorption spectra alone whether in-gap absorptions are produced by polarons or bipolarons$^{3,6,3,7}$. For this reason magnetic experiments are needed to distinguish between polarons, which have spin, and bipolarons, which have no spin.

**Static Magnetic Susceptibility**

In the investigation of the magnetic behavior of materials there exist several experimental techniques (i.e. the Gouy method, the Faraday balance method, AC susceptibility, and electron spin resonance)$^{3,10}$. Each of these techniques have different uses and give somewhat different information, but they all measure the magnetic susceptibility $\chi$. It is found from the definition of the magnetic induction $B$:

$$B = H + 4\pi M$$  \hspace{1cm} 3.15

where $M$ is the magnetization induced by the magnetic field $H$. If the sample’s magnetization has a linear dependence on $H$, then the relation between $M$ and $H$ reads:

$$M = \chi H$$  \hspace{1cm} 3.16

where $M$ and $H$ are vectors and $\chi$ is a second-rank tensor. If the material studied is isotropic, as in amorphous materials, then $\chi$ is diagonal with the same value in all nonzero positions. The energy density of the field is:
and from Equation 3.15:

$$U = \frac{1}{8\pi} B \cdot H,$$  \hspace{1cm} 3.17

$$U = \frac{1}{8\pi} H \cdot H + \frac{1}{2} M \cdot H,$$  \hspace{1cm} 3.18

the second term of which is the energy density associated with the presence of the sample. If the field \( H \) is in the \( z \) direction and has a gradient in the \( z \) direction then the familiar equation:

$$F = -\nabla U$$  \hspace{1cm} 3.19

gives:

$$F_z = \chi H \frac{dH}{dz}.$$  \hspace{1cm} 3.20

Thus a sample in a field \( H \) and field gradient \( \frac{dH}{dz} \) experiences a force \( F \) that is directly proportional to the magnetic susceptibility \( \chi \). This relation is the basis for the measurement of the magnetic susceptibility in several of the above techniques including the Faraday balance method. Since the evaluation of the absolute force on a sample would require very detailed calibrations at the beginning and end of every data run, in our experiments a modification of the original technique is used. Instead of having a constant \( \frac{dH}{dz} \) at a constant value of \( T \) and \( H \), \( \frac{dH}{dz} \) is varied in the form of a trapezoidal wave and the force is measured at the top and bottom of the cycle. The value of \( \chi \) is thus given by:
\[ \chi = \frac{\Delta F}{2H \frac{dH}{dx}}. \]  

With this modification, instead of having to know the absolute value of the force only the change in the force needs to be measured with precision.

The Faraday balance used in these studies is shown in Figure 3.1. With this apparatus, \( \chi \) can be measured as a function of field \( H \) (0-80 kG) and temperature \( T \) (300-2.0 K) and can be measured to an absolute value of \( \sim 10^{-11} \) emu. In these studies, powdered samples were loaded into cylindrical sample holders of 99.99 percent aluminum foil of 1.0 mil thickness and suspended from a Perkin-Elmer model AR-2 microbalance by a 131 cm length of 51 \( \mu \)m diameter tungsten wire of purity 99.95%. The sample was positioned to hang at the center of a superconducting magnet, capable of generating 80kG with field homogeneity of 1 part in \( 10^5 \), and a pair of superconducting Helmholtz coils, which produce a field gradient in the z direction of up to 800 G/cm with a uniformity of 1 part in \( 10^4 \) over the center 2 cm region. Liquid helium is used to keep both magnets at 4.2K and to provide gas for the cooling of the hangdown tube containing the sample.

The main magnetic field is ramped up or down using an AMI 400 power supply programmer in series with an Sorenson SRL 10-100 dc power supply. A heatable superconducting shunt across the magnet leads acts as a persistence switch, while the current is monitored from the voltage drop \( (V_1) \) across a 1.00 m\( \Omega \) resistor in series with the magnet. The gradient magnet current was supplied by a Kepco BOP15-20 bipolar power supply and was monitored by the voltage drop \( (V_2) \) across a 2.00 m\( \Omega \) series resistor. From the voltage measurements, \( H \) is found to be:

\[ H = \frac{V_1}{(1.00 m\Omega)} \times (1032 - \frac{G}{Amp}), \]  

3.22
Figure 3.1. Schematic diagram of the Faraday balance apparatus used for magnetic susceptibility measurements. (Adopted from J.M. Ginder)
and \( \frac{dH}{dz} \) is found to be:

\[
\frac{dH}{dz} = \frac{V_2}{(2m\Omega)} \times (37.35 - \frac{G}{Amp \cdot cm}),
\]

Sample temperature is measured by a Lakeshore calibrated carbon glass resistor, in a four-lead configuration, using a Keithley 220 programmable current source and a Keithley 195A voltmeter. The temperature control system consists of three devices. A helium flow control needle-value that adjusts the helium flow through a capillary tube to the vaporizer (a large copper block at the bottom of the sample space) and two Lakeshore DRC 82C temperature controllers that supply current to 25Ω heater wires wrapped around the hangdown tube and the vaporizer. The temperature of the sample can thus be controlled by adjusting the needle-value (the cooling power), the temperature of the vaporizer (the temperature of the helium gas that flows around the hangdown tube), and the temperature of the hangdown tube.

To ensure that the sample is hanging free and is thus not dragging against the sides of the hangdown tube, the output of the autobalance is monitored while a small perturbation is introduced to the system. If the sample is in fact free, the output is that of a dampened harmonic oscillator and is seen to settle down within a few minutes. If the sample is dragging, the output will in general be very complex; in this case the position of the balance head (therefore the position of the sample) is adjusted until the sample is found to be hanging free. Once this condition is met a data run can begin. Data runs consist of a field scan at constant temperature (usually room temperature) up to the desired field, followed by a temperature scan at constant field. Once the field is set, the magnitude of the force can be varied.
to an acceptable value (by varying the $\frac{dH}{dx}$ value), large enough to have a good signal-to-noise ratio, but not so large that the sample overly perturbed.

Data acquisition is accomplished as shown in Figure 3.2. A Leading Edge IBM compatible personal computer with a National Instruments General Purpose Interface Bus communication card installed is used to read and control all instruments. In general a data cycle begins with the PC executing a global trigger to all instruments. A Wavetek model 75 function generator responds by outputting to the gradient coils a trapezoid function with a 40 second period and a rise time of 2 seconds. A trapezoid wave is used instead of a square wave to decrease ringing effects and to insure that the sample does not experience any large impulses that could force it to oscillate. During this cycle the autobalance reading is averaged for the top of the cycle and for the bottom of the cycle, while $\frac{dH}{dx}$ and $H$ are read from their respective multimeters. In order to remove any Fermi contact potential effects the value of the carbon glass resistor current is reversed several times a second while its corresponding voltage value is read. These values are then used to calculate the temperature from a polynomial fit to the calibration data supplied by Lakeshore. The value of $\chi$ is then calculated from the values of $\Delta F$, $H$, and $\frac{dH}{dx}$ using equation 3.21. The deviations of all values from their average values are used to calculate the relative error in these values and are monitored for indications of any problems with the sample (in general the root mean square deviation of $\chi$ is approximately 0.2%). The autobalance’s output is simultaneously monitored on an XY recorder for a real-time indication of the sample’s condition.

The analysis of the data from a magnetic susceptibility run is then done on an IBM AT personal computer. To understand the analysis procedure one must consider the possible contributions to the magnetic susceptibility. In general the susceptibility can be written as:
Figure 3.2. Schematic diagram of the data acquisition system for the dc magnetic susceptibility measurements.
\[ \chi_T = \chi_c + \chi_{\text{core}} + \chi_{\text{pauli}} + \frac{M}{H} + \chi_{\text{other}}. \] 3.24

The first term \((\chi_c)\) is the Curie susceptibility; it is due to the presence of partially occupied localized electron orbitals and their desire to lower their energy in a magnetic field by aligning with it. The Curie susceptibility's temperature dependence can be found from a statistical mechanics calculation of the partition function of an independent electron in a magnetic field. The result is the Brillouin function, which in the limit \(k_B T \gg \mu_B H\) reduces to the form:

\[ \chi_c = \frac{C}{T}, \] 3.25

where

\[ C = \frac{S(S + 1)g^2\mu_B^2}{3k_B}, \] 3.26

is the Curie constant. The next term \((\chi_{\text{core}})\) is the diamagnetic susceptibility; it is due to the polarization of the core electrons orbiting the nucleus and is given for each atom by \(^3.11\)

\[ \chi_{\text{core}} = \frac{NZe^2}{6mc^2} <r^2> \] 3.27

where \(r\) is the electron orbital radius, \(m\) is the electron mass, \(Z\) is the atomic number, and \(N\) is the number of atoms. There are also bond and other corrections to this term\(^3.11\).

The third term, \(\chi_{\text{pauli}}\), is the Pauli susceptibility. It is associated with the presence of a nonzero density of states at the Fermi energy. Most conduction electrons in a metal have no possibility of aligning their spin with an applied field
because most orbitals in the Fermi sea with parallel spin are already occupied. Only electrons within a range $k_B T$ of the top of the Fermi distribution have a chance to align with the field. A calculation of the difference in concentration between electrons parallel and antiparallel to the magnetic field gives $3.12$:

$$\chi_{\text{Pauli}} = \mu_B^2 N(E_F).$$  

where $N(E_F)$ (for both signs of spins) is the density of states at the Fermi energy.

The $M/H$ term is due to any magnetic impurities (e.g. iron) present in the sample which have constant $M$ below their Curie temperature (the temperature at which the material undergoes spontaneous magnetization) and above magnetic fields that induce saturation magnetization. The last term, $\chi_{\text{other}}$, is the contribution of the susceptibility of the aluminum foil sample holder and the supporting tungsten wire.

The data is reduced by subtracting the different terms in a systematic way. First, a correction is made for the tungsten wire's susceptibility. From the mass of the sample holder, the value of the aluminium susceptibility is removed using a fourth-order-in-$T$ polynomial fit to the susceptibility of aluminum that was measured here and independently at Xerox. Next a plot is made of $\chi_T$ vs. $1/H$ and the slope ($M$) is found from a least square fit; this is assumed to be the magnetic impurity ($M/H$) and is then subtracted from $\chi_T$ to find;

$$\chi_{\text{true}} = \chi_T - \chi_{\text{other}} - \frac{M}{H}. $$  

The last step is to plot $\chi_{\text{true}}$ vs. $1/H$, where the intercept ($\chi_{\text{core}} + \chi_{\text{Pauli}}$) and the slope ($C$) can be found from a least square fit. To find $\chi_{\text{Pauli}}$, the value of $\chi_{\text{core}}$, found from tables $3.13$, is subtracted from the value of the intercept.
Figure 3.3. A Block diagram of the Bruker ESP300 EPR Spectrometer (From reference 3.14).
The EPR SPECTROMETER

The second technique that is used to measure the susceptibility in this work is electron spin resonance (ESR). A block diagram of a typical EPR spectrometer is illustrated in Figure 3.3. A Bruker Instruments ESP 300 9.5 GHz X band EPR was used to take the data. Samples were placed in a TE\(_{102}\) mode rectangular cavity with an optical assess grid and a low temperature cryostat installed. The sample can be photoexcited for LESR experiments by either a continuous wave Ar ion laser or a pulsed Nd:YAG laser. In most conventional EPR spectrometers, data is not taken as direct absorption but as the derivative of the absorption by magnetic field modulation at typically 100KHz using detection by lockin amplification. This results in a greatly enhanced signal-to-noise (S/N) ratio and allows measurement of smaller numbers of spins.

The ESP 300\(^3,15\) consists of a ER04MR microwave bridge which contains all components which generate, control, and detect the microwave radiation of the spectrometer, an electronic control console including the magnetic field controller, a signal channel, time base, field and frequency lock systems, a sample cavity in the TE\(_{102}\) mode, electromagnet, and magnet power supply.

The microwave bridge \(^3,15\) is shown in Figure 3.4 with a simplified version shown in Figure 3.5. The numbers used in the description below refer to Figure 3.5. The microwave bridge contains a low-noise long-life (10,000 hours) klystron with 1 GHz tuning range \(^1\). The microwave bridge has a power range of 0.2 microwatts to 200 milliwatts and contains a power leveling circuit. A low power option allows power incident on the cavity to be reduced to 1 nanowatt. The klystron source power is split into a power arm \(^2\), used to both irradiate the sample and detect the signal response, and a reference arm. The incident power
Figure 3.4. A schematic diagram of the microwave bridge for the Bruker ESP300 EPR Spectrometer. (From Bruker manual)
is altered by rotary vane microwave attenuators (6) and directed to the sample by a unidirectional microwave circulator (7). The circulator directs power from the source to the sample cavity (8) and power emanating from the cavity to the detector (9) only. The reference arm (3) serves the dual function of biasing the detector diode and phase discriminating between the absorptive and dispersive component of the EPR response. The biasing power is determined by the reference arm attenuation level (4) while absorption/dispersion selection is determined by the reference arm phase adjustment (5).

The microwave detection system used is referred to as super heterodyne detection. This terminology arises from the mixing of a second frequency source to convert the microwave frequency to 1 MHz. An alternate configuration in the past has used a second frequency source to mix the two microwave frequencies to a lower intermediate frequency (IF) regime for signal processing. This is referred to as heterodyne detection derived from “different frequency mixing”. In both the heterodyne and the super heterodyne detection schemes, the detector diode is biased to ensure that it operates in the square law response regime. In this regime the diode current is a linear function of the power.

Frequency stability of the microwave source is achieved by locking the klystron frequency to the sample cavity frequency through a feedback loop. The klystron frequency is frequency modulated (10) by modulating the klystron reflector voltage. If the klystron frequency is matched exactly to the cavity resonant frequency, maximum power is transmitted to the cavity. If mismatch occurs, more power is reflected from the cavity at the microwave frequency and at sidebands offset from the microwave carrier by the modulation frequency. These modulation sidebands are phase sensitive detected (11) by mixing with a reference derived from the reflector frequency modulation source. The resulting d.c. voltage forms an error voltage
Figure 3.5. A schematic of the technique of field modulation detection in ESR spectroscopy (from Bruker manual).
which is applied to the klystron reflector tuning voltage to lock the klystron to the cavity frequency. This frequency stabilization feedback control loop is known as Automatic Frequency Control (AFC). AFC gives a short term (2 minutes) stability of 10 ppb and a long term (24 hours) stability of 1 ppm.

The Microwave Cavity

The microwave cavity dictates the operating frequency of the spectrometer, is paramount in determining the sensitivity, may limit stability and resolution, and in some cases may determine whether a particular experiment can be performed. The cavity is a geometric structure of the proper dimensions for the microwave radiation to form standing wave patterns called modes. The standing wave pattern increases the microwave energy density and thus serves as an amplifier. The sensitivity and the available microwave power density are both significantly increased by this amplifying process.

An important characteristic of cavity modes is the spatial separation of the electric and the magnetic fields of the microwave radiation. Microwave electric and magnetic fields oscillate in phase with respect to space and time as traveling waves. As standing waves, however, a spacial separation of the electric and magnetic fields is possible. The sample can thus be situated in a region of maximum magnetic field and minimum electric field. This arrangement minimizes the loss of sensitivity concomitant with situating high dielectric loss materials in electric fields.

Cavity nomenclature is derived from the microwave standing wave patterns (modes) that are formed in the cavity. The modes are designated as transverse electric (TE) if the electric field has no component along the major axis of the cavity, and transverse magnetic (TM) if the magnetic field has no component along the
major axis. The subscripts on these designations further describe the multiplicity of the wavelengths of the corresponding electric (TE) or magnetic (TM) field along the cartesian axis.

Cavities are also characterized by their efficiency for integrating microwave energy. A measure of this efficiency is described by the quality factor or Q factor:

\[
Q = 2\pi \frac{\text{energy stored}}{\text{energy lost per cycle}}
\]  

A higher Q implies a greater capacity for energy storage. A working definition of the Q derived from bandwidth considerations is:

\[
Q = \frac{\nu}{\Delta \nu}
\]  

where \(\nu\) is the cavity resonant frequency and \(\Delta \nu\) is the difference in frequency obtained at the half power absorption. The Q will limit the stability and resolution of the spectrometer as well as the sensitivity.

The Detection System

The standard method of recording EPR spectra is due to the constraints of the cavity. Signal-to-noise (S/N) considerations require the cavity to have a high Q factor, but this implies a narrow bandwidth of frequencies. This rules out the use of conventional frequency swept experiments. The magnetic field dependence of the magnetic eigenvalue spectrum makes it possible to maintain the high Q and constant source frequency needed for high S/N. Thus, the spectrum can be obtained by recording the absorption as a function of applied magnetic field.
Figure 3.6. A block diagram of the signal channel. Section (a) is the signal receiver and filter, section (b) is a tuned lock-in amplifier, section (c) is the analog to digital converter (ADC), and section (d) is the modulation generator and reference (from Bruker manual).
Signal detection is through the use of lock-in detection \(^3,14\) to achieve a significant improvement in the signal-to-noise ratio by virtue of the bandwidth limitations. A frequency source, derived from the signal channel, serves to encode the signal response at the modulation frequency by amplitude modulating the d.c. magnetic field. The EPR signal response is decoded by phase sensitive detection. The EPR signal is generally detected at the first or second Fourier harmonic of the applied field modulation frequency, and in-phase with the frequency of the reference arm. This scheme, known as Zeeman modulation with phase sensitive detection, increases the S/N by limiting the frequency bandwidth of the receiver and by translating the signal to a frequency away from d.c. where the microwave detector diode 1/f noise is quite large. The field modulation scheme also results in excellent baseline stability. The transfer of modulation of the field modulation frequency to the detector system and through the receiver bandpass amplifiers is only possible through the sample response.

The operation of the field modulation detection scheme is shown in Figure 3.5. The modulation frequency source signal (12) is fed to the modulation coils (13) on the cavity. A modulation frequency reference arm (14) supplies the reference frequency and phase to the phase sensitive detector (17). A bandpass amplifier (16) improves the S/N by amplifying only the response at approximately the modulation frequency. Modulation frequencies can be set from 1.56 to 100 KHz with the option of observing the second harmonic from 3.02 to 200 KHz.

Figure 3.6 shows the ER 023m Signal channel. The signal from the detection diode is passed through a 200 kHz low pass filter and an AFC trap to remove the side bands due to the frequency control. After amplification the signal is mixed with a 1 MHz carrier signal and amplified in a tuned amplifier. The signal then goes to a phase sensitive lock-in amplifier, is mixed with 1 MHz reference signal, passes
Figure 3.7. A diagram of the Oxford ESR-900 continuous flow liquid helium cryostat. (from Oxford manual)
a variable low pass filter and amplifier. This analog signal is then converted to
digital by a voltage controlled oscillator, whose frequency (between 0.9 - 1.1 MHz)
depends on the voltage applied, and an event counter whose gating time can be set
from 10 µs to 5 s. This scheme of analog to digital conversion thereby does a real
time signal averaging on a data point by data point basis.

CRYOGENICS

A commercial ESR-900 continuous flow cryostat manufactured by Oxford In­
struments was used for taking data down to liquid helium temperature. The struc­
ture of the cryostat is illustrated in Figure(3.7). The liquid helium or cold helium
gas flows from the nozzle which is positioned 3/16 inches below the sample. A cop­
pper block with a heater wire rapped around it is attached to the nozzle to control
the temperature of the flowing gas. A thermocouple is placed in the helium flow
1/16 inches above the nozzle. An Oxford ITC-4 temperature controller was used
to monitor the thermocouple and to supply power to the heater. Liquid nitrogen
was used for the reference temperature of the thermocouple. Calibration of the
temperature at the sample position was done using a calibrated diode sensor in­
serted in an EPR tube and placed at the samples position. During experiments, a
minimum of 10 minutes was allowed after the temperature reading had steadied to
insure that the sample was at the same temperature as the thermocouple.

When doing low temperature measurements water may condense inside the
cavity decreasing the S/N due to the increased dielectric losses. To protect against
this, dry nitrogen gas is continuously flushed through the waveguide.

Instrumental Considerations
The response of simple linear paramagnetic samples to imposed microwave radiation cannot be addressed without regard to instrumental considerations. The absolute energy absorbed during resonance absorption by a spin system is small in contrast to the inherent noise of the microwave source-detector system. In practice, signals are extracted from the noise by use of lock-in detection during field modulation. To obtain both undistorted line shapes and large S/N, it is important to properly choose both the magnetic field modulation amplitude, the microwave power, and the ratio of the bandpass filter time constant to the field sweep time.

The choice of the modulation amplitude (MA) depends on the information desired. If the goal is to produce the greatest signal, and therefore the largest S/N, then the MA should be set to $\sqrt{3} \Delta H_{pp} (2\ln2 \Delta H_{pp})$ for a Lorentzian (Gaussian) line shape: This will produce the largest signal, but will increase the observed linewidth by a factor of $\approx 1.3$. If one desires an undistorted lineshape then the MA should be set to $1/10$ of $\Delta H_{pp}$ with a concomitant decrease of the S/N by a factor of 300. In most studies in this paper a compromise between these limits was found empirically such that no distortion in line shape was observably by eye with values of MA between $1/2$ and $1/3 \Delta H_{pp}$.

Since the intensity of the signal depend on the intensity of the microwave field $H_1$, where $H_1 \propto P^{1/2}$, a maximum microwave power is desirable for a large S/N. Unfortunately, the $H_1$ field also acts to broaden lines with the onset of saturation. For homogeneous resonance lines $^{3,14}$

$$\Delta H_{pp} = \left(\frac{4}{3\gamma^2T_2^2} + \frac{4H_1^2T_1}{3T_2}\right)^{1/2}$$  \hspace{1cm} 3.32

where $T_1$ is the spin-lattice relaxation time, $T_2$ is the spin-spin relaxation time, and $\gamma$ is the gyromagnetic ratio. For accurate linewidth and lineshape measurements
signal saturation should be avoided. In all experiments discussed in this thesis, saturation was checked for by monitoring the signal height as a function of the square root of the power with final measurements done in the linear dependence regime, usually in the 0.1 - 1.0 milliwatt range.

In conventional CW-EPR measurements the scan rate is such that the scanned magnetic field is effectively constant with respect to the modulated field and changes slowly with respect to the spin-lattice and spin-spin relaxation times. There are no further constraints on the scan rate itself. It is important though that the time constant setting be such that an acceptable S/N is obtained and that the magnetic field scan rate is such that spectral distortion is kept to an acceptable level. What constitutes an acceptable S/N level is arbitrary but the time constant required to maintain a constant noise amplitude varies as the square of the receiver gain. In general, S/N is proportional to the square root of the time constant, thus, to double the S/N the time constant must be quadrupled. If the time constant is set too large with respect to the magnetic field sweep rate, then lineshape distortion will occur and the line position will be shifted. An empirical rule of thumb for the determination of the appropriate time constant \((T_c)\) versus field sweep time \((T_s)\) is

\[
\frac{T_c}{T_s} = \frac{\Delta H_{pp}}{50 \ SW} \quad 3.33
\]

where SW is the sweep width in gauss.

There are many factors that determine either the signal strength or the detection limits of EPR spectrometers \(^{3-14}\). If it is assumed that the susceptibility follows the Curie law and that there is no microwave saturation, then these factors combine to determine the minimum number of spins detectable in a system \(N_{MIN}\).
The effective unloaded Q factor of the cavity is given by the following expression;

\[ \frac{1}{Q_u'} = \frac{1}{Q_u} + \frac{1}{Q_u} \]  \hspace{1cm} 3.35

where \( Q_u \) is the unloaded Q factor in which only losses within the cavity are considered and \( Q_u \) is the dielectric Q factor which is due to material in the cavity having a nonvanishing imaginary part to the dielectric constant. For solid samples dielectric losses are usually not critical, but in the case of doped polyanilines the inherently high microwave loss tangents make it extremely important to use only very small samples.
In the Bruker ESP-300, \( N_{MIN} \approx 10^{12} \) spins for a line with a linewidth of 1 gauss and 4.2K. It is appropriate to note here that in the field modulation technique where the field is modulated at 100KHz the time resolution is limited by the bandwidth of the detection system which is typically 5KHz giving a time constant of 200 \( \mu s \). Therefore, no lifetime dependent information on a time scale shorter than this can be found by use of conventional techniques in EPR.

**Light-Induced EPR**

Data for LESR experiments were performed on the same Bruker EPR system discussed above. All experiments used the optical access microwave cavity with a half power transmission grid. Laser illumination was supplied by either a cw argon ion laser, a variable frequency dye laser, or a pulsed Nd:YAG laser and was routed to the ESR experiment through a 200\( \mu m \) single fiber fiber-optic cable. The output of the fiber-optic cable was collimated and passed through a cylindrical lens such that the resulting beam was rectangular in shape with cross sections of \( w \approx 0.5cm \) and \( h \approx 2.0cm \). The cross section of the sample is \( w \approx 0.3 \) cm and \( h \approx 1.8 \) cm, thus the beam fully covered the sample. The illuminating beam was blocked and unblocked by the use of either a Stanford optical chopper in the frequency range of 5-1000 Hz or an optical shutter in the range of 0.5 Hz. A photo-diode was used to correlate the LESR signal to the time and phase of the illuminating beam.

In general three different methods were used in the LESR experiments and will be described. The three methods are: 1) Detection by signal averaging with chopped illumination, 2) Detection by double lock-in detection with chopped illumination, and 3) Detection under steady-state illumination. Each of these techniques have their advantages and limitations such that a complete understanding of experimental results necessitate the use of all three in our experiments.
Figure 3.8. A block diagram of the LESR experimental setup. Detection can be done with either a signal averager or a lock-in amplifier. For the second case the output from the lock-in amplifier is used for the input of the ESP 300 digitizer.
Figure 3.9. An example of the subtraction of the dark ESR spectra of PNB from the spectra taken while the sample is illuminated at 60K. The top figure shows both the dark ESR signal (dashed line) and the ESR signal during illumination (solid line) that is a combination of the dark ESR and the light-induced ESR. The light-induced ESR is found by subtracting the dark ESR signal from the combination and is shown in the bottom figure.
Detection by signal averaging was found to be the most versatile of the three methods and therefore was usually performed first. The setup for this experiment is shown in Figure 3.8. A Stanford adjustable frequency optical chopper or shutter was used to produce a square wave illuminating pulse from the CW laser beam. A photo-diode detected when the beam was unblocked and served as a reference for the trigger of the signal averager. The output from the ESP 300 lock-in (back panel pin S130) was taken as the input connection to the digitizer. For this a special 6 pin to BNC cable was made. This technique allows the measurement of the time and phase dynamics of the LESR signal once the signal has been identified. LESR signals are taken at constant magnetic field, usually the top of the derivative peak, and were allowed to average for as long as needed for a good S/N ratio. The signal averager used in these experiments has two input channels, the reference signal from the diode and the LESR signal. Both signals can be plotted simultaneously enabling the LESR signal to be distinguished between a heating effect, which is opposite in phase to the reference, and photo-induced spin which has the same phase as the reference (assuming that the photo-induced defects are not quenching previously present spins).

Once the phase and time dynamics have been found from signal averaging, the magnetic field dependence can be found using the double lock-in method. In this method, both outputs used in the signal averager experiments are connected to a second lock-in detector. The change in ESR signal is thus measured with respect to phase and amplitude to the modulating light pulse. Amplitude and phase of the LESR signal can be digitized by connecting the output from the second lock-in detector to the input to the ESP 300 digitizer. This technique has the advantage over the signal averager that the LESR amplitude versus magnetic field can be measured by doing a standard field sweep. In both of the above techniques it is
important to use a short time constant for the first lock-in detector, the one built into the ESP 300, such that the signal that is modulated at the chopping frequency is not distorted by the filter built into the first lock-in. This filter limits the time resolution of these technique to \( \approx 200 \mu s \).

The third technique used in this work was steady-state illumination. In this technique, a steady state condition is created due to the fact that under constant illumination the population of defects becomes constant when the production rate is equal to the decay rate, i.e. the steady-state condition, see Chapter 2. As long as there are no long time effects, the LESR signal can be measured by doing scans in the dark and then scanning under illumination. In our studies, dark scans were done with the laser blocked and stored in memory location 1. The shutter was then opened by a computer signal, illuminating the sample, and new scan was done and stored in memory location 2. This procedure can be repeated for as long as needed with each new scan added to either memory location 1 or 2 depending on whether or not the laser is blocked. The LESR signal was then found by subtracting the dark signal, in memory location 1, from the light on signal, in memory location 2, by computer (Figure 3.9). This enables the linewidth and g-value of the LESR signal to be found. The number of photo-induced defects is found by double integrating both the dark and light-on spectra and comparing the two. Since the number of spins in the dark sample are known from Faraday balance measurements the number of induced defects is equal to

\[
N_{\text{Induced}} = \frac{I_{\text{light-on}} - I_{\text{light-off}}}{I_{\text{light-off}}} N_{\text{Dark}}
\]

where \( I \) is the double integral for the dark or illuminated sample and \( N_{\text{dark}} \) is the number of spins per ring found from Faraday balance experiments. The long time
defect growth experiments for the polyaniline polymers where done similarly to the above technique. For these experiments 5 spectra were taken in the dark and averaged before the sample was illuminated. Spectra were then taken at fixed time intervals while the sample was being illuminated. The average of the dark spectra were then subtracted from the light-on spectra as previously discussed.
CHAPTER IV

DATA and DISCUSSION I

RESULTS IN POLYANILINE

INTRODUCTION

Polyanilines have attracted great interest in the last few years. The nature of the chemically doped polymer and the correspondence to the photo-doped polymer are active areas of investigation. It is expected that polyanilines support solitons, polarons, and bipolarons stabilized by ring angle and/or bond length distortions. Optical absorption spectra and photo-induced absorption spectra have shown there to be defects created in these polymers, but have not been able to differentiate conclusively the type of defects created.

Magnetic susceptibility measurements on one-dimensional systems have been an invaluable probe of the mechanisms at work in these systems. In polyacetylene, the temperature independent $\chi$, the Pauli susceptibility, Figure 4.1, is seen to remain small at low doping levels $(y < 0.04)$, even though the conductivity of the system is already almost at its maximum value, and then to increase rapidly up to a value $\sim 75\%$ that of a hypothetical 1-dimensional metal at its highest doping level. This behavior of polyacetylene has lead to a large amount of theoretical work in an attempt to understand the nature of this insulator-metal transition. Briefly, solitons are created at low doping levels and charge can move by hopping between
Figure 4.1. Dependence of the conductivity and Pauli susceptibility of trans-polyacetylene on doping level (from Reference 4.4).
spinless soliton sites, thus the rapid increase of the conductivity at low doping levels, but no increase in the number of spins. As the doping level is increased the onset of a Pauli susceptibility is indicative of the formation of a metallic density of states at the Fermi level. In protonated polyaniline (PANI), Ginder et al. found that, unlike the polyacetylene case, the $\chi_{\text{pauli}}$ was seen to increase nearly linearly with doping level even at low protonation levels. This result was interpreted as evidence of phase segregation upon doping of the polymer into small "metallic islands" embedded in a matrix of the insulating undoped polymer. These results are consistent with DC and AC conductivity measurements of Zuo et al. and the microwave work of Javadi et al.

The model of Ginder et al. is shown in Figure 4.2. The protonation of the polymer backbone (a) causes a redistribution of the electronic structure such that the quinoid unit becomes a benzenoid unit and (b) two free radicals are formed (the bipolaron model). Since by symmetry the -N- sites are now equivalent, the charges are free to lower their Coulomb interaction by rearranging as shown in (c) (the polaron model). The polaron wavefunctions can then overlap to form a new polaron band in the gap with an associated density of states at the Fermi level. The polymer's conductivity never reaches that of a metal's due to chain defects that lower the coherence length.

Other magnetic studies have shown that polyanilines, and most polymers in general, have a non zero defect concentration even in their undoped forms (base forms). The reason for the non zero defect level at zero doping in polyaniline has not previously been well understood, but was believed to be either defects at the end of a chain or uncompensated doped material that is trapped in the polymer matrix. Both explanations point to the importance of material preparation and therefore it was believed that if the material could be prepared in a more pristine form the
Figure 4.2. Possible chemical structures of the emeraldine salt. (a) and (b): bipolaron lattice structures. (c) and (d): polaron lattice structures (after Reference 4.8).
undoped defects would disappear. For this reason little theoretical work has been done to explain these defects. Similar undoped spins were seen in polyacetylene and were explained theoretically as neutral solitons and later confirmed by EPR and ENDOR studies \(^4.9\). The more recent work of dos Stantos and Bredas \(^4.10\) predicts that PNB should have charged solitons but that these solitons should be spinless. In order to gain insight into these undoped defects several previous works have been analyzed with the purpose of either upholding or refuting the explanation of the undoped defects.

The existence of uncompensated regions in the polymer matrix, is in contrast to the results of Vaca et al. \(^4.11\) who have shown that there is no difference in the number of spins between the two forms of the base material of emeraldine (EB-I and EB-II)\(^2.5\). These materials differ in crystallinity, EB-I is amorphous and EB-II is \(\approx 50\%\) crystalline, and therefore if the spin defects are due to uncompensated areas trapped within the polymer the more crystalline material would have a higher spin concentration. It is also in contrast with the result that the process of doping and undoping the polymer has little effect on the undoped spin concentration even though one expects that the undoped spin concentration would increase if there were trapped regions of doped polymer.

The possible existence of defects at the end of the chain is seen as unlikely in retrospect to work by Tang et al. \(^4.12\). In Tang's work, the undoped spin concentration was measured as a function of average chain length. It was found that the spin concentration had little dependence on the average chain length, in direct contrast with the expectation that if the spins are due to chain ends then the spin concentration should increase linearly with decreasing average chain length.

Figure 4.3 is a plot of the number of Curie spins verses temperature measured on a Faraday balance for LEB and PNB, (EB has the same value and temperature
Figure 4.3. Faraday balance measurement of the temperature dependence of the apparent Curie spin density, i.e. $T \times (\chi(T) - \chi(T \to \infty))$ for LEB and PNB. EB has the same value as that of LEB and is omitted for clarity.
dependence and is omitted for clarity) showing that the number of spins of the undoped as prepared material is $1.9 \times 10^{-3}$ Curie spins per two rings (1 spin per 1052 rings) for both LEB and EB, but is $3.5 \times 10^{-3}$ Curie spins per two rings (1 spin per 571 rings) for PNB. The data also show that the number of spins is not independent of $T$ as one expects. This result is also seen in Faraday balance data for doped polyaniline, but is seen only to a small extent in ESR data on LEB, EB, and PNB. This temperature dependence has cast doubt on the validity of any interpretation of this data and therefore we must address this point before any attempts are made to explain the differences between PNB and EB.

Several explanations have been put forward to account for this temperature dependence of the number of spins $^{4.13,4.14}$; that the system may be a Fermi glass (a system in which there is a large density of localized states near the Fermi energy), or that the difference between the creation energy of polarons and bipolarons might be on the order of $kT$. No explanation seems to resolve the decrease in the number of Curie spins below 40 K. On further investigation, this effect was found in several other types of samples but with much smaller percent changes. From a literature search, Kanda et al $^{4.15}$ showed a similar behavior below 45 K in the AC susceptibility of oxygen. Upon remeasuring this with our own AC susceptibility instrument$^{4.37}$ with a quartz tube filled with oxygen at one atmosphere of pressure, it was seen that the behavior below 50 K is qualitatively the same as found by Kanda et al $^{4.15}$ but above 50 K there was a decrease of the number of spins with increasing temperature and there were several other transitions not shown by Kanda, one at $\sim 70$ K and another at $\sim 90$ K (the boiling point of $O_2$). Reexamination of data on protonated and $CH_3$-doped PANI$^{4.16}$ showed similar transitions at both of these temperatures as shown in Figure 4.4. Since it is well known that powdered polymers absorb $O_2$ readily, the temperature dependence of the number
Figure 4.4. Expanded scale graph of the Faraday balance measurement of the temperature dependence of the apparent Curie spin density, for the 10% $CH_3$-doped emeraldine showing the extra peak at 70K due to $O_2$. 
of Curie spins is qualitatively consistent with the presence of $O_2$ in the sample. It must be added that this temperature dependence is present in EPR data, though to a smaller degree, even when extensive pumping is done on the sample. Therefore it is still possible that there is some temperature dependence to the number of Curie spins, but more likely there is still $O_2$ present in the polymer that could not be removed by pumping.

**Solution ESR**

Since the existence of uncompensated regions and of chain end defects are unlikely what are the undoped spins in polyanilines due to and how can the differences in the number of spins between PNB and EB be explained? The answer to this question is contained in the solution ESR spectra of PNB and EB. It is well known that the solid state effects that average out the hyperfine interactions are not present when a sample is in dilute solution. With the discovery in the last year of low dielectric constant solvents that are capable of dissolving the base forms of polyaniline, solution ESR studies have been undertaken.

Figure 4.5 shows the complete ESR spectrum of a solution of EB dissolved in dioxane at a concentration of 0.26 mg/L. This spectrum was taken after extensive degassing of the solution by the use of the freeze, pump, and thaw method. The spectrum was taken at a microwave power of 2 mW, a modulation amplitude of $\approx 0.25$ gauss, a sweep time of $\approx 10$ minutes, and a low pass filter time constant of $\approx 1/2$ second. As can be seen the solution spectrum has a much higher resolution then the solid sample. There are three major peaks split by $\approx 15.5$ gauss. The same pattern of three lines split by $\approx 15.5$ gauss was observed for PNB dissolved in solution. Even though the heights of the three peaks are some what different, the
Figure 4.5. The full field solution spectrum of EB dissolved in a dioxane solvent. The spectrum of PNB in solution was found to have the same nitrogen hyperfine splitting as EB. The data was taken with a large modulation amplitude to increase S/N.
double integrals of each separate peak are equal showing that there is an equal spin density for each line. The differences in the line heights are due to the variation in the linewidths between the lines. Since the number of equal height lines of an ESR spectrum due to hyperfine splitting is equal to \((2I+1)^{4.17}\) this pattern is explainable in terms of the hyperfine splittings of a nuclear spin \((I)\) of \(1\). Figure 4.6 shows the splitting of electron spin \((1/2)\) energy levels by the presence of a nuclear spin \((1)\) and the resulting three lines expected. The only nuclear spin of one in the polyaniline system is the nitrogen. Thus the large splitting seen in the solution ESR spectrum is attributed to the presence of a spin density on a nitrogen atom in the polyaniline chain.

Figure 4.7 shows the same spectrum but with a much smaller field modulation amplitude used. The spectrum was taken at a microwave power of \(2\) mW, a modulation amplitude of \(\approx 0.05\) gauss, a sweep time of \(\approx 10\) minutes and averaged for 2 hours, and a low pass filter time constant of \(\approx 1/2\) second. The smaller modulation amplitude used results in a lower S/N but there is an increase in field resolution. This spectrum shows the same three line pattern but each line now shows resolved structure contained within. The same type of pattern was observed for PNB dissolved in solution, but quantitative comparisons have not yet been undertaken. Figure 4.8 shows the blowup of the low field line of the full spectrum, the one centered at 3341 gauss. This spectrum shows a nine line pattern with a decrease in line intensity from the center of the pattern outward. The lines are separated by approximately 0.41 gauss and have the intensity ratios of

\[3:10:30:55:70:55:30:10:5\]

where the resonance heights have been normalized to the center line having a height of 70. This simplest way to produce this type of pattern is if the electron spins
Figure 4.6. A diagram of the electron spin energy levels split by the nuclear hyperfine interaction of a Nitrogen atom with nuclear spin (I) of 1.
Figure 4.1. The full field spectrum of the same sample of EB in solution as Figure 4.5, except taken with a much lower modulation amplitude for increased field resolution.
energy levels were split by the presence of 8 equivalent nuclear spin (1/2) hyperfine interactions. The splitting of an electron spin (1/2) energy level by eight nuclear spin (1/2) hyperfine interactions is shown in Figure 4.9 along with the expected ratio of the ESR lines. These ratios are

\[ 1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1 \]

and are in reasonable agreement with the measured intensities. The differences may be due to either the limits of experimental resolution or the possible extra splittings one would expect if all eight nuclear spin (1/2) interactions are not exactly of the same value but differ by up to 30%. The only nuclear spin (1/2) atoms in polyaniline are the hydrogens on the rings and the possible hydrogens on the nitrogens. The possibility of a hydrogen being bound to the nitrogen with a measurable spin density can be ruled out. The reason for this is that if a hydrogen were bound to the nitrogen the amount of time the spin sits on a hydrogen would approximately the same as the amount of time the spin sits on the nitrogen and the splitting of the hydrogen would be close to the splitting of the nitrogen. In this case, there would be 6 major lines instead of only three. Therefore it is concluded that the spin is partly sitting on an imine type of nitrogen. The hydrogen splitting must result from the interactions of the ring hydrogens with the electron spin.

The spin density on individual atoms of a molecule can be estimated from the size of the hyperfine coupling constants from the theory of McConnell. McConnell proposed that there is a linear relation between experimentally observed hyperfine splittings and the unpaired-\(\pi\)-electron densities in \(\pi\) type organic radicals. This relation can be written as
Figure 4.8. A blowup of the low field resonance line of Figure 4.7 showing the presence of a nine line pattern and the possible presence of unresulted shoulders on the outer lines.
Figure 4.9. A diagram of the electron spin energy levels and the expected ratios of their intensities caused by the nuclear hyperfine splitting of eight equivalent nuclear spin (I) 1/2 atoms.
where $Q_i$ is an empirically found proportionality constant, $a_i$ is the measured hyperfine splitting of atom $i$, and $\rho_i$ is the spin density on atom $i$. The value of $Q_N$ has been experimentally found to vary from 23-30 gauss and to depend on whether the nitrogen is protonated or not. Freed 4.19 found that the value of 25.6 gauss is the best value for unprotonated nitrogens. Using this value of $Q_N$ and the measured nitrogen hyperfine splitting of 15.5 gauss the electron spin density on the nitrogen is estimated to be $\approx 61\%$ of an electron. A similar estimate for the hydrogens can be made using the value of $Q_{CH} = 22.5$ gauss, where $Q_{CH}$ is the proportionality constant relating the spin density on a carbon atom that is bond to a hydrogen atom to the hyperfine splitting caused by the hydrogen atom. With a measured hyperfine splitting of 0.42 gauss, the spin density on a ring carbon atom is $\approx 2\%$ of an electron spin per carbon atom. Since the 9 line pattern suggest that there are 8 hydrogens that are interacting the density of all eight atoms is $8 \times 2\% = 16\%$. Adding this contribution to that of the nitrogen density 77% of the spin density can be accounted for. To account for the remaining spin density a model of the spin distribution is required.

All of the above features can be explained by assuming that the spin is localized 60% on a nitrogen atom with the remaining spin density distributed over the two adjacent rings. Figure 4.10 shows the most likely configuration of this defect. This type of defect is a change in phase between double bond/single bond to single bond/double bond configuration similar to the neutral solitons seen in polyacetylene. If it is assumed that the spin defect is localized on the nitrogen and two adjacent rings, a simple representation of this the spin density on the rings can be
found from the MO’s of benzene. Figure 4.11 shows the orbitals of benzene and their energy levels. A lone \( \pi \)-electron on a nitrogen atom would mix with these orbitals to lower it’s energy. This mixing would be mainly with MO 2 such that all non-para carbon positions have equal spin density and the para positions have twice the density of the others. Within this structure there are 8 positions with hydrogens with equal spin density \( \rho_C \) and 4 positions with spin density of \( 2\rho_C \). If \( \rho_C = 2\% \) as found above then the total spin density on both rings is 32\% with a total spin density of 93\% accounted for. Thus, it is felt that this structure is a good model of the experimentally measured defects.

This type of defect, the neutral soliton, would be a stable defect just as in polyacetylene and would be created during the polymerization process and/or during the oxidation of EB to PNB. This would account for the presence of undoped spins in all forms of polyaniline and would also account for the increase in the number of spins observed in PNB. No extra defects should be created during the reduction process of converting EB to LED.

It is interesting to note that the delocalization of the spin defect over the rings is a function of the overlap integral between the nitrogen atom and the para position carbons. Since this overlap integral has a cosine dependence on the ring torsion angle, the delocalization is greatest for a flat ring configuration and decreases as the ring torsion angle increases away from planarity. Figure 4.12 shows a simple Huckel type calculation for an oligomer of two rings and one nitrogen, with all parameters taken from the model of Ginder, for the spin density on the nitrogen atom and the carbon atoms as a function of ring torsion angle. The nitrogen spin density is seen to increase as the ring torsion angle increases, while the carbon spin density decreases as the ring torsion angle increases. This simple model matches the experimental spin density on the nitrogen at a ring torsion angle of \( \approx 45^\circ \).
Figure 4.10. The most likely molecular structure to explain the observed hyperfine splittings. The change in the double bond order is similar to the neutral soliton of polyacetylene.
Figure 4.11. The molecular orbitals of the benzene molecule. The nitrogen lone $p_z$ orbital will mix with these orbitals to lower its energy (From Reference 4.19).
This ring torsion angle is consistent with X-ray experiments\textsuperscript{4,21} and also the ring torsion angles predicted in the Ginder model. With the knowledge that the average ring torsion angle increases as a function of increasing temperature due to the anharmonic nature of the steric potential, it is suggested that the delocalization and thus the nitrogen and hydrogen coupling constants should have a temperature dependence. This could be a powerful probe of the ring dynamics of the polyaniline system (though the thermochromism suggests no more than a 1° or 2° shift of the ring torsion angle with temperature increase from 10K to 400K).

The difference in linewidth from the low field to the high field resonance lines is explained by the presence of the anisotropy of the hyperfine coupling constant (a) and the g-factor\textsuperscript{4,22}. The total contribution to the linewidth can be resolved into the components

\[ \Delta H_{\text{aniso}} = \Delta H^{gg} + \Delta H^{ga} + \Delta H^{aa} \]  \hspace{1cm} 4.2

This type of function is expected only if the π-electron density is high at the nitrogen site as is concluded from the hyperfine coupling constant. Since the hyperfine interaction terms depend on the quantum number \( M_I \), an empirical form of this function can be written as

\[ \Delta H_{\text{aniso}} = A + BM_I + CM_I^2 \]  \hspace{1cm} 4.3

where the terms \( A \), \( B \), and \( C \) are as follows\textsuperscript{3,16}

\[ A = \frac{2}{15}(\Delta g)^2\left(\frac{\beta H_0}{\hbar}\right)^2 \tau + \frac{1}{20}(\Delta a)^2 I(I + 1) \tau \]  \hspace{1cm} 4.4
where \( \tau \) is the average collision time of two chains in solution, and \( \Delta a \) and \( \Delta g \) are defined as

\[
B = -\frac{4}{15}(\frac{\beta H_0}{h})(\Delta g \Delta a)\tau \tag{4.5}
\]

\[
C = \frac{1}{12}(\Delta a)^2 \tau \tag{4.6}
\]

Thus individual resonance line linewidths depend on the quantum number \( M_f \). The squared terms in the equations for A and C constrain these terms to be positive whereas the term B may be positive or negative. The third term in Equation 4.3 acts to broaden resonance lines that are to either side of the center line, while the second term broadens the low field (high field) line and narrows the high field (low field) line if the term B is positive (negative). The results on PNB shows that the resonance lines broaden as \( M_f \) increases from -1 to +1, thus B must be negative and \(-B > C\). From the experimental linewidths \( B = -0.083 \) gauss and \( C = 0.049 \) gauss. The fact that B<0 is almost always the case for a nitrogen atom with a high \( \pi \)-spin density. This result gives conclusive proof that the sign of the coupling constant
Figure 4.12. The results of a Hückel calculation for the spin density on the nitrogen atom and the ring carbons.
$a_N$ is positive whereas the position of the peaks of the spectrum in Figure 4.5 only determined its size. The term $A$ is found from the concentration dependence of the centerline linewidth to follow the equation

$$A = 1.299\text{gauss} + 0.590C\left(\frac{\text{gauss}}{g/L}\right)$$

which is the type of behavior one expects for collisional broadening of a resonance line in solution.

**Solid State ESR of PNB**

With the advent of the solution ESR spectrum discussed above the interpretation of the undoped dark ESR spectrum of the polyaniline family is possible. Figure 4.13 shows the X-band ESR solid state spectrum of PNB powder. The spectrum shows a complicated structure of two positive peaks and two negative peaks. This spectrum can be interpreted in terms of a combination of an anisotropic g-value and an anisotropic hyperfine coupling of a nuclear spin (1). Q-band measurements, also shown in Figure 4.13, showed that there is a small g-value anisotropy but that most of the features must be due to the hyperfine coupling constant anisotropy. Fits for this type of spectrum were able to reproduce the main features of the experimental spectrum, but by itself were not able to give good fits. Much better results were found by including a rotational averaging of the anisotropic interacts with a rotational time on the time scale of $10^{-5} - 10^{-6}$ seconds. This type of rotational averaging is also consistent with initial results of Saturation Transfer ESR (ST-ESR) \textsuperscript{4.23}, where molecular rotations move ESR signals from in-phase/first derivative absorption to out-of-phase/first derivative and second derivative absorptions. Room temperature experiments at a microwave power of 200 $\mu$W revealed that as the
Figure 4.13. The solid state X-band (top) and Q-band (bottom) ESR spectrum of PNB.
spectrum was recorded as a function of lockin phase (\( \phi \)), from in-phase/first derivative absorption (\( \phi = 0^\circ \)) to the out-of-phase/first derivative absorption (\( \phi = 90^\circ \)), the signal intensity fell off as \( \approx (1 - 0.5 \cos(\phi)) \) instead of the \( \cos(\phi) \) dependence expected for non molecules. Also these experiments showed that the character of the spectrum depends on the modulation frequency from 100 KHz to 1 KHz, with the low field peaking increasing in height and moving toward the centerline as the modulation frequency in decreased from 100 KHz to 1 KHz. This type of behavior is indicative of a rotational averaging taking place with the time scale of \( 10^{-6} - 10^{-4} \) seconds. Due to the nature of the ST-ESR experiments this time scale is a difficult one to get quantitative results for and thus at this point no more precise results are attainable. This rotational averaging time scale is consistent with the rotational frequencies of benzeniod ring flips in LED and EB solid samples observed in NMR experiments by Kaplan et al\(^4,24\). Kaplan's experimental results where interpreted in terms of rings that undergo rapid flips (\( \tau < 10^{-7} \) s) and rings that flip slowly (\( \tau < 10^{-4} \) s). Including rotational averaging into the simulated spectrum using a program developed by D.J. Schneider and J.H. Freed\(^4,22\) values of the hyperfine coupling constant were found to be

\[ A_x = A_y = 6 - 10 \text{ gauss} \]
\[ A_z = 25 - 33 \text{ gauss} \]
\[ g_x = g_y = 2.0026 \]
\[ g_z = 2.0053 \]

Using the best found values of \( A_x = 7 \) gauss and \( A_z = 32 \) gauss along with the above g-values in Equations 4.4-4.8 the ratio \( B/C = -1.62 \) is calculated which is consistent with the experimental measured ratio of \( B/C = -1.69 \). This result suggests that the spin density on the nitrogen is not confined solely to the nitrogen
p, orbital but instead ≈ 30% of the time that the spin is on the nitrogen it is distributed over the sp² orbitals that make up the polymer framework.

**LESR Time Dependence of PNB**

Figure 4.14 shows the pernigraniline base (PNB) dark ESR and light-induced ESR signals taken at ≈ 60K. The LESR signal was taken with a pump photon energy of 2.51 eV and laser intensity of 100 mW/cm². The dark signal shows the nitrogen hyperfine structure that was discussed previously, but the LESR signal is a single resonance line which is lorentzian in shape. From Figure 4.14 it can be seen that the LESR signal is positive; i.e. the number of spins is increased under illumination and therefore is not a result of heating.

Figure 4.15 shows the evolution of the height of the derivative peak (A) within the first 80 seconds of sample illumination. A increases monotonically with time over the first 80 seconds. Since the number of spins measured in an EPR experiment is proportional to $A\Delta H^2$, where $\Delta H$ is the peak-to-peak linewidth, in the limit that the linewidth is constant, the number of spins measured is proportional to A. Therefore, by monitoring only A, a time resolution of 10 msec can be achieved. As time increases the assumption that $\Delta H$ is a constant becomes tenuous and the number of spins is no longer proportional to A. In this regime, it is necessary to doubly integrate the full spectrum of the induced spin for accurate spin concentration information.

Figure 4.16 shows a three dimensional plot of the photo-induced defect resonance line as a function of magnetic field and illumination time for the first 80 minutes. The graph shows that the resonance line increases in height by almost a factor of one hundred and fifty from the first minute to minute 80. The line is
Figure 4.14. ESR spectrum of PNB powder for both the dark (smaller signal) and light-induced (larger signal) taken at 60K, a laser intensity of 100 mW/cm², photon energy of 2.54 eV, and after 1 hour of illumination. The dark signal has been multiplied by a factor of 50 for comparison.
Figure 4.15. The light-induced change in the height of the derivative peak height divided by the height of the dark derivative height as a function of time for the first 80 sec for PNB. The data was taken at 60K, a laser intensity of 100 mW/cm², and a photon energy of 2.54 eV.
stationary in field position but a narrowing of the line can be seen. The evolution of the normalized number of light-induced spins found from the double integral as a function of time at 60K and 100mW/cm² of laser power is shown in Figure 4.17. The signal intensity grows continuously during the ≈ 2 hours of laser illumination.

Figure 4.18 shows the normalized decay of the photo-induced defect created at 60K with 2 hours of illumination time and a laser power of 100mW/cm². The decay rate is extremely slow. From an extrapolation of the data to an exponential type of decay law a half-life of ≈ 7 days is found. The decay rate has been investigated as a function of sample temperature, sample type (i.e. LEB and PNB), laser illumination time, and laser photon energy. There is little measurable difference in the decay rate due to any of these variables. The only difference of interest is the fast decay of the defects for all oxidation states when the sample is raised above the temperature of ≈ 250K. Below this temperature there is no measurable change in the LESR defects decay rate.

As discussed in Chapter 2, the time dynamics of the photo-induced defect states give information on the creation and recombination paths that are available to a system. The time dynamics in the polyaniline system do not directly conform to either of the simple unimolecular or bimolecular recombinations pathways already discussed. From a log-log plot of the number of defects versus time, Figure 4.19, it can be seen that the LESR signal growth can be interpreted as following a power law;

\[ n(t) = at^\alpha \]  

4.11

for short times. However, as time increases there is a significant departure from a single power law. In the past, there have been attempts to use multiple power laws
Figure 4.16. A 3-dimensional plot of the light-induced ESR spectra for PNB as a function of magnetic field and illumination time.
Figure 4.17. The light-induced change in the double integral of the ESR spectra divided by the dark ESR spectrum as a function of illumination time for PNB. The data were taken at 60K, a laser intensity of 100 mW/cm², and a photon energy of 2.54 eV.
Figure 4.18. The normalized decay of the photo-induced defects in PNB as a function of time at 60K. An extrapolation of the data gives a half life of $\approx 7$ days.
to fit different types of experimental data for many different systems \(^4\,_.25,\,_.26\), but
this did not give reliable results in our case. A better approach was that of the
"stretched exponential" that was mentioned in the experimental discussion section
of this thesis. We found that the function

\[ n(t) = A(1 - \exp(-\left(\frac{t}{B}\right)^c)) \quad 4.12 \]

produced extremely good fits to the experimental data. As for \( t \ll B \) this function
reduces to the before mentioned power law, this function is consistent with the
observed short time behavior. Figure 4.20 shows the experimental data along with
the best fit curve for the stretched exponential type time dependence.

Derivation of "Stretched Exponential"

The long time growth behavior of the induced spins in the polyaniline system
is suggestive of the type of behavior seen in glassy systems. As stated previously,
relaxation of excited states in simple systems usually follow a Debye type relaxation.
A Debye relaxation is one in which a single relaxation time, \( \tau \), characterizes the
system and the relaxation follows the equation \(^3\,_.12;\)

\[ n(t) = a \exp(-\frac{t}{\tau}). \quad 4.13 \]

In many systems this conventional Debye relaxation is not applicable and more
complicated types of behavior are observed. Relaxation in complex, slowly relaxing,
and strongly interacting materials often follows the stretched exponential form

\[ n(t) = n_0 \exp(-\left(\frac{t}{\tau}\right)^\beta), \quad 0 \ll \beta \ll 1. \quad 4.14 \]
Figure 4.19. A log-log plot of the light-induced change in the double integral of the ESR spectra divided by the dark ESR spectrum as a function of illumination time for PNB. The data was taken at 60K, with a laser intensity of 100 mW/cm², and a photon energy of 2.54 eV.
Figure 4.20. A plot of the best fit of a stretched exponential law to the PNB data taken at 50K using parameters $A=11.5$, $B=26.9$, and $C=0.56$. 
This equation was first suggested by Kohlrausch \(^4,27\) as a description of viscoelasticity. In more recent years, it has been used to describe a wide range of phenomena from dielectric relaxation to spin relaxation in spin-glass alloys\(^4,28\).

The simplest way to obtain a non Debye type relaxation, is to assume a distribution of relaxation times \(\tau\) due to distributions in molecular environments and/or degrees of freedom within a material. With this assumption one can write the equation

\[
n(t) = \int_0^\infty w(t) \exp\left(-\frac{t}{\tau}\right) d\tau
\]

where with a suitable selection of the weighting function \((w(t))\), virtually any desired functional form for \(n(t)\) can be produced. This approach is normally associated with a picture of parallel relaxation, in which each degree of freedom \(z_i\) relaxes independently with characteristic time \(\tau_i\). A distribution of \(\tau\)'s is applicable in amorphous materials where the microscopic environments can be diverse from point to point.

A second approach to the understanding of this type of time behavior was developed by Palmer et al\(^4,29\). Palmer and coworkers put forth a series interpretation with the path to equilibrium involving many sequential and correlated activation steps. In their view, any successful theory of glassy relaxation must satisfy three requirements: (1) The theory must be based on dynamic behavior and not on simple statistics such as is the case in the Debye law. (2) The theory must involve constraints; in our case, defect states are not independent but are strongly coupled. (3) The theory should involve a hierarchy of degrees of freedom, from slow to fast, where the fastest degree of freedom may involve single atoms and the slower ones
might depend on a group of the faster ones moving in just the right way to make
room for the slower ones.

Since both approaches predict the same time behavior one might ask what are
the differences between them and how can these differences be used to interpret
our data. Briefly, "parallel relaxation" assumes that all defect states are indepen­
dent and that there is a distribution of relaxation times in the system, whereas
"serial relaxation" assumes that there is strong coupling between defects and that
the creation or annihilation of a defect is dependent on all other defects that are
coupled to it. In "parallel relaxation" since all defects are independent there should
be a symmetry between the creation process and the decay process. In "serial re­
laxation" since defects are coupled and this coupling may increase with increasing
defect concentration, there need be no symmetry between the creation and decay
processes. Also in "serial relaxation" where defects are coupled there should be
changes associated with this coupling that can be experimentally measured, e.g.
exchange or dipole-dipole interactions in EPR experiments.

Laser Intensity Dependence

LESR experiments can yield more information if the laser intensity and photon
energy dependence are explored. It is usual in photo-induced experiments that the
signal laser intensity dependence gives information on the recombination route
of the excited states. In Chapter 3 it was shown that if the recombination is
unimolecular then the steady state equilibrium is proportional to the laser intensity
I and if bimolecular it is proportional to $\sqrt{I}$. However, in our experiments, an
equilibrium population is never reach since there is a constant increase in defects
with constant illumination, and therefore any such intensity dependences could
only be incidental.
The spin concentration as a function of illumination time for several laser intensities does show a dependence of the induced spin concentration on laser intensity. At first the interpretation of this result was not clear, but on reflection it was realized that the spin concentration should not be a function of time but instead a function of the number of photons incident on the sample. Time is converted to the number of photons by multiplying the time of illumination by the laser power and dividing by the photon energy. When this was done there was no difference found in the growth dynamics of the number of spins due to changes in the laser intensity. The important quantity to monitor in these experiments is the photon flux. The number of defects is therefore dependent only on the number of photons incident on the sample and not on the rate of incidence. Because the creation of defects is dependent on the photon flux rather than on the photon flux rate no information on the defect recombination path is gained from the intensity dependence of the defect generation rate. When this is taken into account it is also found that there is little dependence of the LESR on the photon energy, after adjusting for the sample's absorption curve, that is used to excite the defects.

Temperature Dependence of LESR of PNB

A striking feature of the photo-induced defects in the PNB system is the temperature dependence. Figure 4.21 shows the time dependent growth of photo-induced defects at constant illumination at several temperatures. As can be seen there is an increase in the production of defects as the temperature decreases. This would be what one would expect if the decay time of photo-induced defects were temperature dependent. For example, if the defects recombined by collisions with other defects the decay time would have a thermally activated temperature dependence such as;
Figure 4.21. The concentration of light-induced defects as a function of time for several temperatures for PNB.
$\tau(T) = \exp\left( \frac{\Delta E}{k_B T} \right)$

where $\Delta E$ is the activation energy of the system. This model does not seem to be applicable for the material studied here. As was mentioned previously, the decay times for the defects have been found to be extremely long, the best estimate gives the half-life to be on the order of 7 days, and also that there is little to no temperature dependence to them, at least for temperatures below 200K. Since there is no temperature dependence to the decay rate of photo-induced defects, yet the production of defects increases as the temperature decreases, there must be a temperature dependence to the cross section for production of defects $(g)$. In other words, the production of spin defects per photon becomes more efficient as the temperature decreases.

**Table 1.** Summary of the temperature dependences of the Kohlrausch parameters $A$, $B$, and $C$.

<table>
<thead>
<tr>
<th>Kohlrausch Parameters</th>
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<tr>
<td>$T$(K)</td>
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<tr>
<td>25</td>
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<tr>
<td>50</td>
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<td>75</td>
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<td>150</td>
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Table 1 shows the temperature dependence to the parameters $A$, $B$, and $C$ of Equation 4.6 of the stretched exponential expression used to fit the experimental
Figure 4.22. A plot of the stretched exponential parameter $A$ versus $T$ for PNB. See Table I.
Figure 4.23. A log-log plot of the stretched exponential parameter $A$ versus $T$ for PNB showing a change in behavior at 130K. See Table I.
data for PNB. All three parameters are temperature dependent and increase with decreasing temperature. The fits are reproducible for different samples. From a plot of the parameter A versus T, Figure 4.22, we see that there is a change in the temperature dependence of the parameter A at around 130K. Above 130K the parameter A has a weak temperature dependence, but below 130K there is a rapid increase in the parameter A as the temperature decreases. Figure 4.23 is a log-log plot of the parameter A as a function of temperature. Both above 130K and below 100K the similar slopes in the log-log plot of the parameter A suggests that in both regions the parameter A might follow a thermally activated type behavior but with two different activation energies for the two regions. It is noted that above 130K, additional data is necessary to substantiate the activation. The temperature range of 100-130K is an intermediate region where there is a cross over from one dependence to another. This type of change over is suggestive of a phase transition of some type in the polyaniline system. There is evidence that there is indeed a transition of some type in this temperature regime in the polyaniline system. This evidence will be discussed in detail in following sections (see sections, LESR temperature dependence, Linewidth, Linewidth temperature dependence).

**LESR Linewidth of PNB**

**Time/Concentration Dependence**

The most unexpected result of LESR on PNB is the time dependence of the peak-to-peak linewidth of the ESR signal. Figure 4.24 shows the FWHM linewidth of PNB as a function of illumination time at several different temperatures ranging from 60K to 300K. The linewidth decreases from \( \approx 18 \) gauss at \( t \to 0 \) at all temperatures to a minimum of \( \approx 8 \) gauss as \( t \to 2 \) hours at 60K. Since the concentration
of spin defects is time dependent, the linewidth is plotted as a function of the spin concentration in Figure 4.25. As can be seen the linewidth is a function of the defect concentration. This type of behavior can be explained in terms of narrowing of the ESR linewidth by exchange narrowing that was discussed in Chapter 2. In brief, although individual spins are localized there is a quantum spin exchange interaction $J$ between neighboring spins which narrows the resonance line according to the theory derived by Anderson and Weiss\textsuperscript{4,30}. In the simplest approximation of this theory

$$\Delta H \propto A/J. \quad 4.17$$

where $A$ is a proportionality constant related to the dipole-dipole interactions the spin experiences. For small deviations in the spin-spin distances $r$ and assuming an exponential dependence of $J$ on $r$

$$J = J_0 \exp(-Br) \quad 4.18$$

Equation 4.16 can be expanded to

$$\Delta H \propto A + Er. \quad 4.19$$

Since in three dimensions $r \propto C^{-1/3}$, where $C$ is the defect concentration, a plot of $\Delta H$ versus $C^{-1/3}$ should be linear if the above approximation is correct. As can be seen from Figure 4.26, $\Delta H$ versus $C^{-1/3}$ is in fact almost linear, thus supporting the idea that the narrowing of the linewidth is due to exchange coupling of neighboring spin defects. The three-dimensional dependence of $J$ is somewhat
Figure 4.24. The full width at half maximum (FWHM) linewidth of the LESR spectra of PNB as a function of time at 50K, 75K, 100K, 125K, 150K, 175K, and 200K from the bottom to the top.
Figure 4.25. The full width at half maximum (FWHM) linewidth of the LESR spectra of PNB as a function of photo-induced defect concentration at 60K.
surprising in light of the one-dimensional character of the polymer chain. Attempts were made to fit the data to either one or two dimensional dependences but these produced extremely poor results. The three-dimensional behavior of dependence of $\Delta H$ on the defect concentration is explainable in terms of the random creation and migration processes of the defects. These processes are governed by three-dimensional interactions and therefore the accumulation of regions of high defect concentration that is proposed for this system is a three-dimensional process. Plotting $J$ from Equation 4.16 ($J = A/\Delta H$) shows that the value of $J$ found from this expression increases as the photo-induced defect concentration increases.

A more realistic linewidth dependence does not assume that the value of $A$ is a constant. In a model by Richardson, $A$ is the second moment of the resonance line that was defined in Chapter 2. Making this correction in Equation 4.11 produced the equation

$$\Delta H \propto M_2/J$$  \hspace{1cm} 4.20

The behavior of $J$ as a function of the spin defect concentration $C$ found from this equation is plotted in Figure 4.27 showing that $J$ increases up to $\approx 20$ gauss.

A second method of calculating $J$ is the methods of moments random function model. This model gives the result

$$M_4 = 3M_2^2 + AM_2J^2$$  \hspace{1cm} 4.21

where $M_4$ is the fourth moment and the constant $A$ depends on the lattice structure assumed for nearest neighbor spins and the largest possible value of $A = 3.3$, that for a simple cubic lattice, was used to calculate the value of $J$. Figure 4.28 shows
Figure 4.26. The full width at half maximum (FWHM) linewidth of the LESR spectra of PNB as a function of the cube root of the concentration ($C^{-1/3}$), where $C^{-1/3} \propto r$ the distance between defects.
Figure 4.21. The exchange interaction energy ($J$), in gauss, as a function of the concentration of photo-induced defects in PNB. $J$ was calculated from the equation $J = M_2 / \Delta H$, where $M_2$ is the second moment of the resonance line and $\Delta H$ is the FWHM linewidth.

Figure 4.27. The exchange interaction energy ($J$), in gauss, as a function of the concentration of photo-induced defects in PNB. $J$ was calculated from the equation $J = M_2 / \Delta H$, where $M_2$ is the second moment of the resonance line and $\Delta H$ is the FWHM linewidth.
the result of $J$ versus $C$ by use of this method. As can be seen, the results from this equation follows the same general type of behavior as the previous plot in that both equations give an increase in the value of $J$ of approximately a factor 2, but the size of $J$ differs between the two. An exact value of $J$ is difficult to determine from this type of calculation, but the trend of the increase in the value of $J$ with increasing defect concentration is consistent within both models.

**LineWidth Temperature Dependence of PNB**

Although the zero time linewidth is nearly the same for all temperatures ($\approx 18$ gauss), the time/concentration dependent change in the linewidth is temperature-dependent. Figure 4.29 shows $\Delta H$ versus concentration for temperatures between 50K and 200K. The linewidth versus spin concentration follows three distinct curves for data taken in the ranges $T \gtrsim 130K$, $90K \lesssim T \lesssim 130K$, and $T \lesssim 90K$. The change in slope that occurs below 130K is also accompanied by a change in the temperature dependence of the Kohlrausch parameters as was discussed in the previous section. Similarly, changes are seen in this temperature region in both specific heat measurements by Avlyanov et al.\textsuperscript{33} and Resonance Raman measurements by Bartonek et al.\textsuperscript{34} on slightly doped and undoped polyanilines. We suggest that this change may be due to the freezing out of the quinoid and/or benzeniod ring flip modes in the PNB chain. This would be consistent with the increase in wavefunction overlap that is needed to explain the increase in exchange interaction seen in the LESR experiment along with explaining the specific heat anomaly seen by Avlyanov et al. This temperature range is also consistent with calculations of Ginder\textsuperscript{4,38} on the energy needed to flip a benzeniod ring.

The second change in linewidth behavior seen below 90K, is not accompanied by a change in the Kohlrausch parameters but there is a change seen at this temperature in the temperature dependent stability of induced defects as discussed in
a following section. This change is not well understood but is likely due to either freezing out of the ring flip modes of the benzenoid units, similar to the freezing out of the quinoid units, or possibly a change in the interchain interaction due to a change in the three-dimensional structure of the polymer.

**LineWidth Temperature Dependence of LEB**

So far we have restricted our discussion to the experiments on PNB, but similar results have been found in the other oxidation states of polyaniline. Photoinduced absorption experiments on EB and LEB have demonstrated that the long lived photo-induced defects are present in these materials. LESR experiments on LEB have shown the same type of time dependence to the growth of defects with illumination time as seen in the PNB system, but the maximum number of defects created in LEB is 50 times smaller then the maximum number of defects observed in PNB. Since it is known that during the reduction process of EB to LEB approximately 2-4% of the quinoid rings are left in the final product, this ratio of the number of defects observed in LEB compared to PNB suggests that it is quinoid rings in LEB that are responsible for the observed long lived photo-induced defects.

Figure 4.30 shows the LESR linewidth as a function of induced defect concentration for the temperature of 50K, 100K, and 300K. At high temperature the linewidth for the light-induced defects in LEB narrows somewhat with increasing defect concentration in the same way that was observed for PNB. As the temperature decreases though, the LESR line of LEB no longer narrows, but in fact broadens with increasing defect concentration. The narrowing of the LESR line at room temperature of LEB can be concluded to be due to exchange narrowing as is the case for the LESR of PNB. The broadening of the LESR linewidth of LEB
Figure 4.28. The exchange interaction energy ($J$), in gauss, as a function of the concentration of photo-induced defects in PNB. $J$ was calculated from the equation $M_4 = 3M_2^2 + AM_2J^2$, where $M_2$ is the second moment of the resonance line, $M_4$ is the fourth moment of the resonance line, and $A$ is a parameter that depends on the lattice structure.
Figure 4.29. The full width at half maximum (FWHM) linewidth of the LESR spectra of PNB as a function of photo-induced defect concentration for temperatures in the range of 30K to 200K.
at low temperature, as compared to the narrowing of the LESR of PNB seen at all temperature, is indicative of a dipole-dipole interaction between pairs of spins. In this case, the exchange interaction is small enough that the dipolar broadening is the major factor in determining the LESR linewidth. A possible explanation of dipolar broadening of the LESR of LEB and the differences in the LESR linewidth of PNB and LEB is the presence of the amine sites in the LEB structure. The transfer integral between nitrogens and rings is smaller at amine sites then it is at imine sites because of the lack of the lone $p_z$ electron at the amine sites. Thus, an amine site creates a barrier to the exchange between two neighboring spins and therefore, only a dipolar interaction is observed at low temperature. At higher temperature, as the rings flip more rapidly, there is a greater chance for the spin wavefunctions to overlap and exchange narrowing takes place.

**Temperature Dependent Susceptibility of Defects**

There are two different temperature dependences of the LESR signal of interest, not including the heating effect already discussed in chapter two. The first is the temperature dependences of the creation and decay times and amplitudes. These can be determined by repeating LESR experiments as a function of temperature. This is a standard method in both photoinduced absorption and LESR experiments and is valuable in identifying temperature depend relaxation in photoinduced defect states. The second temperature dependence of the LESR signal is only observable because of the long-lived nature of the defect states in the polyaniline system. In PNB, a large defect concentration can be achieved. Since this large defect concentration is stable below 250K, the temperature dependence of the susceptibility of the induced defects can be measured. Inherent in this susceptibility
Figure 4.30. The full width at half maximum (FWHM) linewidth of the LESR spectra of LED as a function of $\chi_{\text{induced}}/\chi_{\text{dark}}$ $\propto n_{\text{induced}}$ for the temperatures 50K, 100K, 300K.
data is information on the environment of the spins and on the interaction of the spins with each other.

Figure 4.31 shows the temperature dependent susceptibility of the induced defect states in the PNB system. This data was taken after the sample was illuminated for 2 hours at 50K with a laser power of 100mW/cm² and then the laser was blocked for 1/2 hour to allow all heating effects to disappear. Data was taken as a function of temperature as the sample was cooled to 20K and then warmed back up to 50K. The sample was then heated to 95K and then cooled back to 50K, where a measurement confirmed that the defect concentration was in fact stable even after the 5 hours needed for these runs. This procedure was repeated 4 times on the same and different samples to insure that this data was due to the sample studied and not some outside influences.

The data points (circles) on Figure 4.32 represent the number of Curie like spins, \( \chi \times T \), as a function of temperature. As can be seen from the graph, the defect states studied here are not simple Curie spins (i.e. localized non-interacting spin defects) for which there would be no temperature dependence to the number of spins, but must in fact be interacting defect states where the interaction of the defects is a function of temperature. There are two simple models to explain this temperature dependent interaction. The first model is that of a high lying triplet state shown in Figure 4.33. In the triplet model, the ground state of the defect is in fact a singlet state \( (S=0) \) but has a triplet state \( (S=1) \) configuration thermally accessible to the defect. For this case, if the splitting between the singlet and triplet states are greater then the EPR microwave photon energy then the susceptibility is as follows;

\[
\chi(T) = \frac{C}{T} \frac{4}{3 + e^{\frac{A_E}{kT}}} 
\]

\[4.22\]
Figure 4.31. A plot of the susceptibility of the photo-induced spins of PNB as a function of temperature. The defects were produced by 2 hours of illumination at a temperature of 50K. The laser was then turned off. Data was taken and doubly integrated at intervals as the sample was cooled to 20K, then heated up to 95K, and finally cooled back to 50K.
Figure 4.31. A plot of the number of curie spins, $\chi T$, of the photo-induced defects as a function of temperature. Data from plot 4.29 multiplied by $T$. The line is the best fit to the expected behavior of a thermally excited triplet.
Figure 4.32. A diagram of a high lying triplet states split off from the singlet ground state by an energy $\Delta E$. 
where $C$ is the number of defects and $\Delta E$ is the energy difference between the singlet ground state and the triplet excited state. The function $\chi(T) \times T$ has a more compact form and therefore is easier to analyze.

$$\chi(T) \times T = \frac{4C}{3 + e^{\frac{\Delta E}{k_B T}}}$$  \hspace{1cm} (4.23)

This function decreases as $k_BT$ decreases and becomes the size of $\Delta E$. This behavior is the same type of behavior seen in the temperature dependence of $\chi(T) \times T$ for the induced defects of PNB. The solid line on Figure 4.31 is a fit of the function 4.22 to the experimental data with the result that $\Delta E$ is found to be 44K and the number of Curie spins is $4.4 \times 10^{-2}$. In other words the data on PNB is consistent with a photo-induced singlet ground state having a triplet excited state split off from the ground state by 4 meV and is therefore thermally accessible. This model of a thermally accessible triplet state for the photo-induced defects is also consistent with the spin interaction deduced from the behavior of the LESR linewidth as a function of spin concentration.

The second model to explain this data is harder to quantify, but is important enough that it needs to be discussed. The stability of defect states in one-dimension depends on parameters such as the Coulomb interaction. A case in point is polyacetylene where the role of the Coulomb interaction and intra-chain versus interchain interactions is still a contested subject. It is therefore quite possible that there is no most stable defect in the polyaniline system, but there is instead a competition between two defect states (i.e., $P^+ + P^+ \rightleftharpoons BP^{++}$). One expects that the equilibrium concentration for this equation would be temperature dependent. For the case of PNB, if the equilibrium was moved in favor of $BP^{++}$ at low temperatures then it would be possible to get the results that we have found.
Another interesting behavior was found as a function of temperature. While heating the sample with a large concentration of induced defects, when the temperature was raised above 100K there was a decrease in the number of defects present. This was confirmed by the fact that on cooling back to the temperature at which the defects were created the initial defect concentration was not recovered whereas when the temperature was only raised to 95K upon recooling, the measurements were repeatable. This sudden change in the defect stability around 100K leads to the conclusion that there is a "phase transition" of some kind at this temperature. Whether this phase transition is related to the phase transition that is deduced to be at 120K from the changes seen in the defect production rate is unclear at this time. It is quite possible however that the two observed phenomena are due to the same phase transition. There are more indications that there is a phase transition in this temperature regime for polyanilines. Avlyanov et al. observed in specific heat measurements an anomalous temperature dependent specific heat jump in EB. The temperature at which this specific heat anomaly was observed was found to be dependent on the doping level and varied from 165K for emeraldine base to 210K for fully doped emeraldine salt. Previous EPR data of our own on PF$_6^-$ doped LEB showed that there are in fact two phase transition, one at $\approx 170K - 220K$, depending on the oxidative doping level, and another at $\approx 100K$. The phase transition at 100K in PF$_6^-$ LEB is consistent with that seen in the LESR of PNB. It is possible that the transition at 130K in the LESR of PNB is the same one observed by Avlyanov at 170K, but is moved to a lower temperature in the PNB oxidation state as compared to the EB oxidation state. We at first interpreted this EPR data in terms of the freezing out of rotational mode of the PF$_6^-$ molecule, but with the advent of Avlyanov's et al data and our observation of the temperature dependent LESR, we now believe these phase transitions to be inherent to the polyaniline chains.
One possible origin of these phase transitions is a three-dimensional restructuring of the crystal lattice. This is highly unlikely due to the fact that the materials that we have studied do not have a high degree of crystal structure, EB-II is at most 50% crystalline and PNB is has a lower crystalline fraction. A more likely cause for the phase transitions seen is a microscopic one instead of a macroscopic one such as the 3-d restructuring. Since ring containing polymers have more degrees of freedom (i.e. ring rotation, breathing modes, etc.) then linear chain polymers such as polyacetylene, they also have more possible coupling routes between the polymer backbone and the charge on the chain. In particular, the ring rotational mode in the polyaniline system is known to be important for the stability of defect states on the polymer chain \textsuperscript{4.1,4.3}. Ginder \textit{et al} have shown that in all oxidation states of polyaniline, it is possible to have not only the standard bond length dependent defect states but also a new class of defect states due to variations in ring angle along the chain. Since these rings are in fact dynamic, they can have thermally activated rotations, the stability of these new class of ring defect states would be temperature dependent.

\textbf{Short Time LESR}

The monitoring of the derivative peak height with a lock-in amplifier as the light source is chopped at a frequency in the range of 5-1000 Hz is known as double modulation detection. This technique enables the measurement of small (10\textsuperscript{-4}) changes in defect concentration and their dependences on laser intensity, chopper frequency, and sample temperature. These results can be compared to photoinduced absorption experiments to obtain a coherent picture of the induced defect states. This method was used by Flood \textit{et al} \textsuperscript{4.35} to identify the photoinduced defect states in polyacetylene as charged solitons due to the fact that the
LESR experiments put an upper limit of $3 \times 10^{10}$ spins/cm$^3$ as compared to the $5 \times 10^{12}$ cm$^{-3}$ defects seen in trans-photoinduced absorption measurements. From these measurements Flood et al concluded that the branching ratio for the creation of spins and charges has a limit of $2 \times 10^{-3}$ and thus that most of the photo-induced defects in polyacetylene are charged, spinless solitons. A similar attempt was made by us in the polyaniline systems.

Optical experiments on PNB have shown not only that there is a long lived, long creation time defect, that is associated with absorptions at 1.5 and 3.0 eV along with changes in IR modes, as found in LESR experiments but also demonstrated that a short lived defect exists that is most likely independent of the other defect. This short lived defect has an absorption at 1.0 and 1.3 eV. In order to understand the structure and origin of this short lived defect, we attempted to study the spin of this defect by double lock-in detection LESR. In PNB, the long lived, long creation time spin defects discussed in the previous section made it very difficult to use double lock-in detection (DLD) in this system. Since there is a continuous growth of spin defects in this system, it is necessary to wait at least two hours after the sample is illuminated before beginning DLD so that the growth of defects per laser pulse will have fallen below the expected increase in signal that will be seen from the induction of the short lived defects. The derivative peak height is monitored both by a second lock-in detector and by a signal averaging oscilloscope. Both the lock-in detector and signal averager used as a reference the output of a light detecting diode that is arranged to measure the chopped laser output.

The photoinduced absorption experiments of Leng et al$^{34}$ have shown that the ratio between the steady state population of short lived defects and the maximum population of long lived defects is $2.5 \times 10^{-3}$ at 80K with a laser power of 100mW/cm$^2$. If both the short lived and long lived photo-induced defects have spin
associated with them, then a 0.25% change in the ESR spin concentration should be produced during chopped LESR experiments. If the linewidth of the short lived defects is assumed to be the same as that of the long lived defects then a 0.25% change in the resonance line height is expected for short lived defects that have spin. In order to observe this number of short lived spins, heating effects must be carefully taken into account. Since heating causes a decrease of the LESR signal, there will be a competition between any increase in signal caused by short lived defects and the decrease in signal that is produced by laser heating of the sample. For example, a laser heating of the sample of 0.1K per laser pulse at 60K produces a 0.17% decrease in the LESR signal. In our short time LESR experiments, only a signal decrease of 0.25% was observed at 60K both by the lock-in detector and the signal averager. This decrease in signal is consistent with a 0.15K temperature increase per laser pulse, but could also be due to a larger heating effect with a simultaneous increase in spin concentration. It was hoped that phase information from the lock-in and/or time information from the signal averager might show two separate processes, one a decrease due to heating and one an increase due to the induced defects, but this was not the case. Since from photoinduced absorption experiments the temperature and power dependence of the induced defects is known, and it is possible to calculate the dependence of the heating effect on these quantities, detailed temperature and laser power studies of the LESR signal were done in order to quantitatively compare the calculated heating effect and the induced defect effect to the results obtained by the LESR experiments. The decrease in the LESR signal was observed to scale as the laser power, as expected for a pure heating effect, down to 10mW/cm², whereas the photoinduced absorption experiments have demonstrated a $I^{0.7}$ laser power dependence to the short lived defects. Steady state photoinduced absorption experiments at 295K, where
the long lived photo-induced defect concentration measured by both LESR and photoinduced absorption experiments is 40 times smaller than that at 60K, show a short lived defect concentration of $1/2$ of that at 10K. Since the resolution of the LESR experiments is determined by the ratio between the size of the signal without illumination and the change in signal due to illumination, the much smaller number of long lived defects at 295K versus the number at 60K enhances the LESR sensitivity by a factor of 40 while the number of short lived defects only decreases by a factor of 2. Also at 295K the same laser heating of 0.15K will only decrease the background signal by 0.05% versus the 0.25% decrease at 60K. If the short lived defect has spin associated with it, then the short time LESR experiments should measure an increase in signal of $\approx 5\%$ from the background signal. When LESR experiments were done at 295K no signal, increase or decrease, could be observed. Since a maximum decrease in signal of 0.05% can be expected from heating effects and this was not observed, then either there is a photo-induced increase of signal of this same size thus adding to a net zero change in signal or the sensitivity of the instrument is on the order of 0.05%. In either case this value of 0.05% can be used as an upper limit to the increase in the LESR signal. Under the assumption of a constant linewidth this limit gives a branching ratio between the photo-induced change to spin of 100.

Unfortunately this method on its own is at best only circumstantial and at worst is possibly misleading in that the errors associated with the subtraction of large numbers to find small underlying effects are very large. But even if the short lived defect has a larger linewidth and/or is not at the same g-value then the branching ratio could be no smaller than 10. This is one order of magnitude smaller than the number of defects seen by PA experiments. The LESR experiments are therefore consistent with the proposal of Leng et al.\textsuperscript{4,36} that the short lived photo-induced
defects are spinless solitons that are associated with changes in the bond order of the PNB rings and not with the ring angles such as is the case with the long lived spin defects.

Possible Origins of Photo-Induced Defects

Interpretations of experimental data on the polyaniline family of polymers have concentrated on the role of polarons and bipolarons on the polymer chain and have largely dismissed the possible role of solitons because of the presence of spin in these systems. Theories that have proposed the presence of solitons in these systems have concluded that these solitons would be charged, spinless solitons and therefore not relevant to the interpretation of LESR experiments. These charged, spinless solitons would play a role in photoinduced absorption experiments and are consistent with the photoinduced absorption experimental results of Leng et al and short time LESR on PNB where a spinless photoinduced absorption feature was detected at 1.0eV. The photo-production of spinless solitons is also consistent with the observed behavior in polyacetylene where only charged, spinless solitons have been detected. Neutral, spin solitons have been detected in polyacetylene but are known to be created in the polymerization process and are generally believed not to be photo-produced. A defect similar to polyacetylene neutral, spin solitons have been experimentally observed in the undoped solid and solution samples of EB and PNB as discussed at the beginning of this chapter. These defects are also believed to be created during the polymerization and/or oxidation process, but the question is raised as to whether these same type of defects can be photo-produced.

dos Santos and Bredas' predicted the existence of two types of solitons, as shown in Figure 4.34, in PNB but concluded that these independent solitons are
unstable to the creation of a spinless soliton anti-soliton pair. Su\textsuperscript{4,38} has recently calculated that there is a binding energy for the soliton anti-soliton pair, but that there two would separate into two spins with an activation type of behavior. Su's proposal is consistent with the existence of photo-induced spins and the temperature dependence of the long lived defects susceptibility, but does not explain the long lifetimes of the defects.

The long lived defects have been proposed by Ginder et al\textsuperscript{4,1} to be related to a change in the ring torsion angle of the benzene rings on the creation of a ring polaron. In the Ginder model, several different types of polaron defects are needed to explain both the LESR and photoinduced absorption experiments, but many of the observed phenomena of the polyaniline polymers are explainable within this model. One short coming of this model is the difficulty in explaining the formation of interacting spin defects that are observed in LESR experiments. Interacting defects are predicted by Bredas, although these are spinless defects, and similarly by Su, where the defects have spin. In both of the later works ring rotations play a small role in the defects behavior, but the defect is mainly due to bond order changes where benzenoid, quinoid, and semiquinones structures make up the polymer backbone. We believe that any coherent theory of the behavior of the polyaniline family of polymers must incorporate both importance of ring angle, include the creation of interacting defects, and be consistent within all oxidation states of the polymer.

Figure 4.35 shows several possible sequences of the PNB defect states. The first sequence show the two types of solitons of dos Stantos and Bredas \textsuperscript{4,35} where the first type is related to two benzenoid units and the second is two quinoid units in a semiquinone sequence. This is consistent with the observation of interacting spins, but is inconsistent with the observed long decay times. The second sequence
shown is similar to the first except that the semiquinone unit has become unstable to the production of a benzenoid ring that can then rotate out of the plane to lower the steric interaction with the adjacent benzenoid ring. This type of behavior is consistent with the known preference of the polyaniline system to form only regions with either of the benzenoid or the quinoid resonance structures. On conversion to the benzenoid structure, both positive and negative charges are localized on separated nitrogen atoms, but the two interacting spins are still present. This sequence of defects can be represented as two pairs of charged and neutral solitons such as $S_-S_0, S_0S_+$. These pairs can move apart and become trapped by other pairs on the chain or can exchange an electron to become two $S_-S_+$ pairs with no spin. This conversion from two spin $1/2$ pairs to two spin 0 pairs is consistent with the observed temperature dependence of the susceptibility of the long lived defects where a thermal activation of spin is observed. The conversion of a quinoid ring to a benzenoid ring and the subsequent rotation of the ring out of the polymer plane explains the long decay times of these defects. In order for two pairs of defects to recombine a benzenoid ring must rotate back into the plane while the two pairs are in close proximity. The probability of this happening is temperature dependent and would be small at low temperatures in view of the proposal of the freezing out of the rotational modes of the benzenoid rings below 130K. The validity of this model might be investigated by the temperature dependence of the photoinduced absorption of the long lived defects. If the optical absorption of a $S_-S_+$ pair is different from that of $S_-S_0, S_0S_+$ pairs then this model predicts that the absorption of the long lived defects should change as a function of temperature from 100K - 4K with an increase in absorption due to the increase in the population of the charged pair as the temperature decreases. It is unknown at present what changes in the optical spectrum might take place during the conversion of a $S_-S_0, S_0S_+$ pair to
Figure 4.34. The structure of the two types of solitons predicted to be present in PNB. The first structure is termed $S_{BB}$, for benzenoid-benzenoid, and the second structure is termed $S_{QQ}$, for quinoid-quinoid (From reference 4.35).
Figure 4.35. Several possible sequences for defects in PNB. (a) Shows the \( S_{BB} \) and \( S_{QQ} \) defects as predicted by Bredas but with spins as predicted by Su. (b) Shows the same sequence except that the quinone \( S_{QQ} \) defect becomes benzenoid in character with the production of four solitons. (c) Shows the two possible configurations of charged and neutral soliton.
two $S_–S_+$ pairs, but initial Hückel calculations on a 6 ring oligomer have shown that there is a shift in the density of states from the pristine PNB oligomer to a PNB oligomer containing one $S_–S_0, S_0 S_+$ pair. This shift is not simply due to the two new states formed within the gap on the creation of this defect. Instead, there is a change in the band structure of the Peierls LUMO (conduction band) with the result of creating new optical transitions that are larger in energy than the Peierls band gap. These changes in the Peierls LUMO and their associated “supergap” optical transitions are one possible explanation of the long-lived 1.5, 1.8, and 3.0 eV photo-induced transitions observed in PNB.
CHAPTER V

DATA and DISCUSSION II

RESULTS IN POLYTHIOPHENE

Since the first report on the photoinduced absorption and LESR of polythiophene (PT) by Vardeny et al. \(^5\), several other reports pertaining to the nature of the photo-excited defects in the polythiophene family of conjugated polymers have appeared \(^5\). Polythiophene and poly(3-methylthiophene) (P3MT) shown in Figure 5.1 are stable conducting polymers with nondegenerate ground states. The two possible ground states are shown in Figure 5.2, where the first of these is the lowest energy configuration. Since polythiophene possess a nondegenerate ground state solitons are not possible in this system and the stable excitations are polarons and bipolarons. Figure 5.3 shows the 4 new energy levels, along with the possible optical transitions, associated with the creation of polarons or bipolarons on the polymer chain. If polarons are photo-produced in this system three new sub-gap absorptions are expected, whereas if bipolarons are photo-produced then only two new sub-gap features should be observed. In polythiophene, two “mid-gap” photoinduced transitions and a set of infrared bands were observed, all of which behave similarly as the exciting photon energy is changed. LESR, on the other hand, showed a different excitation spectrum, indicating different photo-excited defects. Based on these observations it was concluded that the photoinduced defects observed in the photoinduced absorption (PA) experiments are predominantly
Figure 5.1. Chemical structure of Polythiophene; R=H and poly (3-methylthiophene); R=CH₃.
Figure 5.2. Two possible ground state configurations of polythiophene. The lower configuration is the lowest energy configuration.
Figure 5.3. Schematic energy diagrams of positive and negative polarons and bipolarons and the possible energy transitions associated with each.
Figure 5.4. Dark ESR signal (upper trace) and light induced ESR (lower trace) of P3MT at $\approx 30 \text{ K}$. 
bipolarons. In a different report, Kaneto et. al. concluded, from estimates of the number of photo-excited charges and spins in their experiment, that the photoinduced species are predominantly polarons. In this latter work, however, no detailed comparison of the excitation spectra of the PA and LESR was presented. In order to examine the photo-excited species in more detail, photoinduced absorption and LESR measurements on samples of the methyl derivative of polythiophene (P3MT) at various excitation photon energies were performed. Samples and assistance for this project were received from Professor Eitan Ehrenfreund and Jorge Poplawski (Technion).

The upper trace in Figure 5.4 shows the absorption derivative of a dark ESR spectrum of P3MT taken at \( \simeq 30 \) K. The lower trace shows the absorption derivative of the LESR, defined as LESR=ESR(light)−ESR(dark), at a photon excitation energy \( \hbar \omega_L = 2.008 \) eV. It is seen that: (a) the LESR is positive; i.e. the number of spins is increased upon illumination; (b) the LESR line is shifted towards higher fields- i.e. \( \Delta g < 0 \); and (c) the LESR has a narrower linewidth. Experiments done at different temperatures revealed that whereas the dark ESR indicates a nearly Curie-like behavior, the LESR signal has a stronger temperature dependence and is not observed above 170 K. This suggests that the LESR and dark ESR have different origins.

The upper trace of Figure 5.5 shows the LESR integrated intensity (which is proportional to the number of photo-induced spins) as a function of \( \hbar \omega_L \). It features a sharp peak at 2.05 eV, superimposed on a broad background with a maximum at \( \simeq 1.8 \) eV. The lower trace shows the derivative peak to peak linewidth, \( \Delta H_{pp} \), as a function of \( \hbar \omega_L \). As \( \hbar \omega_L \) is increased, \( \Delta H_{pp} \) decreases from 8.5 G at 1.2 eV to a minimum of 5.7 G at \( \simeq 2.0 \) eV, then slightly increases to 6.1 G above 2.1 eV. The LESR \( g \) value also depends upon \( \hbar \omega_L \). Figure 5.6 shows the time response of the
Figure 5.5. The integrated intensity (upper trace) and the linewidth (lower trace) of the LESR of P3MT as a function of the exciting photon energy.
Figure 5.6. The time response of the LESR signal at \( \approx 30 \) K taken by signal averaging for \( \approx 10 \) min.
Figure 5.7. The LESR signal of P3MT as a function of laser power at \( \approx 30K \). The solid curve is a fit of the data to the function \( n=0.26P^{0.6} \).
LESR signal as the pump light is chopped at a magnetic field which corresponds to the peak of the LESR signal. The figure shows that the time dynamics are slightly longer ($\approx 0.5\text{ms}$) than the response time of the apparatus ($0.2\text{ ms}$ in this case). This makes it difficult to analyze the growth and decay of the signal. Figure 5.7 shows the laser intensity dependence of the LESR signal at an energy of 2.74 eV. As can be seen the power dependence is sublinear at low powers following the power law

$$I(P) = 0.26P^{0.8}.$$  \hspace{1cm} 5.1

At higher powers, the dependence falls off and turns over such that there is a decrease in signal with illumination. This is attributed to sample heating and was expected. A similar laser power dependence of $P^{0.8}$ was observed in the photoinduced absorption experiments. This type of laser power dependence is consistent with a bimolecular decay for which one expects a $P^{0.5}$ type of behavior.

The photoinduced absorption spectrum of P3MT is shown in Figure 5.8. It features two broad asymmetric electronic bands peaked at 0.39 eV (LE band) and 1.28 eV (HE band), followed by a shoulder around 1.6–1.8 eV, and a set of photoinduced IRAV lines below 0.2 eV. Comparing the integrated photoinduced absorption to that of the doping induced absorption, found by subtracting the absorption of a 2% doped sample from an undoped sample, we estimate the photogenerated carrier density to be $\approx 2.0 - 5.5 \times 10^{-5}$ charges/ring. Data taken by the Faraday balance technique show that there are $1 \times 10^{-4}$ spins/ring in P3MT. This gives the maxima number of spins produced in figure 5.2 to be $\approx 5.5 \times 10^{-6}$ spins/ring. From this data we conclude that the number of photo-induced charges, calculated from the photoinduced absorption spectrum, is a minimum of
Figure 5.8. The photoinduced absorption spectrum of P3MT at 80K, excited at $\hbar \omega_L = 2.6$ eV. The low energy peak (LE) 0.4 eV, the high energy peak (HE) 1.3 eV, and the infrared active vibrations (IRAV) are shown.
Figure 5.9. The excitation spectra of the IRAV and HE bands of the photoinduced absorption (lower traces) of P3MT. The excitation spectrum of P3MT of the LESR is shown again here for comparison.
10 times higher than the photo-generated spin density estimated from the LESR experiments.

The excitation spectra of the HE and IRAV bands are shown in Figure 5.9. Both spectra feature a sharp peak around $\hbar \omega_L = 2.10$ eV, a slightly higher value than the peak in the LESR excitation spectrum.

The variations in the LESR intensity, linewidth, and g-value with $\hbar \omega_L$ suggest that there are at least two types of photo-generated spin species. The first type, type I, are those spins that give rise to the sharp peak at 2.05 eV. The second type, type II, are responsible for the broad band with maximum at $\simeq 1.8$ eV in the excitation spectrum. These two type of spins have ESR lines with different g-values and linewidths. Since no LESR signal has been seen at approximately half field, it is not likely that the observed spins are due to triplet excitons (or polaron-excitons) and therefore it is concluded that this spin species is polaronic. The peak at $E_p \simeq 2.05$ eV, may indicate the polaron level.

The most striking result of the simultaneous photoinduced absorption and LESR experiments is that both show a sharp peak at $\simeq E_p$ in their excitation spectra. This may be taken as evidence that the initial photo-generated defects are identical for the two experiments. It does not necessarily mean that the long lived photoinduced defects measured by our steady state experiments are identical. In fact, since the defect density measured by the photoinduced absorption is approximately an order of magnitude larger than that measured by LESR, the photoinduced absorption should originate mainly from other charged defects. These charged defects are most likely bipolarons, as originally suggested for PT and P3MT.

A possible scenario that emerges from this discussion is that the exciting photon creates an electron–hole pair which rapidly decays into a pair of negative and positive polarons;
Figure 5.10. A model of the relaxation processes of photo-excited defect states to produced polarons and bipolarons in P3MT. (From Reference 5.6)
\[ e - h \rightarrow P^+ + P^- \]

Most of these polarons quickly recombine except for those left alone on different chains. These remnant long-lived polarons may eventually form bipolarons with lower total energy than the separate polarons, e.g.:

\[ P^+ + P^+ \rightarrow BP^{++} \]

In this way both the steady state LESR (a single polaron on a chain) and the photoinduced absorption (bipolarons) can be explained: The two different photoexcited defects have the same excitation spectrum since they originate from the same species.

This model is consistent with the proposal of Kaneto et al.\textsuperscript{5,6} on the relaxation processes of the photo-excited state to the ground state of polythiophene, shown in Figure 5.10. In this scheme, photo-generated free electrons and holes produce polarons which can either recombine as \( P^+ + P^- \) or combine as \( P^\pm + P^\pm \) creating \( BP^{\pm} \) which can then decay to the ground state. Our studies have shown conclusively that the branching ratio for this process is a maximum of \( 1 \times 10^{-1} \) polarons for every bipolaron.
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APPENDIX I

Aluminum Sample Holder Susceptibility

The magnetic susceptibility of the aluminum foils used to construct sample holders was measured independently at Xerox and at Ohio States. Foils of thickness 12.5 \( \mu \text{m} \) and purity of 99.99\% were obtained from Reactor Experiments, Inc., 963 Terminal Way, San Carlos, CA 94070. A polynomial function of the form:

\[
\chi(T) = \sum_{n=0}^{4} a_n T^n
\]

was used to fit the temperature dependence of the aluminum foils susceptibility. Also included in this fit is the susceptibility of the tungsten hangdown wire. The two terms were compared by measuring several different masses of aluminum foil but only one tungsten wire. The value of the susceptibility of the tungsten wire was found to be \( 5.0 \times 10^{-9} \text{ emu} \). The best fit values of the coefficients were found from a least-squares routine to be

\[
a_0 = 7.261 \times 10^{-7} \text{ emu} - \text{ gm}^{-1},
\]

\[
a_1 = -5.679 \times 10^{-10} \text{ emu} - \text{ gm}^{-1} \text{ K}^{-1},
\]

\[
a_2 = 2.201 \times 10^{-12} \text{ emu} - \text{ gm}^{-1} \text{ K}^{-2},
\]
\[ a_3 = -1.026 \times 10^{-14} \text{emu} - gm^{-1}K^{-3}, \]

\[ a_4 = 1.582 \times 10^{-17} \text{emu} - gm^{-1}K^{-4}, \]

The polynomial fit was used to correct the data taken on the polyaniline samples for the sample holder contribution.