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PHOTOPHYSICAL STUDIES OF
RING CONTAINING CONJUGATED POLYMERS

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy
in the Graduate School of The Ohio State University

By

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*******
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1995

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To My Parents: Shu-Man Huang and Teng-Chih Lin (1933-1993)
I would like to thank my advisors, Professors Arthur Epstein and Terry Gustafson, for their advice and guidance during my stay at OSU. I appreciate the assistance in the research from Dr. Daniel Morris, Dr. James Leonard and J. J. Lih. Special thanks go to James Blatchford and the other ‘LED subgroup’ members, Scott Jessen, Yun-Zhang Wang and Darren Gebler for their joint adventures in the studies of conjugated polymer-LEDs and the related photophysics. I would like to mention other present and former colleagues of the Epstein group for their friendship and encouragement, Randolph Kohlman, William Brinckerhoff, Stephen Long, X. Wei, Drs. Gang Du, Ping Zhou, and Shashi Jasty. I am also indebted to several former colleagues of the Gustafson group, Lisa Huston, Drs. Koichi Iwata, William Weaver, and Ronda Benson, for their support and collaboration. Finally, samples provided by Dr. H. L. Wang and Gary Min from the research group of Dr. Alan MacDiarmid of the University of Pennsylvania are invaluable to this work.
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PUBLICATIONS

L. -B. Lin, Y. P. Lee and J. F. Ogilvie, “Linestrengths of the band a'\Delta (v'=0)-\Sigma^3

K. Kim, L. -B. Lin, J. M. Ginder, T. L. Gustafson, and A. J. Epstein, “Luminescence and

G. MacDiarmid, “Long Lived Neutral Solitons in Pernigraniline Base”, Molecular
CrystalsLiquid Crystals 256, 399-405 (1994).

**FIELDS OF STUDY**

Major Field: Chemical Physics

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Studies in Ultrafast Spectroscopy. Professor Terry L. Gustafson
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<td>ADA</td>
<td>Ammonium Dihydrogen Arsenate (NH₄H₂AsO₄)</td>
</tr>
<tr>
<td>A/D</td>
<td>Analog-to-Digital Convertor</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>Hydrogenated amorphous Silicon</td>
</tr>
<tr>
<td>BBO</td>
<td>Beta-Barium Borate (b-Ba₂O₃)</td>
</tr>
<tr>
<td>BP</td>
<td>Bipolaron</td>
</tr>
<tr>
<td>BRF</td>
<td>Birefringent Filter</td>
</tr>
<tr>
<td>BS</td>
<td>Beam Splitter</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
</tr>
<tr>
<td>CD</td>
<td>Cavity Dumping</td>
</tr>
<tr>
<td>CFD</td>
<td>Constant Fraction Discriminator</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>DCM</td>
<td>4-(Dicyanomethylene)-2-Methyl-6-(p-Dimethylaminostyryl)-4-H-Pyran</td>
</tr>
<tr>
<td>DQOCI</td>
<td>1-Ethyl-4-[3-(3-Ethyl-2-(3H)Benzoazolylidene)-1-Propenyl]-Quinolinium Iodide</td>
</tr>
<tr>
<td>DODCI</td>
<td>3,3'-Diethyloxadicarbocyanine Iodide</td>
</tr>
<tr>
<td>DPS</td>
<td>trans-4,4'-Diphenylstilbene</td>
</tr>
<tr>
<td>DTDCI</td>
<td>3,3'-Diethylthiadicarbocyanine Iodide</td>
</tr>
<tr>
<td>EB</td>
<td>Emeraldine Base</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>FCB</td>
<td>Fesser-Campbell-Bishop Model</td>
</tr>
<tr>
<td>FE</td>
<td>Free Exciton</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
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<td>GS</td>
<td>Ground State</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>HWP</td>
<td>Half Wave Plate</td>
</tr>
<tr>
<td>ic</td>
<td>Internal Conversion</td>
</tr>
<tr>
<td>isc</td>
<td>Intersystem Crossing</td>
</tr>
<tr>
<td>ITO</td>
<td>Indiumtitaniumoxide</td>
</tr>
<tr>
<td>KDP</td>
<td>Potassium (K) Dihydrogenphosphate (KH$_2$PO$_4$)</td>
</tr>
<tr>
<td>KTP</td>
<td>Potassium (K) Titanyl Phosphate (KtiOPO$_4$)</td>
</tr>
<tr>
<td>LEB</td>
<td>Leucoemeraldine Base</td>
</tr>
<tr>
<td>LED</td>
<td>Light-Emitting-Diode</td>
</tr>
<tr>
<td>LIA</td>
<td>Lock-in Amplifier</td>
</tr>
<tr>
<td>MCP-PMT</td>
<td>Multichannelplate Photonmultiplier</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>ML</td>
<td>Mode Locking</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>OD</td>
<td>Optical Density</td>
</tr>
<tr>
<td>P'/P</td>
<td>Polaron (positive/negative)</td>
</tr>
<tr>
<td>PA</td>
<td>Polyacetylene (CH)$_x$</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PD</td>
<td>Photodiode</td>
</tr>
<tr>
<td>PIA</td>
<td>Photoinduced Absorption</td>
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<tr>
<td>PIB</td>
<td>Photoinduced Bleaching</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>PLE</td>
<td>Photoluminescence Excitation Spectroscopy</td>
</tr>
<tr>
<td>PNB</td>
<td>Perigraniline Base</td>
</tr>
<tr>
<td>PPP</td>
<td>Poly($p$-phenylene)</td>
</tr>
<tr>
<td>PPy</td>
<td>Poly($p$-pyridine) or Polypyrrole</td>
</tr>
<tr>
<td>PPyV</td>
<td>Poly($p$-pyridylvinylene)</td>
</tr>
<tr>
<td>PR</td>
<td>Prism</td>
</tr>
<tr>
<td>PT</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>PZT</td>
<td>Piezoelectric</td>
</tr>
<tr>
<td>R6G</td>
<td>Rhodamine 6G</td>
</tr>
<tr>
<td>SA</td>
<td>Saturable Absorber</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generator</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal to Noise</td>
</tr>
<tr>
<td>SPDL</td>
<td>Synchronously Pumping Dye Laser</td>
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<tr>
<td>SSH</td>
<td>Su-Schrieffer-Heeger Model</td>
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<tr>
<td>Stilbene 420</td>
<td>trans-4,4'-Di(2-Sulfostyryl)biphenyl</td>
</tr>
<tr>
<td>TAC</td>
<td>Time-to-Amplitude Convertor</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time-Correlated-Single-Photon-Counting</td>
</tr>
<tr>
<td>TE</td>
<td>Triplet Exciton</td>
</tr>
<tr>
<td>THG</td>
<td>Third Harmonic Generator</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
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<tr>
<td>YAG</td>
<td>Yttrium-Aluminum-Garnet</td>
</tr>
<tr>
<td>YLF</td>
<td>Yttrium-Lithium-Fluoride</td>
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CHAPTER I

INTRODUCTION

Polymers are best known for their insulator properties. In fact, the insulating properties of polymers are a significant advantage for many applications pertaining to plastics. It is a general concept that plastics and electrical conductivity are mutually excluded. Conjugated polymers stand for a class of polymers with bond alternations (mostly single and double bonds) in their backbones. The conjugation leads to a lower band gap, which makes the polymers more feasible for electrical, electronic and electro-optical applications [1,2]. One of the fascinating properties of conjugated polymers was their ability to conduct charges after being chemically doped or photoexcited. Conducting polymers have now been studied for nearly two decades since the report of the achievement of a highly conducting "metallic" state upon doping of polyacetylene, \((\text{CH})_x\) (see Fig. 1a), with acceptors such as iodine and \(\text{AsF}_5\) and donors such as sodium [3]. The doping resulted in the increase of conductivity by a factor of \(10^7\) to 100 S/cm, transforming the semiconducting polyacetylene to a metallic state. Research in the field of conducting polymers has increased several fold for the past two decades. An important advantage of polymers lies in their structural flexibility both at the molecular and bulk levels. By chemical modification and physical processing one can control the conformation of a given polymer. These approaches provide exciting opportunities to impart multifunctional characteristics to a polymer in that the same polymeric material can perform more than one function.

Fig. 1 gives the basic units of some important conjugated polymers. Trans-polyacetylene is the prototypical and the most studied polymer. Polythiophene and polypyrrole represent a class of heteroatom polymers in which the heteroatoms do not participate significantly in the \(\pi\)-conjugation. Poly(p-phenyl) (PPP) is the simplest phenyl
The basic units of some important conjugated polymers. Their abbreviations are listed in the List of Abbreviations, pages x-xii. In (a), $a$ is the equilibrium spacing along the $x$ coordinates between the neighboring CH groups in the undimerized structure, $u_n$ is the dimerization coordinate for the displacement of the $n$th CH group along the molecular-symmetry axis ($x$), $u_0$ is the displacement of a perfectly dimerized structure.
ring containing polymer, and is considered to have a rigid linear structure [4]. Since the initiative of incorporating conjugated polymers into light-emitting-diode devices (LED) in the late 1980s [5], studies of the class of polymers like poly(p-phenylenevinylene) (PPV) have interested both science and engineering fields. In this work, I studied two groups of ring-containing polymers: aniline-based and pyridine-based polymers (see Fig. 1f-h). Their fundamental photophysical properties are discussed later in this chapter and a more thorough discussion is presented in chapters 3 and 4.

SSH Model

The SSH model was developed by Su, Schrieffer and Heeger in the late 1970's [6] to describe the ground and low-lying excited states of trans-polyacetylene (see Fig. 1a for the basic units). Though using simple Hückel type Hamiltonian without considering electron-electron interactions, the SSH model has become the most widely used theoretical model of π-conjugated polymers [7]. The principle physical properties of the SSH model are summarized in this section. The model treats the σ bonds implicitly as (lattice) potential energy, and the electron-phonon interaction for the π-electrons is treated quantum mechanically. The SSH Hamiltonian is given by the following:

\[ H_{SSH} = H_\pi + H_{\pi-ph} + H_{ph} \]  

(1.1)

where

\[ H_\pi = -t_0 \sum_{n,s} (c_{n+1,s}^* c_{n,s} + c_{n,s}^* c_{n+1,s}) \]  

(1.2)

describes the hopping of π(p\textsubscript{z}) electrons along the chain without spin flip. Here, \( t_0 \) is the adiabatic transfer integral between neighboring π electrons and \( c_{n,s}^* \) (\( c_{n,s} \)) is the π electron creation (annihilation) operator at site \( n \) with spin \( s \). The π-electron-phonon interaction is given by
\[ H_{\text{\text{-}ph}} = \alpha \sum_{n,s} (u_{n+1} - u_n)(c_{n+1,s}c_{n,s} + c_{n,s}^{\dagger}c_{n+1,s}^{\dagger}) \]  

(1.3)

where \( u_n \) is the dimerization coordinate for displacement of the \( n \)th CH group along the \( x \) axis (see Fig. 1a) and \( \alpha \) is the electron-phonon coupling constant. In eq. 1.3, the terms linear in \( u_n \) dominate higher-order terms for the weak-coupling systems, i.e., the mean displacement \( u_n \) in the broken-symmetry phase is \( \sim 0.03 \text{ Å} \) compared to the lattice spacing, \( a \), of order 1.22 Å. Finally, the phonon Hamiltonian is taken to be

\[ H_{\text{ph}} = \sum \frac{p_n^2}{2M} + \frac{K}{2} \sum (u_{n+1} - u_n)^2 \]  

(1.4)

where \( M \) is the mass of the (CH) group, \( p_n \) is the momentum conjugate to \( u_n \), and \( K \) is the spring constant for the \( \sigma \) energy when expanded to second-order about the equilibrium undimerized systems. The Peierls theorem states that such a quasi-1D metal will tend to undergo a structural distortion \([8]\). The CH group tends to dimerize so that the Brillouin zone reduces to half of the original size (the size of the unit cell becomes \( 2a \)) and therefore the valence band becomes completely filled. The uniform dimerization is forcing the atoms to have fixed displacements \( u_n = (-1)^n u_0 \) away from undimerized case, i.e., uniform bond length changes to bond alternating between a single bond 'like' and a double bond 'like'. Consequently, dimerized polyacetylene is a semiconductor with \( E_g = 2\Delta_0 \sim 1.4 \text{ eV} \) \([9]\), where \( \Delta_0 = 4\alpha u_0 \), \( \alpha = 4.1 \text{ eV/Å}, K = 21 \text{ eV/Å}^2 \), and \( t_0 = 2.5 \text{ eV} \) are adopted as parameters for trans-(CH)\(_x\). The bond alternation leads to two-fold degenerate ground state depending on the order of the bond alternation. It is useful to define an order parameter \( \Psi_n = (-1)^n u_n \). The two-fold ground state is then defined by \( \Psi_{n0} = u_0, \) A phase and \( \Psi_{n0} = -u_0 \), B phase (See Fig. 1a).

The two-fold degenerate ground state of trans-(CH)\(_x\) can support an excitation that corresponds to a soliton. If phase A is allowed to change to phase B, a soliton is formed in a trans-(CH)\(_x\) chain. For a long chain, a soliton (antisoliton) corresponds to a phonon field configuration that approaches the B phase as \( N \) approaches negative infinity, and approaches the A phase as \( N \) approaches infinity. There is a preferred width that minimizes the total
energy. Numerical calculations show that the formation energy is \( E_s \sim 0.63A = 0.42 \) eV for a width \( l \sim 7 \). The presence of the strong electron-phonon coupling in polyacetylene implies that changes in the electronic structure will accompany the lattice distortion that occurs when a solitonic defect forms. Fig. 2 schematically displays some of the possible structural defects (solitons, polarons and bipolarons) in \( \text{trans-}(\text{CH})_x \) and other phenyl-ring containing polymers (poly(p-phenylene) and polyaniline). Conventional chemical terms, such as free radical and radical cation that correlate to terms in condensed-matter physics, also are exhibited in Fig. 2. In the view of quantum chemistry, a soliton excitation is a non-bonding state formed in the middle of the energy between bonding and anti-bonding states (see Fig. 3, 4) \([7,10]\). Note that, the soliton has reverse spin-charge relations from conventional charge defects. Charged solitons (positive and negative solitons) are spinless, while positive and negative polarons have spin \( \frac{1}{2} \). Neutral solitons have spin \( \frac{1}{2} \), while negative and positive bipolarons are spinless (see Fig. 2-4 for details).

**FBC Model**

Fesser, Bishop and Campbell presented a theoretical calculation, within a continuum electron-phonon-coupled model, of the optical absorption due to polarons and bipolarons in \( \text{(CH)}_x \) \([11]\) (hereafter this model is referred as FBC model). The FBC model approaches the conventional molecular-crystal model pioneered by Holstein \([12]\) in the weakly bound limit \([13]\). Conjugated polymers can be classified into degenerate or nondegenerate types. In degenerate polymers such as \( \text{trans-}(\text{CH})_x \) and pernigraniline, kink solitons can be induced by photoexcitations or chemical doping for \( \text{trans-}(\text{CH})_x \). The resulting soliton energy level is formed at midgap and has equal contributions from states in valence and conduction bands. Thus, a midgap peak is expected in the optical absorption (see Fig. 4). Polarons and bipolarons are more generic than kink solitons. Owing to charge conjugation symmetry of \( \text{(CH)}_x \), a polaron (bipolaron) has two localized energy levels that appear at \( \pm \omega_0 \) \((\pm \omega'_0)\) symmetrically with respect to the midgap (see Fig. 5). A confinement parameter \( \gamma \) regarding to the degree of nondegeneracy is defined as following:
Fig. 2. Schematic illustration of soliton, polaron and bipolaron defects in trans-polyacetylene and other ring-containing polymers.

Fig. 3. Formation of an soliton-antisoliton pair after an interband photoexcitation. (Adapted from [7])
Fig. 4. The optical absorption due to soliton excitations and the spin-charge relationship of solitons. (Adapted from [7,10])

Fig. 5. The optical transitions due to polaron and bipolaron defects. (a) Positive polaron. (b) Negative polaron. (c) Positive bipolaron. (d) Negative bipolaron. (Adapted from [14])
\[ \gamma = \left( \frac{\omega_0}{\Delta_0} \right) \left\{ 1 - \left( \frac{\omega_0}{\Delta_0} \right)^2 \right\}^{-\frac{1}{2}} \left\{ \sin^{-1}\left( \frac{\omega_0}{\Delta_0} - \frac{\pi}{4} \right) \right\} \]  

(1.5)

where \( \Delta_0 \) is the gap parameter; \( \gamma = 0 \) for \((\text{CH})_x\) and \( \gamma > 0 \) for nondegenerate polymers. The positions of polaron and bipolaron levels depend on the confinement parameter and the number of electrons occupying the \( \pi \omega_0 \) levels. Therefore, polarons (bipolarons) are expected to have three (two) intraband transitions, \( \omega_1, \omega_2 \) and \( \omega_3 \) \((\omega_1 \) and \( \omega_3 \)). Furukawa has pointed out that these three (two) transitions do not have equal oscillator strengths [14].

According to the FBC model, the absorption coefficient, \( \alpha(\omega) \), of each intraband transition is a function of \( \omega_0/\Delta_0 \). For a polaron with \( \omega_0/\Delta_0 > 0.2 \), \( \alpha(\omega_1) \) and \( \alpha(\omega_2) \) are an order of magnitude greater than \( \alpha(\omega_3) \). For a bipolaron, the \( \omega_1 \) transition is dominate for large \( \omega_0/\Delta_0 \) values, while the \( \omega_3 \) transition becomes strong only at small \( \omega_0/\Delta_0 \) values. Recent calculations by Furukawa [14] suggest that only two absorption peaks are observable for polarons, and one absorption peak observable for bipolarons. For degenerate ground state polymers such as \textit{trans}-\((\text{CH})_x\) and xerogranitone base, bipolarons are not stable-splitting into two solitons.

Another consideration of the oscillator strengths comes from the symmetry argument. The bond-alternation nature of conjugated polymers could lead to a \( g \) and \( u \) symmetry alternation in the ordering of the electronic states. This is especially true for linear polyenes, and in fact there were numerous debates over the state ordering of polyenes even before computers were accessible to scientists [15]. The deformation of the lattice by charge defects (polarons and bipolarons) will certainly destroy some global symmetries in the electronic structure. Nonetheless, some local symmetries may still preserve after the formation of polarons (bipolarons). By looking at the ground state and the \( \pi \omega_0 \) levels, assuming the \( g \) and \( u \) symmetry alternation does exist in these states, we can see that the \( \omega_1 \) and the \( \omega_2 \) transitions are symmetry-allowed, whereas the \( \omega_3 \) transition is forbidden in symmetry (see Fig. 6). Therefore, a polaron has two strong absorption bands \((\omega_1 \) and \( \omega_2 \)) and a bipolaron has one strong absorption band \((\omega_1 \).
Fig. 6. A possible symmetry alternation in the state ordering among the ground state and the polaron (bipolaron) states. $\omega_1$ and $\omega_2$ are symmetry allowed transitions, $\omega_3$ is a symmetry forbidden transition.

Polyaniline

Polyaniline is a generic name for a class of polymers with several different oxidation states. The basic repeat unit moieties of polyaniline are shown in Fig. If. The polymer builds up from repeat unit of 1A is the fully reduced leucoemeraldine base (LEB) form, the combination of one 1A and one 2A unit comprise the half oxidized emeraldine base (EB) form, fully oxidized pernigraniline base (PNB) form is consisted of the repeat unit 2A only.

Polyaniline differs from earlier studied polymers like polyacetylene and polythiophene in a number of important aspects: first, both nitrogen atoms and benzene rings are incorporated in the polymer backbone. By contrast, polythiophene and polypyrrole essentially have simple carbon backbones, since their sulfur or hydrogen heteroatoms play a small role in $\pi$ band formation. Thus, polyaniline is an example of a generalized A-B polymer, i.e., it is built from dissimilar units. Second, the filling fraction of the highest $\pi$ band of the undoped insulating forms of polyaniline can be altered by reducing or oxidizing the polymer. In LEB the filling fraction is 1; in EB the filling fraction is 3/4 and in fully oxidized PNB it is equal to 1/2, as in trans-polyacetylene. Third, because the nitrogen heteroatoms are in the conjugation pathway, polyaniline is not a charge conjugation symmetric system. That is the valence and conduction bands (or equivalently, the highest
occupied and lowest unoccupied molecular orbitals) are very asymmetric: the valence band is derived primarily from the benzene π orbitals, which have substantial overlap with neighboring nitrogen heteroatoms and so form a wide band; the conduction band is formed from the benzene π* molecular orbitals, which does not overlap substantially with the neighboring nitrogen sites and thus do not form as wide a band.

Polyaniline and other ring-containing polymers form a unique class of polymers that, in addition to bond length distortion, these polymers possess ring torsional degrees of freedom. Ginder and Epstein have initiated in incorporating a steric potential function in the treatment of polyaniline [16]. They wrote the Hamiltonian as a sum of electronic and steric interactions between adjacent rings: \( H = H_{el} + V_{\text{steric}} \). The electronic part of the Hamiltonian includes terms contributed from the torsional angles between adjacent rings. The transfer integral \( t_{2l+1} \) between the \( l \)th nitrogen \( p_z \) and the \( j \)th molecular orbital of the \( l \)th benzene is represented by \( t_{2l+1} = t_{CN} \times \cos^{2} \phi_{2l+1} \times c'_{2l+1}^{j} \), where \( t_{CN} \) is the carbon hydrogen resonance integral, \( \cos^{2} \phi_{2l+1} \) is the cosine of the torsional angle between the N and ring \( p_z \) electron lobes, and the \( c'_{2l+1}^{j} \) is the coefficient of the \( j \)th molecular orbital at the para carbon atom neighboring the nitrogen. The steric potential is approximated by

\[
V(\psi_{2l+1},\psi_{2l+1}) = -\frac{V_{2,0}}{2}(\sin^{2}\psi_{2l+1} + \sin^{2}\psi_{2l+1})
+\frac{V_{4,0}}{2}(\sin^{4}\psi_{2l+1} + \sin^{4}\psi_{2l+1})
+V_{1,1}(\sin\psi_{2l+1} - \sin\psi_{2l+1})^{2}
\]  

(1.6)

Fig. 7 illustrates the role of the ring-torsion angle order parameters in the ground state and a hole polaron state of LEB. This model demonstrates the importance of the ring rotational order parameters in polyanilines. Charged defects, particularly hole polarons, in polyaniline and other phenyl-ring-containing polymers are associated with localized distortions of the ground state ring torsional angles toward a planar conformation. Readers are referred to literature for other theoretical models regarding polyaniline [17-20].
Summary of cw and Photoexcitation Spectroscopy of Polyaniline

Charge conjugation symmetry or near charge conjugation symmetry is common to polymers such as polyacetylene, polythiophene and polypyrrole. The polyanilines differ substantially from these polymers. Many of the differences arise from the alternating ring-heteroatom backbone structure and from the wide range of forms that polyaniline can have, depending on the number of electrons and protons on the polymer backbone. The fully reduced LEB is an insulator with a large energy gap, $E_g \sim 3.6$ eV. The band gap originates predominately from the difference in energy between the bonding and antibonding molecular orbitals of benzene involved in the overlap of molecular orbitals of neighboring phenyl rings and nitrogen atoms [21]. The EB form of polyaniline is also an insulator with a large extrinsic gap ($E_g \sim 3.6$ eV), similar to that of LEB and an exciton transition centered
at 2 eV. In contrast to LEB and EB, the fully oxidized PNB is a degenerate polymer, with a Peierls gap of 2.3 eV (See Fig. 8).

The results of photoinduced absorption (PIA) spectroscopy studies of three different oxidation states of polyaniline are summarized below. The near-steady-state PIA spectrum of EB is shown in Fig. 9 for $E_{\text{pump}} = 2.54$ eV [22]. The spectrum shows photoinduced bleaching (PIB) peaked at 1.9 and 3.6 eV, and photoinduced absorption (PIA) peaked at 0.9, 1.4 and 2.9 eV. A similar study of PNB revealed PIA peaks at 1.0, 1.3, 1.5 and 3.1 eV, and PIB peaks at 2.0 eV [23]. Photoexcitation of LEB into the $\pi-\pi^*$ gap ($\sim 3.5$ eV) gave PIA peaks of 0.75, 1.4 and 2.8 eV, and a PIB peak of 1.9 eV [24]. Intensity dependence studies of the PIA peaks of all three forms of polyaniline have revealed that the recombination processes are mainly bimolecular. In contrast to the unimolecular dynamics of the exciton bleaching for EB at 2 eV, the decay of the Peierls gap bleaching for PNB is mainly bimolecular.

**Pyridine-Based Polymers: Poly(p-pyridine)**

Interest in studying poly(arylene)s has increased several fold since the advent of light emitting diode (LED) devices using PPV as the active layer [5]. Among the poly(arylene)s, PPP is constituted of the most fundamental aromatic ring and is proved to have a rigidly linear structure [4]. However, the very low solubility of PPP has made it difficult to study its structure, chemical and physical properties on a molecular scale. On the other hand, poly(p-pyridine) (PPy) (see Fig. 1g), constituted of another fundamental aromatic ring: pyridine, has received much less attention [25] as compared to PPP, although it also takes a linear structure similar to that of PPP and may contribute to understanding the physical and chemical properties of such a linear polymer. The preparation of polypyridine is by dehalogenation polycondensation of dihaloaromatic compounds [26], which is based on organonickel chemistry. PPy prepared by this method is soluble in some organic and inorganic solvents. PPy is also considered to have a large fluorescence quantum yield, a preliminary result by the author has shown that the quantum yield exceeds 60% for PPy in
Fig. 8. Absorption spectra of the three different oxidation states of polyaniline. All samples are powders in substrates of KBr. LEB data taken by R. S. Kohlman. PNB data taken by K.A. Coplin.
Fig. 9. Near-steady state photoinduced absorption spectrum of EB in a substrate of KBr. The excitation energies was 2.54 eV, a laser intensity of 0.8 W/cm², a chopper frequency of 21 Hz, and a temperature of 15 K. (after Roe et al. [22]) The ground state absorption spectrum and the basic molecular unit of EB are also shown.
HCOOH (see Chapter 4), which makes the polymer a possible candidate for acting as the luminescent layer in LED devices.

Polarization studies of PPy and poly(2,2'-bipyridine-5,5'-diyl) (PBpy) in formic acid (HCOOH) have revealed that both polymers give a very large degree of depolarization with a $\rho_v$ (ratio of the horizontal and the vertical components of the scattered light) value of 0.33 [26], which is very close to the theoretical value 1/3 of a rodlike molecule [27]. The results strongly suggest that PPy takes a rodlike linear structure, and therefore it may have an extended $\pi$ conjugation system with mobile electrons along the polymer chain. A large refractive index of $n_D = 2.2$ was demonstrated in films of PPy [26]. In contrast to PPy and PBpy, PRPy's (PPy derivatives with side group R) with larger molecular weights give $\rho_v$ values of almost 0, indicating that these polymers take essentially a random-coil like structure as a whole molecule probably due to steric repulsion between the alkyl substituents, twisting out of the $\pi$–conjugation plane, and/or bowing of the long molecular chain. PPy was shown to align in stretched films as well as on substrates [26]. Polarization study of stretched films of PPy on a poly(vinyl alcohol) (PVA) substrate reveals a strong dichroic ratio, $R \sim 40$ ($R = A_1/A_\perp$, where $A_1$ and $A_\perp$ are the parallel and perpendicular absorbance to the preferential orientation of the films, respectively) [26]. A more thorough discussion of photophysical properties of PPy is presented in Chapter 4.

**Nature of Photoexcitations in Conjugated Polymers**

The molecular and one-dimensional semiconductor approaches in treating electronic excitations of conjugated polymers are briefly discussed in this section. Owing to weak interchain interactions and extended delocalization of the electronic structure, the dynamics of photoexcited states in conjugated polymers is often treated as a one-electron semiconductor band picture with strong electron-phonon interaction [7]. An alternative view is by considering the polymers as composed of different lengths of conjugated segments separated by topological defects [28]. The distribution of the conjugated length establishes a manifold of localized chromophores that control absorption, fluorescence as
well as energy and charge transport. According to the recent theoretical work by Mukamel et al., the character of the elementary excitations of conjugated polyenes is intermediate between that of the molecular (Frenkel) and the semiconductor (Wannier) excitons [29].

Molecular solids are defined as solids formed from inert gas atoms or from molecules (containing saturated and/or unsaturated bonds). A large portion of the class of molecular solids consists of organic molecules. Most organic molecular solids are held together by weak intermolecular interactions of the Lennard-Jones type (van der Waals forces). Therefore, molecular solids usually have small cohesive energies. The intermolecular coupling of organic molecular solids is generally in the order of $10^{-2}$ eV [30], which implies low melting and boiling points. In addition to weak intermolecular coupling, organic molecular solids are also characterized by their low dielectric constants ($3 \sim 4$). Consequently, the transport band for charge carriers or excitons is narrow and the mean free path is comparable to the intermolecular spacing. The importance of coulomb effects implies that the elementary optical excitations are excitons of the Frenkel type (binding energy $\sim 1$ eV) [31]. In the case of conjugated polymers, the spacing between neighboring chain controls the strength of the interchain coupling, which is in the order of 0.1 eV [7]. Recent calculations by Vogl et al. have found that in crystalline PPP, the interchain coupling leads to energy band splitting of the order of 0.5 eV [32]. However, the intrachain coupling is on the order of 1 to 10 eV for conjugated polymers [7], therefore, with weakly coupled chains and strong intrachain delocalization of electrons, large anisotropic behaviors are expected for the system. Conwell et al. have studied the effects of interchain couplings on the stability of the interchain polaron pair in PPV [33]. They predicted that an electron or hole added to a conjugated polymer chain causes the chain to distort, forming a large polaron.

Excimers play an important role in the migration of electronically excited energy in molecular solids as well as in polymers [34,35]. Excimers are a type of excited dimer, usually formed in concentrated samples from the association of an excited monomer ($A^*$) and a monomer in its ground state ($A$).
Excimers in organic molecules also are currently recognized as a kind of self-trapping exciton [36]. The formation of excimers is characterized by the presence of a broad emission (with no intrinsic absorption) at longer wavelengths than the corresponding monomer emission. The shift in the emission energy is due to the binding energy of the excimer. The typical excimer binding energies $E_b$ for molecules like benzene and pyrene are 1800 and 4000 cm$^{-1}$, respectively [35]. The radiative lifetime of an excimer is usually longer than its monomer and the formation (rise time) of the excimer is associated with the radiative lifetime of the excited monomer ($10^{-10}$-$10^{-7}$ s). Time-resolved spectroscopic techniques have been used to differentiate excimers from monomers [37-39]. Usually, in the time domain, the formation of excimer is indicative by the following features: the excimer emission appears at a later time than the monomer emission; and the time constant of the rise of the excimer emission is consistent with the decay constant of the monomer emission.

Low temperature fluorescence studies of molecular crystals such as anthracene have revealed a weak exciton-phonon coupling on the order of 1 to 10 cm$^{-1}$ [40]. The situation is quite different for polymers in which both absorption and photoluminescence spectra are broad and usually feature a large Stokes shift of several hundred meVs. In the framework of 1-D semiconductor pictures, large electron phonon interactions would be expected for a Stokes shift of that magnitude (see next section for a more thorough discussion of the electron-phonon coupling including the Huang-Rhys factor). Heeger et al. considered conjugated polymers as arrays of fully elongated infinite chains with strong electron-phonon couplings and weak inter-chain interactions [7]. Photon absorption has been treated in terms of the one-electron semiconductor band picture ignoring coulombic and electron-correlation effects. One of the evidences that support the noninteracting model comes from the absorption spectrum reflecting the von Hove singularity at the band edge [41]. The large Stokes shift of the photoluminescence is attributed to the radiative recombination of a pair of oppositely charged polarons. Another evidence in favor of the above model (as applied
to polyacetylene) comes from the coincidence of the action spectra of photoconductivity with the absorption spectrum [42].

Bassler et al. [28,43] have pointed out several exception rules to the 1D semiconductor picture, which are summarized below. (i) Polydiacetylene (PDA) is known for its crystallinity and extended conjugation, which should make PDA approaching an 1D array of infinite molecular wires, however, the exciton is the lowest transition in crystalline polydiacetylenes (PDA) [44]. (ii) The importance of electron-electron interactions is demonstrated in many theoretical and experimental studies, e.g., electron-electron correlation effects was found to be responsible for the reversal of the $2^1A_g$ and $1^1B_u$ excited state ordering in conjugated polyenes [45]. (iii) The original SSH Hamiltonian [9] does not include interchain interactions, where studies have shown that the occurrence of photoconductivity involves inter-chain effects [46,47]. From the above discussion, it seems that neither the 1D semiconductor nor the simple molecular solid picture can fully describe the nature of photoexcitations in conjugated polymers.

The presence of the disorder in non-crystalline polymers indicates that the polymer chains are electronically interrupted by defects. The defects in conjugated polymers are usually conformational (rotational) or bond-order (e.g. saturated sp$^3$) defects (see Fig. 10a). Studies of site selective fluorescence (SSF) spectroscopy of PPV and its oligomers suggested the notion that the elementary absorbers are segments of the chain with several repeat units long [48]. The distribution of the segments creates a 3D array of localized chromophores similar to chromophores in molecular systems. This random distribution is responsible for inhomogeneous broadening of the absorption bands in the polymers [48]. In this picture, absorption spectroscopy does not probe the joint density of coulombically decoupled valence and conduction band states, but the inhomogeneously broadened manifold of exciton states. It is unique that the dynamics of photoexcitations in conjugated polymers could be controlled by incoherent random walks of neutral excitations migrating among subunits of the same and/or adjacent chains [28]. Therefore, the relaxation processes
Fig. 10. Defects and radiative segments in conjugated polymers. (a) Schematic diagram of a ring-containing $\pi$-conjugated segment with one rotational (torsional angle) and two saturated defects. (b) Correlation of the absorption and emission spectra with a distribution of subunits of a hypothesized polymer chain. Sub-units are terminated at both ends by some types of defects. The inhomogeneous broadening of the radiative transitions (absorption and emission) are resulted from the distribution of the sub-units (arrows indicate different conjugated lengths of the radiative sub-units).
in conjugated polymers are a collective effect influenced by the conformation of subunits, the presence of defects and trap sites, the strength of the exciton-phonon (or electron-phonon) coupling, and the competition between radiative and non-radiative channels. The apparent Stokes shift is the consequence of this migration of neutral excitations from shorter segments to longer segments, in other words, it arises from spectral diffusion (energy transfer in this case) among the subunits of the polymer. The intrinsic 'Stokes shift' should be from the structural relaxation of an emitting segment depending on how strained or confined the segment is. Fig. 10b illustrates this distribution of conjugated subunits, the migration of neutral species, and the corresponding absorption and emission spectra in a hypothetical polymer chain.

**Radiative and Nonradiative Processes of Photoexcited States**

Besides having bands rather than discrete electronic states, extended systems differ from molecules in several important ways. The increase in the degrees of freedom in extended systems also increases the number of nonradiative channels. Therefore, without any argument from symmetry, quantum yields of radiative transitions are likely to be smaller in extended systems than simple molecules. Diffusion and trapping of charged and neutral species are important aspects of extended systems (see next section) but are rarely recognized in simple molecules. An electron, hole or exciton in a deformable lattice can be subject to competition of two opposing interactions: one for delocalization and the other for localization [49-51]. The former is characterized by $B$, the maximum energy released from extended delocalization of a localized electron (hole, or exciton) (see Fig. 11b). Within the tight binding approximation with hopping integral $t$, $B$ is equal to $|t|$ times the number of nearest neighbors, therefore, $B$ is half the bandwidth. The latter are characterized by two kinds of energy: $D$, the fluctuation of the site energy due to lattice vibrations ($D$ is also called as the mean amplitude of the Franck-Condon excitation); $E_{\text{tr}}$, the lattice relaxation energy due to the localized electron (see Fig. 11a-b). Assuming harmonic potentials with an identical spring constant for the excited and ground states and with a zero point energy $kT/2$, $D$ is related to $E_{\text{tr}}$ as $D^2 = 2E_{\text{tr}}kT$. 
Fig. 11. (a)-(b) Configuration coordinate models. (a) Localized excitation (b) Exciton. $V_f, V_g$: adiabatic potential curves. $q$: lattice coordinate. $c$: zero-point displacement. D: mean amplitude of the Franck-Condon excitation. $E_{LR}$: lattice relaxation energy. $E_a, E_e$: vertical transition energy. B: delocalization parameter. FE: free exciton. SE: self-trapped exciton. (Adapted from [49])
(c)-(d) Huang-Rhys factor $S$. (c) Relaxation energy for emission from $f$ to $g$. (b) Spectral distribution of the emission for an approximately symmetric shape. $\omega$: phonon frequency. $\Delta$: lattice displacement. $E_f, E_g$: zero-point energy of the $f$ and $g$ states, respectively. (Adapted from [52-53])
In the absence of transfer (assuming $t = 0$), the adiabatic potential $V_e(r)$ of a localized electron as a function of the displacement coordinate $r$ (lattice vibrational energy is included in the kinetic part) is approximated as the following

$$V_e(r) = E_a - cr + c^2/2 = (E_a - E_{LR}) + (r - c)^2/2; \ E_{LR} = c^2/2,$$  

(1.8)

where $E_a$ is the adiabatic vertical transition energy, $c$ is the zero-point (ZP) displacement ($c = r_{e,0} - r_{g,0}$) of the excited state from the ground state. $c$ is related to the Huang-Rhys factor $S$ by $S = \frac{1}{2}c^2/\Delta E$, in which $\Delta E$ is the ZP energy difference between the two states (see next paragraph). $E_{LR}$ is interpreted as the energy gained by the system when the lattice is distorted to an equilibrium position $r_e = c$. Notice that the Stokes shift of the radiative processes is $\sim 2 E_{LR}$. In an ideal delocalized condition (without any distortion), an excited electron would move freely in a band of a B bandwidth. Similarly, in an ideal localized condition, the electron would be stabilized at the band bottom with energy $E_a \sim B$ (a perfectly ‘free’ exciton). Note that in this case, there is no apparent Stokes shift (see Fig. 11b). From the above discussion, it seems that, for $E_{LR} > B$, the electron is subject to localization with a lattice distortion (SE), and for $E_{LR} < B$, the electron is delocalized without lattice distortion (FE).

Huang and Rhys investigated the radiative and non-radiative transitions in $F$-centers ($F$-center is an electron trapped in an anion vacancy) by taking into account the strength of the coupling between the electron and lattice [52]. The approach is in the framework of the Condon approximation: the separation of nuclear and electronic wavefunctions. The interaction matrix $<g|M|f>$ of the electric moment $M$ between the initial state $g$ and the final state $f$ is written as

$$<g|M|f> = <g_e|er|f_e> \int \chi_{g,n}(Q)\chi_{f,m}(Q) \ dQ$$  

(1.9)

where $<g_e|er|f_e>$ is the matrix element of the electronic part, $r$ is the electronic coordinates, $\chi_{g,n}$ and $\chi_{f,m}$ are the vibrational wavefunctions of the lattice at the $g$ and $f$ states, respectively, and $Q$’s are the nuclear coordinates. The transition probability $W_{gf}$ is proportional to the square of the interaction matrix.
The vibrational wavefunctions are approximated by products of simple harmonic oscillator functions of normal coordinates \( Q_s \): 

\[
\chi_n(Q) = \prod_s \chi_{n_s}(Q_s) \quad (s = 1, \ldots, N).
\]

The electron-lattice coupling is described by the displacements of these normal coordinates (lattice relaxation):

\[
\chi_{gn}(Q) = \prod_s \chi_{n_s}(Q_s - \Delta_g)^s; \quad \chi_{fm}(Q) = \prod_s \chi_{m_s}(Q_s - \Delta_f)^s
\]

where \( \Delta \)'s are the lattice displacement parameters for the state \( g \) or \( f \). Hence, the transition probability \( W_{gf} \) depends on the strength of the electron-phonon interaction:

\[
W_{gf} \propto |\chi_{gn}(Q)|^2 |\chi_{fm}(Q)|^2 \prod_s |\chi_{n_s}(Q_s)|^2 dQ_s
\]

In the absence of the lattice relaxation \( (\Delta = 0) \), \( W_{gf} \) is non-zero only if \( n = m \). But with the presence of \( \Delta_g, \Delta_f \) in the arguments, the optical transition is accompanied with multiphonon transitions, in which the band shape is a reflection of the thermal distribution and the number density of the phonons. For a single mode transition, the average value \( \sigma \) of the squared overlap integral is expressed by:

\[
\sigma = Av |\prod_s \chi_{n_s}(Q_s - \Delta_g)\chi_{n_s}(Q_s - \Delta_f)|^2
\]

So for an \( n \)-phonon transition, the probability would be proportional to \( \sigma^n \). Suppose there are \( N \) modes of the same phonon frequency, the total number of such \( n \)-phonon transitions will be \( N^n/n! \). Huang and Rhys introduced a dimensionless factor \( S \) (also known as the Huang-Rhys factor):

\[
\frac{N^n}{n!} \sigma^n = \frac{S^n}{n!}
\]

where \( S = N\sigma \) represents the sum of the squared overlap integral over all the \( N \) modes. Wagner gave a simple illustration of the configurational coordinate diagram which is reproduced in Fig. 11c [53]. The lattice relaxation energy is expressed as the Huang-Rhys factor \( S \) multiplying an average phonon energy:
\[ S \overline{\lambda} = \sum \frac{1}{2} \omega_i^2 (\Delta_i - \Delta_f)^2 \] (1.15)

Note that \( \Delta_i - \Delta_f \) is the lattice relaxation in the transition from the \( g \) state to the \( f \) state. Fig. 11d shows how the lattice relaxation energy is related to the energy difference between absorption (emission) maximum and zero-phonon line of a symmetric band.

The interplay of recombination and annihilation of excited species with defects is also unique to disordered systems. Nevertheless, as mentioned in the last section, defects and conjugation breaks are common to noncrystalline polymers, thus, their photoexcitations are often viewed from a localized picture \([43,54,55]\). Adiabatic potential energy curves and electronic transitions of a closed shell molecule in a certain coordinate are shown in Fig. 12. Electronically excited states invoke two types of radiationless transitions: internal conversion (ic), a transition between states of the same spin multiplicity; and intersystem crossing (isc), a spin forbidden transition (e.g., \( S_1 \) to \( T_1 \)). Radiative transitions are termed as fluorescence (spin allowed) and phosphorescence (spin forbidden). The lifetime of the radiative process is generally a good guideline for distinguishing fluorescence (< 10^{-8} s) from phosphorescence (> 10^{-6} s). For an excited state of a shallow potential well, the molecule can also dissociate (breaking of the chemical bond) into two or several separated species. Autoionization occurs when the molecule is excited into a quasicontinuum. The inset on the right-hand side of the Fig. 12 illustrates the commonly accepted notion of a Stokes shift (the energy difference between the maximum of absorption energy, \( \omega_1 \), and the maximum of emission energy, \( \omega_2 \)), which arises from the lattice displacement between the ground state and \( S_1 \) state.

**Ultrafast Dynamics of Conjugated Polymers**

In this section, ultrafast spectroscopic studies of conjugated polymers are briefly reviewed, in particular, PPV, polythiophene (PT), polydiacetylene (PDA) and their derivatives. PPV and derivatives have received tremendous attention lately due to their potential uses as active layers in light emitting diode (LED) devices \([5]\). The current
Fig. 12. Potential energy curves and electronic transitions of a molecule along a certain coordinate. Vertical straight lines are radiative transitions. Curly lines are radiationless transitions. Inset: illustration of the Stokes shift: $\omega_1 - \omega_2$. See text for details.
accepting view on the nature of photoexcitations in PPV is coulombically bound excitons [43]. Rothberg et al. have presented a series of studies on the photoexcited dynamics of PPV polymers [56-60]. They proposed that the majority species created by the initial photoexcitation are polaron pairs (quantum yield > 90%), which are non-radiative [56]. The (interchain) polaron pair (also called as spatial indirect excitons) is formed by an interchain photoexcitation, with a charge located on one chain and the counter change located on the neighboring chain. The wavefunctions of the positive and negative charges do not overlap with each other, therefore, the probability of the radiative decay is very low [58]. However, the distance of the charges are close enough to hold up the changes through coulombic forces (2.3 Å). These polaron pair can dissociate and diffuse to find opposite changes and form excitons. And along with the initially created (~ 10%) excitons, these excitons are responsible for the photoluminescence. Stimulated emission from these radiative excitons occurs within 200 fs after the initial photoexcitation [57]. They observed drastic increase in luminescence quantum yield going from films to dilute blends or solution of a soluble PPV derivatives [60]. The PL is quenched by the presence of carbonyl groups in PPV, which explains the nonexponential decay dynamics observed in the PL decays [59]. Vardeny et al. used picosecond transient, cw photomodulation, photoluminescence, and their excitation spectra to study PPV [61]. They determined that the onset of the conduction band was at 3.5 eV, which gave a exciton binding energy, $E_b$, of 1.1 eV in contrast to $E_b$ of ~ 0.3-0.4 eV claimed by Conwell et al. [62]. Readers are referred to other interesting results of the ultrafast spectroscopic studies on PPV and derivatives [28,63-65].

Kobayashi et al. studied relaxation dynamics of photoexcitations in polythiophene (PT) and polydiacetylene (PDA) polymers [66]. The model for the relaxation kinetics in PT and PDA was proposed to depending on free excitons and self-trapped excitons (SE). The free excitons were created by photoexcitations at the band edge, and they cross over to (SE) within ~ 200 fs. The decay kinetics of the SE were governed by potential crossing and tunneling between two potential curves of the SE and the ground state. There are a wealth of ultrafast spectroscopic studies on PT, PDA and their derivatives [66-70].
Ultrafast Interactions in (Inorganic) Semiconductor Solids

There is a many-fold increase in the applications of ultrafast optical techniques to solid-state phenomena over the past decade. However, most of the works have emphasized conventional semiconductor materials [71,72]. I briefly review some phenomena observed in the dynamics of conventional semiconductor materials, especially, exciton screening, exciton relaxation and electron-hole dynamics. These concepts may be useful to the interpretation of the dynamics of radiative and radiationless processes in conjugated polymers.

Excitons represent the lowest intrinsic electronic excited states of semiconductors. The binding energy of an exciton depends on the spacing of the charges and the dielectric constant of the lattice. Typical binding energies for excitons formed in inorganic semiconductors are on the order 1 to 100 meV, e.g., the exciton binding energy of indirect gap materials such as Si and Ge, and direct gap materials such as GaAs is 14.7, 4.1 and 4.2 meV, respectively [73]. The presence of intrinsic carriers (or impurities) in these materials would probably obscure the exciton transitions at room temperature. Only for fairly pure samples at low temperatures, can the exciton feature be distinguished at the absorption edge.

Excitons interact in various ways with other intrinsic elementary excitations, with impurities and defects of the semiconductor crystal, and of course, with other excitons. These interactions cause rapid relaxation, redistribution and recombination phenomena, which are interesting topics of ultrafast spectroscopy. The covalent forces between two excitons can lead to the formation of an excitonic molecule, or a biexciton [74]. Excitonic molecules can be produced either directly via resonant two-photon absorption, or else by collisions of two singlet excitons. Excitonic molecules were first observed in CuCl crystals owing to its simple bandstructure and large binding energy $E_{\text{hex}}$ of the complex [75]. A simple treatment of exciton is the Hartee-Fock effective Hamiltonian approach [75]. The exciton Hamiltonian can be written as
where $E_0$ is the ground state energy of the system, $H_{HF}(e)$ and $H_{HF}(h)$ are the one-particle electron ($e$) and hole ($h$) operators, obtained in the Hartree-Fock approximation, and $W(e,h)$ represents the exchange energy between the electron and the hole. A similar treatment for biexciton would be

$$H_{exc} = E_0 + H_{HF}(e_1) + H_{HF}(h_a) + H_{HF}(e_2) + H_{HF}(h_b) - \epsilon^2 \left( \frac{1}{r_{12}} - \frac{1}{r_{ab}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right) + W_{1a} + W_{1b} + W_{2a} + W_{2b}$$

where 1,2 denote electrons, a,b denote holes. The equation is in analogy with the covalent bond treatment of a hydrogen molecule.

In the tight-binding limit, an exciton can be expressed from Bloch-type wavefunctions, $\psi_k(r) = \psi_k(r) \exp(ik \cdot r)$, where $r$ is the position vector, $k$ is the wavevector, and $\psi_k(r)$ has the periodicity of the lattice, [73]. An exciton carries a polarization $P \exp(ik \cdot r)$, where $P$ is the polarization vector of the exciton. The polarization of the exciton is called longitudinal when $P \parallel k$ or transverse when $P \perp k$. In simple non-perturbed systems, the allowed optical transition from the valence band is to the transverse exciton. Therefore, the exciton splits into two branches: longitudinal and transverse. When coupling between the transverse excitons and the photons are strong, excitons and photons lost their identity and quasi-particles called ‘exciton-polariton’ are formed [76]. There have been extensive studies on the frequency-wavevector dispersion relation and the propagating properties of the exciton-polariton in inorganic materials [76].

An exciton coupling to the phonon field can result in a lattice distortion around itself. An exciton accompanied by a lattice distortion is defined as an excitonic polaron. An excitonic polaron that is mobile at weak coupling becomes immobilized or self-trapped at strong coupling [72]. The motion of a phonon-coupled exciton in a deformable lattice is
hindered by its accompanying distortion. The factors that affect the lattice distortion are the magnitude and spatial range of the carrier-phonon coupling, and the dimensionality of exciton motion [72]. For instance, if an exciton couples strongly with the surrounding lattice displacements, a short-range distortion arises leading to a small excitonic polaron. A strong exciton-phonon coupling would imply a large lattice distortion (a large Huang-Rhys factor $S$). The distortion in one dimension (1-D) is of long range (spatially extended) at weak coupling and gradually reduced in spatial extent as the coupling increases. Fig. 13 illustrates schematically the adiabatic energy dispersion curves of the valence, the conduction, the free exciton (FE), and the self-trapped exciton (SE) bands. It is important to recognize the presence of a self-trapping barrier, $E_b$, which separates the free and self-trapped excitons [50]. Generally, photoexcited states in a strong exciton-phonon coupled system can relax to the self-trapped state via two paths: direct and indirect paths. A direct path relaxes to the self-trapped state without passing through the free exciton band bottom. A transition from the bottom edge of the free exciton band (indirect) to the self-trapped exciton state can occur via three possible channels: quantum tunneling at low temperatures, thermally assisted tunneling at intermediate temperatures, and thermally activated transfer at high temperatures.

A self-trapping state can be observed through the luminescence spectra. The typical experimental technique is to excite the free exciton band in a crystal and then observe the luminescent energy. A Stokes shift of the luminescence spectrum to the excitation energy represents the existence of a self-trapping state.

Interesting changes of the excitonic properties occur when the exciton density becomes high [77]. Excitons behave as non-interacting boson-like particles only in the limit of vanishing number density. However, as the density increases, the fermion character of the basic constituents may become noticeable and lead to a variety of interesting phenomena, including nonlinear optical effects such as bleaching of the optical absorption and shifting of the band gap to a lower energy [78]. The shift in the band gap is attributed to the
Fig. 13. Adiabatic potential energy curves for strong exciton-phonon interaction system. $E_b$ is the barrier height between the free and self trapped states. Trapping can take three routes: direct, indirect and tunneling. (Adapted from [50])

renormalization of the band gap at high exciton densities [78]. Other interesting high density effects are related to the screening of the Coulomb interaction. When the exciton density exceeds a critical value, the binding between individual electron-hole pairs is screened out, and the excitonic system undergoes a transition from an electrically non-conducting phase of neutral excitons to a conducting plasma of collectively interacting electrons and holes, in analogy with the insulator-metal Mott transition [79]. The Coulomb forces between the electron and the hole can also be screened by the injection of free carriers. Excitons become unstable, if the density of free carriers exceeds the Mott density.

**Exciton Relaxation**

Exciton relaxation phenomena have been a field of active research for many years. In the earlier work photoluminescence has often been used to obtain information about
recombination and relaxation of excitons [80]. More recently, nonlinear optical techniques have been used to study the dynamics of exciton-polariton distributions [81]. An exciton-polariton is a quasi-particle formed by coupling of a photon and a dipole-active exciton. For example, one can make use of transitions from a populated exciton-polariton branch to biexciton states; this is a form of excited state spectroscopy. Masumoto and Shionoya have reported a detailed investigation of the time evolution of the exciton-polariton distribution in CuCl [81]. The photon energy of the excitation pulse was chosen to exceed the longitudinal exciton energy of CuCl, $E_L = 3.208$ eV. From the photon energy of the induced absorption, the energy and the wavevector of the exciton-polariton involved in any given excited-state transition can be unambiguously determined, because the energy wavevector relation of both the exciton-polariton and the biexciton are precisely known in CuCl [75]. They have observed the growth of the longitudinal and the transverse exciton induced absorption. The initial generated polaritons, i.e., polaritons in states directly pumped by the excitation pulse ($h\nu = 3.215$ eV), disappear quite rapidly, very nearly following the excitation pulse. The relaxed polaritons, on the other hand, follow the integration of the excitation pulses. The decay time of the exciton-polariton population was observed to increase with the thickness of the samples [81]. This observation is in agreement with the decay being dominated by radiation losses, i.e., losses due to polaritons that propagate to the boundaries of the crystals and escape as free-space photons. The characteristic time for this radiative escape is obviously proportional to the sample thickness. It is concluded that the average energy of the exciton-polariton decreases faster than their number [81]. This was also concluded from the time-resolved luminescence lifetime measurement of exciton-polariton relaxation in CdSe [82].

**Exciton Screening**

The screening of the Coulomb interaction is of great importance for the understanding of high excitation density phenomena in semiconductors. The principal changes of the spectra caused by high excitation density can be described briefly as follows.
Screening weakens the attractive forces between electrons and holes and impairs the mutual bindings. Bound, hydrogen-like states can no longer exist, and the discrete excitonic absorption peaks disappear. The exciton spectra are replaced by the broad continuum spectra of the electron-hole plasma, which is at lower energies than conduction band bottom. This shift reflects the renormalization of the band gap, which is a characteristic manifestation of the electron-hole interaction of the many-body system. Shank et al. concluded from their results that the screening of the exciton and the shift of the band edges occurs in less than 0.5 ps [83]. The changes of the spectra at later time were explained by band-filling effects due to the relaxation of the hot carrier distribution. Fehrenbach et al. studied the transient absorption of GaAs at different pair density [84]. They noticed that: (i) up to a pair density as high as \(2 \times 10^{16} \text{ cm}^{-3}\) the exciton spectrum is hardly changed at all; (ii) for higher densities progressive bleaching of the exciton absorption is observed; the peak broadens asymmetrically, and the wavelength of the maximum absorption decreases; (iii) up to the measured maximum density of about \(2 \times 10^{17} \text{ cm}^{-3}\) the energy of the 1s (the transition from the ground state to the 1s exciton state) exciton peak remains practically constant. The authors point out that for resonant excitation (photon energy resonant with transition energy between states), distinct exciton resonances persist for densities exceeding the Mott density by approximately a factor of one hundred.

**Electron-Hole Dynamics**

Electrons and holes are the basic carriers of electrical change in semiconductors. The fundamental importance of understanding the dynamics of charge carriers hardly needs to be emphasized. A wealth of useful information about carrier interactions has been obtained in the past from electrical transport measurements [85,86]. Electrical transport experiments usually give information involving averages over various individual processes. The study of the dynamics of photoexcited carriers, on the other hand, is in principle capable of providing more selective information. Optical excitation with visible light promotes electrons and holes to states with excess energies of typically several hundred meV with respect to the
ground state. There is a hierarchy of relaxation mechanisms that cause the excited electrons and holes to return to thermal equilibrium. Relaxation involves a number of different steps with rates ranging from $10^{14}$ s$^{-1}$ to about $10^9$ s$^{-1}$ [71].

The fate of the photoexcited carriers may be qualitatively described as follows [71]. The first step is the scattering of the carriers out of the primary optically coupled valence and the conduction band states. This process is believed to be dominated by very fast carrier-carrier scattering. A quasi-thermal distribution is eventually established among the electrons and the holes by carrier-carrier collisions and carrier-phonon scattering processes. At this stage the energy distributions of the electrons and the holes are given by Fermi-Dirac distributions characterized by an electron temperature $T_e$, and a hole temperature $T_h$. Usually it is assumed that the interaction between electrons and holes is sufficiently strong that the carriers possess a common temperature, $T_e = T_c = T_h$. The carrier temperature may still be substantially greater than the lattice temperature. The further evolution can then be described as cooling of the carriers resulting from coupling of the electronic system to the cold lattice. The carriers lose their energy primarily by emission of phonons. The energy loss is usually dominated by optical phonons, mainly because on the average they carry away more energy than acoustic phonons. The life of the electrons and holes is finally terminated by carrier recombination processes, which may occur even before the carriers have equilibrated with the lattice temperature. In radiative recombination an electron-hole pair is destroyed and a photon carrying away the pair energy is created. Non-radiative recombination processes may also play a role. For example, at high electron-hole density the recombination may be dominated by a non-radiative Auger process in which the recombination energy of the electron-hole pair is given to a third carrier rather than to a phonon.
CHAPTER II

EXPERIMENTAL TECHNIQUES

Overview of Ultrafast Spectroscopy

The advent of ultrafast lasers enables researchers to investigate elementary processes involved on picosecond and femtosecond time scales [63,87-98]. It has been several decades since the first ultrafast pulses were demonstrated by passive mode-locking of a ruby laser [99]. The first picosecond laser, a Nd:glass laser, was reported in 1966 [100]. Since that time we have witnessed a dramatic advancement in pulse generation technology (Fig. 14). Optical pulse durations as short as 6 fs have been produced, approaching the uncertainty principle limit in the visible spectrum [89]. The studying of ultrafast phenomena is beneficial to both the optical engineering and physical science communities as understanding of a wide range of optical phenomena and development of devices owe their existence to the development of lasers. We emphasize the importance of ultrafast spectroscopy by stating some of the elementary processes within a nanosecond time scale: electronic relaxation ($10^{-8}$-$10^{-12}$ s), molecular rotation ($10^{-9}$-$10^{-12}$ s), vibrational relaxation ($10^{-10}$-$10^{-13}$ s), vibrational dephasing ($10^{-11}$-$10^{-13}$ s), solvent relaxation ($10^{-12}$-$10^{-13}$ s) and electronic dephasing ($10^{-13}$-$10^{-14}$ s) [101]. Two concepts are necessary for a description of both electronic and vibrational relaxation in condensed phases: dephasing and population relaxation. The dephasing process is a quasi-elastic process that destroys the coherent macroscopic dipole via interactions with the environment. In this work, we studied photoexcited (photoinduced) properties of organic conjugated polymers with regard to phenomena mainly arising from population relaxation. To investigate the elementary photophysical properties of conjugated polymers, we need a variety of ultrafast laser sources, in terms of energy and power density of laser pulses, and a variety of detection
techniques. In the Gustafson group, I have been involved in the construction of two laser systems, which can provide picosecond pulses with spectral range from near-IR to UV [102,103]. Although most components in the systems are commercialized products, one still needs to understand the principles of operation behind each instrument to some extent. It is naive to assume that the whole laser system would behave like household appliances (i.e., 'just push the button'). I was fortunate to study each component by trouble shooting the system when various components broke down and through intensive reading of literature. I will give a brief description of the fundamentals of ultrafast lasers and a brief outline of the laser systems used for this study. For abbreviated terms, the readers are referred to the List of Abbreviations, pages x to xii.

**Mode Locking**

Mode locking is the most employed technique for generating ultrafast pulses [101,104]. The basic idea of mode locking is that modes inside a resonant cavity are forced to follow the direction of some impressed force either internally or externally. In short, the
modes are locked in phase (synchronized). For each transverse mode, a laser resonator usually supports a number of longitudinal modes. These modes are separated in frequency by

\[ \omega_{n+1} - \omega_n = \frac{\pi c}{L} = \omega = 2\pi v \]  

(2.1)

where \( L \) is the cavity length and \( c \) is the velocity of light. In order to generate short pulses using mode locking, the laser resonator must support a large number (\( 10^4 \) to \( 10^5 \)) of longitudinal modes. Thus, a broad emission profile is one of the basic requirements for choosing a lasing medium for ultrafast lasers. The number of allowed modes is limited by the mode spacing \( v \) and the bandwidth \( \Delta v \) over which the laser gain exceeds the loss of the

\[ \Delta t \sim \frac{1}{\Delta v} \]

Fig. 15. (a) Allowed modes in a resonant cavity of optical length \( L \). (b) The temporal output of a laser with all modes locked in the proper phase.
resonator (see Fig. 15a). The total optical electric field, \( E(t) \), at some arbitrary point in a laser cavity can be expressed as:

\[
E(t) = \sum_{-\infty}^{\infty} e^{i(\omega_0 + n\omega)t} = e^{i\omega_0 t} \frac{\sin(N\omega t/2)}{\sin(\omega t/2)}
\]

(2.2)

where \( N \sim \Delta v/v \) is the number of longitudinal modes in the cavity. If it is assumed that the modes are nondegenerate and the phase shift is zero between oscillating modes, thus

\[
I(t) \propto \frac{\sin^2(N\omega t/2)}{\sin^2(\omega t/2)}
\]

(2.3)

\( I(t) \) is periodic in \( T = 2L/c \). The peak laser intensity is \( N^2 \) times the amplitude of a single mode, and the pulse width, defined for this illustrative case as the time between the peak and the first zero of \( I(t) \), is \( \tau = T/N \sim 2\pi/\Delta \omega = 1/\Delta v \). It can be seen that the pulse width depends inversely on the gain linewidth of the laser. In Fig. 15b, a mode-locked train is illustrated. Mode locking can be grouped by the way the signal is applied to the modulation of the losses. Active mode locking requires an external source applied to the laser cavity. However, passive mode locking does not require any external source. It is done by periodic modulation of the cavity by inserting a 'shutter' into the cavity. Often, a saturable absorber is inserted into the laser cavity. The essential feature of a saturable absorber is that its transmission at the laser wavelength increases nonlinearly with increasing light intensity. When a laser pulse encounters a saturable absorber, the peak of the pulse is enhanced relative to edges of the pulse. At each round trip, pulse compression occurs until the gain approaches unity.

**Ultrafast Laser Systems**

In this section, the laser systems used in this study are described. The popular ultrafast pump sources are solid state lasers, in particular, mode-locked Nd:YAG (Yttrium Aluminum Garnet) and Nd:YLF (Yttrium Lithium Fluoride) lasers. Fig. 16 displays laser head diagram of a continuous wave (CW) mode-locked (ML) Nd:YAG laser (Coherent model Antares 76-s). The fundamental output for the Nd:YAG laser is at a wavelength of
Fig. 16. Schematic diagram of a Nd:YAG laser (Coherent, model Antares 76-S). See text for details. (Adapted from "Operator's Manual: Antares 76-S" Coherent Laser Group)

1064 nm, the pulse duration is ~ 100 ps and the average power is 22 W (76 MHZ) in $\text{TEM}_{\infty}$ mode. The pulsewidth of the 1064 nm pulses is monitored by a picosecond photodetector (Antel Optronics, model AR-S2) through the leakage of the intracavity pulses from the high reflector. The near-IR fundamental is frequency doubled with an KTiOPO$_4$ (KTP) crystal to generate the second harmonic output of 532 nm (~ 3 W, $\tau_\text{p} \sim 70$ ps), which pumps two synchronously pumped dye lasers. Briefly, the major components and the principles of operation of the Coherent Antares laser system are illustrated. The round trip of the optical path is ~ 3.95 m for a 76 MHZ repetition rate. The overall length of the Antares is minimized with a folded resonator design (fold mirror assembly). The POT assembly is the 'heart' of the laser, which contains the Nd:YAG rod and two krypton arc lamps housed inside a gold-plated cavity. The aperture discriminates against higher transverse modes and sustains only the $\text{TEM}_{\infty}$ mode. The Brewster plate is used for preserving the vertical polarization of the 1064 nm light. Vertically polarized light will be transmitted through the plate with no reflection loss. (Active) Mode locking is achieved by inserting a Piezoelectric Transducer (PZT) inside the cavity. An RF drive signal (38 MHZ) is applied to the PZT to produce a
standing acoustic wave, which results in a periodic diffraction loss inside the laser cavity. The phase matching condition for the KTP is TYPE II and the crystal is angle tuned to achieve phase matching. The assembly for the KTP crystal provides three rotational degrees of freedom. The polarization of the second harmonic beam is 45 degrees with respect to horizontal and the polarization of the residual IR becomes elliptical with one component at horizontal and one component at vertical polarization. The PROD (polarization, rotation and discrimination device) separates the 532 nm beam from the residual 1064 nm beam and rotates the polarization of the 532 nm beam so that it is vertical or horizontal.

I used a third harmonic generator (Coherent, model 7950) to produce 355 nm light. For the third harmonic operation, the PROD is displaced and the KTP crystal is rotated 45 degrees from ordinary setting with respect to the optical axis. Phase matching conditions for the THG setup are exhibited in Fig. 17. The phase matching is Type II for the KTP crystal and is Type I for the $\beta$-BaB$_2$O$_4$ (BBO) crystal. Therefore, two half wave plates (HWP) are incorporated in the optical path; one is between the output coupler and the SHG, which changes the polarization of the IR to 45 degrees from vertical polarization; the other one is placed between the SHG and the BBO crystal, which makes the polarization of the IR parallel to the 532 nm beam. I have obtained average power of 0.9 W of 355 nm from the THG setup with mixing of 3 W of 532 nm and 18 W of 1024 nm. Note that, with Type II phase matching of the KTP crystal, the residual IR becomes elliptical polarized, therefore, the 'useful' power of the 1064 nm is roughly half of the residual power, i.e., 9 W.

![Fig. 17. Phase matching conditions for the third harmonic generation of 1064 nm. HWP: half wave plate. (Adapted from "Operator's Manual: 7950 Third Harmonic Generator" Coherent Laser Group)]
The schematic for a synchronous pumping cavity dumped dye laser (Coherent, model 702) is shown in Fig. 18. The laser operates with a hybrid mode-locking configuration, which combines synchronous mode-locking and pulse shaping by a saturable absorber. The dye laser can be dissected into several compartments: the pump mirror, the gain jet assembly, the delay arm, the saturable absorber assembly, the tuning element, and the cavity dumper. The pump mirror (P) is a 10-cm radius concave mirror that reflects the frequency doubled or tripled Nd:YAG or Nd:YLF lasers. The gain jet assembly consists of mirrors $M_1$ ($f = 10$ cm) and $M_2$ ($f = 15$ cm), and a dye jet (oriented at the Brewster's angle to the optical path). Mirrors $M_3$ and $M_4$ are both flat high reflectors and are used to lengthen the optical path. The dye jet for the saturable absorber assembly is similar to the one for the gain jet and the focus lengths of mirrors $M_5$ and $M_6$ are both 5 cm. Tuning of the dye laser is achieved by inserting a birefringent filter inside the laser cavity. The filter consists of one or several flat and parallel quartz plates. They function as full wave plates that change the effective extraordinary index of refraction as the plates are rotated. Mirror $M_7$ ($f = 15$ cm) functions as a folding mirror for the cavity dumper and the mirror $M_8$ ($f = 7.5$ cm) is the end mirror for the whole cavity of the dye laser. The Bragg cell, an acousto-optic (A.O.) modulator, is used to deflect selectively out part of the light traveling inside the laser cavity.

The A.O. modulator consists of a fused silica slab with a PZT transducer bonded on one side. The PZT transducer converts the RF signal from a cavity dumper driver (Coherent, model 7200) to an acoustic wave. This acoustic wave modulates the refractive index (creating a phase grating) of the fused silica through the photoelastic effect. The cavity dumped beam is diffracted from the main light at the Bragg regime. Readers are advised to refer to the operation manuals for more details of the lasers outlined above.

I briefly discuss some fundamental principles of synchronous mode-locking with passive mode-locking by a saturable absorber. The optimum optical path for a synchronously-pumped dye laser should be identical to the length of the pump laser. This results in a modulation in the gain of the laser at the round-trip frequency. Synchronous pumping is viewed as active mode-locking since the pumping source acts as a master while the optically pumped laser is the slave. The rise time of the gain is determined by the time integral of the optical pumping pulse, thus, the optical pulsewidth of the slave laser is typically much shorter than the pumping pulse (see Fig. 19a). When the pulse in the cavity passes through the gain medium, stimulated emission depletes the upper state dye population and reduces the gain to equal the level of the threshold. The temporal evolution of the pulses is shown in Fig. 19b. The effect of a saturable absorber to an intra-cavity pulse is illustrated in Fig. 19c. The leading edge of the pulse is truncated (absorbed) which induces a narrower pulse width.

Pump-Probe Experiments

The basic experimental principle of pump probe experiments is discussed in this section. Fig. 20 shows the basic setup for a pump-probe experiment in this work. The second harmonic output from a CW ML Nd: YAG laser was divided with a beam splitter and served as the pump source for two synchronously pumped dye lasers (R6G and/or DCM). When a blue light source was needed for experiments, the fundamental and second harmonics were mixed in a BBO crystal to generate the third harmonic (355 nm). The 355 nm and the residual of 532 nm then served as the pump sources for a blue dye (Stilbene 420) and a red
Fig. 19. Hybrid mode locking by synchronous pumping and passive mode-locking. (a) Active mode-locking of a dye laser by synchronous pumping. (b) Temporal evolution of the dye laser pulse and the pump pulse in a synchronously pumped dye laser. (c) Illustration of the effect of a saturable absorber on a short pulse. (Adapted from [101,104])
dye laser (R6G). Experiments were usually run at a 1 MHz or 500 kHz repetition rate. The laser power was measured with a power meter (Laser Precision, model RT-30-cal or Coherent, model 210). The typical average pulse energies (at 1 MHz) generated from the dye lasers were as follows: R6G, 100 nJ (~ 2.1 eV) with 1.4 W pump energy; DCM, 25 nJ (~ 1.9 eV) with 1.3 W pump energy; Stilbene 420, 18 nJ (~ 2.9 eV) with 0.9 W pump energy. The pulse widths of the R6G and DCM lasers were characterized with an autocorrelator (Coherent, model FR103 or Femtochrome Research, model FR-103XL). Typical pulse widths ranged 4 ~ 8 ps at 1 MHz. The pulse width of the blue light was optimized by achieving a minimum rise time for transient absorption of a well-known system (DODCI or DTCI) with the blue light serving as the probe beam (see below).

The pump energy was usually 2.1 eV (~ 590 nm) generated from a R6G dye laser. In case of high peak intensity was required, the 2.1 eV pulses were amplified with a six-pass amplifier pumped by a cavity dumped Ar\textsuperscript+ laser [102]. The cavity dumper of the Ar\textsuperscript+ laser was synchronized with the ones for the dye lasers. The typical cavity dumped pulse from the Ar\textsuperscript+ laser was ~ 10 ns and ~ 1.8 μJ (at 1 MHz). A 100 nJ pulse of 2.1 eV can be amplified to 500 nJ in an ideal situation. To generate UV pulses, the amplified 2.1 eV pulses were frequency doubled with an angle tuned crystal, KH\textsubscript{2}PO\textsubscript{4} (KDP), or a temperature tuned crystal, NH\textsubscript{4}H\textsubscript{2}AsO\textsubscript{4} (ADA). The conversion efficiency exceeded 15% for pulse energies larger than 200 nJ. The probe energy was usually 1.9 eV (~ 650 nm) or 2.9 eV (~ 428 nm). The probe beam was passed through a delay line consisting of a retroreflector mounting on a computerized translational stage (Compumotor, model F-L5A-P54). The motor can scan at steps of 2 μm which yields a 6.6 fs resolution. The motor/drive was interfaced with a PC through a microprocessor-based indexer (Compumotor, model PC-21).

The pump and probe pulses were combined and collimated with an appropriate beam splitter. In the case of 2.1 eV pump and 1.9 eV probe, a 50% non-polarized visible beam splitter was used. A dichroic beamsplitter with reflection centered at 430 nm (~ 2.88 eV) and a transmission range of 550 to 700 nm (2.25-1.77 eV) was used for the 2.1 eV pump and 2.9
eV probe experiments. An UV reflector (308 nm or 4 eV) was used to reflect the 4.2 eV pulses and served to transmit the probe beam (1.9 or 2.9 eV) for the UV pump and visible probe experiments. The pump and probe beams were focused with a lens of \( f = 5 \) cm, and the beam waist of the focused spot was usually 100 \( \mu \)m. The radiant energy density of the laser beams was, therefore, in the order of 10 to 100 \( \mu \)J/cm\(^2\). When the power density of the lasers was a concern, a neutral density filter was used to reduce the radiant intensity. In most cases, the pump and probe beams were collinear, however, a non-collinear configuration was also adopted for some experiments. There was no apparent difference between the experimental results for both setups.

Solution samples were placed in cylindrical quartz cells (O.D. \( \sim \) 1 mm; I.D. \( \sim \) 0.8 mm). Each cell was housed in a sample holder that allowed the cell to be spun with compressed air. The purpose of spinning the cell was to reduce thermal effects created from local heating of samples by the laser light. The focused point of the pump and the probe beams was usually on the surface of the inner sphere of the cell. A metal clip was used to hold film samples. In the case of air sensitive samples or for low temperature experiments, samples were placed in a home made sample holder that was housed inside a vacuum chamber. The intensity of the laser for solid state samples was usually kept as low as possible (< 10 \( \mu \)J/cm\(^2\)) to prevent too much heating of the samples. The transmitted laser beams were recollimated with a lens of \( f = 10 \) cm. Then, the pump and the probe beams were separated with a grating or a Pellin-Broca prism. The probe beam was passed on a photodiode with or without a focus lens depending on the size of the beam waist.

A lock-in amplifier (Ithaca, model 3981) was incorporated in the data collection. The lock-in amplifier connected with a PC interface board, which was controlled by PC software. The signals detected by the photodiode were sent to a transimpedance amplifier (UDT, model 101C). The amplified signal was then sent to the lock-in amplifier. The reference frequency for the lock-in detection was from a mechanical chopper (Stanford Research, model SR540) placed in the optical path of the pump beam before hitting the sample. The
chopping rate was typically 1 to 2 kHz. DC signals of the probe beam were obtained by converting the analog signals from the transimpedance amplifier to digital signals by an A/D converter (Metra Byte, model DAS-8), which is also an interface board for the IBM-PC compatible computer. The ratio between the signal obtained from the lock-in and the signal obtained from the A/D converter would be $\Delta T / T$: the change of the probe field under the presence of the pump field.

Lock-in technology employs phase sensitive detection and extracts signal by synchronous rectification according to a reference frequency. The process converts a noisy ac signal into a clean dc output and rejects dc offsets, incoherent frequency components, and random noise. The Ithaca lock-in amplifier produces two dc outputs, in phase ($x = A \cos \phi$) and in-quadrature ($y = A \sin \phi$) signals (see Fig. 21). Phase zero is defined as the positive-going zero crossing of the mean value of the reference ac input (from the reference voltage input of the mechanical chopper). Notice that, the phase here is determined from the ac reference frequency, the period in which as many as $10^3$ pulses being averaged. It is, therefore, not the true phase between the individual pump and probe pulses, which is very important in determining the absolute photoinduced change of the probe field, i.e., whether it is a photoinduced absorption or bleaching. Photoinduced absorption (bleaching)

![Dual phase lock-in vector diagram.](image)

**Fig. 21.** Dual phase lock-in vector diagram.
corresponds to the probe field being reduced (increased) by the presence of the pump field.

I now discuss the real signals obtained in pump-probe experiments. To obtain the photoinduced signals, the pump and the probe beams needed to be spatially and temporally overlapped. All the cavity dumpers for the dye lasers were synchronized to the mode locker driver for the Nd:YAG laser. Rough temporal overlap between the probe and the pump was achieved by monitoring the relative delay between the two beams with a ns photodiode. The signals from the photodiode were sent to a sampling scope, and the time delay between the pump and probe was adjusted by switching the delay of the cavity dumper drivers. The relationship of the timing between the pump and the probe is shown in Fig. 22. The time delay between pump and probe pulses is adjusted by varying the optical delay line of the probe beam. In Fig. 23, the typical picosecond photoinduced (transient) signals are displayed. The inset of Fig. 23a shows how the time zero is determined by the rise of a transient signal, the half height of the rise of a transient signal with decay much longer than the pulse widths of the laser is considered as the time zero. I will discuss the reasoning behind this in more detail in the next paragraph. Shown in Fig. 23a is the photoinduced absorption decay of DODCI in methanol with a 2.1 eV pump and a 2.9 eV probe from -20 to 4000 ps (-20 to 20 ps in the inset). The decay can be fit to a single exponential with a time constant of 910 ps, which is certainly long enough as compared to the typical pulse duration of 5 ps for the probe beam. Notice that, the forward and reverse scans coincide with each other—an indication of good S/N and spatial alignment. Shown in Fig. 23b is the photoinduced decay of hydrogenated amorphous silicon (a-Si:H) with a 2.1 eV pump and a 2.0 eV probe from -20 to 4000 ps.

The transient photoinduced signal \( \Delta T(t) \) is actually derived from a convolution of the probe field \( E(t) \) and the population decay of the photoexcited states \( P(t) \): \( \Delta T(t) \equiv E(t) \otimes P(t) \). The temporal profile of a cavity dumped laser pulse is best approximated by a hyperbolic secant square function \( \text{sech}^2\left(\frac{1.76t}{\Delta t}\right) \), where \( \Delta t \) stands for the pulse width (see Fig. 24a). If the \( \text{sech}^2 \) function is convoluted with a single exponential of 1 ns lifetime
Fig. 22. Relative time delay between the pump and the probe pulse train. (a) The pump and the probe pulses are in near coincidence. The repetition rates of the lasers are shown as ~ 1 MHz. (b) The probe pulse train arrives about 26 ns after the pump pulse. (Adapted from [105])
Fig. 23. (a) Picosecond photoinduced absorption of DODCI in methanol from -20 to 4000 ps. The pump and the probe energies were 2.1 and 2.9 eV, respectively. Inset: The same decay from -20 to 20 ps. Notice that the time zero is set at the half height of the rise. (b) Picosecond photoinduced absorption of a-Si:H from -20 to 4000 ps. The pump and the probe energies were 2.1 and 1.9 eV, respectively.
Fig. 24. Convolution of a laser pulse and a population decay of an excited state. (a) A 5 ps cavity dumped dye laser pulse. (b) A single exponential decay of 1 ns. (c) Plot of the convolution of the above two functions from 0 to 2 ns. Inset: Solid line--replot of (c) from -20 to 60 ps. Open circle: convolution of a single exponential decay of 10 ps and a 5 ps laser pulse.
(Fig. 24b), the numerical result is shown in Fig. 24c. The initial rise is determined by the convolution of the temporal profile of the light fields and the population decay of the transient species. Moreover, for short lifetime species, it is difficult to determine the real time zero since the half height of the rise has shifted to negative time delay. The inset of Fig. 24c illustrates this point by displaying results of convolutions of 10 ps and 1 ns lifetimes with a 5 ps pulse. For a lifetime \( \tau \) much longer than the pulse duration \( \Delta t \), the half height of the rise of photoinduced signals is assured to be the zero time delay between the pump and probe fields. However, as shown in the graph, for a lifetime on the order of the pulse width, the half height is no longer the true time zero.

Gustafson et al. have developed a unique technique called time-modulation for pump-probe experiments using cavity dumped dye lasers [105]. Instead of using a mechanical chopper to modulate the pump, electronic modulation of the probe beam is used in time-modulation techniques. Electronic modulation is accomplished by electronically switching the time delay between the pump and the probe beams through the cavity dumper driver of the probe laser. The cavity dumper driver electronics were modified to allow the delay increment and decrement control of the RF signal at high repetition rates. A pulse generator (HP 8011A) applied a square wave and its compliment to the delay increment and decrement controls, respectively, of the cavity dumper driver for the probe laser. Recall Fig. 22, in (a), the probe and the pump are near coincidence, in (b), the probe pulse is 26 ns before the pump beam. Time-modulation takes its name as the probe pulse is modulated between these two stages and the corresponding change in intensity is detected with a lock-in amplifier. This method reduces the thermal (or long-lived) background in transient signals owing to the fact that both pump and probe beams are always present: the dc background is subtracted out by modulation between these two stages. Electronic modulation also allows pump-probe experiments to run at higher repetition rates than conventional chopping methods. In Fig. 25a, I compare photoinduced signals of an a-Si:H sample obtained using conventional amplitude modulation with that obtained using time modulation (the latter delay is artificially shifted +100 ps). Only traces of the background signal were observed in
Comparison of a time modulation and a mechanical modulation techniques. (a) Upper curve: picosecond photoinduced absorption of a-Si:H by mechanical modulation (the curve is time shifted -200 ps) Lower curve: same temporal and spatial overlaps as the upper curve but using the time modulation method. (b) Upper curve: the variation of the probe intensity from -40 to 40 ps by using mechanical modulation when the spatial overlap between the pump and the probe beam was not perfect. Lower curve: same conditions as the upper curve but using the time modulation method.
the latter decay, and the S/N was improved as the experiment was run at a higher repetition rate than that of the formal decay. I close the discussion of time-modulation techniques by showing a transient signal that was difficult to distinguish using amplitude modulation but was easily accessible with time modulation. Shown in the upper curve of Fig. 25b is the variation of the probe field for an a-Si:H sample from -40 to 40 ps when the pump beam and the probe beam did not have perfect spatial overlap. I could only observe a small ‘dip’ (transient) signal of the probe intensity buried in a huge thermal background. However, when time modulation was applied to the same setting, an obvious transient signal had appeared and the huge thermal background had reduced to a negligible level (see the lower curve of Fig. 25b).

**Luminescence Studies**

The experimental methods in steady-state and time-resolved luminescence studies of conjugated polymers are described in this section. Photoluminescence is a term referring to emission of photons (radiative decay) after photoexcitation. Generally, it covers spin-allowed (fluorescence) and spin-forbidden (phosphorescence) transitions. Radiative decay can involve in a wide distribution of time scales: from tens of femtoseconds to several hours. To elucidate the nature of radiative processes in complex systems like conjugated polymers, spectrally and temporally, a variety of spectroscopic techniques have to be applied in photoluminescence studies.

A fluorimeter (Instrument SA, model Fluorolog-3) was used for steady-state luminescence studies. The light source for the fluorimeter is a xenon lamp with an excitation range from 250 to 800 nm (5 to 1.5 eV). The instrument allows luminescence to be detected at 90° or 23.3° with respect to the excitation beam, emission is dispersed with a grating pair and is detected in step-scan by a photomultiplier. Emission profiles of the luminescence spectra obtained were corrected to the instrument response of the fluorimeter. I also obtained cw luminescence spectra by using the ultrafast lasers described above as photoexcitation sources. The emission was detected in a back scattering configuration. A lens pair was used
to collimate and to direct the luminescence into a monochromator (Instrument SA, model HR640). A charged coupled detector (CCD) setup was used as the detection mechanism (Photometrics, model CCD 9000). This setup has an advantage of detecting a wide range of the luminescence spectra at once (the width of the CCD chip is 1.12 cm, with which a 100 gr/mm grating inside the HR 640 will yield a dispersion of ~ 220 nm in the visible range).

Time-correlated single photon counting (TCSPC) techniques were used in the picosecond and nanosecond time-resolved luminescence studies. A schematic of a typical TCSPC setup is shown in Fig. 26. The light source for photoexcitation was usually from a cavity dumped synchronous pumping dye laser. To generate UV light, the R6G dye laser, either amplified or not, was frequency doubled. Luminescence was measured at 90° with respect to the excitation beam and was dispersed by a subtractive double monochromator (American Holographic, model DB10-S). The monochromator preserves the transit time for different wavelengths in the same dispersion order. MCP-PMT is a microchannel plate photomultiplier tube (Hamamatsu, model R2809U-07) with a transit time spread of 55 ps and a rise time of 150 ps. A time-to-amplitude converter (TAC; Tennelec, model TC 864) is the key element of the TCSPC technique. It determines the timing of a fluorescence decay by registering a start pulse and a stop pulse from a pair of constant fraction discriminators (CFD; Tennelec, model TC 455). A start pulse triggers the charging of a capacitor in the TAC until a stop pulse is detected, and the time interval between the start and the stop pulses generates a voltage across the capacitor. The start pulse is initiated from a photodiode and the stop pulse is initiated by the arrival of a fluorescence photon. The voltage pulse is stored by a multi-channel analyzer (MCA; Tennelec, model PCA-2). By repeating the ‘start’-’stop’ cycle many times, a histogram of the fluorescence decay is stored in the MCA. The parameters can then be extracted from the histogram. For more thorough discussion of the TCSPC technique, the readers are advised to refer to more detailed reviews in literature [106,107].
CHAPTER III

PICOSECOND PHOTOINDUCED ABSORPTION SPECTROSCOPY OF POLYANILINE

Ring rotational hindrance in lattice relaxation of the emeraldine and pernigraniline base forms of polyaniline: picosecond photoinduced bleaching studies

Introduction

Ultrafast spectroscopy has played an active role in understanding the dynamics of photoexcitations and novel defects (solitons, polarons and bipolarons) in conjugated polymers [63,66,108]. Polyacetylene, a prototypical conjugated polymer, has generated a lot of interest both in theoretical and experimental studies. Previously, a subpicosecond photoinduced absorption (PIA) study of polyacetylene has demonstrated that the induced absorption of gap states appears in less than 150 fs [96]. The PIA was interpreted as kink (charged soliton-antisoliton) pairs converted from initial photoexcited intrachain electron-hole pairs \((e+h)\) [109]. Subsequently, polarization dependence studies of the PIA of oriented \(trans-(CH)_x\) in picosecond and microsecond time scales have revealed that inter-chain photoexcitations create polaron pairs \((P^+ + P^-)\) [110]. It is fair to infer that the dynamics of the photoexcitations of polyacetylene are thoroughly investigated. However, for conjugated polymers with more complexity in conformation and structure than polyacetylene, the evolution of photoexcited species on fast time scales is less clear and many issues remain to be explored [57,68,108].

Polyaniline is a generic term for a class of polymer with three different oxidation states: fully reduced form leucoemeraldine base (LEB), half oxidized form emeraldine base (EB) and fully oxidized form pernigraniline base (PNB). In recent years, these polymers
have been studied extensively, and each oxidation state shows novel physical and chemical properties [24,111-115]. Polyaniline has been recognized for its strong correlation of optical, electronic and chemical properties with the torsional angles of benzenoid and quinoid rings of the polymer [116]. Several theoretical studies have shown that the ring-rotational conformation is important in determining the ground-state electronic structure and geometry of polyaniline [16,20]. Polyaniline, owing to the alternating ring-nitrogen backbone structure, can have a wide range of forms that depend on the number of electrons and protons on the polymer backbone. The half-oxidized emeraldine base (EB) has been extensively studied for its fascinating physical and chemical properties and stability [111,114,117]. The fully oxidized pernigraniline base (PNB) has a two-fold degenerate Peierls ground state, which too has attracted more attention recently [19,23,112,118-121]. The 2 eV optical transition of EB has been attributed to a charge transfer molecular exciton bound to a locally distorted (ring-torsion) segment of the polymer backbone [122]. A theoretical calculation has suggested the exciton formation is followed by a 60° to 90° rotation of the quinoid moiety relative to its ground-state conformation [123] (see Fig. 27). The negative charge is centered on a quinoid ring with the positive charge equally distributed between the adjacent phenyl rings. The Peierls gap transition of PNB is centered at 2.3 eV. Previously, a near steady state photoinduced study of the emeraldine base form of polyaniline revealed the existence of a long-lived (> ms) exciton and a unimolecular dependence of the relaxation of the exciton [22]. PNB also exhibits a long-lived bleaching of the Peierls gap in near-steady state conditions, which carries a relaxation behavior approaching a bimolecular dependence [23,113]. Picosecond photoinduced bleaching (PIB) of the exciton band of EB with pump energy at 2.1 eV and probe energy at 2.0 eV has shown a temperature independent dispersive decay, $\sim t^{0.11}$, for $40 \text{ ps} < t < 4 \text{ ns}$, for EB as a film [117]. The long-lived excitons and polarons that were observed in the near-steady state photoinduced absorption experiment of EB were suggested to be stabilized through ring rotations or other conformation changes that inhibit charge recombination [22]. A similar proposal was also suggested for the photoinduced bleaching of the Peierls gap of PNB [23].
**Fig. 27.** The conformations of the molecular exciton and its ground state in a monomer unit of EB. The exciton formation is followed by a 60°-90° rotation of the quinoid moiety relative to its ground-state conformation. The rotation is accompanied by a redistribution of charge described by charges of e/2 moving from each of the two adjacent phenyl rings to the quinoid ring.

To evaluate this proposition using PIB, I seek to reduce the rotational hindrance within the polymer backbone by increasing the free volume and minimizing inter chain packing of the polymer. Ideally, one would dissolve the polymer in a solvent. The bulky size and long chain length of polymers limit the number of available solvents. N-methyl-2-pyrrolidinone (NMP) is the only solvent used that has enough solubility for EB and PNB to give substantial photoinduced signals for this study. Note that in NMP, emeraldine base adopts a coil-like structure [124], which makes spatial hoping of charges between nonadjacent units of the same chain likely to happen.
Picosecond photoinduced bleaching studies of EB photoexcitations in NMP solution and in solids are reported in the first part of this chapter. Picosecond photoinduced bleaching of PNB in NMP also is discussed. To reduce possible thermal effects induced from heating of the samples by laser radiation [125], I used a spinning quartz cell (8 mm i.d.) or a flowing jet with a nozzle in closed circulation. For solid samples, the radiant density was kept below 5 μJ/cm² to minimize heating effects. Powders of EB and PNB were ground into fine particles, stirred in NMP for several hours, and filtered before use. Filtration was generally done in two steps: 1. gravity or suction filtration using filter papers like VWR No. 454 (10 μm particle retention), 2. syringe filtration using syringe filters (Acrodisc PTFE 25 mm, 1 μm pore size), syringes (B-D Multifit Syringe BD2136 or BD2131), and needles (Hamilton 90022 or 90122). Some solution samples of EB and PNB were sealed under a vacuum in quartz cells to make comparison with open-air samples. The concentrations of the samples in the spinning cell were 0.02-0.1 mg/1 ml (~ 10⁻⁵ M monomer unit; the atomic mass for an EB (PNB) monomer unit is 361.15 (180.07) amu). Since the thickness of the jet was 0.02-0.1 mm, to create ample photoexcitations, the concentration of the jet solution was kept at 0.5-2 mg of EB (~ 10⁻³ M monomer unit) in 1 ml of NMP. In order to compare the dynamics of the photoexcitations in solution with the dynamics of the photoexcitation in solid form, a ~ 0.2-μm-thick EB film (cast onto quartz substrates) was also used in this experiment. All experiments of NMP solutions were performed at room temperature.

Picosecond photoinduced bleaching measurements were made using a dual synchronously pumped, cavity dumped dye laser system that has been described in detailed in chapter 2. Both dye lasers were operated at repetition rates of 500 kHz or 1 MHZ with pulse duration: \( t_p \sim 5 \) ps. Rhodamine 6 G dye was used to generate the pump photon energy, 2.09 eV. DCM dye was used to generate the probe photon energy, 1.88 eV, which is close to the maximum of the near steady state PB peak of the exciton band (1.8 eV) [22]; see also Fig. 9 in chapter 1. For the intensity dependence study, the pump beam was amplified with a six-pass amplifier pumped by a cavity dumped argon ion laser [102]. By adjusting the RF level of the cavity dumper and employing combinations of neutral density filters, the energy
of the pump pulse was varied from 4 nJ to 250 nJ (10 to 625 μJ/cm² for a beam waist of 100 μm). A UV source was also employed to excite polyaniline into π–π* bands. The 4.2 eV pulses were obtained by frequency doubling the amplified 2.1 eV sources. The radiant energy of the UV pulse can be as high as 30 nJ. The time resolution of the experiment was limited by the 8 ps cross correlation of the pump and probe pulses. Besides mechanical modulation, a time modulation technique was also incorporated in this study [105]. The great advantage of this technique is that there is no artifact due to heating of samples from the pump and probe laser beams. Time modulation of the probe delay also provides full access to pump beam power with energy losses due only to the mirrors and beamsplitter.

**Results and discussion**

Shown in Fig. 28 are transient photoinduced signals of EB in NMP and 3,3'-diethylxadicarbocyanine iodide (DODCI) in methanol from delay time of -20 to 20 ps. The pump energy was 2.09 eV and the probe energy was 1.88 eV. The total radiant energy of the pump and the probe pulses was 50 nJ, which is equivalent to a radiant energy density of 160 μJ/cm² for a beam waist of 100 μm. Ratios between the intensity of the pump and the probe beams were normally kept above 5 to 1. The time zero was set at the half height of the rise of the photoinduced absorption (PIA) of DODCI in methanol. Care was taken to recheck the time zero frequently using the PIA of DODCI in methanol throughout each experiment. As discussed in chapter 2, the rise and the maximum of the photoinduced signals are the outcome from the convolution of the light fields (pump and probe) and the decay of the photoexcited states. The maximum of the photoinduced bleaching of EB in NMP was at +4 ps relative to the time zero of the PIA of DODCI in methanol. The PIB changes can be fit to a convolution between an exponential decay (time constant of 6 ps) and the probe field (a hyperbolic secant function: \( I(t) = I_0 \text{sech}^2(t/\tau_p) \), where \( \tau_p = 5 \) ps) (see Fig. 28). The PIA of DODCI was fit with a convolution of the probe field and a biexponential form of \( 0.4 \times \exp(-t/50 \text{ ps}) + \exp(-t/1.2 \text{ ns}) \), where the short component was put in artificially to match the fast decay observed in the PIA.
Fig. 28. Photoinduced absorption of DODCI in methanol and photoinduced bleaching of EB in NMP. (Note that the absolute values, $|\Delta T/T|$ are plotted here.) The pump and probe energies were 2.1 eV and 1.88 eV, respectively. Simulations of the photoinduced changes also are shown in the graph, open circle for EB in NMP and open square for DODCI in methanol (see text for details). Shown in the top left corner of the graph are conformations of the molecular exciton and its ground state in a monomer unit of EB.
The transient photoinduced bleaching of EB in NMP relaxed to the background level (comparable to signals at negative delay time) within 50 ps (See Fig. 29). No appropriate function was found to fit the PIB decay well. A possible explanation is pointed to the fact that the decay is derived from a convolution of the light fields (pump and probe) and the nonlinear response function (which is a subset of the third order polarizability) of the polymer. Since the pulse durations of the dye lasers in this work were ~ 5 ps, a short-lived component of less than 10 ps cannot be deconvoluted properly, without knowing some details of the third order polarizability, from the fast decay. I can only emphasize that the time constant of the fast decay of the PIB of EB in NMP is within 10 ps as demonstrated from the convolution fit of the PIB signal of EB in NMP (Fig. 28). A similar picosecond photoinduced bleaching of EB in NMP was also observed in a flowing jet setup (See Fig. 29 inset). Owing to spinning or circulation of samples, no notable thermal effects were observed throughout the span of experiments. There were no significant changes in the transmission of the laser pulses, and the photoinduced signals for EB in NMP were reproducible for several hours. The reproducibility of the photoinduced signals for solutions indicates that those photon energies absorbed by EB were dissipated well by spinning or circulating of the solutions.

Transmission of the probe beam was 5 to 15% for samples being investigated, and losses from reflection and scattering of the sample cell and solutions were 15 to 20%. It was pretty straightforward to determine the transmission, i.e., by the ratio of the intensities of the probe beam with sample and solvent and with only solvent in a cell. The intensity was measured by a photodiode (UDT 101C) placed in the optical path. To estimate the diffraction and scattering losses, intensity of the probe beam with a sample cell and NMP was subtracted with the intensity of the unperturbed probe beam \( I_0 \), which yielded the portion of the diffraction and scattering losses by the cell and the solvent (~ 10-15%). Then, a 50% beamsplitter was placed in the optical path before the sample cell, and another photodiode (UDT 101C) was placed in the optical path of the 45° back reflection beam (see Fig. 30). When the cell was filled with only solvent the second diode gave a near zero reading
Fig. 29. Picosecond photoinduced bleaching of EB in NMP (using a spinning cell) with pump and probe energies of 2.1 and 1.88 eV, respectively. Forward and reverse scans match up with each other very well, which shows the consistency of the photoinduced signals. Shown in the inset is a similar PIB done with a flowing jet setup.
Fig. 30. Schematic diagram for the measurement of the transmission and losses (from scattering and reflection) of the probe beam. BS: beamsplitter, S: sample cell, PD: photodiode.

(below 0.05% of the $I_0$). The intensities were $\sim 1.2$-2.2% with samples filled in the cell. I have found that a concentration of 0.05 mg EB in 1 ml of NMP gave the best result. At this concentration, the transmission was $\sim 10\%$ with reflection and scattering losses of $\sim 20\%$. Assuming the minimum unit for the formation of the molecular exciton contains four rings, the number of available and excited sites at certain concentration of solution can be estimated. Thus, for a pulse of radiant density of 20 $\mu$J/cm$^2$, the maximum excited sites are $4.6 \times 10^9$ sites at the above mentioned concentration. I estimate the total available sites, for a beam waist of 100 m, are $\sim 1.5 \times 10^{12}$. Ratios between the excited and available sites are very close to the observed photoinduced bleaching changes: $\sim 10^{-3}$.

In contrast to picosecond photoinduced bleaching in solution, there were long-lived components ($> \text{ns}$) observed in the picosecond photoinduced bleaching of EB films (Fig. 31). In order to minimize heating effects, data for films were collected with radiant densities less than 5 $\mu$J/cm$^2$. The pump and probe energies for EB films were the same as those of EB in NMP. The rise of the exciton bleaching of EB films was comparable to that of EB in NMP, which correlated well with the pulse durations and the cross correlation between the pump and the probe pulses. This indicates that the formation of the exciton in either solid or
Fig. 31. Picosecond PIB of an EB (spin-cast) film at probing energies of 2.01 and 1.88 eV. The excitation energy was 2.1 eV.
solution is within the instrumentation limit (< 5 ps or < 2 ps by deconvolution of the data). The rise and decay for the EB film were also similar to previous results with probe energy of 2.0 eV [117]. Specifically, an instrumentation-limited rise and a multi-component decay with 40% of the exciton population that was present at 10 ps remained after 4 ns. The drastic difference in the lifetime of the molecular exciton in solution and as a film clearly indicates the importance of local environment in the dynamics of photoinduced species of EB. Fig. 31 also displays the photoinduced bleaching of an EB film at two probing energies: 2.04 and 1.88 eV. It is interesting to note that the exciton band contains a faster initial decay when probing at 1.88 eV than probing at 2.04 eV. Photoinduced changes from both probing energies possess long-lived (> ns) components, which are probably related to ms components observed in the near-steady state photoinduced studies of EB (see Fig. 9). Although the 1.88 and the 2.04 eV experiments were done on an identical film, these results need to be reproduced. The bleaching at 1.88 eV could arise from states that subject to less lattice relaxation, and therefore, the excited species should exhibit a faster decay than the states probing at 2.04 eV. These results support the important role of ring-rotational hindrance in lattice relaxation and the formation of novel defects of polyaniline. The frequency of the ring-torsional mode should be ~ 100 cm$^{-1}$, which makes the direct measurement of the transition difficult even for the polymer in the ground state. At the present stage, most ultrafast photoinduced IR experiments are only capable of studying relatively high frequencies, > 600 cm$^{-1}$ [126]. This work represents an indirect probe to the ring-torsional degrees of freedom by studying the dynamics of photoexcited states in different environments. To date, this is likely to be the only feasible approach. (The author has tried every effort to obtain picosecond photoinduced Raman of EB and PNB but unfortunately the scarce data collected were probably due to vibrational population depletion (thermal effects) of the solvent (NMP).)

The dynamics of the exciton band was found to behave unimolecularly in near-steady-state conditions [22]. It is worthwhile to address the intensity dependence of the picosecond photoinduced bleaching of EB in NMP. At the peak of photoinduced bleaching
(or absorption), the derivative of the number of the photoinduced species over time $dn/dt$ should be $\sim 0$, therefore, it can be treated as quasi-equilibrium condition (see eq. 3-1 in next section). Data for the intensity dependence were taken at the peak of the initial photoinduced signals and at a delay time of 50 ps. The excitation intensities were corrected for transmission and reflection losses of samples. Shown in Fig. 32 are photoinduced changes for several excitation intensities. A more pronounced long tail was present in the PIB at higher radiant intensity. Nevertheless, if the peaks of photoinduced changes were normalized, there is no apparent distinction between different excitation intensities. This means that there is no intensity dependent decay in this system, which is a signature of one-photon process. The logarithm plot of PIB intensities of the exciton band vs. pump intensities is exhibited in Fig. 33. The intensity dependence of the PIB has revealed an unimolecular relaxation at radiant densities range from 5 $\mu$J/cm$^2$ to 80 $\mu$J/cm$^2$. The unimolecular rate has demonstrated that the nature of photoexcitation for the 2 eV band of EB is truly excitonic. This result is consistent with previous study on near-steady-state photoinduced bleaching of EB, which showed a linear intensity dependence in ms time scale. Notice that the intensity dependence at 50 ps delay time follows a superlinear behavior (a slope of 1.2 from the logarithm plot of the photoinduced changes vs. excitation intensities). A possible origin is that at high number densities, screening of the Coulomb interaction impairs the mutual binding of the electrons and holes, and the molecular excitons prevail longer.

The photoinduced bleaching of EB in NMP was reproducible for every fresh sample and the signal persisted for several hours in each experiment. However, there was evidence for the existence of long-lived species (> ns), for experiments in which the samples sat for several days after extensive exposure to laser (See Fig. 34). This happened in both spinning cell and flowing jet setups. These long-lived components can be fit to a single exponential ($\tau \sim 3$ ns). As samples kept aging, the photoinduced intensity of the long-lived components gradually increased (see Fig. 35 inset). Eventually, the long-lived components dominated for aged samples of EB in NMP. The decay of the long-lived species can be fit to single
Fig. 32. Picosecond PIB of EB in NMP at several different radiant intensities.
Fig. 33. Logarithm plots of $\Delta T/T$ vs. pump intensities at the maximum (open circle) of the photoinduced changes and at a delay time of 50 ps (open square). Solid lines are linear fit of the data.
Fig. 34. Picosecond PIB of EB in NMP for a sample with four hours of constant exposure to laser light. Notice that there are traces of photoinduced changes after time delay of 200 ps. Inset: A single exponential fit of the long-lived decay.
Fig. 35. Picosecond PIB of an aged sample of EB in NMP via a flowing jet setup. Inset: Photoinduced changes of a ten days old sample of EB in NMP.
exponential with a time constant of 4.5 ns (Fig. 35). The absorption spectra of EB in NMP for fresh and aged (after irradiation) samples are shown in Fig. 36. The exciton band and the \( \pi-\pi^* \) transitions of EB peak at 2.0 and 3.81 eV, respectively, for fresh samples. The color of aged EB solution has changed from dark blue to light purple. The absorption spectrum of aged samples of EB/NMP peaks at 2.39 and 3.9 eV with a side band of 4.2 eV (see Fig. 36), which resembles that of PNB (see Fig. 8). A vibrational structure study via infrared absorption is not possible for polyanilines in NMP solution owing to the fact that NMP absorbs too strongly in the IR, which obscures the IR absorption of polyanilines.

This result seems to imply that the photoinduced bleaching from photoexcitations of the Peierls gap of PNB in NMP would persist for a longer time than photoexcitations of the exciton of EB in NMP. Nonetheless, like EB in NMP, PNB in NMP solution only possesses very short-lived components with photoexcitations into the Peierls gap. Shown in Fig. 37 is a photoinduced bleaching rise and decay of PNB in NMP with an excitation and a probe energy of 2.1 and 1.95 eV, respectively. The inset (1) of the Fig. 37 displays the variation the photoinduced intensity for probing energies range from 1.84 to 1.95 eV. From the trend of the spectrum of the photoinduced bleaching, the maximum of the bleaching energy at picosecond time scale should be closer to the Peierls gap (2.35 eV). The ps PIA results are in good agreement with the results of the near-steady-state study of the photoinduced bleaching of the Peierls gap of PNB, which peaks at 2.15 eV. This indicates that the lattice relaxation is completed within picosecond for photoexcitations of the Peierls gap of PNB. Preliminary results of the intensity dependence study show a linear behavior for the PIB from radiant energy densities of 10 to 35 \( \mu J/cm^2 \) (see Fig. 37 inset(2)). This seems to contradict with the conception that the 2.3 eV transition is a band to band transition for PNB. A possible origin lies in the separation of the charges which is correlated with the escape probability of the charges after initial (light) field. In other words, there is competition between geminate recombination and charge diffusion. It is important to recognize that, for photoinduced bleaching studies, the recovery of the ground state can be look upon as a unimolecular dynamics at low depletion percentages.
Fig. 36. Absorption spectra of fresh EB and aged EB in NMP.
Fig. 37. Picosecond PIB of PNB in NMP with pump and probe energies of 2.1 and 1.95 eV, respectively. Inset (1): Photoinduced changes at different probing energies ranged from 1.84-1.95 eV. Inset (2): Preliminary results (dots) of the intensity dependence study of the PIB at 1.95 eV. (The solid line is a linear regression of the data) The intensity dependence is linear for radiant densities ranged from 5 to 20 μJ/cm².
Since fresh samples of PNB in NMP did not possess long-lived photoinduced components, it was important to clarify that the long-lived components were not some kind of artifact. A good spatial overlap between the pump and the probe beams is critical to photoinduced experiments. The simply way of maintaining a good spatial overlap is by letting the beam waist of the probe beam larger than that of the pump beam at the front surface of the focus lens. Usually, after producing the initial photoinduced signals, I would adopt procedures similar to those described in the following to check and improve the alignment.

The absolute intensity of the probe pulses for aged EB samples was examined. Figure 38-39 show the probe intensity changes for typical photoinduced scans of an aged solution at various time delays. The changes of the transmission of the probe beam ($T_{\text{probe}}$), while processing a picosecond photoinduced scan at various time delays from -50 to 5000 ps, are reproduced in the inset of Fig. 3.38b. The $T_{\text{probe}}$ was obtained by measuring the DC signal from a photodiode. The photoinduced change of the transmission of the probe field, $\Delta T_{\text{probe}}$, was recorded from the AC signal (reference to the modulation frequency of the pump beam) of the photodiode. (Note that the photoinduced decay in Fig. 35 is created from the ratio between the described $\Delta T_{\text{probe}}$ and $T_{\text{probe}}$.) It is typical for a 10% change in $T_{\text{probe}}$ to occur when the optical delay is varied from 0 ps to 5 ns, owing to the divergence of the probe beam at longer optical path.

Furthermore, I adjusted the timing between the pump and probe pulses by an additional 26 ns delay ($t_{\text{pump}} - t_{\text{probe}} = 26$ ns). This was achieved by switching the time delay between the cavity dumper drivers for the pump and probe pulses. Therefore, the timing between pump and probe pulses were no longer coincidence. What I was monitoring was the change of the probe field with only spatial overlap but no temporal overlap of the pump field. This should examine the presence of any artifacts that might occur in the data collection configuration. Shown in Fig. 38a are the $T_{\text{probe}}$ ($\Delta t + 26$ ns) and the $\Delta T_{\text{probe}}$ ($\Delta t + 26$ ns). The ratio of the above two values is shown in Fig. 38b, where the change of the $\Delta T/T$...
(a) Variations of the transmission of the probe beam propagating through a sample of EB in NMP with the geometrical overlap of the pump field but at -26 ns delay time. $T_{\text{probe}}$ and $\Delta T_{\text{probe}}$ are obtained from an DC and an AC measurements, respectively. 

(b) Ratios of $\Delta T_{\text{probe}}$ over $T_{\text{probe}}$. Shown in the inset is the variation of $T_{\text{probe}}$ while taking a real photoinduced scan.

Fig. 38.
is around 20% from 26 ns to 26 + 5 ns. Nonetheless, the data presented above resemble each other in the trend of the variation of $T_{\text{probe}}$ with respect to time delays.

I have also investigated the variation of the $T_{\text{probe}}$ by monitoring the $T_{\text{probe}}$ with a mechanical modulation (by applying a mechanical chopper in the light path of the probe beam) under the presence of the pump beam on the sample. In Fig. 39a, the solid line displays the AC changes of the probe intensity, and the dots represent the DC average of the probe intensity. The decrease of the transmission of the probe pulses with an increase of the time delay is again probably due to the divergence of the probe beam at longer delays (longer light paths). The ratio between the AC and DC signals gives $\Delta T/T$: the modulated changes of the probe pulses under the presence of the pump pulses (see Fig. 39b). Although the intensity of the probe field decreases as the time delay increases for either AC (from a lock-in) or DC (voltage readings from a photodiode) measurements, the modulated intensity of the probe pulses rises as the delay between the pump and probe gets longer. These results have shown that the long-lived components observed in aged samples of EB/NMP were not due to 'artifacts' from the data collection.

These data suggest that photoexcitations might create more quinoid sites in the polymer through oxidation of phenyl moieties. Along with the process of the oxidation of phenyl rings, interchain cross-linking might also occur. It requires further investigation to justify if the long-lived components are due to the obstruction of (e-h) recombination by cross-linking of the polymer. (See later in this chapter for a discussion of crosslinking in polyaniline)

The dynamics of the PIB of EB and PNB also was studied with $\pi-\pi^*$ photoexcitation. This was accomplished by frequency doubling the 2.1 eV pulses. Even though substantial peak power (35 nJ) of the UV source could be obtained by amplifying the 2.1 eV pulses with a six-pass amplifier as described in chapter 2, the radiant intensity was kept below 10 $\mu$J/cm$^2$ (2 nJ per pulse). The reason for this will be clear from the following results. Shown in Fig. 40a is a photoinduced bleaching of EB in NMP at 1.9 eV with 4.2 eV
Fig. 39. (a) Transmission of the probe beam propagating through a sample of EB in NMP obtained by modulations of the probe beam with an AC ($\Delta T_{\text{probe}}$) and an DC ($T_{\text{probe}}$) measurements. Note that the pump beam was geometrically and timingly overlapped with the probe beam. (b) Ratios of $\Delta T_{\text{probe}}$ over $T_{\text{probe}}$.
Fig. 40. (a) $T_{\text{probe}}$ (1.88 eV) of EB in NMP with 4.2 eV excitation scanning from -20 to 50 ps (forward scan) then from 50 to -20 ps (backward scan). (b) $\Delta T/T$ for forward and backward scans. The photoinduced signals disappeared within several minutes of exposure of the UV laser.
pump. The data collection time was about two minutes. Radiant densities of the pump and probe pulses were 8 and 4 μJ/cm², respectively. A pump pulse of 8 μJ/cm² (1.5 nJ per pulse) was the low end of the radiant density that gave photoinduced signals. The forward and backward scans of the ps PIB did not coincide with each other. The PIB also disappeared within several scans of experiments—that was about 30 min of exposure time. I estimate there were ~ 7 x 10¹⁶ excitation photons received by the sample within the period of the experiment. The total monomer moieties were ~ 8 x 10¹⁶ in the sample. The Tprobe of the photoinduced bleaching is shown in Fig. 40b. The transmission of the probe field increased with the evolution of the photoinduced experiment and eventually saturated at certain level. This demonstrates that the photobleaching of the ground state was very rapid and was not recovered by spinning the solution. The photobleaching was also irreversible as the Tprobe saturated after some exposure time.

In comparison to the ps PIA of trans-4,4'-diphenylstilbene (DPS) in dioxane (Fig. 41a), the Tprobe and the ΔT/T of DPS almost mirrored each other and the PIA stayed constant for a substantial period of time (in terms of the exposure time, it can last at least several days at comparable radiant intensity). Fig. 41b shows the Tprobe (1.9 eV) for PNB in NMP at pump energy of 4.2 eV, which underwent a initial sharp rise and saturated swiftly. The ΔT/T of PNB in NMP with 4.2 eV pump was very noisy and without obvious feature. The color of the PNB and the EB solutions bleached and turned transparent after the photoinduced experiments. The absorption spectra of the above solutions are shown in Fig. 42. Notice that the visible bands of EB and PNB disappeared after the exposure. The peak positions in the spectra are also displayed in the enlarged view of the spectra. Notice that there is a spike at 3.9 eV in the absorption spectrum of the PNB solutions, which is probably due to some artifacts. These data suggest that quinoid moieties in PNB and EB underwent some photochemical reactions by photoexcitation into π-π* states. As a final note of the study of PIB by π-π* photoexcitations, Tprobe for UV and visible photoexcitations of EB are shown in Fig. 43. In contrast to 4.2 eV pump, the Tprobe for 2.1 eV excitation stayed at a constant level for a lengthy period (exposure time of several hours for 100 mW average power for a sample
Fig. 41. (a) $\Delta T/T$ and $T_{\text{probe}}$ of DPS in dioxane with pump at 4.2 eV and probe at 1.9 eV. (b) $T_{\text{probe}}$ of PNB in NMP with pump and probe energies same as in (a). The $T_{\text{probe}}$ saturated instantly after the application of the pump field.
Fig. 42. Absorption spectra of EB and PNB in NMP after 4.2 eV irradiation (30 \( \mu \)J/cm\(^2\)) of several hours. Peak positions of the spectra are indicated in the enlarged view. The absorption spectra for fresh samples of polyaniline are also shown. The spike at 3.9 eV is probably due to some artifacts.
Fig. 43. Variations of the probe field (1.88 eV) from -20 to 100 ps with 2.1 or 4.2 eV photoexcitations. The fluctuation of the $T_{\text{probe}}$ was less than 2% from -20 to 100 ps for 2.1 eV photoexcitations.
of $10^{17}$ monomer units). Thus, UV excitation is the likely cause of the observed results in which photoinduced crosslinking might have occurred (see next paragraph).

Yan Sun et al. investigated thermal degradation of polyaniline [127]. They obtained a series of UV-VIS absorption spectra for an EB film heated at 540 K with increasing time periods. The exciton transition at 1.96 eV shifted to 2.06 eV after the first two minutes of heating and then remain essentially constant. The intensity of the exciton peak also decreased continuously with heating time while the intensity and the peak position of the $\pi-\pi^*$ transition remain unchanged. So, the quinoid units, which are responsible for the exciton transition, are thermally converted to other units which do not have any absorption in the region of 1.4 to 4.8 eV. Sun et al. proposed a crosslinking scheme for the polymer (see Fig. 44). Notice that the mass is conserved in this scheme, which is confirmed by an elemental analysis [127].

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**Fig. 44.** A proposed mechanism for reductive thermal crosslinking of EB. After [127].
The differences observed in the dynamics of polyaniline in different environments (free volume and inter-chain packing) are very unique. Most organic polymers, degenerate or nondegenerate, do not possess a large excited population at ns delays after photoexcitation \([61,63,108,128]\). Following the initial photogeneration, electron-hole pairs are more likely to recombine quickly due to screened Coulomb interaction and confinement of lattice energy. The exciton formation of EB is due to a charge transfer from two neighboring benzenoid moieties to the quinoid ring. It is stabilized through a ring torsional twist of the quinoid ring with respect to the plane formed by the nitrogen atoms. In solid form, the deactivation of this ring twist is constrained by inter-chain packing. Thermal activation of free volume for rotation is required for charge recombination. The free volume is larger in solution than in the solid, so inter-chain interactions are less likely to occur in the solutions I studied. Therefore, excitons formed in solution are not as stable as the ones formed in the solid and should relax more quickly. To substantiate that the excitons are formed only with light parallel to the polymer chain, I have also studied the polarization behavior of the photoinduced bleaching. I did not observe any significant differences in the intensity of the photoinduced signals or in the relaxation dynamics with pump and probe lasers parallel or perpendicular to each other. This strongly supports the localized picture of exciton formation and suggests initial inter-chain excitations are less likely to occur. The linear power behavior for EB and PNB in the two types of samples suggests the initial charge separation mainly recombined geminately. Near steady state PIB study of PNB has shown bimolecular power dependence for the Peierls gap. The discrepancy in power dependence between the initial photoexcitations and the near steady state condition may be because the initial excitations are mainly intra-chain excitations. Since the magnitude of the photoinduced changes is small \((\Delta T/T \leq 10^{-3})\), the apparent linear effect may also have a contribution from other sources such as the existing neutral soliton defects in the PNB, which absorb around 1.6-2.0 eV \([121,129]\).

The direct charge recombination of EB and PNB in solution behaves differently than usual geminate recombination, \(i.e.,\) the decays at different excitation energies do not fit to
either an exponential or an error function well [96]. The initial photoinduced signal decays nonexponentially with a time constant less than 20 ps. There is a possible crossover to a power decay, which is the signature of dispersive controlled multiple trapping [130,131]. The 20 ps time constant is larger than the subpicosecond recombination time usually observed in electron-hole correlated pairs [96,132], therefore, the direct recombination of photoexcited charges may have to go through a small barrier. The temperature independence earlier observed [117] in the film can be explained by a tunneling effect of the barrier [133]. The linear energy dependence of the photoinduced bleaching intensity at low power supports the unimolecular relaxation dynamics observed in the near-steady state experiment. This is particularly true in solution, where the inter-chain processes are less likely to occur.

The cross-section for two-photon absorption increases with the square of the intensity of photon energy. At high pump photon energies, two photon absorption processes can contribute substantial to the photoexcitation of EB. A two-photon absorption in EB will be a π-π* transition, which is localized primarily on the benzenoid ring. The fluorescence decay life time of (fully reduced and partially oxidized) LEB with 3.65 eV excitation is on the order of 1 ns to 100 ps [134]. Charge transfer from the excited benzenoid ring to neighboring quinoid ring is expected to occur on a ps time scale. These energy transfer induced excitons, which pass a large amount of internal energy, will cause the broadened long tail observed in picosecond photoinduced bleaching of EB in NMP at high pump powers. The significance of this multiphoton effect is indicated by the intensity dependence of photoinduced bleaching scaled to 1.2 at 50 ps.

In summary, the effects of ring rotational hindrance on lattice relaxation of exciton band of EB and the Peierls band-to-band transition of PNB were studied. The experimental results provide further evidence that long-lived defects of EB are stabilized through ring rotational and inter chain packing effects. The charge recombination of the excitons behaves differently from geminate recombination. Power dependence study of the photoexcitation supports the unimolecular relaxation dynamics at low power and shows a profound multiphoton absorption at high power.
Diffusion and trapping of polarons in polyaniline: picosecond photoinduced absorption studies of leucoemeraldine, emeraldine and pernigraniline bases in solution and solid forms

Introduction

One of the common features of the three oxidation states of polyaniline is a broad photoinduced absorption band around 3 eV appearing at near-steady state upon photoexcitation of the polymers [24,113,114]. This photoinduced band was assigned to a positive (hole) polaron band since the intensity dependence of the photoinduced absorption band under near-steady state conditions scales bimolecularly. And the overall number of photoinduced bands was consistent with features that typically arise from polaronic type defects. These bands match up well with new bands that are produced from protonation [135]. The polaron is attributed to a positive charge centered on a phenyl ring (see Fig. 45). One of the unsolved issues in these polaron defects is the nature of the defect and its relation to molecular conformation and electronic structure of the polymer backbones. Theoretical calculations on pentamers of the polymers have shown that the induced positive polaron extends over about four amine units for LEB [136]. The polarons are more localized in EB and PNB, with the positive charge confined to one ring and its neighboring C-N bonds. Room temperature frequency dependent studies at near-steady-state conditions of the polaron bands for EB, PNB and LEB have shown a frequency behavior of $f^{-0.1}, f^{-0.3}$ and $f^{-0.2}$, respectively [24,113,114]. This frequency behavior represents a faster recombination rate in near-steady-state condition for LEB than for EB or PNB. This suggests that more delocalized polarons are more likely to recombine with each other. It is speculated that at near-steady state conditions, the relaxation mechanism of the polarons follows bimolecular recombination from “well relaxed” photoexcited species. Therefore, the relaxation should derive from the probability of defect-defect annihilation and phonon-assisted processes and
Fig. 45. The hole polaron is centered on a phenyl ring with the ring rotated certain torsional degrees relative to its the ground state configuration.

cannot be realized just from a local picture of an individual polaron.

In order to probe the nature of the formation of the polarons and their dynamics, picosecond photoinduced absorption (PIA) spectroscopy of the three types of oxidation states of polyaniline was investigated. I have studied samples in solution of NMP, spin-cast films, and powders in KBr substrates. Solution samples were prepared under an inert gas environment and sealed under vacuum. The reason for studying samples in solution and solid forms is that interchain packing is expected to play an important role in the formation and relaxation of the polarons. Picosecond photoinduced absorption (PIA) experiments were performed with a dual synchronously pumped, cavity-dumped dye laser system that has been described previously (see Chapter 2). The third harmonic output of a YAG laser fundamental was used to excite stilbene 420 dye to generate 2.9 eV pulses for the probe
beam. Pumping energy of 2.1 eV was obtained from a Rhodamine 6G dye laser and used to excite EB into the molecular exciton band or PNB into the Peierls gap. For pumping intensity dependence studies, the 2.1 eV pulses were amplified with a six-pass dye amplifier pumped by a cavity dumped Ar ion laser. The pump intensity was varied by combinations of neutral density filters and by adjusting the intensity of the acoustic wave for the cavity dumper. The amplified output was frequency doubled with a nonlinear optical crystal to generate 4.2 eV pulses, when a UV source was required to excite polyaniline into the $\pi-\pi^*$ transitions [137]. Throughout the experiments, the radiant intensity of the probe pulse was kept below 20% of the pump pulse. The total radiant energy density was ranged from 10 to 200 $\mu$J/cm$^2$ for solution samples and was kept below 20 $\mu$J/cm$^2$ for samples in solid form. The time resolution was limited by the 8 ps cross correlation of the pump and probe pulses. Besides mechanical modulation, a time modulation technique [105] was incorporated in the pump-probe experiments to eliminate heating artifacts in the samples during data collections. Spinning of the solution samples served to remove effects due to heating and possible thermal lensing.

Results

2.1 eV photoexcitations and 2.9 eV probe

Fig. 46 shows a typical PIA from -20 to 200 ps for EB in NMP. A PIA from -100 to 4000 ps for a EB film is also presented in the inset. The rise of the PA signals was instrument limited (< 10 ps) for both solution and film. The PIA in solution decays within 20 ps and the FWHM of the peak is about 15 ps. Notice that this is even more rapid than the exciton bleaching of EB in NMP (see last section). The initial PIA signal of the EB solution was found to follow closely to a convolution of a single exponential of 3 ps and the laser pulse envelop. There were only traces of background signals observed beyond 50 ps, which could arise from long-lived species. In contrast, the PIA in EB film persisted for several ns, with 50% of original signal at 5 ps still remaining at 4 ns. Several attempts were made to fit the decay of EB/NMP to some functional form(s). These attempts met with of limited
Fig. 46. Picosecond PIA of EB in NMP with pump and probe energies of 2.1 and 2.9 eV, respectively. Inset: Photoinduced absorption decay of an EB film with experimental conditions similar to those of the EB solution.
success. It appears that, $\Delta T/T = A\exp(-t/\tau_1) + B\exp(-t/\tau_2) + C$ provides the best fit with $\tau_1 = 8$ ps, $\tau_2 = 1$ ns, $B/A = 0.18$, and $C/A = 0.086$. The decay mechanism is certainly not a simple geminate recombination controlled by 1D diffusion as seen in polyacetylene: $\Delta T(t) = \text{erf}\left(\frac{\tau_0}{t}\right)$ ($\tau_0^{-1}$ is the jump rate of 1D diffusion) [96]. The fast decay components retain traces of probe pulses which obscured the true decay. In contrast, the decay for the polaron bands in a film follows a dispersive transport decay scheme [130]:

$$\frac{\Delta T}{T} = \frac{n_1 - n_2}{1 + \left(\frac{t}{\tau}\right)^\beta} + n_2$$  \hspace{1cm} (3.1)

with $\tau = 130$ ps and $\beta = 1.2$. A biexponential form also gives a good fit, with $\tau_1 = 130$ ps and $\tau_2 = 1.3$ ns. It is suggested that the polarons (in films) perform random walks from trap to trap along the polymer chain or hopping to neighboring chains before recombining with other polarons. The dynamics of the polarons is controlled by the rate of diffusion and the rate of polaron-polaron recombination. It is important to recognize that the microscopic 'friction' could affect the dynamics of the conformational change (torsional angles and bond lengths) in polymers. In photoinduced states, a larger 'friction' leads to a larger probability of localizing the photoinduced states to some trap states. Therefore, the chances of forming stabilized polarons in films are better than in solution. In solution, the escape probability for a hole polaron is low, in other words, the rate of recombination of a hole polaron with an electron (or a negative polaron) is high with a small microscopic 'friction' (esp. for the torsional degrees of freedom).

Results for PNB in NMP were very similar to those for EB with only fast decay components relaxing within 20 ps (Fig. 47). The PIA of PNB in NMP appears to have less background traces than that of EB/NMP. Deconvolution of the photoinduced signal gives an exponential decay of $\tau \sim 1$ ps. The shape of the decay can also be fit to a power law of the form $A t^{-\beta} + C$, with $\beta = 0.8$. It appears that the recombination rate is larger in PNB/NMP than in EB/NMP. This implies the hole polaron in PNB/NMP adopts a decay closer to usual geminate recombination [138]. However, it requires caution in interpreting results of fittings
Fig. 47. Picosecond PIA of PNB and LEB in NMP from -20 to 50 ps. The pump and the probe energies were 2.1 and 2.9 eV, respectively.
from fast decays close to or within the instrument limit. Fitting results could be just some artifact created from limited data distributions, which have no true physical meanings. Normally, it can only be stressed that the decay observed is within the instrument limit. I have also investigated the dynamics of LEB with subband gap photoexcitation. Depending on preparation and preservation methods, LEB may contain certain amount of residual quinoid rings. These quinoid moieties can be subjected to yellow light absorption (~ 2 eV) which should create molecular excitons with negative charge centers on quinoid ring. It would be interesting to compare ‘excitons’ created in LEB with those of EB. Shown together with the PIA of PNB/NMP, is the PIA dynamics from –20 to 50 ps for LEB in NMP with 2.1 eV photoexcitations (Fig. 47). The PIA of LEB in NMP is similar to those of EB and PNB but has a larger FWHM and a longer tail. The decay follows closely to power law with a slope of 0.9. It appears that the polaron in LEB sustains longer than the polarons in EB and PNB, which is a contradiction to the phenomenon observed under near-steady-state conditions (see the introduction section). It is suggested that, under near-steady-state or steady-state conditions, the dynamics of the polaron is controlled by the rate of polaron-polaron annihilation, i.e., mainly related to the population of the polaron. On a picosecond time scale, the initial charge separation also affects the dynamics. Since the hole polaron is more delocalized in LEB than EB and PNB, the rate of geminate charge recombination for the polaron is smaller in LEB than in EB and PNB.

Photoinduced absorption of PNB powder in substrates of KBr is shown in Fig. 48a. The PIA also possesses long components which are similar to those of EB films. However, the long components in PNB powder have a faster decay time with less than 10% of the original signal remaining at 4 ns. The transient decay of PNB powder was found to fit closely to a biexponential or a power law form. Briefly, in biexponential form, \( \tau_1 = 100 \) ps and \( \tau_2 = 1.5 \) ns; the index is 0.31 for the power law form.

I now focus on the issue of the variation of \( T_{\text{probe}} \)'s (2.9 eV) in picosecond photoinduced absorption of polyanilines. Shown in Fig. 49a is a decay of the 2.9 eV polaron
Fig. 48. (a) Photoinduced absorption of PNB powder in substrates of KBr from -20 to 4000 ps. The pump and probe energies were 2.1 and 2.9 eV, respectively. Shown in the inset in the PIA from -20 to 100 ps. Note that the forward (open circles) and reverse (open squares) scans coincided with each other. (b) Variations of the phase angle and the $T_{\text{probe}}$ from -20 to 100 ps.
Fig. 49.  (a) Photoinduced absorption of EB in NMP from -20 to 200 ps. The experimental conditions were the same as above mentioned in Fig.48.
(b) Variations of the phase angle and the $T_{\text{probe}}$ from -20 to 50 ps.
band of EB in NMP from -20 to 200 ps. Fig. 49b displays the corresponding changes of the phase angle and $T_{\text{probe}}$ of the PIA from -20 to 50 ps. Notice the dip of the $T_{\text{probe}}$ scanning from negative time delay toward positive time delay. As mentioned in chapter II, the phase of the lock-in detection is from the reference frequency, which can have nothing to do with the 'real phase' between the pump and probe pulses. Nonetheless, I did observe a change of phase around zero time delay. This indicates that the picosecond transient photoinduced absorption is correlated with the µs or ms photoinduced absorption. Polaron created in the subpicosecond time scale survive after several ms. Normally, it is difficult to determine the absolute phase change in picosecond photoinduced absorption. Thus, in order to determine whether it is a photoinduced absorption or photoinduced bleaching, it is generally a good practice to compare changes of the $T_{\text{probe}}$ of the system under study with some well known systems.

Fig. 50 shows the $\Delta T/T$, the $T_{\text{probe}}$ and the phase change for the PIA of DODCI in dioxane. Depending on the experimental conditions, the $\Delta T/T$ of DODCI can range from a few to ten percent. The PIA of DODCI is also a good reference for time delays between the pump and the probe fields. The variation the $T_{\text{probe}}$ from negative toward positive time delays clearly indicates the change of the probe field is a photoinduced absorption. The phase angle of the lock-in detection changed from ~ $110^\circ$ to ~ $10^\circ$ from -20 to 10 ps for the PIA of DODCI. I compared trends of the phase angle, $\Delta T/T$ and $T_{\text{probe}}$ between DODCI and polyanilines to determine the sign of the $\Delta T/T$ for polyanilines. For most experiments of 2.9 eV probe, the photoinduced changes reduced the intensity of the probe field (photoinduced absorption). However, thermal effects, photophysical and photochemical alternation of the polymer structure could all lead to variations of the oscillator strengths of the corresponding states. I observed sample damage at high radiant density, which gave peculiar photoinduced behaviors; photoinduced changes can be reduced or increased with the probe field. Sometimes, the probe field increased in transmission not due to a removing of states but by physically removing the absorption sites: probably the results of some photochemical transformation of the interacting sites. It is extremely important to keep the total radiant
Fig. 50. (a) Variations of $T_{\text{probe}}$ and $\Delta T/T$ of DODCI in methanol. Conditions were the same as above mentioned in Fig. 48. (b) A plot of phase angle vs. time delay for the PIA of DODCI in methanol.
density low on solid samples. I had seen many unusual photoinduced behaviors in films and powder studies of polyanilines. Since the photoinduced changes are usually small for polyanilines in solid form, it took great effort to maintain the balance between substantial photoinduced changes and to minimize local heating and thermal effects. As for solution samples, situation is much simpler since most radiant heat will be dissipated well by spinning or flowing of solutions. Care still needed to taken to avoid too much light power going into samples, which might cause some sample damages.

As a final note for the 2.1 eV photoexcitation experiments, a PIA of PNB/KBr at low temperature (~ 200 K) is presented in Fig. 51. The phenomenon resulted from a medium radiant energy density (25 µJ/cm²) of the pump beam, which provoked a thermal effect at the absorption spot. The forward and backward scans deviated from each other, the discrepancy was more pronounced around zero time delay (Fig. 51a). I suggest that the oscillator strength for the polaron band or the number of defects decrease as the temperature of absorption spot increases. $T_{probe}$ also decreased during the exposure of light (see Fig. 51b). So that, instead of the decrease in number of defects, the decrease of the $\Delta T/T$ could also arise from a larger $T_{probe}$ that is, the decrease of absorbing sites. Notice that the phase change had a smaller response for the backward scan, which was consistent with the reduce in $\Delta T/T$.

4.2 eV photoexcitations and 2.9 eV probe

It is worthwhile to discuss the results of the photoinduced experiments with a 4.2 eV pump and a 2.9 eV probe. Shown in Fig. 52 are the PIA of the 2.9 eV band of LEB and EB in NMP. It is obvious that with 4.2 eV pump, the 2.9 eV polaron band of EB in NMP persists longer than with 2.1 eV pump. In contrast to photoexcitation of exciton band, positive polarons generated from $\pi-\pi^*$ photoexcitation lasted ~ 300 ps for EB in NMP. The 2.9 eV PIA of LEB in NMP demonstrates the long-lived nature of the positive polaron in LEB. The PIA decay is similar to PIAs or PIBs of solid forms of PNB and EB with 2.1 eV photoexcitations. The decay of LEB/NMP was found to fit closely to a stretch exponential form: $\Delta T/T \sim \exp\left(-\frac{t}{\tau}\right)^{0.38}$. A fit to a dispersive transport form gave a time constant of 300
Fig. 51. (a) Picosecond PIA of PNB in substrates of KBr from -20 to 4000 ps at 200 K. Inset: The forward (open circles) and reverse (open squares) scans of the PIA. Notice the reduction of the oscillator strength for the reverse scan of the PIA. (b) Variation of the phase angle and $T_{probe}$ of the PIA from -20 to 50 ps.
Fig. 52. Photoinduced absorption decays of LEB and EB in NMP from -20 to 2500 ps with pump and probe energies of 4.2 and 2.9 eV, respectively.
ps for LEB/NMP. For EB in NMP, at \( \Delta t > 40 \) ps, the decay can be fit to a biexponential form with time constants of \( \tau_1 = 100 \) ps and \( \tau_2 = 7 \) ns.

The rise time of PIAs for EB and LEB in NMP were comparable to each other (Fig. 53). The time shift of the rises were \( \sim -5 \) ps relative to the zero delay determined from the rise of 2.9 eV PIA of DODCI in methanol. This signifies the similarity of the fast decay of positive polarons in EB and LEB, which is less than 1 ps as obtained from deconvolution of the rise time of the PIAs. I have also studied the PIA of PNB in NMP and the results were similar to those of EB in NMP. Fig. 54 displays the 2.9 eV PIA of LEB/NMP at several radiant energy densities. The normalized decays for different intensities coincided with each other fairly well--there is no intensity dependent decay for positive polarons of LEB. The intensity dependence study for the above has shown a superlinear dependence (slope \( \sim 1.5 \)) for a logarithm plot of intensity vs \( \Delta T/T \). Notice that, for fresh LEB samples, the PIA persisted longer initially for a constant level till time delay \( \sim 500 \) ps (see the forward scan of the PIA, Fig. 55a). This phenomenon disappeared as samples were exposed a few minutes to the UV laser. There was nothing peculiar about the \( T_{\text{probe}} \) for the PIA of LEB/NMP (see Fig. 55b). Both forward and backward scans tracked each other well. It is suggested that initially the photoexcitation caused highly populated electrons and holes, which lead to the stabilization of the positive polarons (Coulombic screening effect).

**Intensity dependence study for 2.1 eV photoexcitations**

I now consider the intensity dependence studies of the positive polaron bands created from 2.1 eV photoexcitations. Logarithm plots of \( \Delta T/T \) vs radiant density of several samples of EB and PNB are collected in Fig. 56. The intensity dependence study depicts a linear behavior for the PIAs of polyanilines. Note that at low radiant densities \((< 50 \mu J/cm^2)\), the slope is 0.8 for EB in NMP. The intensity dependence shifted toward linear (1.1) as the radiant density increased. Solid form samples of polyanilines also behaved linearly in the variation of \( \Delta T/T \)'s as illustrated from the results of a EB film and PNB powder. The results
Fig. 53. Comparison of rises for LEB, EB in NMP and DODCI in methanol under the same experimental conditions. The pump and probe energies were 4.2 and 2.9 eV, respectively.
Fig. 54. Photoinduced absorption decays of LEB in NMP at three different radiant densities from -20 to 2500 ps. The pump and probe energies were the same as mentioned above in Fig. 53. Shown in the inset are the normalized decays.
Fig. 55. (a) Variations of the probe field from -20 to 2500 ps in a photoinduced absorption scan of LEB in NMP. The experimental conditions were similar to above mentioned in Fig. 53 (see text for details). (b) $\Delta T/T$ from -20 to 2500 ps. Notice that the forward and reverse scans were not consistent.
Fig. 56. Logarithm plots of $|\Delta T/T|$ vs. $T_{\text{probe}}$ for EB and PNB. The photoexcitation energy was 2.1 eV and the probe energy was 1.88 eV. The slope are 0.8, 0.9, 0.85, 1.1 and 1.1 for EB/NMP, EB (film), PNB (in KBr), EB/NMP (high radiant intensities) and PNB/NMP, respectively. The radiant intensities are in the range from 0.2 to 150 $\mu$J/cm$^2$ (The 'INTENSITY' axis scales as $1 = 1$ $\mu$J/cm$^2$).
of PNB in NMP were distinct from the results of EB/NMP in that the variation of $\Delta T/T$'s followed a linear behavior for radiant densities ranged from 10 to 200 $\mu$J/cm$^2$.

Discussion

The experimental results of the PIA studies are discussed in this section. There was no delay in the rise of the photoinduced absorption signals for the polaron bands for any polyaniline sample that was studied. This indicates the polarons in polyaniline were generated within our time-resolution limit, 10 ps. The kinetics for the rate of polaron generation can be expressed as:

$$\frac{dn}{dt} = \alpha I \gamma [n_o] - \beta [n]^\nu + \frac{D \partial^2 n(x,t)}{\partial x^2}$$

(3.2)

where, $n$ is the number density of the polarons, $n_o$ is the number density of valence electrons, $\alpha$ is the absorption coefficient, $I$ is the flux of photons, $\gamma$ is the order of intensity law, $\beta$ is the recombination rate, $\nu$ is the order of recombination, and $D$ is the diffusion coefficient. The multiphoton transition probability is enhanced by the resonance effect of $\pi-\pi^*$ transition as can be seen by the superlinear power dependence observed in the LEB experiments. Multiphoton absorption is also the possible explanation for the power dependence of PNB and EB with slightly superlinear dependence at high radiant intensities.

While the creation of polarons (or polaron excitons) is rapid in polyaniline, it is important to recognize the intrinsic difference in the creation mechanism of polarons for LEB, EB and PNB. The 2.1 eV excitation of EB generates molecular excitons. According to Duke et al.[123], the formation of a molecular exciton on a quinoid ring in EB results in a rotation of the ring of approximately 90° relative to its ground state conformation. The rotation is accompanied by a redistribution of charge that can be described by charges of $e/2$ moving from the two neighboring benzene rings, forming a charge of $e$ on the quinoid ring (see Fig. 27). The charge distribution spreads over three rings and two imine units between the rings. Recalling the PIB results in this chapter, a time resolution limited rise was
observed for the picosecond photoinduced bleaching of the exciton band of EB. A fast decay (< 30 ps) for the exciton band in NMP also was observed. As pointed out above, the positive polaron in EB is mainly localized in a phenyl ring and adjacent amine units (70% of a positive charge). The phenyl ring and adjacent C-N bonds adopt a semiquinoid geometry and the ring becomes coplanar with the nitrogen plane. It is possible that the initial rise of the PA for the 2.9 eV polaron band is due to the +e/2 localized positive charge from the molecular exciton. In solution, the conformation of polymers is subjected to a larger free volume for ring rotation as compared to polymers in solid form. The molecular exciton or polaron exciton is promptly prone to geminate recombination if the conformational change of the ring torsional angle is free to rotate back to its ground state conformation. Therefore, the rise and decay of the PA of the positive polaron of EB in NMP should coincidence with the formation and decay of the molecular exciton band in NMP. The situation of photoexcitation of EB films differs from EB in NMP in that the present of neighboring chains can lead to separated charged polarons (P⁺ P⁻) excitations. These P⁺ P⁻ pairs can either geminately recombine or diffuse away from each other and form isolated P⁺ and P⁻ on separated chains. The two-fold decay components in films can be realized by components originated from intra- or interchain decaying processes. As shown above, decays of polarons of EB in NMP also have two components, which could be due to the curly nature of polyaniline in NMP [124]. The polymer chain of EB in NMP was found to be coil-like. Therefore, some rings along a single chain with some distance apart can come into contact, which are accessible to polarons hopping between rings in contact. Comparing the overall features of the PIA of EB in NMP and as a film, the ring torsional degree of freedom definitely has an important impact on the life time of positive polarons in polyaniline.

Pernigraniline is one of the few conjugated polymers beyond trans-(CH)ₓ with a two-fold Peierls degenerate ground state [139]. Therefore, solitonic excitations are expected for this polymer. dos Santos and Brédas have found that two types of charged solitons are stable in PNB [140]. Su and Epstein incorporated both bond length and ring torsional degrees of freedom into an SSH-like Hamiltonian to study PNB [19]. They predicted that neutral
soliton pairs should be stable excitations in PNB. In addition to solitonic excitations, both calculations predicted that polarons are stable excitations. In contrast to solitonic defects that are nitrogen centered defects, the polaron excitation is centered on a phenyl ring. Libert and Brédas have shown that the positive polaron in PNB is formed with the positive charge mainly localized in one aromatic ring and its adjacent C-N bonds which adopt a semiquinoid geometry [141]. The ring becomes perpendicular to the nitrogen plane which breaks the conjugation along the chain. This pinning of the defect implies the migration of the polaron should be of limited rate. The fast dispersive decay (power law) observed in the PA of PNB in NMP is consistent with this defect pinning picture.

Excitation into the $\pi-\pi^*$ band gap creates free electron and hole carriers, which then lead to trapping and lattice deformation to create polarons. The maximum, for the PIA of EB/NMP with 4.2 eV excitation, was at delay time of $\sim 0$ ps, which demonstrated a faster decay than with 2.1 eV excitation. This implies hole carriers of EB generated from $\pi-\pi^*$ excitation have a larger diffusion rate than those of EB generated from 2.1 eV excitation. This phenomenon can be understood by the mobility of the hole carriers, which should have more kinetic energy at higher excitation energy.

The dependence of the peak of $\Delta T/T$ was studied as a function of pump intensity. A logarithm plot of $\Delta T/T$ vs pump intensity for EB/NMP shows a slope of 0.75 at radiant densities less than 90 $\mu$J/cm$^2$ and a slope of 1.2 at higher radiant densities. The intensity dependence for EB films has a slope of 0.85 for low radiant densities and scales linearly at higher radiant densities. The intensity dependence of PNB in NMP scales close to linear with a slope of 1.1 throughout the range of the radiant density for the experiment (20 to 300 $\mu$J/cm$^2$). For PNB in KBr, the intensity dependence scales linearly both at the peak of the initial decay and at delay time of 4 ns. A low temperature experiment (200 K) of PNB/KBr showed a slope of 0.9 for the intensity dependence study. At 2.1 eV excitation, the generation and annihilation of the positive polarons of EB seem to follow the prediction of the rate law. At lower pump intensity, the relaxation scales between unimolecular and
bimolecular recombinations, while at higher pump intensity, the relaxation scales up to unimolecular or even superlinear behavior. In addition to the issue of multiphoton absorption, there is an appreciable rate of diffusion for photocarriers, which also changes the intensity dependence behavior.

I now discuss the superlinear behavior of the intensity dependence data observed in polyaniline. Assuming a non-degenerate two-level system with population densities $N_1$ and $N_2$ (the total population density, $N = N_1 + N_2$), and $N_1$ being the lower energy level (see Fig. 57), the absorption coefficient is expresses as:

$$\alpha = \sigma_{12}[N_1 - N_2], \quad (3.3)$$

where $\sigma_{12}$ is the optical absorption cross section between 1 and 2 states for the probe field. The attenuation of the probe beam propagating along the $z$ direction through the medium is $I(z) = I_0 e^{-\alpha z}$ or $T(z) = I(z)/I_0 = e^{-\alpha z}$. The variation of $\alpha$ under the presence of the pump field can be expressed as

$$T' = e^{-(\alpha + \Delta \alpha) z}, \quad (3.4)$$

![Fig. 57. Schematic diagram of a two-level system.](image-url)
where $\Delta \alpha (= \Delta N_2 \times \sigma_{12})$ is the change of the optical absorption coefficient, $\alpha$, under the influence of the probe field. Equation 3.2 is rewritten as $dN_2 = \alpha IN_2 - \beta N_1^\mu$, for $\gamma = 1$. If the diffusion in eq. 3.2 is ignored, at the peak of the photoinduced changes, $dN_2/dt \sim 0$, therefore,

$$\Delta T/T \sim N_2 = [\alpha IN_1/\beta]^{1/\mu}$$

(3.5)

At low excitation intensity ($N_1 >> N_2$), the linear relationship between $\Delta T/T$ and $I$ holds, assuming other terms being constant. Nonetheless, at larger intensities, $N_1$ and $N_2$ are functions of $I$ and therefore $dI$ (or $\Delta T$) is no longer proportional to $I$. A saturation parameter is defined as: $S = \rho B_{12}/A_{12}$, where $B_{12}$ and $A_{12}$ are the Einstein coefficients of stimulated and spontaneous absorption, respectively. The time derivatives of $N_1$ and $N_2$ can be written as

$$dN_1/dt = -dN_2/dt = -B_{12} \rho N_{12} + B_{21} \rho N_2 + A_{21} N_2$$

(3.6)

Under stationary conditions, $dN_1/dt = -dN_2/dt \sim 0$, it can be shown that, with $I = cp$ and $B_{12} = B_{21}$,

$$N_1 = N (A_{21} + B_{21} I/c)/(A_{21} + 2B_{21} I/c) = N(1 + S)/(1 + 2S)$$

(3.7)

and

$$N_2 = NS/(1 + 2S)$$

(3.8)

At high radiant densities, the absorption coefficient $\alpha$ gets smaller as $N_2$ increases. Thus,

$$\Delta T/T \sim N_2 = [\alpha IN_1/\beta]^{1/\mu},$$

(3.9)

no longer yields a linear relationship as $\log(\Delta T/T)$ vs. $\log(I)$ is plotted. The increase of $\Delta T/T$ ($N_2$) and the decrease of $N_1$ will cause the slope $(1/\mu)$ to increase, which gives a smaller $\mu$. The slope obtained from the logarithm plot of $\Delta T/T$ vs. $I$ can no longer give the appropriate intensity dependence. The other possible source of giving a larger slope is multiphoton absorption, $I'$, with $\gamma$ greater than one; the slope will be larger than $(1/\mu)$ (see eq. 3.9).
Multiphoton absorption should be more pronounced at high pump intensities, which is consistent with the observed superlinear behavior. In summary, multiphoton absorption and non-linear absorption could be the reasons for the superlinear behavior observed in the picosecond photoinduced experiments.

It is worthwhile to compare the results of the PIA and the PIB of polyanilines obtained in this work. In Fig. 58a, the 2.9 eV PIA and 2.1 eV PIB of EB films at room temperature are reproduced. It is suggested that, for EB in solids, the positive polaron retains longer than the molecular exciton. This is also true for EB in NMP, in which the ps PIA contains more long-lived components than in the ps PIB (Fig. 58a Inset). Note that in comparing the rise of the PIA and PIB, the polaron appears to have a fast decay component (~ 3 ps) that is shorter than the fast decay component of the exciton (~ 6 ps). Further experiments are required to elucidate the phenomenon. It is indicated from the results that the hole polaron is more environmental sensitive than the exciton. In contrast to the PIB of the molecular exciton (see the introduction section in the beginning of this chapter and [16]), the PIA of the positive polaron bands of EB is moderately temperature dependent (see Fig. 58b). This can be realized from the general acceptance that polarons encounter some lattice distortion, which cause polarons to be subject to more environmental dependence. Last but not least, in Fig. 59, a distinction is drawn between the dynamics of PNB and EB in NMP. In PNB/NMP, the hole polaron decays faster than the photoexcitation of the Peierls gap, which is distinct from the results of EB in NMP (see Fig. 59a). The hole polaron in PNB/NMP also decays faster than the hole polaron in EB/NMP (see Fig. 59b). In contrast, the photoexcitation of the Peierls gap persists longer than the exciton bleaching of EB/NMP (see Fig. 59c).
Fig. 58. (a) Comparison of picosecond photoinduced absorption (2.9 eV) and bleaching (1.9 eV) of EB as a film with 2.1 eV pump. Inset: a similar comparison of EB in NMP from -20 to 50 ps. (b) Temperature dependent decay of the 2.9 eV polaron bands of EB as a film.
Fig. 59. Comparisons of the ps PIA and PIB of PNB and EB in NMP from -20 to 50 ps. The pump energy was 2.1 eV and the probe energies for the PIA and PIB were 2.9 and 1.88 eV, respectively. (a) PIA and PIB of PNB. (b) PIA of EB and PNB. (c) PIB of EB and PNB.
CHAPTER IV

PHOTOPHYSICS OF POLY(p-pyridine)

Introduction

While polymers have traditionally been used in electrical applications only as insulators (e.g., coverings for wire), there is much interest in their potential ability to conduct electricity and radiate light. Polymers offer major advantages in that they are durable, are easy to make, and open doors for chemical tailoring. Early research was limited primarily to their uses as pressure sensors, electrical conductors, and light modulators [3,142,143]. However, with the current high interest in developing ultrathin computer monitors and television sets (i.e., flat-panel displays), research on polymer light-emitting diodes (LEDs) and thin-film transistors (TFTs) has been receiving much attention. Since the pioneer work by Friend’s group on poly(p-phenylene vinylene) (PPV), there has been a great interest in using organic polymers as active layers in fabricating light emitting diodes (LED) [144-147]. Conjugated polymers were initially discussed in connection with their high electrical conductivity on doping with either donors or acceptors. The Su-Schrieffer-Heeger (SSH) model of non-interacting $\pi$-electrons provides a general framework of self-localized states such as solitons, polarons and bipolarons. Major efforts were subsequently devoted to the nonlinear optical (NLO) properties of conjugated polymers in their pristine, semiconducting state in connection with optical switching elements and third harmonic generation. Large ultrafast NLO responses are due to virtual $\pi-\pi^*$ excitations of the delocalized electrons, which are the polymer’s neutral excited states [148,149]. The Pariser-Parr-Pople model for interacting $\pi$-electrons in conjugated molecules accounts naturally for such neutral
excitations, including key two-photon states.

The most commonly studied polymer LED consists of two electrodes sandwiching a light-emitting polymer layer of PPV, or poly(p-phenylene vinylene). PPV is a semiconductor first reported by scientists at Cambridge University [5] to emit green-yellow light. Subsequent work from Santa Barbara [147] describes a version of a PPV which was an almost-all-plastic, flexible LED device: the positive electrode, traditionally metallic, was made of a polymer, polyaniline, although the negative electrode was made of calcium, a metal. The device was easily bendable and had a quantum efficiency of 1%. However, despite its excellent ability to inject electrons into the PPV, calcium is highly reactive and unstable. A remarkable improvement in efficiency to about 4% was then reported by the Cambridge group [145], who put another, modified PPV layer (CN-PPV) in contact with the original PPV: this modified layer facilitates the electron transport to the PPV interface and enables use of more stable metal electrodes such as aluminum.

While the negative electrode supplies electrons to the PPV layer, the positive electrode draws electrons away from the PPV, creating positively charged holes. An electron and hole can temporarily join with each other, forming transient pairs called excitons that can travel through the polymer. When such excitons eventually migrate to radiative subunits of the polymer, they release their excess energy in the form of light. But the electron-hole pairs responsible for producing light are created rather inefficiently. Based on measurements at AT&T Bell Laboratories [56,57] it was proposed that a competing species preferentially forms. This species, a short-lived molecular complex known as a charge-transfer exciplex (also called spatial-indirect exciton pair or interchain polaron pair), does not radiate light and thereby reduces luminescence. Another major question regarding performance of these PPV polymers has been their stability. These materials have been known to be air-sensitive, and scientists at AT&T Bell Laboratories have shown that the major culprits are carbonyl groups. The carbonyl groups form as defects on the chain during making of PPV. Luminescence was shown to correlate inversely with carbonyl content, and
the manyfold increase light emission obtained when the manufacturing process was carried out in a hydrogen atmosphere that suppresses oxidation and carbonyl formation [59,150].

Much progress has also been made recently on the color obtainable from such polymeric LEDs. Most of the PPV materials emit green-yellow light, but tailoring the structure of a light-emitting polymer can change the color. Scientists at the University of Massachusetts [151] have recently reported a blue polymer LED consisting of chains in which short PPV groups alternate with another building block, polyethylene. A similar approach by the University of Groningen resulted in color-tunable polymeric films using units of another simple molecule, thiophene (C\textsubscript{2}H\textsubscript{4}S), in alternation with alkylsilanylene blocks [152]. By varying the number of thiophene groups per bloc from two to six, the emitted colors ranged from blue to orange-red. An alternative ingenious approach has just recently been reported [153] using microcavity structures, sandwiches of electrically active and inert layers each about 10-200 nm thick. By controlling the thickness of the layers, different colors can be made to reflect out of the cavity.

In the context of semiconductor devices, the particular interest lies in the scope for fabrication of thin-film devices over large areas, which, with the exception of amorphous and polycrystalline silicon, has proved difficult to achieve with inorganic materials. An early interest in polymer-based devices was in the field-effect transistor (FET), with the discovery in the late 1980s that the field effect could be routinely achieved in devices made by the deposition of conjugated polymers onto insulator layers such as silicon dioxide [154]. This work has now been extended to the use of well-defined oligomers of thiophene, principally \(\alpha\)-sexithiophene, which exhibit the highest field-effect mobilities among organic FETs, on the order of 0.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\).

Poly(pyridine-2,5-diyl) (PPy) has a band gap of 3.3 eV and large photoluminescence (PL) quantum yield. It is also soluble in most acids and slightly in benzene, alcohol and acetone. These are a potential candidate for blue emitting LEDs. And unlike PPV, PPy is relatively easy to process and fabricate. The photophysics of the polymer was studied by
using conventional and ultrafast spectroscopic techniques. This chapter is organized as followings: the basic physical and chemical properties of the polymer are introduced. Then, experimental methods are described briefly. The results of steady state and transient PL are presented next. Finally, discussion and conclusions are presented.

**Spectral diffusion and luminescence decays of a rigid linear chain polymer poly(p-pyridine): observation of phosphorescence**

The results of luminescence lifetime and steady state photoluminescence (PL) studies of poly(p-pyridine) (PPy) are presented in this chapter. The outcome of the spectral behavior (the apparent Stokes shift) in PPy is interpreted as contributions from one or more of the following factors: intrinsic Stokes shift, spectral diffusion and self-absorption. The PL of PPy features a minimum Stokes shift when chains of the polymer are unconstrained, such as in solution. A persistent Stokes shift is present for the PL occurring in a confined environment, such as films. I observe spectral diffusion in the PL and the peak position of the PL depends on excitation energies. Phosphorescence was detected at photoexcitation energies significantly above the band edge for PPy films. In addition to PL from thermalized (π−π*)† states, fluorescence from (n-π*)† states also was observed. A possible photophysical pathway, including the enhancement of inter-system crossing and the migration and structural relaxation of the photoexcited species, are discussed. The physical model that governs the apparent Stokes shift observed in the PL of PPy is discussed in terms of Stokes shift, spectral diffusion and self absorption. The results indicate that the photoexcited nature of PPy is primarily excitonic.

A great deal of attention has been recently devoted to the nature of radiative processes in conjugated polymers since the advent of polymer light emitting diodes [5]. Although the elementary photoexcitations for nondegenerate conjugated polymers have been attributed primarily to excitons [48], there is still debate on the pertinence of this picture. [43,155]. Excitonic radiative emission is also considered to be responsible for photoluminescence (PL) as well as electroluminescence (EL) in most conjugated polymers
Recently, a polarized fluorescence study of poly(p-phenyl vinylene) (PPV) films has demonstrated that the photoexcited electron-hole pairs maintain their correlation across the entire absorption spectrum of PPV (from 2.4 to 4.7 eV) [43]. The interplay between photoexcitations and the correlation-energy gap $U$ and dipole-dipole interaction $V$ in conjugated polymers has been addressed recently [158]. The relationship between the electron-hole correlation (electron-hole separation) and the binding energy of excitons remains unclear. An analysis of the phonon modes of PPV has found that all allowed modes for luminescence are within an almost dispersionless ground-state phonon branch [159]. Moreover, the role of the higher lying states in elementary excitations of conjugated polymers is not well documented, which could be significant due to the fact that prior to generating radiation in the process of electroluminescence, electrons and holes recombine and create 'hot excitons'.

In this work, I studied photophysical properties for a wide band-gap arylene polymer: PPy, the pyridine analog of poly(p-phenylene) (PPP). The non-bonding orbitals of nitrogen atoms in PPy facilitate the dissolution of the polymer in acidic solvents, which allows the conformation and inter-chain stacking of PPy to be addressed by studying the polymer in many different forms: films, powder and solution. PPy is similar to PPP, which is considered to have a rigidly linear structure [4]. Previously, a polarization study of PPy has revealed a rodlike structure in a solution of formic acid (protonated) as well as films [26]. The luminescent behavior of PPy was attributed to the formation of excimers in concentrated solution and films [160]. (It would be clear from the results of this work that the excimer picture is not justifiable.) To address the nature of the radiative processes of PPy, time-resolved, cw, and near-steady-state studies were performed. I observed spectral diffusion in the PL of PPy and the polymer possesses a very unusual feature that the emitting energy depends on excitation energy. The luminescent properties of PPy are strongly correlated with the migration of excitons, the conformation and the local structure of the emitting segments of the polymer. PPy is also distinguished from other luminescent polymers in that the non-bonding orbitals of the nitrogen atoms play an important role in inter-system
crossing that can lead to phosphorescence emission. The inter-system crossing is further substantiated by the observation of fluorescence from \((n-\pi^*)^1\) states.

**PPy was synthesized by dehalogenation of dibromopyridine with a zerovalent nickel complex as described in detail elsewhere [25]. Samples were provided by H.-L. Wang (under the supervision of Prof. Tim Swager) from the research group of Prof. Alan MacDiarmid at the University of Pennsylvania. The average chain length of the polymer ranges from repeat units of 20 to 50 depending on the method of preparation. Thin films of PPy were obtained by spin casting onto ITO-glass substrate using a solvent of formic acid (HCOOH). Optical experiments were performed on several forms of PPy: thin films, powder (0.02 wt % in KBr) and in solution of HCOOH. For ps and ns luminescence decay measurements, time-resolved single photon counting techniques were used. Picosecond UV (4.27 eV) excitation was generated by frequency doubling a 2.15 eV output from a cavity dumped synchronously pumped R6G dye laser pumped with the second harmonic output of a mode-locked Nd:YAG laser. The 2.15 eV output from the dye laser was amplified by a cavity dumped Ar+ laser and frequency doubled with an angle tuned nonlinear crystal [102]. 2.9 eV excitation generated from a Stilbene 420 dye laser pumped by the third harmonic of a YLF or YAG laser was also used in this study. Millisecond and microsecond lifetime measurements were accomplished by mechanical modulation of the UV pump source, and the decay was monitored by an analog oscilloscope. Steady state PL measurements were obtained with a commercial fluorimeter (SPEX, fluorolog-2, Instruments SA, Inc.) or with the pulsed sources described above coupled with a spectrograph and a charge coupled detector. The photoluminescence spectra (steady-state and time-resolved) were collected with a front reflection geometry. Unless specified otherwise, the PL and PLE spectra in this work were obtained with the fluorimeter.

**CW absorption, photoluminescence and excitation spectra of PPy**

In Fig. 60 the absorption spectra for several concentrations of PPy in HCOOH are shown. The absorption peaks at 3.351 eV for a concentration of 0.65 mM (monomer unit)
Fig. 60. Absorption spectra of PPy in HCOOH. The concentration is accounted from monomer units. Inset: A plot of maximum absorbance vs. concentration (cross) and the linear regression of the corresponding data (solid line).
and through a path length of 2 mm. Shown in the inset of Fig. 60 are absorbances (at 3.35 eV) for several concentrations of PPy and the linear extrapolation of the corresponding data. The molar absorptivity of PPy in HCOOH at 3.351 eV is determined as $1.207 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ or $1.207 \times 10^7 \text{ mol}^{-1} \text{ cm}^2$. Typical molar absorptivity for organic dyes such as R6G and DODCI is in the order of $10^7$-$10^8 \text{ mol}^{-1} \text{ cm}^2$ at the absorption maximum [161]. For comparison, the molar absorptivity of trans-stilbene is $2.8 \times 10^7 \text{ mol}^{-1} \text{ cm}^2$ at 4.16 eV [162]. Several different types of solid-state PPy samples were prepared: spin-cast films on surfaces of ITO, glass and quartz; pellets consisting of PPy powder in substrates of KBr (0.005 and 0.01% in weight). Absorption spectra for these different samples and the absorption spectrum of PPy in HCOOH are reproduced in Fig. 61. The thickness of the films was adjusted to make the maximum of absorbance close to 1 for all films. Note that the peak (~3.31 eV) of the absorption of PPy powder is red shifted with respect to the corresponding peak (~3.35 eV) of PPy in HCOOH. (It is pointed out that PPy in HCOOH is likely protonated while the solid forms of the polymer are not protonated (assuming all traces of the acid in the films have been removed during drying).) The maximum of absorption for PPy films is even further red shifted to ~3.25 eV. Taking the molar absorptivity of PPy powder as the same as that of PPy in HCOOH, the moles of PPy in a pellet (0.005% in weight) was estimated from the absorbance (2.12), which gives a value of 3% less than the real value. The discrepancy could be due to losses from scattering, diffraction and reflection of light by the pellet. Notice that, the variation of the FWHM of the absorption for different PPy samples. In general, thin films of PPy give a larger FWHM (~0.8-1 eV), then PPy powder has a slightly smaller FWHM (~0.7 eV), and finally the FWHM for PPy in HCOOH is ~0.45 eV. In contrast to the absorption spectrum of PPy solution and powder, PPy films demonstrate a development of a low energy tail into the near-IR and a larger inhomogeneous width in the absorption spectrum. These indicate the presence of substantial disorder in PPy films.

Absorption, photoluminescence and excitation spectra of PPy in HCOOH are collected in Fig. 62. The PL spectrum was obtained with excitation energy of 3.35 eV in a concentration of $3 \times 10^{-3} \text{ M}$ (monomer unit). The collection path was 23.3° to the excitation
Fig. 61. Absorption spectra of PPy films, powder and in HCOOH. Peak position for each absorption spectrum are indicated in the figure.
Absorption (solid line), photoluminescence (dots) and excitation (dashed line) spectra of PPy in HCOOH ($10^{-4}$ M, monomer unit). The PL spectra were obtained with excitation energy of 3.4 eV and the PLE spectrum was done monitoring at 2.2 eV.
beam. The peak position of the PL is at 2.952 eV with a shoulder band at 2.666 eV. At the present stage, the origin of the shoulder band remains unknown. The shoulder band is Stokes shifted ~ 2300 cm$^{-1}$ with respect to the peak of the PL. This shift cannot be assigned to a phonon sideband straight forwardly since other than nitriles (-CN) there are very few fundamental groups vibrated in this frequency region. Besides variations in intensities, there are no observable differences in the PL for excitation energies ranging from 3 to 4.8 eV. The PLE (monitored at 2.2 eV) for the same solution peaks at 2.97, 3.38 and 4.5 eV. And there is no energy dependence in the PLE spectrum—that is, peak positions do not change for excitation energies ranging from 3 to 5 eV. The peak at 2.97 for the PLE signifies a minimum Stokes shift for the chromophore; with excitation energy around 2.95 eV, PPy in HCOOH can emit without significant structural relaxation. This phenomenon signifies the 'excitonic' nature of luminescence of PPy.

The preliminary result has shown that the fluorescence internal quantum yield for PPy in HCOOH is ~ 60%. The procedures of the estimation are described below. The absolute quantum yield for Stilbene 420 in methanol is known to be ~ 84% at 3.35 eV excitation [163]. I adjusted the absorbance of a Stilbene/methanol solution at 3.35 eV to be ~ 1 at 1 cm path length. A solution of PPy in HCOOH also was prepared with an absorbance of ~ 1 at 3.35 eV (1 cm path length). The emission intensity of the Stilbene solution was compared to the emission intensity of the PPy solution. The relative quantum yield of PPy in HCOOH is determined by

$$\Phi_{\text{PPy}} = \frac{\int A_{\text{PPy}} d\nu}{\int A_{\text{Stilbene420}} d\nu} \times \frac{\int E_{\text{PPy}} d\nu}{\int E_{\text{Stilbene420}} d\nu} \times \Phi_{\text{Stilbene420}}$$  \hspace{1cm} (4.1)

where $A_{\text{PPy}} (A_{\text{Stilbene420}})$ is the absorbance for the PPy (Stilbene 420) solution, $E_{\text{PPy}} (E_{\text{Stilbene420}})$ is the emission intensity for the PPy (Stilbene 420) solution, and $\Phi_{\text{PPy}} (\Phi_{\text{Stilbene420}})$ is the quantum yield for the PPy (Stilbene 420) solution.
Absorption and photoluminescence spectra of a PPy film (PPy/ITO/glass). The PL spectra were obtained by photoexcitations at 4.4 (solid line) and 3.4 (open circle) eV. The excitation beam was directly on the polymer and the collection path was 23.3° to the excitation beam.
Fig. 64. Photoluminescence spectra of a PPy film (PPy/ITO/glass) with excitation energies of 3.53 and 4.27 eV. The 3.53 eV was from the third harmonics of the fundamentals line of a Nd:YLF laser. The generation of the 4.27 eV line is described in the text. The excitation was directly on the polymer film and the collection path was 45° to the excitation beam.
Dramatic changes in the PL and PLE for different forms of PPy were observed. For the PL of films (PPy/ITO/glass), the emission energy depends on the excitation energy (Fig. 63). The PL was taken by directly exciting the polymer film using a front surface reflection configuration (the collection path was 23.3° to the path of the excitation beam). The Stokes shift of the PPy films is ~1 eV, with a trend of thicker films yielding larger shifts. The PL of 2.3 eV of the PPy films blue shifts to ~2.5 eV as the excitation energy changes from 3.35 eV to 4.4 eV and two additional bands appear at 1.87 and 1.77 eV. To understand the phenomenon, I studied the PL of PPy films with photoexcitation at 2.95 eV (420 nm), 3.53 eV (351 nm), 4.13 eV (300 nm) and 4.28 eV (290 nm) using excitation from the picosecond pulse lasers. The excitation was directly on the PPy/ITO and the collection path was 45° to the excitation beam. Indeed, at higher excitation energies, an extra band at 1.77 eV shows up in the PL (see Fig. 64). Note that as the excitation spot and penetration depth of laser beams varied for different laser lines, the absolute peak position of the PL could be irrelevant here. Moreover, the issue of exact peak positions of the PL cannot be settled without doing experiments for every laser line at the same spot of the same film, which is difficult to achieve in any case.

The quantum yield ($10^{-3}$) for the PPy film (ITO/glass) is at least two orders of magnitude lower than the quantum yield for PPy in HCOOH. This was determined by comparing the integrated areas of the absorption spectra and the emission spectra of the film and solution samples. I have neglected effects from self-absorption, since it is difficult to discern the contribution from self-absorption without knowing the thickness of the film. The possible sources for the lowering of the quantum yield are discussed later in this chapter.

I now consider the PLE of PPy films. Shown in Fig 65 are the PLE spectra monitoring at 2.3, 1.87 and 1.77 eV running from 2.5 to 5 eV. The PLE spectra for all three bands embody a peak around 3.35 eV (the peak of the absorption of PPy in HCOOH), with a tendency of a small red shift of the peak for lower energies (~0.02 eV). Notice that the low energy tail in the absorption of films does not contribute to the PL, this implies the important
Fig. 65. Photoluminescence excitation spectra of a PPy film (PPy/ITO/glass) monitored at 2.3 eV (open circle), 1.87 eV (open square) and 1.77 eV (open triangular). Experimental conditions were similar to above mentioned in Fig. 63.
Fig. 66. Absorption (dashed line), photoluminescence (solid line) and excitation (open triangular) spectra of PPy powder in substrates of KBr (0.005% in weight). The PL was excited with 3.8 eV, and the PLE was monitored at 2.6 eV. The PL was collected at 23.3° to the excitation beam.
roles of structural relaxation and self-absorption in the emission process of PPy as a film. The PLE recorded at 2.3 eV displays a profile close to the ground state absorption of PPy. However, the PLE of the 1.77 eV band shows that the emission is derived primarily from 4.6 eV excitation (> 60%). These data imply that the majority of the 1.77 eV band is induced from populated high lying states. Note that most of the emission of the 1.87 eV band is still derived from the 3.35 eV absorption band. The origin of the 1.87 eV band is unclear at this stage, the majority of the emission is still from the tail of the 2.3 eV band which overlaps with the emission from the blue end of the 1.77 eV band.

Fig. 66 shows absorption, photoluminescence and excitation spectra of PPy powder in substrates of KBr (0.001% in weight). The geometry between the excitation beam and the collection path was the same as previously mentioned for the films. The PL of the PPy pellet peaks at 2.65 eV (apparent Stokes shift ~ 0.6 eV). The PLE for the pellet peaks at 2.98, 3.38 and 4.5 eV as monitored at 2.5 eV. There was no difference in the PLE profile as the monitoring energy was scanned from 2.8 to 1.8 eV. The peak of 2.98 eV for the PLE again demonstrates the location of favorable emitting sites, which is very close to the ones in PPy solution. However, as in PPy films, a persistent Stokes shift exists for PPy powder.

The Stokes shift and the spectral diffusion observed in the PL of PPy are discussed here. It is interesting to note from the PLE of PPy films that the low energy absorption for the films does not contribute substantially to the generation of PL. While PLEs for all forms of PPy have shown huge peaks or shoulders at ~ 3 eV and 3.38 eV, it is seen from the PLE of PPy in HCOOH (~ 10^-5 M) that emission can occur at most favorable low energy sites without any significant Stokes shift. Also that, in the PLE spectra of solution and powders (see figures 62 and 66), there are peaks at ~ 4.5 eV contributing to the PL spectra (peaks at 2.98 and 2.65 eV for PPy in HCOOH and PPy/KBr, respectively). In the PLE of PPy films (PPy/ITO/glass), this 4.5 ~ 4.6 eV peak contributes to the PL peaked at 1.77 eV (see Fig. 65). The results of the PL and PLE indicate that the PL in PPy originated from the migration of photoexcited species to some radiative segments of the polymer and concurs with some
lattice relaxation at emitting sites, which are strongly correlated with the environment and disorders of the polymer. The difference in the Stokes shift among films, powder and solution of PPy is attributed to the difference in conjugation lengths and the difference in the conformation of radiative segments. Large or essentially zero Stokes shifts may both occur depending on the local structure of the emitting sites. In a well delocalized π electron chain and without any significant local confinement of the emitting segment, the Stokes shift could reach zero, such as the PL of PPy solution. However, even though there may be migration of excitons in an extended conjugation chain (site selective fluorescence), if the local structure of the emitting segment is confined by the inter-chain packing or torsional strain, lattice relaxation can be substantial, such as the PL observed from PPy films. PPy powder is likely to adopt a coil-like structure as the polymer is precipitated from DMF during preparation [43]. The migration of the excitons could be hampered by this coil chain and the Stokes shift of PPy powder can be understood by this coil-like structure, which can induce some lattice relaxation at emitting sites. Therefore, the Stokes shift of the PL of PPy powder is in between the corresponding Stokes shifts of PPy solution and films. These results suggest that the emitting species of PPy are from a distribution of different ‘conjugation lengths’ of polymer segments. However, the emission is environmental or conformational dependent as can be seen from the drastic difference in the luminescence spectral of different forms of PPy.

**Time-resolved Spectroscopic Study of PPy**

In this section, the transient behavior of the PL of PPy is discussed. For PPy films (PPy/ITO/glass), experiments were done on three similar films with the excitation beam directly on the polymer. Unless specified otherwise, the concentration of the solution (PPy in HCOOH) was typically 10⁻⁴-10⁻⁵ M. Every photoluminescence decays was collected at 45° to the pump beam and was reproduced at least twice on the same or different samples (esp. for films). Multiple decay components were present for the PL for different forms of PPy. The main feature of the PL of PPy exhibits nonexponential decays and the emission
demonstrates **spectral diffusion** with the evolution of time which is consistent with the scheme of the migration of excitons. The spectral diffusion is illustrated in the difference of fluorescence decays at 2.3 and 2.95 eV for a PPy film with 4.27 eV photoexcitations (see Fig. 67). The short component (~ 50 ps) of the PL increases in time as the emission energy decreases. The decays can be fit to biexponential form, for e.g., time constants are 60 and 450 ps for the 2.3 eV band. Shown in the inset of Fig. 67 are the PL decays at 3.45 and 2.3 eV. There is a long-lived component for the luminescence decay of the 3.45 eV band. Recall the presence of 1.87 and 1.77 eV bands, I found out that the lifetime of the 1.77 eV band is much longer than 400 ns, which cannot be differentiated by the TCSPC setup. Later, the lifetime of the 1.77 eV band obtained under near-steady conditions will be presented.

Temperature and intensity dependence studies of the PL of PPy films are discussed here. The temperature dependence study of the PL has revealed that the dynamics of the short component (~ 50 ps) exhibit a nominal temperature dependence (see Fig. 68 a-b). The curve labeled IRF stands for instrument response function, which was from the signals of the excitation pulses. It is very interesting to find that emission at 3.45 eV possesses a 35 ns component, which is essentially temperature independent (Fig. 69). This band is attributed to fluorescence from \((n-\pi^*)\) states, which should lie above in energy of the \(S_1\) state to account for the strong luminescent property of PPy. Fig. 70 displays fluorescence decays of a PPy film at 2.3, 2.7 and 3.45 eV from 0 to 130 ns. The 35 ns component dominates the 3.45 eV emission, but can only be seen as a small trace in the 2.7 eV emission, and is essentially gone in the 2.3 eV emission. This long-lived component is indeed from high lying states, which can only occur when excited with energy (4.27 eV in this work) substantially higher than the \(S_0\)-\(S_1\) transition (3.35 eV). The intensity dependence studies of the 3.45 and the 2.3 eV bands are presented in Fig. 71. Basically, from 0.1 to 1 nJ (3 to 30 μJ/cm² for a beam waist of 100 μm) both decays show no obvious dependence on excitation intensities. The 2.3 eV band also exhibits similar dynamics with excitation energy (2.9 eV) slightly lower than the band edge. More importantly, for 2.9 eV excitation, I did not observe any luminescence decays with a lifetime longer than ns for emission energies ranging from excitation energy
Room temperature photoluminescence decays of a PPy film (PPy/ITO/glass) at emission energies of 2.3 (open circle) and 2.95 eV (open square). Inset: The PL decays of 3.45 and 2.3 eV bands. (Pump was 4.27 eV and directly on the polymer; the collection path was 45° to the pump beam.)
Fig. 68. Photoluminescence decays of a PPy film (on substrates of ITO) at 80 (open circle) and 230 K (open square). (a) PL at 2.3 eV. (b) PI at 3.45 eV. IRF: Instrument response function. The excitation and collection geometries were similar to the above mentioned in Fig. 67.
Fig. 69. Photoluminescence decays of the 3.45 eV emission band of a PPY film (PPy/ITO/glass) at temperature of 80, 130 and 230 K from 0 to 20 ns. The decays are temperature independent with an exponential lifetime of 35 ns. The pump beam was directly on the polymer and the PL was collected at 45° to the pump beam.
Fig. 70. Photoluminescence decays of a PPy film (PPy/ITO/glass) at emission energies of 3.45, 2.7 and 2.3 eV from 0 to 130 ns (T = 230 K). The arrangements for the excitation beam and the collection of the PL were similar to the above mentioned in Fig. 69.
Photoluminescence decays of a PPy film (PPy/ITO/PPy) with different excitation intensities (pump at 4.27 eV). (a) The PL decays at 3.45 eV (0 to 30 ns). The radiant energy ranges from 0.1 to 1 nJ (3 to 30 μJ/cm²). The decays at 2.3 eV (subnanosecond) is also shown in the graph. (b) The 2.3 eV decays (0 to 500 ps) for radiant intensities range from 0.1 to 1.2 nJ. The arrangements for the excitation beam and the collection of the PL were similar to the above mentioned in Fig. 69.
(2.9 eV) to the lower energy limit of the detector (1.6 eV). It is suggested that the emission at 2.3 eV is from lowest $\pi-\pi^*$ transitions ($S_1-S_0$); the emission at 3.45 eV, however, is from $n-\pi^*$ transitions.

I now consider the time-resolved fluorescence studies of PPy in HCOOH. The fluorescence decays of 2.95 and 1.62 eV bands at room temperature along with the IRF are displayed in Fig. 72. The results of the time-resolved fluorescence are consistent with phenomena observed in the CW studies of the PL and clearly indicate the origin of the spectral diffusion and the Stoke shift in PPy. Again, the luminescence decays of PPy in HCOOH exhibit strong spectral diffusion induced from the structural relaxation of the chromophores and the migration of excitons in the polymer. The decays are nonexponential and can be fit to a biexponential form, for e.g., time constants for the 2.95 eV band are 100 and 350 ps. I investigated the temperature dependence of the time-resolved fluorescence of PPy in HCOOH. Shown in Fig. 73 are decays for 2.95 and 1.62 eV emission of the polymer in HCOOH from −10 to 60 degrees. Arrhenius plots, for the short component, of the 2.95 and 1.62 eV emission show activation energies of $E_a \sim 380$ cm$^{-1}$ and $\sim 650$ cm$^{-1}$, respectively (see Fig. 74). I examined the fluorescence decays of PPy solution in several different concentrations (Fig. 75). It was found that even in very dilute solution (< $10^{-8}$ M, monomer unit), the fluorescence decays still appear to be nonexponential, the short component in the 2.95 eV emission changes from 100 to 250 ps for a concentration change from $\sim 10^{-5}$ M to $10^{-8}$ M, correspondingly, the long component changes from 350 ps to 2 ns.

The lifetime for the 1.77 eV band of PPy films (ITO/glass) was determined by a near-steady state measurement to be 0.5 ms and 15 ms at 280 and 20 K, respectively (Fig. 76). The data were taken with a mechanical modulation of the excitation laser (4.27 eV) and the phosphorescence signals were collected with an oscilloscope. A cutoff filter ($\sim 2$ eV) was used to cut down the fluorescence band and allowed only emission of energies below 2 eV to pass through.
Fig. 72. Photoluminescence decays of PPy in HCOOH at 1.62 (solid line) and 2.95 eV (dashed line). IRF (short dashed line) is displayed for comparison. Shown also in the figure is a photoinduced absorption of PPy in HCOOH (dots) with pump and probe at 4.2 and 2.1 eV, respectively.
Fig. 73. Photoluminescence decays of PPy in HCOOH at different temperatures. (a) PL at 2.95 eV. (b) PL at 1.62 eV. (Pump at 4.27 eV)
Fig. 74. Arrehenius plot of decay rate vs. temperature of PPy in HCOOH (~ $10^{-5}$ M).

Fig. 75. The 2.95 eV decay of PPy in HCOOH at several different concentrations.
Fig. 76. Time-resolved phosphorescence spectra of PPy (PPy/ITO/glass). Square waves are referring to modulation frequencies, 'ON' and 'OFF' stand for the light field is turned on (off). (a) 280 K (b) 20 K.
**PLE of PPY in HCOOH-Revisited**

I investigated the PLE spectra of PPY in HCOOH for a wide range of concentrations (from $10^{-3}$ M to $< 10^{-9}$ M). Shown in Fig. 77 are the PLE spectra (monitored at 2.5 eV) at concentrations of $~ 10^{-4}$, $~ 10^{-7}$ and $< 10^{-9}$ M, the absorption spectrum of a PPY solution of $10^{-5}$ M is also presented in the figure. For very dilute solution of PPY, the PLE profile follows closely to the ground state absorption, there is only a trace of emission derived from energies below 3 eV, and a small portion of emission is obtained from photoexcitation around 4.5 eV. The difference in the PLE spectra can be explained by the reabsorption of photons in concentrated PPY solution. Fig. 78 shows PLE spectra, for a PPY solution of $2 \times 10^{-5}$ M, monitored at several different energies, for comparison, the corresponding absorption spectrum is also displayed. The peak of the PLE ($~ 3$ eV) shifts to lower energy as the monitoring energy shifts from 2.9 eV toward low energy, but stays constant at 3.024 eV for emission below $~ 2.3$ eV. The transition at 3.024 eV appears to be the most favorable site (conjugation length) for emission in that particular solution. The above results further substantiate the proposal that emission of PPY is mainly from excitons, which can have a wide distribution of different conjugation lengths inside a single polymer chain.

**Discussion**

The evidence presented above clearly indicates that the PL from $(n-\pi^*)^1$ states and the phosphorescence emission are generated by populating high lying states. In contrast to the PL of films, only short decays were observed in the PL of solution with no component longer than 2 ns. This can be understood by the fact that non-bonding states of the nitrogen atoms vanish after protonation (i.e. the non-bonding states become bonding states). Summarizing the time-resolved results of PPY in solution and as films, it is suggested that disorder and constraint in the local structure of PPY can lead to substantially different exciton dynamics. Compiling the spectral and time-resolved data and with the aid of semiempirical quantum chemical calculations [164], a possible photophysical pathway for the essential states of PPY is proposed (Fig. 79).
Fig. 77. Excitation spectra of PPy in HCOOH at concentrations of ~$10^{-4}$ M (solid line), ~$10^{-6}$ M (open circle) and < $10^{-9}$ M (open square). Absorption spectrum is also included (triangle).
Excitation spectra of PPy in HCOOH (~ 10^-4 M) monitored at 2.88 (solid line), 2.63 (triangular), 2.33 (circle) and 2.13 eV (open square). Absorption (circle) spectrum of the solution is also displayed. $v_{loc}$ corresponds to the minimum energy of the peak (~ 3 eV) of the excitation spectra monitored at energies ranged from 2.9 to 1.9 eV.

Fig. 78.
Fig. 79. A possible photophysical pathway for the essential states of PPy. \( \omega_1 \) represents an excitation into high-lying states (> 3.5 eV). \( \omega_2 \) is an excitation with energy below the lowest \((n-\pi^*)^1\).
The lifetime on the order of ms for the 1.77 eV band is several orders of magnitude larger than a usual time constant for fluorescence decays [35]. Earlier, phosphorescence of pyridine was detected at 2.78 eV (lifetime, $\tau_p \sim 2$ s at 77 K and quantum yield, $Q_p \sim 10^{-6}$) [165,166]. Previously, phosphorescence ($\tau_p \sim 15$ s) from polymers was reported for thin films of poly(3-hexylthiophene) [167]. In addition to a long lifetime, the PLE of the phosphorescence confirms that the 1.77 eV band is mainly generated from high lying states. The relative quantum yield of the 1.77 eV band is approximately 12 to 1 for excitation energy of 4.4 eV as compared to 4.1 eV. We have also detected photonduced species on a ms time scale with a linear intensity dependence for the creation and relaxation of the species [168]. The near steady state photoinduced absorption at 1.7 eV is attributed to a T-T* transition. The observation of phosphorescence is further substantiated by the presence of the 3.45 eV emission, which is attributed to a (n-$\pi^*$) transition. The 3.45 eV transition is higher in energy than the peak of the absorption (3.26 eV) for PPy films. The quantum yield of the 3.45 eV band with 4.4 eV excitation is increased at least three-fold compared to 4.1 eV excitation. The lifetime of 35 ns for the 3.45 eV band indicates that the oscillator strength of the transition is relatively small. Overall, the experimental evidence strongly suggest that the 1.77 eV band is phosphorescence from $T_1$, which is similar to classic examples of the enhancement of the inter-system crossing through non-bonding orbitals in a molecular system [169,170].

Luminescence of PPy is different from other luminescent polymers in one other way: the emission energy is dependent on excitation energy. It could arise from the fact that the nature of excitation is band to band at high energy (4.4 eV) for PPy . The process of the recombination of electron and hole can have a different statistical distribution than the migration of neutral species. For charged species, spectral diffusion and structural relaxation (at radiative sites) could behave differently than for neutral species. ‘Hot luminescence’ is probably more dominant after charge recombination.

The apparent Stokes shift is the consequence of the intrinsic Stokes shift, spectral diffusion and self-absorption. It is shown from the excitation spectrum that the intrinsic
Stokes shift is minimum (~ 0) for PPy in HCOOH. Spectral diffusion also is demonstrated by the time-resolved PL studies of PPy in every type of sample. Besides spectral diffusion, it is important to determine the source for the apparent Stokes shift observed in films and powders of PPy: the contribution from self-absorption and/or intrinsic Stokes shift. As I have estimated, the concentration of the film (ITO/glass) is ~ 10 M, with a penetration depth (thickness) of 1000 Å and a fluorescence yield of ~ 10^3, it is obvious that self-absorption cannot fully account for the lowering of the quantum yield and the apparent Stokes shift. The reason for this can be drawn from a qualitative analogy: for a 5x10^-2 M PPy/HCOOH solution, the maximum of the excitation spectrum is still at 2.95 eV. Owing to the limit solubility, it is impossible to prepare a 10 M solution, but from the trend of the excitation spectra, it is unlikely that self-absorption will shift the maximum of the excitation spectrum toward higher energy. The lower quantum yield in PPy films could be attributed to the increase of nonradiative channels in films. I suggest that not only the interchain effects but also the structural relaxations are more pronounced in films. There is also the possibility that aggregate states are present which do not contribute to the emission but do absorb.

It is worthwhile to compare the results of this work with previous results of some polyarylenes and polyaryl vinylenes. The Stokes shift of 1.05 eV for PPy films is comparable to the Stokes shifts observed in PPP (1.1 eV) [144] and in soluble poly(m-phenylene) (PMP) (1.62 eV) [171]. For PPV and derivatives, the PL displays vibronic progressions, and the Stokes shift is on the order of 0.1-0.2 eV [172]. In particular, the Stokes shifts are also similar in solution and as films for soluble derivatives of PPV and PMP. The PLE studies of PPV and derivatives have shown that the excitation profiles are in close resemblance to the absorption spectra of these polymers [172,173]. However, the relationship between PL and high lying states of PPV and derivatives has not drawn much attention. I suggest the difference in Stokes shifts between polyarylene and polyaryl vinylene could be due to the presence of the vinyl group in polyaryl vinylene. In comparing the Stokes shifts of bismethylstyrylbenzene (a three rings oligomer of PPV) and terphenyl, terphenyl shows a larger Stokes shift than bismethylstyrylbenzene. A progressive general
trend is also found in Stokes shifts of oligomers of PPV, PPy and PPP. Excited state conformational changes were given to explain the deviation from mirror images between absorption and emission spectra of phenyls and phenyl vinylenes [174]. In general, the geometry relaxation between ground state and excited state is larger for phenyls than phenyl vinylenes.

PPy differs from PPV and derivatives in that absorption and PLE do not match well with each other in several different forms. This could be due to the presence of (n−π) states in PPy, which complicates the state ordering and the excited state energy transfer. I now refer to the PL of PMP and PPP. Since the Stokes shift for PMP [171] is similar for films and solution, the mechanism for the Stokes shift of PPy is different from the Stokes shift of PMP in that for PMP the spectral diffusion and Stokes shift happen in geometric relaxation at local order, which is similar to molecular systems due to the fact that the conjugation length of PMP is limited within two phenyl rings. The conjugation length in PPy films can be extended by forcing the planarity of the polymer chain due to inter-chain packing. The planarity could account for the red shifting in emission energy. Moreover, lattice relaxation can also be profound in films as compared to solution and powder. These results imply that the spectral diffusion in conjugated polymers is indeed from the migration of correlated electron-hole pairs to low energy sites. Spectral diffusion was observed in PPV and its derivatives [48]. It is also strong evidence for the excitonic nature of the photoexcitation in PPV and derivatives. The minimum Stokes shift observed in PPy solution reveals a similar mechanism obtained from the site-selective fluorescence studies of PPV: the major emitting species are a statistical distribution of different conjugation lengths in PPy. The large Stokes shift in films could also be the results of the absorption and re-emitting of photons by the low energy tail. The forcing of planarity in films could cause conjugation to extend in the polymer chain. This is particularly true in the case of thin films since the inter-chain packing plays a more important role than other forms, such as powder. The extended conjugation should favor the migration of neutral species, such as excitons. As for the luminescence lifetime of PPy solution, the absence of long components as seen in films can be well
understood by lattice relaxation and distribution of energy sites in the films. In solution, the forced conjugation and the enhancement of migration rate disappear. Therefore, the PL of PPy solution is mainly due to localized excitations. Spectral diffusion in solution is probably due to structure relaxation on a local order.

Finally, it is important to point out that 'excimer-like' model does not fully account for the photophysics of PPy. For time-resolved experiments, I did not observe any rise time (or formation time) for lower energy emissions of PPy relative to the decays of higher energy emissions, e.g., see Figures 67 (film) and 72 (solution). This certainly rules out the possibility that excimers form beyond the time-resolution (~ 35 ps or 10 ps by deconvolution) of the experiments. Yamamoto et al. [160] claimed that, for concentrated PPy solution (0.5 M; HCOOH), they observed a 10 ps rise time for emission at 2.17 eV, which is consistent with the 10 ps decay constant observed at 2.8 eV emission. The longer components of the luminescence decays were fit to a bi-exponential with lifetimes of 90 and 300 ps for both 2.8 and 2.17 eV. Yamamoto et al. were using a PMT with a 80 ps time-response (For comparison, in this work, the time-response of the PMT is ~ 35 ps, and the electronic components in the TCSPC setup are perhaps more advance than the ones used by Yamamoto et al.). In this case, a 10 ps rise time is certainly not justifiable even with the deconvolution of the data. Moreover, the excimer model does not explain the time evolution of spectral diffusion, the progression of the Stokes shift, and the dependence of the emission on excitation energy.

In conclusion, I demonstrated the unique photophysical properties of PPy. The polymer displays fluorescence from (\(\pi-\pi^*\))\(^1\) and (\(n-\pi^*\))\(^1\) states and phosphorescence emission. Spectral diffusion and Stokes shift are shown to be in close relation to the migration of excitons and geometric relaxation of the radiative segments in PPy. I stress the difference in luminescence properties between polyarylene and polyaryl vinylene by pointing out the presence of vinyl groups in PPV and derivatives.
CHAPTER V
CONCLUSIONS

Polyaniline

The photoexcited states of the three oxidation states of polyaniline: LEB, EB and PNB have been studied by ultrafast spectroscopy, in particular, picosecond photoinduced absorption (2.9 eV) and bleaching (1.9 eV) spectroscopy. For photoexcitation at 2.1 eV, the photoexcited species were the molecular excitons in the cases of EB (and LEB) and free electron-hole pairs in the case of PNB. Free carriers were generated for all three forms of polyaniline by photoexciting the polymers into the $\pi-\pi^*$ transition (used a pump energy of 4.27 eV). The probe energy of 1.9 eV was studying the recovery of the ground state of EB and PNB. Previously, in the near-steady state photoinduced studies of polyaniline, the transition of ~ 2.9 eV was attributed to a hole polaron ($P_{\beta}^+$) [24].

The important roles of ring-torsional degrees of freedom were demonstrated by investigating the dynamics of photoexcitations in restrained (solid) and unrestrained (solution) environments. When excited into the exciton band (EB) or the Peierls gap (PNB), the photoexcited species in NMP solution decayed within 30 ps. However, under similar experimental conditions, a long-lived component (> ns) appeared in thin films and powder samples of EB and PNB. In contrast to 1D diffusion dynamics observed in polyacetylene [96,109], the recombination kinetics of the photoexcited species in NMP (excitons in the case of EB and electron-hole pairs in the case of PNB) exhibited unusual behaviors as the relaxation do not follow an exponential or a power law ($t^{0.5}$) form. It was found that, in solid form, the dynamics of the photogenerated species mainly followed a dispersive transport scheme, which should arise from random walks of charged or neutral species along the
polymer chains before the occurrence of trapping or hopping and recombination. Nonlinear behavior of the excited species was observed at high radiant intensities and there was evidence for the presence of sample damage.

For EB in NMP or EB solid, the hole polaron lasted longer than the exciton ($\tau_{\text{polaron}} > \tau_{\text{exciton}}$). The situation was reversed for PNB in NMP, in which the polarons decayed faster than the recovery of the ground state ($\tau_{\text{polaron}} < \tau_{\text{free carrier}} (> 10 \text{ ps})$). (Data for picosecond PIB of PNB in solid form were not available for comparison.) In comparing the PIA results, the lifetime for hole polaron was longest in LEB (e.g., in NMP, $\tau_{\text{polaron (LEB)}} \sim 100 \text{ ps}$, $\tau_{\text{polaron (EB)}} \sim 10 \text{ ps}$ and $\tau_{\text{polaron (PNB)}} \sim 2 \text{ ps}$). Apparently, quinoid moieties act as trapping (quenching) sites for the hole polarons ($P_{B}^+$). Intensity dependence studies have revealed that the decay mechanism is mainly unimolecular for both the 2.0 eV band (PIB) and the 2.9 eV band (PIA) of EB and PNB. These results indicate that in polyaniline the confinement length is longer than the typical decay length of the photoexcited species created from 2.1 eV pump. Superlinear behavior appeared in the intensity dependence study of high radiant power on samples of EB in NMP. It is suggested that exciton screening and nonlinear absorption (intense bleaching of the ground state) are the possible causes of the superlinear behavior.

When EB/NMP or PNB/NMP was excited into the $\pi-\pi^*$ transition (used 4.27 eV), the visible absorption of the exciton band and the Peierls gap disappeared rapidly, and the quinoid sites appeared to be quenched by the free electrons and holes. No consistent transient decay of the exciton band and the Peierls band was obtained. Nevertheless, for the polaron bands, longer lived components (> 200 ps) existed for EB/NMP and PNB/NMP with 4.27 eV excitation as compared to results obtained with 2.1 eV excitation. This feature was even more pronounced for the 4.27 eV excitation of LEB in NMP as there was the presence of ns components in the decays of the $P_{B}^+$. For the UV excitation, the 2.9 eV photoinduced absorption is due to hole polarons that centered on phenyl rings, $P_{B}^+$ [175], which should persist longer since there are fewer quinoid sites after the photoexcitation of 4.27 eV. These results strongly suggest that the quinoid moiety in polyaniline can act as a quenching site for $P_{B}^+$.
Polyp(p-pyridine)

Photophysical properties of pyridine-based polymers were investigated via time-resolved and steady state fluorescence and picosecond photoinduced absorption spectroscopy. It is suggested that the nature of the photoexcitations in PPy is primarily excitonic. PPy is soluble in acidic solvents, which facilitates the study of photophysical properties in a variety of sample forms: solution, thin films and powder. Results of the photoluminescence and excitation studies have confirmed the notion that optically active species in conjugated polymers are comprised of sub-units of the chain likely separated by topological defects. The PL of PPy features a minimum Stokes shift when chains of the polymer are unrestrained, such as in solution. Whereas, a persistent apparent Stokes shift is present for the PL occurring in a confined environment, such as films. Spectral diffusion is revealed from the excitation spectra of different concentrations of PPy in HCOOH. For a solution of $10^{-4}$ M (monomer unit), a favorite emitting site (a peak of the PLE) was found to locate at 3.024 eV when the excitation spectra were probed at progressively lowering the monitored energy. This result should compliment data obtained from low temperature site selective fluorescence (SSF) spectroscopy, one of the very few methods applicable to nonsoluble polymers like PPV. I observed that peak position of the PL of PPy films (PPy/ITO/glass) depends on excitation energies. Phosphorescence (1.77 eV) was detected at photoexcitation energies significantly above the band edge for PPy films. In addition to PL from thermalized $(\pi-\pi^*)^1$ states, fluorescence from $(n-\pi^*)^1$ state also was observed in films ($\sim$ 3.45 eV).

Time-resolved fluorescence studies revealed red shifting of the PL with the evolution of time, which is a signature of spectral diffusion and is further proof for the statistical nature of the chain segments. The decay of the primary PL (from $(\pi-\pi^*)^1$ states) was found to be nonexponential ($< 1$ ns), which is a characteristic feature of neutral excitations executing an incoherent random walk. Intensity and temperature studies of the primary PL have shown
that the PL was intensity independent and nominally temperature dependent. The temperature dependence can be attributed to the structural relaxation of the emitting sub-unit. The intensity independence of the PL is also a signature arising from random walks. There was a 35 ns component in the \((n-\pi^*)^1\) emission, which was shown to be temperature and intensity independent. We attribute the temperature independence to the fact that the \((n-\pi^*)^1\) orbital is almost orthogonal to the conjugation path. I have determined, from a near-steady-state measurement, a phosphorescence lifetime of 0.5 and 15 ms at 280 and 20 K, respectively, for the 1.77 eV band. Initial picosecond photoinduced studies of PPy in HCOOH have shown that the PIA at 2.1 eV decayed at a faster rate than the corresponding PL at 2.95 eV. Further studies are required to expose the photophysical picture of the photoinduced absorption.
LIST OF REFERENCES


[164] PM3 calculations done by J. W. Blatchford.


