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Structure and long-lived defects in polyanilines

Józefowicz, Mikolaj Edward, Ph.D.

The Ohio State University, 1991
STRUCTURE AND LONG-LIVED DEFECTS IN POLYANILINES

A 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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1991

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This work explores the major role structure and, in particular, ring torsion angles play in determining chemical and physical properties of polyanilines.

The structure of various forms of polyaniline and of poly-o-toluidine is studied with x-ray diffraction. Two separate classes of emeraldine are described: materials originally precipitated in the form of salt (Class 1) characterized by amorphous base form EB-I and partially crystalline (space group P1) salt form ES-I. Materials originally precipitated in the base form belong to Class 2 and are partially crystalline both as base EB-II (Pbcn) and as salts ES-II (Pc2a). Differences in crystallinity affect solubility and other properties. C₈ rings are flatter in salt samples, aiding electron delocalization. Leucoemeraldine has ES-I-like structure, whereas pernimгранiline has structure similar to EB-II. Poly-o-toluidine (POT) exhibits structural features similar to Class 1 emeraldines, but with greater interchain spacing. This is seen as an origin of the greater electron localization observed in POT.

Temperature dependent structural studies of oriented EB-II films show that the average ring-tilt angle decreases by about 1° when the temperature is lowered from room temperature to 135 K. This is correlated with previous theoretical calculations. Polarized IR absorption studies on oriented films confirm IR mode assignments and allow estimation of the degree of orientation in the material. They offer also an independent estimate of non-planar ring conformation.

Photoinduced FTIR studies of long-lived defects in polyanilines show that the defect number growth curve is a stretched-exponential, which is typical for disordered systems. Several models giving this type of non-Debye behavior are discussed. Electronic photoinduced spectra show the same behavior and it is concluded that mass of the photoinduced defects does not change with time. Photoinduced defects involve ring torsion changes, which explains their large mass and stability.
To Ela
Eli
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CHAPTER I

INTRODUCTION

In the first section of this chapter, the field of conducting polymers will be introduced, with particular emphasis placed on polyacetylene. The polyaniline class of polymers will be described in the second section. The scope of this work is presented in the section three.

1.1 INTRODUCTION TO CONDUCTING POLYMERS

Electrical conductivity is not a property that one would commonly associate with organic polymers. Yet in the past fifteen years or so a whole new class of polymers was discovered, polymers that can be chemically treated (doped) to approach the conductivity of metals. The one that is simplest in structure and that has attracted the most attention thus far is polyacetylene (Fig. 1). It was synthesized first as a powder in 1958 using the so-called Ziegler-Natta catalyst [1] and then as a silvery-black film by Shirakawa et al. in 1974 [2]. Three years later it was discovered [3] that semiconducting pristine polyacetylene can be doped to become conducting. Since then numerous dopants have been discovered, both acceptors, such as AsF₅ or iodine, and donors, such as sodium. Quite recently it was reported that iodine-doped polyacetylene attains the conductivity of $\sigma \approx 10^5$ S/cm - approaching that of copper [4, 5].

The discovery of conductivity in polyacetylene spurred research in the area of physics describing properties of one-dimensional systems. Trans-polyacetylene
Figure 1: Structural formulas of polyacetylene isomers: (a) - cis-transoid, (b) - trans-cisoid, (c) - trans-transoid. Isomer (c), called “trans” for short is energetically most favored and stable.

(Fig. 1c) is an ideal system to compare theory with experiment due to its structural simplicity. The four valence electrons in a single carbon atom in polyacetylene are hybridized into a $sp^2p_z$ configuration. Two $sp^2$ electrons form $\sigma$ bonds with neighboring carbon atoms and one forms a $\sigma$ bond with a hydrogen atom. The simplest Hamiltonian describing the behavior of the remaining $p_z$ electrons is the Su-Schrieffer-Heeger (SSH) Hamiltonian [6]. Even though it was developed for polyacetylene, it introduces concepts that are important in studying other conducting polymers, and therefore will be briefly described here. A detailed description of the SSH Hamiltonian and its extensions can be found in [7].

The SSH Hamiltonian contains several assumptions: the $p_z$ (or $\pi$) electrons are treated explicit, the $\sigma$ bonds are treated as “springs”, electrons respond instantaneously to changing atomic positions, and electron-electron interactions are unimportant. The SSH Hamiltonian has the following form:

$$H_{SSH} = \frac{1}{2} \sum_n M \dot{u}_n^2 + \frac{1}{2} \sum_n K (u_{n+1} - u_n)^2 - \sum_{n,s} t_{n+1,n} (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s})$$  (1.1)

The first term is the kinetic energy term, with $M$ being the mass of an CH unit and $u_n$ being the displacement of the $n$th C atom in a chain from an equal-bond-length position (see Fig. 2 for schematic picture of the model discussed here). The second
Figure 2: Schematic polyacetylene chain for SSH Hamiltonian. $\sigma$ bonds are indicated as springs and individual $p_z$ orbitals are marked. One electron occupies each orbital (From Ref. [8]).

term is a the $\sigma$ bond potential energy ("spring" term) where $K$ is the effective spring constant. The third term is the $\pi$ electron energy within the tight-binding approximation. The transfer integral between neighboring sites is given by $t_{n+1,n}$ and $c_{n,s}^\dagger$ and $c_{n,s}$ are creation and annihilation operators for a $p_z$ electron with spin $s$ at site $n$. The transfer integral is assumed to vary linearly with interatomic spacing: $t_{n+1,n} = t_0 - \alpha (u_{n+1} - u_n)$; this relation constitutes the interaction of electrons and phonons in the system, i.e. the electron-phonon coupling.

For a uniform, undimerized chain ($u_n = 0$) with atoms at a distance $a$ apart, the Hamiltonian is easy to solve. The classical expression for energy dispersion is

$$\epsilon(k) = \epsilon_0 - 2t_0 \cos ka$$

(1.2)

A plot of the energy dispersion and of the density of states calculated for an undimerized chain (after Ref. [8]) is given on Fig. 3.

Polyacetylene in such an undimerized state would possess a half-filled band and therefore would be metallic. It is well known, however, that such a one-dimensional chain undergoes a Peierls distortion, that is dimerization. Indeed, the SSH Hamiltonian can be solved for a uniformly distorted chain of alternating shorter and longer bonds ($u_n = (-1)^n u$) and it is found that the overall energy decreases. This result is intuitively evident from a chemical point of view - a system of conjugated double bonds is much more stable than system with unpaired $p_z$ electron at every carbon atom. Plots of the calculated energy dispersion and density of states for a dimerized chain is given in Fig. 4. In Fig. 5 the energy per -CH- unit calculated as a function of the dimerization parameter $u_0$ is drawn.

As can be seen from Fig. 4, an energy gap opens at $k = \pi/2a$ and the system
Figure 3: (a) energy dispersion and (b) density of states calculated for an undimerized polyacetylene chain. The filled states are marked in (b) (From Ref. [6]).

Figure 4: (a) energy dispersion and (b) density of states calculated for a dimerized polyacetylene chain. The filled states are marked in (b) (From Ref. [6]).
becomes a semiconductor with a gap of about 1.4 eV. Figure 4 also explains what drives the Peierls distortion: energy of the highest occupied states is lowered which more than offsets the energy required to compress and expand the “springs” of σ bonds. From Fig. 5 it can be seen that two degenerate ground states exist. They are represented schematically in Fig. 6a (from Ref. [9]) as regions in the polymer with double bonds tilted to the left (\) or right (/\). The border between those two phases (called “A” and “B” phases) can be thought of as a domain wall. An order parameter $\Psi$ can be defined: $\Psi = (-1)^n u_n$. The evolution of such a parameter around such a domain wall can be calculated within a continuum version of the SSH Hamiltonian [10]. The result is shown in Fig. 6b. The domain wall takes the form of a bond-length defect which spreads over several bond lengths $a$. Such a defect is called a soliton. From a chemical point of view it is an unpaired $p_z$ electron, or a “dangling bond”, as denoted by the dot in Fig. 6a.

Solitons occur naturally in pristine, as-polymerized polyacetylene or can be created by doping. Acceptors (e.g., iodine, SF$_5$) create positively charged solitons, donors (e.g., sodium) create negatively charged solitons. Charged solitons are spinless, whereas neutral solitons have spin. Soliton defects create additional states in the middle of the polyacetylene energy gap. A schematic diagram of all three types of solitons is shown on Fig. 7. At this point it is clear that polyacetylene (and

---

**Figure 5**: The energy per CH repeat unit as a function of dimerization amplitude $u$. Two degenerate states exist at $u = \pm u_0$ (From Ref. [7]).
Figure 6: (a) chemical bond and (b) order parameter $\Psi$ diagrams of a soliton (From Ref. [9]).
other conducting polymers) differ from classical semiconductors in the nature of the defects. For polymers, the dopant atoms (or molecules) are positioned interstitially between polymer chains, accept or donate charge to the polymer, and create (via electron-phonon coupling) a distortion in the order of the polymer backbone. As will be seen later, defects can also be created by photoexcitation.

The discovery of conductivity in polyacetylene prompted intensive search for other conductive polymers and soon it was discovered that there exists a whole class of polymers with similar properties to polyacetylene. Repeat units of representative examples are shown in Fig. 8. Numerous variations of these basic polymers, with various side groups, were synthesized. It can be noted that all the polymers presented in Fig. 8 are in a sense structural variations of polyacetylene - they all contain a carbon chain with conjugated double bonds (chemically speaking). This chain can be bridged by heteroatoms (as in polypyrrole, polythiophene) or additional carbon bridge (as in poly-p-phenylene). Such polymers can still be analyzed within the polyacetylene framework, but with significant modifications. For example, the two dimerization states (Fig. 5) are no longer degenerate for those materials. This can be easily visualized by exchanging single and double bonds on
Figure 8: Repeat units of representative conducting polymers (insulating forms, before doping).
the carbon chain in any of the polymers from Fig. 8. One phase becomes strongly favored energetically and as an effect soliton states are no longer stable in such polymers. Instead, other "bond alternation" defects are expected to be stable - polarons and bipolarons. Those can be thought of as a soliton and an antisoliton bound together. If for example an energetically less stable phase is named B, than solitons A|B and B|A will be confined together to minimize the extent of phase B. Polaron and bipolarons can be thought of as soliton pairs bound so closely that all that remains from phase B is a small change in the order parameter. Order parameter diagrams for polarons and bipolarons with corresponding electronic levels created in the gap and their occupancy are shown in Fig. 9. Again, polarons or bipolarons can occur spontaneously in the polymer or can be created by doping or photoexcitation.

1.2 POLYANILINE

Common features in all the conducting polymers mentioned in the previous section (see Fig. 8, p. 8) are: (1) - the conjugated carbon backbone and (2) - the fact that electrons are taken from or transferred to the polymer backbone when the polymer
is chemically (or electrochemically) doped. Polyaniline is very different in both aspects. It contains nitrogen in the conjugation path and can be doped with the transfer of a proton to the backbone, with no change in the overall number of electrons.

Polyaniline has been known for about 150 years now. Originally it was used as a dye, called “aniline black”, along with a whole family of dyes based on aniline. Due to the fact (as we know now) that it may exist in several chemical variations, its exact chemical composition and structural formula were, for a long time, a matter of controversy. The British periodical *Journal of the Society of Dyers and Colourists* from January 1908 prints two papers discussing the subject [12, 13]. In the two papers, authors analyze elemental composition of various polyaniline powders and propose several possible formulas. The term “emeraldine” is used as a description of a moderately oxidized polyaniline powder. In the same issue, the Society of Dyers and Colourists offers a £10 prize for “the most satisfactory method of using Formic Acid on a practical scale, as a substitute for hydrochloric or other acids, in dyeing cotton piece goods or yarns an aged Aniline Black”. This probably may be regarded as the first grant for the study of polyaniline.

Extensive work on the electrochemical, electrical and chemical properties of polyaniline was carried out by M. Jozefowicz and coworkers in the 1960’s [14,15]. It was discovered for example that chemically prepared polyaniline pellets are highly conducting, and that the mechanism of conductivity is electronic. M. Jozefowicz and coworkers also discovered that conductivity of polyaniline salts is affected by the oxidation and protonation state of the polymer, as well as the amount of water absorbed. The use of polyaniline electrodes in batteries was proposed. This work however was not pursued further and, in particular, no origin of the electronic conductivity was proposed.

The renewal of interest in polyaniline occurred after the discovery of the doped form of polyacetylene. Searching for conducting polymers other than polyacetylene, researchers rediscovered polyaniline. Synthetic methods and chemical mechanisms of doping and redox reactions have been firmly established in the early 1980’s [16]. For a review of the chemical literature on polyaniline, see Ref. [17].

Figure 10 presents structural formulas of three oxidation states of polyaniline. They can be characterized by the relative concentration $y$ of fully reduced repeat units \(-\text{NH}-\text{C}_6\text{H}_4\text{NH}-\text{C}_6\text{H}_4\)-. Thus, fully reduced leucoemeraldine (i) has $y = 1$, \(y = 0\),
Figure 10: Three oxidation states of polyaniline: (i) - leucoemeraldine, (ii) - emeraldine, (iii) - pernigraniline.
emeraldine (environmentally stable and the most studied form) (ii) has \( y = 0.5 \) and pernigraniline (iii) has \( y = 0 \) because it contains only oxidized repeat units (\(-N-C_6H_4-N=C_6H_4=\)) \[46\]. A given oxidation or reduction state can be obtained both chemically and electrochemically. Nitrogen valence electrons are \( \text{sp}^2 \text{p} \text{z} \) hybridized, so that polyaniline is expected to have a zig-zag form in all of its oxidation states. Oxidation or reduction changes the number of nitrogen \( p \text{z} \) electrons - from 1 per N in pernigraniline to 2 per N in leucoemeraldine.

Another reaction occurring in the polyaniline system is an acid-base reaction. Polyaniline can react with aqueous solutions of acids of appropriate pH to form salts. Since the conductivity of the polyaniline-emeraldine can increase from \(10^{-10} \text{ S/cm} \) (base form) to \(10^2 \text{ S/cm} \) (salt form), this process is also referred to as doping. Doping of emeraldine base does not involve change in the number of electrons on the backbone but does involve proton transfer to the nitrogen atom. This is a unique process in polyaniline and is due to the fact that nitrogen atoms in the polyaniline backbone are active basic sites. The formula of the emeraldine base and proposed formulas of emeraldine salt are given on Fig. 11. Based on magnetic studies \[18\], the polaronic formula (Fig. 11(ii) ) is accepted as the appropriate one for ordered regions of emeraldine salt, while bipolaronic form, Fig. 11(iii), is more appropriate for the disordered form \[19\].

All properties of polyaniline change dramatically with oxidation/reduction and doping. Each polyaniline sample has to be therefore uniquely characterized in both doping and oxidation levels. Figure 12 (from Ref. \[20\]) shows a three-dimensional plot of relative conductivity versus the potential of polyaniline with respect to SCE electrode and versus the pH of the equilibrating solution. This is an example of the rich chemistry and related physics in polyaniline.

Calculations of the electronic structure of polyaniline are by far more complicated than for polyacetylene: polyaniline contains more \( p \text{z} \) electrons per repeat unit, and is geometrically more complex. It contains rings which can rotate, affecting the \( p \text{z} \) transfer integral and through this the overall electronic energy. Electronic structure calculations can be divided into two groups: molecular orbital calculations on small oligomers (two-three rings) that approximate polyaniline and band structure calculations on ideal, infinite, and isolated chains.

Calculations on oligomers indicate that benzenoid rings are tilted with respect to the plane of the molecule and quinoid rings are flat \[21\]. Electronic spectra pro-
Figure 11: Emeraldine base and salt: (i) - base, (ii) - salt, polaronic form, (iii) - salt, bipolaronic form.
Figure 12: Relative room-temperature (compared to emeraldine salt) conductivity of polyaniline as a function of potential and pH. Emeraldine base is marked with • and emeraldine salt is marked with ■ (from [20]).

jected from (phenyl)-N-(quinoid)-N-(phenyl) model agree well with experimental spectra of oligomers and do not differ substantially from those found in polymer [22]. An absorption feature occurring at 1.4 eV is attributed to an exciton involving charge transfer from neighboring benzenoid rings to the quinoid rings, accompanied by change in the quinoid ring tilt angle $\phi$ from essentially zero to approximately 60° out of the plane of the nitrogen zig-zag [21]. This was the first indication that defects (and photoinduced defects in particular) in polyaniline involve significant changes in ring rotations.

Band structure calculations indicate that leucoemeraldine (LEB) (fully reduced form of polyaniline, Fig. 10(i)), has an energy gap that originates from the $C_6$ electronic structure [23]. Emeraldine (EB, Fig. 10(ii)) in addition to the large (3.6 eV) gap, similar to that of LEB, has an absorption at 2 eV attributed to $\pi \rightarrow \pi^*$, a transition from the benzenoid based highest occupied band to the quinoid based lowest unoccupied orbital [24, 25]. Pernigraniline (PNB), Fig. 10(iii), a fully oxidized form of polyaniline ($y - 1 = 1$) differs in that it has a degenerate ground state with the gap (2.3 eV) arising from Peierls distortion involving both bond length [26] and ring-torsional [23, 27] dimerization. Recently, it was calculated that those two contributions to the gap are additive and nearly independent [28].
Photoinduced and doping-induced defects in polyanilines are expected to include significant changes in the C₆ ring torsion angle. Calculations on leucoemeraldine [23, 29] indicate that a ring-rotational hole polaron (P⁺) is a stable excitation, with a binding energy of ~ 0.6 eV. Figure 13 shows a schematic structure and energy level diagram for a ring-rotational hole polaron in leucoemeraldine. Near-steady state photoinduced absorption studies in leucoemeraldine [30] show photoinduced absorptions at 0.75 and 2.85 eV which are consistent with absorptions expected in this scheme (marked as ω₁ and ω₂ in Fig. 13b). The mass of this defect is calculated to be on the order of 50 mₑ. Such a large mass is due to the moment of inertia of the C₆ ring undergoing torsional motion about the N-N axis. The presence of a hole polaron centered on a benzenoid ring causes this ring and its neighbours to assume more planar configuration. Hole polarons are associated with new states in the gap, giving rise to two in-gap absorptions whose energies sum to the gap energy. Such transitions have been observed experimentally in near-steady photoinduced absorption studies [30]. Also observed are photoinduced

![Figure 13: Ring rotational hole polaron in leucoemeraldine: (a) - schematic structure, (b) - energy level diagram (from Ref. [23]).](image)
infrared features, due to lowering of the symmetry around the \( p \)-disubstituted benzene rings. Other defects described as possible in LEB are ring-rotational solitons \[23, 31\] and electron polarons \[30\]. Existence of solitons has not been confirmed experimentally, some may form however during preparation of leucoemeraldine.

Bond-alternation solitons have been predicted as stable defects for pernigraniline \[26\]. Such defects, due to small changes in the bond lengths involved, are expected to have small effective mass, of the order of \( 5m_e \). Pernigraniline however, in contrast with polyacetylene, has an additional ring torsional degree of freedom. Hence ring-torsional polarons are expected to be stable, large mass defects in pernigraniline \[23\]. Recent experimental study confirmed existence of both types of defects \[32\]. Experimental evidence suggests that the dominant defect species in emeraldine base, at least on long time scale are ring-rotational polarons \[30, 33\].

1.3 The Scope of this Work

This dissertation can be divided into two parts. The first part deals with the very broad issue of the influence of sample preparation history and chemical state of the sample on the x-ray structure and crystallinity of the sample, with particular stress placed on the evaluation of ring tilt angles. Before this study the structure of polyaniline had not been systematically studied at all. Given the overall high level of interest in polyaniline, the lack of reliable information about its x-ray structure may seem surprising. Crystallinity in some polyaniline samples was reported \[34, 35\], without an attempt, however, to correlate it in a broader context with the preparation methods or to solve the crystalline structures. Baughman et al. \[36\] studied crystals of ClO\(^-\) and BF\(_4^-\) salts of tetramers and dimers of aniline. Figure 14 presents the structure of the phenyl-end-capped tetramer of polyaniline. Ring angles are found to be alternately \(+15^\circ\) and \(-15^\circ\) out of the plane defined by the nitrogen atoms. Bond length data from Ref. \[36\] will be used in calculations of x-ray structures in the present work.

Electronic structure calculations \[23\] predict that rings in undoped leucoemeraldine are tilted out of the plane due to steric interactions. Figure 15 presents a calculated total energy curve as a function of ring tilt angle. The function is asymmetric, implying that average ring angle should change with temperature. The right plot in Fig. 15 shows the calculated variation of this angle with temperature.
Figure 14: Structure of aniline tetramer ClO₄⁻ salt (from Ref. [36]).
Figure 15: Calculated total energy per site vs ring torsion angle in leucoemeraldine (left) and calculated variations in the average ring angle and energy gap with temperature (right) (From Ref. [23]).

Results and discussion of x-ray experiments are given in Chapter IV. It will be seen that the crystallinity and structure of polyaniline samples depend not only on the chemical state of the sample but also (and with surprising results) on the sample history. In some cases, detailed structural parameters will be elucidated, in particular ring tilt angle, which is expected to influence electron delocalization and defect stability. Ring tilt angle with respect to the plane of nitrogen atoms varies with polymer oxidation state, doping and derivatization. Thermal evolution of emeraldine base structure will be correlated with electronic calculations mentioned above.

The second part of this work deals with the time evolution of the very long-lived photoinduced defects in polyanilines and its intimate relationship to motion of the C$_6$ rings. While emeraldine is the least described by theory, it is the most studied experimentally form of polyaniline. Of particular interest is the broad range of time scales exhibited by photoinduced features in emeraldine: from femtoseconds
to hours and even days.

**Femtosecond** nonlinear optical response of emeraldine was measured with degenerate four-wave mixing (DFWM) setup [37]. The pump energy was 2 eV (excitonic peak). A transient DFWM signal with a decay time of the order of 300 fs was observed at 2 eV. Even shorter relaxation times may exist.

**Picosecond** photoinduced exciton bleaching was observed using pump and probe technique [38]. At time scale 40 ps < t < 4 ns bleaching varies as t^-\beta where \beta \sim 0.115 and is not dependent on temperature. (At even shorter time scale, t < 40 ps, decay follows a power law, but with \beta \sim 0.2). It was pointed out that this result supports central role of exciton formation with subsequent lattice relaxation, probably through rotations of the C6 rings. Long-time photoinduced bleaching effects were observed and it was estimated that about one in 10^7 excitations present at 10 ps after photoexcitation gives rise to long-lived (~minutes) photoexcitation. Recent study [39] explored picosecond photoinduced absorptions of emeraldine base pumped at 2.1 eV and probed at 1.5 eV and 2.9 eV. Both show rapid decay, but 1.5 eV peak decays more rapidly (~ 100 ps) and does not show a substantial residue on the nanosecond time scale, in contrast with 2.9 eV absorption and 2 eV bleaching, measured earlier [38]. 2.9 eV peak decay rate slows down when the temperature is decreased. In addition, the 2.9 eV picosecond photoinduced absorption in emeraldine solutions has a very fast decay with no long-lived component. These results support the importance of ring torsions and environmental conditions in the dynamic of photoexcited defects.

**Millisecond** time scale near steady state (chopping) experiments were performed on emeraldine base and leucoemeraldine [30, 40]. The excitonic bleaching in emeraldine shows weakly temperature dependent frequency behaviour f^-0.47 and scales linearly with pump beam intensity, indicating unimolecular decay. 1.4 eV and 3.0 eV photoinduced peaks show different chopping frequency behaviour, slower than excitonic bleaching and are signatures of polaronic states.

**Seconds** and **minutes** time scale was explored in “long-time” photoinduced experiments [30, 33]. IR and near-IR studies at low temperatures (80 K) were combined with results from near-steady state experiments to provide assignments for the origin of long-lived photoinduced features. Both the near-IR 1.4 eV (11,150 cm^-1) photoinduced peak and the mid-IR photoinduced peaks and bleachings are described as signatures of a hole polaron centered on a benzene ring and trapped
near quinoid, \( P_{BQ}^+ \). Mid-IR photoinduced modes are activated by the lowering of symmetry around disubstituted benzenoid and quinoid rings. Those modes are substantially weaker than the electronic photoinduced mode at 1.4 eV, indicating that \( P_{BQ}^+ \) has a large mass, calculated as \( M_{\text{polaron}} > 60m_e \). Long-lived photoinduced features in leucoemeraldine base were also studied, and were found similar in character but much weaker than those in emeraldine. They are associated with the presence of residual quinoids, essential to the stabilization of \( P_{BQ}^+ \)'s, in the leucoemeraldine samples.

This study extends the time scales studied to hours. Long-time monitoring of photoinduced IR peaks, both with the pump light on and with the pump light off is employed. Results of FTIR experiments are presented and discussed in Chapter V. Photoinduced defects are found to follow a "stretched-exponential" growth curve and have very long decay times, on the order of days. The mass of the photocreated defects does not change with time.

A broad range of samples has been used in this work. Chapter II has been devoted entirely to the description of the details of chemical methods of sample preparation. Chapter III describes the experimental setups used. Chapter VI offers a summary and a conclusion.
CHAPTER II

CHEMISTRY AND SAMPLE PREPARATION

Chemical methods used to obtain desired samples of polyaniline and its derivatives are given in the first section of this chapter. Methods of sample preparation in forms suitable for x-ray and FTIR experiments are described in section two.

2.1 CHEMISTRY OF POLYANILINES

2.1.1 EMERALDINE MATERIALS

Polyaniline in its emeraldine form is stable in air and doping/dedoping reactions are conducted in aqueous media. Emeraldine samples were prepared in various ways, in order to examine the relationship between the preparation method and properties of the material. A scheme of the preparation of various emeraldine powders is presented in Fig. 16.

Emeraldine salt "as prepared" ES-I powder was synthesized\(^1\) by adding oxidant \((\text{NH}_4)_2\text{S}_2\text{O}_8\) to a solution of aniline in 1.0 M HCl [41]. The reaction vessel was cooled in an ice bath and the solution was constantly stirred. After about one hour, the polyaniline in the emeraldine form was collected as a precipitate, filtered, and washed with aqueous 1.0 M HCl solution. Detailed studies [41, 42] suggest that "as prepared" EB-I powder prepared in this way is 42% protonated (degree of

\(^{1}\text{Frequently by various members of Prof. A.G. MacDiarmid research group at University of Pennsylvania.}\)
Emeraldine

Class I

aniline (HCl) → (NH₄)₂S₂O₈ → emeraldine salt

"as prepared" ES-I

↓ NH₄OH

emeraldine base EB-I

HCl  NH₄OH

↓  ↓

emeraldine salt ES-I

↓

HCl gas/NMP solution

Class II

emeraldine base EB-II

THF/NMP

↓

emeraldine base EB-II'

↓ HCl

emeraldine salt ES-II

NH₄OH  HCl

Figure 16: Preparation scheme for emeraldine samples.
protonation or doping level $x$ is defined as $[\text{Cl}]/[\text{N}]$ ratio. Alternatively, polyaniline was synthesized at -13°C and treated with HCl to obtain a doping level of 50%. X-ray data obtained on this ES-I powder, named “low temperature” ES-I, will serve as a basis of most of the structural evaluations on emeraldine salt ES-I in chapter IV.

Emeraldine base EB-I powder was prepared by washing emeraldine salt “as prepared” ES-I with a large excess of 0.1M $\text{NH}_4\text{OH}$ for 24 hrs, followed by repeated washing with distilled water and pumping in dynamic vacuum. This emeraldine powder was subsequently used to produce “Class II” powders (see Fig. 16) as well as NMP- and DMSO-cast films. Recent studies [42] suggest that emeraldine base EB-I prepared in this way has an oxidation level $(1-y) \approx 0.6$, or slightly overoxidized with respect to “ideal” emeraldine with $(1-y) = 0.5$. Therefore, samples referred to here as “emeraldine” possess oxidation state of approximately $(1-y) = 1/2$.

Emeraldine salt ES-I powder was prepared by equilibrating emeraldine base EB-I with HCl solutions of concentrations ranging from 0.001 M to 1 M for 48 hours, followed by drying in dynamic vacuum for 24 hrs. The pH of the doping solution was measured and the percent doping was obtained from the previously published doping level/pH curve [43], Fig. 17. Note that the doping reaction is reversible - ES-I samples can be dedoped with 0.1 M $\text{NH}_4\text{OH}$.

Emeraldine base EB-II powder was prepared by extracting the emeraldine base EB-I with tetrahydrofuran (THF) until the liquid was colorless, then extracting with $N$-methyl-2-pyrrolidone (NMP) until the liquid was almost colorless, and vacuum drying for 48 h in room temperature [44]. The THF extract was collected during the above extraction process and vacuum dried. It was shown [44, 46] that the extracted material has significantly lower molecular weight than emeraldine base powder.

Emeraldine salt ES-II powder was prepared by equilibrating emeraldine base EB-II powder with HCl solutions of concentrations ranging from 1M to 0.001M for 48 hrs, then drying in dynamic vacuum for 24 hrs. Since doping curve was not known in advance, elemental analysis was performed on each sample$^4$. The

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$^3$Emeraldine synthesized and dedoped under argon has oxidation level $(1-y) \approx 0.4$.

$^4$Originally by Xun Tang, Department of Chemistry, University of Pennsylvania.

$^4$By Robertson Laboratory Inc., P.O. Box 927, Madison, NJ 07940.
Figure 17: Plot of the doping level $x = [\text{Cl}] / [\text{N}]$ of emeraldine versus pH of hydrochloric acid. The squares (●) represent "Branch I" data [43] and dots (●) represent "Branch II" data. (□) represents doping level of emeraldine base EB-II' sample.
doping level was calculated as \( x = \frac{[C_1]}{[N]} \). In this way a new doping curve was constructed for ES-II samples (solid line ---- , points marked by (●) on Fig. 17). It differs from the curve for ES-I samples (broken line - - - -), particularly around pH=2. The origin of this difference will be discussed in Chapter IV.

Emeraldine salt ES-II powder, when dedoped, does not transform back to emeraldine base EB-II, but forms **Emeraldine base EB-II’** powder. This reaction is reversible. EB-II’ when doped forms emeraldine salt ES-II. Emeraldine base EB-II’ is soluble in NMP. When HCl gas is bubbled through this solution, emeraldine salt ES-I is precipitated. This completes the circle of transformations for emeraldine powder [44].

**NMP-cast film (EB-II)** was made by dissolving the emeraldine base EB-I powder in NMP. The solution was filtered, cast on a glass substrate and dried in air in an oven at 70 °C for 16 h [47]. The film was removed from the substrate by immersing it in water. As-prepared film contains significant amounts of residual NMP. It can be washed out by doping/dedoping the film. The typical thickness of the NMP film was of the order of 100 μm.

**Oriented NMP film** - some of the as-prepared NMP film samples were uni-axially oriented by stretching at ca. 110 °C in argon [48]. Films were maintained under stress of approximately 2 × 10⁷ Pa while being heated in an vacuum oven. Upon increasing the temperature beyond 60 °C there is continuous increase in sample length, with rapid increase and necking above 110 °C. Residual NMP acts as a plasticizer, as samples with no NMP do not stretch well. Maximum elongation obtained was 450%.

**Electrochemically prepared film** of emeraldine hydrochloride was the only polymer sample used in this study not synthesized chemically via emeraldine salt “as prepared” ES-I. The film was deposited on a Pt electrode 1/4 inch wide and 2 inches long by cycling the potential of the electrode (50 mV/s) from -0.15 to +0.75 V vs SCE in an aniline solution in 1 M HCl for four hours [49]. The film was removed from the solution at a potential of ~0.40 V characteristic of the emeraldine oxidation state. Some of the films were later dedoped in 0.1 M NH₄OH.

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5 The difference between emeraldine bases EB-II and EB-II’ is sample crystallinity; EB-II is partially crystalline whereas EB-II’ is amorphous. This will be discussed in Chapter IV. Note that the material labels here (EB-I, EB-II, etc.) follow conventions introduced in Ref. [45].

6 In most instances in Department of Chemistry, University of Pennsylvania by Elliot Scherr.
2.1.2 PNB, LEB, POT

**Pernigraniline PNB** (fully oxidized form of aniline) powder was prepared by oxidizing emeraldine base EB-I with solution of m-chloroperbenzoic acid in glacial acetic acid \([50]\). The brown-grey powder is air-sensitive and was handled in glove-box.

**Leucoemeraldine LEB** (fully reduced form of aniline) powder was made by reducing emeraldine base EB-I with hydrazine monohydrate \(\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\) for 12 hrs under static vacuum at 50 °C. The powder was then dried under dynamic vacuum and washed with methanol. The light grey powder is air-sensitive, therefore all the operations were performed in the vacuum line or glove-box \([51]\).

Preparation of **poly-o-toluidine (POT)** is very similar to preparation of emeraldine samples, with the exception that no evidence of the existence of an analog of “Class II” materials was discovered. **Poly-o-toluidine salt “as prepared” POT-ES** was synthesized by treating a solution of o-toluidine in HCl with ammonium peroxydisulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) similar to the synthesis of emeraldine salt \([52]\).

**Poly-o-toluidine base POT-EB** was prepared by stirring “as prepared” POT-ES with 0.1M \(\text{NH}_4\text{OH}\) for 24 hrs, then drying under dynamic vacuum for 24 hrs.

**Poly-o-toluidine salt POT-ES** was prepared by equilibrating poly-o-toluidine base POT-EB with aqueous HCl solutions of concentrations ranging from 0.001 M to 1 M. Since the doping curve for poly-o-toluidine was not known, each sample was analyzed for C, H, N, and Cl and the doping level directly calculated as \(x = [\text{Cl}]/[\text{N}]\). This produced doping data which are presented on Fig. 18. The doping reaction is reversible, as in the emeraldine case.

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7By Yan Sun of Department of Chemistry, University of Pennsylvania.
8In most cases by Jim Masters of Department of Chemistry, University of Pennsylvania.
9Again, by Jim Masters.
Equilibrium pH (HCl aq.)

Figure 18: Plot of the doping level $x = [\text{Cl}]/[N]$ of poly-$\omega$-toluidine versus pH of hydrochloric acid (solid line and ●). The squares (■) and broken line represent emeraldine "Branch I" data [43], shown for comparison.
2.2 Sample Preparation

Polymer powders to be studied by x-ray spectroscopy were put in Lindemann glass capillaries\(^{10}\). These capillaries are made of light-element glass and have very thin walls (0.01 mm) to minimize scattering. The sample needs to be firmly compacted at the bottom of the capillary in order to maximize the x-ray scattering from the sample. The task of putting very fine and light powders into the thin capillaries was tricky. Particularly, insulating samples were difficult to handle, due to the static charge buildup. It was discovered that the best way to compact powder on the bottom of the capillary is to put some powder in the small funnel at the top of the capillary and then to drop the capillary several times down the 30 cm glass tube onto a hard table (or glovebox) surface. Then, some more powder is put into the funnel and the process is repeated until the column of powder at the bottom is about 0.5 cm high. Sometimes the powder became blocked inside the capillary. Delicate pushing with a thin steel wire would usually unclog the passage. Care should be taken not to use wires coated with or made from soft metals, e.g. aluminum, as they will contaminate the walls of the capillary to an extent very clearly detectable by x-rays. Capillaries were sealed with a match flame or, in the case of air sensitive leucoemeraldine or pernigraniline which were handled in glove-box, first sealed with a bit of vacuum grease, taken out of the glove-box and then sealed with a flame. This procedure gave reproducible results.

Electrochemical films, grown on Pt electrodes, have a powdery appearance and could easily be scraped off the electrode. Powders obtained that way were put in Lindemann glass and studied the same way as regular powders.

NMP cast films were studied free-standing in the x-ray spectrometer. Usually, a single layer of film sufficed, but for some experiments (on oriented films) several layers folded together were used.

For infrared studies, powder samples were prepared in KBr pellets. The KBr powder was dried by heating in a vacuum oven overnight at temperature of 120 °C, then transferred to the glove-box. All the operations were conducted in the glove-box as the potassium bromide is hygroscopic. First, a 1% solid solution of the organic powder sample was prepared, by mixing powder with KBr (typically 5 mg

\(^{10}\) Made by Glas (Berlin, Germany), distributed in US by Charles Supper Co., Natick, MA 01760, size: 0.7 mm outer diameter.
of sample diluted with KBr to 500 mg) in a Wig-L-Bug. Then, a 25 mg portion of this solid solution would be further diluted to 500 mg with KBr and pressed in a special evacuable die. A 13 mm diameter pellet, 1 mm thick, containing 0.05% of the organic material resulted. When this recipe was strictly followed, pellets were reproducible within a single material. There were however some differences in material dispersion between various polyaniline powders, probably due to differences in crystallinity, grain size, etc.

For studies in the near-IR region, an NMP film was prepared on a quartz slide, following the recipe from the previous section.

For transmission-reflection experiments in mid- and far-IR regions, thin (about 1 μm thick) polyaniline base film was coated on a polished platinum foil. Platinum was put into a polymerizing aniline solution and kept immersed in the solution until the polymerization was complete. Then the film was dedoped with 0.1 M NH₄OH. Resulting film is uniform, semi-transparent, with rough surface and adheres strongly to the platinum substrate, offering good thermal contact.

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11 By Crescent, Hauppauge, NY. Milling session would consist of 10 "shakes", each 10 s long.
12 From Wilmad Glass. Pressure of 3.3 × 10⁸ Pa (4.8 × 10⁴ PSI) on the die was used.
13 By Sanjeev Manohar, Department of Chemistry, University of Pennsylvania.
CHAPTER III

EXPERIMENTAL

This chapter describes the experimental setups used. Details on x-ray experiments are given in the first two sections. FTIR experimental details are discussed in sections 3.3 and 3.4.

3.1 DEBYE-SCHERRER X-RAY EXPERIMENT

Weakly scattering organic samples pose problems for x-ray data collection. With modern counters, slow scanning speeds are required to obtain sufficient signal/noise ratio. For this reason, a photographic method was used for this work. Photographic film has this advantage that during the exposure it registers intensity from all scattering directions simultaneously, and in two dimensions, instead of only small angle at a time and usually in one (equatorial) plane as counters do. Therefore, a single photographic exposure lasting, say, 6 hours, will give much more information than a counter scan lasting as long.

The experimental setup\(^1\) used in taking Debye-Scherrer powder data is shown schematically in Fig. 19. A Philips PW 1010 generator was operated with copper sealed cathode tube at 40 kV and 20 mA. Monochromatized CuK\(\alpha\) radiation (\(\lambda = 1.542 \text{ Å}\)) was used. The experimental setup was placed in a vacuum enclosure to minimize air scattering during long exposures. Inside the enclosure (cf. Fig. 19), there was a pinhole collimator with an additional shield to minimize stray scat-

\(^1\)Dr Jean-Paul Pouget's lab at Université Paris-Sud, Orsay, France.
Figure 19: X-ray Debye-Scherrer setup geometry (projected on the equatorial plane).
tering, a sample on the goniometer, a lead beam stop and a film in a cylindrical cassette. Typical exposure times for powders in capillaries described in chapter II were 6 hours; for single, free standing polymer films - up to 24 hours. Exposed films were developed in a standard way and read (usually in the equatorial plane) with a Joyce-Loeble analog photodensitometer. The scattering intensity vs. scattering angle 2Θ data obtained as a result were used in structural investigations (Chapter IV). Additional data were also obtained with x-ray synchrotron radiation (λ = 1.596 Å and λ = 1.551 Å) at the station D-16 at LURE (Orsay). Synchrotron radiation offers higher resolution and intensity.

3.2 VARIABLE TEMPERATURE X-RAY EXPERIMENT

An attempt was made to investigate the evolution of stretched emeraldine base film structure with temperature. A diagram of an experimental setup is presented in Fig. 20. A standard 1.5 kW sealed Cu tube with a focusing graphite 004 monochromator (λ = 1.542 Å) was used. The sample was placed on a Joule-Thompson cooling microdevice. Nitrogen gas (200 PSI) was used as a cooling medium. The temperature was controlled with an integral heater, thermocouple and a temperature controller. For scans in the equatorial plane (reflections (hk0)), the sample was placed with its stretching axis perpendicular to the instrument plane. For scans in the longitudinal plane (reflections (00l)), the sample was placed with its stretching axis parallel to the instrument plane. The sample and the cooler were enclosed in an evacuated aluminum can, with 360° beryllium window. A single detector in the equatorial plane was used. Soller slit was put between the sample and the detector.

2Kodak diagnostic film.
3By Dr Jean-Paul Pouget, Université Paris-Sud.
4Prof. Jack E. Fischer's lab, University of Pennsylvania.
5By MMR Technologies, Mountain View, CA
Figure 20: X-ray geometry for variable temperature measurements (projected on the equatorial plane).
3.3 Polarized FTIR Experiment on Oriented Films

The EB film used for polarized FTIR studies was stretched by passing it between two pinch rollers, then across a heated (~140°C) Teflon coated roller, and then finally between a second set of pinch rollers rotating at a higher speed than the first set. This method of processing allows precise control of the stretching ratio, something that was not available in the “hanging weight” method described in Chapter II.

A Nicolet 60SXR Fourier-Transform Infrared spectrometer was used. The polarizer was placed before the sample in the FTIR spectrometer sample compartment. Polarization direction was set such that the $E$ vector was parallel or perpendicular to the sample stretching direction. The sample was not moved during the experiment. Sample spectra were ratioed to the background spectra taken with no sample but with the polarizer in the appropriate orientation.

3.4 Time Evolution of Photoinduced Infrared Signal

The general scheme of the experimental setup is presented in Fig. 21. The sample was mounted in a continuous helium transfer cryostat. The temperature was stabilized by an integral heater controlled by a heater controller with an accuracy of ±0.1°C. The cryostat containing the sample was placed in the sample compartment of the Nicolet 60SX FTIR spectrometer. The sample was illuminated by an argon ion laser via fiber optic cable. In all the experiments reported here, 488 nm (blue) line was used. A shutter controlled by a spectrometer computer was placed in the optical path. A typical experiment would follow the sequence below:

1. The sample is cooled in the dark to a desired temperature.
2. A background set of (typically) 256 scans is taken and coadded.
3. The shutter blocking the pump beam is opened.

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8By E.M. Scherr, M.A. Dray and P.J. Glatkowski at Foster-Miller Co, Inc., Waltham, MA.
7Heli-tran by APG Cryogenics, Allentown, PA.
8Model 3700 APDE by Scientific Instruments, Inc., W. Palm Beach, FL.
9Innova 70 by Coherent, Palo Alto, CA.
Figure 21: Schematic diagram of the FTIR experiment (see text for details).
4. Sets of scans are continuously taken and coadded at a rate of 2 sets of 256 scans per minute.

5. The shutter is closed, typically after ~ 1 hour of exposure.

6. Sets of scans continue to be taken for a desired time.

7. The sample is warmed up to room temperature to erase the photoinduced effects.

8. Coadded scans are Fourier-processed, ratioed to the background and converted to absorbance to obtain the desired photoinduced spectra.

9. A selected photoinduced IR peak is integrated in all time-resolved spectra to obtain a relative measure of the photoinduced defect concentration.

A complete set of macro commands used to control this experiment is available from the directory [ROOT.USER.MIK] in the spectrometer computer and also is listed with the explanations in Appendix A.

Usually, the experiment was performed with samples in the form of a 0.05% KBr pellet in normal transmission configuration, Fig. 22a. However, for comparison purposes, as well as to measure photoinduced spectra in the far-IR region (10 cm\(^{-1}\) - 400 cm\(^{-1}\)), a transmission-reflection configuration was used, Fig. 22b. Measurements in far-IR region require either a free-standing sample or a sample suspended in a medium that transmits far-IR wavelengths, typically paraffin or polyethylene. Free standing polyaniline samples cannot be used for low-temperature photoinduced experiments due to their poor thermal conductivity. Pellets made from polyaniline mixed with paraffin or polyethylene were made, but their performance in photoinduced experiment was not satisfactory. Because of a poor thermal contact between polyaniline and the pellet material, laser light heats polyaniline by sometimes more than 100 K above set temperature, completely obscuring (and perhaps erasing) any photoinduced spectral features. Entirely different method of taking photoinduced spectra had to be devised.

Instead of using a classical transmission method, a transmission-reflection method was used, Fig. 22b. Polyaniline film polymerized directly on reflective platinum foil\(^{10}\) was mounted on a specially modified cryostat cold finger. The vacuum cryostat shield was fitted with 1/8 inch thick polyethylene window and placed in a

\(^{10}\)See previous chapter for a description of a preparation method.
Figure 22: Details of sample placement in: a)-transmission experiment, b)-transmission-reflection experiment (details in text).
reflection spectroscopy attachment. The pump laser beam was supplied through the same window. The probe IR beam would pass through the polyaniline layer, then reflect from the platinum, then pass through polyaniline again. Changes in polyaniline absorbance can in this way be monitored. Specular reflection from polyaniline is not expected to contribute much to the spectrum due to the roughness of the polyaniline surface. Specular reflections from the cryostat shield window surfaces are eliminated from the detection path by placing windows at a slightly different angle than the platinum/polyaniline foil. Thermal conductivity between platinum and polyaniline film in this system is excellent and no significant heating effects upon laser illumination were detected.
CHAPTER IV

X-RAY EXPERIMENTAL RESULTS AND DISCUSSION

This chapter describes the results of x-ray experiments performed and their interpretation. Results of x-ray Debye-Scherrer experiments on emeraldine samples are given in the first section. Those results are discussed in section two. Outcomes of x-ray experiments on leucoemeraldine, pernigraniline and poly-o-toluidine are discussed in the third section. The variable temperature x-ray experiment on stretched emeraldine base films is described in the fourth section.

4.1 DEBYE-SCHERRER EXPERIMENTS ON EMERALDINE

The Debye-Scherrer pattern of emeraldine salt “as prepared, low temperature” ES-I (cf. Fig. 16) is shown in Fig. 23b. Chemically and electrochemically synthesized emeraldine show essentially identical ES-I patterns. However, the pattern of “as prepared, low temperature” emeraldine salt possesses the best defined peaks and therefore will be used for structural evaluations.

The pattern shown in Fig. 23b is only partially crystalline and contains a significant amorphous contribution, only part of which can be attributed to the Lindemann glass holder. The fraction of crystallinity, $X_c$, estimated by comparing the integrated intensity of the rings above the amorphous halo with the total scattered intensity (minus glass contribution) is approximately 50%. Moreover, crystalline peaks are broadened with respect to the natural, instrumental width ($\Delta(2\theta) \approx 0.05^\circ$) which indicates that crystalline regions have very limited size. Table 1 summarizes the data obtained from the pattern in Fig. 23b. The $d$-spacings
Figure 23: Debye-Scherrer patterns of: (a) Emeraldine base EB-I and (b) Emeraldine salt “as prepared” ES-I. In (a), double arrows point towards maxima of the broad, amorphous rings. In (b), results of the intensity calculations for the ES-I in the pseudoorthorombic cell are shown.
Table 1: Emeraldine salt “as prepared, low temperature” ES-I crystalline peak parameters: d-spacing \( d \), domain length \( L \), intensity, and indexation \( (hkl) \). \( \{(hkl)\} \) denotes set of reflections with permutation of the sign of the indices.

<table>
<thead>
<tr>
<th>( d, ) Å</th>
<th>( L, ) Å</th>
<th>intensity</th>
<th>( (hkl) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.57</td>
<td>45</td>
<td>s</td>
<td>(001)</td>
</tr>
<tr>
<td>5.94</td>
<td>35</td>
<td>s</td>
<td>(010)</td>
</tr>
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<td>4.26</td>
<td>35</td>
<td>s</td>
<td>(100)</td>
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<td>3.51</td>
<td>70</td>
<td>vs</td>
<td>{(110)}</td>
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<td>w</td>
<td>(020)</td>
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<td>2.85</td>
<td>vw</td>
<td>{(112)}, {(021)}</td>
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</tr>
<tr>
<td>2.47</td>
<td>w</td>
<td>{(120)}</td>
<td></td>
</tr>
<tr>
<td>2.34</td>
<td>vw</td>
<td>{(121)}, {(113)}</td>
<td></td>
</tr>
</tbody>
</table>


were calculated from the angular position of the rings according to the Bragg formula:

\[
\lambda = 2d \sin \Theta
\]

where \( \lambda \) is the x-ray wavelength used. The crystalline domain size \( L \) can be estimated from the rings’ angular width \( \Delta(2\Theta) \) (full width at half-maximum) using the Scherrer formula [53]:

\[
L = \frac{0.9\lambda}{\Delta(2\Theta) \cos \Theta}
\]

Table 1 also contains the intensity description and pseudoorthorhombic indexation of the observed peaks.

Sharp rings of ES-I disappear upon compensation with NH4OH. A typical x-ray pattern for a dedoped material, emeraldine base EB-I (see Fig. 16) is shown in Fig. 23a. It consists mainly (double arrows) of one intense broad ring centered at about \( 2\Theta \sim 20^\circ \) \((d \sim 4.6\text{Å})\) having a shoulder at about \( 2\Theta \sim 30^\circ \) \((d \sim 3\text{Å})\) and of a weak ring at about \( 2\Theta \sim 45^\circ \) \((d \sim 2.1\text{Å})\). These broad structures are characteristic of the diffraction by an amorphous polymer. The inner ring at about \( 2\Theta \sim 10^\circ \) (single arrow), which is very intense in ES-I, is probably due to remaining traces of ES-I in the “dedoped” material.
EB-I when redoped with HCl becomes ES-I again, with a continuous evolution of its diffraction spectrum. This is clearly illustrated by the microdensitometer reading shown in Fig. 24 for different \( x = [\text{Cl}]/[\text{N}] \) ratios (concentrations).

The evolution of the x-ray pattern for increasing \( x \) consists of:

- A gradual emergence of Debye-Scherrer rings from the EB-I amorphous halo together with a decrease of the amorphous content. The percent crystallinity \( X_c \) roughly increases from near 0 at \( x \sim 0 \) to a maximum of about fifty percent at maximum doping level (\( x = 0.5 \)).

- A slight shift of the 2\( \Theta \) position of the Debye-Scherrer rings. This shift is clearly expressed in Fig. 25 in terms of \( d \)-spacings, according to Equation (4.1).

- A sharpening of the rings, indicating an increase of the crystalline domain size \( L \) with \( x \). Only the evolution of \( L \) associated with the inner ring (2\( \Theta \sim 10^\circ \) i.e. \( d \sim 9\AA \)) can be measured quantitatively. This is shown in Fig. 26.

Class II materials exhibit entirely different x-ray patterns. Treatment with THF/NMP causes emeraldine base EB-I material to recrystallize and form partially crystalline emeraldine base EB-II (compare preparation scheme, Fig. 16, p. 22). Similarly, THF extract and films cast from NMP and DMSO all were precipitated in the base form and exhibit EB-II structural features. They differ in percent crystallinity (from over 50% for THF extract to sometimes 0% in NMP-cast films), but share characteristic EB-II structural features. Also, when doped, EB-II materials change structure into ES-II crystalline structure, not ES-I.

Fig. 27a shows the Debye-Scherrer pattern of THF extract emeraldine base EB-II. This material exhibits the highest crystallinity and coherence lengths of all the EB-II samples and therefore was used (along with stretched NMP films) to solve the EB-II structure. Parameters (\( d \)-spacings, coherence lengths \( L \) and intensities) of the THF extract pattern are given in Table 2.

THF/NMP extracted EB-II powder when doped with HCl retains its structure up to approximately \( x \sim 0.25 \). At this concentration a new structure, labeled ES-II below, appears. The ES-II and EB-II structures coexist at \( x = 0.25 \). Only the ES-II structure is observed for \( x = 0.4 \) and \( x = 0.5 \). Figure 27b shows an x-ray pattern from an emeraldine salt ES-II powder. The relative intensity and position of the
Figure 24: Evolution of the x-ray Debye-Scherrer pattern with the doping level $x=[\text{Cl}]/[\text{N}]$, from EB-I (top curve, $x = 0$) to ES-I (bottom curve, $x = 50\%$).
Figure 25: Variation of the d-spacings of selected reflections with doping level for EB-I - ES-I system.
Figure 26: Increase of the in-chain crystalline domain length, $L$, deduced from the width of the (001) reflection (Eqn. 4.2) as a function of the doping level.
Figure 27: Debye-Scherrer patterns of: (a) Emeraldine base EB-II (THF extract) and (b) Emeraldine salt ES-II. Results of the intensity calculations for the EB-II in $Pbcn$ cell and ES-II in $Pc2a$ cell are shown.
Table 2: Emeraldine base THF extract EB-II crystalline peak parameters: $d$-spacing $d$, domain length $L$, intensity, and indexation (hkl).

<table>
<thead>
<tr>
<th>$d$, Å</th>
<th>$L$, Å</th>
<th>intensity</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.56</td>
<td>100</td>
<td>vs</td>
<td>(110)</td>
</tr>
<tr>
<td>3.83</td>
<td>100</td>
<td>s</td>
<td>(200)</td>
</tr>
<tr>
<td>3.41</td>
<td>vW</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>3.02</td>
<td>70</td>
<td>m</td>
<td>(211)</td>
</tr>
<tr>
<td>2.82</td>
<td>w</td>
<td></td>
<td>(020)</td>
</tr>
<tr>
<td>~2.70</td>
<td>vW</td>
<td></td>
<td>(212)</td>
</tr>
<tr>
<td>~2.48</td>
<td>vW</td>
<td></td>
<td>(121)</td>
</tr>
<tr>
<td>2.33</td>
<td>w</td>
<td></td>
<td>(213), (310)</td>
</tr>
<tr>
<td>2.19</td>
<td>w</td>
<td></td>
<td>(114), (221)</td>
</tr>
<tr>
<td>1.95</td>
<td>w</td>
<td></td>
<td>(024)</td>
</tr>
<tr>
<td>1.84</td>
<td>w</td>
<td></td>
<td>(321), (115)</td>
</tr>
</tbody>
</table>

reflections show striking differences from those of ES-I (Fig. 23b). The $d$-spacings, relative intensity of the reflections and crystalline domain length associated with some reflections for the ES-II powder are shown in Table 3. Other materials (THF extract, NMP-cast film) when doped, show a similar Debye-Scherrer pattern, however with lower coherence and crystallinity. Therefore, emeraldine salt ES-II powder pattern was chosen for further investigation. Details about other materials can be found in Ref. [45].

ES-II when dedoped becomes amorphous. This material is called emeraldine base EB-II' 1. Its x-ray pattern consists solely of a broad and intense ring centered at about $d \sim 4.5\text{Å}$. However, when doped again with HCl, amorphous EB-II' becomes ES-II, not ES-I. This demonstrates that the two amorphous phases EB-I and EB-II have local structural differences. In this respect, emeraldine exhibits an interesting "memory effect": upon doping it "remembers" the (base) state from which it was prepared.

1The EB-I, EB-II, etc. nomenclature in this work follows one introduced in Ref. [45]. EB-II' is introduced to distinguish this amorphous material from partially crystalline EB-II. Both EB-II and EB-II' however, when doped, form partially crystalline ES-II salt.
Table 3: Emeraldine salt ES-II crystalline peak parameters: *d*-spacing *d*, domain length *L*, intensity, and indexation (hkl).

<table>
<thead>
<tr>
<th><em>d</em>, Å</th>
<th><em>L</em>, Å</th>
<th>intensity</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.66</td>
<td>55</td>
<td>s</td>
<td>(010)</td>
</tr>
<tr>
<td>4.32</td>
<td>55</td>
<td>m</td>
<td>(012)</td>
</tr>
<tr>
<td>3.96</td>
<td></td>
<td>vw</td>
<td>(020), (021)?</td>
</tr>
<tr>
<td>3.49</td>
<td>45</td>
<td>s</td>
<td>(200)</td>
</tr>
<tr>
<td>~3.23</td>
<td>vw</td>
<td></td>
<td>(210)</td>
</tr>
<tr>
<td>2.90</td>
<td>w</td>
<td></td>
<td>(113), (030)</td>
</tr>
<tr>
<td>~2.57</td>
<td>vw</td>
<td></td>
<td>(131), (123)</td>
</tr>
<tr>
<td>~2.44</td>
<td>vw</td>
<td></td>
<td>(014), (222)</td>
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<tr>
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<td>vw</td>
<td></td>
<td>(230), (311)</td>
</tr>
<tr>
<td>~1.90</td>
<td>vw</td>
<td></td>
<td>(034), (313)</td>
</tr>
<tr>
<td>~1.74</td>
<td>w</td>
<td></td>
<td>(400)</td>
</tr>
</tbody>
</table>

### 4.2 Analysis of the Crystalline Structures

Analysis of the crystalline structure is simplest with the EB-II and ES-II samples, for which Debye-Scherrer patterns from oriented films exist, helping in indexing of the crystalline peaks by separating them into equatorial (hk0), longitudinal (00l) and mixed (hkl) reflections. Therefore the EB-II structure will be discussed first, followed by ES-II and ES-I structures.

#### 4.2.1 Emeraldine Base EB-II

The *d*-spacings of the Bragg reflections observed from EB-II x-ray diffraction patterns are compatible with an orthorhombic lattice symmetry. Table 2 presents an indexation of the reflections of the longest *d*-spacings for this lattice symmetry. The lattice parameters have been obtained from a least square fit of the 20 positions of those reflections having a single (hkl) contribution. The orthorhombic parameters found are: *a* = 7.65 Å, *b* = 5.65 Å, *c* = 10.40 Å, *V* = 450 Å³ (for the THF extract EB-II powder).
The value of parameter \( c \) given corresponds to a zigzag repeat unit containing two rings. If the polymer contains an ordered sequence of benzenoid and quinoid rings as shown by Fig. 11(1), page 13, the actual periodicity must be \( 2c \). However, the subtle differences in the C-C and N-C bond distances between these two sequences, and the linking of H to the N atoms terminating the benzenoid sequence may not be detected by x-rays.

Because of the limited number of reflections observed, the determination of the orthorhombic space group of EB-II cannot be performed directly from the diffraction spectrum alone. However, it has been previously determined that poly-paraphenylene sulfide (PPS) [54] and oxide (PPO) [55], composed also of X-ring-X [X=S or O instead of N and N-H for the emeraldine] zigzag polymer chains, crystallize in the \( Pbcn \) orthorhombic space group with lattice parameters similar to that of the polyaniline. The indices of the reflections allowed by the \( Pbcn \) space group [56] are compatible with those quoted in Table 2. Furthermore, the intensities estimated in Table 2 follow approximately those measured in PPS and PPO [54, 55]. A schematic drawing of the EB-II structure in accord with the \( Pbcn \) orthorhombic symmetry elements is given in Fig. 28. The \( Pbcn \) space group holds if one neglects the difference between the benzenoid and quinoid sequences of the emeraldine chain and the hydrogen atoms bound to the amine nitrogens. Thus the \( Pbcn \) space group describes either the polymer backbone array of the polyaniline base if there is order between the benzenoid and quinoid sequences or an average structure if these sequences are disordered.

In order to check quantitatively this structure, the x-ray powder pattern was calculated with polyaniline chains located in the orthorhombic unit cell according to the above model. The program used was called LAZY PULVERIX\(^2\) (Detailed description and instructions for running this program are in Appendix B). No distinction was made between the quinoid and benzenoid units. Bond lengths were assumed to be: C-C = 1.41 Å, C-N = 1.36 Å, C-H = 1.08 Å, based on oligomer values from Ref. [36] (Fig. 14, p. 17). The only parameter which is variable in this model is the ring tilt angle \( \phi \) (the angle between each \( C_6 \) ring plane and the plane defined by the positions of the nitrogen atoms). It is assumed that the angles \( \phi \) alternate in sign for adjacent rings along a chain to minimize steric repulsion between neighboring \( C_6 \) rings [29, 23]. The calculated relative intensities of the most intense reflections normalized to the strongest reflection, as a function of ring

Figure 28: Projection along the chain axis and side view of the average structure of (a) - the polyaniline chain, (b) - EB-II structure.
The relative intensities of the (110) and (200) reflections depend strongly on \( \phi \), as shown in Fig. 29. It has been found that the calculated pattern agrees best with the experimental pattern for \( \phi \sim 30^\circ \). The angle \( \phi \sim 30^\circ \) compares well with \( \phi \sim 45^\circ \) obtained from the structural refinement of PPS and PPO [54, 55]. A comparison between the experimental and calculated pattern is shown in Fig. 27a. Figure 30 shows stereoscopic view of the emeraldine base EB-II structure.

### 4.2.2 Emeraldine Salt ES-II

The \( d \)-spacings of the Bragg reflections observed from ES-II x-ray diffraction patterns are also compatible with an orthorhombic lattice symmetry. The indexation for the reflections of the largest \( d \)-spacing is given in Table 3. A least square fit of their 2\( \Theta \) angular positions leads to the following orthorhombic parameters:

\[
\begin{align*}
a &= 7.0 \text{ Å}, & b &= 8.6 \text{ Å}, & c &= 10.4 \text{ Å}, & V &= 620 \text{ Å}^3 \\
\end{align*}
\]

for the emeraldine salt ES-II powder (doping level \( x = 0.5 \)). From the \( c \) (polymer chain repeat) parameter, assuming an N-ring-N length of 5.52 Å, a ring-N-ring angle \( \delta \) close to 141\(^\circ\) is deduced.

With the small number of reflections observed, it is difficult to derive the structure of ES-II directly. Since the volume of the ES-II cell is only 30% greater than that of EB-II, it should contain similarly two polymer chains per unit cell. (The excess volume of about 150 \( \text{Å}^3 \) is however three times larger than the volume of two \( \text{Cl}^- \) ions). The absence of the (100) reflection shows that the structure projected along \( a \) axis has an \( a/2 \) translational symmetry. This is not the case in the \( b \) direction, since the (010) reflection is allowed. Although the reflections in the polymer chain (c) direction are difficult to observe, one can assume from the absence of a strong (001) reflection that the structure projected along \( c \) still possesses the \( c/2 \) translational symmetry. Two orthorhombic space groups of maximal symmetry compatible with the extinctions mentioned above are \( P2_12_2_1 \) and \( Pc2a \) [56]. The most likely placement of the nitrogen atoms (with the constraint of 4N per unit cell) is, as in the EB-II structure, to form a N-backbone in the \((b,c)\) plane. As the unit cell must also accommodate two times less Cl atoms than N atoms, (for \( x = 0.5 \)), the Cl must also belong to a special position in the unit cell. The more likely possibility compatible with the large increase of the parameter \( b \) from EB-II to ES-II is to place the Cl on the two-fold axis parallel to \( b \), in the hollow of the polymer zigzag.
Figure 29: Calculated variation of the relative (to the strongest reflection) intensity of the five strongest reflections in EB-II as a function of the ring tilt angle $\phi$. The vertical dashed line represents the best fit to the experimental data at $\phi = 30^\circ$. 
Figure 30: Stereoview of the emeraldine base EB-II structure (ring tilt angle $\phi = 30^{\circ}$). The drawing can be viewed with a stereoviewer. Alternatively, the unaided eyes can be trained to defocus, so that each eye sees only the appropriate diagram. This process may be aided by placing a white card edgeways between the drawings.
Calculations were made for theoretical powder patterns in both the $P2_12_2_1$ and $Pc2a$ structures, similarly as for EB-II. There are three variable parameters in the first structure: middle chain shift $u$, Cl-N distance $d$, and ring tilt angle $\phi$. In the second structure, only the Cl-N distance $d$ and the angle $\phi$ can vary. In $P2_12_2_1$ structure a strong (110) reflection not observed experimentally is obtained unless a large shift of the middle chain (close to $b/2$) is introduced. The (110) reflection is not allowed in $Pc2a$ structure [56]. In addition, the out of phase order of polymer chains along the $a$ direction of a $Pc2a$ structure leads to lower interchain interaction than the in phase order in the $P2_12_2_1$ structure with large middle chain shift. Model calculations show that the experimental data can be well accounted for by the $Pc2a$ structure. A schematic diagram of this structure is presented in Fig. 31.

The relative intensities of the (010) and (200) reflections are sensitive to the ring tilt angle $\phi$ and to the Cl-N distance $d$. The best agreement between the experimental and calculated spectra is obtained with $\phi = 0 - 10^\circ$ and $d = 5 - 6$ Å. Fig. 27b compares the experimental and calculated ($\phi = 0^\circ$, $d = 5$ Å) spectra.

4.2.3 EMERALDINE SALT ES-I

In the absence of data from stretched films, the indexation of the reflections from the crystalline part of ES-I is more difficult to obtain. The $d$-spacings of the 4 strongest reflections are 9.6 Å, 5.9 Å, 4.26 Å and 3.51 Å. The largest $d$-spacing is close to a polymer repeat distance. Thus it can correspond to the (001) reflection if, as before, we take $c$ as a polymer repeat periodicity. However, the decrease of this $d$-spacing from 9.6 Å (for $x \sim 0.5$) to about 8.6 Å ($x \sim 0$) (Fig. 25) suggests that the chains can be tilted with respect to the (a,b) basal plane, with an angle which decreases upon dedoping. The three other $d$-spacings are close to the $b$, \(ab/\sqrt{a^2 + b^2}\) (i.e. $d_{110}$) and $a/2$ distances of EB-II, respectively and they approach these EB-II values upon dedoping (Fig. 25). This suggests that they correspond to the transverse (interchain) distances. Such an assignment is in agreement with an independent result [35] obtained from oriented fibers.

All the main reflections observed in the “low temperature” ES-I, (Table 1) can be indexed in a pseudoorthorhombic cell with lattice parameters: $a = 4.3$ Å, $b = 5.9$ Å, $c = 9.6$ Å, $V = 245$ Å³. The volume $V$ thus obtained is slightly larger than that of an emeraldine base chain repeat unit (225 Å³ or half the volume of
Figure 31: Projection along the chain axis and side view of the proposed ES-II structure. Circles represent Cl\textsuperscript{−} ions.
the EB-II cell); the difference in volumes is close to the ionic volume of a Cl\textsuperscript{−} anion (\(\sim 25 \, \text{Å}^3\)). Thus, the ES-I unit cell contains a single polymer zig-zag and a Cl\textsuperscript{−} anion in compact packing. Its volume per chain repeat unit is significantly smaller than that of the ES-II structure (\(\sim 300 \, \text{Å}^3\)). The value of the pseudoorthorhombic \(c\) parameter at \(x \sim 0.5\) leads to a ring-N-ring angle \(\delta\) close to 120°. A proposed ES-I structure is shown in Fig. 32. A very compact structure is obtained by assuming the placement of Cl\textsuperscript{−} anions in the hollow of the polymer zig-zag.

A Debye-Scherrer pattern was calculated for such a structure assuming that:

- the lattice is pseudoorthorhombic
- the bond lengths are identical to those used previously
- the Cl\textsuperscript{−} is positioned in the plane of the nitrogens (parallel to the \((a,b)\) plane) with distances to two neighboring nitrogens equal to 3.5 Å, which is approximately the sum of the N-H bond length and the Cl\textsuperscript{−} ionic radius.

This model contains two variable parameters: the ring tilt angle \(\phi\) and the polymer chain setting angle \(\Psi\) (defined in Fig. 32). The calculated pattern contains the four previously discussed strongest reflections and agrees best with the experimental results for \(\phi \sim 0 - 15°\) and \(\Psi \sim 20 - 30°\). Figure 23b compares the experimental powder pattern and the calculated intensities for \(\phi = 0°\) and \(\Psi = 20°\) for which there is the best agreement.

Data for materials not mentioned here, such as stretched NMP-cast films are discussed in detail in [45]. The summary of structural data obtained for various emeraldine materials is presented in Table 4.

### 4.2.4 Discussion

The first phenomenon that needs to be addressed is the doping process. Clearly, amorphous emeraldine base materials EB-I and EB-II', retain "memory" of the kind of salt which they were prepared from. Evidently, even though both are amorphous, local order differs in them. Studies of this amorphous order are currently underway [57].

\(^3\)See footnote on page 47.
Figure 32: Projection along the chain axis and side view of the proposed ES-I structure. Circles represent Cl$^-$ ions.
Table 4: Summary of structural parameters for various emeraldine materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sgrp</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$V$, Å$^3$</th>
<th>$\Psi$</th>
<th>$\phi$</th>
<th>$X_e$ %</th>
<th>$L$, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB-II powder</td>
<td>Pbcn</td>
<td>7.65</td>
<td>5.75</td>
<td>10.20</td>
<td>445</td>
<td>0</td>
<td>30</td>
<td>40-50</td>
<td>50</td>
</tr>
<tr>
<td>THF extr</td>
<td></td>
<td>7.65</td>
<td>5.65</td>
<td>10.40</td>
<td>450</td>
<td>0</td>
<td>30</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>NMP film</td>
<td></td>
<td>7.80</td>
<td>5.75</td>
<td>10.05</td>
<td>450</td>
<td>0</td>
<td>30</td>
<td>10(?)</td>
<td>150</td>
</tr>
<tr>
<td>NMP film powder</td>
<td>Pc2a</td>
<td>7.0</td>
<td>8.6</td>
<td>10.4</td>
<td>620</td>
<td>0</td>
<td>0-10</td>
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<td>50</td>
</tr>
<tr>
<td>ES-II powder</td>
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<td>7.1</td>
<td>7.9</td>
<td>10.4</td>
<td>565</td>
<td>0</td>
<td>?</td>
<td>10(?)</td>
<td>25</td>
</tr>
<tr>
<td>NMP film ES-II Powder</td>
<td></td>
<td>4.3</td>
<td>5.9</td>
<td>9.6</td>
<td>245</td>
<td>0</td>
<td>0-15</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Electrochem film</td>
<td>P1</td>
<td>4.3</td>
<td>5.7</td>
<td>9.2</td>
<td>226</td>
<td>?</td>
<td>?</td>
<td>50</td>
<td>40</td>
</tr>
</tbody>
</table>

Differences in crystallinity explain the difference between EB-I base (amorphous) and EB-II base (crystalline) in their doping behaviour (Fig. 17). Crystalline EB-II is more difficult to dope than EB-I, until a pH of about 2 is reached. Also, EB-II is insoluble in many solvents that dissolve EB-I, including NMP and DMSO.

Doping of EB-I materials causes an almost linear increase in crystallinity, (see Debye-Scherrer patterns in Fig. 24) with a clear trace of an ES-I structure even in the lowest levels of doping. Subsequent doping does not change the $d$-spacings significantly (Fig. 25), rather the crystallite size (correlation length) $L$ increases with an increase in doping level (Fig. 26). This clearly suggests that there is separation of phases into a doped phase and an undoped phase - and that the spacial extent of the former increases with the doping level. Such a formation of a separated doped phase agrees with the expected reduction of the elastic energy costs associated with the insertion of the bulky chlorine ions into the polymer. The inhomogeneous structure points to the role of undoped amorphous regions that form barriers to conduction at intermediate doping levels [58]. The EB-II - ES-II system is quite different in this aspect. Up to a doping level of $x \approx 0.25$ the base structure is still visible with unchanged cell parameters. Above a doping level of $x \approx 0.25$, the ES-II structure appears. Thus, the initial doping occurs primarily within amorphous regions of the polymer.

*Preliminary results suggest that the ring tilt angle decreases with doping even in this otherwise unchanged EB-II chain array.*
Figure 33: Pauli susceptibility $\chi^P$ vs doping level $x$ for EB-I (•, solid line, from Ref. [59]) and EB-II (×, dashed line). $x$ values are based on Fig. 17, p. 24.

These differences in doping behaviour correlate well with magnetic studies. Plot of spin susceptibility versus doping level of emeraldine samples is given in Fig. 33. A linear increase of spin susceptibility [59], which accompanies the gradual increase of crystallinity of EB-I material with doping level as well as its rapid increase in the EB-II material for doping levels $x > 0.25$ (when crystalline regions of EB-II become doped) [19] suggests that metallic regions are associated with the crystalline parts of the sample.

The ring tilt angle $\phi$ is an important structure parameter. Within the crystalline EB-II, the benzene rings are tilted alternately (on average, neglecting differences between benzenoids and quinoids) by $\pm 30^\circ$. The structure allows room for the change of local ring angle that is expected to occur upon photoexcitation of charges to form a positive ring-torsional polaron [29, 23, 30, 33]. The ring torsion
angle $\phi$ appears to decrease to a value close to zero as the doping level reaches $x \approx 0.5$ (Table 4). A small tilt angle will cause increased delocalization of individual charge carriers along the chain [29, 23]. It can be added that movement of charge in the polaronic fully doped structure (Fig. 11(ii), p. 13) is not expected to involve a change of the ring angle because all the rings in the polymer have the same electronic structure. This is not the case in the bipolaronic structure (Fig. 11(iii)). In the crystalline part of ES-I and ES-II, larger ring motions are strongly inhibited by the interaction with neighboring chains.

### 4.3 Other Debye-Scherrer Experiments

#### 4.3.1 Pernigraniline, Leucoemeraldine

In this section, Debye-Scherrer experiments on pernigraniline base (PNB), leucoemeraldine (LEB) and poly-$o$-toluidine (POT) will be described. The crystallinity $X_c$ and coherence lengths $L$ in those materials are generally lower than in polyaniline powders, thus precluding calculations of exact chain placement in the unit cell. Structures are analyzed in terms of analogous emeraldine structures.

A densitometer tracing of the Debye-Scherrer pattern of PNB powder (from THF extract emeraldine base) is shown in Fig. 34a. PNB powder is partially crystalline, with the percent crystallinity on the order of $X_c \sim 30\%$ and a coherence length estimated at $50\,\text{Å}$. The diffraction pattern from PNB obtained from emeraldine base EB-I powder is similar, but less crystalline. The diffraction pattern in Fig. 34a is similar to that of EB-II (Fig. 27a). Observed peaks are given in Table 5. All the peaks can be indexed in a way analogous with EB-II structure, within an orthorhombic cell with parameters: $a = 7.25\,\text{Å}$, $b = 6.2\,\text{Å}$, $c = 8.95\,\text{Å}$. Parameter $c$ is smaller than that of EB-II, therefore it is likely that polymer chains are tilted with respect to the $(a,b)$ plane. The volume per polymer repeat unit (two benzene rings and two nitrogens, there are two repeat units in the unit cell) is $V_{PNB} \sim 200\,\text{Å}^3$.

The diffraction pattern of leucoemeraldine film cast from NMP is shown in Fig. 34b. Leucoemeraldine powders exhibit identical patterns, but are less crystalline. For this reason, film data were used for structural evaluation. The LEB x-ray pattern is significantly different from patterns of PNB and EB-II. Again,
Figure 34: Debye-Scherrer diffraction patterns of: a) pernigraniline (PNB) and b) leucoemeraldine (LEB). $\lambda = 1.542\text{Å}$.
Table 5: Pernigraniline (from THF extract EB-II) peak parameters: $d$-spacing $d$, domain length $L$, intensity, and indexation (hkl).

<table>
<thead>
<tr>
<th>$d$, Å</th>
<th>$L$, Å</th>
<th>intensity</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.95</td>
<td>60</td>
<td>vw</td>
<td>(001)</td>
</tr>
<tr>
<td>~7.10</td>
<td></td>
<td>vw</td>
<td>(100)</td>
</tr>
<tr>
<td>4.75</td>
<td>30</td>
<td>s</td>
<td>(110)</td>
</tr>
<tr>
<td>3.62</td>
<td>40</td>
<td>m</td>
<td>(200)</td>
</tr>
<tr>
<td>3.10</td>
<td></td>
<td>w</td>
<td>(020)</td>
</tr>
</tbody>
</table>

The sample is partially crystalline with a coherence length of about 50 Å, but this time strong reflections (Table 6) can be indexed with an ES-I-like lattice, with parameters: $a = 6.15$ Å, $b = 4.3$ Å, $c = 9.8$ Å. The volume per polymer zigzag is found to be $V_{LEB} \sim 260$ Å$^3$. The fact that the LEB structure is different than that of PNB and EB-II may be caused by hydrogen bonding between neighboring chains in LEB.

It is interesting to note that the volume per polymer zigzag decreases as the oxidation level of the polyaniline increases: $V_{LEB} \sim 260$ Å$^3 > V_{EB} \sim 225$ Å$^3 > V_{PNB} \sim 200$ Å$^3$. This can be due to the decrease of the average ring tilt angle $\phi$ (out of the plane of nitrogens) as the number of quinoidal rings increases.

### 4.3.2 Poly-o-toluidine

Poly-o-toluidine (POT) is chemically similar to polyaniline, but for a methyl group on benzene rings (Fig. 35). It is therefore expected that POT will crystalize in structures similar to that of polyaniline.

A Debye-Scherrer pattern of “as prepared” POT-ES is shown in Fig. 36a. It exhibits well defined reflections characteristic of crystalline order on top of a broad scattering feature from amorphous regions of the sample and the Lindemann glass sample holder. The $d$-spacings calculated from the angular positions of the reflections of “as prepared” POT-ES are given in Table 7, together with the calculated coherence lengths and estimates of relative peak intensity.
Table 6: Leucoemeraldine (NMP film) peak parameters: d-spacing $d$, domain length $L$, intensity, and indexation (hkl).

<table>
<thead>
<tr>
<th>$d$, Å</th>
<th>$L$, Å</th>
<th>intensity</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.65</td>
<td></td>
<td>w</td>
<td>($\frac{1}{3}$,00)</td>
</tr>
<tr>
<td>6.15</td>
<td>45</td>
<td>s</td>
<td>(010)</td>
</tr>
<tr>
<td>4.89</td>
<td></td>
<td>vw</td>
<td>(002)</td>
</tr>
<tr>
<td>4.29</td>
<td>40</td>
<td>vs</td>
<td>(100)</td>
</tr>
<tr>
<td>3.53</td>
<td>50</td>
<td>m</td>
<td>(110)</td>
</tr>
<tr>
<td>3.26</td>
<td>45</td>
<td>s</td>
<td>(111),(102)</td>
</tr>
<tr>
<td>2.72</td>
<td>30</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>2.34</td>
<td></td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>2.04</td>
<td></td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>1.86</td>
<td></td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>1.71</td>
<td></td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td></td>
<td>vw</td>
<td></td>
</tr>
</tbody>
</table>

Figure 35: Structural formulas of poly-o-toluidine: (i) - base, (ii) - HCl salt.
Figure 36: Debye-Scherrer diffraction patterns of: a) poly-o-toluidine base and b) poly-o-toluidine salt. Dashed line shows contribution from the Lindemann glass sample holder.
Table 7: Poly-o-toluidine peak parameters: \( d \)-spacing \( d \), domain length \( L \), intensity, and indexation \((hkl)\).

<table>
<thead>
<tr>
<th>( d ), Å</th>
<th>( L ), Å</th>
<th>intensity</th>
<th>((hkl))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.95</td>
<td>40</td>
<td>s</td>
<td>(001)</td>
</tr>
<tr>
<td>6.5</td>
<td>35</td>
<td>m</td>
<td>(010)</td>
</tr>
<tr>
<td>( \sim 4.7 )</td>
<td>broad</td>
<td></td>
<td>(100)</td>
</tr>
<tr>
<td>3.61</td>
<td>40</td>
<td>s</td>
<td>(110)</td>
</tr>
<tr>
<td>3.38</td>
<td>w</td>
<td></td>
<td>(111)</td>
</tr>
<tr>
<td>( \sim 3.25 )</td>
<td>vw</td>
<td></td>
<td>(020)</td>
</tr>
<tr>
<td>( \sim 3.03 )</td>
<td>vw</td>
<td></td>
<td>(021)</td>
</tr>
<tr>
<td>( \sim 2.45 )</td>
<td>vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sim 2.10 )</td>
<td>vw</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sharp, crystalline rings of POT-ES disappear when the sample is dedoped, that is converted to the base form, POT-EB. A typical Debye-Scherrer pattern of the POT-EB is shown in Fig. 36a. It was taken using the CuK\( \alpha \) radiation (\( \lambda = 1.542 \) Å). It consists mainly of one broad reflection centered around \( 2\Theta \sim 19^\circ \) (\( d \sim 4.75 \) Å) and weaker broad features at \( 2\Theta \sim 23^\circ \) (\( d \sim 3.9 \) Å) and \( 2\Theta \sim 44^\circ \) (\( d \sim 2.05 \) Å). A small bump also exists at \( 2\Theta \sim 30^\circ \) (\( d \sim 3 \) Å). For reference, the scattering from an empty glass capillary is indicated.

POT-EB when redoped with HCl becomes partially crystalline again, with continuous evolution of the x-ray pattern with doping level. Figure 37 shows Debye-Scherrer patterns for POT samples with doping levels from \( x = 0.0 \) to 0.5. Reflections characteristic of crystalline order emerge gradually as the crystallinity of the sample increases from \( \sim 0\% \) for the base sample to \( \sim 40 - 50\% \) for the fully doped sample. Their \( d \)-spacings shift slightly with the increased doping level, as can be seen in Fig. 38. Figure 37 also shows how, upon doping, the broad reflection in POT-EB, corresponding to \( d \sim 4.75 \) Å (\( 2\Theta \sim 19^\circ \)), transforms into the asymmetric one at about the same angle in POT-ES.

Diffractometer tracings of as-prepared POT-ES (Fig. 36) and dedoped and subsequently redoped POT-ES (Fig. 37) are almost identical, showing that there is no significant degradation of the crystalline order in POT-ES upon this dedoping-
Figure 37: Evolution of x-ray Debye-Scherrer pattern with the doping level, from POT-EB (top curve, doping level 0) to POT-ES (bottom curve, doping level 50%).
Figure 38: Variation of the $d$-spacings of selected strongest reflections with doping level for EB-I - ES-I system.
doping cycle. However, the long d-spacing reflection at about 20Å (2θ ~ 4.6°, Fig. 36) has disappeared.

It can be seen by comparing POT data on Figures 37 and 38 with emeraldine data on Figures 24 and 25, respectively, that x-ray scattering patterns and their evolution with the doping level are remarkably similar in both materials. The analysis of structural features of POT will for this reason follow the lines of analysis of emeraldine Class I structures (Attempts to synthesize a POT equivalent of emeraldine Class II were not successful).

When the positions of the broad features of POT-EB are compared with data for EB-I (page 41) it can be seen that there is an increase of d-spacing from EB-I to POT-EB. However, the general features of the scattering patterns are similar. It can be concluded that the local chain array is similar in both materials. On the assumption that the peaks in the quasi-amorphous spectra of POT-EB correspond to fundamental distances \( d_{110} \), \( d_{200} \) and \( d_{020} \) (by analogy to EB-II), approximate interchain lateral distances of \( a \sim 7.8 \) Å and \( b \sim 6.0 \) Å can be calculated, which yield a cross-sectional area for two chains of \( A = ab = 47 \) Å². This value can be compared to 44 Å² in EB-I and EB-II. This represents an approximately 6% increase in \( A \) or ~3% increase in the average POT-EB interchain distance with respect to EB. This increase is probably due to the bulky \(-\text{CH}_3\) groups in POT.

The main peaks in the Debye-Scherrer pattern of “as prepared” POT-ES (Table 7) can be indexed with ES-I - like pseudoorthorhombic cell (cf. Fig. 32, p. 57). The c parameter, corresponding to one zigzag period of the POT chain, is 9.9Å. Comparing with \( c = 9.6\) Å for ES-I, we conclude that the C-N-C angle of POT-ES is larger. This increase is likely due to steric interactions between hydrogen and methyl groups of neighboring benzene rings.

The interchain order is not as well defined in POT-ES as compared with ES-I. An asymmetric reflection is visible where the (100) peak is anticipated. Such a feature could be explained by a broadening of the (100) reflection in directions perpendicular to a reciprocal direction \( \alpha^* \). In contrast, the (010) and (110) reflections remain clearly defined. However, the (110) reflection is significantly broader when compared to the equivalent reflection in ES-I. The (010) reflection is not significantly broadened. These features could be caused by disorder in the placement of Cl⁻ ions due to some randomness in the position of the methyl groups caused by ring flips. When \( d_{010} \) and \( d_{110} \) distances of redoped POT-ES and ES-I are com-
Table 8: Summary of structural parameters for pernigraniline (PNB), leucoemeraldine (LEB), and poly-o-toluidine (POT).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spgrp</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>V</th>
<th>Xc %</th>
<th>L, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNB powder</td>
<td>Pbcn</td>
<td>7.25</td>
<td>6.2</td>
<td>8.95</td>
<td>402</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>THF extr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LEB powder</td>
<td>P1 ?</td>
<td>6.1</td>
<td>4.3</td>
<td>9.8</td>
<td>260</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>THF extr</td>
<td></td>
<td>6.15</td>
<td>4.3</td>
<td>9.8</td>
<td>260</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>NMP film</td>
<td></td>
<td>6.15</td>
<td>4.3</td>
<td>9.8</td>
<td>260</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>POT-EB powder</td>
<td>amorph</td>
<td>7.8</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>POT-ES powder</td>
<td>P1</td>
<td>~4.7</td>
<td>~5.5</td>
<td>9.9</td>
<td>50</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

Apart from the resemblance of the Debye-Scherrer patterns of “as prepared” ES-I and POT-ES, perhaps the strongest argument for the similarity of their structures is parallel evolution of their x-ray patterns with doping level. In both materials the $d_{001}$ and $d_{010}$ distances increase with increasing doping level whereas $d_{110}$ decreases. However, while the $d$-spacings of POT-ES vary for the entire [Cl]/[N] range (Fig. 38, p. 67), those of ES-I saturate above $x_c \sim 0.2 - 0.3$ (Fig. 25, p. 44).

Table 8 summarizes structural data for pernigraniline (PNB), leucoemeraldine (LEB), and poly-o-toluidine base (POT-EB) and salt (POT-ES).

Similarity of the structures of emeraldine salt ES-I and poly-o-toluidine POT-ES makes possible meaningful comparisons of electronic properties between the two. Though the electronic structures of POT-ES and ES-I should be very similar [60], their transport properties are dramatically different, with POT-ES having one-dimensional localization [60] and ES-I showing features of three-dimensional delocalization [61]. Since the only difference in structure between the two polymers is $\sim 5\%$ increased interchain separation and reduced interchain order it can be concluded that this is the cause of the differences in electronic properties. This points out to the critical role of the interchain conduction electron transition rate as compared with intrachain scattering rate. This conclusion should also apply to
other conducting polymers.

### 4.4 Variable Temperature X-ray Experiment

Several scans at various temperatures were performed on stretched NMP-cast EB-II film in the equatorial plane (reflections (hk0)) in order to estimate the variations of the unit cell parameters $a$ and $b$ with temperature. Stretched films were chosen because they offer good crystallinity and good separation of the (110) and (200) peaks from the amorphous background (see section 4.2, page 48, also [62]). The temperature range accessible with the experimental setup was 135-298 K. Figure 39 presents part of the collected x-ray patterns ($T=135$ K and $T=298$ K). Both the (110) and (200) peaks show a moderate shift towards lower $d$ values as the temperature is lowered. Shifts in the unit cell parameters $a$ and $b$ (see Fig. 28 on page 50 for a scheme of EB-II unit cell), relative to the values at 298 K ($a_{298}$ and $b_{298}$, respectively) are plotted in Fig. 40. The change in $a$ is larger than in $b$. This is probably caused by changes in the average ring tilt angle $\phi$ with temperature (see below). Such changes would affect the $a$ direction more than the $b$ direction. The absolute values are $a_{298} = 7.76$ Å and $b_{298} = 5.75$ Å (compare with Table 4, p. 58).

Relatively small changes with temperature in the $a$ and $b$ distances for polyaniline (and in poly-$p$-phenylene-vinylene (PPV)) have been contrasted with large changes in those parameters in polyacetylene (CH)$_z$ and polyethylene (CH$_2$)$_z$ [63]. It has been observed that polyacetylene and polyethylene structures evolve with temperature increase towards regular triangular lattice of chains in the $(a, b)$ plane, that is towards the $b/a$ ratio equal $\sqrt{3}$. This was attributed to thermal motions in the $(a, b)$ plane which make the thermally averaged chain projections onto this plane more circular and therefore the structure tends to approach a close-packed triangular lattice at higher temperatures. In contrast to the behaviour of (CH)$_z$ and (CH$_2$)$_z$, polyaniline does not show a significant change in the $b/a$ ratio with temperature, which changes from 1.345 to 1.350 as the temperature is raised from 135 K to 295 K. Similar behaviour was observed in PPV [63]. It has been suggested that polymers containing rings possess an additional degree of freedom involving ring torsions. These ring motions are of lower energy than chain motions and therefore are turned on first when the temperature increases. An effective thermally averaged chain projection onto an $(a, b)$ plane remains non-circular and the structure does not evolve towards close-packing in this plane. The change in ring
Figure 39: Evolution of the stretched NMP-cast EB-II film x-ray pattern with temperature - part of the equatorial x-ray pattern, showing change in positions and intensities of (110) and (200) peaks.
Figure 40: Evolution of the stretched NMP-cast EB-II film structure with temperature - changes in $a$ and $b$ cell parameters, relative to $a_{298}$ and $b_{298}$, respectively.
tilt angle $\phi$ can be calculated from polyaniline data obtained (see below).

Several scans at various temperatures were performed in the longitudinal plane, in search for (weak) reflection (002). In contrast to (110) and (200) reflections, the position of (002) reflection does not change with temperature, implying that the zig-zag chain periodicity $c$ stays constant at $c = 9.92 \text{ Å}$.

An attempt was made to calculate changes in the ring tilt angle $\phi$, based on the comparison of the observed $I_{200}/I_{110}$ value at various temperatures with the calculated ratio $I_{200}/I_{110}$ of (200) and (110) peak intensities vs ring tilt angle. This method was used previously to determine the absolute value of the ring tilt angle in EB-II powders - see Fig. 29, p. 52. While the absolute value of $\phi$ can be calculated only with relatively large error (perhaps $\pm 5^\circ$), changes in $\phi$ can be calculated more accurately, with an error of only of the order of $\pm 0.5^\circ$. Plot of the ring tilt angle change with temperature is given in Fig. 41.

It should be noted that the ring tilt angle calculations do not take into account the influence of the Debye-Waller factor. Thermal atomic motions will cause decrease in absolute intensity of both reflections with increasing temperature. While intensity of the (200) peak decreases with increased temperature (from combined effect of the Debye-Waller factor and ring tilt angle changes), the intensity of the (110) peak actually increases. This shows that the ring tilt angle change is a primary factor causing spectral changes with temperature.

From Fig. 41 it can be seen that the ring tilt angle decreases by about $1 \pm 0.5^\circ$ when the temperature of the sample decreases from 298 K to 135 K. Due to the lack of information on the magnitude of influence of the Debye-Waller factor on the x-ray spectrum, this value should be treated as approximate. A decrease of the average ring tilt angle with decreasing temperature is consistent with the proposition that potential energy curve for polyaniline is asymmetric with respect to the ring tilt angle and similar to that of leucoemeraldine (Fig. 15 (left), p. 18). The size of that decrease in ring tilt angle (about $1^\circ$) with a temperature change from 295 K to 135 K is consistent with the calculations of Ginder et al. [23] on leucoemeraldine. According to those calculations, the ring angle $\phi$ is expected to decrease by about $0.7^\circ$ over the same temperature range (see Fig. 15 (right)). Unfortunately, no leucoemeraldine sample of sufficient crystallinity is available to directly test the calculations. However, a ring tilt angle calculated for emeraldine samples is an average value of three benzenoid rings, which probably have larger
Figure 41: Evolution of the stretched NMP-cast EB-II film structure with temperature - changes in ring tilt angle $\phi$, relative to a value of $\phi = 30^\circ$ at 298 K.
ring tilt angle, and of quinoid ring, which probably lies almost in the plane of the nitrogen atoms. Therefore, the observed change in average ring tilt angle is most likely an effect of benzenoid rings contribution. The $\Delta \phi = 1^\circ$ is a small change and is on the limit of the resolution of the method. An investigation over larger temperature range would provide more accurate data. An absolute value of $\phi$ in this sample (stretched NMP-cast EB-II films) was found to be $\sim 30^\circ$, identical as in EB-II powders (Table 4).
CHAPTER V

FTIR EXPERIMENTAL RESULTS AND DISCUSSION

The x-ray structural studies demonstrated how polymer structure, and in particular ring tilt angles change with oxidation level, protonation and derivatization. In this chapter results of Fourier Transform Infra-Red (FTIR) experiments are described and discussed. The outcome of polarized absorption experiments in stretch-oriented emeraldine films is discussed in the first section. Results of long-time photoinduced FTIR experiments on emeraldine and derivatives are given in the second section of this chapter. These results imply important role of the ring conformations and motions in creation and trapping of photoinduced defects.

5.1 INFRARED ABSORBANCE OF ORIENTED EMERALDINE FILMS

Polarized infrared spectra of several samples of stretched NMP-cast EB-II films, with various stretching ratios (length of the film after stretching \( l \) divided by length of film before stretching \( l_0 \)) were taken. Figure 42 presents a typical pair of spectra (taken with electric field \( E \) parallel and perpendicular to the stretching direction) for a film with \( l/l_0 = 2 \).

It can be seen that all the modes absorb more strongly when \( E \) is polarized parallel to the stretching direction, with the exception of modes at 833 and 852 cm\(^{-1}\), which absorb less and the mode at 1672 cm\(^{-1}\) which has an equal strength in both orientations of \( E \). The 1672 cm\(^{-1}\) mode can be identified as an NMP (solvent) mode, so the fact that it is not affected by polymer stretching comes as no surprise and provides additional information that the solvent is not in any way bound to
Figure 42: Polarized FTIR spectra of stretch-oriented NMP-cast EB-II film. Stretching ratio $l/l_0 = 2$. $E_{||}$ and $E_{\perp}$ indicate the $E$ vector polarized parallel and perpendicular to the stretching direction, respectively.
Table 9: Assignments of molecular vibrations in emeraldine base in terms of modes of \( p \)-disubstituted benzene (after [30]): wavenumber, relative intensity \( I \), and mode assignment.

<table>
<thead>
<tr>
<th>mode [cm(^{-1})]</th>
<th>( I )</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>835</td>
<td>m</td>
<td>( b_{2u} ) C-H out-of-plane, benzenoids</td>
</tr>
<tr>
<td>852</td>
<td>w</td>
<td>same as above, quinoids ?</td>
</tr>
<tr>
<td>1170</td>
<td>m</td>
<td>( a_g ) C-H in-plane ring deformation or ( a_g ) ring-N stretching, activated by asymmetric ring substitutions</td>
</tr>
<tr>
<td>1308</td>
<td>s</td>
<td>( b_{1u} ) benzenoid-amine stretching</td>
</tr>
<tr>
<td>1507</td>
<td>vs</td>
<td>( b_{1u} ) C-C stretching mode</td>
</tr>
<tr>
<td>1600</td>
<td>vs</td>
<td>C-C ring stretching, quinoids + ( a_g ) C-C ring stretching mode of benzenoids, activated by asymmetry</td>
</tr>
</tbody>
</table>

the polymer and its molecules possess no preferential orientation in a stretched polymer.

Individual chains in a stretched polymer film or fiber acquire preferential orientation along the polymer direction. Also, the absorption of a given mode is proportional to \( \cos^2 \Theta \) where \( \Theta \) is the angle between the dipole transition moment vector of a given mode and the electric field vector \( E \) (see Ref. [64], p. 23). From these two statements it can be concluded that modes that absorb more intensely with \( E_\parallel \) have dipole transition moment vectors in or near the direction of the chain axis, whereas modes that absorb more with \( E_\perp \) are transverse modes. Applying this to the spectra observed in stretched emeraldine films (Fig. 42) it is concluded that modes at 835 and 852 \( \text{cm}^{-1} \) have dipole transition moments close to perpendicular to the chain directions, whereas all other emeraldine modes have dipole transition modes close to parallel to the chain direction. This observation is consistent with the previous mode assignments detailed in Ref. [30]. Table 9 gives the summary of these assignments.

Dichroism of the sample can be used to estimate the degree of the orientation of the polymer chains around stretching direction. If we assume that the sample is
anisotropic in the plane perpendicular to the stretching direction (for a relatively thick sample this should be the case) then the sample orientation can be described by an orientation function $f_\Theta$:

$$f_\Theta = \frac{3\cos^2 \Theta - 1}{2}$$  \hspace{1cm} (5.1)

where $\Theta$ is the angle between the polymer chain axis and the stretching direction [64]. For perfect chain alignment, $\Theta = 0$, $\cos^2 \Theta = 1$, and therefore $f_\Theta = 1$. For random orientation, $\cos^2 \Theta = 1/3$ and $f_\Theta = 0$. The orientation function $f_\Theta$ can be calculated (see Ref. [64], p. 162) from the dichroic ratio $D = \frac{I_\parallel}{I_\perp}$, where $I_\parallel$ and $I_\perp$ are the IR absorption with $E$ parallel and $E$ perpendicular to the stretching direction respectively:

$$f_\Theta = \frac{D^0 + 2}{D^0 - 1} \times \frac{D - 1}{D + 2}$$  \hspace{1cm} (5.2)

where $D^0$ is the value of $D$ corresponding to perfect orientation. It can be shown that $D^0 = \cot \alpha$ where $\alpha$ is an angle between a dipole transition moment direction and the polymer chain axis. Thus the first term in equation 5.2 is a purely geometrical term which should be constant within a given mode for all stretching ratios and in principle can be calculated if the polymer structure and mode assignment is known.

Figure 43 shows dichroic ratios $D_{835}$ and $D_{1170}$ for the 835 cm$^{-1}$ and 1170 cm$^{-1}$ modes, respectively, observed in stretch-oriented emeraldine base films with $l/l_0$ up to 4. The 1170 cm$^{-1}$ mode is assumed to be polarized along the N-N direction of a polymer zig-zag, according to the assignment in Table 9, page 78. Since the zig-zag (C-N-C) angle can be calculated from the x-ray data and is found to be 131° in stretched emeraldine films, the angle $\alpha_{1170}$ between the chain axis and 1170 cm$^{-1}$ mode dipole transition moment is $(180° - 131°)/2 = 24.5°$. Thus $D_{1170}^0 = \cot \alpha_{1170} = 2.19$ and values of $f_{\Theta_{1170}}$ can be calculated from experimental $D_{1170}$'s using Equation 5.2. Results are presented in Fig. 44. It can be seen that the polymer alignment is far from perfect (when $f_\Theta = 1$). This is probably caused by the fact that emeraldine films are to a large degree amorphous and the amorphous fraction is weakly aligned (see section 4.2 and Ref. [62]).

Calculations of orientation functions $f_\Theta$ should yield the same result for all the modes observed. This can be used to calculate the direction of a dipole transition moment of an unknown mode, when some other mode is known. In the case of

---

$^1$Using the value of parameter $c$ from Table 4 and N-N distance of 5.54 Å after Ref. [36].
Figure 43: Dichroic ratio $D = I_{\parallel}/I_{\perp}$ for the 835 cm$^{-1}$ mode ($D_{835}$) and for the 1170 cm$^{-1}$ mode ($D_{1170}$) vs stretch ratio $l/l_0$. 
Figure 44: Orientation function $f_{\Theta,117\theta}$ vs $l/l_0$. $f_{\Theta} = 0$ for an unoriented sample and $f_{\Theta} = 1$ for perfectly oriented sample.
stretch-oriented emeraldine films, this can be used to obtain a ring tilt angle \( \phi \). The 835 cm\(^{-1}\) mode is assumed to be polarized perpendicular to the ring. From geometrical calculations it can be shown that

\[
\sin \phi = \frac{\cos \alpha_{835}}{\sin \alpha_{1170}}
\]

(5.3)

where \( \alpha_{1170} \) was calculated previously and found to be 24.5°. Equation 5.3 can be rearranged and solved for \( \phi \):

\[
\phi = \arcsin(2.411 \cos \alpha_{835})
\]

(5.4)

The value of \( \alpha_{835} \) can be obtained using the assumption that \( f_{\phi,835} = f_{\phi,1170} \). Using this, and Equation 5.2, the following relation is readily obtained:

\[
\frac{D_{835}^0 + 2}{D_{835}^0 - 1} \times \frac{D_{835} - 1}{D_{835} + 2} = f_{\phi,1170}
\]

(5.5)

\( D_{835} \) is obtained experimentally (Fig. 43). Equation 5.5 can be solved for \( D_{835}^0 \) and a value of \( \alpha_{835} \) is calculated from the relation \( D_{835}^0 = 2 \cot^2 \alpha_{835} \). The value of \( \alpha_{835} = 69.9° \) is obtained from experimental data on emeraldine films. This value, when used in Eq. 5.4 gives a ring tilt angle \( \phi = 56° \). A complicated and indirect way of evaluating this angle, and particularly the relative insensitivity of the value of \( D_{835} \) with respect to \( \phi \), result in a large error in the absolute value of \( \phi \), on the order of ±15°. One also cannot rule out the possibility that the directions of the transition moments of 835 and 1170 cm\(^{-1}\) modes are somewhat different than those assumed. The x-ray value of \( \phi = 30 ± 5° \) is more reliable.

### 5.2 PHOTOINDUCED FTIR SIGNAL IN EMERALDINE MATERIALS

Long-time evolution of photoinduced infrared spectrum was studied in emeraldine powder EB-I. Sample was prepared in the form of KBr pellet. Figure 45 shows 5 spectra taken in 1 minute intervals, with the laser light\(^2\) (488 nm, 200 mW/pellet) continuously on. It can be seen that the photoinduced spectrum does not change shape in time, only the intensity. The purpose of this section is the analysis of the change of this photoinduced spectrum with time.

\(^2\)In all photoinduced experiments reported here, 488 nm argon ion laser line was used as a pump beam. Pump beam power is reported throughout this work in mW at the sample position.
Figure 45: Photoinduced spectra of emeraldine base powder EB-I. Change in absorbance is plotted with respect to the background spectrum taken before laser was turned on. The temperature was 90 K. The laser light was on continuously (200 mW, 488 nm). The time interval between spectra is 1 minute.
The photoinduced spectrum in polyaniline was analyzed previously [30]. The photoinduced absorptions at 1130 and 1570 cm\(^{-1}\) are associated with symmetry breaking of \(p\)-disubstituted benzene rings due to defect photocreation. Photoinduced bleachings at 1510 and 1600 cm\(^{-1}\) indicate a decrease in the intensity of benzenoid and quinoid modes, caused by some rings becoming asymmetric (see Table 9 for straight absorbance mode assignments). All those features are traces of photoinduced defects created in emeraldine, expected to be polarons trapped near quinoids, \(P_{BQ}^{+}\) [30]. It is assumed that the number of long-lived defects is proportional to the intensity of any given photoinduced mode. For further analysis, the 1130 cm\(^{-1}\) mode has been chosen because there is little thermal activity underneath it\(^3\). This mode was integrated and the value of the integral was assumed to be proportional to the number of defects. Figure 46 presents the integrated 1130 cm\(^{-1}\) peak intensity as a function of time.

The photoinduced signal initially grows rapidly, then more slowly, but does not saturate even after 3.5 hours. The growth of the signal (during "laser on" stage) can be described by adapting the Kohlrausch-Williams-Watts (KWW) [65, 66] function. The typical KWW function describes decay of some physical feature (like number of defects \(N(t)\) for example):

\[
N(t) = N_0 \exp(-t/\tau)^\beta
\]

where \(N_0\), \(\tau\), and \(\beta\) (0 ≤ \(\beta\) ≤ 1) are parameters. For the purpose of describing growth\(^4\) of the photoinduced signal in emeraldine, the following modification of Kohlrausch-Williams-Watts function, called "stretched-exponential" function is introduced:

\[
\Delta A(t) = \Delta A_\infty \{1 - \exp[-(t/\tau)^\beta]\}
\]

where \(\Delta A_\infty\) (asymptotic value of \(\Delta A\) when time \(t \to \infty\)), \(\tau\) (characteristic time) and exponent \(\beta\) are all fitted parameters. A stretched-exponential fit to the experimental data is marked on the Fig. 46 with a continuous line. The fit is very good and covers data taken over several hours.

When the laser is turned off, initially a small decrease in the photoinduced signal occurs, within the first minute or two, due to sample cooling, but later the

---

\(^3\) Laser light not only photoproduces defects, but also heats the sample. In this case, heating effects contribute little to the overall photoinduced spectrum.

\(^4\) What is considered "growth" and "decay" is in a sense a matter of definition. Equation 5.7 can be rewritten: \(\Delta A_\infty - \Delta A(t) = \Delta A_\infty \exp[-(t/\tau)^{\beta}]\) to conform to a classical Kohlrausch decay equation (Eq. 5.6).
Figure 46: Integrated 1130 cm$^{-1}$ peak intensity as a function of time (emeraldine base EB-I). $T = 90$ K, pump beam power (at the sample) $P = 200$ mW. The continuous line represents stretched exponential fit.
Table 10: Stretched-exponential parameters for photoinduced signal growth in emeraldine base obtained by fitting Function 5.7 to the data from Fig. 49.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>$\Delta A_{\infty}$</th>
<th>$\tau$ [min.]</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>1.24</td>
<td>20.0</td>
<td>0.43</td>
</tr>
<tr>
<td>110</td>
<td>1.08</td>
<td>15.2</td>
<td>0.42</td>
</tr>
<tr>
<td>130</td>
<td>0.84</td>
<td>10.9</td>
<td>0.41</td>
</tr>
<tr>
<td>150</td>
<td>0.59</td>
<td>5.8</td>
<td>0.42</td>
</tr>
<tr>
<td>180</td>
<td>0.34</td>
<td>2.4</td>
<td>0.40</td>
</tr>
<tr>
<td>210</td>
<td>0.18</td>
<td>1.0</td>
<td>0.48</td>
</tr>
<tr>
<td>240</td>
<td>0.13</td>
<td>0.9</td>
<td>0.39</td>
</tr>
</tbody>
</table>

signal is stable and persists with only a slight decay for a long time. It has been estimated from the data pictured in Fig. 46 that the half-time of the photoinduced signal decay in emeraldine base at temperature 90 K is on the order of 6 days. Other forms of polyaniline exhibit similarly long defect decay times. The fact that the signal decay is so slow precludes any qualitative investigation of it because of instrumental drift over such a long time period.

Figure 47 shows photoinduced data taken at a temperature $T = 90$ K with various laser powers (at the sample, $\lambda = 488$ nm), from $P = 20$ mW to $P = 600$ mW. The same data are shown in Figure 48, but this time plotted against total energy delivered to the sample. It can be seen that the photoinduced signal intensity or the number of defects depends only slightly on the laser power used and that there is only small defect decay. What matters most is the total number of photons delivered to the sample and number of defects already created. The photoinduced signal grows more slowly as the number of defects increases, probably because defects already created block possible defect stabilization sites.

Data taken at different temperatures are presented on Figure 49. Parameters $\Delta A_{\infty}$, $\tau$ and $\beta$ obtained by fitting function 5.7 to the data from Fig. 49 are given in Table 10. Clearly, less and less long-lived photoinduced defects are observed when the temperature is increased. Above ca. 260 K, no photoinduced effects are observed and defects created at lower temperatures are annealed above that temperature. This feature is used to erase previously photocreated defects. All
Figure 47: Integrated $\Delta A$ for the 1130 cm$^{-1}$ peak for various laser power at the sample, versus time. $T = 90$ K.
Figure 48: Integrated $\Delta A$ for the 1130 cm$^{-1}$ peak (data from Fig. 47), plotted as a function of total energy of the light delivered to the sample (pellet).
Figure 49: Integrated $\Delta A$ for the 1130 cm$^{-1}$ peak for experiments performed at different temperatures. Power of laser light at the sample $P=320$ mW.
the data presented in Figs 47 and 49 were taken with a single pellet\(^6\) (0.5% of EB-I powder in KBr), which was repeatedly exposed to light in low temperatures and then “erased” at room temperature. This mechanism of “writing” and “erasing” photoinduced defects in polyaniline is the basis for a proposal of possible use of polyaniline as an information storage medium [67, 68]. An interesting feature about the data listed in Table 10 is the fact that the exponent \(\beta\) is almost constant with temperature. Models discussed below all postulate that \(\beta\) changes with temperature.

Kohlrausch-William-Watts decay of a physical quantity occurs often in disordered systems and in glasses. Kohlrausch first suggested (in 1847) a formula of the type of Equation 5.6 as a description of an evolution of viscoelasticity [65]. Later Williams and Watts postulated the same function for dielectric relaxation in glasses [66]. Since then many other phenomena in disordered materials were discovered to follow this time behavior. A good overview with many examples from a surprisingly broad range of systems is given in [69]. In the following paragraphs a short summary of the field of this complex (sometimes called “non-Debye”) decay will be given. After that, some connection will be made to the stretched-exponential growth.

The decay rate of a given quantity \(N(t)\) can be written as proportional to the value of \(N(t)\):

\[
\frac{dN(t)}{dt} = -k(t) \ast N(t) \tag{5.8}
\]

where \(k(t)\) is a rate coefficient. In a classical, Debye system, \(k\) would be constant with time and the solution would be a Debye relaxation

\[
N(t) = N_0 \exp(-kt) \tag{5.9}
\]

However, if a particular time-dependent form of \(k(t)\) is assumed:

\[
k(t) = \frac{\beta}{\tau} \left(\frac{t}{\tau}\right)^{\beta-1} \tag{5.10}
\]

then equation 5.8 can be solved to give the stretched-exponential time dependence 5.6. This can be considered as a “diffusive” model - \(k\) may be a function of time because defects diffuse with a time-dependent diffusion constant.

\(^6\)Parameters for data taken on different pellets of the same material are reproducible to \(\sim\)10%. Variations are due to differences in pellet transparency and in dispersion of polyaniline powder in the KBr. For this reason, only data taken from single pellet can be used for comparative temperature and power dependency studies.
Another way of arriving at a non-Debye decay law is to realize that Debye decay is described by a single characteristic time $\tau$. One may, however, assume that there exists a continuum of characteristic decay times due for example to the disorder in the sample. Then the total value of $N(t)$ can be described as an integral over all characteristic times:

$$N(t) = \int_0^\infty w(\tau) \exp(-t/\tau) d\tau$$

(5.11)

Any reasonable $N(t)$ can in this way be obtained by a suitable choice of the weight distribution function $w(t)$. This can be regarded as a "parallel" model - there exist a continuum of independent parallel processes, each with its characteristic time $\tau$.

This is about where the simplicity ends. Both approaches are rather arbitrary and do not advance our knowledge of exact, molecular scale mechanisms involved. It may be that there are no single mechanism and simply a distribution of decay times $\tau$ caused by disorder must suffice as an explanation. But many authors, seeing a very broad range of systems exhibiting a stretched-exponential behavior have attempted to explain it in more detail. A broad overview of those efforts is given by Ngai and Wright [70]. Only a few of the simplest and/or most typical models will be mentioned below.

Palmer et al. [71] proposed models based on hierarchically constrained dynamics. The degrees of freedom of a strongly disordered material are divided into a sequence of levels such that those in level $n + 1$ are locked except when some of those in level $n$ form the right combination to release them. This represents a hierarchy of constraints in real systems. It corresponds to a situation when an atom (or cluster) $A$ cannot move until an atom (or cluster) $B$ moves out of the way. For appropriate combination of the number "atoms" $\mu_n$ out of total of $N_n$ at each level $n$ that needs to be in the correct position for the $n+1$ level to relax, the authors obtain a relation that is essentially a stretched-exponential with a small correction. This can be considered a completely "serial" model.

A variation of this model is a hierarchical energy barriers model by Kumar et al. [72]. Hopping over hierarchical (in "height") barriers in many dimensions is shown to yield a stretched-exponential decay for appropriate (and somewhat arbitrary) assumptions about the "height" of the barrier and the attempt frequency to overcome that barrier. Other authors have also explored this model [73, 74, 75] and concluded that it is a variation of a "serial" model, because lower barriers get crossed first, then taller barriers, etc.
J.L. Skinner et al. in a series of papers [76, 77, 78, 79] analyzes results of light scattering experiments in polymers. Such light scattering experiments are sensitive to polymer chain conformations. The authors view relaxation in such polymers as arising solely from two processes: the migration (random walk) of defects and the creation/annihilation of defect pairs. When defects are assumed to be non-interacting, a stretched exponential decay function of the form 5.6 is found, with $\beta = 1/2$. For the case of interacting defects, $1/2 \leq \beta \leq 1$ is obtained. When the distribution of defect hopping times is included, $\beta \leq 1/2$ can be obtained.

One experimental result that can be related to the time dependence of photoinduced signal in emeraldine is an effect of illumination on defects in hydrogenated amorphous silicon (a-Si:H). The observation of changes in a-Si:H upon illumination goes back to the work of Staebler and Wronski [80] who found that the dark conductivity and photoconductivity of a-Si:H can be reduced significantly by prolonged illumination of the sample with intense light. The interest in the effect was significant, due to commercial potential of a-Si:H. Numerous experiments prove that the creation of defect states in the gap of the amorphous silicon occurs upon illumination. Diffusion of the hydrogen atoms plays a crucial role in defect creation and annihilation. It was discovered [81] that the hydrogen diffusion rate in a-Si:H is a function of time and is proportional to $(t/P)^{-1}$, where $P$ is some characteristic time. A good review of experimental results is given by Stutzmann et al. [82].

Bube and Redfield [83] postulated that the change in the number of defects upon illumination of a-Si:H can be written as:

$$\frac{dN}{dt} = C_1 G (N_T - N) - C_2 G N$$

(5.12)

where $N$ is a number of defects, $G$ is the volume photoexcitation rate (proportional to light intensity), $N_T$ is maximum density of sites in the material that can be photoexcited and $C_1$ and $C_2$ are effectiveness coefficients for the production of defects and optical annealing of already created defects. Thermal processes are neglected and both effectiveness coefficients are assumed to have a form: $C_1 = C'_1 (t/P)^{-(1-\beta)}$ and $C_2 = C'_2 (t/P)^{-(1-\beta)}$. This is justified by the fact that hydrogen diffusion rate has the same form. Using these forms, equation 5.12 can be written as:

$$\frac{dN}{dt} = \left( \frac{t}{P} \right)^{-(1-\beta)} [C'_1 G N_T - (C'_1 + C'_2) G N]$$

(5.13)
This equation can be integrated to give:

\[ N(t) = N_\infty \left\{ 1 - \exp\left[-\left(t/\tau\right)^\beta\right]\right\} \tag{5.14} \]

where \( N_\infty = \left[ C'_1/(C'_1 + C'_2) \right] N_T \) and \( \tau = \beta P^{\gamma - 1} G^{-1}/(C'_1 + C'_2) \). This is a stretched exponential solution that is identical to the equation of the growth of photoinduced signal in emeraldine (Eq. 5.7).

It is not clear at this moment what mechanism is responsible for the stretched-exponential growth of photoinduced signal in polyaniline. It may be that there is some distribution of characteristic times \( \tau \) due to the largely amorphous nature of the sample which gives stretched-exponential behavior in the manner of Eq. 5.11. The existence of a very broad range of time scales in emeraldine was postulated from NMR investigations [84]. There is however some indication from studies of light-induced EPR signal [85] that the photoproduced defects aggregate. If this is the case, then the defects must diffuse along the polymer chains until a suitable stabilization site (like naturally occurring conformational defect) or another photoinduced defect can be found. The diffusion rate may be time-dependent (shortest and fastest routes are utilized first and blocked by defects?), as in the model of Bube et al, discussed above and that would give rise to a stretched-exponential behavior 5.7.

Long-time changes in the spectrum of emeraldine base are visible not only in the mid-IR region but also in the near-IR, where a large photoinduced peak at 11,150 cm\(^{-1}\) (1.4 eV) is observed. Detailed analysis of the photoinduced spectra of emeraldine [30] describes this peak as an electronic transition associated with a hole polaron trapped near a quinoid site. This peak can be monitored with the same FTIR setup (and in the same pellet sample) used for the observation of mid-IR peaks, with the addition of a visible source and silicon detector. Photoinduced spectra taken in the near-IR region during the first 5 minutes of laser illumination are presented in Fig. 50. In Fig. 51, the integrated 11,150 cm\(^{-1}\) peak intensity is plotted.

The electronic photoinduced peak at 11,150 cm\(^{-1}\) exhibits the same type of growth as the vibrational peaks. The growth can be fitted to the same stretched-exponential function (Eq. 5.7) that was used to describe the behavior of the vibrational modes. In this case, parameters obtained from the fit are: \( \Delta A_\infty = 1381.8 \), \( \tau = 6.95 \), \( \beta = 0.47 \). The 11,150 cm\(^{-1}\) peak is stronger than vibrational peaks (compare vibrational peaks visible at the left side of Fig. 50). This indicates that
Figure 50: Photoinduced near-IR spectra of emeraldine base powder EB-I during the first five minutes of laser irradiation. The change in absorbance ΔA with respect to the background spectrum taken before laser was turned on is plotted. Temperature was 90 K. Laser pump light was on continuously (400 mW, 488 nm). The time interval between spectra is 1 minute.
Figure 51: Integrated 11,150 cm$^{-1}$ peak intensity as a function of time. $T = 90$ K, pump light power (at the sample) $P = 400$ mW.
photocreated defects are massive \( M > 60m_e \) \cite{30, 68}. In the amplitude mode \cite{86} or bond-order polaron \cite{87} formalism the defect mass is proportional to the ratio of electronic photoinduced peaks intensity to the vibrational photoinduced peak intensity. In Fig. 52 the 11,150 cm\(^{-1}\) peak intensity is plotted against the 1130 cm\(^{-1}\) peak intensity obtained in the analogous experiment (thus each point in Fig. 52 corresponds to some point in time after the laser was turned on). The fact that the line of experimental points is almost exactly straight (or that the ratio of intensities \( I_{11,150}/I_{1130} \) is constant) tells us that the average defect mass remains constant as the experiment progresses.

To conclude the investigation of photoinduced defects in emeraldine base it will be noted that no significant differences in photoinduced spectra between amorphous emeraldine base EB-I and partially crystalline emeraldine base EB-II were recorded. Photoinduced spectra taken from EB-I and EB-II after 48 minutes of laser irradiation (200 mW, 90 K) are shown in Figure 53. The photoinduced modes look very similar in both materials.

Additional spectra were taken in transmission-reflection configuration (see Chapter III for experimental setup description). The mid-IR photoinduced spectra have identical features and similar kinetics to those spectra described above, confirming the fact that long-lived photoinduced effects are characteristic to polyaniline polymer, and not for example to polyaniline-KBr solid solution. The main reason why the transmission-reflection experiment was undertaken however was search for far-IR ring-torsional mode. This mode is expected to occur approximately at 90 cm\(^{-1}\). The search not successful however - no photoinduced peaks were observed in far-IR in emeraldine sample. The reason may be that the ring-torsional peak has a very small transition moment - ring-substituted materials may show more active mode. Otherwise, it is possible that the mode is IR active, but is very broad, resulting in very small change in absorbance.

5.3 PHOTOINDUCED SIGNAL IN PNB AND LEB

A photoinduced FTIR spectrum of pernigraniline base is presented in Fig. 54. It was obtained in the same experimental conditions as the two emeraldine base spectra shown in Fig. 53 (after 48 min. of 400 mW laser light, \( T = 90 \) K). It is significantly different from photoinduced spectra of emeraldine base (compare
Figure 52: The integrated 11,150 cm$^{-1}$ peak intensity plotted versus the 1130 cm$^{-1}$ peak intensity. The ratio of $I_{11,150}/I_{1130}$ remains constant as the experiment progresses, indicating that the average mass of a photocreared defect is constant.
Figure 53: Photoinduced spectra for emeraldine base EB-I and EB-II. Conditions in both cases are the same: 48 minutes of 200 mW laser light, $T = 90$ K, 0.05% KBr pellets mixed using the same procedure.
Table 11: Stretched-exponential parameters for photoinduced signal growth in pernigraniline, emeraldine base EB-I and leucoemeraldine obtained by fitting Function 5.7 to the integrated 1130 cm⁻¹ photoinduced peak intensity experimental data. $T = 90$ K, laser power $P = 400$ mW (488 nm) at the sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta A_{\infty}$</th>
<th>$\tau$ [min.]</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pernigraniline</td>
<td>0.72</td>
<td>188</td>
<td>0.38</td>
</tr>
<tr>
<td>emeraldine</td>
<td>1.11</td>
<td>12.5</td>
<td>0.43</td>
</tr>
<tr>
<td>leucoemeraldine</td>
<td>0.11</td>
<td>1.4</td>
<td>0.23</td>
</tr>
</tbody>
</table>

with Figures 45 and 53). PNB photoinduced features are less intense than in emeraldine. The 1570 cm⁻¹ peak, quite large in emeraldine, is rather small here. The 1510 cm⁻¹ bleaching is almost nonexistent. On the other hand, features associated with the breaking of the symmetry of the quinoids (1600 cm⁻¹ bleaching and 1130 cm⁻¹ photoinduced absorption) are prominent. This is consistent with the fact that in pernigraniline every other ring is in quinoidal form (Fig. 10(iii)). Particularly interesting is the large photoinduced peak at 830 cm⁻¹, associated with a bleaching at 860 cm⁻¹. It is stronger in PNB than in emeraldine base. It may also be associated with the change in local symmetry around quinoids.

As in the case of emeraldine, the 1130 cm⁻¹ photoinduced mode was chosen for integration. The plot of integrated 1130 cm⁻¹ peak intensity vs time is shown in Fig. 55. It exhibits the same stretched-exponential growth (Eq. 5.7) as observed in emeraldine base. Fitted parameters are given in Table 11, together with parameters for emeraldine base and leucoemeraldine.

The photoinduced spectrum of leucoemeraldine form of polyaniline, taken after 48 minutes of 400 mW of laser light (488 nm) irradiation in $T = 90$ K is shown on Figure 56. It is weaker than the photoinduced spectra of both emeraldine and pernigraniline. This may be due in part to the fact that leucoemeraldine absorbs much less radiation at 488 nm. The photoinduced spectrum of leucoemeraldine has been analyzed previously [30], so it will only be mentioned here that the absence of a photoinduced bleaching at 1600 cm⁻¹, which is so prominent in emeraldine

*Note that scale on Fig. 56 is ten times smaller than on Figures 53 and 54.
Figure 54: Photoinduced FTIR spectrum for pernigraniline (PNB) in KBr pellet. Experimental conditions: spectrum was taken after 48 minutes of irradiation with 400 mW, 488 nm laser light, $T = 90$ K.
Figure 55: Integrated 1130 cm\(^{-1}\) peak intensity as a function of time (pernigraniline). \(T = 90\) K, power (at the sample) \(P = 400\) mW.
Figure 56: Photoinduced FTIR spectrum of leucoemeraldine (LEB) in KBr pellet. Experimental conditions: the spectrum was taken after 48 minutes of irradiation with 400 mW, 488 nm laser light, T = 90 K.
base and in pernigraniline is very characteristic. This is a confirmation that this bleaching is due to the depletion of quinoid rings. Since leucoemeraldine contains only small amounts of quinoid rings as impurities, and otherwise has only benzenoid rings (Fig. 10(i)), thus little quinoidal bleaching is expected.

As for emeraldine base and pernigraniline, the 1130 cm$^{-1}$ photoinduced mode can be integrated and a stretched-exponential curve in the form of 5.7 was fitted. Parameters obtained are given in Table 11. The resulting curve is plotted in Fig. 57. It should be noted that with such weak signals the accuracy of the fitted parameters is not very good.

It is difficult to compare photoinduced signal parameters for different materials due to variations in sample preparation. Even with the same material and the same pellet preparation method the stretch-exponential parameters can differ from pellet to pellet by as much as 10%. This difference must be larger when samples are different (in chemical composition and crystallinity). The differences in dispersion and miscibility of various polyaniline samples in KBr obscure the real differences in photoinduced signal parameters between those samples. For this reason, data in Table 11 should be compared with caution.
Figure 57: Integrated 1130 cm\(^{-1}\) peak intensity as a function of time (leucoemeraldine). \(T = 90\) K, power (at the sample) \(P = 400\) mW.
CHAPTER VI

Conclusions

A summary of the structural results is presented in the first section of this chapter. Importance of the local structure and crystallinity on polyaniline chemical and physical properties is stressed. In particular, ring tilt angle is found to vary with doping level and derivatization. In the second section, the conclusions of the long-lived photoinduced defect study are given. Long-lived defects are proposed to involve ring angle changes. The third section reviews the work done on the oriented samples.

6.1 Structural Results

X-ray structures of a wide range of polyaniline samples have been studied. The results in polyaniline-emeraldine can be summarized as follows:

- Emeraldine samples prepared originally in the salt form (this includes emeraldine hydrochloride, but also other salts, such as fluoride or sulfide) are amorphous in the base (EB-I) form and partially crystalline in the HCl salt (ES-I) form. Examples of materials belonging to this category are: emeraldine salt "as prepared", electrochemically prepared film, and film cast from acetic acid [47].

- Emeraldine samples precipitated or recrystallized in the base form are partially crystalline in the base form (EB-II) and partially crystalline in the
salt form (ES-II), with the crystalline structure different from the ES-I samples. Examples of materials belonging to this category are: emeraldine base THF/NMP extracted material, low molecular weight THF extract, and films cast from NMP and DMSO.

The reason for the existence of two different classes of emeraldine is apparently the fact that the local polymer chain arrangements are significantly different in the base forms than in the salt forms. When emeraldine is precipitated in the salt form, the polymer chains are arranged to accommodate bulky counterions. When the polymer is subsequently dedoped, and counterions removed, the long range order collapses (which is why emeraldine base EB-I is amorphous), but local order retains “memory” of the salt structure. When the sample is redoped, the ES-I partially crystalline structure is restored. Coulomb forces between counterions and the backbone, much stronger than Van der Waals forces, help restore the structure.

Amorphous base EB-I probably has highly strained chain arrangement due to removal of counterions. Therefore it rearranges itself when the polymer is dissolved in NMP, or DMSO or swelled in THF. Rearrangement produces the more compact and ordered, partially crystalline EB-II structure. This form of the emeraldine is more difficult to dope (Fig. 17, p. 24), as there is no space in the material left for Cl⁻ counterions. The EB-II materials are doped by inserting layers of Cl⁻ counterions between layers of polymer chains, resulting in the ES-II structure, different from ES-I.

In emeraldine base EB-II the average ring tilt angle (out of the plane of nitrogen atoms) is 30°. This angle decreases to 0-15° in the salt samples. Doping-induced defects thus involve considerable changes in ring tilt angle φ towards planar configuration. Planar configuration is expected to increase electron delocalization along the polymer chain.

This study has an impact on polymer processing. Amorphous forms of emeraldine are soluble in NMP and DMSO, and partially soluble in THF, whereas crystalline bases and salts are not. Improved order in the polymer should result in improved electrical and mechanical properties. It has been shown that in stretched NMP-cast films, not only individual chains are oriented but also crystallinity is nucleated [62]. On the other hand, oriented films show an improved electrical conductivity and tensile strength [88].
Future work in emeraldine might include further study of the EB-II - ES-II system, particularly investigation of the change in the ring tilt angle as the doping progresses. Another study should concentrate on analysis of the structure of oriented emeraldine fibers spun from sulfuric acid solution and redoped in hydrochloric acid. Such fibers should be of oriented, highly crystalline ES-I form.

The analysis of pernigraniline and leucoemeraldine structures is significantly hampered by the lack of materials with sufficient crystallinity. Better knowledge of the structures of those materials would enable one to make direct comparisons with electronic calculations. The results presented in this work, namely that pernigraniline crystallizes in EB-II-like structure ($P_{bcn}$) and leucoemeraldine in ES-I-like structure ($P1$) should be treated as preliminary. Many efforts to synthesize highly crystalline LEB or PNB either by reduction/oxidation of highly crystalline emeraldine or directly were not successful thus far. Pernigraniline is likely to exhibit small average ring tilt angle due to presence of quinoids whereas leucoemeraldine, having no quinoids, should have large angle, perhaps of the order of $\phi = 56^\circ$, as predicted from electronic calculations [23]. Determination of the ring conformation was not possible with the low crystallinity materials studied.

Poly-o-toluidine has been found to resemble the EB-I - ES-I system, with increased interchain spacing and disorder. This has been directly related to the transport measurements which indicate larger electron localization in POT. It is intriguing that no equivalent of the “Class II” phase has been found in POT. The reason may be that POT will not crystallize from a solvent in a tightly packed EB-II-like structure due to a somewhat random orientation of the $-\text{CH}_3$ groups. The study of POT can be naturally extended to systems with other substituent groups. Some preliminary studies suggest however that polyanilines with side groups larger than the methyl group are largely amorphous.

Other groups of materials which await more careful study are salts of emeraldine other than hydrochloride. It has been reported previously [34, 35] that emeraldine sulfide is partially crystalline. Comparison of its Debye-Scherrer pattern with that of ES-I or ES-II clearly shows that its structure is different. After this structure is solved it can be compared to the structures of emeraldine hydrochloride in terms of its impact on electronic properties.
6.2 Long-lived Photoinduced Defects

It has been shown that the growth of the photoinduced IR signal in all oxidation forms of polyaniline follows "stretched exponential" behaviour over many hours and that the decay of signal is slow. The photoinduced signal is relatively weakest in leucoemeraldine. The signal scales with light intensity and is strongest at low temperatures. Above ca 260 K no signal is observed.

Long-lived photoinduced features are attributed (after Ref. [30]) to ring-rotational polarons trapped near quinoids, $P^+_R$. Ring rotational polarons are regions in the polymer chain where rings lie somewhat more in plane of nitrogens than the surrounding rings. Such conformational defects would be stabilized by quinoid rings, which are expected to be more planar than benzenoid rings. They might be stabilised by other similar defects as well. This would cause defect aggregation. Emeraldine base and pernigraniline contains large numbers of quinoids, offering large number of trapping centers for photoinduced defects. Therefore long-lived photoinduced signal in emeraldine and pernigraniline is strong. On the other hand, leucoemeraldine samples have very little quinoids, offering few defect trapping sites and the photoinduced signal in leucoemeraldine is weak.

Stretched exponential behaviour of the photoinduced signal can arise from many different origins: from a distribution of independent relaxation times $\tau$ (parallel model), from a time-dependent diffusion (diffusion model), and from highly hierarchical mechanism of relaxation (serial model). Some evidence from EPR studies shows that photoinduced defects congregate suggesting that defects have to diffuse, and thus the diffusive model would be appropriate.

The electronic part of the spectrum evolves in parallel with the vibrational part which suggests that the average mass of the defect does not change as more and more defects are created. Attempts were made to measure photoinduced defects in the far-IR part of the spectrum (10-600 cm$^{-1}$) in the transmission-reflection experiment (Fig. 22b, p. 37) in the search for a photoinduced ring-torsional mode. No photoinduced features were found in this region in emeraldine. Future work should include polyaniline materials with side groups (poly-o-toluidine, polyethylaniline), which should give a clearer indication of ring twists.
6.3 Oriented Materials

Oriented emeraldine films possess improved electrical properties, orientation, and crystallinity. X-ray variable temperature studies revealed a change in the cell parameters and more importantly a change in the average ring tilt angle of emeraldine base that is qualitatively consistent with electronic calculations. This is a direct confirmation of those calculations and of the proposed origin of the thermochromic effect in polyanilines [89]. Future studies of the same type should span a larger temperature range. Studies on pernigraniline and leucoemeraldine will be possible only if more crystalline materials are produced. As a substitute for leucoemeraldine, a highly crystalline poly-p-phenylene oxide (PPO) or sulfide (PPS) can be used. These polymers are structural analogues of leucoemeraldine, with oxygen and sulfur, respectively in place of leucoemeraldine's -NH groups. The study of temperature dependence of the PPO or PPS structures could provide information about the electron structure dependence on the ring twists which could be applicable to leucoemeraldine.

Infrared dichroic studies confirmed previous assignments of direct absorptions in polyaniline. The calculated orientation function $f_\phi$ reaches a maximum of ca 0.4 for four times stretched emeraldine films. This is far from $f_\phi = 1$ for perfectly alligned polymer. There is clearly room for improvement. Better oriented materials should give significantly better electrical and mechanical properties. A search should be continued for better methods of orienting polyaniline; perhaps fibers spun from thick NMP or sulfuric acid solutions, new solvents or new plasticizers.
Appendix A

Macro Commands for Time Evolution FTIR Experiment

A large amount of data collected with the FTIR spectrometer during a long-time experiment requires special macro commands (short programs consisting of series of spectrometer instructions) to efficiently store and handle data. Macros described here are to be run on the Nicolet 60SX spectrometer. Text of the macros is capitalized. Comments are put in lower case and are not actually input into the computer.

- **FSC** - File Size Change. This command changes the file size in order to accommodate more files in the scratch area and lowers the resolution in order to lower the noise of a final peak intensity vs time curve.

```
NSK=0
COR=NO
NPD=200
OMD

ENTER RESOLUTION (4, 8, 16, 32 CM^-1)
RTN *this is approximate resolution*
NDP=16384/RTN+799
NTP=2*NDP
FSZ=NTP
FXI=0
LXI=NDP
```
OMD
   ENTER VELOCITY 1-180 (SEE TABLE)
VEL
DFN=9
NSD=2*RTN
CLD  *a scan is collected to check of the system*
END

• LTP - Long-Time Photoinduced experiment. This is a primary macro controlling the long-time photoinduced experiment. This macro calls short macro SOO - Shutter On/Off which opens/closes the shutter.

OMD
   ENTER NUMBER OF "LASER ON" MEASUREMENTS
QIT
OMD
   ENTER NUMBER OF "LASER OFF" MEASUREMENTS
VII
OMD
   ENTER SCAN PARAMETERS
NSB
NSS
SRT=QIT
BFN=10
DFN=11
PAU  HIT <RETURN> WHEN READY
CLB  *collect background into scratch file 10*
SOO  *open the shutter*
NSD=NSS
FOR XXX=1 TIL QIT
PRN SRT  *collect spectra into scratch files starting
CLD
   at 11 until QIT files are collected*
DFN=DFN+1
SRT=SRT-1
NXT XXX
SOO
   *close the shutter*
NSD=NSS
SRT=VI1
FOR YYY=1 TIL VI1
PRN SRT *collect spectra into scratch files starting at
CLD last file collected in previous loop + 1 and
DFN=DFN+1 continuing until VII files are collected*
SRT=SRT-1
NXT YYY
OMD
FILE "BEFORE LASER" IS PLACED IN BFN=10
OMD
FILES "DURING AND AFTER LASER" ARE PLACED FROM DFN=11 TILL:
DFN=DFN-1
PRN DFN
END

Macro SOO:

NSD=1
ITR=4
RSC *spectrometer collects short Rapid Scan to
DFN=DFN-4 generate pulse which triggers the shutter*
END

• **FPA** - *Fourier-Process All files. Converts collected interferograms into one-beam spectra.*

OMD
FOURIER-PROCESSES FILES FROM SRT TILL QIT
SRT
QIT
DFN=SRT
FOR XXX=SRT TIL QIT
FPD
DFN=DFN+1
NXT XXX
END

• **RSN** - *ReSolutioN - calculates actual resolution.*
TEM=NDP-PEK+SSP
VF3=32000/TEM
TEM=3
NPR
OMD
CURRENT RESOLUTION IS:
PRN VF3
NPR
END

- **CDT** - Calculate Delta Transmittance - calculates $-\Delta T/T$ for collected files and stores resulting files in consecutive scratch files beginning at a specified file.

OMD
  CALCULATES $-\Delta T/T$ FOR FILES FROM SRT TILL QIT
SRT
QIT
OMD
  ENTER THE BACKGROUND FILE NUMBER
BFN
OMD
  ENTER THE NUMBER OF THE FIRST FILE TO STORE PIA
SFN=QIT+1
SFN
FCS=-1
FCB=-1
OFN=SRT
FOR XXX=SRT TIL QIT
MOS
BKS
RAS
OFN=OFN+1
SFN=SFN+1
NXT XXX
SFN=SFN-1
OMD
LAST PIA FILE IS STORED IN
PRN SFN
END

- **CDA** - Calculate Delta Absorbance - same as CDT, except it calculates $\Delta A$ instead.

**OMD**

CALCULATES DA FOR FILES FROM SRT TILL QIT
SRT
QIT
OMD

ENTER THE BACKGROUND FILE NUMBER
BFN
OMD

ENTER THE NUMBER OF THE FIRST FILE TO STORE PIA
SFN=QIT+1
SFN
OFN=SRT
FOR XXX=SRT TILL QIT
MOS
RAS
ABS
OFN=OFN+1
SFN=SFN+1
NXT XXX
SFN=SFN-1
OMD
LAST PIA FILE IS STORED IN
PRN SFN
END

- **DPZ** - Display/Plot files in Z format. Prepares parameters for display/plotting of consecutive files on the same page with (optional) "z-axis" offset. The actual display is triggered by macro **DPZ** - Display in Z format and plotting by macro **PLZ** - Plot in Z format.
OMD

DISPLAYS/PlOTS FILES FROM SRT TILL QIT

SRT
QIT

OMD

ENTER THE FILE INCREMENT FOR DISPLAY/PLOT

RTQ *will plot every n-th file, n=1,2 ...*

DFN=SRT

OMD

ADJUST XPN AND YPN FOR Z-AXIS OUTPUT

XPN=0.1 *XPN, YPN should set to zero if plots are to be superimposed*

YPN=0.2

YPN

TEM=108

NPR

ASD

DSD

OMD

ROLL AND ZOOM TO AREA OF INTEREST

OMD

STRIKE <RETURN> WHEN READY

PAU

OMD

INPUT AXES PARAMETERS     9/6

XSP
XEP

XSL *XSL controls the width of the plot - normally 9 in.*

YSP
YEP

YSL *YSL controls the height of the plot - normally 6 in.*

OMD

PRESS DSZ TO DISPLAY, PLZ TO PLOT

END

DSZ - DiSplay in Z-axis format.

VI0=QIT-SRT+1/RTQ
DFN=SRT
TEM=108
NPR
FXF=XSP
LXF=XEP
FOR XXX=1 TIL VIO
DSD
TEM=9
NPR
DFN=DFN+RTQ
NXT XXX
END

PLZ - PLOT in Z-axis format.

VIO=QIT-SRT+1/RTQ
OMD
WILL PLOT DELTA A DATA ONLY!
TIT=YS
DFN=SRT
TEM=111
NPR
FXF=XSP
LXF=XEP
CXF=XEP-XSP/XSL
FYA=YSP *to plot transmittance data, change FYA, LYA, CYA
LYA=YEP to FYT, LYT, CYT in these substitutions*
CYA=YEP-YSP/YSL
AXS=YS
PAG=NO
ZPN
PLD
DFN=DFN+1
VIO=VIO-1
TIT=NO
AXS=NO
FOR XXX=1 TIL VIO
PEN
PLD
DFN=DFN+RTQ
NXT XXX
ZPN
VF3=YPN
YPN=−VF3*VI0−8.5
PEN
YPN=VF3
END

* SMA - SuM All files. Integrates FXF-LXF region of the spectrum for all files from SRT to QIT. Integration can be carried out to the zero line or to the baseline, which is a straight line from data point at SRT to data point at QIT. This program uses two FORTRAN programs to store integration results on the disc.

OMD
INTEGRATES SPECIFIED REGION FOR ALL FILES FROM SRT TILL QIT:
SRT
QIT
OMD
ENTER INTEGRATION RANGE:
FXF
LXF
OMD
INTEGRATE TO THE ZERO LINE (BAS=NO) OR TO
OMD
THE BASELINE (BAS=YES)?
BAS
OMD
ENTER TIME BETWEEN SCANS
VFO
OMD
FIRST FILE HAS TIME COORDINATE = VFO*(VI2−0.5)
VI2 *normally put to 1*
DFN=SRT
GFN
GETNAM.FCP *this FORTRAN program opens file NAME and inputs a filename of a data file to be created into it*
VI1=0
OMD

VF2 IS TIME FOR A FILE, FCD IS A PEAK INTENSITY:
FOR XXX=SRT TIL QIT
TEM=4
NPR
SMD *desired region is integrated*
VF2=VI2-.5*VF0
NPR
TEM=3
PRN VF2 *results are printed on the screen*
NPR
PRN FCD
NPR
GFN
DATPUT.FCP *FORTRAN program is called and values of VF2 and FCD added to a data file*
DFN=DFN+1
VI1=VI1+1
VI2=VI2+1
NXT XXX *loop is executed until XXX=QIT*
END

Program GETNAM.FOR

C THIS PROGRAM GETS A FILENAME
C AND STORES IT IN A FILE 'NAME'
C
C GET THE FILENAME
C
CHARACTER N*20
PRINT *, 'ENTER FILENAME FOR DATA STORAGE '
READ(1,10) N
10 FORMAT(A)

C STORE THE FILENAME IN FILE 'NAME'
C
OPEN (11,FILE='NAME',STATUS='UNKNOWN',FORM='FORMATTED')
WRITE(11,10) N
CALL EXIT
END

Program DATPUT.FOR

C THIS PROGRAM GETS VALUES OF VII, VF2 AND FCD FROM MEMORY
C AND STORES VF2 AND FCD IN A FILE. VII IS A COUNTING
C VARIABLE, FCD IS PEAK INTENSITY AND VF2 IS SOME OTHER
C PARAMETER, C FOR EXAMPLE TIME.
C
C
INTEGER I
REAL TIME,INT,FTIME,FINT
CHARACTER N*20

C GETS VALUES FROM MEMORY:
C
I=IRVAL(6131,1)
TIME=RVAL(6138,1)
INT=RVAL(6194,1)

C GETS FILE NAME FROM FILE 'NAME':
C
OPEN(11,FILE='NAME',STATUS='UNKNOWN',FORM='FORMATTED')
READ(11,10) N
10 FORMAT(A)

C OPENS STORAGE FILE:
OPEN(UNIT=12,FILE=N,STATUS='UNKNOWN',FORM='FORMATTED')
C
C READS STORAGE FILE I TIMES TO GET TO THE END:
C
   DO 15 J=1,I
      READ(12,20) FTIME,FINT
   15 CONTINUE
C
C WRITES NEXT PAIR OF DATA:
C
   17 WRITE(12,20) TIME,INT
   20 FORMAT(3X,G12.5,3X,G12.5,)
      CALL EXIT
      END

• PDA - Put on the Disc All files. This macro will copy into the directory area all files from scratch area, from scratch file SRT till QIT. Only FXF-LXF portion of the data will be stored.

OMD
      PUTS FXF-LXF PORTION OF DATA FILES FROM SRT TIL QIT
OMD
      ONTO HARD DISK. ENTER SRT AND QIT
SRT
QIT
OMD
      ENTER WAVENUMBER LIMITS
FXF=500
FXF
LXF=2300
LXF
OMD
      ENTER FILENAME (SIX CHARACTERS MAX, NO DEVICE CODE)
IFN
OMD
      ENTER FIRST EXTENSION NUMBER
EXT
DFN=SRT
FOR XXX=SRT TIL QIT
ASP
EXT=EXT+1
DFN=DFN+1
NXT XXX
EXT=EXT-1
OMD
LAST EXTENSION NUMBER IS
PRN EXT
EXT=EXT+1
END

• **GDA** - Get from Disc All files. This macro will copy all files with specified `FILENAME` and extensions from SRT till QIT from directory into the scratch area.

OMD

ENTER FILENAME
IFN
OMD

ENTER EXTENSION RANGE (SRT TILL QIT)
SRT
QIT
OMD

ENTER FIRST DFN TO WRITE FILE INTO
DFN
EXT=SRT
FOR XXX=SRT TIL QIT
AFG
EXT=EXT+1
DFN=DFN+1
NXT XXX
DFN=DFN-1
OMD
LAST DFN USED IS:
PRN DFN
DFN=DFN+1
END
Appendix B

Program for Powder Scattering Patterns Calculation

Program LAZY-PULVERIX for calculation of x-ray and neutron scattering powder patterns was written in 1977 by K. Yvon, W. Jeitschko and E. Parthé of Université de Geneve. It calculates the intensity of the peaks in the powder scattering patterns. Below is a shortened version of the program description. A full version can be found at the beginning of the main segment LAZY.FOR and in *J. Appl. Cryst.* 10, 73 (1977).

Program calculates peak intensity as

\[ I_{hkl} = MLPF_{hkl}^2 \]  \hspace{1cm} (B.1)

where \( M \) is multiplicity factor, \( L \) is a Lorentz factor, \( P \) is a polarization factor. The structure factor \( F_{hkl} \) is defined by:

\[ F_{hkl} = \sum_{\text{unit cell}} f_j O_j \exp[2\pi i(h x_j + k y_j + l z_j)] \exp(-B_j \frac{\sin^2 \Theta}{\lambda^2}) \]  \hspace{1cm} (B.2)

where \( f_j \) is an atomic scattering factor of atom \( j \), \( O_j \) is an occupation factor of site \( x_j, y_j, z_j \) for atom \( j \) and \( B_j \) is a Debye-Waller factor in Å² for atom \( j \). Program is given only the information about the experimental geometry, crystalline unit cell, and atomic positions. All other parameters needed for calculation of \( I_{hkl} \)'s are generated from cell symmetry and atomic labels.

The program consists of the main segment LAZY.FOR and a routine PULVER.FOR. A compiled version, LAZY.EXE (available from [MIKOLAJ.LAZY])
is run on the Physics Department VAX via a short program LAZY.COM, by executing the command "@lazy" at the $ prompt. LAZY.COM defines the names of certain transitory files and of output/input files. Below is an example of a LAZY.COM file:

```
$ set noverify
$ assign/user lazy1.tmp for001
$ assign/user lazy11.tmp for011
$ assign/user lazy12.tmp for012
$ assign/user pani.inp; for005
$ assign pani.out for006
$ run lazy
$ del lazy1.tmp;,lazy11.tmp;,lazy12.tmp;
$ deassign for006
$ exit
```

Assigned input file which must be prepared before running LAZY is in this example pani.inp; . Program output is directed to (ASCII) file pani.out; . An example of typical input file is provided below.

```
TITLE     EB-II    THETA =     30   PHI =      O SP GROUP P B C N
CONDIT    1.551   0.   30.  1DS
CELL      7.65    5.75   10.2
SPCGRP   P B C N
ATOM    N 1 0 0.188 0.25
ATOM    N 1 0 0.096 0.127
ATOM    C 2 -0.08 -0.121 0.104
ATOM    C 3 0.08 0.217 0.023
ATOM    H 2 -0.141 -0.215 0.184
ATOM    H 3 0.141 0.384 0.041
ENDSET
FINISH
```

Below is the description of the lines which must be included in the input file.
For historical reasons lines are called "cards". For full description with a list of allowed symbols, see beginning of LAZY.FOR.

General remarks:

Calculations for several structures may be done in one run. The order in which data cards are given within a set is not important. When reading the data cards, the program identifies the kind of data by labels in columns 1-6 (e.g. TITLE, CONDIT). One END card must terminate each set and one finish card must follow the last end card.

The minimum of input cards must contain a TITLE-, CELL-, SPCGRP-, ATOM-, END- AND FINISH-card. The SPCGRP-card may be replaced by LATICE and SYMTRY cards and vice versa.

TITLE card - Title

FORMAT(A2,A3,1X,17A4)

COLS
1- 5 TITLE Label *TITLE*
7-74 COMPND Any alphanumeric information

CONDIT card - Experimental conditions.

FORMAT(3A2,4X,A4,F6.0,2F5.0,1X,A1,I2,A2,1X,A1)

COLS
1- 6 CONDIT Label *CONDIT*
11-14 SYMWL Symbol for wavelength (adjust to the left)
Example: CUA1 = Cu K alpha1 radiation.
Wavelengths for which no symbol exists must be given explicitly in cols 15-20. If left blank, Cu K alpha radiation is assumed.
15-20 WL  Wavelength in Angstrom.
            Need not be given if SYMWL is specified.
21-25 TL  Lower Theta - limit of calculation.
26-30 TH  Upper Theta - limit of calculation.
            If left blank, TL=0 and TH=89 degrees.
32 NORM  Tabular representation of the powder pattern.
            Blank      Intensities normalized to 1000.
            A         Intensities not normalized.
            N         No tabular representation.
33-34 IMAGE Graphic representation of the powder pattern.
            Blank      No graphic output
            Integer   Graphic output of intensities
            in Theta steps of 1/(2*INTEGER)
35-36 SYMLP Experimental technique:
            DS         Debye-Scherrer
            Blank      Powder diffractometer/monochromator
            NE         Neutron diffraction
            GN         Guinier - DeWolff camera
            GH         Guinier - Haegg camera
38 IANO  Correction for anomalous dispersion (x-rays):
            Blank      Correction is made
            N          No correction is made

If no CONDIT card is given, copper radiation and Debye-Scherrer
technique is assumed, correction for anomalous dispersion will
be made and a complete powder pattern will be calculated.

CELL card - Lattice constants.

FORMAT(3A2,7X,3F8.0,3F9.0)

1-4 CELL  Label *CELL*
14-21 A  Lattice parameters in Angstroms and degrees.
22-29 B  cubic -  omit B,C,ALPHA,BETA,GAMMA.
30-37 C  hexagonal -  omit B,ALPHA,BETA,GAM=120.
            rhombohedral -  see note below.
38-46 ALPHA  tetragonal -  omit B,ALPHA,BETA,GAMMA
47-55 BETA orthorombic - omit ALPHA,BETA,GAMMA
56-64 GAMMA monoclinic - omit ALPHA,GAMMA

Note: Rhombohedral should be calculated with hexagonal axes. If rhombohedral axes are desired, the structure must be described in the triclinic system.

LATICE card - Symmetry center and Bravais lattice.
This card may be replaced by SPCGRP card.

FORMAT(3A2,2X,A1,2X,A1)
COLS
1- 6 LATICE Label *LATICE*
  9 ISYMCE Center of symmetry at origin?
      C Yes (centric).
      A No (acentric)
 12 SYMBR Bravais lattice indicator
      P Primitive
      I Body centered
      R Rhombohedral
      F Face centered
      A A centered
      B B centered
      C C centered
      Blank Primitive

If no LATICE card is given, a non-centrosymmetric structure and a primitive lattice is assumed.

SYMTRY card - Equivalent point positions.
These cards may be replaced by a SPCGRP card.

FORMAT(3A2,45A1)
COLS
1- 6 SYMTRY Label *SYMTRY*
  7-51 IPOE Equivalent position coded in verbatim form.
Include one card for each position.
Rules for coding:
- coordinates are separated by commas.
- fractions are written as two integers separated by a slash.
- blank spaces are ignored.

Example: space group P 21/C

```
SYMTRY X, Y, Z
SYMTRY X,1/2-Y,1/2+Z
```

Notes: If ISYMCE=C then only one of any two centro-symmetric positions needs to be given. If SYMBR= I,R,F,A,B or C, only one of the positions related by centering needs to be given.

If no SYMTRY card is given, X,Y,Z is automatically assumed, but if SYMTRY cards are given, X,Y,Z position must be explicitly included.

**SPCGRP card** - Space group.

This card may replace LATICE and SYMTRY cards.

**FORMAT(3A2,35A1)**

**COLS**

<table>
<thead>
<tr>
<th>1- 6</th>
<th>SPCGRP</th>
<th>Label <em>SPCGRP</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>8-17</td>
<td>IPOS</td>
<td>Hermann-Mauguin symbol for the space group. Adjust to the left of the field.</td>
</tr>
</tbody>
</table>

Rules for coding:
- Symmetry operators are separated by blanks
- The bar operator is coded as minus *-
- Screw axes are given by two integers that are not separated by a blank.

Examples: P B C N, P 21/C, P -3

Notes: For centrosymmetric groups, the program assumes the
setting having the center at the origin.
For R space groups hexagonal setting is assumed.

ATOM card - Atom identifier and coordinates.
Use one ATOM card for each atom in the assymetric unit

FORMAT(3A2,IX,A4,A2,3F8.0,F6.0,F5.0)

COLS
1- 4 ATOM Label *ATOM*
8-11 ELEM Symbol of element and ionisation state
Adjust to the left of the field.
Examples: CA - calcium (neutral)
CA2+ - calcium (ionized)
12-13 IDE Sequence number or atom label (may be left blank).
It is convenient to label atoms of the same type
14-21 X X coordinate
22-29 Y Y coordinate
30-37 Z Z coordinate
Only coordinates between -1. and +1. allowed.
Fractions may be given by integers separated
by a slash.
Example:
ATOM H 1/3 2/3 0.512
is equivalent to:
ATOM H .33333 .666667 0.512
38-43 BTEMP Debye-Waller factor.
If left blank, no temperature factor
 correction will be made.
44-48 FOCCU Occupation factor.
This factor is usually 1 (full occupancy of
the site), but may be smaller in disordered
structures. If left blank, FOCCU=1 is assumed.

END card - Terminates each set of data cards.

COLS
1- 3 END Label *END*
FINISH card - Terminates the run.

COLS
1-6 FINISH Label *FINISH*

Note: This card must come after the last END card. It initiates the execution of the program.

Full description of the program, including lists of allowed wavelengths, atom labels and space groups is provided at the beginning of main segment LAZY.FOR.
Bibliography


