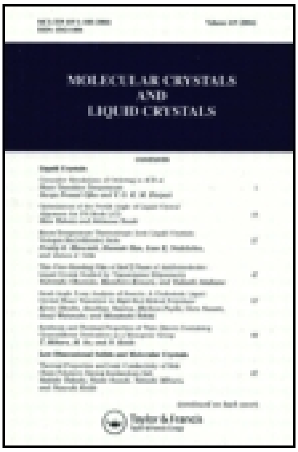

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TORSIONAL DEFECTS AND PHOTOINDUCED CHARGE TRANSFER IN RING-CONTAINING POLYMERS

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Abstract The importance of ring torsion angle for photoinduced charge generation and transfer in phenyl-ring-containing polymers such as polyaniline and polyparaphenylene sulfide is discussed. The magnitude of the ground state ring torsion angle in these materials is determined by the competition between electron delocalization, favoring planar rings, and the steric repulsion between rings, favoring rings twisted far out of the plane. Upon photoinduced charge transfer, the hole formed upon removal of an electron from the valence band becomes self-localized into a polaronic state in part through changes in ring torsion angle; the effective mass of this defect is estimated to be at least an order of magnitude greater than that of bond-alternation defects. The existence of these ring-torsional defects is borne out by the experimental observation of large effective masses, long relaxation times, and weak photoconductivity for photoexcited defects, as well as by x-ray structural evidence of the dependence of torsion angle on doping level.

Keywords: Polyaniline, photoinduced absorption, polarons, polyparaphenylene sulfide

INTRODUCTION

Reports [1,2] in the mid-1980's of an insulator-to-conductor transition induced by the protonic-acid doping of polyaniline have stimulated a tremendous variety of studies of this unusual conducting polymer. Unlike those polymers – polyacetylene, polythiophene, and polydiacetylene – whose physical properties are dominated by their carbon-atom backbones [3], the polyanilines incorporate a nitrogen heteroatom in their backbone structures. The polyaniline family thus belongs to a broad class of alternating phenyl ring-heteroatom polymers, which includes the important engineering polymers polyparaphenylene sulfide (PPS) and polyparaphenylene oxide (PPO). Unlike PPS and PPO, the chemical flexibility provided by the nitrogen atom in polyaniline allows the existence of several insulating ground states, distinguished by their oxidation level [4]: reduced leucoemeraldine base (LB), partially oxidized emeraldine base (EB), and fully oxidized pernigraniline base (PN); see Fig. 1.

The polymers LB, EB, PPS, and PPO all possess lone pairs of electrons formally in heteroatomic p_z orbitals; their $\pi - \pi^*$ band gaps originate from the electronic structure of the backbone C_6H_4 (phenyl) rings [5]. The one-electron nature of the gaps in the reduced polymers causes severe asymmetry between valence and conduction bands and also negates a bond-alternation defect description of the charge states of these materials. Nonetheless, the nature of the ground and defect states is dependent on electron-lattice coupling; in particular, the unique role of the ring torsion angle in describing the photoexcited defect states of these ring-containing polymers will be explored [6-8].

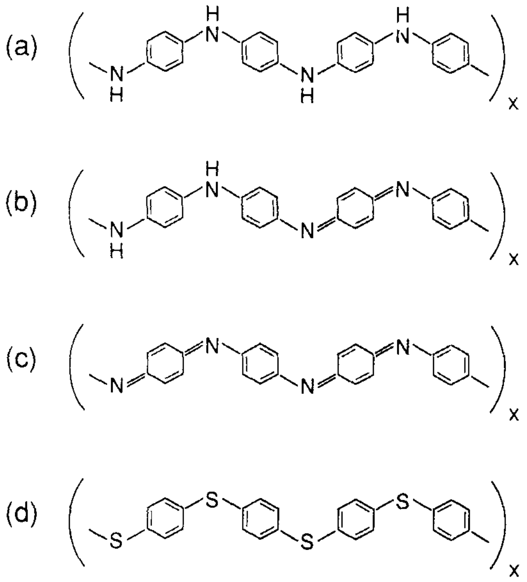

FIGURE 1 Schematic illustration of the (a) leucoemeraldine (LB), (b) emeraldine (EB), and (c) pernigraniline (PB) base forms of polyaniline, and (d) the LB analog polyparaphenylene sulfide (PPS).

The defect species originating from photoexcitation across the $\pi - \pi^*$ gaps of LB and PPS are probed by various photoinduced optical experiments in picosecond through hour time scales and infrared through visible spectral ranges. These studies suggest that the defect species formed upon photoexcitation or p-doping are long-lived, massive polarons [9] whose character is distinct from the solitonic or polaronic defects of the carbon-backbone polymers. Instead, an understanding of these phenomena is based upon the role of the phenyl ring torsional degrees of freedom of the LB and PPS chains. The existence of ring-torsional polarons is proposed to explain the photoinduced phenomena; further evidence for these defects is found from structural studies [10,11]. Other consequences of this perspective are discussed.

EXPERIMENTAL OBSERVATIONS

Techniques for the measurement of linear and photoinduced absorption are described elsewhere [9]. Fig. 2 shows the linear absorption spectrum of a $\sim 6 \times 10^{-5}$ M solution of LB in N-methyl pyrrolidinone (NMP) at room temperature. In addition to the $\pi - \pi^*$ transition peaking at $\sim$ 3.65 eV, a weak absorption feature at $\sim$ 2.0 eV is observed, consistent in position and strength with the presence of a low density of oxidized quinoid units in this nominally fully reduced material. The near-steady-state photoinduced absorption spectrum of a $\sim$ 0.1 μm thick film of LB cast from NMP solution is shown in Fig. 3. Upon photoexcitation into the $\pi - \pi^*$ transition via a mechanically chopped ultraviolet source, photoinduced absorptions at 0.75 eV and 2.85 eV are identified, as is a photoinduced bleaching at 1.9 eV. Photoinduced absorption measurements performed in the near- to mid-infrared at second to hour time scales reveal the growth of an induced absorption peaking at 1.4 eV, as well as photoinduced infrared active (IRAV) modes indicative of structural distortions associated with the photoexcited species. Application of the amplitude mode formalism to these IRAV modes suggests that the photoexcited charged defects are quite massive, $M^* \sim 60\ m_e$ [9,12]. The photoproduction of massive, relatively immobile charged defects is also consistent with the observation of weak photoconductivity in the LB [13] and EB [14] forms of polyaniline.

Preliminary near-steady-state photoinduced absorption studies of PPS films also reveal two photoinduced absorptions, peaking at 0.85 and 3.05 eV. No long-lived photoinduced absorption features were observed. The two induced absorptions correspond well to those observed in studies [15,16] of the oxidative p-doping of PPS; ESR studies [17] suggest that some of the dopant-induced defects possess spin-1/2, i.e. they are polarons.

The perspective which evolves from these photoinduced and doping-induced optical studies is that massive polaronic defects play an important role in these ring-heteroatomic polymer systems. Both the large mass and the existence of only two induced absorptions contrast with the behavior observed widely in the carbon-backbone polymers. These unusual results can be understood, however, by explicitly considering the important role of the phenyl ring torsion angle in describing the ground state and charged defect geometries in this class of materials.

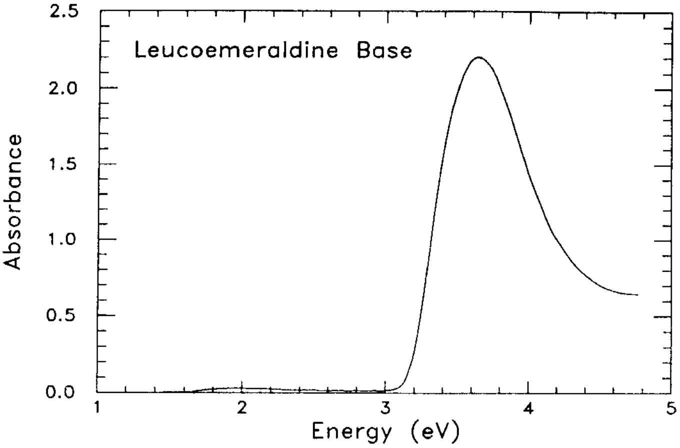

FIGURE 2 Linear absorption spectrum of LB in NMP solution.

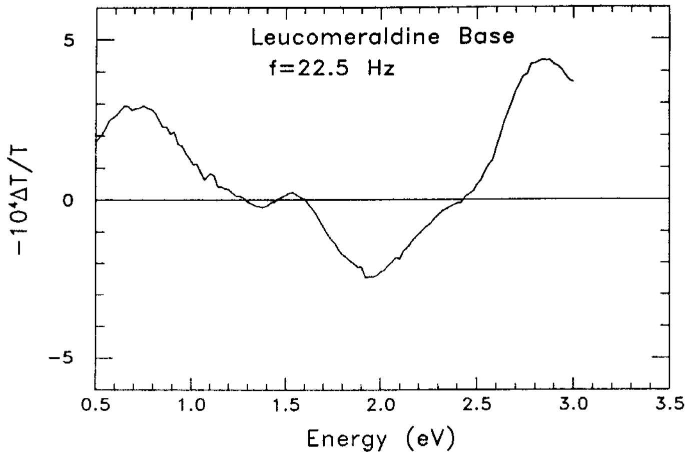

FIGURE 3 Near-steady-state photoinduced absorption spectrum of a LB film on quartz substrate at 10 K.

RING-TORSIONAL DEFECTS

A Hamiltonian describing single LB or PPS chains can be constructed [6,7] from a sum of electronic (including electron-lattice coupling) and steric interactions between adjacent phenyl rings: $\mathcal{H} = \mathcal{H}_{el} + V_{steric}$. In the following developments, LB is considered for specificity. The LB chain is built from unit cells that each contain one N-H (bearing 2 electrons in a p_z orbital assumed to be perpendicular to the C-N-C plane) and one C_6H_4 ring (6 p_z electrons); the lth phenyl ring is twisted at a torsion angle ϕ_{2l+1} out of the C-N-C plane. Within a one-dimensional linear combination of molecular orbitals approximation, the electronic part of the Hamiltonian can be written as

$$\mathcal{H}_{el} = \sum_{l,s} \alpha_N a^{\dagger}_{2l,s} a_{2l,s} + \sum_{l,s}\sum_{j} \epsilon_j b^{j\dagger}_{2l+1,s} b^{j}_{2l+1,s} - \sum_{l,s}\sum_{j} [t^{j}_{2l,2l+1}(a^{\dagger}_{2l,s} b^{j}_{2l+1,s} + b^{j\dagger}_{2l+1,s} a_{2l,s}) + t^{j}_{2l+1,2l+2}(b^{j\dagger}_{2l+1,s} a_{2l+2,s} + a^{\dagger}_{2l+2,s} b^{j}_{2l+1,s})]. \qquad (1)$$

The operator $a^{\dagger}_{2l,s}$ $(a_{2l,s})$ creates (destroys) an electron of spin s at the lth nitrogen atom, with site energy α_N, and $b^{j\dagger}_{2l+1,s}$ $(b^{j}_{2l+1,s})$ creates (destroys) an electron of spin s in the jth MO of the lth benzene ring, with site energy ϵ_j.

The transfer integral $t^{j}_{2l,2l+1}$ between the lth nitrogen p_z and the jth MO of the lth benzene ring is given [18] by $t^{j}_{2l,2l+1} = t_{C-N} \times cos\phi_{2l+1} \times c^{j}_{2l+1}$, where t_{C-N} is the carbon-nitrogen transfer integral, $cos\phi_{2l+1}$ is the cosine of the angle between the N and ring p_z electron lobes, and c^{j}_{2l+1} is the coefficient of the jth MO at the *para* carbon atom neighboring the nitrogen. In light of the steric repulsion between adjacent phenyl rings, the ring rotation angles ϕ_{2m+1} are expected to alternate in sign. Therefore, we define an order parameter ψ_{2m+1} such that $\phi_{2m+1} = (-1)^m \psi_{2m+1}$. LB and PPS have filled valence bands so that no tendency toward Peierls distortion exists; nonetheless, two degenerate ground states defined by $\psi_{2m+1} \equiv +\psi$ and $\psi_{2m+1} \equiv -\psi$ are anticipated to exist.

Both the effective site energy (i.e. band center) and bandwidth of the seven energy band solutions to the electronic Hamiltonian are modulated by the ring angle ψ. For nearly planar ring systems, application of first order perturbation theory leads to a $\cos\psi$ dependence of the energy gap and transfer integrals between unit cells. For systems further removed from planarity, second order perturbation theory yields transfer integral variations as $t = t_{eff} \times \cos^2\psi$.

Lattice Energy: Steric Repulsion Between Rings

In polyaniline, the π electron delocalization energy that favors phenyl rings in the plane of the nitrogen atoms is countered by a substantial steric repulsion between adjacent rings, forcing them out of the plane [19]. The angular dependence of the effective lattice energy is commonly approximated by a ϕ^4-like function of the ring angles, i.e.

$$V(\psi_{2l-1},\psi_{2l+1}) \simeq -\frac{V_{2,0}}{2}(sin^2\psi_{2l-1} + sin^2\psi_{2l+1}) + \frac{V_{4,0}}{2}(sin^4\psi_{2l-1} + sin^4\psi_{2l+1}) + V_{1,1}(sin\psi_{2l+1} - sin\psi_{2l-1})^2 + constant \quad (2)$$

with ψ_1 and ψ_2 the torsion angles of adjacent rings and $V_{2,0}$, $V_{4,0}$, and $V_{1,1}$ constants; the equilibrium ring angle ψ_0 is given by $sin^2\psi_0 = V_{2,0}/(2V_{4,0})$. For example, the interaction of neighboring benzene rings in diphenyl oxide [25] (and thus PPO) can be described by $V_{2,0} \simeq 1.50$ eV and $V_{4,0} \simeq 1.45$ eV. The approximate dependence of lattice energy on torsion angle for LB can be obtained by modifying the PPO steric parameters (setting $V_{2,0} \simeq 2.0$ eV) to yield $\psi_0 \sim 56°$ as suggested by band structure results [6,7].

The anharmonicity of the steric potential about the ground state ψ_0 implies that the average ground state ring angle increases with increasing temperature [7], analogous to thermal expansion in conventional solids. Given the dependence of the electronic structure on ring angle, thermally-induced increases in the energies of optical transistions are anticipated. Substantial thermochromic blue shifts have been observed in LB solutions [20]; absorbance peak energies exhibit temperature coefficients of the order of 1 meV/K.

Defect States in LB and PPS: Ring-Torsional Polarons

The existence of a ring-angle order parameter ψ and the ϕ^4-like steric potential suggests that the ground state of LB can support soliton and polaron defects associated with distortions of the ground state ring angle. Two types of solitonic defects in the ring torsion angle order parameter can be identified [7,21], one associated with near-zero ring angles and thus involve substantial steric energy, and another involving rings twisted to near 90°. Polaronic defects are also possible; to facilitate their study, a one-band Hamiltonian similar to that appropriate for Holstein polarons [22] can be constructed to describe holes in the otherwise filled valence band of LB. The solutions of this Hamiltonian are ring-torsional polarons stabilized by the increase in delocalization energy involving local ring angles distorted toward planarity. Iterative solutions of the discrete Hamiltonian for a hole polaron (P^+) wavefunction have been found [7], utilizing the *ansatz* that the polaron ring-angular order parameter varies with position as $sin^2\psi_{2m+1} \equiv sin^2\psi_0 - A\ sech((m - m_0)/l)$, where l and A are dimensionless length and depth parameters, respectively, and m_0 is the site index of the polaron center. Solutions corresponding to a single energy level split off into the band gap by an energy ϵ_P from the valence band are found. Fig. 4 shows the variation of ring angle and hole charge density with position of the minimum-energy solution for $\epsilon_P \simeq 0.8$ eV, with the defect length $l \simeq 1.5$ and depth $A \simeq 0.19$. Nearly the same characteristics are found for ring or nitrogen-centered defects. These ring-torsional polarons are predicted to be stable, since the associated increase in steric energy is $\simeq 0.2$ eV, yielding a binding energy $\epsilon_B \simeq 0.6$ eV, not accounting for changes in the valence band density of states induced by the defect. Assuming that the polaron translates without distortion along the chain at a velocity v_{pol}, its effective mass M_{pol} is estimated by equating its translational kinetic energy with the sum of the rotational kinetic energies of the rings associated with the polaron; i.e.,

$$\frac{1}{2}M_{pol}v_{pol}^2 = \frac{1}{2}I\sum_m\left(\frac{d}{dt}\psi(m - v_{pol}t/a)\right)^2, \tag{3}$$

where $I \simeq 89$ amu-Å^2 is the moment of inertia for phenyl ring rotations about the *para* axis. For the defect shown in Fig. 4, $M_{pol} \sim 50\ m_e$, where m_e is a free electron mass. Removal of a second electron from the polaron yields a spinless bipolaron exhibiting increased ring-torsion-angle distortion – analogous to the increased order parameter deviation in bond-order bipolarons – and thus possessing an even larger effective mass.

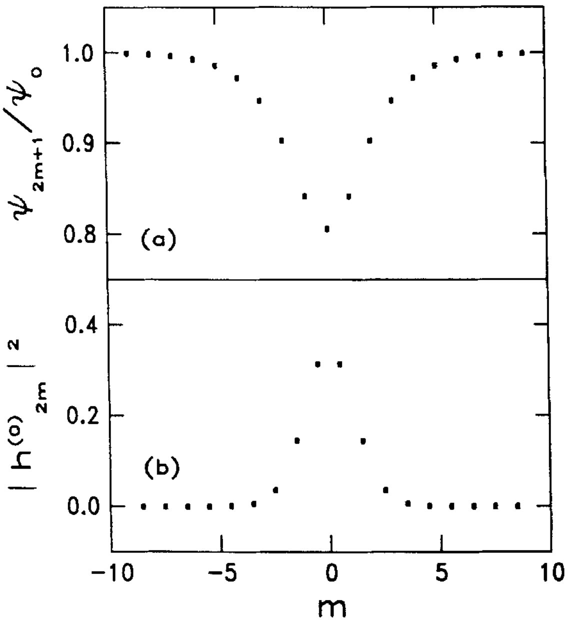

FIGURE 4 Spatial variation of the (a) order parameter and (b) hole charge density for a ring-rotational polaron in LB.

Two in-gap optical transitions, whose energies sum to the gap energy, are associated with the P^+ energy level; by contrast, a polaron induces *three* optical transitions in nearly charge-conjugation-symmetric systems [3]. This energy level scheme is consistent with the near-steady-state photoinduced absorption spectra on LB and PPS, as well as doping-induced spectra on PPS. The association of the positively-charged defects with a flattening of the rings is also in agreement with x-ray structural studies of doped polyaniline oligomers [11] and the emeraldine salt polymer [10], as well as theoretical studies of the PPS oligomer diphenylsulfide [23]. These ring-torsional polarons can indeed reconcile the extremely long-lived, massive polarons inferred from the photoinduced absorption [9,12,24] and photoconductivity [13,14] experiments described previously with NMR studies [25] suggesting that large-amplitude ring rotations are thermally activated: it is possible that polarons are trapped via constrained chain packing arrangements, and that charge recombination is thus hindered by the lack of free volume for ring rotation.

A full description of the electronic states of all forms of polyaniline is likely to require a two-component order parameter including both ring-torsion and quinoid bond-length effects. The likely importance of both these degrees of freedom in describing the charge-storing states in the various forms of polyaniline suggests that a wide variety of stable states may exist, depending on local order, crystallinity, and oxidation state. The complex photoinduced absorption features found in various forms of polyaniline, revealing a variety of characteristic optical transitions and temporal dynamics, may be a manifestation of these many types of stable states.

SUMMARY

By virtue of their chemical flexibility, the polyanilines provide a unique system to explore the physical role of conformational changes in determining the nature of photoexcited charged species. The importance of electron-torsion angle coupling as well as the more usual electron-longitudinal phonon coupling is emphasized; the consequent ring-torsional character of the polaron defect states in LB and PPS is consistent with the large mass and long lifetimes of the photoinduced phenomena in these systems.

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