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RING-TORSIONAL POLARONS IN POLYANILINE AND POLYPARAPHENYLENE SULFIDE

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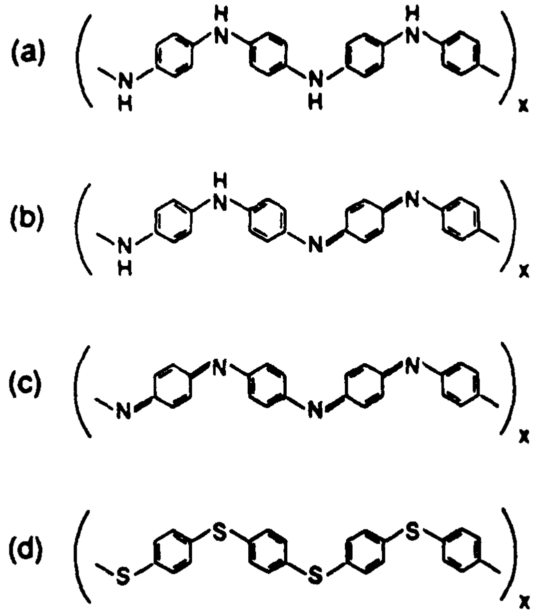
ABSTRACT

The role of the dihedral angle of the backbone phenyl rings in determining the electronic structure and charge storage mechanism in polyaniline (PAN) and polyparaphenylene sulfide (PPS) is reviewed. The sensitivity of the average ring torsion angle to the effects of steric repulsion and electron delocalization is manifest in the effects of derivatization and temperature on the optical spectra of these materials. It is shown that charge is self-trapped into localized defect states in part via changes in ring angle, leading to novel ring-torsional polarons which induce only one defect level into the energy gap and possess a very large kinetic mass (50 – 500 m_e). Evidence for the existence of these defects in PAN and PPS is discussed.

INTRODUCTION

The polyaniline (PAN) system is readily transformed among the three insulating forms shown schematically in Fig. 1 [1]: leucoemeraldine base (LEB), emeraldine base (EB), and pernigraniline base (PNB). Within a tight-binding approximation, the energy bands result from the mixing of doubly occupied nitrogen $2p_z$ and benzene π molecular orbitals (MOs), leading to a broad valence band of width ~ 3 eV and a flat conduction band [2-4]. Substantial charge conjugation asymmetry results [3], accompanied by a large energy gap ~ 3.7 eV whose magnitude is controlled in part by the average ring torsion angle [2]. PPS, Fig. 1(d), is isoelectronic to LEB and is thus expected to exhibit similar physical properties; that its gap energy, ~ 4.0 eV [5], is slightly larger than in LEB probably reflects the reduced overlap expected between the phenyl ring and the sulfur heteroatom. The energy gap in the degenerate-ground-state PNB form of PAN originates not only from the dimerization of the bond lengths [6], yielding an alternating benzenoid/quinoid ring structure, but also from ring-torsion-angle dimerization [7].



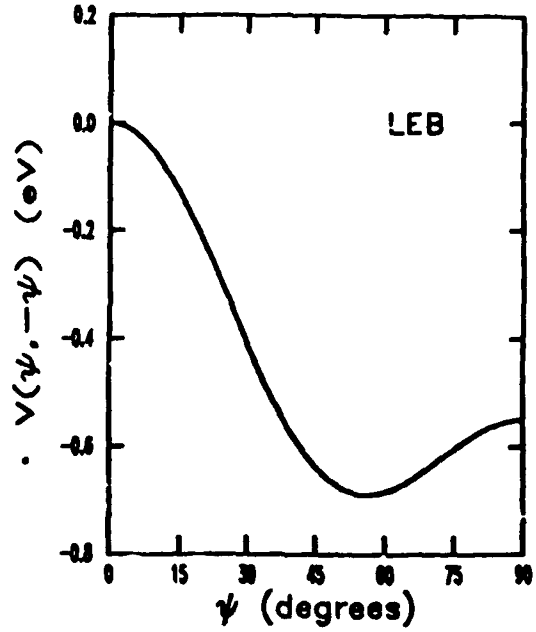


Figure 1: (Left) Schematic illustration of the (a) leucoemeraldine (LEB), (b) emeraldine (EB), and (c) pernigraniline base (PNB) forms of polyaniline; (d) polyparaphenylene sulfide (PPS).

Figure 2: (Right) Approximate variation of the total energy of interaction between neighboring phenyl rings in LEB (from Ref. 2).

We have constructed a ring-torsional order parameter ψ in order to describe the ground states of LEB and PPS; it is found [2] that a valence-band hole is self-trapped in part by localized changes in ψ along the chain. No self-trapping of electrons in LEB due to defects in ψ is expected [2], another manifestation of the charge-conjugation asymmetry in these materials. Ring-torsional polarons are predicted to possess several unusual properties, including kinetic masses much larger than their bond-alternation-defect counterparts. Experimental evidence for these defects includes the weak associated photoinduced infrared activity [8-10] and photoconductivity [8,11], as well as x-ray evidence that doped PAN indeed exhibits an average ring torsion angle much smaller than in undoped forms [12,13]. Ring-torsional solitons have also been predicted as possible excitations [2,14].

RESULTS AND DISCUSSION

Because the dihedral ring angles ϕ_n in LEB and PPS alternate in sign due to the substantial steric repulsion between near-neighbor rings, a ring-torsion-angle order parameter ψ can be constructed: $\psi_n \equiv (-1)^n \phi_n$ [2]. The ground state value of the order parameter, ψ_0, is determined by a competition between the π delocalization energy and the steric repulsion between neighboring rings. The variation of the total energy for pairs of neighboring rings with equal-but-opposite torsion angle magnitudes is shown in Fig. 2. Because of the anharmonic variation of the total energy as the ring angle is increased away from the minimum value ψ_0, the thermal average of ψ is a strong function of temperature, leading to a gradual thermochromic blue shift of the $\pi - \pi^*$ transition consistent with observations on LEB [15]. Harmonic oscillations of ψ about ψ_0 should result in a torsional mode (Raman active in

LEB) having an estimated frequency $\sim$ 100 cm^{-1}. It is noted that a torsional mode has been assigned [16] to an infrared feature at $\sim$ 130 cm^{-1} in nitrogen-derivatized PAN.

That the details of the steric potential - particularly the value of the equilibrium ring angle ψ_0 - are sensitive to the interaction of neighboring phenyl rings suggests that these parameters may be tunable by chemical derivatization of the rings. The absorbance spectra of N-methyl pyrrolidinone solutions of underivatized LEB as well as the methyl-substituted form of LEB, poly-(orthotoluidine), Fig. 3, show that despite the expected weak inductive effect of the methyl group on the benzene MOs, derivatization *increases* the $\pi-\pi^*$ gap energy to $\sim$ 3.9 eV [17]. This blue shift is consistent with a sterically-induced increase in ring angle and the concomitant valence band narrowing upon substitution. Similar observations have also been reported in the optical spectra of the conducting emeraldine salt (ES) forms of alkyl-substituted polyanilines [18]: the partially-filled polaron band [3] is narrowed slightly, leading to a reduction of the $\sim$ 1.5 eV transition energy associated with polarons. The small polaron bandwidth reduction, while likely to enhance somewhat the localization of charge carriers, is not sufficient to explain the severity of the changes in transport and magnetic properties found when emeraldine salt is derivatized; Wang *et al.* [19] have suggested that increased interchain spacing and disorder induced by derivatization are the most important factors in enhancing the effects of localization in substituted PAN.

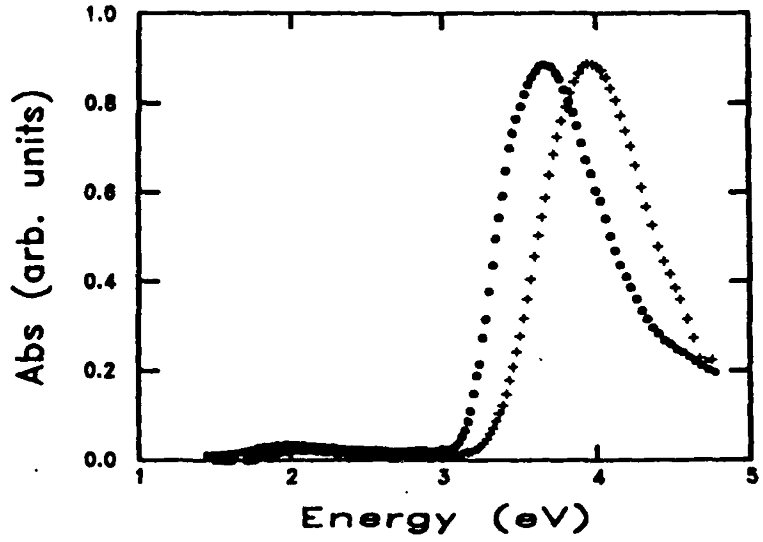


Figure 3: Absorbance spectra for LEB in unsubstituted (•) and poly(ortho-toluidine) (+) forms in NMP solution. The weak absorbance peaks at $\sim$ 2 eV are due to slight residual oxidation of these nominally fully reduced materials (from Ref. 17).

Photoinduced absorption (PA) spectroscopy has become a widely-used probe of the electronic structure and population kinetics of photoexcited defect states in conducting polymers. PA spectra have been measured for the LEB [20], EB[8-10,20,21], and PNB [22] forms of PAN, as well as for PPS [23]. The near-steady-state PA spectrum of an LEB film held at 10K and excited by ultraviolet photons from a Hg:Xe arc lamp is shown in Fig. 4(a): two photoinduced absorption peaks, at 0.75 and 2.75 eV, and one photoinduced bleaching,

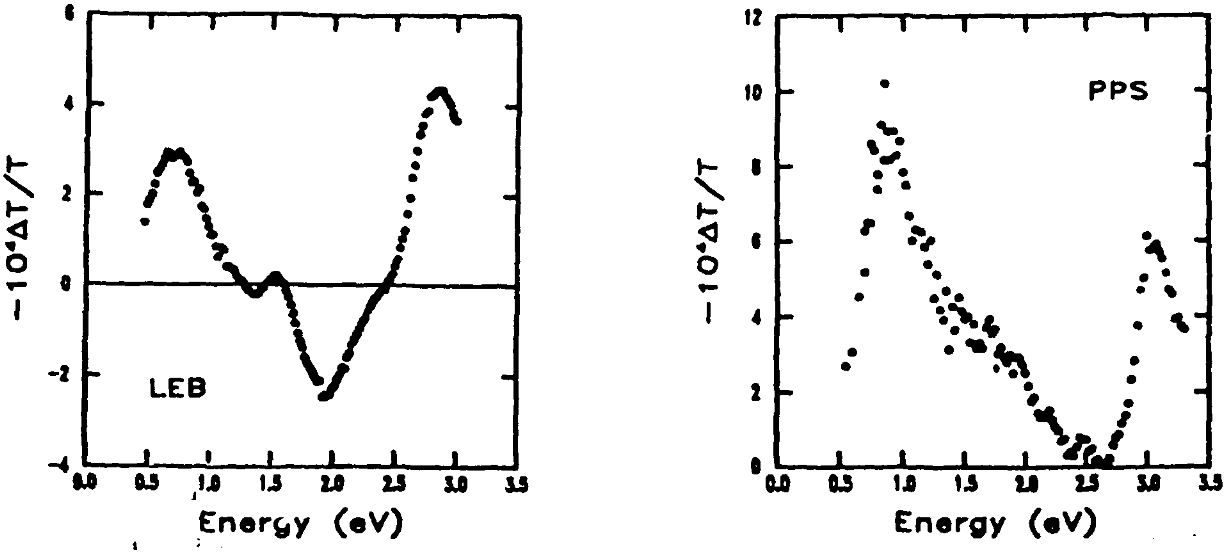


Figure 4: Photoinduced absorption spectra of LEB (left) and PPS (right) films obtained upon ultraviolet photoexcitation.

at 2.0 eV, are observed on this (millisecond) time scale [20]. Similarly, induced absorption features at 0.9 and 3.1 eV are found upon pumping into the $\pi - \pi^*$ gap of PPS, Fig. 4(b) [23]. The absence of bleaching at ~ 2 eV in PPS is due to the lack of oxidized quinoid units in this material. Changes in the optical spectrum of PPS induced by p-type AsF_5 doping also exhibited [5] two absorptions at nearly the same energies as the PA peaks; EPR studies [24] revealed that these doping-induced hole defects possess spin-1/2, and thus are polaronic in nature. Studies of the photoinduced changes in the infrared-active vibrational modes (IRAV) of LEB [20], EB [8-10,20,21], and PNB [22] reveal them to be very weak relative to the observed photoinduced electronic transitions, suggesting that the photoinduced charged defects possess very large kinetic mass; for example, in EB a mass $M_{pol} \sim 60\ m_e$ is estimated [9]. The increase in M_{pol} in going from LEB ($\sim 60\ m_e$) to PNB ($\sim 300\ m_e$) likely reflects the increased localization of the polarons with increasing quinoid content [20,25]. M_{pol} also increases with derivatization [25], e.g. $M_{pol} \sim 60\ m_e$ in EB but is $\sim 200\ m_e$ for the EB state of poly-(orthotoluidine), probably a consequence of the increase in ring moment of inertia and average ring angle, a 'softer' steric energy potential minimum allowing larger changes in ring angle at the polaron sites, or enhanced interchain crowding. Recent experimental results, including the absence of long-lived defects in crystalline PPS and their presence in amorphous and partially crystalline PAN, suggest that the long-lived polarons reside primarily in the amorphous regions of the sample [25]. The potential relevance of the average ring torsion angle, ring angle alternation [7], and benzenoid-quinoid bond length alternation [6] in fully describing the conformational state of PAN and PPS suggests that a plethora of defect states involving independent or correlated changes of each these parameters could be present in various phases or morphologies of the bulk polymer. While detailed information on the structure of the defects is difficult to infer from infrared studies, x-ray studies on undoped and fully doped PAN [12] and oligomeric model compounds [13] do indicate that one effect of doping is to reduce the phenyl ring torsion angles toward planarity with the nitrogen heteroatoms: for example, an average torsion angle $\sim 30°$ is estimated in EB, reducing to $\lesssim 10°$ upon doping to ES [12].

The observations described above for the charged defects in PAN and PPS are to be contrast with the characteristics exhibited by bond-alternation defects in, e.g., polythiophene [26]: polarons in the carbon-backbone polymers are anticipated to induce *three* optical transitions within the band gap, the in-gap defect levels are roughly centered about midgap, and the kinetic masses of the bond-alternation defects are $\sim 1\ m_e$. The optical features found in the PA of LEB, as well as the photoinduced and doping-induced spectra in PPS, suggest that *one* in-gap energy level is split off from the valence band; this defect energy level structure is consistent with the existence of severe charge-conjugation asymmetry in PAN and PPS. The effective masses observed in PAN are also inconsistent with a defect involving only small distortions of the equilibrium bond lengths.

SUMMARY

The consequences of the existence of a steric potential between neighboring phenyl rings in the alternating heteroatom-phenyl ring polymers PAN and PPS have been discussed: the predicted existence of a torsional mode; thermochromism resulting from thermal expansion of the average ring angle; the decrease in the VB width and increase in the gap energy upon derivatization of the phenyl rings; and the existence of charged defect states involving changes in ring torsion angle. Various photoinduced and doping-induced studies of PAN and PPS exhibit the effects of strong charge-conjugation asymmetry in these systems, and are consistent with the absorptions expected if the defect induces *one* level in the gap. The optical spectra, the large kinetic mass, and the flattening of the phenyl ring angles observed in various experiments are consistent with a model of the defect states involving, at least in part, local distortions of the rings toward planarity. This concept is likely quite general, perhaps relevant in other systems in which the ring angle is a degree of freedom of the polymer conformation, such as polyparaphenylene [27,28] and substituted polythiophenes and polypyrroles [29], although the degree of electron-torsional coupling is likely weaker in those systems with nearly planar rings [2].

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