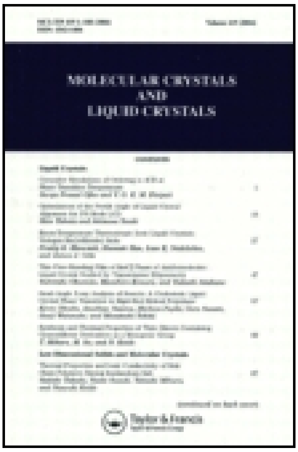

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LONG LIVED NEUTRAL SOLITONS IN PERNIGRANILINE BASE

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Abstract Pernigraniline base is the first Peierls degenerate ground state polymer beyond *trans*- polyacetylene. It is similar to *trans*- polyacetylene in that is sustains neutral and charged solitons and charged polarons as photoexcitations. Pernigraniline base differs substantially from *trans*-polyacetylene in that photoexcited neutral solitons are stable for long times for temperatures below 150 K and that at high photoexcitation densities, photoexcited neutral solitons are stable, even at room temperature. The origin of this anomalous behavior is attributed to the central role of ring rotations and interchain interactions in the system.

INTRODUCTION

Polyanilines are a family of polymers[1] that include three neutral insulating ground states, the fully reduced leucoemeraldine base (LEB), the half oxidized emeraldine base (EB) and the fully oxidized pernigraniline base (PNB), shown schematically in Figure 1. The leucoemeraldine base form is a wide band gap (~3.8 eV) insulator, the energy gap of which arises from the even number of electrons present in the C_6NH repeat unit.[2] In contrast, the simple repeat unit for pernigraniline base polymer, C_6N, has an odd number of π electrons as

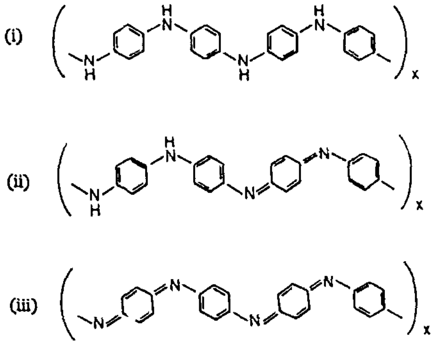

Figure 1: Idealized structural formulae of (i) leucoemeraldine base (LEB), (ii) emeraldine base (EB) and (iii) pernigraniline base forms of polyaniline.

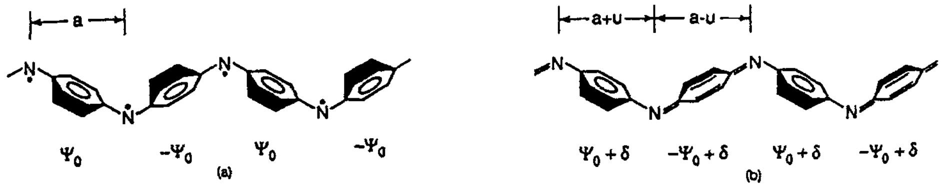

Figure 2: Schematic chemical structure of (a) undimerized and (b) bond length and ring torsion angle dimerized pernigraniline base polymer. (From reference 6).

shown schematically in Figure 2a. Dos Santos and Brédas,[3] predicted that the pernigraniline base polymer would act as a degenerate polymer similar to *trans-* polyacetylene. They calculated the effects of bond length changes (resulting in the formation of alternating benzenoid- and quinoid-like rings) and predicted the formation of charged excitations of this polymer which have soliton and polaron features. Ginder, et al.[2,4] introduced the important role of ring rotational dimerization. The torsion of the C_6 rings dihedral angle ψ out of the plane formed by the nitrogen atoms leads to a reduction of carbon-nitrogen p_z transfer by a factor of cos ψ. Hence a Peierls distortion can be introduced into this polymer through two mechanisms, changes in the effective bond length and changes in the effective ring torsion angle. Figure 2b schematically illustrates the chemical structure of pernigraniline base after bond length and ring torsion angle dimerization. Later calculations[5] demonstrate that the two order parameters contribute independently to the Peierls gap with the ring torsion dimerization contributing about 40% of the full band gap value and the bond length dimerization contributing approximately 60% towards the full band gap value. Leng et al.[6] reported the observation of photoexcited charged solitons and charged polarons in near steady state (millisecond time scale) photoinduced absorption experiments. They also reported that polaron excitations can be very long lived in the system.

More recently is was suggested[7] that unlike charge conjugation symmetric *trans-* polyacetylene, neutral solitons may be directly photocreated in pernigraniline base because of the charge conjugation asymmetry of this polymer. The neutral solitons are shown schematically in Figure 3. Two types can be distinguished, those that bring together two benzenoid-like rings adjacent to the central nitrogen, and those that bring together two quinoid-like rings adjacent to the central nitrogen. The benzenoid-N-benzenoid-type soliton (BNB) is predicted to be the most stable form. A long lived photoinduced absorption near 1.8 eV has been reported for pernigraniline base by Coplin et al.[8] The absence of associated infrared active vibrational

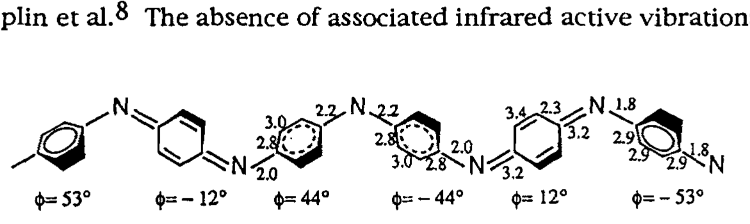

Figure 3. Bond orders and torsional angles in the vicinity of a neutral soliton in PNB. (From reference 7).

modes and the results of light-induced electron spin resonance experiments identify the photoexcited defects as disorder confined neutral soliton pairs with a temperature dependent antiferromagnetic exchange interaction. In parallel studies, Long et al.[9] have reported the electron spin resonance hyperfine spectra of pernigraniline base powder and solutions. These data provide a direct measure of the internal structure of neutral soliton defect. Calculations based on the Hubbard model of the π electron spin density for the BNB S^0 yield an estimate of the onsite Coulomb repulsion of $U \sim 2.5$ eV similar to that for S^0 in *trans*- polyacetylene[9]. Here we summarize some recent advances in the study of the long-lived photoexcited neutral solitons in pernigraniline base.

It is of interest to compare the ground state of the half oxidized of the emeraldine base to that of the fully reduced leucoemeraldine base and the fully oxidized pernigraniline base polymers. Figure 4a shows the four ring-nitrogen repeat unit for this system. The emeraldine base polymer has two additional electrons (and two additional protons) for the four ring repeat as compared to the similar length of pernigraniline base polymer. (Alternatively the emeraldine base polymer may be viewed as having two fewer electrons (and two fewer protons) than the corresponding four ring-nitrogen length of leucoemeraldine base polymer.) The energy of the polymer shown schematically in Figure 4a can be reduced by introducing a "tetramerization" of the lattice, shown schematically in Figure 4b. In a matter similar to that of pernigraniline base, Figure 2, bond length (i.e., formation of a quinoid structure) and ring torsion angle changes will take place. The final structure consists of the alternation of three benzenoid and one quinoid ring. Though this may be considered as a Peierls distorted ground state form of the undistorted four ring repeat system, it is noted that the final distorted state of emeraldine base does not have a degenerate ground state structure because of the absence of protons adjacent to the nitrogens on either side of the quinoid ring and the presence of protons adjacent to the other two nitrogens of the four ring repeat. The fixed periodicity of the protons introduces a periodic potential commensurate with the Peierls distortion, making the emeraldine base, a non-degenerate ground state Peierls insulator. The fraction of the band gap due to this "external potential" caused by the alternating proton pairs is of major consequence. The periodicity of the lattice distortion of emeraldine base together with its cooperative alternating pairs of NH(amine) and -N=(imine) sites is a stable point for the system. It has been

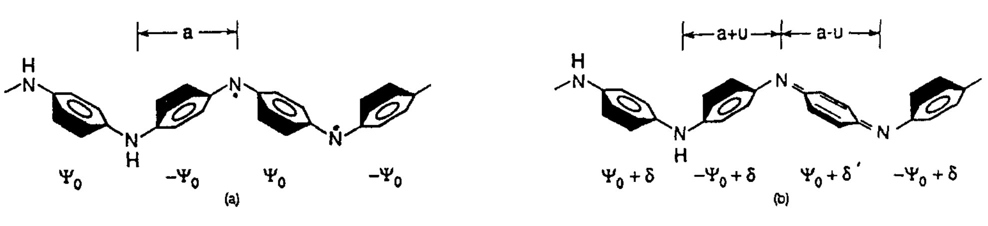

Figure 4. Schematic chemical structure of (a) uniform chain, and (b) bond length and ring torsion angle tetramerized emeraldine base polymer. It is noted that the three benzenoid rings may not have identical bond lengths and torsion angles.

shown that excess amine or imine units in the chain segregate to form segments of leucoemeraldine base or pernigraniline base system, respectively.[10] Electronic structure of forms of emeraldine base have been reported earlier.[11,12] Because the tetramerized ground state of emeraldine base is nondegenerate, it will not have neutral or charged soliton excitations.

EXPERIMENTAL METHODS

Pernigraniline base powder samples were synthesized via the oxidation of the emeraldine base with an acetic acid solution of *m*-choloroperbenzoic acid followed by deprotonation with triethylamine.[13] The experimental techniques for steady-state photoinduced absorption,[6] long time low power photoinduced absorption,[8] and high power density picosecond photoinduced absorption[14] are reported elsewhere.

SUMMARY OF EXPERIMENTAL RESULTS

Figure 5 presents results of near steady state photoinduced absorption experiments for pernigraniline polymer of Leng, et al.[6] This figure summarizes the photoinduced absorption results in the near steady state at 10K and the long photoinduced experiments at 80K. The near steady state shows the presence of both the low energy peak (~1.0 eV) and a second weaker peak (1.5 eV). Photoinduced infrared active vibration modes (IRAV) are found.. In contrast in a long lived photoinduced absorption experiment, photoinduced absorption is found at 1.5 eV. The long lived photoinduced IRAV modes are much weaker. The short lived defects at 1.0 and 1.3 eV have been assigned to charged solitons (S^+, S^-) and the short and long lived peaks at

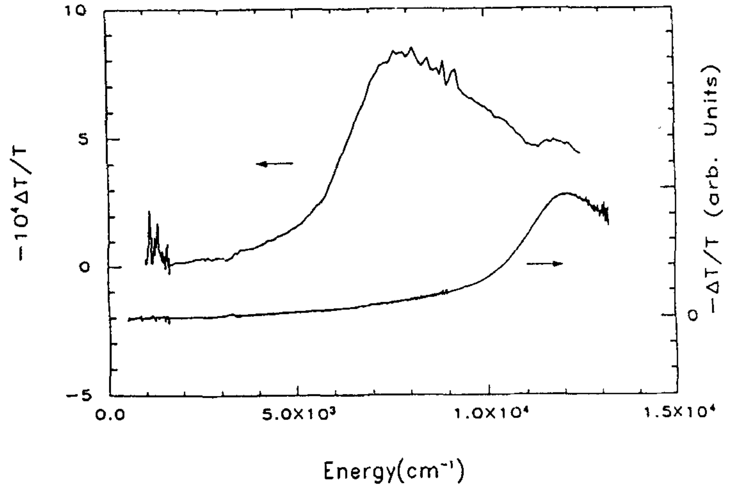

Figure 5 Photoinduced absorption spectra of pernigraniline base polymer as powder mixed with KBr, obtained with pump laser intensity I_0 = 250 mW cm^{-2}. Left scale: near-steady state (22.4 Hz light modulation) at 10 K. Right scale: long-lived (reduced by a factor ~400) at 80 K. (From reference 6).

1.5 eV have been assigned to the negative polaron (P^-). It has been suggested that the other absorptions in the negative polaron and those of the positive polaron are not observable due to the disorder present in pernigraniline.[8]

More recent long lived photoinduced studies (Coplin et al.[8]) demonstrate the presence of a second longer lived photoinduced absorption peak at 1.8 eV. It is noted that the intensity of the 1.8 eV photoinduced absorption decreases more slowly than that of the 1.5 eV photoinduced absorption with increasing laser excitation power, demonstrating that the 1.8 eV absorption arises from a separate defect. There are no infrared active vibrational modes associated with the presence of the 1.8 eV peak, supporting its assignment to the presence of the neutron soliton.

We have recently carried out extensive picosecond photoinduced absorption studies of this system. The photoinduced absorption spectrum differs substantially depending upon the amount of time for which the sample is exposed to the pump beam before conducting the experiment. Figure 6 presents the photoinduced absorption for two limiting cases, both data sets for zero delay of the probe pulse following the pump pulse. The initial photoinduced absorption profile, with the exposure time to the pump beam less than three seconds ($t_{exp} \approx 0$), matches that expected for the formation of charged polarons (at ~1.4 eV), bleaching of the absorption due to isolated (preexisting) neutral solitons(1.8-2.0 eV), and absorption due to the production of a neutral soliton lattice (at >1.6 eV). After 10 minutes of exposure of PNB to the high photon flux used for picosecond spectroscopy the photoinduced absorption shifts so that bleaching now extends from ~1.5 eV through to >2.0 eV, as may be expected for the broadening of the S^0 absorption with creation of an increasing density of long-lived neutral solitons. The 1.4 eV photoinduced absorption has a power law decay, though the total oscillator strength of this peak decreases with exposure time. In contrast, in the 1.5-1.6 eV region, the pump/probe time dynamics change from a fast-decaying absorption at zero exposure time to a slowly-decaying bleaching at long exposure times (> 10 min.). The intermediate decay rate for the bleaching at 1.8-2.0 eV remains the same, independent of exposure time. The photoinduced absorption obtained after 10 minutes of pumping is found to persist for several hours after the pump beam is turned off.

This anomalous long-lived behavior compliments the earlier reported

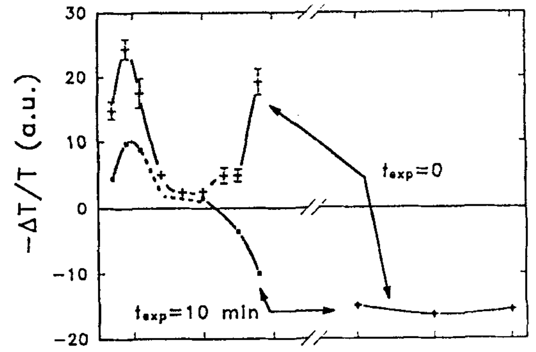

Figure 6. Picosecond photoinduced absorption at zero pump/probe time delay for PNB pumped at 2.1eV with average power 100 W/cm^2 (peak power of 20 MW/cm^2), immediately after pump exposure (t_{exp}=0) and after exposure to the pump beam for 10 minutes (t_{exp}=10 min).

stability of photoinduced neutral solitons and charged polarons at low densities and low temperature. As there is of order one pump photon absorbed per 1000 polymer C_6 units for each ~5 ps pulse (i.e., of order 500 photons absorbed per C_6 unit per second), it is suggested that this stability at room temperature arises from the excitation of a very high density of neutral solitons, leading to the formation of a neutral soliton lattice. As noted in Figure 2, the formation of neutral solitons involves ring torsion in addition to the bond alternation changes. The ring torsions on neighboring chains may be coordinated so that it is difficult for the rings to relax back to their initial starting point. Also, for the neutral excitations there is no Coulomb driving force for the defect species to recombine. The identification of the 1.6 eV feature as due to a neutral soliton lattice is supported by the presence of only fast decays for photoexcitation of PNB in solution and the absence of the 1.6 eV long-lived feature in the nondegenerate ground state emeraldine base polymer.

SUMMARY

The polyaniline family of polymers provides a flexible system for studying a wide range of concepts. In particular, pernigraniline base polymer is shown to be a degenerate Peierls ground state system that sustains photoexcited charged and neutral solitons in addition to charged polarons. The unusual decay dynamics for photoinduced charged solitons, especially when created at high densities, is suggested to arise from the important role of interchain steric interactions preventing rapid relaxation of the polymer back to the ground state.

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