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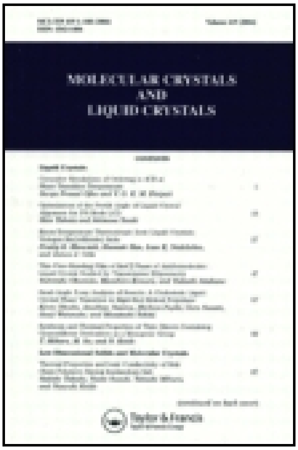

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Electroactivity in Polyaniline

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ELECTROACTIVITY IN POLYANILINE

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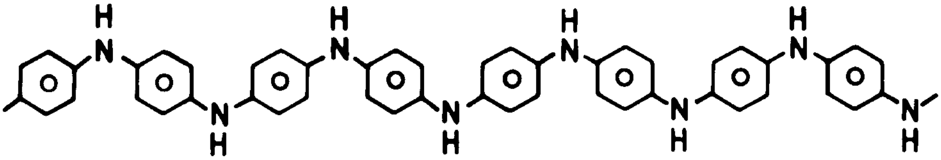
INTRODUCTION

Twenty years ago, if someone had asked for a material with which they could fabricate a yoghurt pot, as quickly as they could with polyethylene, but had the electrical properties as if it were made of aluminium, both chemists and physicists would have laughed them away. Today, we have conductive polymers which can rival copper as a conductor, and materials which can be processed in simple ways, however, the yoghurt pot still seems a little to technical at present! At the forefront of this field, one increasingly finds polyaniline (PANi). The polymer can be processed [1], and is air stable, making it a good candidate for many electrical applications. Along with these most desirable properties, PANi and its family members also have a large number of interesting optical properties, and it is to these that research groups are now turning. In this lecture, I will review some of the salent points about the optical nature of PANi, and hopefully point out some of the potential avenues that they might take us down in the future.

THE POLYANILINE FAMILY

Polyaniline should be thought of as a family of three polymers, depending on oxidation state. The fully reduced form, known as leucoemeraldine, has the simplest polymer backbone. Electro-chemically, this corresponds to an oxidation state of −0.2V vs calomel. See fig.1 for optical spectrum.



LEUCOEMERALDINE

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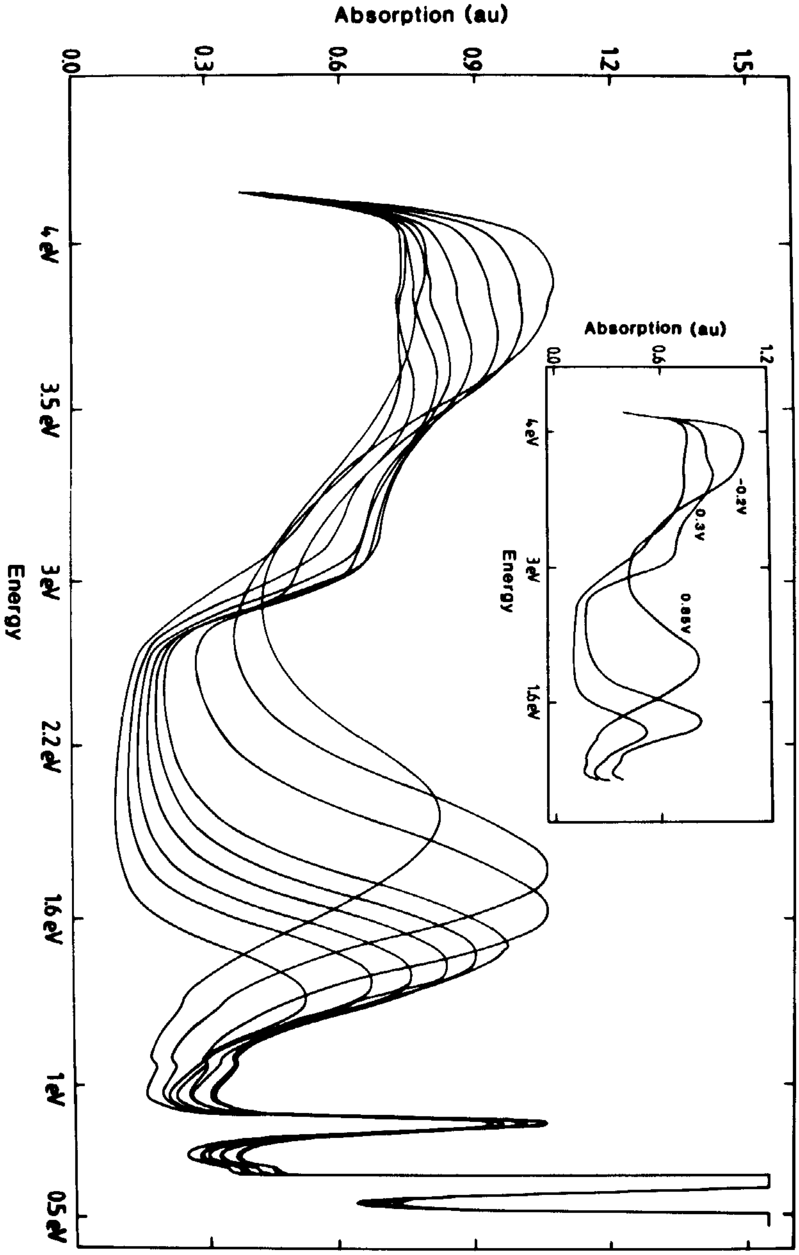

Fig. 1. Insitu absorption spectra of polyaniline.

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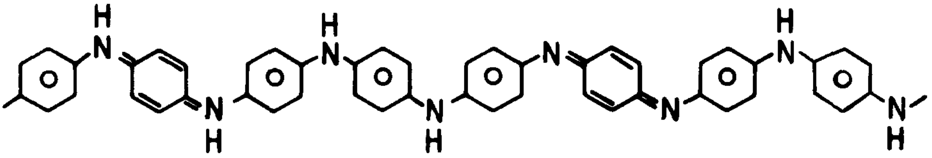
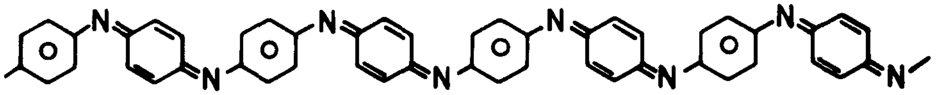
Electrically, the most interesting state is emeraldine. When this material is protonated it becomes conductive, and has a metallic-like optical absorption and reflection spectrum (fig.2). The oxidation potential of emeraldine is 0.2 to 0.4V vs calomel. Again, its optical spectrum can be seen in fig.1.



EMERALDINE

Optically, the most intriguing material is pernigraniline, the fully oxidised material. Here the polymer is 50:50 benzenoid/quinoid. Its oxidation potential is 0.7–0.9V vs calomel. On inspection it can be seen that pernigraniline possesses a degenerate group state, and so could support solitonic excitations [2]. See fig.1 for absorption spectrum.



PERNIGRANILINE

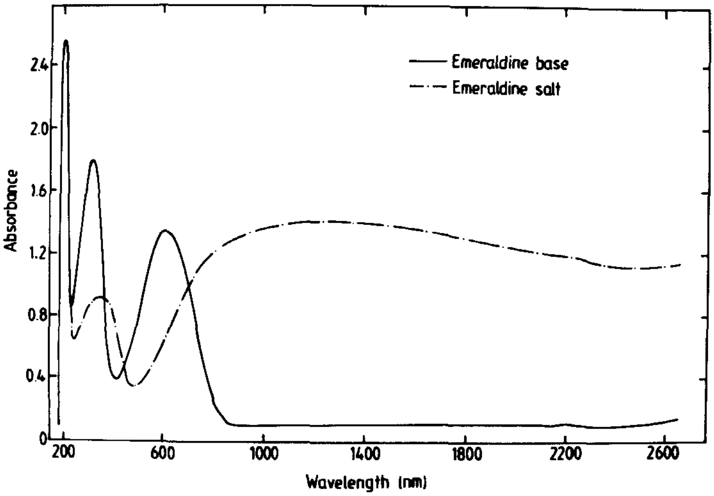


Fig. 2. Absorption spectra of emeraldine salt and base form.

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Polyaniline Synthesis

Polyaniline can be synthesised either chemically or electrochemically. The former yielding longer average chain length [3]. For a detailed electrochemical route, see ref.4. Briefly an aqueous electrolyte of 2 molar HCl was used. The monomeric analine was vacuum distilled after being treated with stanous chloride. Films were deposited galvanostatically, at an oxidation potential of 0.75V vs SCE. PANi being deposited on either Pt or ITO electrodes.

Chemical synthesis of the polymer [1] follows a modified version of that used by Angelopoulos et al [5]. Again briefly this entails oxidation of aniline hydrochloride with aqueous ammonium persulphate. The resultant PANi powder after washing is deprotonated with ammonia to yield emeraldine base. This can be dissolved in n-methyl-pyrrolidinone (NMP), from which free standing cast films and thin films via spin coating [6] can be made. Further, these free standing films can be partially oriented via the application of uniaxial stress [7], increasing conductivity and introducing anisotropy in both electronic and optical properties.

Optical Properties

From the insitu spectra, one can see the characteristic absorption bands of the component parts of the polymer backbone. Taking the leuco form (fully reduced) first, one sees one main peak at 4 eV, ascribed to the $\pi \rightarrow \pi^*$ of the benzenoid rings. The small absorption in the NIR is due to irreversible oxidative products, with the sharp peaks below 1 eV being water overtone bands. In the emeraldine state, the 4 eV band is reduced in intensity, and two new bands are seen. The main NIR band being indicative of a charge transfer band associated with a semi-quinone amine/imine moiety, and a band in the blue/violet at 3 eV, ascribed to excitation of charge amine moieties. A small NIR tail is visible, indicative of low conductivity (NB. the sample was only moderately protonated). In the case of highly conductive films this NIR absorption is far more prominent and metallic-like, see fig.2.

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For optical phenomena, the more interesting electronic transition are found in the emeraldine base and in pernigraniline. In fig.2, along with the absorption spectrum of the salt form, one can also find the absorption spectrum of emeraldine base. Here one observes two prominent peaks. One at 320 nm (3.65 eV) ascribed to the benzenoid $\pi \rightarrow \pi^*$, and a second broader band at 600 nm (2 eV). This second band is ascribed to the $\pi \rightarrow \pi^*$ of the iminoquinoid moiety, and has been postulated to be due to the formation of a self trapped exciton at such a site [8]. As can be seen from the spectrum, the emeraldine base is transparant in the NIR region, and has a window in the green/blue region of the spectrum. This offers a good cenario for NLO applications as the pump wavelength will be a long way from resonance, and there should be only a low re-absorption of the 3rd harmonic emission. With the possibility of photoexcitation of the trapped excitons, one might well be able to observe a large enhancement in 3rd harmonic output, due to the large dipole of the exciton, and the possibilities of interactions with the large manifold of excited states.

The formation of self trapped excitons at iminoquinoid sites also affords another possible optical application. That of optical data storage. This comes about through the self trapping mechanism which Duke et al [8], ourselves [9], and Epstein et al [10] have put forward to be caused by ring rotations. Inspection of the "polyaniline" backbone reveals that due to the heteroatomic coupling between adjacent rings there is an extra degree of freedom along the polymer backbone, e.g. rotation of a ring with respect to its neighbour. This rotation is in fact an equilibrium. Stearic interactions would like a 90° torsion angle (between adjacent rings) whereas conjugation tends to drive the system planar (0° torsion). In the case of protonation, this equilibrium is driven more to low torsion angles, thus a higher degree of conjugation and so increasing conduction, as well as producing vacancies along the chain for electrons to hope to [11]. In the case of emeraldine salt we have estimated this torsion angle to be around 35° [12,13].

For iminoquinoid moieties, the p_z orbitals of the nitrogen are orthogonal to those of the rings, thus to form the imine bonds the

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rings are driven to large torsion angles (approaching 90°). In this case, the iminoquinoid is 'localised' and not conjugated with its adjacent neighbours. This should be observed strongly in the perinigraniline case which contains 50% iminoquinoids. Evidence for this can be seen in the optical spectrum of the pernigraniline, formed at an oxidation potential of 0.8 V vs SCE. Here one observed that the NIR band has broadened dramatically but also is shifted to nearly 2.2 eV, indicating an increased localisation of the iminoquinoid moieties. Further evidence of this is seen in the Resonance Raman spectra measured insitu, fig.3. With a laser excitation wavelength of 488 nm (2.4 eV), one observes first one resonance with the absorption band at 3.1 eV. The spectra being characteristic of a paradisubstituted phenyl ring [9] and then at high oxidation potentials a second resonance is observed. This spectrum is characteristic of an aminobenzinoid-iminoquinoid (two ring) unit [9]. In both cases the Raman bands are relatively sharp, characteristic of a localised system.

Photoexcitation of such moieties, at low temperature yields long lived excited states. Initial evidence for this phenomena has been shown by Epstein et al [14]. One can then see that if this ring twist mechanism is producing such phenomena, simple but careful ring substitution should lead to long lived photoinduced states at room temperature, a very desirable objective for optical data storage. As yet, however, no evidence for optical de-excitation has been shown.

SUMMARY

The polyaniline family of polymers offers not only the possibility of a useable, processable conductive polymer, but also a potential optical material. Because of the mechanism and type of excited state observed on the quinoid moieties along the backbone, emeraldine and pernigraniline may well offer good NLO and excited state NLO responses and the potential use of long lived self trapped excitons as a means for optical data storage. In both cases these phenomena arise from the 'extra' degree of freedom on the polymer backbone afforded by ring rotations with the possibility of further

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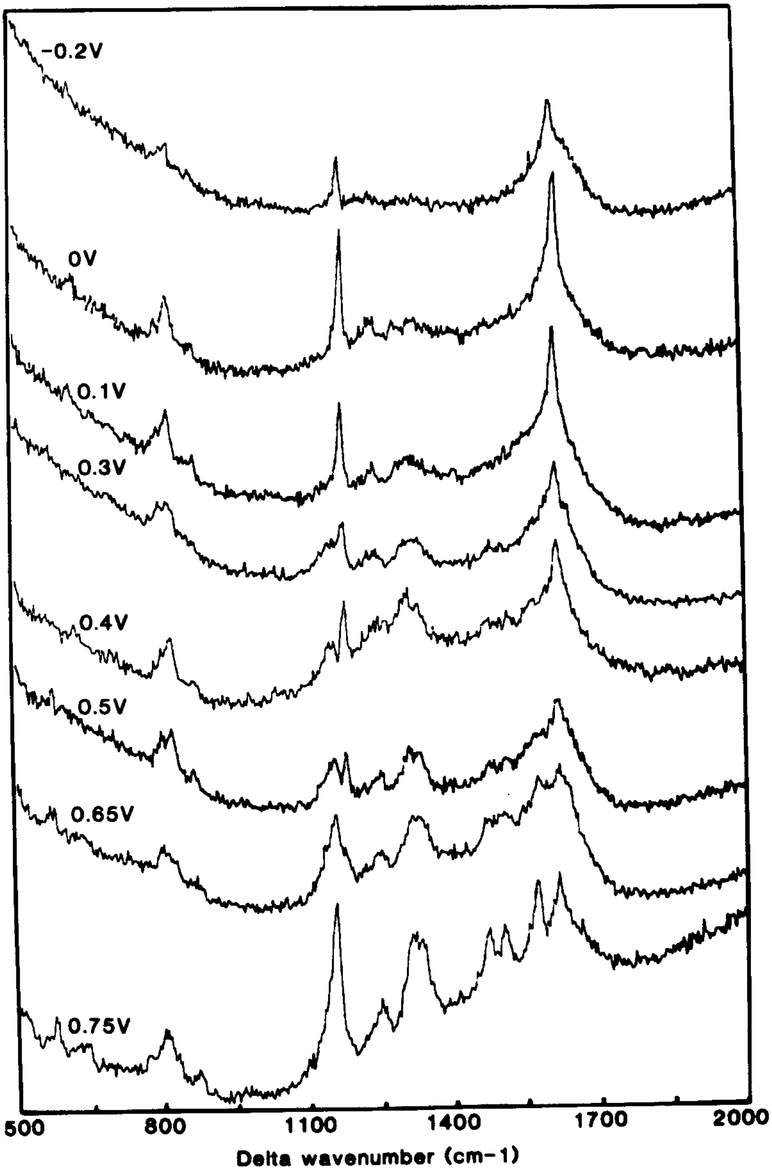

Fig. 3. Insitu resonance Raman spectra of polyaniline with 2.4 eV laser excitation.

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controlling this properly by simple chemical modification of the rings. PANi may well be the stepping stone required by organics to venture into the optical data storage market.

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