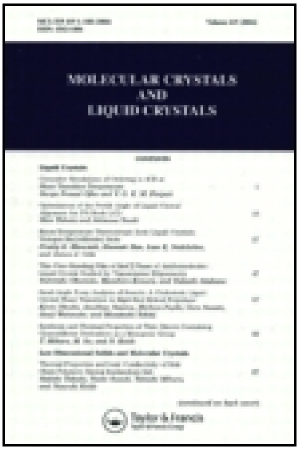

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

What Do Ring Rotations Do for Polyaniline?

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Version of record first published: 05 Dec 2006.

To cite this article: A. P. Monkman, P. Adams, A. Milton, M. Scully, S. Pomfret & A. M. Kenwright (1993): What Do Ring Rotations Do for Polyaniline?, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 236:1, 189-197

To link to this article: http://dx.doi.org/10.1080/10587259308055227

Mol. Cryst. Liq. Cryst. 1993, Vol. 236, pp. 189–197
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Printed in the United States of America

WHAT DO RING ROTATIONS DO FOR POLYANILINE?

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Abstract

Polyaniline in its many forms has potential optical data storage possibilities along with its known electrical properties. Here we discuss the role which mechanical motions of the polymer chain play in the delocalisation of electrons on the backbone, and the consequences this has on the optical properties of the polymer.

INTRODUCTION

Workers in the conventional (insulating) polymer field know well that most of the mechanical properties of polymers are controlled or at least influenced by the motion of part or hole repeat units, along the polymer backbone. In the main these will be either rotations of the units or the movement of pendent side groups. In all cases these movements will affect the free space encompassing the chain which will in turn effect the intermolecular forces, ie. Van Der Waals etc. We in the conducting polymer field know full well that any change in the backbone geometry directly effects the electronic properties of our polymers, see for example Su [1]. What many in the conductive polymer field have failed to take on board, so far, is what role do such intrinsic motions along the polymer chain play in the conductive polymers? Here, polyaniline offers a wealth of opportunity to the experimentalist, as it possess heteroatomic coupling within the conjugation path, this directly influences possible configurations of the backbone and sets up configurational equilibria for rotational motions along the backbone.

This degree of freedom, namely ring rotations, will be strongly manifest in polyaniline, and has been discussed in various forms by ourselves [2] and other research groups [3,4,5] to explain the physical nature of polyaniline. In this paper we report evidence for such ring motions in polyaniline, shed light on there thermal equilibrium report a new phase transition, and show how the electronic structure of polyaniline is affected by these motions. Lastly, we discussed the feasibility of using these motions for a new data storage medium.

POLYANILINE SAMPLES

All polyaniline samples used in our studies were synthesised using our well document procedure [6]. Analysis was performed either on solutions of emeraldine base in n-methyl-pyrolidinone (NMP) or on free standing films cast from NMP solution. Further, thin films have been spun from NMP solution, to yield high quality, optically transparent films for optical characterisation. In the latter case both glass and sapphire substrates are used. All material used is characterised by molecular weight determination and consistency of FTIR spectra. In the vast majority of cases, especially the thin film work, samples where exposed to air for the minimum time possible, but total anaerobic conditions are not possible, hence some aerial oxidation of samples is inevitable.

C^{13} NMR SPECTROSCOPY

The best starting point for any study of structural property relations has to be proof you know what you are dealing with, and the most appropriate way to do that is to use high resolution NMR spectroscopy. We have started an extensive study of polyaniline using this powerful analytical tool and to date have discovered a wealth of structural information. Sample preparation and instrumental techniques can be found elsewhere [7]. One of our key experiments was to verify the chain structure of emeraldine, the conducting form of polyaniline. The proposed structure, with the numerous possible resonance structures available to it and large number of inequivalent carbon sites should yield a complex NMR spectrum. We found this to be the case figure 1a. To aid in unravelling this complex spectra, DEPT-90 and quantitative studies where also made [7]. Further we took some of our starting emeraldine base, and under the best oxygen free conditions available, chemically

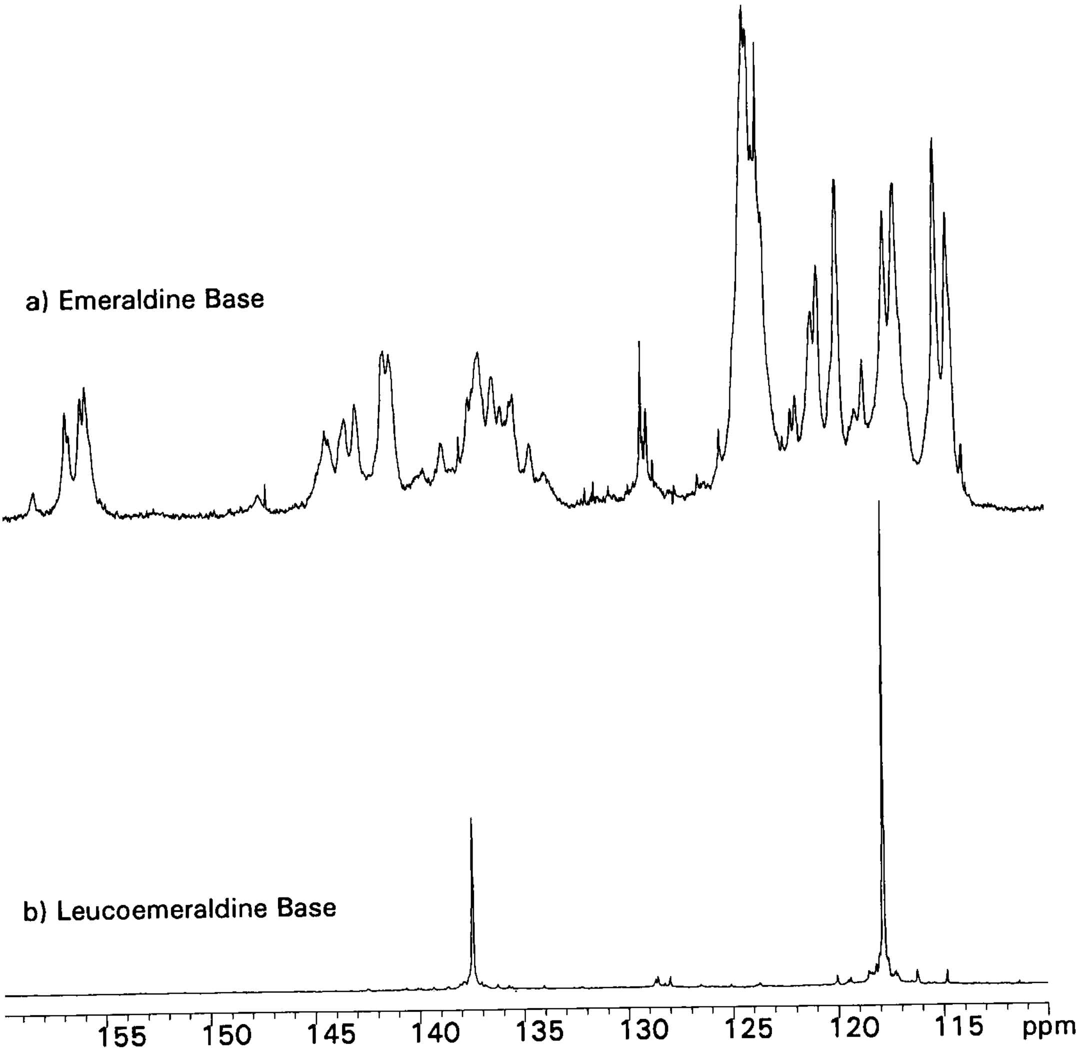

Figure 1 Normal proton decoupled ^{13}C spectra of emeraldine and leucoemeraldine base.

reduced the emeraldine to leucoemeraldine using phenylhydrazine. We then quantitively measured the NMR spectrum of this, more simple polymer. The recorded spectrum is seen in figure 1b. Now we observe just two major lines, 117.84 and 137.44 ppm, with intensity ratio 2:1. These lines account for more than 95% of our spectrum, ie. leaving some 4% to be accounted for. This spectrum is consistent with the postulate structure for leucoemeraldine. The final step in the process was to reoxidize the leuco back to emeraldine. From this we recovered essentially an identical spectrum to our starting material, with only minor differences being found in the relative intensities of peaks.

GPC analysis revealed that no chain scission or cross linking had occurred. Thus the backbone of emeraldine must be as postulated, ie. six membered carbon rings separated by para-coupled nitrogen atoms, with an average one in every three for rings being quinoid, although the precise statistical distribution cannot be determined, however, the number of peaks seen in the spectrum is far greater than the number of inequivalent carbon sites in the emeraldine structure. These main peaks cannot be due to 'non-para' coupling, from the leuco data, and so must be due to conformational effects and or reduced

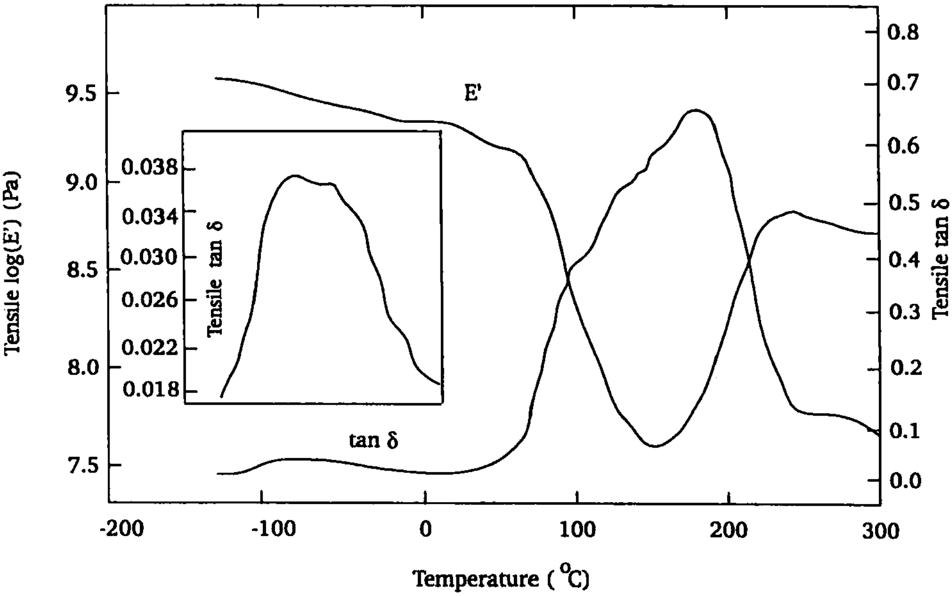

Figure 2 The storage modules, E', and loss tangent tan 5 as a function of temperature for emeraldine base. The insert shows an expand scale to bring out a feature at 190°K.

ring symmetry. Note on the NMR time scale, rapid 180° phenyl ring flips would not be seen. However, in emeraldine the quinoid bonds prevent such ring flips in all but the middle benzenoid ring, and this must be a cooperative effect. This will lead to stiffening the chain.

The stiffening will help to lock in the torsion angle between adjacent phenyl rings, leading to inequivalency between carbon sites on opposite sides of the phenyl rings. Different quinoid phenyl ring conformations, eg. all trans symmetric, trans anti symmetric, cis symmetric and cis antisymmetric can be postulated. Such conformers will give rise to many new peaks in the NMR spectrum of emeraldine, which we observe, bearing in mind that from our leuco samples we also find some 5% of 'impurities'. Therefore, this shows that not only are the proposed chain structures of both leuco and emeraldine correct, it also shows that in emeraldine, we will also have to consider different conformers, due to ring rotations, and there effect on inter and intra chain electronic properties.

DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

To access the mechanical properties of emeraldine base, cast into free standing films, we have used DMTA, this enables us to access the direct bearing which backbone modes have on the mechanical properties of the polymer, and thus gauge there effect on the electronic (and optical) properties of polyaniline. Experimental details can be found elsewhere [8]. In figure 2 we present a DMTA scan from 173° K to 573°K, both the storage modules E' and loss tangent (tan δ) ie. dynamic Youngs modules divided by the loss component, are shown. The large broad peak in tan δ above 300° K, peaking at 453° K, signifies the onset of film softening. The shoulder observed at ca. 370° K can be thought of as a glass transition temperature, although we have found that this Tg is strictly dependent on the NMP content of the film. Films heated beyond 453^0 K are found to thermally cross link.

As well as this behaviour, we also observe a tan δ peak at 190° K. We ascribe this beta transition to the torsional motion of the rings along the polymer backbone. Further, we observe this transition in films with no NMP content and in both base and salt films. Hence it has to be considered as an intrinsic phase transition of emeraldine due to ring rotations, and so we should observe discontinuities in the physical properties of polyaniline at this transition temperature. At present we do not have enough information as to the precise nature of this transition, eg. whether it involves the quinoid segments turning fully 90^0 out of plane with respect to the neighbouring benzenoid sites, or some motion of the benzenoid sites with respect to each other, also whether the transition drives the system to a more planar or non planar configuration.

DO RING ROTATIONS MANIFEST THEMSELVES IN THE OPTICAL PROPERTIES OF EMERALDINE

Emeraldine base is the most delocalised 'base' member of the polyaniline family, thus if ring rotations play any part in electronic wavefunction delocalisation/localisation it must be most easily seen in the emeraldine base system. In figure 3 we show the optical absorption coefficient α multiplied by $\hbar\omega$ as a function of photon energy, $\hbar\omega$. Full experimental details can be found in [9].

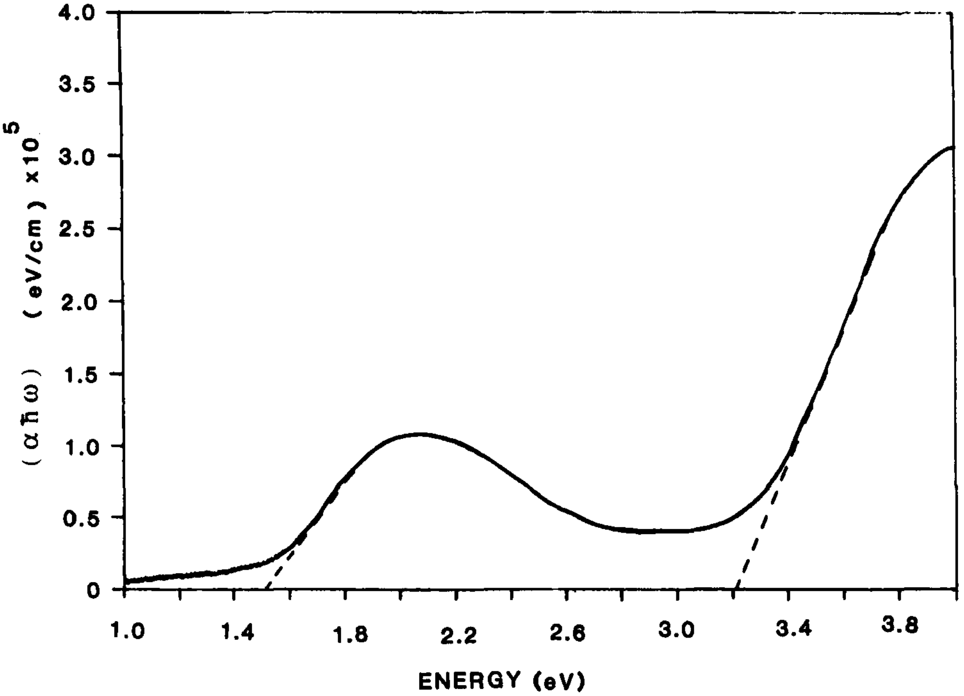

Figure 3 Photon energy dependence of the absorption coefficient (multiplied by $\hbar\omega$ [10]) to reveal the true onset of band absorption in emeraldine base.

Using this analogy to Tauc theory [10] the plot of $\alpha\ \hbar\omega$ vs.$\hbar\omega$ yieldsonsets for the observed absorption bands at 1.47 eV and 3.19 eV respectively. These values are in excellent agreement to values calculated by Bredas [4], however, these calculations for the emeraldine base, have as yet not been analysed to ascertain the contribution which ring torsion angle makes to the band gap compared to the conventional bond length alternation component. However, experimentally we can ascertain if ring torsion is important in the measured optical gap of emeraldine, and the magnitude of its contribution. We have done this by measuring the temperature dependence of the absorption bands of emeraldine to observe thermochromic shifts, band narrowing and to see if vibrational structure appear in these bands. In figure 4 one can observe the high temperature behaviour of the quinoid absorption band. In the case of the benzenoid $\pi \rightarrow \pi^*$ transition 320 nm (4 eV) [2], there is a similar change in oscillator strength and peak position up to 420° K, but this shift is in the opposite direction to that seen in the quinoid band. In the 620 nm (2 eV) absorption ascribed to the formation of self trapped excitons at the quinoid sites [2,11] a large blue shift is observed, which saturates at about 420°K. The shift is measured at 1.4 meV/K. This phenomena is ascribed to the

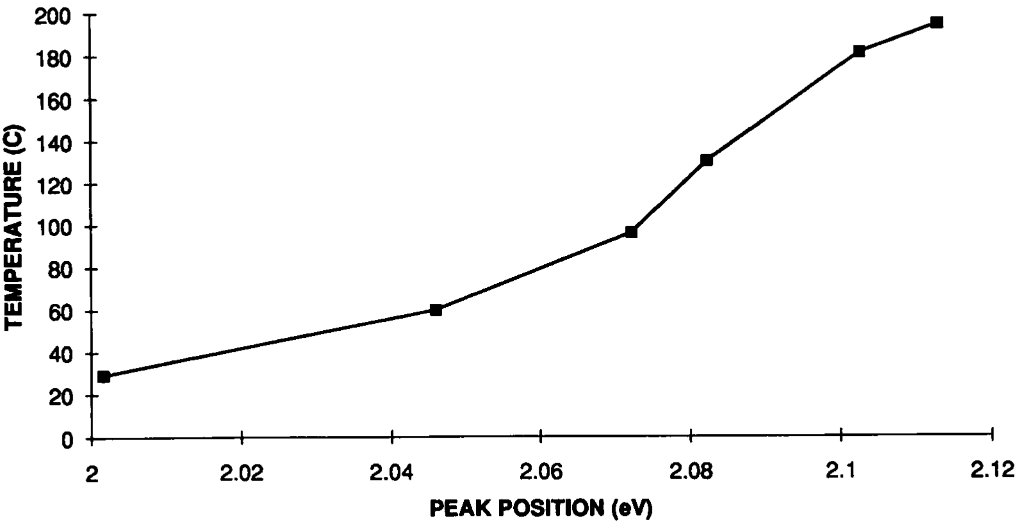

Figure 4 Thermochromic shift in peak position of the quinoid imine absorption band.

localisation of this excitonic transition ie. the quinoid rings increase there torsion angle with respect to the adjacent benzenoid rings, saturating at or near 90^0. Lowering the temperature below the ring torsion phase transition shows that these shifts continue until the phase transition occurs and then no further shift in peak positions is observed. At present it would seem that below the phase transition, the emeraldine is in its most planar configuration and that thermal excitation disrupts the planarity above the phase transition.

DC PHOTOCURRENT MEASUREMENTS

At present we cannot say a great deal about dc photoconductivity in emeraldine base. It is very small, extremely difficult to measure at room temperature and seems to only arise when exciting well into the UV. This last comment is consistent with the self trapped exciton picture, ie. the band at 2 eV is not a band gap transition in the semiconductor sense, but is a truly localised molecular phenomena. We do measure large dark currents in our samples, and bearing in mind that our NMR can only account for some 95% we assume that a large proportion of the defects, act as either very effective trapping sites, or are easily ionisable sites. Thus all data resulting from sensitive measurements must take account of the fact that at best, materials have some 4% impurity, ie. one defect every 20–25 rings.

SUMMARY

Do ring rotations play a role in the physics of emeraldine? From our results we think that they play a large and important role. The degree to which electronic wave functions are delocalised through out the chain is critically dependent on torsion angle, and temperature seems to directly influence this. We have shown that emeraldine goes through a phase transition, directly ascribed to ring torsional motion at 190^0 K. From our NMR results we can prove the definitive chain structure of emeraldine base, and further can show that many conformations of this basic structure coexist. These conformers must be a direct consequence of ring torsional degrees of freedom. The measured physical properties of any sample must also be dependent on the type and distribution of these conformers. It has been proposed [2,3] that on photoexcitation of the quinoid sites, a ring flip occurs along with the loss of quinoid nature of the ring upon excitation. Again remembering that at best one in every twenty to twenty five rings are defect sites, this ring flip leads to a long lived photoexcited state which could be used for optical data storage. Noting that if this is a truly intrinsic property, and the fact that many different conformers exist, there should be many inequivalent quinoid sites giving rise to many possible discrete wavelengths at which excitation, and this storage can be made. This can be thought of as an analogue, but at high temperature, to the photo-chemical hole burning phenomena and may lead to very high room temperature storage capacities. Although at present this is not tenable with the current purity and material understanding of emeraldine base polymer.

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