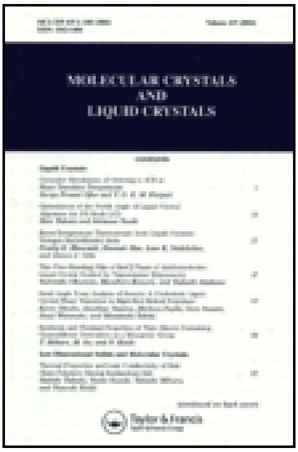

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Structure-Property Relationships in Conductive Polymers

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Version of record first published: 22 Sep 2006.

To cite this article: D. Bloor , A. P. Monkman , G. C. Stevens , K. M. Cheung & S. Pugh (1990): Structure-Property Relationships in Conductive Polymers, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 231-239

To link to this article: http://dx.doi.org/10.1080/00268949008036047

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 231–239
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Printed in the United States of America

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ABSTRACT

Detailed studies of the structure-property relationships for conductive conjugated polymers are important for the proper understanding of the impact of morphological details on chemical and physical properties. This understanding is necessary for the development of realistic theoretical models. The particular cases of poly- and oligo-pyrroles and polyaniline are described.

1. INTRODUCTION

The recent history of electrically conducting conjugated polymers has been marked by apparently conflicting viewpoints. On the one hand physicists and theoretical chemists have considered the action of donors and acceptors to produce high conductivity values as 'doping' and the elementary excitations of ideal, isolated polymer chains as solitons, polarons, bipolarons, etc.[1] The concepts have proved stimulating and fruitful as a new class of fundamental excitations in solids. The idealised models used have, however, been questioned as a proper basis for understanding real materials. In particular, synthetic chemists and polymer scientists have been concerned with the morphological complexity of these polymers, the chemical nature of the oxidation and reduction processes and the consequent occurrence of radicals, cations, dications, etc.[2] Though some of these differences can be regarded as a question of semantics, e.g. the terms 'bipolarons' and 'dications' describe similar entities, there are underlying differences in philosophy which have presented a barrier to progress. There is, however, a growing realisation that a detailed understanding of sample morphology and chemical behaviour is essential if a correct understanding of physical properties is to be obtained.

Studies of two 'typical' conductive polymers, polypyrrole and polyaniline, which illustrate the complexity of structure-property relationships in these materials, are summarised.

Polypyrrole is an excellent example of a 'non-ideal' material. Electrochemically polymerised samples are cationic network polymers which have morphologies and mechanical properties that are dependent on factors such as the electrolyte composition, the electrode materials and the incorporated counter-ion. Counter-ions with an extremely wide range of molecular shapes can be incorporated. Careful examination reveals a hierachy of inhomogeneities and differences in structure and physical properties. Despite this the features in the optical spectra attributed to bipolarons are hardly affected. These results are discussed further below.

Parallel studies of stereoregular soluble oligopyrroles have been undertaken. The spectroscopic properties of oxidised oligomers can be interpreted in terms of a dication (bipolaron) model. However, there is evidence for other effects, such as proton abstraction and complex formation, which demonstrate that the chemical aspects of the interaction of the oligomers with their environment cannot be ignored.

Polyaniline has been extensively studied both experimentally and theoretically. Again the preparative route has a profound effect on structure and properties. In an attempt to obtain reproducible samples a simple electrochemical synthesis was adopted. Material produced by this 'standard' route was characterised electrochemically and studied by a variety of experimental methods.

2. STRUCTURE-PROPERTY RELATIONSHIPS : CASE STUDIES

2.1. Polypyrrole

Polypyrrole can be produced by the electrochemical oxidation of pyrrole in a range of solvents, e.g. H_2O, acetonitrile, propylene carbonate, and a wide variety of supporting electrolytes.[3] We have found that the use of propylene carbonate and tetraethyl toluene sulphonate enables dense films up to 1mm thick and with good electrical and mechanical properties to be fabricated.[4] Such samples have fracture surfaces typical of tough elastomers and show no sign of any macroscopic anisotropy even though the growing surface has a slightly nodular structure. The surface in contact with the electrode has a smooth and featureless appearance except where there are flaws in the electrode surface. These conclusions are confirmed by scanning electron microscope images taken under normal operating conditions. However, images recorded at low beam currents reveal inhomogeneity. This disappears on prolonged exposure. We presume that these inhomogeneities are due to variations in conductivity that are washed out by electron beam damage (or 'doping').

These observations prompted further studies using techniques sensitive to sample conductivity, i.e. electron beam induced current (EBIC) and secondary electron (SE) imaging. Micrographs obtained by a variety of methods are illustrated in Figures 1-4. The materials are clearly inhomogeneous. Complementary images are obtained for absorbed current (EBIC) and secondary electron emission (SE). At high electron beam energies the average structure extending through the film is seen to be a network of conductive regions which map the boundaries between the surface nodules. While it is tempting to regard these as grain boundaries reflecting the initial nucleation and growth of the film, the absence of structure in the fracture surfaces is a contraindication. At low beam energies, ie. small penetration depths, a finer more random granularity is observed. Though the image is of the near surface region it seems plausible that this finer structure extends throughout the film. Finally, inclusions of a second phase can be seen. These have been reported previously and though their true nature has not been ascertained their number, size and distribution have been shown to be dependent on the material used for the electrode.[5]

Many different counter-ions can be incorporated into electro-polymerised polypyrrole films.[6-8] In general these materials have been studied in isolation. However, much can be learned from comparative studies. Electro-polymerisation has been performed with toluene sulphonate (TS), pyrene sulphonate (PSA), pyrene tetra-sulphonate (PTSA), dodecylbenzene sulphonate (DBS), bis(decyloxycarbonyl)-ethane sulphonate (DES) and octachlorodirhenate counter-ions. The tetraphenylborate counter-ion could not be incorporated as it reacted electrochemically at a

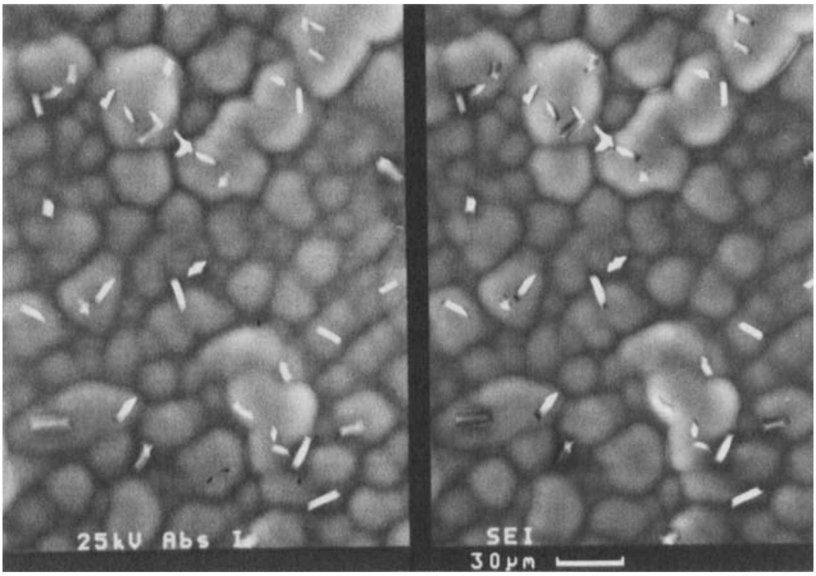

Figure 1 Electron micrographs of polypyrrole polymerized on platinum : EBIC (left) and SEI (right) images recorded with a 25kV electron beam.

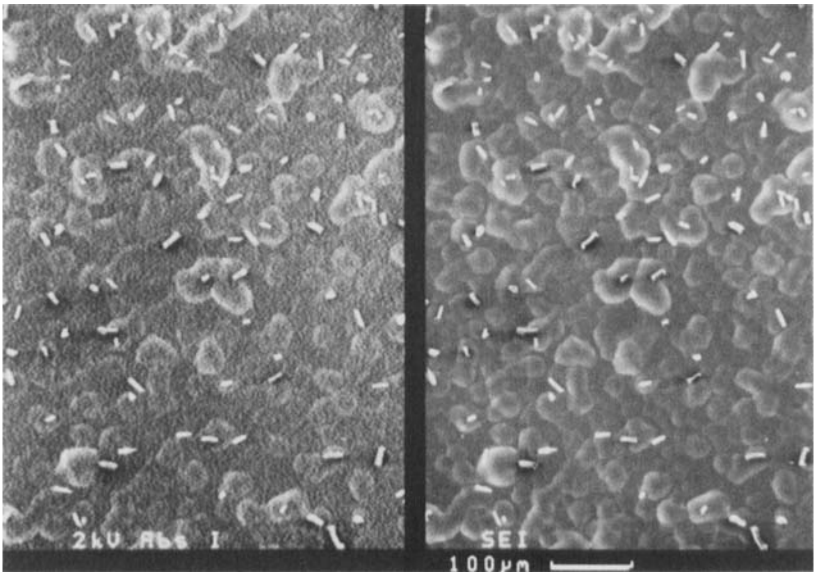

Figure 2 Electron micrographs of polypyrrole polymerised on platinum : EBIC (left) and SEI (right) images recorded with a 2kV electron beam area from top left of figure 1 at higher magnification.

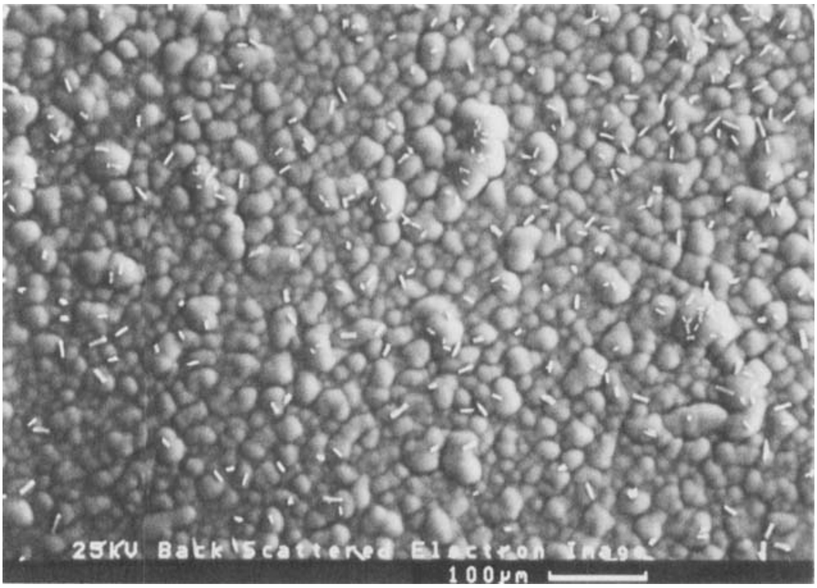

Figure 3 Electron micrographs of polypyrrole polymerised on platinum : image obtained with a Robinson back scattered electron detector, 25kV beam.

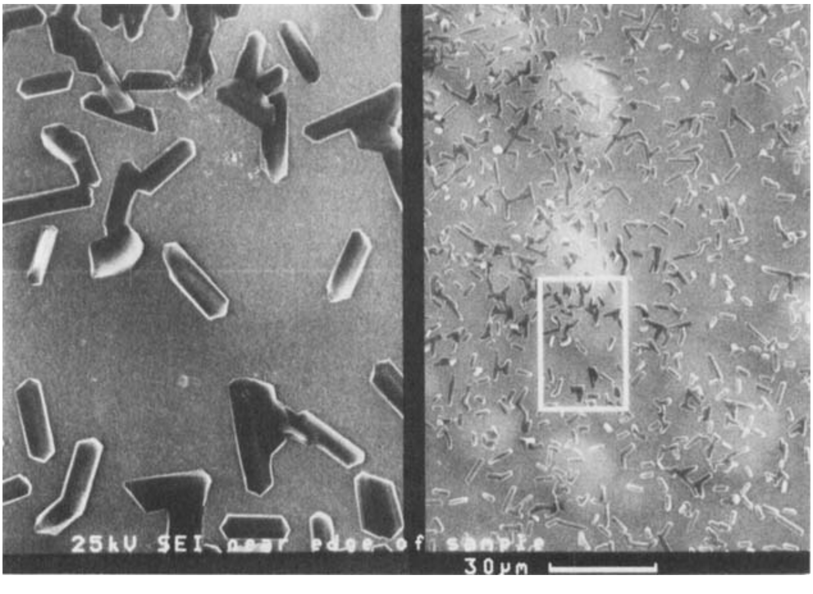

Figure 4 Electron micrographs of polypyrrole polymerised on platinum : SEI images at different magnifications, 25kV beam.

potential less than that required for pyrrole polymerization. Octachlororhenate electrochemistry occurs simultaneously with pyrrole polymerization. The product is a layered film with a strong X-ray reflection corresponding to a layer separation of about 3nm. TS containing films were dense and void free, for the remaining counter-ions the films were either voided or non-continuous on the growing surface. Electrical conductivities ranged from about 50 Scm^{-1} (TS films) to $2x10^{-3}$ Scm^{-1} (PSA film)), the former being the least voided film, the latter the most. The stability of the polymer films depends on the incorporated ion; PTSA containing films exhibit much greater resistance to degradation during electrochemical cycling than TS containing films.

In most respects the properties of the films differ. C:H:N ratios were markedly different and though for TS, PTS, DBS, the ratio of incorporated positive charge to pyrrole units is about 1:3, ratios of 1:1, 1:9 and 1:6 were found for PSA, DES and the chlororhenate ion respectively. Raman spectra for films containing different counter-ions have similar main bands, i.e. similar pyrrolic structures, but distinctly different detailed features, i.e. different local structures. These results suggest marked differences in the composition and microscopic structure of polypyrrole films containing different counter-ions. Despite this the optical spectra of reduced, partially and fully oxidised films display absorption bands with similar widths and energies. Thus the electronic states probed by optical absorption are insensitive to the details of polymer structure. These have been considered to be characteristic of bipolarons (dications) on defect free pyrrole chains. The fact that similar concentrations of perfect chains exist in such dissimilar materials is surprising. The alternative, that charge exchange occurs at localised defects, which occur in all the materials investigated, seems equally plausible. If more perfect material were available it would be possible to decide between these alternatives.

2.2 Oligopyrroles

Chemical synthesis of linear oligopyrroles is difficult for more than four or five repeat units. An alternative method is the electro-polymerization mixtures of 3,4-dimethyl- and 2,3,4-trimethylpyrrole (DPY and TPY). Use of DPY ensures ideal α - α linkages and the TPY acts as a chain terminator. Material is deposited as a black film from acetonitrile electrolyte and can be subsequently dissolved in common solvents, e.g. methanol, if the mean oligomer length is of the order 20 repeat units or less. Preparation and investigation of these oligomers have been reported in more detail elsewhere[9] and is reviewed briefly below. More complex terminating groups can be used with similar results.[10]

Oligopyrroles form true solutions which can be filtered unchanged through 0.1 μm pore filters. Laser light scattering gives an upper limit of 'particle' size of 5nm. Optical spectroscopy has been used to study solutions in different solvents and with different counter-ions.[9,11] These reveal structural relaxation, solvatochromic shifts and complex formation involving deprotonation. Spectra typically show three absorptions, an 'interband' transition at circa 3.3eV and 'bipolaron' peaks at circa 2.5 and 1.2 eV. Since the positive charges of the dication will not reside at the ends of the oligomers, excitation is possible in structurally unchanged regions at the ends of the oligomers. Solvation effects are consistent with screening of the positive charges by more polar solvents. The most dramatic effects occur with variation in counter-ion. For ions with greater proton affinity, e.g. Br^- and TS^-, the 'bipolaron' peaks move apart and weaken and finally disappear. Similar effects occur as the pH of methanolic solutions is varied.

Thus, the 1.2 and 2.6eV absorptions are characteristic of cations on pyrrolic chains. However, they are sensitive to changes in the environment of the oligomers, a sensitivity which is surpressed in polypyrrole. This suggests that the behaviour of polypyrrole is dominated by defects in the polymer, ie., oxidation and reduction occurs at defects. However, in this case the energy levels of the catonic defects must be similar to those of cations on ideal chains. More detailed studies of poly and oligopyrrole are needed to resolve this question. It should be noted that oligopyrrole solutions are stable over periods of years indicating that the degradation of polypyrrole is also controlled by defects.

2.3 Polyaniline

The role of protonation in the properties of polyaniline has been realised for some time.[12] The polymer can be prepared either chemically or electrochemically and details of structure depend on the exact method employed. Despite this and the acknowledged morphological complexity, the models used to describe the properties of the polymer have assumed ideal chains free from defects.

We have studied polyaniline prepared from HCl-water electrolyte.[13-15] The physical property studies have been reported previously and a few results will be highlighted below.

Polyaniline has two oxidation peaks. Various structures have been proposed for the three oxidation states. For fully protonated materials these have been described as benzenoid, 1:1 benzenoid-quinoid and quinoid structures respectively. Optical spectra were recorded as a function of oxidation state for different pH values. An isosbestic point is seen for the first oxidation peak only at low and intermediate pH it is lost at high pH. There is no isosbestic point at any pH value for the second oxidation peak. In situ ESR studies show reversible creation of paramagnetic species for the first oxidation peak and an irreversible generation for cycling beyond the second oxidation peak. This is accompanied by the growth of a third oxidation peak located between the intrinsic oxidation peaks in the cyclic voltammogram. The second oxidation peak therefore involves multiple reactions including hydrolysis in the aqueous medium employed. Near infrared spectra show that the lowest 'bipolaron' absorption band remains at finite energy, for all oxidation states. ESCA spectra do not provide any evidence for a closed gap but do indicate chemical reaction with the chlorine counter-ions. Finally resonant Raman spectroscopy reveals that the visible and NIR absorption bands derive from different chromophores. They are not, therefore, absorptions resulting from a single bipolaronic species. Thus, detailed examination of polyaniline reveals complex chemical behaviour which had not been adequately taken into account in the discussion of models of the electronic properties of the polymer.

3. CONCLUSIONS

Detailed investigations of conductive polymers show that many of the chemical and physical properties are influenced by the microscopic structure. In particular, deviations from ideal extended chain morphology, on which much theoretical discussion is based, play a crucial role in the behaviour of electrochemically prepared polyaniline and polypyrrole. This view is reinforced by the absence of the clear cut effects, seen in oligopyrroles with stereoregular structure, from polypyrrole obtained by a similar electrochemical route. Detailed structure-property evaluation is thus central to efforts to obtain a better understanding of the fundamental properties of conductive polymers. This will require purer, better oriented samples such as those obtained by the use of precursor polymers. Even in this case care must be exercised since orientation does not necessarily mean that the polymer chains are fully extended. Enhanced orientation by alignment of pre-existing microcrystallites is a well known effect. Whether the polymer chains are fully extended or not can be established by the observation of the anharmonic shifts in backbone vibrational frequencies for stressed samples. These are clearly seen for extended chains, e.g. polydiacetylenes[16], but are absent for oriented microcrystals, e.g. polyparaphenylene vinylene.[17]

The need for detailed characterisation of samples and for theoretical models incorporating realistic defect structures is now clearly recognised. As progress is made in both areas a more coherent picture of the interrelation of properties and structure of conductive polymers is emerging.

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