Molecular Crystals and Liquid Crystals

The Structure and Mechanical Properties of Polypyrrole

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THE STRUCTURE AND MECHANICAL PROPERTIES OF POLYPYRROLE.

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Abstract   The evidence for the presence of the pyrrole moiety in electro-chemically prepared polypyrrole is reviewed together with structural and IR data obtained for the crystalline dimer and trimer of pyrrole. The modification of the mechanical properties of polypyrrole by formation of graft copolymers with polystyrene, by polymerization of the pyrrole monomer within the matrix of a swellable polymer film and by polymerization of the pyrrole on vitreous carbon electrodes is described.

EVIDENCE THAT THE PYRROLE MOIETY IS MAINTAINED ON POLYMERIZATION.

Before discussing the structure of polypyrrole, it is important to assess the evidence that the pyrrole moiety persists in the polymer. Chemical analysis and coulometry measurements during preparation[1] and switching are consistent with the formation of the polymer occuring by elimination of 2 hydrogens from each pyrrole unit followed by linking the pyrroles together *via* the carbons from which the hydrogen was eliminated. The fact that the hydrogen on the β-carbons is largely retained has been demonstrated by studies of the polymerization of pyrrole tritiated at all four carbon sites. The XPS spectrum of conducting polypyrroles[2] shows the same features observed for pyrrole monomer. The ^{13}C NMR studies of both the neutral and oxidized forms of the polymer formed from pyrrole or β,β'-dimethyl pyrrole are both consistent with the presence of the pyrrole moiety.[3] In the case of the polypyrrole itself, the shift of the position of the α-carbon resonance which occurs on polymerization is consistent with the formation of an α-substituted pyrrole. Finally convincing evidence for the presence of the pyrrole moiety comes from the strong similarity of the IR spectra of the neutral form of polypyrrole with that of the dimer and trimer of pyrrole as will be discussed below.

STRUCTURE OF POLYPYRROLE AND PYRROLE OLIGOMERS

All forms of polypyrrole reported so far are extremely poorly crystalline, which means that much of our knowledge of the structure of these
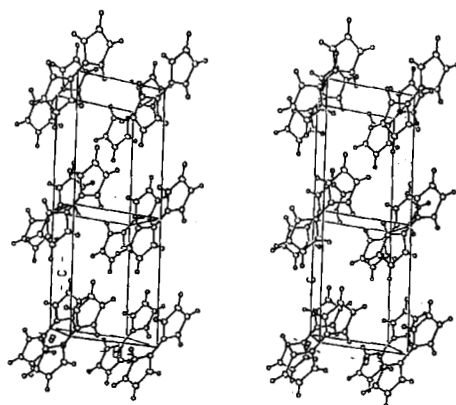
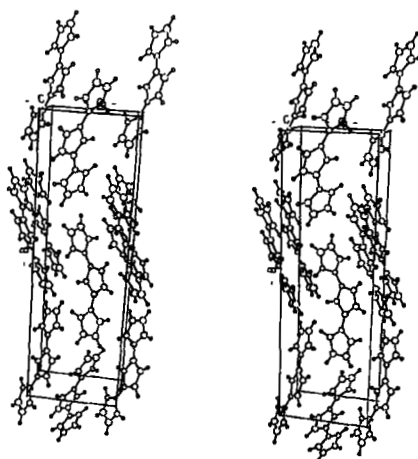G. B. STREET *et al.*

Figure 1. Monoclinic structure of pyrrole dimer.

Figure 2. Orthorhombic structure of pyrrole trimer.

systems is obtained from a variety of indirect measurements. Assuming a completely α,α -bonded polymer, a planar cyclic structure with all the pyrrole nitrogens pointed to the center, would require 10 pyrrole molecules to complete the ring. It has been suggested that the structure of polypyrrole is analogous to the ring structure of the porphyrins or phthalocyanines.[2] This would require considerable chemistry to take place to provide the NH or CH linkages between the pyrrole moieties necessary to form a planar ring from only four pyrrole rings and would be inconsistent with the coulometry. Alternatively, one could consider a spiral arrangement. However, we believe that a linear, completely planar, exclusively α,α'-bonded chain in which the orientation of the pyrrole molecules alternate is the best model for the ideal
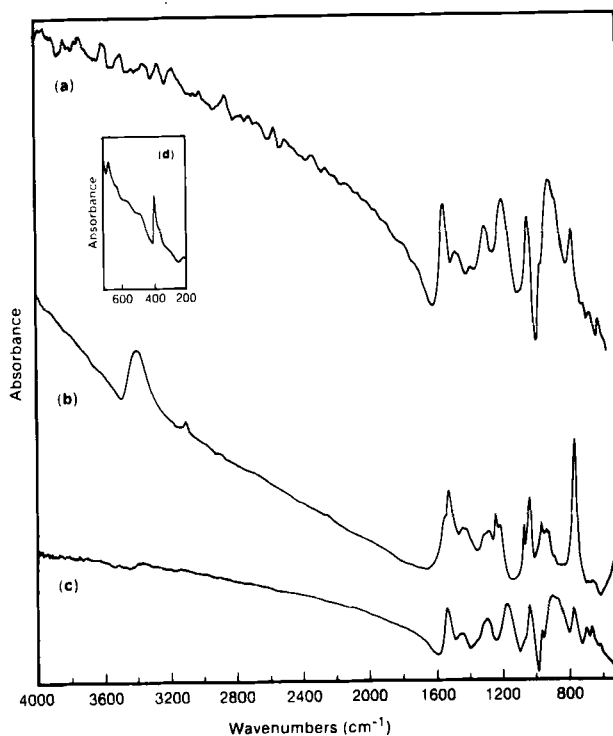

Figure 3. IR spectra of (a) polypyrrole perchlorate, (b) neutral polypyrrole ((a) and (b) have same thickness) (c) polypyrrole hexafluoroarsenate and (d) shows AsF_6^{-1} bands of the polypyrrole.

structure of polypyrrole. Electron diffraction studies[4] indicate that the chains lie flat in the plane of the film. The diffraction patterns of

β,β'-dimethylpyrrole show that within the plane of the films, the chains are oriented parallel to one another, whereas in polypyrrole itself, the alignment of the chains within the film plane is random. Strong evidence for the assumed planar chain geometry has now been obtained from an x-ray determination of the structure of pyrrole dimer and trimer. Both these molecules are linear and planar, with an alternating arrangement of the pyrrole rings. In the dimer, the pyrroles are stacked on top of one another in parallel chains (Fig. 1). A similar situation arises for the trimer, except that adjacent trimers in the chain do not lie in the same plane (Fig. 2).

IR SPECTRA OF POLYPYRROLE AND PYRROLE OLIGOMERS.

The infrared spectra of polypyrrole in its oxidized and neutral forms was first reported by Street *et al.*[5] The spectra of polypyrrole perchlorate and neutral polypyrrole films of the same thickness are shown in Fig. 3. The spectrum of the polypyrrole perchlorate shows a featureless decrease in absorption from 4000 cm^{-1} to 1600 cm^{-1}, which is the tail of the ~1 eV peak seen in the absorption spectrum.[6] The region from 1600 cm^{-1} to 400^{-1} contains the pyrrole ring vibrations and the perchlorate anion vibrations. The perchlorate bands are masked by the pyrrole ring vibrations, as were the tetrafluoroborate anion bands in the spectra published earlier.[5] In order to see the anion bands in the conducting polypyrroles, it is necessary to select an anion which absorbs in a window in the pyrrole spectra, *e.g.*, below 800 cm^{-1}. This can be done with the hexafluoroarsenate anion which absorbs at ~ 780 cm^{-1} and ~ 400 cm^{-1}, as shown in Fig. 3. In the region above 800 cm^{-1}, the spectra of the perchlorate polymer and the hexafluoroarsenate polymer can be overlaid, a convincing demonstration that the perchlorate bands are masked by those of the pyrrole moiety. The NH and CH bands are also not visible in the spectra of the conducting polypyrroles, because they are masked by the tail of the ~1 eV peak in the absorption spectrum. This ~1 eV peak is absent in the neutral form of the polymer, and the NH and CH bands can then be seen (Fig. 3). The bands in the region below 1600 cm^{-1} are similar in the oxidized and neutral polymer, as would be expected, because they contain the same pyrrole moiety; however, this similarity may also be due, in part, to the fact that the neutral polymer has become slightly oxidized, a difficult problem to avoid experimentally. The spectra of pyrrole dimer and trimer are shown in Fig. 4. Comparison of these spectra with that of neutral polypyrrole provides convincing proof that the structure of the polymer chain is predominantly the same as in these oligomers *i.e.*, an α,α'-bonded planar linear chain.
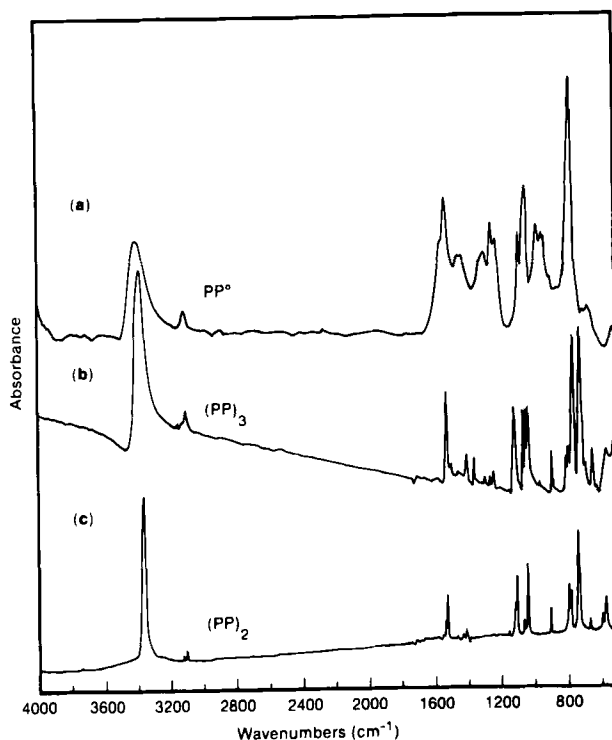
Figure 4. IR spectra of (a) neutral polypyrrole (same as Figure 3b) but base line has been linearized), (b) pyrrole trimer and (c) pyrrole dimer.

Before leaving the description of the IR spectra of these polymers, it is interesting to note, that there is an important distinction between the changes observed in the spectra of neutral polypyrrole on oxidation, and those observed on oxidation of neutral polyacetylene.[7] In the case of polyacetylene, the spectrum of the neutral polymer is characterized by a series of sharp peaks, whereas that of the oxidized polymer consists of a few, more intense, very broad peaks. The situation is completely different in the case of polypyrrole, where both the neutral and oxidized forms of the polymer are characterized by similar relatively sharp spectra. Although the intensity enhancement of the spectrum of the oxidized form of the polymer is noticeable, relative to the neutral form (Fig. 3), the degree of enhancement is much less than observed by Rabolt et al.[7] in the case of polyacetylene. The reasons for these differences are not yet understood. It is interesting to note that the

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spectra of other conducting polymers, which like polypyrrole, have nondegenerate ground states, show changes in spectral features on oxidation which are more similar to the case of polypyrrole, than polyacetylene. These differences may also relate to the fact that polypyrrole, unlike polyacetylene, never becomes metallic even at the highest doping levels achievable.

CHAIN LENGTH IN POLYPYRROLES

Electrochemically prepared films of polypyrrole have the mechanical properties, usually associated with somewhat a fairly high molecular weight polymer. However the insolubility of the polymer prevents a direct determination of the molecular weight. Fortunately in the case of the β,β'-dimethylpyrrole polymer, the molecular weight has been measured directly by radiochemical techniques, using the corresponding α,α'-tritiated monomer.[8] electrochemically polymerized, all the tritium is eliminated except that located at the chain ends. The average chain length can then be determined by comparing the activity of the monomer, with that of the final polymer. It was demonstrated, that under the conditions of the experiment, the tritium in the polymer did not exchange with the solvent, or with the hydrogen on the nitrogen. The average molecular weight determined in this fashion varied between 100-1000 pyrrole units depending on the polymerization conditions. If all of the α,α'-protons are not eliminated, then this number of 100-1000 pyrrole units represents the average separation along the chain between pyrrole rings containing a tritium atom, and is the upper limit for the average conjugation length and the lower limit for the average molecular weight. Obviously, the chain length of polypyrrole itself could be very different, particularly in view of the involvement of the β-carbons in the chain linking in this case.

MECHANICAL PROPERTIES OF POLYPYRROLE

The mechanical properties of polypyrrole are enhanced by incorporating 4-toluenesulfonate as the counter ion.[9] We have now found three other ways of manipulating the mechanical properties: by forming graft copolymers, by polymerizing the pyrrole in the matrix of a swellable polymer and by using vitreous carbon as the cathode material.

PYRROLE-STYRENE GRAFT COPOLYMERS.

Copolymers offer a versatile approach to the systematic modification of the mechanical properties of polypyrrole. In general copolymers exhibit physical and mechanical properties far different than those of homopolymers, and different from those of blends of the same individual homopolymers. The properties of copolymers can be modified by systematically varying

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the nature, number, and ratios of the polymers copolymerized with polypyrrole. We describe here the pyrrole-styrene copolymer system.

Styrene was copolymerized with 4-chloromethylstyrene[10] in a 9:1 ratio (neat) using 2,2′-azobis(2-methylpropionitrile) as a radical initiator(1%). The polymerization was allowed to proceed for 3 days at 80 C°. and the copolymer was then purified by repeated precipitation from a dichloromethane solution by adding to hexane. No attempt was made to characterize the molecular weight or molecular weight distribution of the polymer, but elemental analyses indicated that the copolymer (I) contained about 12% chloromethyl groups. The copolymer was dissolved in THF and added to a THF solution of potassium pyrrole at reflux and allow to react overnight. The new copolymer (II) was purified in a similar manner as (I). Elemental analysis of (II) indicated that about half of the chloromethyl groups had reacted with the potassium salt.
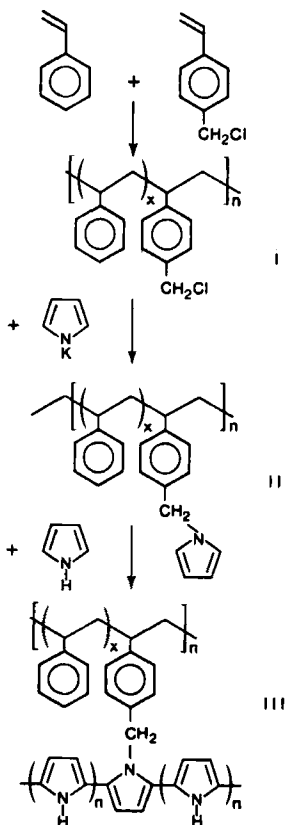

Figure 5. Reaction scheme for preparation of pyrrole-styrene graft copolymers.

This copolymer(II) was then used to grow the the graft copolymer (III) by electrooxidation in a one compartment electrochemical cell with 2 platinum electrodes. The electrolyte solution consisted of 0.1N tetrabutylamonium tetrafluoroborate, 0.1N pyrrole and a varying amount of (II) in dichloromethane. This reaction scheme is summarized in Fig. 5. The films were grown at a constant current density of about 0.1 mA/cm^2 The films produced vary in their properties depending on the initial ratio of (II) to pyrrole. Films with high concentration of (II) were tough and brittle like polystyrene but with electrical conductivities ~10 S/cm similar to polypyrrole. Films with low concentrations of (II) had higher conductivity ~50 S/cm but their mechanical properties were similar to polypyrrole tetrafluoroborate.

This polymer system is but one of several that can be synthesized in a similar manner For example the chloromethylstyrene can be copolymerised with many commercially available vinyl-type monomers and combinations of these monomers. The chloromethyl group will still be available both before and after polymerization to be derivatized with pyrrole and then used in the manner described above to give large variety of pyrrole copolymers.

CONDUCTIVE COMPOSITES FROM SWELLABLE POLYMERS AND POLYPYRROLE

This approach involves electrochemically polymerizing the pyrrole in the matrix of a polymer attached to the electrode. The requirements of the host polymer are that it have superior mechanical properties to polypyrrole and that it swell in the electrolyte solution, permitting the electrolyte solution access to the oxidizing electrode surface. Under these circumstances the polypyrrole then grows in the matrix of the swelled polymer producing a composite combining the conducting properties of polypyrrole with some of the superior mechanical properties of the host polymer. We have utilized this technique to grow conducting composites of polypyrrole with polyvinyl alcohol (PVA) from aqueous electrolyte solutions in an attempt to improve the mechanical properties of the aqueous prepared polypyrrole films which are inferior to similar films grown from acetonitrile solutions.[11]

Composite films of PVA/polypyrrole (PVA/PP) were prepared in a one compartment, two electrode cell. The electrolyte was a 0.1M CuSO$_4$, 0.1M pyrrole in water.[12] The anode was a platinum coated glass slide, on which a 3-4μ thick film of PVA had been spin-coated from a 10% aqueous PVA solution. This film on the electrode was heated at 60° C for 30 min. and then 150° C for 30 min., to cause partial cross-linking such that the PVA became sufficiently water insoluble but still water swellable. The solubility of the PVA was also controlled without thermal cross-linking by using 50/50 mixtures of water/acetonitrile as the electrolyte solvent.

As the electrochemical polymerization of the pyrrole proceeds, the PVA film darkens, indicating the growth of PP within the swollen polymer matrix. The final thickness of the composite is always greater than the initial PVA film. By controlling the polymerization time, composites can be

produced which are equally conducting on both sides, or conducting on one side but not on the other.   If PP is allowed to grow for sufficiently long periods of time PP forms throughout the matrix and a PP film also begins to grow on the solution side of the PVA/PP matrix, giving a laminated film. However if the PP is grown for a shorter time such that the PP has not had time to grow throughout the matrix then depending on the current density either those regions of PVA adjacent to the electrode or those regions of the PVA adjacent to the electrolyte interface remain insulating. At high current density, the polypyrrole forms initially at the solution/ PVA interface whereas at lower current densities the polymerization takes place initially at the electrode/ PVA interface.This suggests that the diffusion of the pyrrole in the PVA is slow and is limiting the polymerization process at high current densities. The rate of polymerization of the pyrrole must depend on the rate of diffusion of the pyrrole monomer to the electrode which in turn must be dependent on the extent of the swelling of the matrix polymer and perhaps the existence of channels within the matrix. The composites have good mechanical strength and can be readily peeled off the electrode, using a razor blade, to give free-standing films.   The electrical conductivity of these PVA/PP composite films is in the range of 0.1-10 S/cm compared to 1-30 S/cm observed for regular PP films grown from aqueous solution.[12]   The composites show negligible change in their electrical conductivity on expo- sure to the atmosphere as is observed for polypyrrole itself.

The mechanical properties of the PVA/PP films, are superior to those of the aqueous prepared films of PP sulfate. The former are flexible and can be creased without breaking whereas the latter are very brittle, much more so than similar films prepared from acetonitrile solution. Although the Young's modulus is much the same for both kinds of films, the ultimate tensile strength for the composites increases by a factor of two, while the elongation to break increased by a factor of 10.

Thus PVA/PP composite films can be prepared electrochemically which combine the advantageous mechanical properties of the host polymer with the electrical properties of PP. This technique can also be employed to grow composites of polyvinyl chloride and PP[13] and is readily applicable to other host polymers as well as other electrochemically prepared conducting polymers.

PREPARATION OF POLYPYRROLE ON VITREOUS CARBON ELECTRODES

Polypyrrole can be grown on vitreous carbon electrodes.[14] These electrodes permit the use of high voltages and high currents which allows growth of thick films in relatively short times. The films adhere well to the carbon electrodes but may be readily peeled off. Using 10 cm x 10cm elec- trodes ~ 74 mm apart, in a one compartment cell, with 3V across the elec- trodes the current was ~80mA and a ~ 100μ thick film was obtained in 2-3 hrs. The supporting electrolyte was tetraethylammonium toluenesulfonate dissolved in acetonitrile which was not dried or deoxygenated. The electrolyte

salt, which is very hydroscopic was also not dried before use. The films obtained in this way had excellent mechanical properties. They were tough and flexible and could be stretched by as much as 60%. The tensile strength of the films is $\sim 3 \times 10^3$ psi and a Youngs modulus of 1×10^5 psi. The films are plasticized by acetonitrile/ water from the electrolyte solvent. Drying the films in vacuo causes the modulus and tensile strength to increase by $\sim 33\%$ and the elongation to break to decrease to $\sim 15\%$. The degree of oxidation of these films was significantly higher than has been observed in previous polypyrrole films. Chemical analysis gave 0.43 toluenesulfonate anions per pyrrole. Despite the fact that the anion comprizes more than 50% of the weight of the polymer the electrical conductivity was ~ 100 ohms^{-1}cm^{-1}.

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