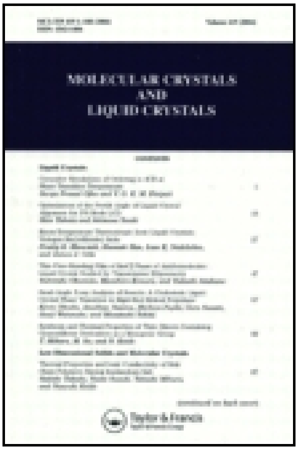

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Characterization of Polypyrrole

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CHARACTERIZATION OF POLYPYRROLE

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Abstract The renewed interest in the conducting polymer polypyrrole in 1968 was due to the efficient electrochemical synthesis of the polymer which made it possible to grow thin films with appropriate mechanical properties to facilitate the characterization of the polymer. Since then we have been able to grow thick films of polypyrrole with very good mechanical properties without compromising their electrical properties. In addition, good films can also be grown from aqueous media. Modifications can be achieved through copolymers with N-methylpyrrole and by alloying with other polymers. An insight into the structure of the polypyrrole polymers can be gained through the x-ray structural determination of some oligomers of pyrrole.

INTRODUCTION

Polymers of pyrrole have been known for a long time. They were produced by chemical oxidation of pyrrole[1]. The lack of interest and poor characterization of these polymers was due to their lack of solubility and poor crystallinity. Despite these difficulties it was established the these polymers consisted of intact pyrrole units linked predominantly at the α,α' carbons. Linkages through β carbons contributes to the disorder of the polymer making classical structural characterization techniques difficult. Improved electrochemical techniques which were developed later to prepare free standing films of the polymer with good physical properties[2] helped to rearouse interest in these polymers. This was largely due to the good mechanical properties of the polymer which are comparable to carbon filled polymers[3]. Another attractive feature is the stability of the oxidized conducting form of polypyrrole. The conductivity of films which have been exposed to air for a period of one year decreased only by 20%.

MECHANISM OF POLYMERIZATION

The electrochemical polymerization of pyrrole involves the generation of the radical cation at the anode. Chain propagation proceeds by the coupling of two radical cations and the elimination of two protons to produce a neutral dimer. The oxidation potential of the dimer and higher oligomers is less than that of the monomer[4] and they are oxidized further to the corresponding radical cation which will react with other radical cations present, (mostly monomers), to elongate the chain. We have shown that the presence of the monomer cation is not essential for the formation of the polypyrrole as it can be formed using bipyrrole or terpyrrole as starting material. When chains becomes sufficiently long they will become insoluble and precipitate on the electrode. From elemental analyses the composition of the final polymer corresponds to the presence of one positive charge on the backbone of the polymer every 3-4 pyrrole rings[5].

PREPARATION

The original preparation of polypyrrole used aqueous solution of pyrrole acidified with sulfuric acid[1]. The conductivity of the polymer produced was good ~10 S/cm however their mechanical properties were poor when compared to films produced in acetonitrile[2]. We have now found that films with good electrical properties can be grown from aqueous solution of copper salts. The presence of copper ions in solution provides a facile reduction reaction on the cathode by depositing copper. Using this method many multivalent ions can be incorporated in the polymer. It is interesting to note that the presence of multivalent ions does not change the degree of oxidation of the polypyrrole produced. In contrast to films grown in acetonitrile in an inert atmosphere the stoichiomerty of films grown from water is not as well defined and contain excess oxygen even though the nitrogen to carbon ratio is close to 4:1.

Smooth thick films of polypyrrole can be grown quickly from acetonitrile if glassy carbon is used as a working electrode. Films hundreds of microns thick can be grown in relatively short periods. They have good electrical and excellent mechanical properties[6].

MODIFICATION OF POLYPYRROLE

Copolymers of pyrrole and N-methylpyrrole have been used to modify the conductivity of polypyrrole[5]. Alloys of polypyrrole in combination with other insulating polymers can also be prepared. Those alloys are prepared by coating a working electrode with a suitable polymer such as partially crosslinked polyvinyl alcohol[7] or polyvinyl chloride[8,9]. This coated electrode is then used in an appropriate solvent to grow polypyrrole in the matrix of that swellable polymer.

Another approach is to graft the polypyrrole to a polymer with the desired physical properties. As an example polystyrene can be modified by attaching pyrrole to some of its building blocks[10](Fig. 1).

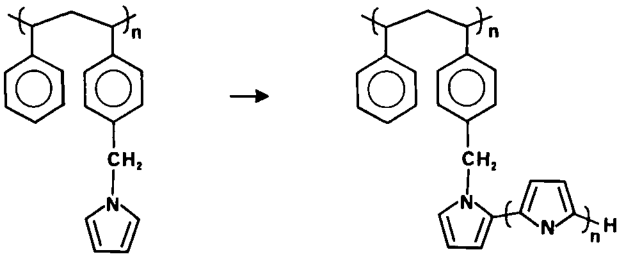

FIGURE 1

Using that modified polymer one can grow polypyrrole using the attached pyrrole as anchor points to the other polymer. This results in a copolymer with some of the properties of both polymers. The properties of the resulting composite can be varied over a wide range by varying the relative concentration of polymers involved.

CHAIN LENGTH OF POLYPYRROLES

Although no way has yet been found to measure the chain length of polypyrrole itself, that of β,β'-dimethylpyrrole can be conveniently measured using a tritiated monomer in the α position[11] (Fig. 2).

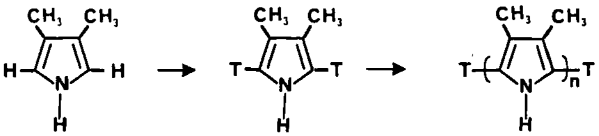

FIGURE 2

Assuming that the tritium in the final polymer is located at the chain ends, the average number of repeat units can be determined by comparing the activity of the polymer with that of the monomer. The average repeat unit determined in this fashion varied between 100-1000 dimethylpyrrole units depending on preparation conditions. If all the protons at the α-position were not eliminated this number would represent the average separation of pyrrole units containing tritium and would be the upper limit of the average conjugation length of the polymer. Obviously the chain length of polypyrrole itself can be different in view of the involvement of the β carbon in the chain linking.

STRUCTURAL MODEL FOR POLYPYRROLE

It is usually assumed in a ideal structure ignoring the presence of non α,α' bonding that polypyrrole has an alternating structure of pyrrole rings. This assumption is required if polypyrrole is to be a linear polymer of considerable number of repeat units. The presence of non α,α' bonding will give rise to bend in the chain and is

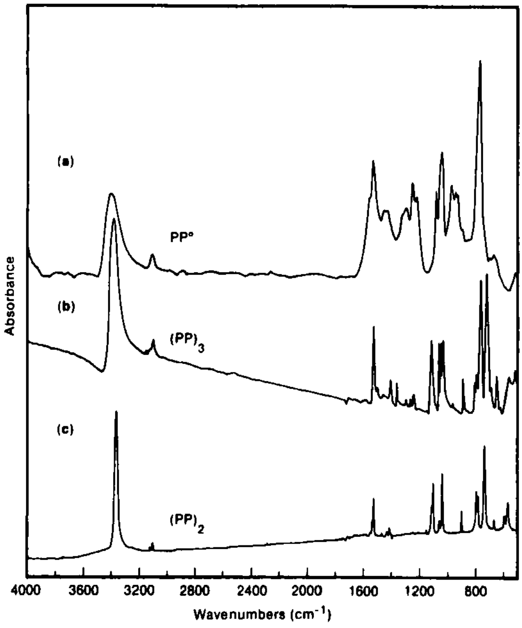

FIGURE 3

probably responsible for the large degree of disorder present in the polymer. The assumption that the polymer is linear with alternating rings is made more valid by ir and x-ray structural data on some oligomers of pyrrole namely bipyrrole and terpyrrole.

The X-ray structural determination of bi-and terpyrrole reveals a structure of coplanar ring in both molecules with the nitrogen in the ring occupying alternate sites. The pyrrole ring itself is not very different than that in pyrrole. The bond length between the rings is about 1.45 A° somewhat less than a single bond but larger than a double bond which indicates some degree of conjugation between the rings.

The ir spectra of neutral polypyrrole $(PP)^{\circ}$ shows a great deal of similarity to that of bipyrrole (PP)2 and terpyrrole (PP)3 (Fig. 3). This strongly suggests that the pyrrole rings in the polymer are still largely intact. It also suggest a large degree of similarity in the structure of the dimer and trimer to that of polypyrrole

CONCLUSION

The idealized structure of polypyrrole seem to be that of a linear polymer of intact pyrrole rings with the nitrogen occupying alternate positions. It has a molecular weight in the range of 10000-100000.

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