

# ON THE STRUCTURE AND TRANSPORT PROPERTIES OF POLYPYRROLES

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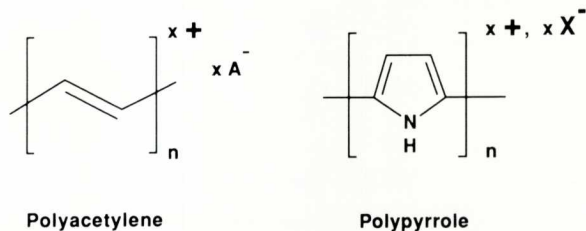
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Conducting organic polymers have attracted much attention as electronic materials, since Shirakawa et al. reported [1] an increase of several orders of magnitude in the electrical conductivity of polyacetylene after reaction with oxidants. This oxidative process - giving positively charged structures - is known as «doping» owing to its analogy with the doping process for inorganic semiconductors. However, from a chemical point of view, the two types of doping correspond to different types of chemical transformation [2]: the oxidative process upon the non-conducting neutral polymer results in an positively charged oxidized molecule which in its solid structure requires the incorporation of a counter anion. Obviously, the nature of this anion determines the physical properties of the material.

In spite of the high electrical conductivities reported for polyacetylene [3] (see Scheme 1) it rapidly degenerates in air. Other  $\pi$  conjugated organic conductors are thus attracting more attention for technical applications. One of these organic polymers is polypyrrole, films of which show a wide range of potential applications [4]. However, neither the chemical structure of polypyrroles in their reduced (electrically isolating:  $\sigma = 10^{-8} \text{ S cm}^{-1}$ ) or oxidized forms (conducting:  $\sigma = 10^2 \text{ S cm}^{-1}$ ) nor the role of the ions acting



Scheme 1

as dopants is clear at the present. In this paper we report on the more important questions about polypyrrole structure and on our results which are related to this topic.

The preparation of thick films of organic polymer conductors is usually carried out by oxidative coupling of the monomer to the polymer and simultaneous oxidation of the polymer to its charged conducting form. The anodic oxidative electrodeposition of the polymer from monomer solutions is the most usual method. In this method the «doping» counter anion is the corresponding anion of the supporting electrolyte.

Industrial applications of organic conductors depend on progress in the preparation of reproducible structural materials. In this sense, the dependence of the physical properties of materials, particularly in the case of polymers, on the hierarchical organization of the structure from the molecular- to the macrolevel is well known [5]. However, before studying the effect of the physical properties of polypyrrole on the organization of its structure at the micro- and macrolevels, efforts should first be directed to understanding its structure at the molecular- and nanolevels. In contrast to the non-conducting organic polymers, and despite the wide range of publications on polypyrrole and other related organic conductors, many aspects of its molecular structure are not yet understood.

Polypyrrole structure is very difficult to characterize because no solvent has yet been found to yield single crystals and little information has been obtained from X-ray diffraction studies, principally as a consequence of polymer degradation. Nevertheless, some results have been obtained from X-ray, neutron and electron diffraction techniques [6,7]. Polypyrrole (electrochemically obtained) is poorly crystalline, with crystalline regions mostly random oriented and the polymer chains lying with the pyrrole rings coplanar to the film surface. Actually, polypyrrole films obtained so far in practice are structurally disordered. In fact, they show a charge-transport mechanism with similarities to the amorphous semi-conductors of tetrahedral type [8]. The semiconductor character and the positive charge carriers of polypyrrole are shown by the temperature variation of its thermoelectric power (see Figure 1). As in the case of amorphous semiconductors, polypyrrole shows an electrical conductivity ( $\sigma$ ) according to the Mott law of variable range hopping:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{4}}$$

(see e.g. Figure 2). However, polypyrrole also presents experimental evidence of the presence of bipolaron carriers, i.e. spinless dications trapped on its own phonon coupling. The microscopic hopping mechanism in polypyrrole is not

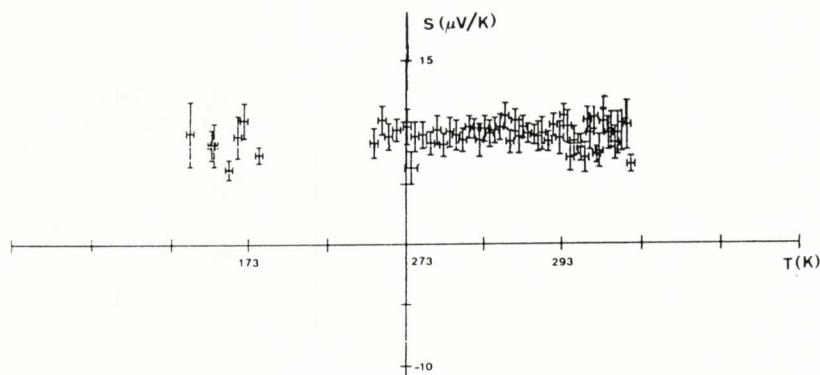


Figure 1. Variation in thermoelectric power ( $S$ ) with temperature ( $T$ ) for *p*-toluensulphonate doped polypyrrole (0.15 mm thick film).

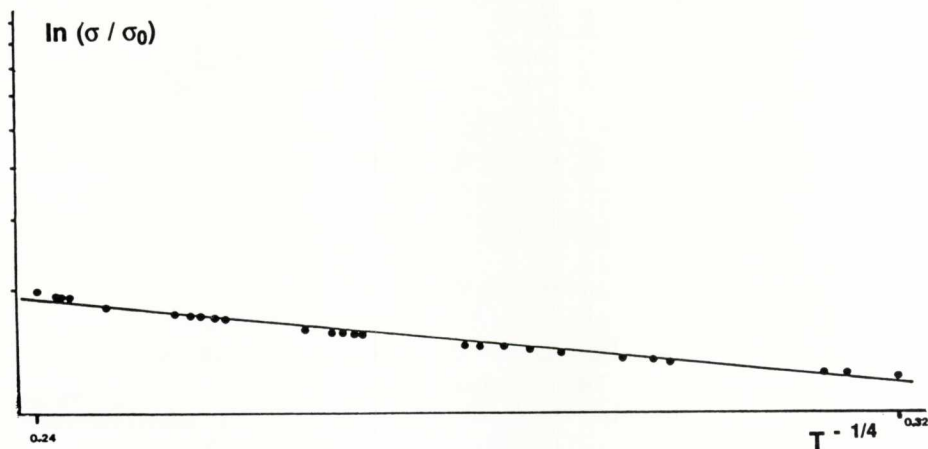


Figure 2. Variation of electrical conductivity ( $\sigma$ ) with temperature ( $T$ ) [ $\ln(\sigma/\sigma_0)$  in front of  $T^{-1/4}$ ] for *p*-toluensulphonate doped polypyrrole.

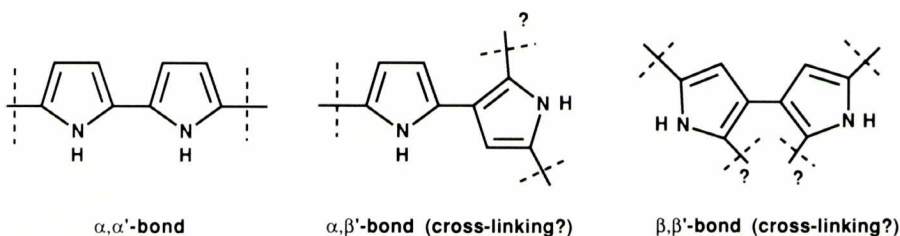
known, but a bipolaron hopping mechanism is probably acting. The degree of disorder in polypyrrole is fairly high and they are other hopping mechanisms at higher organization levels, which do not allow to infer the mechanism at microscopic level.

For an ideal structure of polypyrrole this bipolaron hopping mechanism could be more effective than the bipolaron mechanism of charge transport in the polymer chain. The preparation of more ordered and crystalline structures of polypyrrole is needed to determine the conducting mechanisms of polypyrrole. Furthermore, these studies are necessary in order to establish the industrial potential of organic conductors of polymer type.



*Primary structure of the polypyrrole chain*

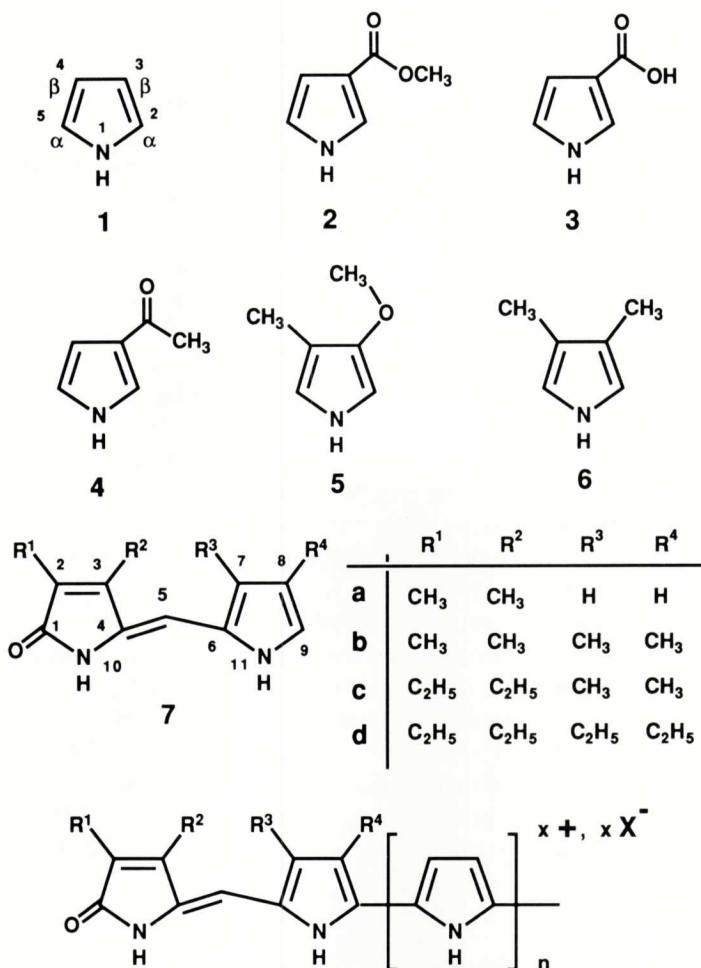
The commonly accepted structure of polypyrrole is that of a plane array of the monomer joined by  $\alpha, \alpha'$  bonds. However, its physical data point to more disordered structures. The most important factor in the structural disorder in polypyrrole is probably the presence of bonds other than the ideal and predominant  $\alpha, \alpha'$  bonds (see Scheme 2):  $\alpha, \beta'$  and  $\beta, \beta'$  bonds introduce structural disorder in the polymer chains but the presence of  $\beta$  bonds in addition to the  $\alpha, \alpha'$  ones could result in polymer cross-linking. Another important aspect concerning the structure of polypyrrole at the molecular level is the chemical state of the oxygen, which is irreversibly absorbed and remains in significant amounts.



Scheme 2

With these two targets in mind - presence of other C-C bonds apart from or in addition to the  $\alpha, \alpha'$  links and the chemical state of the absorbed oxygen - we have performed the electrochemical synthesis of polypyrroles from some  $\beta$ -substituted monomers (1-6, see Scheme 3) and from the copolymerisation of pyrrole (1) or 3,4-dimethylpyrrole (6) with dipyrin-1(10*H*)-ones (7), which act as polymer end groups. The comparison of these copolymers with the polymers obtained from pyrrole alone (1) in the same experimental conditions gives structural information about polypyrrole, e.g. chain length and the presence or not of cross-linking. These results have been published in more detail elsewhere [9]. Here we only report them in summary and in relation to structural aspects of polypyrrole.

The polymer obtained from pyrroles substituted by electron withdrawing groups (2,3 and 4) is an electrical insulating material, which stops the growth of the anodic material after the deposition of the first monolayers [9b]. In contrast, the pyrroles substituted by electron donor groups (5 and 6) give conducting polymer films. Poly(3,4-dimethyl pyrrole) has already been described in the literature [10]. It shows physical properties analogous to those of polypyrrole but with lower electrical conductivity. One characteristic this polymer is its hydrogen content (see Table 1), which is higher than that corresponding to the ideal formula



**Polypyrrole with dipyrrole-1(10H)-one end group**

Scheme 3

and that normally reported for other polypyrroles. This observation has been attributed to the presence of saturated carbon atoms in the rings [10], the presence of which would reduce the electrical conductivity as a consequence of the shortening of the  $\pi$  conjugation. Furthermore, their presence would indicate that non-oxidative acid catalyzed polymerisation of pyrrole competes with the expected oxidative polymerisation. This interpretation should be taken into account in the design of preparation methods for structural non-disordered polypyrrole.

Poly(3-methoxy-4-methyl pyrrole) is a new polymer, which in contrast to poly(3,4-dimethyl pyrrole), shows electrical conductivity and thermopower coefficient of the same order of magnitude as polypyrrole obtained in the same experimental conditions. Unfortunately, film preparation of poly(3-methoxy-4-methyl pyrrole) is not easy, as it is sensitive to many factors which govern electrochemical synthesis. The results shown in Table 1 correspond to the only set of experimental conditions which enabled us to obtain preparative films.

In the case of  $\beta,\beta'$ -disubstituted monomers the yields of deposited polymer are lower and the relative amounts of soluble fractions higher than for polypyrrole. These results point out to the presence of branching and cross-linking in polypyrrole: reticulation would transform soluble short polymer chains into insoluble polymer. The presence of cross-linking is confirmed by the results of our copolymerisation experiments of pyrroles with 7 (see Table 2): in the case of pyrrole (1) copolymerisation generates materials which are very similar to the parent polypyrrole, but incorporating end groups in the approximate ratio (determined by chemical analysis) of two end groups every 20-50 rings. According to reported data [11], such polypyrrole chains, in the absence of cross-linking, would be soluble (in acetonitrile or propylene carbonate as electrolysis solvents). In the case of the copolymerisation experiments of the  $\beta,\beta'$ -disubstituted monomer 6 with derivatives of type 7, no end groups were detected in the small amount of polymer deposited. Furthermore, a high amount of soluble material was isolated.

In summary, from our results and from the results previously reported in the literature, the presence of  $\beta,\beta'$  cross-linking is inferred from the following findings:

– Studies on  $\beta,\beta'$ -dimethyl pyrrole polymer [11], which cannot give  $\beta,\beta'$  cross-linking, show that the polymer chain length should be between 100 and 1000 pyrrole rings. It is also known that  $\beta,\beta'$ -dimethylpyrrole chains about 20-40 rings are soluble materials [12].

Table 1. Properties of p-toluenesulphonate (PTS) doped films (0.1 to 0.3 mm thick) obtained by galvanostatic preparation at Pt-coated titanium electrodes ( $0.7-1.0 \text{ mA} \cdot \text{cm}^{-2}$ ; corresponding to potentials about 0.05-0.1 V below the monomer  $E_p$ ).

Polymer monomer	Conductivity <sup>a)</sup> ( $\text{S} \cdot \text{cm}^{-1}$ )	Thermopower ( $\mu\text{V} \cdot \text{K}^{-1}$ )	Density <sup>b)</sup> ( $\text{g} \cdot \text{ml}^{-1}$ )	Elemental analysis <sup>c)</sup>
1	3	$8 \pm 1$	1.3	$\text{C}_{4.15}\text{N}_{3.53}\text{N}_{1.00}\text{PTS}_{0.28}\text{O}_{0.41}$
5	2	$9 \pm 1$	1,24	$\text{C}_{5.99}\text{H}_{7.21}\text{N}_{1.00}\text{PTS}_{0.33}\text{O}_{1.37}$
6	$2 \cdot 10^{-4}$ <sup>d)</sup>	...	1.37	$\text{C}_{6.18}\text{H}_{7.98}\text{N}_{1.00}\text{PTS}_{0.32}\text{O}_{0.48}$

a) four-point method.

b) flotarium method.

c) oxygen directly: PTS doping level direct from S analysis.

d) pressed pellet.

Table 2. Data of preparative films obtained from pyrroles (1 or 6) and from copolymerisation of pyrroles with dipyrin-1(10H)-ones (7) (molar ratio 10:1):  $0.05 \text{ mol} \cdot \text{l}^{-1}$  supporting electrolyte solutions (for details see ref. 9).

Supporting electrolyte <sup>a)</sup>	Solvent <sup>b)</sup>	Monomers	Film thickness (mm)	Density <sup>c)</sup> ( $\text{g} \cdot \text{ml}^{-1}$ )	Film Properties Conductivity <sup>d)</sup> ( $\sigma \cdot \Omega^{-1} \text{ cm}^{-1}$ )	Elemental analysis molar ratios <sup>e)</sup>				
						C	H	N	O	
TBAP	AN	1	0.2	1.43	28	4.03	3.28	1.00	0.29	0.33
		1 + 7a	powderf)	...	...	4.25	3.42	1.00	0.30	0.26
		1	0.3	1.36	3	4.26	3.53	1.00	0.50	0.26
TEAPTS	PC	1 + 7a	0.1	1.36	4	4.74	3.87	1.00	0.58	0.22
		1	0.6	1.37	3	4.15	3.54	1.00	0.41	0.28
		1 + 7a	0.6	1.31	4	4.28	4.27	1.00	0.59	0.20
	AN	6	0.1	1.30	0.05	6.18	7.98	1.00	0.48	0.32
		6 + 7c	0.08	1.30	0.05	6.18	8.07	1.00	0.43	0.34
		6 + 7d	very thin	1.30	...	5.22	8.01	1.00	0.45	0.30
TBATF	PC	1	0.2	1.42	51	4.04	3.19	1.00	0.72	0.25
		1 + 7a	0.2	1.45	37	4.21	3.21	1.00	0.63	0.25
	AN	1 + 7b	0.3	1.48	19	4.33	3.72	1.00	0.74	0.34
		1	0.2	1.42	31	4.02	3.46	1.00	0.72	0.20
		1 + 7a	0.7	1.37	2	4.28	3.75	1.00	0.63	0.21

a) tetrabutylammonium perchlorate (TBAP), tetraethylammonium p-toluensulphonate (TEAPTS), tetrabutylammonium tetrafluoroborate (TBATF).

b) propylene carbonate (PC), acetonitrile (AN).

c) flotation method.

d) four-point method.

e) C, H, N and O calculated from direct analysis; oxygen values on the table do not include oxygen content of the doping anion. Doping anion evaluated indirectly in the case of TBATF and from the Cl and S direct analysis in the case of TBAP and TEAPTS.

f) film converts to a powder during the wash up procedure with methanol.



– Copolymerisation of pyrrole (1) with pyrroles substituted in one of its positions (7) results in materials [9a,9d] with similar physical properties to the parent polypyrrole. Such copolymerisates show two end groups every 20-40 rings and are insoluble.

These results indicate that linear polypyrroles are insoluble (acetonitrile or propylene carbonate) for chain lengths about 50 rings and that polypyrrole is a mixture of chains of very different length, the shorter ones being insoluble because of the presence of cross-linking. The presence of these  $\beta, \beta'$  bonds giving cross-linking also implies the presence of other  $\alpha, \beta'$ - and  $\alpha' - \beta$ -bonds, which will generate structural disorder, because of the changes in chain linearity and planarity (see below).

The high oxygen contents reported in Tables 1 and 2 (1 *O* for 1.3 - 3 *N*) are typical for polypyrrole. The presence of oxygen, not deliberately introduced through some species (pyrrole substituent or doping anion), may be attributed to two origins: it is incorporated to the film either during its growth from the nucleophiles of the medium (e.g. water) or from air contact. In our case, most of the oxygen must derive from air dioxygen adsorbed after the film preparation, owing to the low water contents of our electrolyte solutions and the absence of dioxygen during the electrolysis (Ar atmosphere). The irreversibility of this oxygen absorption [13,14] points out to the covalent bonding of oxygen with the polymer. From XPS data N-oxide [15,16] and peroxide [9c] functional groups have been proposed to be present in doped polypyrrole.

An accurate description of the primary structure of conducting polypyrrole must take into account the doping ratio, i.e. the content of doping anion, and the distribution of the positive charges in the polymer. To our knowledge polypyrrole dopant molar ratios relative to nitrogen above 0.33 have not been reported [9d], but values of 0.33 or thereabouts appear frequently. Values near to 0.25 are also common for complete polypyrrole doping. According to our results and the reported ones in the literature, values near to 0.25 or to 0.33 appear more often than intermediate values. Doping values under 0.25 are attributed to incomplete doping, which has been linked -through its relation with ESR signals, electronic absorption spectra and electrical conductivity values- to polaron charge transport mechanism. On the other hand, complete doping shows evidence of the presence of a spinless bipolaron charge transfer mechanism [17]. Furthermore, studies of cyclic voltammetry of polypyrrole show that the presence of some radical species (polarons) instead of dications (bipolarons) may be attributed to the difficulties for structural arrangements in the solid structure [18]: the bipolaron carrier being more stable in polypyrrole than the polaron. These results point to an ideal conducting polypyrrole structure, in which a dication every six or eight rings, corresponds to the doping ratios 0.33 and 0.25 respectively. Such dication structure may also be explained through the well known chemistry



of pyrrole in solution and, in fact, represents a junction between the physical models describing the solid structure of polypyrrole and the models describing its solution chemistry (see Figure 3). Two-electron oxidation of pyrroles with one free  $\alpha$  position gives  $\alpha,\alpha'$  bipyrrroles (I): neutral non-conducting polypyrrole is structurally related to this dimer. Bipyrrroles (I) can easily be oxidized to azafulvenic systems (II). In fact, most of the oxidative reagents

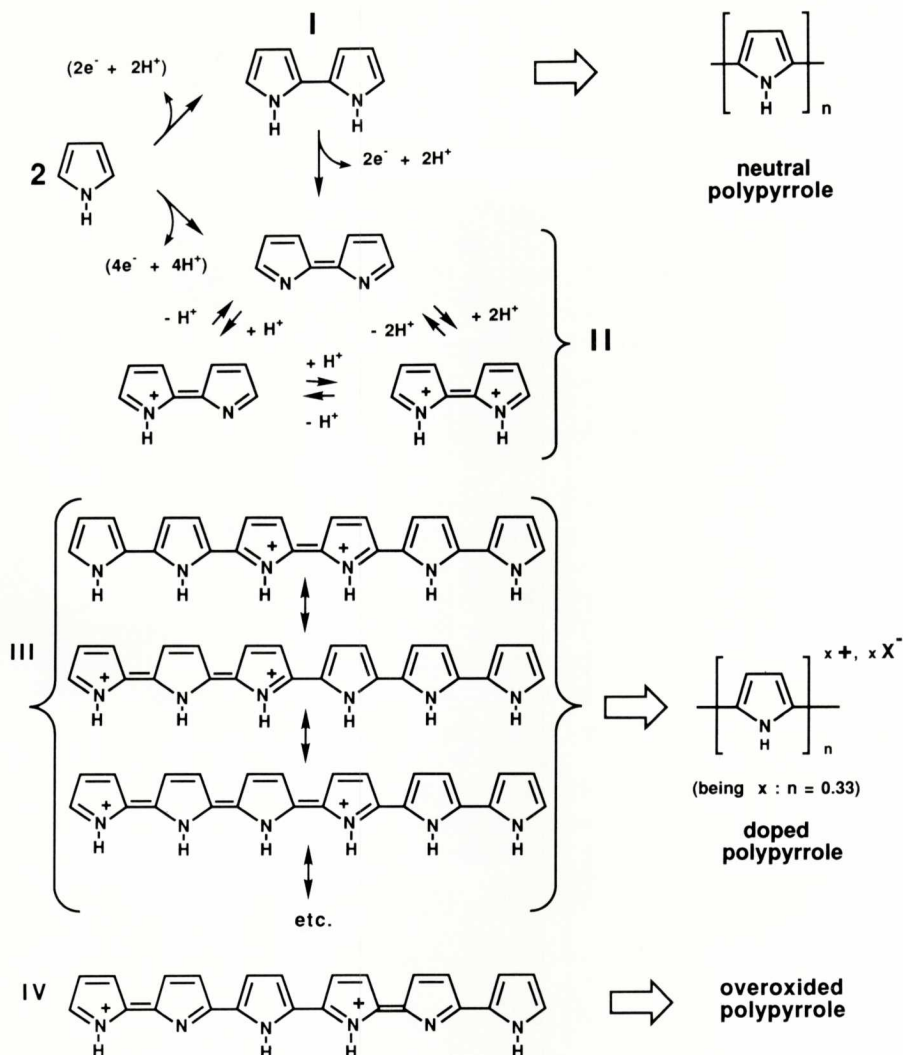


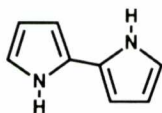
Figure 3. Oxidation chemistry of polypyrrole in solution and its relation to the redox processes of polypyrrole.

used for the preparation of bipyrroles give **II** directly. **II** has basic nitrogen atoms, in contrast with the nitrogen atoms of pyrrole rings, and is more stable in the form of salts of its conjugated acid. The two-electron oxidation of **I** to **II** goes with the protonation of at least one of the nitrogen atoms: the charge field effect hinders the protonation of both nitrogens. However, in the case of a polymeric structure, resonance with the neighbouring rings can lead to the diprotonation of the system. Doping ratios and coulometry measurements point to the presence of two «protonated azafulvenic rings» every six or eight rings (**III**). Such dication stabilized by resonance with the remaining non-oxidized pyrrole rings is structurally related to the bipolaron unit of doped polypyrrole.

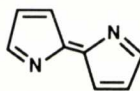
The above model suggests other sources of structural disorder in polypyrrole. Overoxidation of doped polypyrrole to azafulvenic structures (**IV**) not accompanied by protonation is possible because of the electrostatic repulsion between charges: i. e. in chemical terms, because of the progressive increase of pKa with the number of azafulvenic nitrogen atoms. This behaviour of polypyrrole as a polyelectrolyte agrees with the acid-base chemical properties of polypyrroles.

### Secondary structure of polypyrrole

Chemical reasoning points to, and conformational energy calculations [19,20] confirm, that the lowest energy arrangement for  $\alpha,\alpha'$  linked bipyrroles is the planar *anti* conformation of both rings: planar, because of the better p orbital overlap between rings and *anti* because of the interaction between the partial dipole moments of the pyrrole rings [20]. The same arguments allow to infer that the *E* configuration is the more stable configuration of the exocyclic double bond of the oxidized azafulvenic derivatives (see Scheme 4): an additional argument for this *E* configuration is the structure (from X-ray determination) of some substances which have this azafulvenic unit [21]. Consequently, an ideal polypyrrole chain would present a linear shape with planar rings in alternate *anti* arrangement of their nitrogens, in the neutral as well as in the doped state (see Figure 4a). However, from a chemical point



*anti* conformation



*E* configuration

Scheme 4

of view, conformational planarity must be understood as near to plane structures: deviations from planarity in the order of some degrees ( $\pm 15^\circ$ ) can be expected, especially in the case of *b* substituted pyrroles (see below). Nevertheless, doping, which implies the presence of exocyclic double bonds which are more or less delocalized, must increase the double bonding character of the links between rings: consequently, in the case of the doped polymer an increase in chain planarity would be expected. An interesting open question is the effect of the Peierls distortion on the structure of a single polypyrrole chain and other related heteroaromatic polymers [22]: here a distortional change both in the bonding distance between rings and in their dihedral angle could be expected.

Polypyrroles obtained from  $\beta$ -substituted monomers show deviations off plane owing to the higher steric hindrance of the substituent compared to hydrogen. This loss of planarity between rings decreases the  $\pi$  orbital overlap, which implies -in addition to a lower electrical conductivity of the material- more anodic redox peaks by cyclic voltammetry and absorption spectra at lower energies than non-substituted polypyrrole [23]. When the value and sign of this dihedral angle between rings is conserved, helicoidal chains are generated: Figure 4b shows this effect for a  $20^\circ$  dihedral angle.

Introduction of  $\alpha, \beta'$  (2, 4') bonds, instead of  $\alpha, \alpha'$  (2, 2') bonds, does not introduce changes in the polymer chain planarity but they break its linearity. This loss of linearity has important consequences for the structural organization between chains and doping anions (see below). Change of the dihedral angle of  $\alpha, \alpha'$  chains from  $180^\circ$  to  $0^\circ$  (i. e. from *anti* to *syn* planar conformation) introduces the same effect as 2,4 substitution: conservation of planarity but not of linearity. When  $\alpha, \beta'$  (2, 3') bonds are introduced instead of  $\alpha, \alpha'$  bonds greater structural disorder is generated because, in addition to the breaking of linearity, conformational angles of about  $90^\circ$  must be expected [7]. This will also be the case for the  $\beta, \beta'$  bonds giving chain branching. The effect of these links on the shape of the polymer chain is shown in Figure 4c.

In accordance with the above arguments from  $\beta, \beta'$  substituted pyrroles, in spite of the generation of non-planar chains, less disordered structures must be obtained. We have observed that the morphology and growth of 3,4-disubstituted pyrrole monomers are different from common polypyrrole. For example, comparison of the SEM images of polypyrrole and poly( $\beta, \beta'$ -disubstituted) pyrrole shows that the  $\beta, \beta'$ -disubstituted polymer, when it is obtained in the form of macroscopic compact film, does not have the typical cauliflower structure of polypyrrole, which is also characteristic of the copolymerizates of pyrrole with dipyrinones. Figure 5 is a particularly good example of this difference, at the microscopic level, between these two types of polypyrrole. The difference of microstructure between poly(3-methoxy-4-methyl pyrrole) and the parent polypyrrole suggests an expression at microscopic level of the absence of reticulation for the  $\beta, \beta'$  disubstituted polymer.



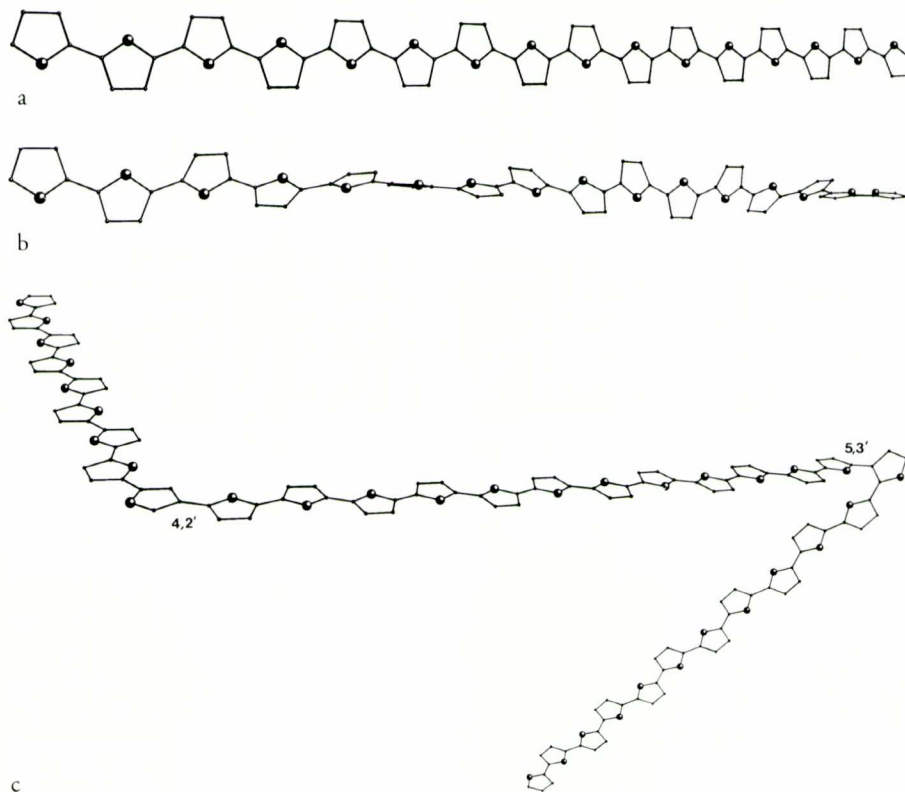


Figure 4. Influence of links between rings on the shape of polypyrrole chains. a: only  $\alpha, \alpha'$  (2,2') bonds at  $180^\circ$  dihedral angle. b: only  $\alpha, \alpha'$  bonds at  $200^\circ$  dihedral angle. c: one  $\alpha, \alpha'$  (2,4') at  $180^\circ$  dihedral angle and one  $\alpha, \beta'$  (2,3') bond at  $90^\circ$  dihedral angle (see text).

### *Tertiary structure of polypyrrole*

Polypyrroles, according with its ideal molecular structure, must have an electronic structure and a conduction mechanism corresponding to an unidimensional system. The experimental evidences against such type of behaviour has been attributed to structural disorder. However, we think that these evidences point to the existence of a better conduction mechanism than that of an unidimensional polymer chain. In fact, the conduction mechanism through the  $\pi$  conjugation cannot be very effective because the chain is not very long (see above). Characteristic for an unidimensional conduction mechanism is that its effectivity decreases (i.e., the energy barrier increases) strongly when the carrier approaches to the chain end [24]. In addition the chain presents structural disorders, which break the  $\pi$  conjugation: addition



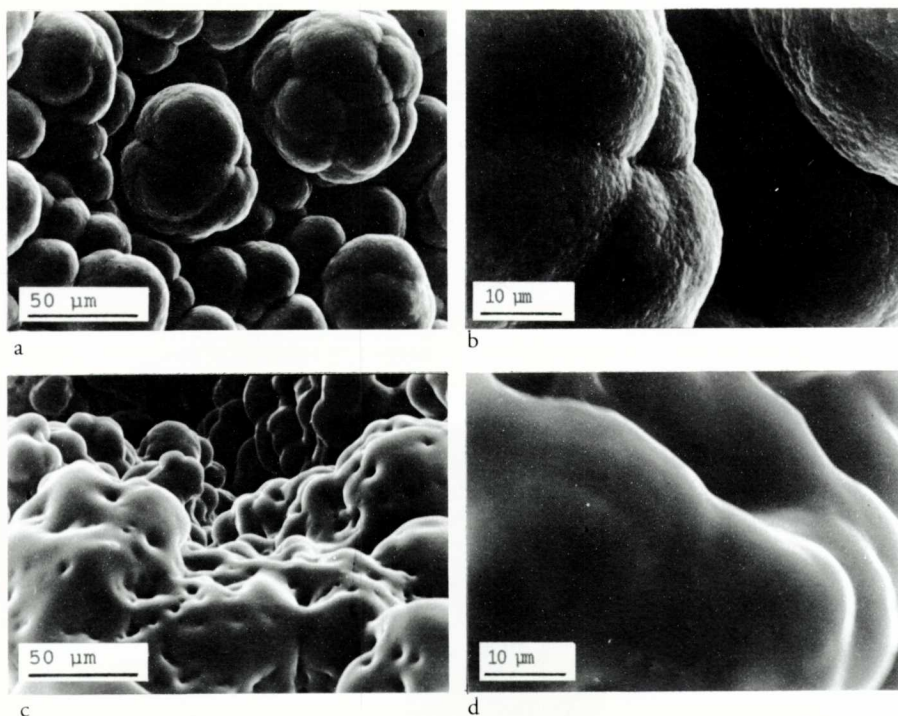


Figure 5. SEM images of polypyrroles. a and b: tetrafluoroborate doped polypyrrole. c and d: *p*-toluensulphonate doped poly(3-methoxy-4-methyl pyrrole).

of nucleophiles (coming from the preparation solution), derivatives from the reaction with dioxygen and presence of saturated rings (non-oxidative acid catalyzed pyrrole polymerization).

The solid structure of polypyrrole is not only due to the organization between the polymer chains but to the arrangement between polymer chains and dopant anions. Doped polypyrrole shows a doping level corresponding to two positive charges for each six or eight rings. The doping level depends on the electrochemical variables of the synthesis and of the dopant anion. This substantial level of doping, corresponding to one anion each three or four ring, must require a structural molecular organization. Furthermore, the better found anions are those with high molecular volumen. The commonly used *p*-toluenesulphonate dopant anion represents about 50%(!) of the volumen of doped polypyrrole. This fact opens the question if other conduction mechanism exists implicating both the polymer chain and the doping anion, i. e. the whole solid structure of doped polypyrrole.

For the progress in the development of polyheterocyclic conducting systems it is necessary to prepare structurally well-defined entities in order to be able to infer the molecular and supramolecular origins of the electronic conductivity. In this sense the results obtained until now with well-ordered structures are significant these efforts led to well-defined structures but to low electrical conductivity values. Doped polypyrrole chains obtained in zeolite channels (0.8 nm windows) shows insulating character [25]. In contrast to the low conductivity of this «molecular wire», thicker polypyrrole fibrils obtained in porous membranes ( $\approx 30$  nm) show enhanced electronic conductivity [26]. Polydiacetylenes can be obtained with very low structural

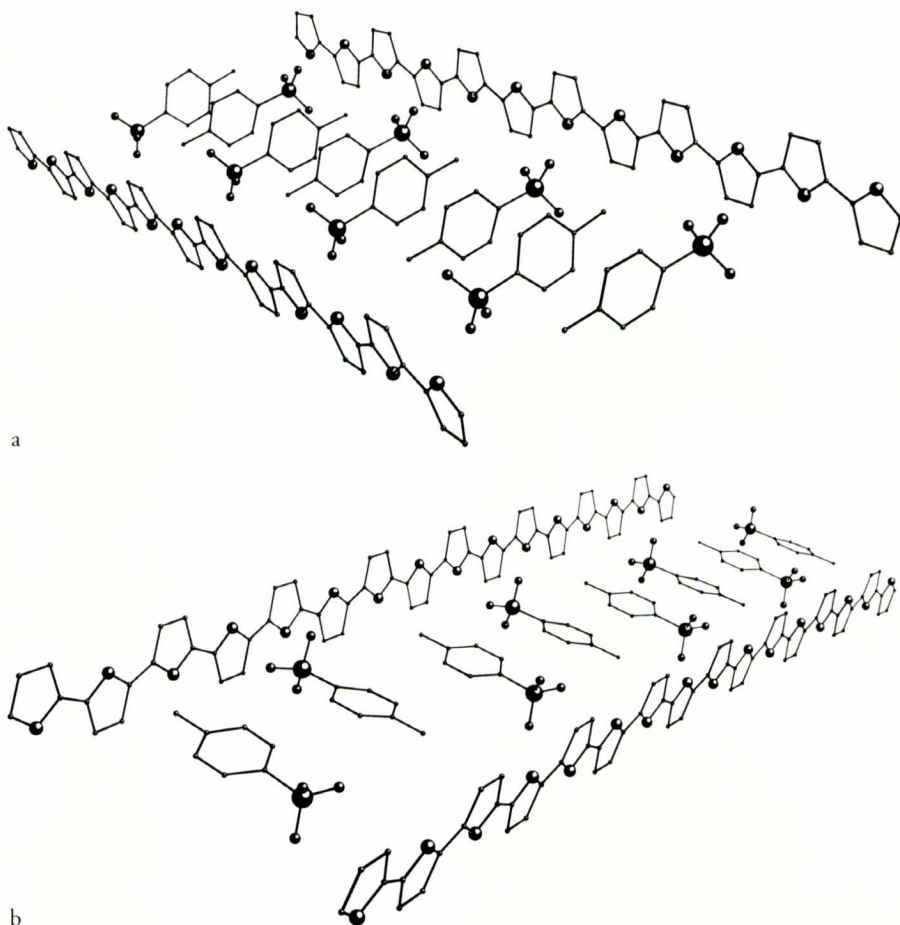


Figure 6. Molecular models on the intercalation of *p*-toluenesulphonate anions (PTS) between polypyrrole chains. a: *N* to PTS 0.25. b: *N* to PTS 0.33.

disorder, because they are prepared from intermolecular arrangements of their monomers, which show structural parameters near to those of the corresponding polymer chains [27]. Nevertheless, polydiacetylenes are very difficult to obtain in the conducting form, and their doping is very difficult [28]. These results can be interpreted assuming that the origin of the conduction mechanism lies on the supramolecular arrangement between polymer chains and doping anions.

Assuming that this hypothesis is true, efforts must be directed to prepare linear and planar polypyrrole chains without structural disorders, that will allow to design supramolecular arrangements between chains and doping anions. In this sense, it is encouraging to observe with molecular models the easy intercalation of *p*-toluensulphonate -until now the better dopant for polypyrrole- between two polypyrrole chains, for both the 0.33 and the 0.25 nitrogen-dopant ratios (see Figure 6). Such kind of models must be related, in the design of new types of experiments, with the already published data on the effect of the dopant molecules on the molecular order and conduction properties of polypyrroles (see e. g. ref. [29]).

#### SUMMARY

Doped polypyrrole shows electronic conduction mechanisms in agreement with a disordered structure. A hitherto unanswered question is the physical characteristics of an ideal structurally ordered polypyrrole. The chemical factors which contribute to preparation of structurally disordered materials in the polypyrrole obtained to date are presented. The importance of the arrangement of doping anions in or between polypyrrole chains is emphasized.

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