On the structure of polypyrrole: polypyrroles with dipyrrin-1(10*H*)-one end groups

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Film obtained by the electrolytic polymerization of pyrrole monomer and pyrrole under addition of dipyrrin-1(10*H*)-ones, which can act as polymer chain end groups, are compared. The effect of the doping anion and of ageing on electrical conductivity are studied. Elemental chemical analysis of the film materials points to the presence of short polymer chains: comparison with similar polymerizations of 3,4-dimethyl pyrrole suggests the presence of β,β' cross-linking in the polypyrrole structure.

(Keywords: anodic electrolytic deposit; copolymerization, polypyrrole cross-linking; poly(3,4-dimethyl pyrrole))

INTRODUCTION

The commonly accepted structure of polypyrrole is that of a plane array of monomer units joined by α,α' bonds. Nevertheless, chemical structures of the polypyrroles reported in the literature are not known in detail. In this respect, two unknown chemical structural details are of importance: (i) the chemical form of the oxygen captured by polypyrrole from air[1]; and (ii) the presence and extension of C–C linkages other than the α,α' ones, especially additional β,β' linkages which afford polymer cross-linking.

Our aim here is to detect the presence of such β,β' cross-linking through the comparative study of the copolymerizates of pyrrole monomers with pyrrole derivatives which act as chain end groups and normal polypyrrole. The end group used is dipyrrin-1(10*H*)-ones (see *Scheme 1*) unsubstituted at the C_9 atom. It is already known that these dipyrrinones show a chemical regiospecificity of electrophilic attack and oxidative behaviour located on the pyrrole ring, and similar to an alkyl substituted pyrrole ring[2]. Thus, the oxidative dimerization of dipyrrin-1(10*H*)-ones such as IIIb and IIId is described, giving the derivative coupled at free α-positions of the pyrrole ring[3]. Consequently, the simultaneous electrochemical oxidation of pyrrole or pyrrole derivatives with free α-positions (I and II) and of dipyrrinones (III) without substituent at the C_9 atom should give polypyrrole polymers with 5-methylen-3-pyrrolin-2-one end groups. Comparison of these polymers with the polymers obtained from the corresponding pyrrole alone would indicate some aspects of the polymer chain length and the presence or absence of cross-linking. A preliminary communication of the results reported here has already been published[4].

In spite of the large amount of literature data on the oxidative electrodeposition preparation of polypyrrole films ($\simeq$0.1 mm thickness) the reproducibility of the published results is quite low. This may be attributed to the many uncontrolled factors that influence the electrodeposition of the polypyrrole, e.g. electrochemical cell geometry, solvent and supporting electrolyte impurities and working electrode surface[5]. This means that each study must involve a preliminary investigation in order to find the best experimental conditions. It is particularly important in our methodology, based on the comparison of the electrodeposits obtained by polymerization and copolymerization, to choose the experimental conditions which afford reproducible films. Consequently, a preliminary study on the electrodeposition of polypyrrole was undertaken.

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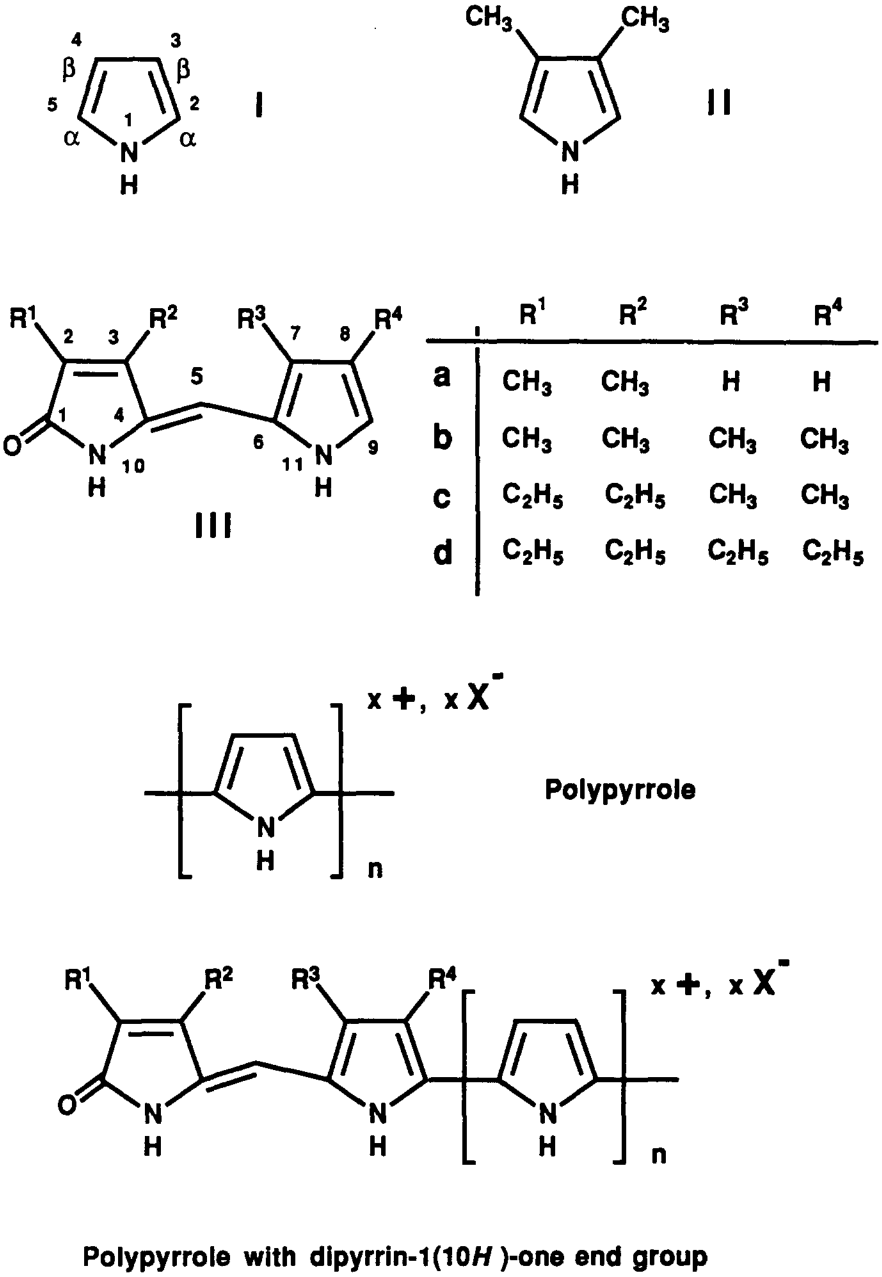

I

II

III

	R^1	R^2	R^3	R^4
a	CH_3	CH_3	H	H
b	CH_3	CH_3	CH_3	CH_3
c	C_2H_5	C_2H_5	CH_3	CH_3
d	C_2H_5	C_2H_5	C_2H_5	C_2H_5

Polypyrrole

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

Scheme 1

RESULTS AND DISCUSSION

Preliminary study on the experimental conditions of electrodeposition

Experiments at a wide range of pyrrole concentrations in acetonitrile (AN) and propylene carbonate (PC) solutions were undertaken using tetraethylammonium *p*-toluensulphonate (TEAPTS) as supporting electrolyte; cell geometry, current intensity, current density and polymerization times were varied and the corresponding potentials were measured (between working and counter-electrode, and working and counter-electrode surfaces *versus* s.c.e.). Although most experiments were performed at galvanostatic conditions, potentiostatic conditions were also tested. The conclusions drawn from the experiments, although already familiar to those working on polypyrrole, have not to our knowledge been published or treated in depth. Thus the following factors that affect the growth of polypyrrole films are noted.

(1) Galvanostatic conditions afford better films than obtained under potentiostatic conditions. Nevertheless, at galvanostatic conditions the experimental conditions chosen (volume of solution, concentration of substrate, time of electrolysis, etc.) must give the smallest possible variation of the potential between electrodes during film growth. Under galvanostatic conditions, satisfactory films can only be obtained while the potential remains nearly constant. A decrease below a critical value of the monomer concentration, or of the concentration of soluble oligomers able to nucleate on the electrode, is detected by a clear change in potential between working and counter-electrode. This change in potential coincides with the formation of polypyrrole deposits with non-compact morphology. This can be prevented if the volume of solution is large enough. However, there is no linear relationship between volume of solution and the time at which uniform polymerization of the film is disrupted, i.e. at lower volumes of solution 'useful' polymerization times are much shorter.

(2) In the preparation of polypyrrole films the potential

Table 1 Effect of monomer concentration on the polypyrrole electrical conductivity (σ, S cm^{-1}). Films were obtained at a current density of 2 mA cm^{-2} on 7 cm^{2} platinum-coated titanium electrodes, in AN solutions using TEAPTS as supporting electrolyte

Initial pyrrole conc. (mol l^{-1})	TEAPTS conc. (mol l^{-1})	Electrolysis time (h)	Film thickness (mm)	Conductivity, σ (S cm^{-1})[a]
0.05	0.1	3	0.13	8.2
0.10	0.2	6	0.27	16.3
0.15	0.3	9	0.35	22.8
0.15	0.1	3	0.14	19.2

[a] Four-point method[9] (see Experimental)

of the counter-electrode can also be important. When the counter-electrode potential is too negative, reductive processes (generally upon the supporting electrolyte) other than the reduction of protons can occur. The products of these reduction processes can be anions which migrate to the working anode and in some cases give non-conducting deposits incorporated into the polypyrrole matrix (detected by SEM and EDAX observation). Too negative counter-electrode potentials can be generated by too large an ohmic fall (e.g. two-compartment cells) or by the absence of protons reaching the electrode, i.e. at the end of the polymerization process.

(3) A series of experiments was performed at different current densities, concentrations and similar working electrode potential. According to our results, low current density affords more compact films if an adequate working potential is attained. At the same current density for more concentrated solutions, more compact polymer deposits are obtained. Obviously, films of this type, which differ only in their density, show differences in electrical conductivity, the more compact being more conductive. However, the electrical conductivities for such films are of the same order of magnitude, although in some cases the conductivity values differ by 50–100%. Most of the experiments described in the literature on the effect of current density performed under galvanostatic conditions are not reliable because in most cases a change in intensity involves a change in the working electrode potential. Our experimental procedure involves several electrolyses formed with the same galvanostatic electrolysis parameters and cell geometry, but with varying electrode areas to vary the current density.

(4) More concentrated solutions of pyrrole afford more conductive films, for films prepared with either the same electrical charge used in the electrolysis or the same ratio of reacted substrate (see *Table 1*). Although the materials of *Table 1* show similar densities by the flotation method (1.36–1.37 g ml^{-1}), SEM observations indicate more compact and even structures for the more conductive ones. These results suggest that there is a sort of Mullins–Sekerka instability[6], originating in the diffusion control of the electrochemical reaction.

The objective of this work was to study the differences obtained when adding dipyrrinones (III) to the polymerization of pyrrole. Experimental conditions were chosen to give good films in AN and PC solutions using TEAPTS as supporting electrolyte and dopant. However, in order to make the experiments sensitive to the different factors acting on the polymerization, the monomer concentration was kept low and the ratio of volume of solution to electrical charge consumed was chosen in order to obtain a useful polymerization limit of 15 h; i.e. 0.5 mol l^{-1} pyrrole and 100 ml solution for current densities of about 2 mA cm^{-2} and platinum-coated titanium electrodes of 7 cm^{2}.

In a typical experiment at galvanostatic conditions (0.5 mol l^{-1} pyrrole, 100 ml propylene carbonate solutions and 0.1 mol l^{-1} tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, 15 mA for 7 cm^{2} electrodes at 1 cm separation), the potential between the electrodes is 4.65 V at the beginning of the experiment and increases very slowly to 4.95 V in the first 16 h, after which it increases at a higher rate. The initial working potential is 1.03 V (s.c.e.) and shows a small increase in the first hour ($\simeq$5 mV) remaining nearly constant up to the first 16 h, after which it decreases at a rate of about 1 mV h^{-1}. The counter-electrode initial potential is -1.95 V (s.c.e.) and increases by about 10 mV in the first 7 h, after which it increases at a rate of 1.5 mV h^{-1} for 9 h and then at a higher rate.

These experimental conditions, which are very similar to those proposed in the literature to obtain preparative polypyrrole films, give an ideal pyrrole electrolysis potential (I shows a voltammetry peak at $+1.15$ V (s.c.e.)), i.e. the same potential that we would choose for electrolysis at potentiostatic conditions, but with the advantages of the galvanostatic conditions in order to obtain a uniform, smooth deposition. The change of potential of the working electrode accounts for a higher potential of the initial step of polymerization (i.e. the pyrrole monoelectronic oxidation) rather than the potentials required for the polypyrrole doping and for the reaction between deposited polymer and soluble oligomers. The basic reaction on the counter-electrode should be the reduction of the protons generated by coupling the pyrrole ring; the increase in the potential of the counter-electrode during electrolysis results from the decrease of the anode oxidative processes generating protons (polymerization couplings) and the increase of other oxidative processes, e.g. doping and oxidation of soluble oligomeric fractions followed by nucleophile addition.

In the case of the copolymerization of pyrrole in the presence of 10 mol% dipyrrinone (IIa), the initial potential between the two electrodes and its change over time is analogous to pyrrole alone, but the initial working potential is lower (e.g. $+0.9$ V for IIIa and $+0.8$ V (s.c.e.) for IIIb) and shows a slight tendency to decrease in the first 4 h ($\simeq$50 mV), after which it maintains the same value. On the other hand, the counter-electrode potential shows a regular increase at a rate of 1 mV h^{-1}. These initial working potentials agree with the finding that dipyrrinones (III) first show anodic voltammetric potentials at more negative potentials than pyrrole ($\simeq$0.4–0.6 V)[7,8].

Three supporting electrolytes — TEAPTS, TBAP and tetrabutylammonium tetrafluoroborate (TBATF) — were tested. The perchlorate doping proved to be very sensitive to changes in the electrolysis conditions; e.g. in PC it gave only powders, not films, although in the same experimental conditions in AN (see *Table 2*) satisfactory films were obtained. In contrast, *p*-toluensulphonate doping also yielded films of similar quality in both PC and AN. Good preparative films were also obtained with tetrafluoroborate, but this was found to depend on the origin (and batch) of the TBATF. Although purification

Table 2 Data of preparative films obtained from pyrroles (I or II) and from copolymerization of pyrroles with dipyrrin-1(10*H*)-ones (III) (molar ratio 10:1): $0.05\,\mathrm{mol\,l^{-1}}$ substrate and $0.1\,\mathrm{mol\,l^{-1}}$ supporting electrolyte solutions (for details see text)

					Film properties					
						Elemental analysis (molar ratios)[e]				
Supporting electrolyte[a]	Solvent[b]	Monomers	Film thickness (mm)	Density[c] $(\mathrm{g\,ml^{-1}})$	Conductivity, σ $(\mathrm{S\,cm^{-1}})$[d]	C	H	N	O	Doping anion
TBAP	AN	I	0.2	1.43	28.1	4.03	3.28	1.00	0.29	0.33
		I+IIIa	Powder[f]	–	–	4.25	3.42	1.00	0.30	0.26
TBAP	PC	I	0.3	1.36	3.4	4.26	3.53	1.00	0.50	0.26
		I+IIIa	0.1	1.36	4.4	4.74	3.87	1.00	0.58	0.22
TEAPTS	AN	I	0.6	1.37	2.9	4.15	3.54	1.00	0.41	0.28
		I+IIIa	0.6	1.31	4.1	4.38	4.27	1.00	0.59	0.20
		II	0.1	1.30	0.05	6.18	7.98	1.00	0.48	0.32
		II+IIIc	0.08	1.30	0.05	6.18	8.07	1.00	0.43	0.34
		II+IIId	Very thin	1.30	–	6.22	8.01	1.00	0.45	0.30
TBATF	PC	I	0.2	1.42	51.2	4.04	3.19	1.00	0.72	0.25
		I+IIIa	0.2	1.45	36.8	4.21	3.21	1.00	0.63	0.25
		I+IIIB	0.3	1.48	19.1	4.33	3.72	1.00	0.74	0.34
TBATF	AN	I	0.2	1.42	31.0	4.02	3.46	1.00	0.72	0.20
		I+IIIa	0.7	1.37	2.4	4.28	3.75	1.00	0.63	0.21

[a] TBAP, tetrabutylammonium perchlorate, TEAPTS, tetraethylammonium *p*-toluensulphonate; TBATF, tetrabutylammonium tetrafluoroborate

[b] PC, propylene carbonate; AN, acetonitrile

[c] Flotation method

[d] Four-point method[9] (see Experimental)

[e] C, H, N and O calculated from direct analysis. Oxygen values do not include the oxygen content of the doping anion. Doping anion calculated indirectly in the case of TBATF and from the Cl and S direct analysis in the case of TBAP and TEAPTS. See Experimental for the significance of elemental ratios

[f] Film converts to a powder during the wash-up procedure (see Experimental)

of TBATF by crystallization improved the film quality, we could not find a reliable purification method. Experiments performed with II using poor TBATF batches as supporting electrolyte resulted in films showing elemental analysis with C, H, and N molar ratios indicating that oxidative reactions other than polymerization and doping were occurring.

Occurrence of copolymerization by the electrolysis of pyrrole in the presence of dipyrrinones (III)

In the experiments of *Table 2* performed with addition of III, the dipyrrinone was still detected (t.l.c. and i.r.) at the end of the experiments. The dimers of the dipyrrinones IIIa–IIId were not detected (for these types of dimer see ref. 3). In contrast, polymerization experiments at lower working electrode potentials, which give polymeric material but poor films, show the presence in the solution of dimers of the dipyrrinones (t.l.c. and mass spectrometry). In the electrolysis experiments in the presence of dipyrrinones the final solutions were dark and not transparent, in contrast with the paler transparent solutions of the experiments with pyrrole alone. In the presence of dipyrrinone the yield of deposited polymer was always lower than for the corresponding experiment with pyrrole alone. In experiments using AN as solvent, after evaporation and water extraction, it was shown that the weight of the residue was higher in the presence of dipyrrinone than in its absence. To sum up, chemical reasoning points to the presence of termination reactions involving dipyrrinone dominating over the dimerization of the dipyrrinone itself. On the other hand, chemical elemental analysis (see *Table 2*) confirms the incorporation of dipyrrinone in the anodic polymer deposit. In the case of polymerization experiments with 3,4-dimethyl pyrrole (II) no dipyrrinone incorporation was detected, a finding which will be discussed below.

Properties of the copolymers

When each copolymerizate (I + IIIa or IIb) is compared with the corresponding polymer obtained from I alone, the characteristics of the polymers are very similar. The clearest difference between the materials is in their elemental chemical analyses and the more open structure for the copolymerized polymers (SEM observation). However, all films observed by SEM show the same compact microstructure on the surface in contact with Pt, while in the growing surface they show the typical cauliflower patterns of polypyrrole[9].

Film densities are very similar for each pair of films. the two clear differences shown in *Table 2* (TEAPTS, AN, I and I+IIIa, and TBATF, AN, I and I+IIIa) would be due to the open structure of the copolymeric material, which prevents the complete exclusion of air in the density determination by the flotation method.

Electrical conductivities (σ) of each pair of films are of the same order of magnitude and decrease on ageing in a similar way. The observed differences in conductivity could be attributed to the more open structure of the copolymer films. With respect to the ageing, we have observed two modes of change in the conductivity with ageing (in contact with air and in the absence of water): films which maintain the same conductivity for more than 5 months after their preparation, and films with high

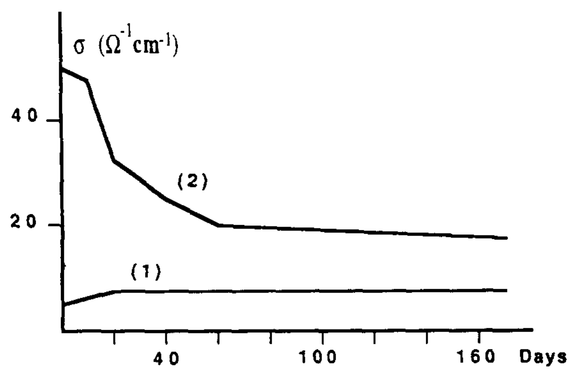

Figure 1 Change of the electrical conductivity (σ) with time: (1) film obtained from pyrrole in propylene carbonate and TEAPTS as supporting electrolyte (reported in *Table 1*); (2) film obtained from pyrrole in propylene carbonate and TBATF as supporting electrolyte (reported in *Table 1*). Curves (1) and (2) correspond to the two basic patterns of ageing observed (see text)

initial conductivity values which show a fast decrease in their conductivity down to a stable value. This last conductivity value is of the same order of magnitude as the value for the films which do not show significant change. These two types of behaviour are represented in *Figure 1*. In our experiments, *p*-toluensulphonate-doped films show the first type of ageing behaviour (curve 1 of *Figure 1*) and perchlorate and tetrafluoroborate-doped films show the second (curve 2 of *Figure 1*). In this respect it must be stressed that *p*-toluensulphonate-doped polypyrrole films, which are more conductive than those given in *Table 2* (20 S cm^{-1}), also show an ageing behaviour corresponding to curve 1. These more conductive films can easily be obtained by electrolysis at the same galvanostatic conditions, but using more concentrated pyrrole solutions and shorter polymerization times.

We have already reported[4] that electroanalytical films of some of the pairs in *Table 2* show similar cyclic voltammetry behaviour. These previous results are confirmed for the other pairs in *Table 1* and for different film thicknesses.

Doping ratio and the oxygen content

Doped polypyrrole takes up oxygen irreversiby[10,11]. In fact such high oxygen values as those of *Table 2* (1 O for 1.3–3 N) are typical values for polypyrrole when it is obtained or stored in the presence of air. Not all published papers on polypyrrole report this, because some do not include direct oxygen analysis. In some studies, in which the doping anion ratios are calculated indirectly and oxygen is supposed to be absent, doping ratios higher than the actual ones are reported.

We conclude that for the dopants studied, doping molar ratios relative to nitrogen higher than 0.33 do not exist. Two 0.34 values of *Table 1* can be attributed to the margin of experimental errors. On the other hand, values near to 0.25 also appear frequently. According to a bipolaron charge transfer mechanism, these doping ratios imply two positive charges every eight or six pyrrole rings. Values lower than 0.25 can be attributed to incomplete doping and intermediate values between 0.25 and 0.33 to mixed states.

Oxygen in pyrrole films comes from two sources, in addition to any deliberately incorporated species; it is incorporated in the film during its growth from the media nucleophiles (e.g. water) and from air in contact with the doped film after its preparation[10–14]. In our case most of the oxygen should derive from air, owing to the low water content of our electrolyte solutions. The irreversibility of this form of oxygen absorption points to some type of chemical reaction giving covalent bonded oxygen: N-oxide[15,16] and peroxide[1] functional groups have been proposed. However, more work must be performed comparing polypyrroles in the absence and in the presence of oxygen to clarify this point.

β,β' Linkage in polypyrrole

Elemental chemical analysis shows small but significant differences between the polymerization experiments for pyrrole and those for pyrrole with dipyrrinone. For polypyrrole, relative ratios between C, H, and N correspond closely to the ieal formula $C_4H_3N_1$: the small excess values for C and H could be attributed to the incorporation of either supporting electrolyte or solvent. *FT*i.r. (KBr) spectra show weak C_{sp^3}-H_s stretching bands for all polypyrrole films but these bands disappear when $LiClO_4$ is the supporting electrolyte. Therefore, these excess values are probably due to the incorporation of supporting electrolyte.

In the case of films from pyrrole (I), C and H values are higher, in each pair, for the experiment under addition of dipyrrinone (IIIa or IIIb). These differences are accounted for by the incorporation of dipyrrinone in most of the experiments (see Experimental section for the significance of the elemental analysis ratios of *Table 2*): differences are also observed depending on the C and H ratios of the incorporated dipyrrinone. Assuming a regular distribution of dipyrrinone units on the polymer, the differences in C and H ratios, for the experiments under addition of dipyrrinone compared to the corresponding polypyrrole, imply one dipyrrinone residue every 10–25 pyrrole units. This represents polymer chains of 20–50 units terminated by two dipyrrinone end groups. However, the lower solubility of this material compared with oligomers of similar chain length derived from 3,4-dimethyl pyrrole[17], which is not able to give new β bonds, suggests the presence of β,β cross-linking.

To test this assumption we have performed the same type of experiments under addition of dipyrrinones but with 3,4-dimethyl pyrrole. In these experiments the dipyrrinones tested (IIIc and IIId) were chosen in order to have a different C/H ratio with respect to II and substituted β positions in the pyrrole ring to avoid β linkage. The results show an excess of C and especially of H compared to the ideal poly(3,4-dimethyl pyrrole), formula $C_6H_7N_1$, but no differences were detected by the presence of dipyrrinone. However, under addition of dipyrrinone the polymer yield is 25% lower and the soluble residue in AN (after evaporation and water extraction) is 200% higher. These results can be interpreted assuming that only long polymer chains are insoluble; either these chains do not have dipyrrinone end groups, or their contribution to the C/H ratio is too small to be detected. Small chains are soluble and the presence of dipyrrinone termination reactions is detected by the smaller polymer yield and the increase in soluble fractions. In the case of pyrrole, the small chains can be incorporated to the anodic deposit by β linking oxidative polymerization. This assumption is also in agreement with the fact that 3,4-disubstituted pyrroles give polymeric deposits in lower yield than pyrrole (e.g. here with

II and in ref. 18 with 3-methoxy-4-methyl pyrrole about 50% of the yield with I).

The presence of a smaller number (each 20–50 rings) of β bonds giving cross-linking also implies the presence of α,β links and β,β' links, which would not give cross-linking. The presence of this type of bond would have important consequences for the stereochemical structure of polypyrrole.

EXPERIMENTAL

PC was anhydrous (Aldrich) and AN was of h.p.l.c. quality (Lab-Scan). The supporting electrolytes were of commercial origin and had been dried before use: TEAPTS (Fluka, 'purum'), TBAP (Fluka, 'puriss.'), TBATF (Fluka, 'purum'). Pyrrole (Fluka, 'purum') was freshly distilled under reduced pressure before use. The remaining monomers were obtained and identified according to the literature: 3,4-dimethyl pyrrole (II)[19], 2,3-dimethyl dipyrrin-1(10*H*)-one (IIIa)[20], 2,3,7,8-tetramethyl dipyrrin-1(10*H*)-one (IIIb)[21], 2,3-diethyl-7,8-dimethyl dipyrrin-1(10*H*)-one (IIIc)[22], 2,3,7,8-tetraethyl dipyrrin-1(10*H*)-one (IIId)[23].

*FT*i.r. spectra were recorded on a Bomem MB 120 instrument. Mass spectra were recorded on a Hewlett Packard 5700-A instrument in electron impact and chemical ionization (NH_3) modes. SEM observation was performed on a Philips SEM 515 instrument equipped with an EDAX accessory. A potentiostat (AMEL 555A) was used as electrical source for the electrolytic preparation of films. For the cyclic voltammetry measurements a Belport HQ305 sweep generator, a Belport HQ105 potentiostat with i.r. compensation and a Houston 2000 X-Y recorder were used.

Cyclic voltammetry measurements of solutions of monomers (5×10^{-3} to $3\times10^{-2}\,mol\,l^{-1}$) were made with a Pt sphere, using a saturated calomel electrode as reference electrode, a Pt wire as counter-electrode and $0.1\,mol\,l^{-1}$ supporting electrolyte. Electroanalytical samples of the polymer on a Pt sphere were similar when measured using a blank solution of supporting electrolyte; samples of the polymer on the Pt sphere were obtained by 5–30 s polarization at potentials 0.05–0.1 V below the E_{pa} of the monomer or of the mixture of monomers.

Preparative polypyrrole films were obtained following the galvanostatic method described in ref. 24. Two platinum-coated titanium electrodes, back protected with epoxy resin, of rectangular form and of the same area were used at 1 cm distance as working- and as counter-electrode. In separate experiments the electrode potentials were measured using a saturated calomel electrode as reference and a Luggin capillary. Air was excluded (nitrogen blanket) during the electrochemical procedure but not in the washing and drying work-up procedure. The polymer film was separated from the electrode, washed several times with methanol and vacuum dried. The films were stored under water exclusion and in contact with air.

Elemental analysis of C, H, N, Cl, S and O was carried out by the CSIC (Barcelona) analysis service. The presence or absence of other elements was checked using energy dispersive spectroscopy on the SEM. For each element, per cent values were calculated as the mean of two experimental measurements differing by less than 0.4% (the accuracy of the method was to the second decimal place). When all the elements in the polymer were directly determined, i.e. except when TBATF was used as dopant, the percentages obtaind added up to $100\pm1\%$.

All films were routinely observed by SEM. Electrical conductivity of the films was measured by the four-point method[25], within 4 h of their preparation and thereafter at regular intervals for a period of 170 days. The relative error in the electrical conductivity measurements is estimated to be less than 5%; this is determined mainly by the geometry of the samples. Sample thickness error is usually about 2%, and inhomogenities in the thickness are probably also within this range. For each sample the conductivity of both sides was measured; the results always indicated a slightly higher ($\leqslant 2\%$) conductivity for the electrode side than for the electrolyte side. For some films, the change of conductivity (σ, $S\,cm^{-1}$) with temperature was also measured. However, the narrow range of temperatures available ($\simeq$140–300 K), did not allow us to distinguish between Arrhenius and Mott charge transport mechanisms.

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