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# Structure of Polyindoles from Anodic Coupling of Indoles: An Electrochemical Approach

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The structure of polyindoles from anodic coupling of indole, 5-carboxyindole, 5-cyanoindole, and biindoles were investigated by cyclic voltammetry (CV), FTIR and UV–vis spectroscopies and in situ conductivity. The presence of the NH signal in the IR spectrum of the neutral polymers indicates that the polyindoles are coupled at the 2 and 3 positions. The shape and the pH dependence of the CV response, the potential window of conductivity, the disappearance of the NH band upon oxidation and the pH-dependent electrochromism, analogous with those of polyaniline, are due to a regular alternance of 2,2 and 3,3 couplings. Polyindoles of different chain length are produced from anodic coupling of 2,2′- and 3,3′-biindoles.

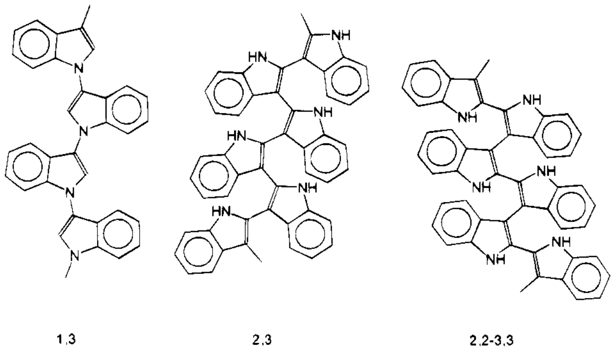
## Introduction

Among polyconjugated conducting polymers, polyindoles from anodic coupling of indoles display a noticeable interest since they have been considered in applications such as sensors[1–3] and because they may be model polymers for biopolymers such as melanines.[4–6] Nevertheless, their structure as well as their redox processes are still not well defined.

Anodically coupled polyindoles have been obtained from indole, 5-carboxyindole, and 5-cyanoindole in acetonitrile.[7,8] Their probable structure was inferred by comparing the ability to polymer deposition of methyl-substituted indoles and by spin density calculations.[8] The latter excluded the benzene ring as the site of coupling and suggested as the most likely sites of coupling the 1 and 3 positions (Scheme 1).

In any case coupling at the 1 position appears to be unusual since chemical oxidation of 2,3-diphenylindoles,[9] acid polymerization,[10] and chemical oxidative coupling of indoles[11] do not involve the NH group. Moreover indole oligomers reported in the literature[12] are coupled at the 2 and 3 positions. Therefore, we thought that a similar coupling could occur also in the anodic coupling of indole and decided to reexamine the characteristics of the electrochemically produced polymers.

**Scheme 1. Structures of 1,3-, 2,3-, and 2,2–3,3-Coupled Polyindoles**



This paper considers the electrochemistry of oxidatively coupled polyindoles from indole (**1**), 5-carboxyindole (**2**), 5-cyanoindole (**3**), the biindoles 2,2′-biindole (**4**), 3,3′-biindole (**6**), and 2,3′-biindole (**8**) and the corresponding 1,1′-dimethyl-substituted biindoles (**5**, **7**, and **9**;) (Scheme 2) in order to better assess the structure of this interesting class of materials.

## Experimental Section

**Chemicals and Reagents.** Acetonitrile (AN) was distilled twice over $P_2O_5$ and once over $CaH_2$. The supporting electro-

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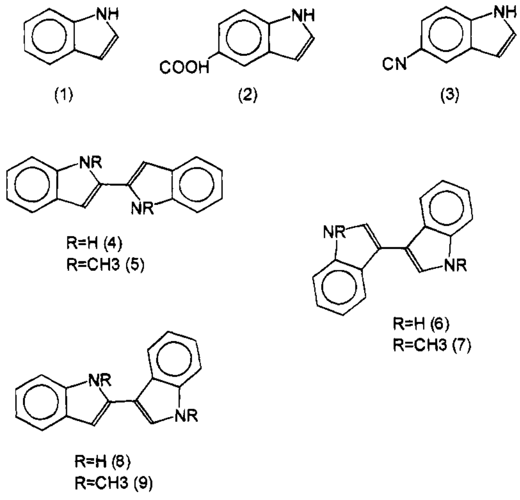
**Scheme 2. Formulas of Investigated Indoles**



lyte tetraethylammonium perchlorate (TEAP) was previously dried under vacuum at 70 °C.

Indole (**1**), 5-carboxyindole (**2**), and 5-cyanoindole (**3**) were reagent grade and used as received. The following compounds were prepared according to literature prescription: 2,2′-biindole (**4**),[13] 1,1′-dimethyl-2,2′-biindole (**5**),[13] 3,3′-biindole (**6**),[14] and 2,3′-biindole (**8**).[15] 1,1′-Dimethyl-2,3′-biindole (**9**) was prepared from **8** by reaction with NaH followed by alkylation with MeI, as described in the literature;[16] 1,1′-dimethyl-3,3′-biindole (**7**) was analogously prepared as described below.

**Synthesis of 1,1′-Dimethyl-3,3′-biindole (7).** A 60% suspension of NaH in mineral oil (0.12 g, 3.00 mmol) was added portionwise to a solution of **6** (0.35 g, 1.50 mmol) in DMF (15 mL) under nitrogen atmosphere and keeping the temperature at 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 2 h. After cooling to 0 °C, a solution of MeI (0.51 g, 3.60 mmol) in ether (10 mL) was added dropwise, and stirring was continued overnight at room temperature. The solution was poured into water and extracted with ether, the organic phase dried ($Na_2SO_4$) and the solvent evaporated. Flash chromatography of the residue (silica gel, eluent: petrol ether/ether, 8/2) afforded the title compound **7** (0.27 g, 70% yield), mp 183−185 °C (lit.[17] 185−187 °C).

**Apparatus and Procedure.** Experiments were performed at 25 °C under nitrogen in three-electrode cells. The counterelectrode was platinum; the reference electrode was SCE for acid solutions and a silver/0.1 M silver perchlorate in AN (0.34 V vs SCE) for AN solutions. The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a platinum minidisk (0.003 cm$^2$) or a glassy carbon (0.02 cm$^2$) electrode. For electronic spectroscopy a 0.8 × 2.5 cm indium−tin−oxide (ITO) sheet (ca. 80% transmittance, ca. 300 Ω/square resistance, from Balzers, Liechtenstein) was used. Platinum sheets or glassy carbon plates (15 cm$^2$) were used in reflection−absorption IR spectroscopy and preparative electrolyses.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer, IR spectra in reflection−absorption with a Perkin-Elmer System 2000 FTIR spectrometer and mass spectra on a VG ZAB 2F spectrometer operating under the electron impact condition (70 eV, 200 μA).

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.[18] The relevant working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband spacing of 20 μm, typically polymer-coated with the passage of 20 mC, which ensured the attainement of limiting resistance conditions. Poly(3-methylthiophene) (60 S/cm[19] ) was used as conductivity standard.

## Results and Discussion

**Electrochemical Synthesis and Characterization of Polyindoles.** Polyindole films were obtained by anodic coupling of indoles according to the literature[8] using cyclic voltammetry (CV) in order to evidence the reversible charging process.

The voltammogram of indole (1−5) x $10^{-3}$ M in AN + 0.1 M TEAP displays an oxidation peak at 0.85 V corresponding to the exchange of $n_{\text{app}}$ = ca. 2.5 e/mol. With continuous cycling of the potential beyond the peak and up to 1.0 V, a redox cycle, due to the growing polymer, develops. The CV response of polyindole (poly(**1**)) in monomer-free solution appears as a broad cycle with two round features imposed over a capacitive plateau extending up to the anodic limit of 0.8 V (Figure 1a). Beyond this potential the polymer is overoxidized with insertion of carbonyl groups in the benzene ring, as evidenced by IR spectroscopy and as previously observed in some polybenzodipyrroles.[20] The charge yield, i.e., the ratio of the reversible charge to that used for polymerization measured at the neutral state, is rather low (ca. 8%) in comparison with, e.g., pyrrole, due to the formation of soluble products. At higher monomer concentrations the polymer deposits with lower yields and $n_{\text{app}}$ decreases so that at 0.1 M concentration the charge yield is less than 1% and $n_{\text{app}}$ = 0.8 e/mol. The drop of polymer formation in concentrated monomer solution is unusual since this condition in general favors anodic coupling: some substituted thiophenes cannot be polymerized on the electrode unless concentrations higher than 2% are used.[21]

Films of poly(5-carboxyindole) (poly(**2**)) and poly(5-cyanoindole) (poly(**3**)) are obtained by CV oxidation of the monomers 5 × $10^{-3}$ M in AN + 0.1 M TEAP, where they display an oxidation peak (at 0.9 and 0.93 V respectively) corresponding to $n_{\text{app}}$ = ca. 2 e/mol. The redox cycle of poly(**2**) and poly(**3**) in monomer-free solution (Figure 1b, c) is quite different from that of poly(**1**) as it appears as a neat symmetrical couple of processes with complete absence of a capacitive range at full oxidation. The charge yield of the overall cycle is ca. 20% for poly(**2**) and 11% for poly(**3**). In these cases formation of soluble species is less than for indole and does not appear to be concentration dependent (for poly(**3**) the charge yield is constant in the range 5 × $10^{-3}$−5 × $10^{-2}$ M).

The redox potentials $E°$ of the polyindoles, summarized in Table 1, follow the electronic properties for poly(**2**) and poly(**3**) as the latter, with the stronger electron-withdrawing substituent, is oxidized at higher potentials than the former. Poly(**1**) behaves anomalously since it was expected to be oxidized at lower potentials yet displays $E°$ values intermediate between those of poly(**2**) and poly(**3**) and with a lower potential separation $\Delta E°$ (0.3 vs 0.6−0.7 V).

**IR Analysis of Polyindoles.** Neutral poly(**1**) films display in the IR spectrum (Figure 2a), beside a single

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[13] Bergman, J.; Eklund, N. *Tetrahedron* **1980**, *36*, 1439.

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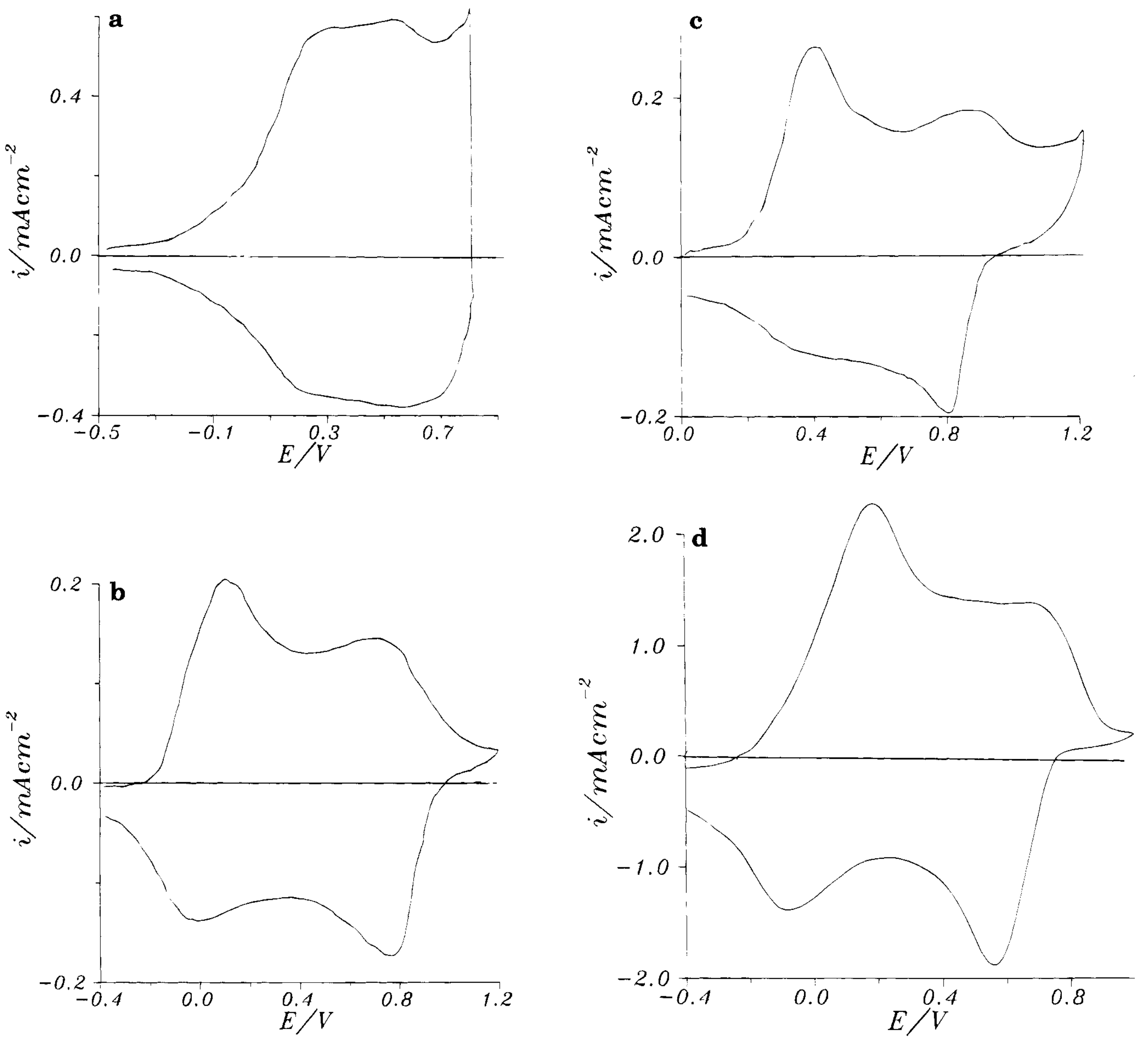


**Figure 1.** Cyclic voltammetry of poly(**1**) (a), poly(**2**) (b), poly(**3**) (c), and PANI (d) deposits in AN+0.1 M TEAP. Scan rate: 0.1 V/s; $Q_r$ = 3 mC/cm$^2$ (a); 1.65 mC/cm$^2$ (b); 1.3 mC/cm$^2$ (c); 14 mC/cm$^2$ (d).

strong out-of-plane CH deformation band at 745 cm$^{-1}$, a NH stretching band at 3400 cm$^{-1}$ as strong as in the monomer with reference, e.g., to the corresponding CH deformation band. This result clearly indicates that the 1 position is not involved in coupling. Also, as 2,3-dimethylindole displays a single band at 740 cm$^{-1}$, the band at 745 cm$^{-1}$ indicates that coupling does not involve the benzene ring, in agreement with previous suggestions.[8] It is therefore inferred that the coupling positions are 2 and 3 and not 1 and 3 as previously suggested on theoretical grounds.[8]

Analogous results have been obtained from poly(**2**) and poly(**3**). In the IR spectrum of neutral poly(**3**) (Figure 2c), beside a single strong CH band at 805 cm$^{-1}$, a strong NH band is present at 3330 cm$^{-1}$ as in the monomer. Neutral poly(**2**) (Figure 2b) shows the CH band at 770 cm$^{-1}$ and the NH band at 3360 cm$^{-1}$, close and partly merged with the carboxylic frequencies.

From these data it appears that all polyindoles are coupled at the 2 and 3 positions. The structure resulting from coupling through the 2 and 3 positions could be a random sequence of linkages or a regular sequence of either 2,3′;2′,3″; etc., or 2,2′;3′,3″, etc., couplings, hereafter named 2,3 and 2,2–3,3 couplings, respectively (Scheme 1). We have been able to discriminate among these possibilities analyzing the polyindole films in acid at different pH conditions.

**Table 1. Redox Potentials for Polyindoles**[a]

| polymer | medium | $E°_1$/V[b] | $E°_2$/V[b] |
|---|---|---|---|
| poly(**2**) | AN | 0.02 | 0.74 |
| | 1 M HClO$_4$ | 0.2 | 0.82 |
| poly(**3**) | AN | 0.35 | 0.97 |
| | 1 M HClO$_4$ | 0.35 | 0.7 |
| poly(**1**); poly(**4**) | AN | 0.3 | 0.6 |
| | 1 M HClO$_4$ | | |
| poly(**6**) | AN | −0.53 | −0.05 |
| | 1 M HClO$_4$ | −0.2 | 0.2 |

[a] As average of oxidation and reduction peak potentials ($E° = (E_{pa} + E_{pc})/2$). [b] Vs Ag/Ag$^+$ for AN and vs SCE for 1 M HClO$_4$.

**pH Dependence of Polyindole Oxidation.** The twin cyclic voltammogram of poly(**2**) and poly(**3**) is surprisingly similar to that of polyaniline, PANI (Figure 1). For this polymer oxidation consists of a two-step oxidation to a half-oxidized conducting state (0.5 e/aniline

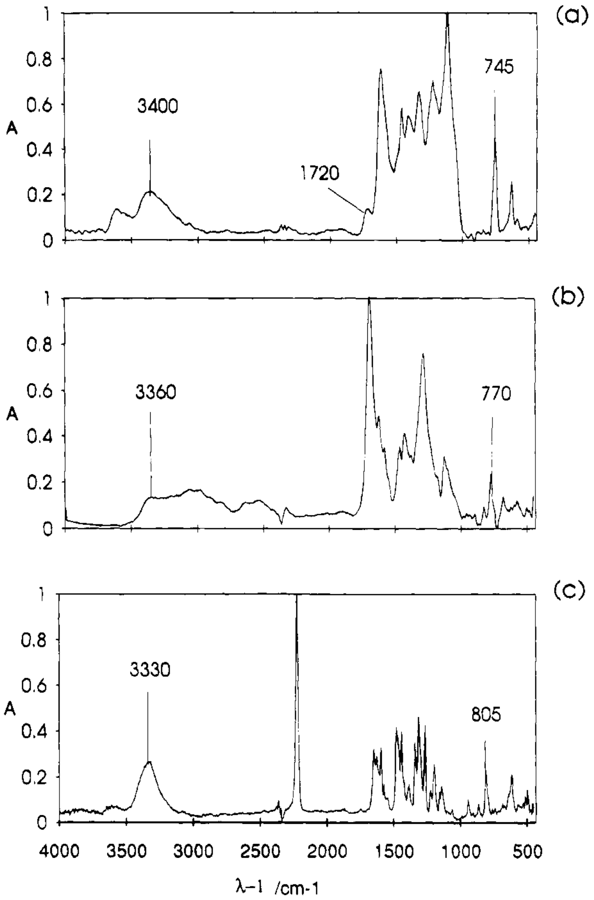


**Figure 2.** IR spectra of neutral poly(**1**) (a), poly(**2**) (b), and poly(**3**) (c) deposits.

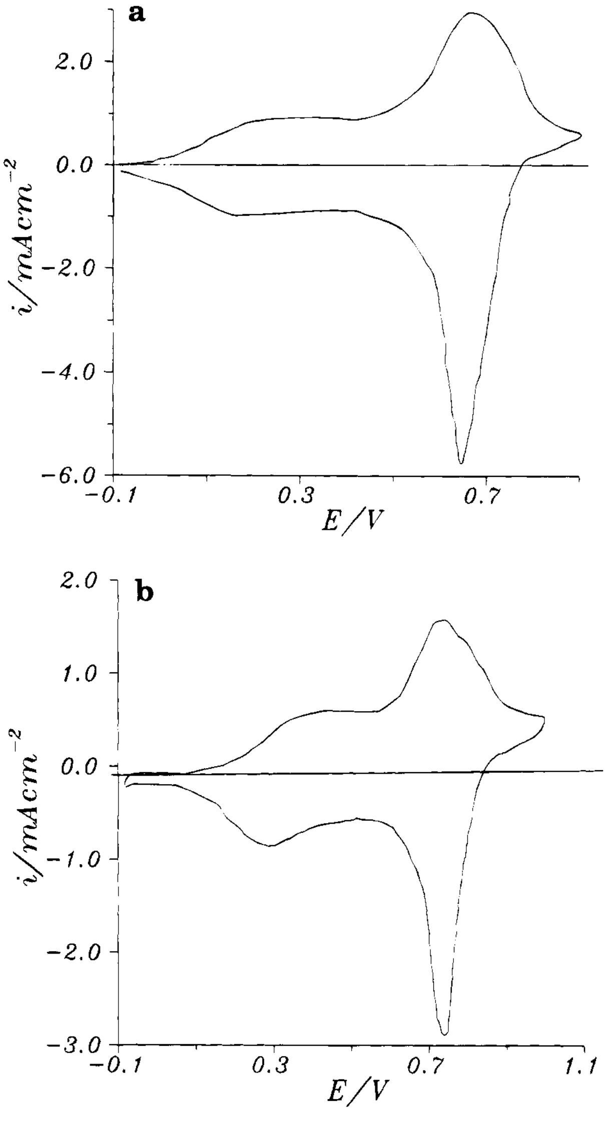
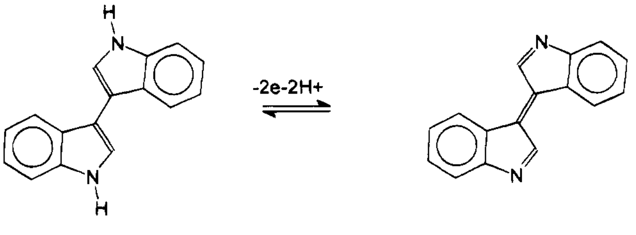


**Figure 3.** Cyclic voltammetry of poly(**2**) (a) and poly(**3**) (b) deposits in 1 M $HClO_4$. Scan rate: 0.1 V/s; $Q_r$ = 12.6 mC/cm$^2$ (a); 6.0 mC/cm$^2$ (b).

**Scheme 3. Enediamine–Diimine Redox System in 3,3′-Biindole and Polyindole**



unit, emeraldine form) and subsequently to a fully oxidized insulating state (1 e/aniline unit, pernigraniline form).[22] The latter process in water is pH dependent (−120 mV/pH) as it is accompanied by the reversible loss of two protons per ejected electron.[23] This fact suggested that the similarity of polyindoles with PANI could be confirmed by CV at different acid conditions.

In $HClO_4$ the redox cycle of poly(**2**) (Figure 3a) appears as a couple of processes involving the same overall charge as in AN. The analogy with PANI appears from the pH dependence of the processes as the first is not pH dependent whereas the second shifts toward positive values as the acidity is increased. The shift (ca. −90 mV/pH for pH between 0 and 3), in substantial agreement with the result reported in the literature[3], is in any case lower than for PANI. The same picture is displayed by poly(**3**) (Figure 3b) and also in this case the more anodic process is pH dependent (ca. −75 mV/pH in the same pH range). For poly(**2**) proton exchange could in principle involve the carboxylic groups, as suggested previously[24] but in the case of poly(**3**) the only possible sources of protons are the NH groups. Since the most likely (i.e., energetically favored) way of involving the NH groups in a pH-dependent redox process is provided by the enediamine–diimine system (Scheme 3) for which a 3,3′-linkage is required, it is inferred that the polymer is 2,2–3,3 coupled. This suggests that the same redox process operates also in poly(**2**) and therefore that this polymer is similarly structured. On these grounds and considering that at pH values lower than 3 the carboxylic group is undissociated, the previous attribution of the pH-dependent oxidation of poly(**2**) to proton release from the carboxylic groups in a 1,3-coupled polymer[24] is ruled out. It must be finally pointed out that the pH dependence of the second oxidation process in the investigated pH range is intermediate between −60 and −120 mV/pH, which indicates an incomplete proton release following the oxidation.

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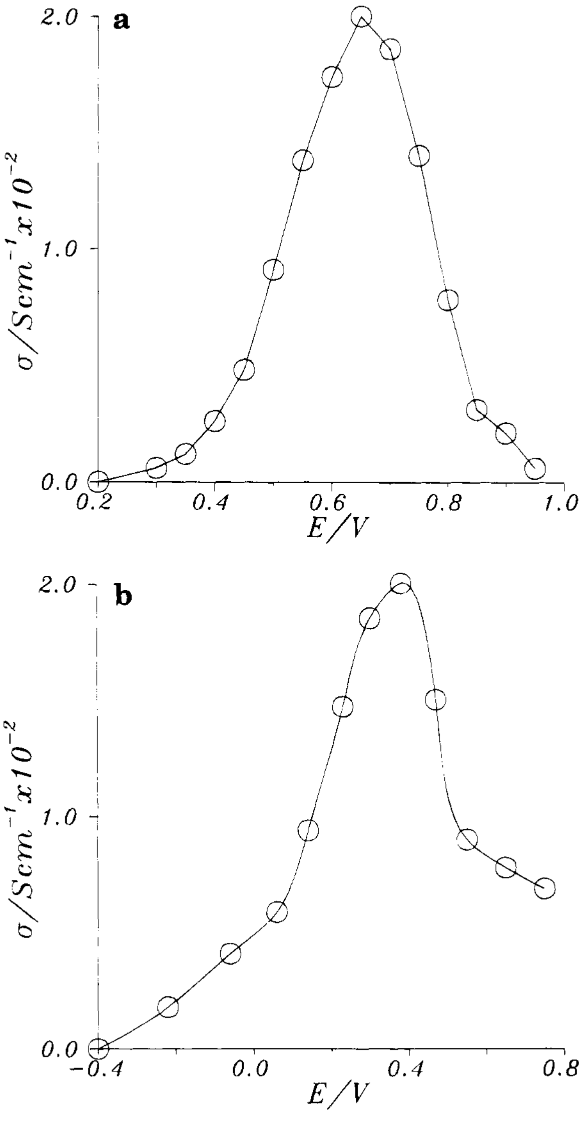

**Figure 4.** In situ conducitvity of poly(**3**) in 1.0 M $HClO_4$ (a) and of poly(**1**) in AN + 0.1 M TEAP (b).

The suggestion that oxidation involves proton dissociation from the NH moiety was confirmed by IR and UV–vis spectroscopy on poly(**3**). The NH stretching IR band is removed upon oxidation and is restored by reduction. Oxidation of the yellowish polymer ($\lambda_{max}$ = 420 nm) turns the color to blue, and the oxidized polymer shows an acid–base transition of the color similar to that for PANI (blue in acid, $\lambda_{max}$ = ca. 700 nm; pink-violet in base, $\lambda_{max}$ = ca. 500 nm). For comparison, the corresponding acid-base transition in PANI is from 590 to 520 nm.[25]

The correspondence of these polymers with PANI was evidenced also by in situ conductivity measurements. Like PANI, poly(**3**) (Figure 4a) and poly(**2**) show a finite window of conductivity as they become conductive at an intermediate oxidation state (maximum conductivity of ca. 2 × $10^{-2}$ S/cm) and are switched to an insulating state at full oxidation.

As far as poly(**1**) is concerned, also its CV shows a twin-peak feature, but its pH dependence is not well defined due to the broadness of the response and the high oxidation potential, close to that of oxidative degradation. Instead, the highly positive $E°$ values, their low separation $\Delta E°$ and the capacitive behavior seemingly indicate a different structure. Poly(**1**) behaves differently also in the conductive properties since though it becomes conductive upon oxidation, with a maximum conductivity of ca. 2 × $10^{-2}$ S/cm at an intermediate potential, its conductivity is appreciably high at the maximum oxidation level (Figure 4b).

In an attempt to clarify the structure of poly(**1**) we investigated the behavior of differently coupled biindoles.

**Electrochemistry of Biindoles.** As a first approach we considered the anodic coupling in AN+0.1 M TEAP of biindoles with *N*-methyl substitution, to overcome complications from possible proton dissociation of the nitrogen position in the course of the overall oxidation process.

The 3,3′ dimer **7** is oxidized in two one-electron reversible steps at $E°$ = 0.21 and 0.56 V and the one-electron oxidation product is a stable radical, in agreement with the literature.[26] The 2,3′ dimer **9** is oxidized in an irreversible process which at high scan rates (>100 V/s) appears as a reversible one-electron oxidation ($E°$ = 0.33 V). In fact electrolysis, requiring ca. 1 e/mol, does not produce polymer, which may be due to parallel reactions competing favorably with the polymerization process. The 2,2′ dimer **5** is oxidized at $E_p$ = 0.60 V with $n_{app}$ = 1.3 e/mol and in this case polymer deposition is observed. The redox cycle of the polymer, similar in shape to that of poly(1), is centered at $E°$ = 0.45 V with a charge yield of only 2%, due to losses of soluble products. The coupling rate of the radical cation is very fast as no reversibility is observed in the CV of **5** up to a scan rate of 1000 V/s.

The fact that **5** polymerizes is first of all a confirmation that the N-position is not involved in coupling. Furthermore the absence of coupling in **7** and the high rate of polymerization in **5** indicate that the 3 position is more reactive than the 2, which agrees with the suggestion provided by spin density calculations.[8]

These results predict that oxidation of the unsubstituted biindoles will result in polyindole formation only in the case of 2,2′-biindole, which was punctually found. Oxidation of 2,2′-biindole **4** beyond the oxidation peak ($E_p$ = 0.44 V) is accompanied by polymer formation. The redox cycle which is developed is the same as for polyindole produced from indole, poly(**1**) (Figure 1a), with the same charge yield (8% in $10^{-3}$ M solution). Also the IR and electronic spectrum of poly(4) match those of poly(**1**). Since poly(**4**) must inevitably originate by coupling at the 3 position, the obvious conclusion is that poly(**1**) is 2,2–3,3 coupled like poly(**2**) and poly(**3**).

After all these findings, we may suggest that indole polymerization proceeds through the following pathway: initially formed radical cations dimerize to yield the 3,3′-dimer and, to a lower extent, the 2,3′ and 2,2′ dimers; further oxidation of the 3,3′ and 2,3′ dimers produces radical cations which are less reactive to coupling and follow therefore parallel degradative routes or are further oxidized, whereas oxidation of the 2,2′ dimer yields a very reactive radical cation which polymerizes.

Though oxidation of 3,3′-biindole under the same conditions did not provide polymers, it showed unex-

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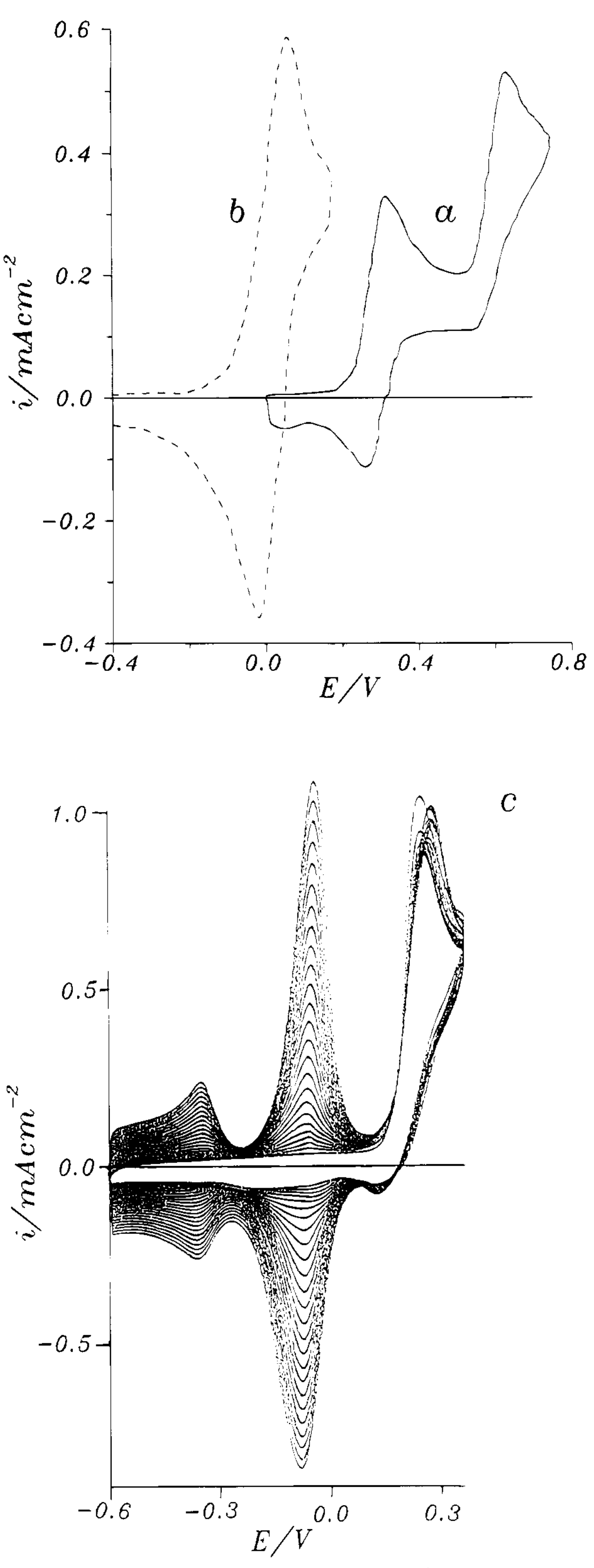

**Figure 5.** Cyclic voltammetry of **6** $1 \times 10^{-3}$ M in AN + 0.1 M TEAP (a), in AN + 0.1 M TEAP + $2 \times 10^{-3}$ M collidine (b) and in AN/$H_2O$ + 1M $NaClO_4$ + $10^{-3}$ M $HClO_4$ (c) at a glassy carbon electrode. Scan rate: 0.1 V/s.

pected features which allowed the obtaining of a novel polymeric material as reported in the following section.

**Electrochemistry of 3,3′-Biindole.** The oxidative behavior of 3,3′-biindole (**6**) shows features different from those of the N-methyl-substitued homologue. Its CV in AN+0.1 M TEAP (Figure 5a) is similar as it shows two one-electron steps at 0.28 and 0.62 V, the first of which is fully reversible. Nevertheless the radical cation in this case is not stable in the long run as electrolysis at the first step requires 2 e/mol with production of a material which in the mass spectrum shows main peaks corresponding to dimeric and trimeric species (*m/e* = 462 and 690). These data indicate that the radical cation is only moderately stable, producing in the time of electrolysis low oligomers, inevitably 2,2-coupled. The fact that the radical cation of the N-substituted dimer is conversely stable suggested that the oligomerization is promoted by proton dissociation of the 3,3′-biindole radical cation at the NH group, which prompted us to investigate its oxidation in the presence of suitable proton scavengers.

In fact the electrochemical pattern of 3,3′-biindole is altered by the addition of a base. Collidine (2,4,6-trimethylpyridine), a base relatively strong yet inert to oxidation and radical attack, if present over a 2:1 ratio changes the two one-electron oxidations into a two-electron process which on a glassy carbon electrode appears quasi-reversible at $E^\circ = -0.05$ V (Figure 5b). Electrolysis requires 2 e/mol with production of a yellow solution ($\lambda_{max}$ = 410 nm) with the same CV (in reduction) of the pristine solution and which on backward reductive electrolysis requires the same charge and reproduces the starting material. This clearly indicates that the overall process is reversible and suggests that the two-electron oxidation is accompanied by release of protons from the nitrogen atoms to yield the neutral diimmine, 3,3′-biindolylylidene (Scheme 3). As a confirmation the electronic spectrum of the oxidized product matches that reported in the literature for 3,3′-biindolylylidene.[27]

Collidine is thus a too strong base to promote coupling. Instead if a weaker base such as water is progressively added, the first one-electron process increases in height until at a water content >10% (vv) a single three-electron process is displayed at $E_p = 0.25$ V. At this point repetitive CV displays the development of a twin redox cycle due to a growing electroactive deposit (Figure 5c). The response develops with a rate proportional with the concentration of perchlorate salt and is better resolved by acid in $10^{-3}$ M concentration. Typically in AN/$H_2O$ 1:1 (vv) and 1.0 M $NaClO_4$ the charge yield for a $10^{-3}$ M solution is 3%.

The shape of the redox response recalls clearly those of poly(**2**) and poly(**3**), but this analogy is more than formal. The deposit, transferred in $HClO_4$ or AN, shows two redox processes (Figure 6). In acid the first process is pH independent, whereas the second involves proton exchange with a pH dependence of −70 mV/pH between pH 0 and 3. The film, insoluble in all organic solvents, is almost colorless as neutral and violet at full oxidation ($\lambda_{max}$ = 550 nm). In this oxidation state it becomes pink after deprotonation ($\lambda_{max}$ = 490 and 750 nm) and reverts to violet in acid. All these features, common to poly(**3**) and poly(**2**), suggest that the material is polyindole, forcedly 2,2–3,3 coupled, i.e., with the same sequence of linkages of poly(**1**) but with $E^\circ$ values lower than for poly(**2**) and poly(**3**), as formerly expected. Final confirmation of the formulation as polyindole came from IR and elemental analysis data. In the oxidized form (the neutral form is air sensitive) the IR spectrum shows a single CH band at 749 cm$^{-1}$, no NH band at 3400 cm$^{-1}$ and three strong bands at 1521, 1555, and 1607 cm$^{-1}$,

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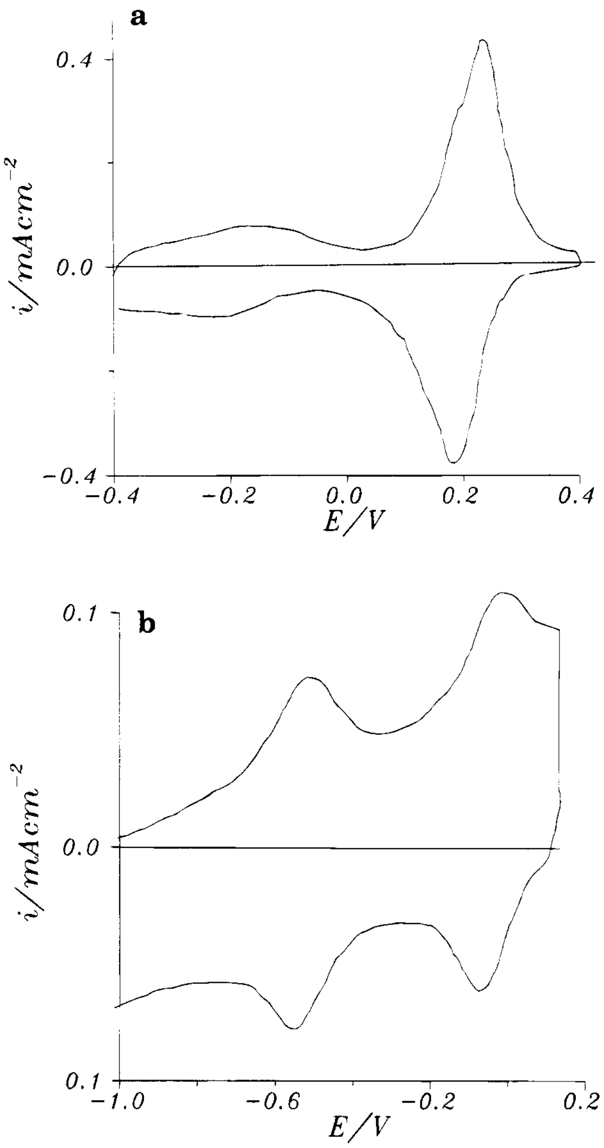
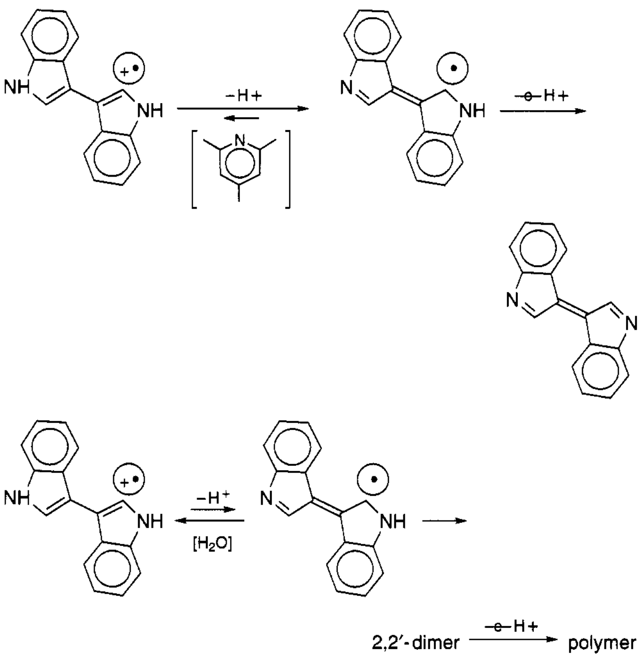


**Figure 6.** Cyclic voltammetry of poly(**6**) (a) in 1.0 M $HClO_4$ and (b) in AN + 0.1 M TEAP.

absent in the spectrum of 3,3′-biindole and attributable to the conjugated C=C and C=N bonds in the diimine moiety; elemental analysis gives the expected formulation $C_8H_4N$.

To explain the different oxidative behavior of 3,3′-biindole in the presence of collidine and water, we suggest that the initially formed radical cation is deprotonated to an extent which depends on the base strength (Scheme 4). Deprotonation is complete with collidine and the neutral radical is further oxidized at the electrode to the diimine; with water the neutral radical is formed to a limited extent so that coupling may compete favorably with the electrode oxidation and polymer is obtained. From the suggestion that coupling at the 2 position is activated by proton loss, it is conceivable that for cyano- and carboxyindole the electronwithdrawing substituents promote proton dissociation of the relevant radical cations, thus inducing the observed alternating 2,2−3,3 coupling.

**Scheme 4. 3,3′-Biindole Oxidation in the Presence of Collidine or Water**



The fact that poly(**4**) (and poly(**1**)) on one hand and poly(**6**) on the other are all 2,2−3,3 coupled but differ markedly for the voltammetric properties deserves at least a tentative explanation. The higher redox potentials of poly(**4**) compared with poly(**6**) may be due to a lower degree of polymerization and/or the presence of oxidative defects. This result may be the outcome of the high reactivity of the 3 position in the radical cation of **4** not only vs coupling but also vs parallel competitive attack of nucleophiles in the medium (e.g., traces of water) which could limit polymer growth to a relatively low degree of polymerization. For this point it is worthwhile mentioning that a weak carbonyl band at 1720 $cm^{-1}$, attributable to overoxidized polymer chain ends, is present in the IR spectrum of poly(**1**) (Figure 2a) and poly(**4**). The insertion of electron-withdrawing carbonyl groups would also contribute to the observed positive shift of the polymer redox potential. Conversely the reactivity of the 2 position in the radical cation of **6** is activated by proton loss and the resulting neutral radical, free from nucleophilic attack, would couple to a polymer composed of chains long, regular, and relatively defect-free.

## Conclusions

The results of this investigation may be summarized as follows:

Polyindoles from anodic coupling of indoles are shown to be coupled at the 2 and 3 positions of the pyrrole ring and not at the 1 and 3 positions as previously assumed.

Coupling to polymer originates from initially formed 2,2′-dimers, and the resulting structure is a regular alternance of 2,2−3,3-couplings.

Coupling of 3,3′-biindole, promoted by proton dissociation of the radical cation, results in a polyindole much more defect-free than the polymer from coupling of indole.

The peculiar structure of polyindoles makes their redox behavior pH dependent, with involvement of the 3,3′-coupled indole units in an enamine−diimine redox transition. As a consequence the redox pattern of polyindoles and their overall behavior are similar to those of polyaniline.

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