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Vibrational properties and structural studies of doped and dedoped polyindole by *FT*i.r., Raman and EEL spectroscopies

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Polyindole obtained by oxidizing coupling of indole, C_8NH_7, was studied either in the doped or the undoped state by *FT*i.r., Raman and electron energy loss (EEL) spectroscopies. Interpretation of the vibrational modes was facilitated by comparison of the absorption spectra of polyindole and those of related molecules acting as standards. The change from the doped to the dedoped state of polyindole is accompanied by a reordering of the Π bonds of the system characterized by the disappearance of $C = N$ bonds and the reappearance of N–H bonds. Detailed analysis of the different spectral manifestations gives evidence for a monomer coupling involving the positions 2 and 3 of the carbon atoms. © 1997 Elsevier Science Ltd.

(Keywords: polyindole; EEL spectroscopy; *FT*i.r. and Raman spectroscopies)

INTRODUCTION

Polyindole is an electroactive polymer which can be obtained either by anodic or by chemical oxidation of indole, C_8NH_7. This polymer and its derivatives appear to be good candidates for applications in various domains like electronics, electrocatalysis and pharmacology. They can be also models for certain biopolymers like melanines[1]. However, despite the number of publications related to the electropolymerization and the mechanisms of interconnection of indole and some of its oligomers, the identification of the polymerization sites is still debated[2–8]. *Figure 1* presents the geometry of the molecule of indole and the different possible structures for polyindole. Tourillon and Garnier[6], based on the fact that the electrooxidation of N-methylindole did not result in the formation of a conducting polymer and that the i.r. absorption band of the N–H bond was no longer present in the doped polyindole, proposed a coupling via the 1,1 positions of the monomer unit. They did not give the second site of polymerization. Waltman *et al.*[7] who carried out tests of polymerization of indole substituted at different positions and who studied the effects of electron donating and accepting substituents on the position 5 by spin densities calculations on the radical-cations, suggested that indole polymerization occurred mainly via the 1 and 3 positions.

Recently, Zotti *et al.*[8] studied the polymerization of biindoles and, by analogy with polyaniline, proposed a stereoregular coupling for these compounds at the 2,2–3,3 positions. Finally, an analysis of i.r. and X.p.s. spectra of doped polyindole suggested that the polymer structure resulted in a regular alternation of 1,1–3,3 couplings[9].

Taking into account these previous contradictory data, it appeared necessary to provide new experiments for the accurate determination of the polymerization sites of indole.

In this communication, we present some vibrational properties of doped and dedoped polyindoles based on the analysis of their i.r. and Raman spectra. The comparison on the evolution of the vibration modes appearing in polymers and in some simpler related molecules acting as references usually facilitates the interpretation of the experimental absorption spectra. Thus, we have selected some molecules based on substituted monomers in order to analyse the differences observed in the spectra of doped and dedoped polyindole. EELS studies were also carried out to support our interpretation of the structure of polyindole.

EXPERIMENTAL

Electrochemical synthesis of polyindole doped with perchlorate ClO_4^- anions was carried out after anodic oxidation in the galvanostatic mode of indole on either polished stainless steel or indium-tin-oxide (ITO) glass electrodes[11,12]. The electrolyte was composed of acetonitrile containing indole (0.05 M) and lithium perchlorate (0.1 M). The current density was equal to 1 mA cm^{-2}. Dedoping of such a polymer was achieved in a solution which did not contain indole either in the galvanostatic mode (cathodic reduction) or by linear sweep voltammetry carried out at low scan rates

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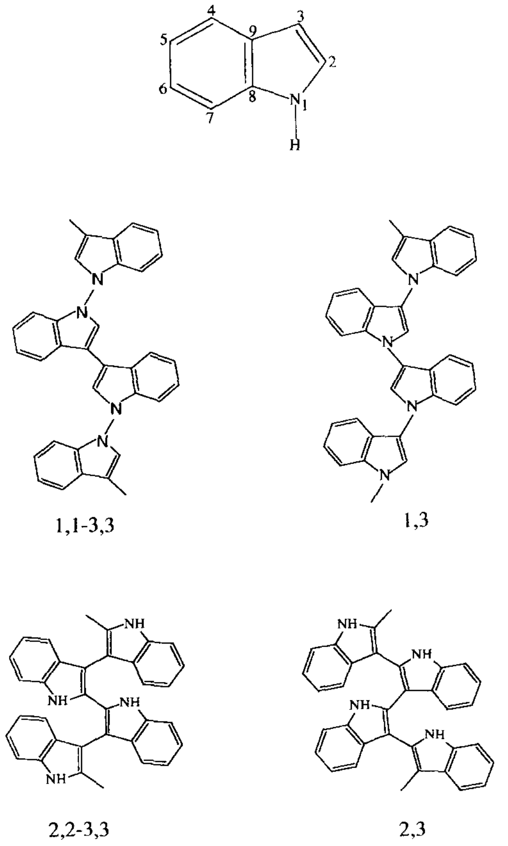

1,1-3,3

1,3

2,2-3,3

2,3

Figure 1 Representation of indole monomer and of the different possible structures of polyindole

($0.05\,mV\,s^{-1}$) to obtain an homogeneously dedoped material. These operations (synthesis and dedoping) were monitored by a computer-controlled potentiostat–galvanostat (EG&G 273). Polyindole can be also obtained in the doped state by chemical techniques as previously described by Billaud *et al.*[13]. In this case, when ferric chloride ($FeCl_3$) is used as oxidizing agent, chloride anion Cl^- is found as dopant species. Dedoping of such a chemically synthesized and doped polyindole can be obtained after treatment in a sodium hydroxide solution (NaOH, 2 M) for 10 min. Further reaction of such a reduced polyindole with HCl (6 M) for 10 min results in the redoping of the polymer[10].

The i.r. absorption spectra are obtained at room temperature with a Fourier transform infrared (*FT*i.r.) spectrometer (Perkin–Elmer 2000). The powder samples are mixed with potassium chloride at about 3 wt% and are pelletized. The single beam transmission spectra of sample pellets are obtained with a resolution of $4\,cm^{-1}$ in 20 scans. The absorbance spectra, shown in this paper, result from the ratio between the intensity of the single beam through the sample pellet (I_S) and the intensity of the single beam of the reference KCl pellet (I_R) for which the spectrum is recorded in the same physical conditions (temperature, pressure, water vapour pressure in the spectrometer) in order to avoid any artefact. The absorbance is defined then as

$$\mathrm{Abs}(\bar{\nu}) = \log_{10}\left(\frac{I_R(\bar{\nu})}{I_S(\bar{\nu})}\right)$$

where $\bar{\nu}$ is the wavenumber. Sample and detector compartments are purged with a continued flow of dried air.

The Raman spectra of pure powders are obtained with the T64000 Raman spectrometer of Jobin Yvon. The Raman spectra are excited by the laser line at 514.5 nm of an argon laser (Spectra Physics 164). The sample is positioned under a microscope which focuses the laser beam on the sample and which collects the backscattering light. In order to avoid photoeffects and hence degradation of the materials strongly absorbing in the excitation range, the power of the incident laser beam on the sample was minimized and was of about 1 mW. The backscattering Rayleigh is eliminated by a notch filter, while the backscattering Raman is dispersed by a grating (1800 grooves mm^{-1}) on a multichannel detector (a charged coupled device camera cooled at the liquid nitrogen temperature). The spectral resolution is of $2.5\,cm^{-1}$. The precision of the wavenumber is better than $1\,cm^{-1}$. The integration time on the detector is 1 s for the indole sample, and 30 s for the polyindole samples.

Electron energy loss spectroscopy (EELS) was performed using a transmission electron microscope (TEM, Philips CM 20) coupled with a parallel EEL spectrometer (Gatan 666). Samples were milled, then dispersed by ultrasonic waves into ethanol and finally deposited on a copper microscope grid covered with a holey amorphous carbon film. EEL spectra were collected at 200 kV in the diffraction coupling mode. The energy resolution, measured as the full width at half height of the zero loss energy peak was equal to 1.4 V. A cryogenic sample holder cooled down at 170 K was used in order to reduce the irradiation damage caused by the high energy electrons.

RESULTS AND DISCUSSIONS

FT*i.r. study of electrochemically synthesized polyindole and comparison with indole and reference compounds*

Figure 2 shows the *FT*i.r. and Raman spectra of crystalline indole. In *Figure 3* are presented the i.r. spectra between 4000 and $500\,cm^{-1}$ of polyindole electrochemically doped (PIE) with ClO_4^- and then electrochemically dedoped. *Figure 4* displays some extended parts of the i.r. spectra of *Figure 3* between 1650 and $1300\,cm^{-1}$ (*Figure 4a*) and between 1100 and $600\,cm^{-1}$ (*Figure 4b*). The different vibration modes of indole and electrochemically doped polyindole as well as their assignments are listed in *Table 1*. These assignments are provided both on the basis of literature data and after our previous experimental determinations[9,18].

The main differences observed in the i.r. spectra of doped and dedoped polyindole are presented in *Table 2*. The most important points are the appearance of two absorption bands at 3380 and $1540\,cm^{-1}$ and the disappearance of three bands at 1370, 1145 and $635\,cm^{-1}$ in the spectrum of dedoped polyindole. Since the peaks at 1084 and $635\,cm^{-1}$ are characteristic of ν_3 and ν_4 vibrational modes of the dopant anion ClO_4^- the absence in the spectrum of dedoped polyindole of the peak at $635\,cm^{-1}$ and the presence of a very ill-defined hump at $1084\,cm^{-1}$ would indicate the presence of trace amounts of remaining doped parts (*Figure 4b*). In *Figure 5* are presented for comparison the i.r. spectra of indole, doped and dedoped polyindole in the frequency range $3800–2800\,cm^{-1}$; the strong and narrow peak at $3400\,cm^{-1}$ observed in the indole spectrum is characteristic of the N–H bond. This peak is broader and shifted

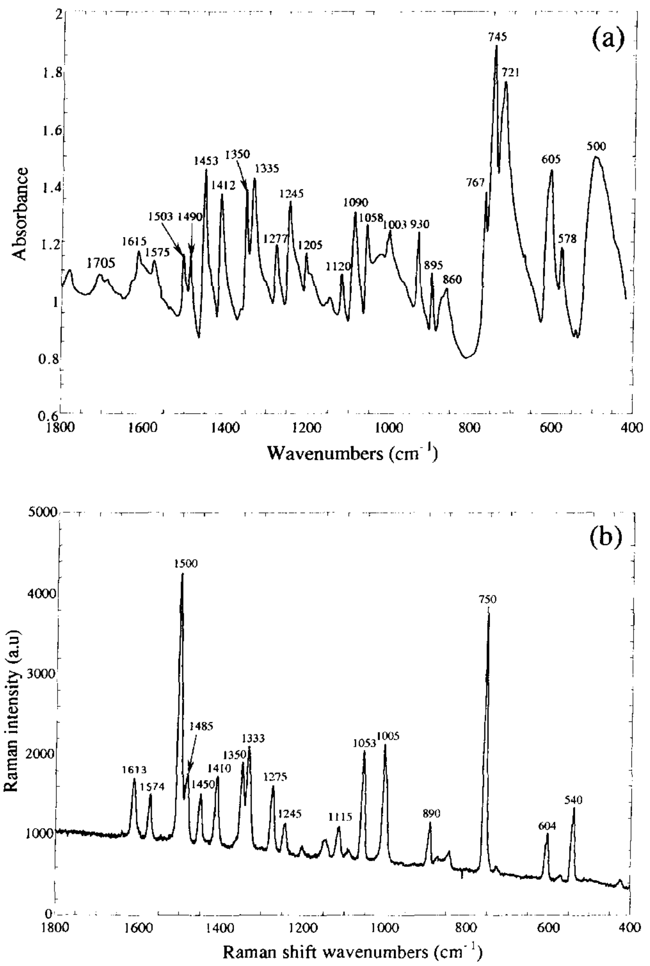

Figure 2 *FT*i.r. (a) and Raman (b) spectra of solid indole

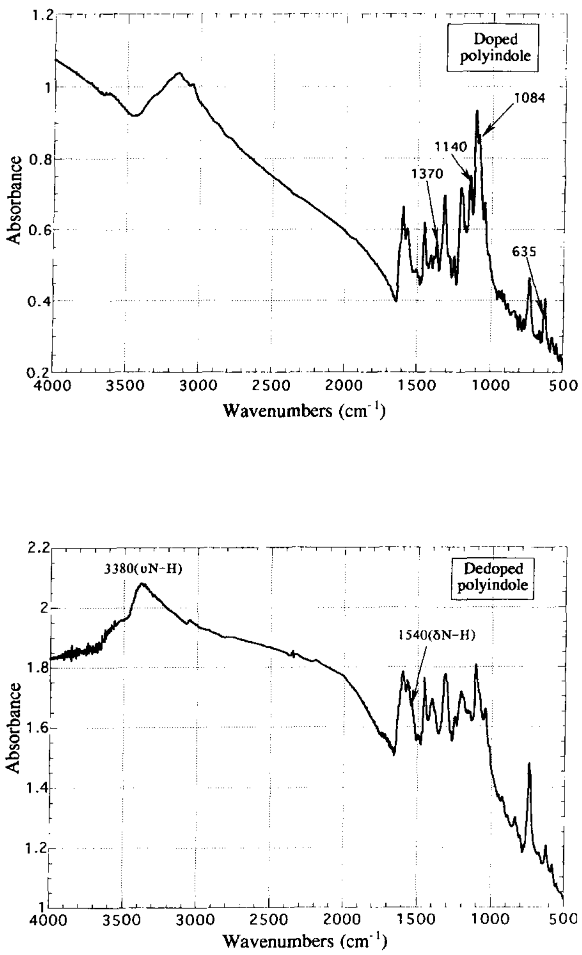

Figure 3 Comparison of the *FT*i.r. spectra of doped and dedoped polyindole

to 3380 cm^{-1} in the spectrum of neutral (dedoped) polyindole; to the contrary, when the polymer is doped, this peak is absent and is replaced by a large and negative band around 3450 cm^{-1} attributable to plasmons (free carrier absorption) typically generated in highly absorbing and conducting systems. In the i.r. spectra of dedoped polyindole, the presence of the NH band at 3380 cm^{-1} seems to be associated to that of a low intensity band at 1540 cm^{-1} and that of a shoulder centred at 1410 cm^{-1} (*Figure 4a* and *Table 2*). There is no absorption at 1540 cm^{-1} for indole but in related mono- and disubstituted monomers (2-methylindole, 3-methylindole, 2,3-dimethylindole) absorptions at 1548, 1554 and 1567 cm^{-1} are present respectively[23]. This observation suggests that the band at around 1550 cm^{-1} is related to a deformation mode of the NH bond strongly coupled to vibration modes involving the C_2 and C_3 atoms (*Table 2*). Thus, this mode which would appear at 1503 cm^{-1} in indole where C_2 and C_3 are both bonded to only one hydrogen atom, would be shifted to around 1540 cm^{-1} as soon as one C_2 or C_3 carbon atom is bonded with another carbon atom. The strong band at 1412 cm^{-1} observed in indole and corresponding to a mode where the NH deformation is coupled to the C_2–C_3 elongation, is shifted to 1430 cm^{-1} for 2,3-dimethylindole and only 1418 and 1410 cm^{-1} for 3-methylindole and 2-methylindole respectively. In neutral polyindole, this band centred at 1405 cm^{-1} is now asymmetrical and has broadened, which suggests a configuration comparable to that of 2,3-dimethylindole. In the doped polymer, this band is absent. Therefore, according to these observations, the band appearing at 1540 cm^{-1} in the dedoped polymer can be the result of the combination of the NH bond deformation and of the double C = C bond stretch between C_2 and C_3 attributed by analogy with the parent elongation observed in pyrrole[14]. The reappearance of this band at 1540 cm^{-1} in the dedoped polymer confirms the presence of the NH bond and therefore supports the fact that the nitrogen species is not a polymerization site. Moreover, it can be concluded that the bond alternation in the pyrrolic cycle is modified during the transformation of the doped form of polyindole into the dedoped one, in agreement with the previous suggestions of Zotti *et al.*[8].

The bands at 1570 and 1505 cm^{-1} assigned respectively to the vibration of the C = C aromatic bonds typical of indoles[15] and to the stretch of the C–N aromatic bonds become more intense in the dedoped polymer which is probably related to a reinforcement of these bonds especially in the pyrrolic cycle.

As shown in *Figure 4a*, the band at 1370 cm^{-1} appears in the spectrum of doped polyindole which does not contain NH bonds, and is absent for dedoped polyindole. The origin of this band is questionable but a reasonable hypothesis is that it could be related to modes involving the atoms C_8, N, C_2, and C_3[14,18]. As a matter of fact, if we turn to indole, the two bands (doublet) at 1352 and 1330 cm^{-1} are attributed to a mode involving the C_2–C_3 stretch coupled to the C_8–N elongation in Fermi

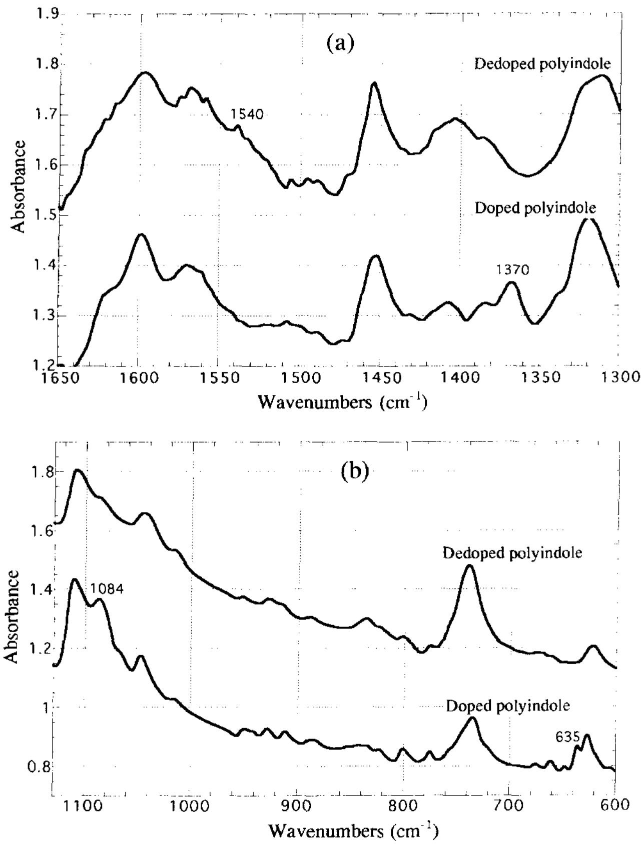

Figure 4 Extended scale of *FT*i.r. spectra of *Figure 3*: between 1650 and 1300 cm^{-1} (a) and between 1100 and 600 cm^{-1} (b)

resonance[18]. This mode is very sensitive to the substitution on the atom C_2 since in 2-methylindole and in 2,3-methylindole, only one component is apparent at 1360 cm^{-1} and at 1330 cm^{-1} respectively while in 3-methylindole the two components of the doublet are present. In the case of polyindole, the dopant can influence this mode which appears at 1370 cm^{-1} for the oxidized $(C_8\ N\ C_2\ C_3)^+$ state and disappears in the reduced $(C_8\ N\ C_2\ C_3)$ form. In the last case, the frequency of this mode can be shifted to a position where other vibration modes are already present.

Investigation of the band centred around 735 cm^{-1} (*Figure 6*) shows that the peak at 721 cm^{-1} assigned to the out-of-plane deformations of the two C_2–H and C_3–H bonds is only present in the case of indole[18]. Its disappearing in the reference materials and in the polymer can be related either to the substitution of the hydrogen atom by a methyl group (as in 2- and 3-methylindole) or to the occupancy of two sites (as in 2,3-methylindole and in doped and dedoped polyindole). The peak located at 767 cm^{-1} and assigned to the out-of-plane deformation of the C_2–H bond is obviously present in the case of indole and 3-methylindole and is absent in the case of 2-methylindole and 2,3-dimethylindole. Dedoped and doped polyindole spectra exhibit a peak at 735 cm^{-1} and a small component at 774 cm^{-1}. This observation indicates that the benzene ring is not affected in the polymerization process of indole and that the remaining C_2–H bonds correspond probably to the non-bound ends of polymer chains; on the contrary, all the C_3 atoms appear to be involved in the connection between the monomer units, in agreement with previous calculations indicating that C_3 is more reactive than C_2 and with experiments of polymerization of substituted indoles[7].

FT *i.r. study of chemically synthesized polyindole (PIC)*

A similar *FT*i.r. study was carried out on chemically synthesized polyindole (PIC). I.r. spectra of the different states of the polymer (doped, dedoped and redoped) are presented in *Figure 7*.

Dedoping of the polymer PIC results in the appearance of bands at 3400, 1540 and 1290 cm^{-1} typical of vibrations involving the N–H bonds. These bands disappear totally when the dedoped polymer is redoped which gives evidence for the reversibility of the doping reaction, as observed ahead in the case of PIE. The bands located at 1215 and 1190 cm^{-1} disappear after dedoping. They are related to the doping and are attributed to the quinonic form of the doped state which is transformed into the benzonic form, after internal bond reorganization, in the dedoped system.

All the spectra of PIC exhibit a low intensity band at 1708 cm^{-1}. This band, present in the case of oxidation and electrochemical overoxidation of polypyrrole by oxygen[16], is attributed to the elongation of carbonyl groups[17]. Such a band is absent for doped PIE but exists as an ill-defined hump in the dedoped PIE indicating the relative sensitivity of this material towards oxidation. Moreover, the band always present at 3600 cm^{-1} on the spectrum of dedoped PIC and attributed to the stretch of O–H bonds shows that this material contains large amounts of O–H groups. In the spectrum of the doped PIC, this band is also apparent but it is probably screened either by the strong free-carrier absorption or by intermolecular interaction.

Moreover, this band appears also in the spectrum of PIE synthesized in acetonitrile containing water (5% w/w). In the absence of water, no peak at around 3600 cm is present. Therefore, it can be concluded that the existence of OH groups in the material is related to water present in the reaction medium. Such OH groups act on the carbon bond alternation and consequently on the electrical conductivity which is found equal to 10^{-4} and 5×10^{-2} S cm^{-1} for PIC and PIE respectively.

Raman spectroscopic study of PIE

Figure 8 shows the Raman spectra of the doped and dedoped states of polyindole (PIE). We did not observe any sample degradation due to thermal or photochemical effects related to the laser beam. The spectra are intense and exhibit a good signal over noise ratio even for low excitating laser power (1 mW). Laser excitation at 514.5 nm was used to obtain resonance effects that intensify the Raman spectra. In order to better observe the spectral modifications due to the chemical transformations of polyindole, we made the subtraction (*Figure 9*) of the spectra presented in *Figure 8* and normalized on the band at 1600 cm^{-1} characteristic of the benzenic ring (*Table 1*). Such a band is supposed to be insensitive to the doping effects. The resulting spectrum of *Figure 9* exhibits four important spectral modifications. Firstly, two bands at 1265 and 1555 cm^{-1} appear when doped polyindole is dedoped. These bands can be attributed by analogy with the spectrum of the indole monomer to the modes (νN_1C_2, δC_2H, δN_1H) and (δN_1H, νC_8N) at 1503 and 1277 cm^{-1} respectively (*Table 1*).

Table 1 Frequencies and assignments of the major absorption bands for solid indole and doped polyindole (the attributions are given either on the basis of theoretical data or by comparison with reference compound spectra)

Monomer (indole)	Assignment for indole monomer[18]	Assignment for doped polyindole
3400 (s)	νNH	
1615 (m)	$\nu C_7C_8 + \nu C_5C_6 + \nu C_8C_9$	Shifted to 1600 (s) (broad)
1575 (w)	$\nu C_9C_4 + \nu C_6C_7 + \nu C_7C_8$	1570 (m) broad as shoulder of previous band
1503 (s)	$\nu N_1C_2 + \delta C_2H$	Broad weak band centred at about 1510 cm^{-1}
1490 (s)	$\nu C_8C_9 + \delta C_4H + \delta C_7H$	Broad weak band centred at about 1510 cm^{-1}
1453 (vs)	$\delta C_5H + \nu C_8N + \nu C_4C_5$	1450 (s)
1412 (s)	$\delta NH + \nu C_2C_3 + \delta C_6H$	–
–		1370 (m) C = N stretch
1350 (vs)	$\nu C_8N + \delta C_6H + \nu C_2C_3$	–
1335 (vs)	Stretch of pyrrole ring	1320 (s)
1277 (s)	$\delta NH + \nu C_8N + \delta C_6H$	-
1245 (s)	$\delta C_7H + \delta C_4H$	Shifted to 1250 (m)
1205 (m)	$\nu C_3C_9 + \nu C_7C_8 + \nu C_5C_6$	1205 (s)
1145 (w)	$\delta C_6H + \delta C_7H + \delta C_5H$	1145 (s)
1120 (m)	$\nu C_6C_7 + \delta C_5H + \delta C_4H$	1110 (vs)
1090 (s)	$\delta C_2H + \delta C_3H + \nu NC_2$	–
–		1084 ν_3 (ClO_4^-) stretch mode
1058 (s)	$\delta C_3H + \nu NC_2$	–
1010 (s)	$\nu C_4C_5 + \nu C_5C_6 + \nu C_6C_7$	Shifted to 1040 cm^{-1} (vibrational mode of benzene ring)
930 (s)	$\pi C_4H + \pi C_6H + \pi C_7H$	Four very weak bands
895 (m)	$\nu C_8C_9 + \gamma NC_2C_3 + \gamma C_2C_3C_9$	Four very weak bands
860 (m)	Skeletal	
767 (s)	πC_2H	774 (w)
745 (vs)	$\pi C_6H + \pi C_5H + \pi C_3H$	735 (s)
721 (vs)	$\pi C_3H(\pi C_2H + \pi C_3H^9$	–
–		635 ν_4 (ClO_4^-) Bending mode
605 (s)	$\pi C_2H + \pi C_6H + \pi NH$	–
578 (m)	πC–C out of plane	577 (w)
500 (s)	ρNH	–

vs: very strong, s: strong, m: medium, w: weak

As previously described by the i.r. studies, the Raman spectra indicate the reappearance of the NH bond in the dedoped form of polyindole. Secondly, the broad massif around 1400 cm^{-1} (*Figure 9*) is composed of several peaks, the indexation of which remains still uncertain due to the resonance effects that are probably different in the doped and dedoped states of the polymer. The third spectral modification is related to bands at 1190 and 1224 cm^{-1} which are intense for the doped polymer and almost absent for the dedoped material as seen in *Figure 8*. These bands can be related to a quinoic form of the doped polymer that can evolve to an aromatic form upon dedoping. Finally, the last structural modification corresponds to the low intensity band at 1680 cm^{-1} (*Figures 8* and *9*) present in the doped polyindole spectrum. This band could be

Table 2 Differences in the spectra of doped and dedoped polyindoles. The signs + and – correspond respectively to the presence and the absence of the absorption peak

Wavenumbers (cm^{-1})	Doped polyindole	Dedoped polyindole
3380 (N–H)	–	+
1540 (N–H)	–	+
1370 (N = C)	+	–
1140	+	–
1084 (ClO_4^-)	+	–
635 (ClO_4^-)	+	–

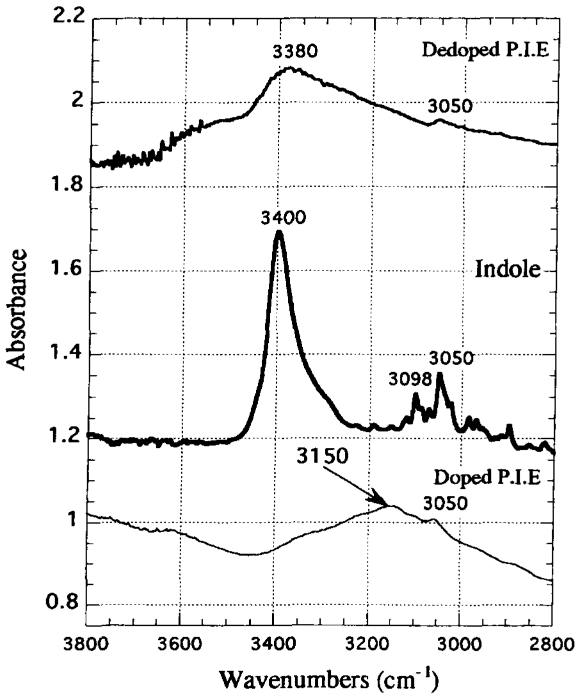

Figure 5 *FT*i.r. spectra around the N–H stretch position for indole, dedoped and doped PIE

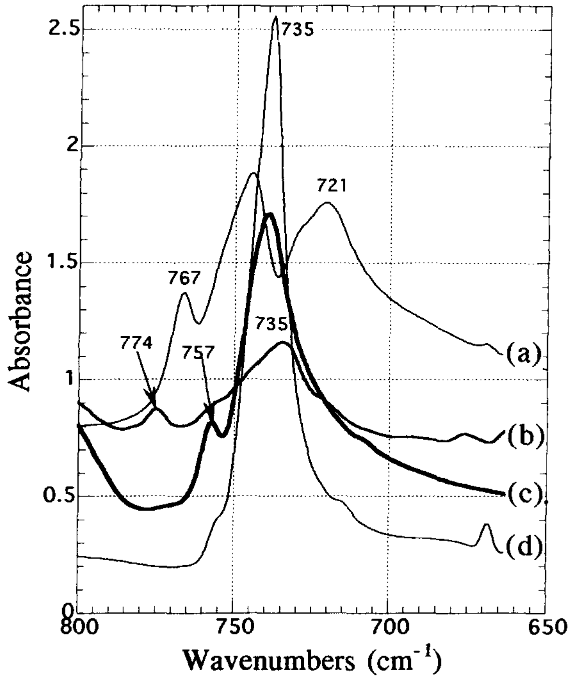

Figure 6 *FT*i.r. spectra in the range 800–650 cm^{-1} for indole (a), doped PIE (b), 3-methylindole (C) and 2,3-dimethylindole (d)

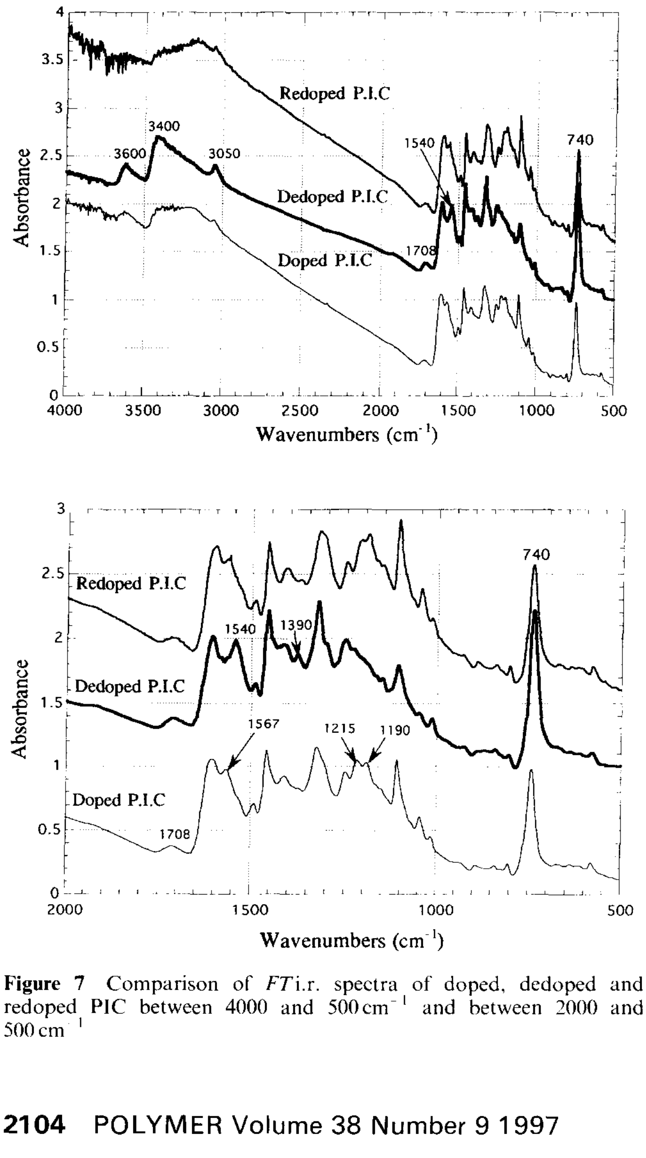

Figure 7 Comparison of *FT*i.r. spectra of doped, dedoped and redoped PIC between 4000 and 500 cm^{-1} and between 2000 and 500 cm^{-1}

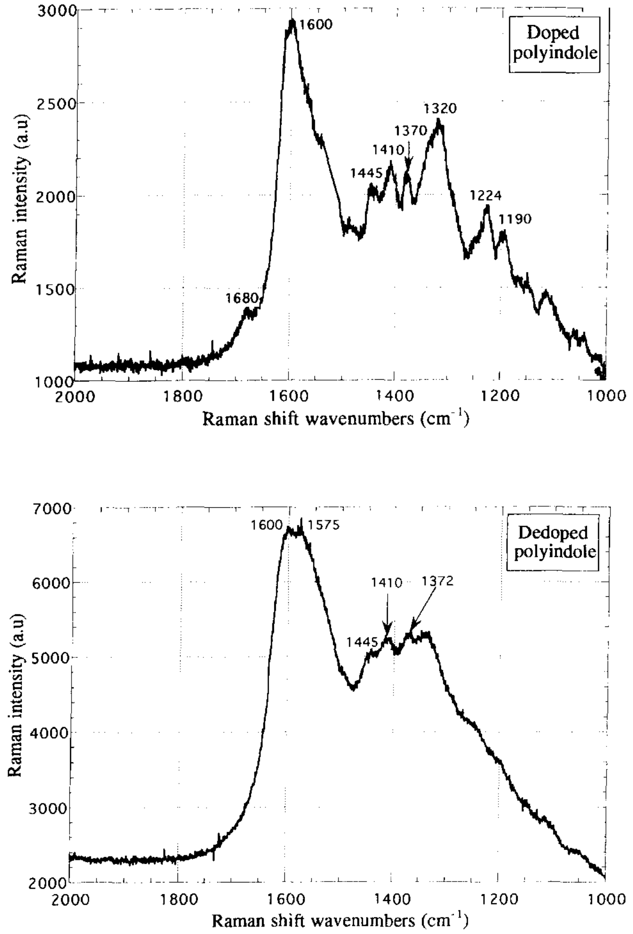

Figure 8 Raman spectra of doped and dedoped polyindole

assigned to a vibration mode which involves C = N bonds not involved in the conjugated system and located at the ends of the polymeric chain.

Tourillon and Garnier[6] suggested that polyindole contains dimeric units with N–N bonds between the monomers. However, two observations allow to rule out this suggestion. The first one is that the band corresponding to the stretch of the N–N bond at 1100 cm^{-1} is intense in the hydrazine Raman spectra and is absent in the case of polyindole. The second observation is the presence of vibrations related to N–H bonds.

Therefore, Raman and *FT*i.r. spectroscopic results

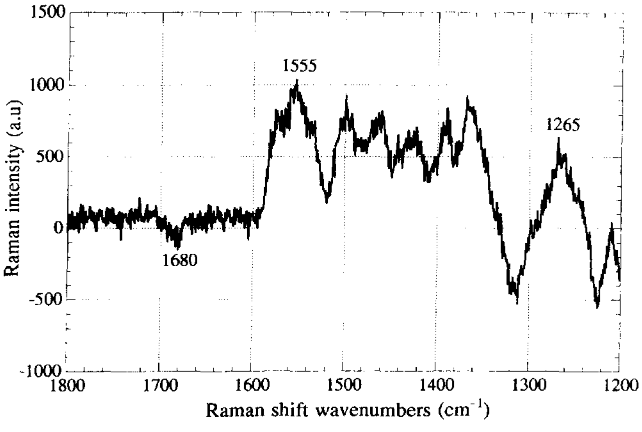

Figure 9 Subtraction of the spectra presented in *Figure 8*

studies agree with the existence of a quinonic structure along the doped polymer chain.

EELS study of doped and dedoped PIE

Figure 10 shows the EELS spectra collected at the *K*-edge of nitrogen both for doped and dedoped PIE. The fine structures present in both spectra can be interpreted in terms of electronic transitions from the 1s atomic orbital level toward antibonding molecular orbital (MO) levels[20–22].

In the case of both doped and dedoped material, the *K*-edge of nitrogen displays a common fine structure at 406 eV corresponding to the transition of 1*s* electron to the antibonding MO σ^* related to the single C–N bond. For doped PIE, a second peak is observed at 398 eV that is attributed to the transition of 1*s* electron to the antibonding MO Π^* characteristic of the double C = N bond. In the spectrum of the dedoped polymer this peak is also present but in the form of a bad defined hump of low intensity. It can be originated either from some doped parts still remaining in the material or to the persistency of the double C = N bond in the ends of chains. The last possibility is the most probable since the disappearance of chlorine is always observed in the EEL spectra of dedoped polyindole.

Like *FT*i.r. and Raman studies, these EELS data confirm the structural change occurring during the redox transformation of polyindole and characterized by the disappearance of the C = N bond in the dedoped material. The possible trace amounts of doped polyindole which could remain trapped in the dedoped matrix during the dedoping process do not really modify this interpretation. These results are in agreement with the formation of a quinonic state in the doped polymer even if this state is not so pronounced as in aromatic polymers like polyparaphenylene, polyparaphenylene–vinylene and polyaniline. According to our data, we suggest that the monomeric indole units are linked via the carbon positions 2 and 3, either in a regular, or a statistical or in a random sequence.

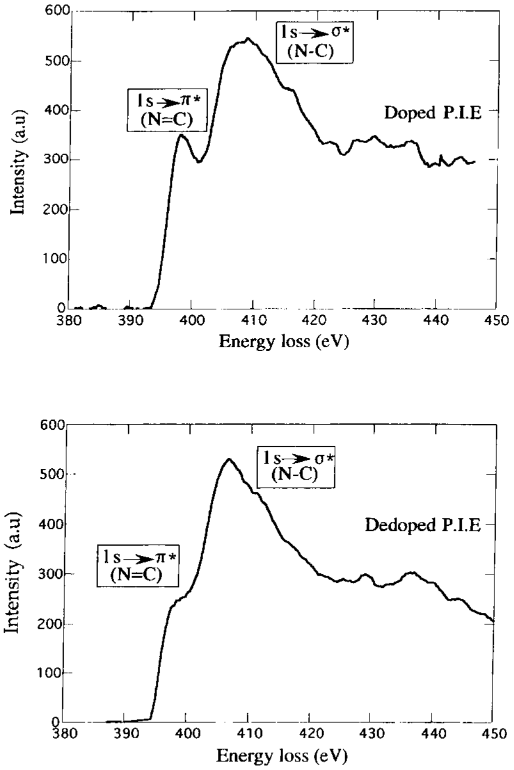

Figure 10 EEL spectra of doped and dedoped PIE at the *K*-edge of nitrogen

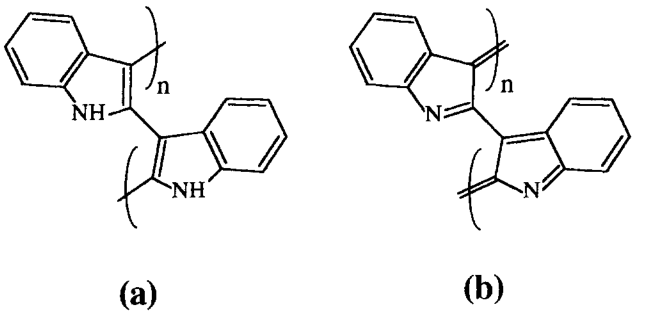

Figure 11 Aromatic structure of the dedoped polyindole (a) and quinonic form of the doped polymer (b)

Moreover, our results show that the doping–dedoping processes of polyindole implies to basic structural states present in *Figure 11*: the quinonic form would correspond to the doped polymer while the aromatic structure would be related to the dedoped material.

CONCLUSION

Polyindole synthesized by electrochemical or chemical techniques was studied in the doped and the dedoped states by *FT*i.r., Raman and EEL spectroscopies. It was shown that the change from the doped state to the dedoped one was accompanied by an internal reordering of the conjugated system of bonds, characterized by the disappearance of the C = N bonds and the reappearance of the N–H bonds. Such a mechanism can originate from protonation–deprotonation reactions as previously discussed in the case of polypyrrole[17]. Compared analysis of the different spectral manifestations allowed to propose the carbon atoms C_2 and C_3 as sites of polymerization. However, it was not possible to state precisely if the monomer sequence is regular, statistical or at random. Comparison of calculated and experimental i.r. and Raman spectra are currently in progress[23] in order to answer the question whether the structure of polyindole is stereoregular or not.

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