Spectroscopic studies of protonation, oxidation and light irradiation of polyaniline solutions

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The absorption spectra of emeraldine base and the fully reduced leucoemeraldine in *N*-methylpyrrolidinone (NMP) indicate that the former is stable in this solvent but the latter undergoes oxidation of the amine units to imine units in the presence of dissolved oxygen. The presence of imine units is confirmed by X-ray photoelectron spectroscopy and infra-red absorption spectroscopy. Under light irradiation, this oxidation process is accelerated. Both this polymer and emeraldine base undergo further degradation of the polymer chain. Comparison of the spectra of leucoemeraldine and emeraldine base solutions with aqueous $HClO_4$ added indicates that protonation can occur at the amine units of the former, although this process is not as effective as protonation of the imine units of emeraldine base. The polymers gradually undergo deprotonation resulting in quinoid-imine structures in both cases when oxygen is present, and the deprotonation process is also accelerated by light. On the other hand, the addition of $Cu(ClO_4)_2.6H_2O$ to the leucoemeraldine and emeraldine base solutions results in the polymers approaching the fully oxidized state which is much more stable under light irradiation than the pristine polymer solutions. The similarities and differences between the results obtained in solution and in solid-state are also discussed.

(Keywords: polyaniline; spectroscopic analysis; irradiation)

INTRODUCTION

The existence of polyanilines in various oxidation states and the wide range of electrical conductivities achievable through reversible doping or protonation[1–6] of these forms make polyanilines unique conducting materials with potentially useful applications. Another attractive feature of this class of materials is its solubility in certain solvents. It has been found that the polyaniline salt, emeraldine-hydrochloride (EM-HCl) is generally not soluble in common organic solvents such as THF and chloroform[7,8] but it dissolves completely at room temperature in concentrated sulphuric acid[9]. In contrast, the polymer in the 50% oxidized poly(paraphenylene amine imine) base form, emeraldine (EM) base, is partially soluble in THF, DMF and DMSO and completely soluble in *N*-methylpyrrolidinone (NMP)[10], and concentrated H_2SO_4 (ref. 9).

A number of spectroscopic studies on polyanilines in solution or in films cast from solutions have been carried out[11–16]. These measurements together with band structure calculations[17,18] have provided a better understanding of the electronic structure of the different forms of polyaniline. The optical absorption spectrum of the fully reduced form of polyaniline, poly(paraphenylene amine) or leucoemeraldine (LM), shows a strong peak at 3.6–3.8 eV which has been assigned to the π–π^* transition[14,15,18]. The absorption spectrum of EM base has an additional peak at ~2.0 eV. The 2 eV absorption has been earlier attributed to an n–π^* transition from the nitrogen lone pair to the conduction (π^*) band[11]. However, spectroscopic experiments with EM base with improved structural order show that the relative amplitude of this absorption peak compared to the 3.7 eV peak is similar to that found from amorphous films, suggesting that the 2 eV absorption is probably not due to an n–π^* transition which could only be strongly allowed if the local structure were highly disordered[15]. Theoretical calculations suggest the assignment of this absorption band to a charge-transfer exciton-like transition from the highest occupied energy level to the lowest unoccupied energy level[14,15]. Upon protonation of EM base, the 2eV absorption disappears and new absorptions appear, centred at 2.9 eV, 1.5 eV and 1.0 eV with a large tail extending into the infra-red (i.r.) region[12,13]. This long tail has been assigned to intraband-free carrier excitations[19,20].

In this paper, we report on the structural changes of LM and EM base in NMP with and without u.v.–visible light irradiation. These results are compared with the data obtained when an acid or oxidizing agent is present in the polyaniline-NMP solution. The structural changes are monitored with u.v.–visible absorption spectroscopy, i.r. absorption spectroscopy and X-ray photoelectron spectroscopy (x.p.s.).

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EXPERIMENTAL

Emeraldine hydrochloride (EM-HCl) was first prepared by the oxidative polymerization of aniline by ammonium persulphate in HCl according to the method reported in the literature[1]. It was then converted to EM base by treatment with excess 0.5 M NaOH and then dried by pumping under reduced pressure. LM was obtained by treating EM base with excess phenylhydrazine according to the method of Green and Woodhead[21]. The LM and EM base were dissolved in NMP and these solutions of various concentrations were either kept in the dark or exposed to irradiation from a 150 W Xe arc lamp (Kratos LH151). Unless otherwise stated, the NMP was used as received ($>99\%$ purity) and no special efforts were taken to eliminate air from the solvent or the vessel containing the polymer solution during the experiment. At selected time intervals, the u.v.-visible absorption spectra of the solutions were determined using a Shimadzu UV-260 spectrophotometer. The experiments were repeated with 0.1 M aqueous $HClO_4$ or 0.1 M $Cu(ClO_4)_2.6H_2O$ in NMP added to the LM and EM base solutions. For selected conditions, the solid was recovered from solution after evaporation of the NMP and its structure was compared with that of the pristine sample. The recovered solid was washed with ethanol to remove residual NMP before i.r. absorption spectroscopy and x.p.s. were performed. The i.r. absorption spectroscopy was carried out on a Perkin-Elmer Model 682 spectrophotometer with the solid dispersed in KBr. The x.p.s. measurements were carried out on a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons). The polymer samples were either cast from solution as a film directly on the sample studs, or in the case of powder samples, double-sided adhesive tape was used for mounting the samples on to the studs. The X-ray source was run at 12 kV and 10 mA. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. All binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. In spectral deconvolution, the full width at half maximum (FWHM) of the Gaussian peak components was kept constant in a particular spectrum.

RESULTS AND DISCUSSION

Leucoemeraldine and emeraldine base solutions

The u.v.-visible absorption spectrum of freshly prepared LM in NMP (*Figure 1*, $t = 0$ curve) reveals a strong absorption band centred at 345 nm (3.6 eV) and a very weak residual absorption at 635 nm (~ 2 eV). The latter peak indicates a very small fraction of quinoid groups present in the sample[14] which is consistent with the i.r. absorption spectrum (see later section). However, there is an increase in the intensity of the 635 nm peak and a decrease in the intensity of the 345 nm peak with time. These changes are accelerated under u.v.-visible light irradiation (compare *Figure 1b* with *1a*). With a 2×10^{-4} M LM solution, a maximum in the intensity of the 635 nm peak is obtained after about 30 min of irradiation (*Figure 1b*). At this point, the relative intensity of the 635 nm peak compared to the 345 nm peak approaches that of EM base (see later section). Under further irradiation, this peak exhibits a blue shift and a decrease in intensity. A similar blue shift and decrease in intensity are also observed for the 345 nm peak. The u.v.-visible absorption spectra of a 2×10^{-3} M LM solution with and without u.v.-visible irradiation are shown in *Figures 1c* and *1d*. (For these spectroscopic measurements, the more concentrated solution was diluted with NMP to obtain the absorbance values in the range shown.) With the more concentrated solution, the rates of change of the intensity of the 635 nm peak relative to that of the 345 nm peak have decreased. The spectra in *Figure 1d* indicate that after 6 h of u.v.-visible light irradiation of the more concentrated solution, the 640 nm peak has not shifted to lower wavelengths even though its intensity has increased significantly. When the NMP used was purged with N_2 and the LM solutions were kept under N_2, the optical spectra of the solutions show no significant changes over a 24 h period if u.v.-visible light irradiation is absent. Under u.v.-visible irradiation, the blue shift and decrease in intensity of the 345 nm are also observed but the increase in intensity in the 635 nm region is minimal. Hence these experiments illustrate that dissolved oxygen plays a role in the degradation of LM in NMP solution.

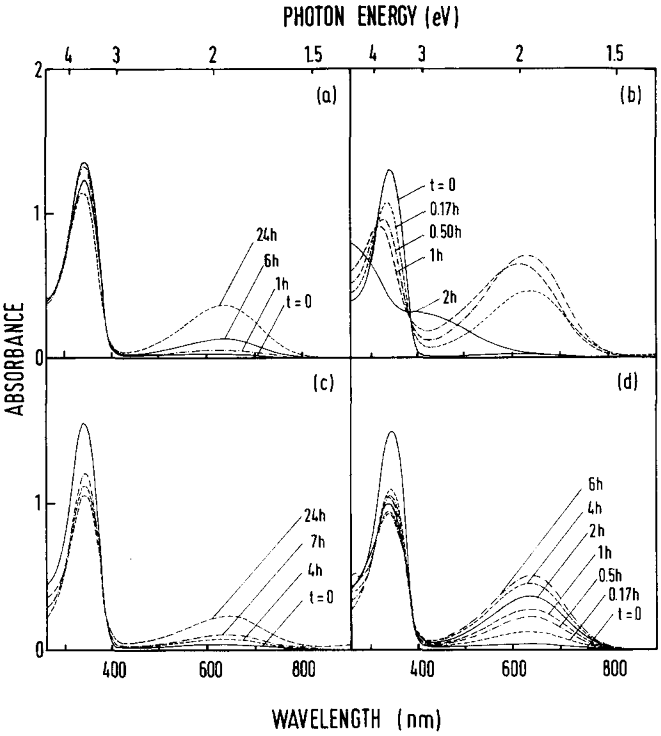

Figure 1 U.v.-visible absorption spectra of leucoemeraldine in NMP solutions: (a) 2×10^{-4} M, not irradiated; (b) 2×10^{-4} M, under u.v.-visible light irradiation; (c) 2×10^{-3} M, not irradiated; (d) 2×10^{-3} M, under u.v.-visible light irradiation

Since the 635 nm peak can be used as a measure of the oxidation state of polyaniline[14], the spectra in *Figure 1* suggest that LM in NMP loses hydrogen from some of its amine groups. X.p.s. and i.r. absorption spectroscopy were carried out on the solid recovered from the 2×10^{-3} M solution after 6 h of u.v.-visible light irradiation and the results are presented in *Figures 2* and *3* respectively. In *Figure 2a* the x.p.s. N1s spectrum of the freshly prepared LM sample exhibits only a single nitrogen environment at a binding energy (BE) of 399.3 eV, which is characteristic of the amine structure[22–24]. After the pristine LM sample is exposed to dry air for two months, the N1s spectrum is skewed towards the low BE side and a new peak component at 398.1 eV

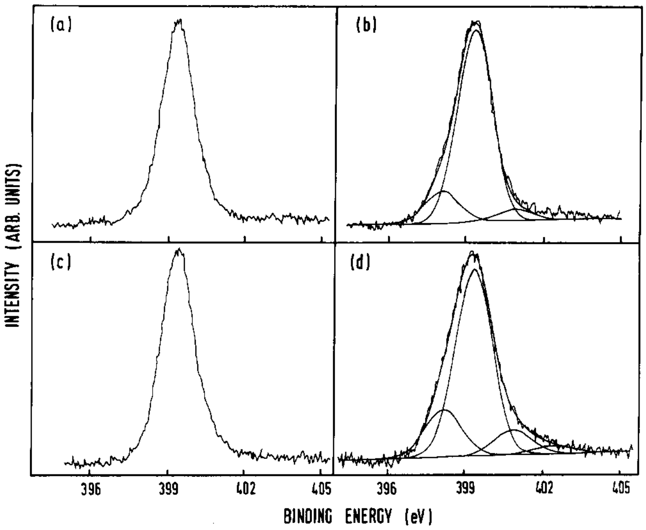

Figure 2 X.p.s. N1s core-level spectra of: (a) freshly prepared leucoemeraldine; (b) leucoemeraldine after exposure to dry air for two months; (c) leucoemeraldine after immersion in deionized water for six months; (d) the solid recovered from a 2×10^{-3} M leucoemeraldine solution after 6 h of u.v.–visible light irradiation

is resolvable (*Figure 2b*). This BE is characteristic of the imine units[22–24], and thus some of the amine units are oxidized by the oxygen in air, albeit rather slowly, to imine units. However, LM can be kept in deionized water over six months and yet its N1s spectrum (*Figure 2c*) does not deviate significantly from that of the pristine LM. In contrast, the N1s spectrum of the solid recovered from NMP solution (with dissolved oxygen present) after u.v.–visible light irradiation (*Figure 2d*) shows that ~18% of the nitrogen exists as imine units. Thus, the oxidation of this LM sample can be represented as follows

$$[\text{-B-NH-B-NH}]_n \rightarrow [(\text{-B-NH-B-NH-})_{1-Y}(\text{-B-N=Q=N-})_Y]_n$$

where B denotes the C_6H_4 ring in the benzenoid form, Q denotes the C_6H_4 ring in the quinoid form and Y is equal to 0.18. In addition, the presence of a high BE (~401 eV) tail can be seen in *Figure 2d*. This tail probably arises from charge-transfer interactions with oxygen and partial contribution from the satellite structure of the imine component[24]. The C1s core-level spectrum of this sample is quite similar to that of pristine LM except for a slight broadening of the peak towards the high BE side in the former.

The i.r. absorption spectra of freshly prepared LM and the solid recovered from NMP solution after u.v.–visible light irradiation are shown in *Figures 3a* and *3b* respectively. Earlier studies[11,25] have suggested that the modes at about 1500 cm^{-1} and 1600 cm^{-1} are associated with the aromatic ring stretching. Tang *et al.*[26] have associated the peak at about 1500 cm^{-1} with the benzenoid ring and the absorption at 1600 cm^{-1} with the quinoid ring. The i.r. spectrum in *Figure 3a* exhibits a very low 1600 cm^{-1}/1500 cm^{-1} intensity ratio and hence the peak assignments support a structure rich in benzenoid units. The spectrum in *Figure 3b* shows an increase in the 1600 cm^{-1}/1500 cm^{-1} intensity ratio and the presence of a weak absorption band at 1380 cm^{-1}. In fact, this spectrum shows close resemblance with that of EM base (see below). The 1380 cm^{-1} peak which has been qualitatively linked to the existence of quinoid units[26,27] and the increase in the 1600 cm^{-1}/1500 cm^{-1} intensity ratio suggest the oxidation of amine units to imine units. This is consistent with the x.p.s. and u.v.–visible absorption data. A peak at 1680 cm^{-1} is barely discernible in *Figure 3b*. This is attributed to C=O structures[28] and may indicate a trace amount of NMP present in the sample or slight oxidation of the aromatic rings.

It should be emphasized that the x.p.s. and i.r. data shown in *Figures 2d* and *3b* respectively are for an 'aged' sample whose u.v.–visible absorption spectrum shows two prominent peaks at 345 nm and 635 nm (*Figure 1d*). As shown in *Figure 1*, further ageing of the LM in NMP under light irradiation may lead to a blue shift of both peaks. This suggests further degradation of the oxidized polymer. The degradation of the oxidized polymer should show similarities with that of EM base. *Figures 4a* and *4b* show the u.v.–visible absorption spectra of EM base in NMP solutions having concentrations of 2×10^{-4} M and 2×10^{-3} M respectively, and under light irradiation. It is again observed that spectral changes occur much more rapidly in the less concentrated solution. At a concentration of 2×10^{-4} M, the optical spectra of LM after the initial 30 min (*Figure 1b*) show essentially the same features of those of EM base (*Figure 4a*). The spectroscopic study of aniline oligomers of different number of aniline units (n) and of different degrees of oxidation[25] shows a red shift of the π–π^* transition peak from 288 nm for $n = 2$, to 309 nm for $n = 4$ and to 326 nm for EM base cast from DMF solution. The position of the exciton band is also dependent on the chain length, as well as on the distribution of benzenoid and quinoid rings. For a tetramer with one quinoid ring, the peak appears at 589 nm and for oligomers with alternating benzenoid and quinoid chain structure, it is shifted to the higher energy side at 412 nm for $n = 2$ and 476 nm for $n = 4$. Thus, the spectra in *Figure 4a* suggest further oxidation and/or a decrease in the chain length of the

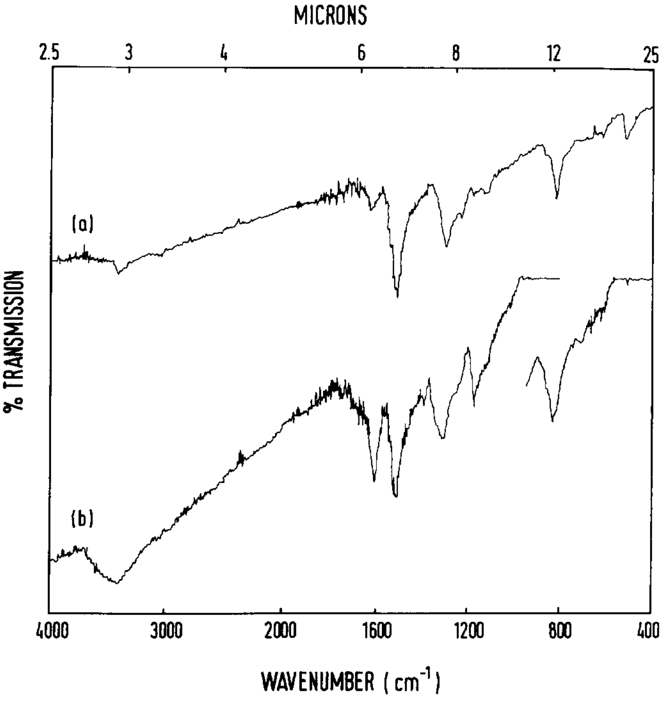

Figure 3 I.r. absorption spectra of: (a) freshly prepared leucoemeraldine; (b) the solid recovered from a 2×10^{-3} M leucoemeraldine solution after 6 h of u.v.–visible light irradiation

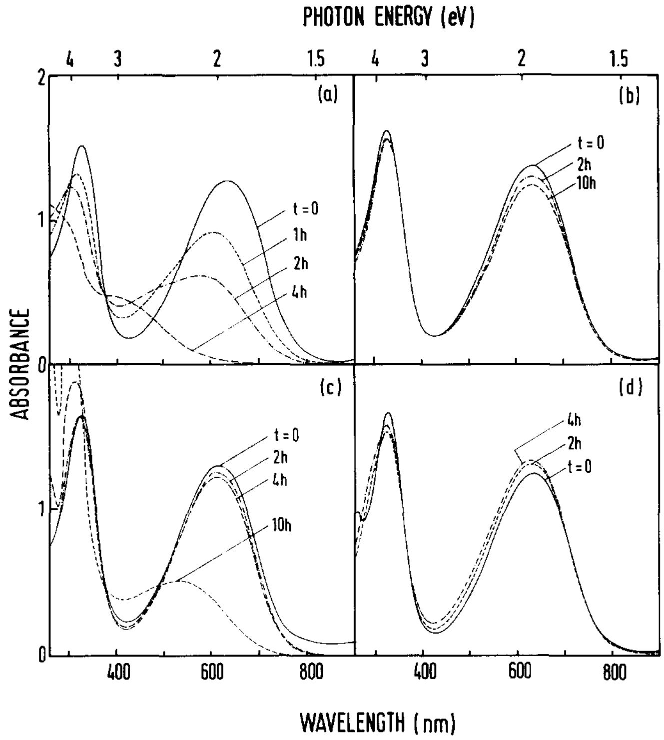

Figure 4 U.v.–visible absorption spectra of emeraldine base in NMP solutions: (a) 2×10^{-4} M, under u.v.–visible light irradiation; (b) 2×10^{-3} M under u.v.–visible light irradiation; (c) 2×10^{-4} M 90% THF–10% NMP solution, under u.v.–visible light irradiation; (d) 2×10^{-4} M, 50°C, not irradiated

polyaniline upon light irradiation. In the absence of oxygen, light irradiation of the 2×10^{-4} M EM base solution results in the almost complete disappearance of the exciton band at 635 nm within an hour. The π–π^* transition peak progressively undergoes a blue shift and decrease in intensity with further irradiation, similar to that shown in *Figure 4a*.

In addition to the experiments carried out with different concentrations, a 90% THF–10% NMP solution was also used. Under light irradiation, the EM base also degrades, but at a much reduced rate than in NMP alone (comparing *Figure 4c* with *Figure 4a*). In the absence of light irradiation, the optical spectrum of EM base in NMP after several days shows no significant changes from that of the freshly prepared solution. Under prolonged heating of the EM base solution at 50°C, only minor spectral changes are observed (*Figure 4d*). Thus, the NMP molecules can only react effectively with the EM base in the presence of u.v.–visible light. Experiments with various cut-off filters indicate that light of wavelength greater than 460 nm has only minor effects on the EM base solution. The lower wavelength limit is determined by the walls of the glass vessel containing the polymer solution which prevent the transmission of most of the irradiation below 300 nm. The critical combination of light and selective solvents for degradation to occur has also been observed with poly((*o*-(trimethylsilyl)-phenyl)acetylene) in chlorinated solvents[29]. This process is also characterized by a blue shift in the main absorption band, and a decrease in the extent of conjugation and molecular weight of the polymer.

Figure 5 compares the x.p.s. C1s and N1s core-level spectra of the solid recovered from a 2×10^{-4} M EM base solution (with dissolved oxygen present) after 1 h light irradiation and those of pristine EM base. A significant broadening of the C1s spectrum is observed in the degraded sample (*Figure 5c*). The presence of oxygen-containing groups such as carbonyl and ether-like structures in the sample would result in peak components having positive BE shifts from the main component peak at 284.6 eV attributable to the normal C atoms in the polymer[30]. At around 291 eV, a shake-up satellite can also be resolved in *Figure 5c*. The presence of the shake-up peak may be attributed to a more localized electronic structure[31,32] consistent with a loss of conjugation. The N1s spectrum of the freshly prepared EM base (*Figure 5b*) can be deconvoluted into two major peak components at 398.1 eV and 399.3 eV, consistent with the proposed EM base structure[1]. The slightly lower amount of imine structure observed is probably associated with the presence of a small amount of positively charged nitrogen as indicated by the residual N1s high BE tail. The N1s spectrum of the degraded sample (*Figure 5d*) indicates a higher amine/imine ratio than that observed in the pristine EM base. Thus, the x.p.s. data do not indicate further oxidation of the amine units of EM base to imine units during the degradation process. The i.r. absorption spectrum of pristine EM base (*Figure 6a*) shows the absorption bands of the quinoid and benzenoid units at *ca.* 1590 and 1500 cm^{-1} respectively[26] to be of about equal magnitude. Both bands are still prominent in the i.r. absorption of the degraded sample (*Figure 6b*). However, this spectrum shows a strong absorption band at 1680 cm^{-1}, attributable to the C=O group[28]. Thus, the i.r. data are again consistent with the x.p.s. data.

As mentioned earlier, it is possible that there is residual NMP in the solid sample and this will contribute to the presence of C=O structures and to an increase in amine/imine ratio. However, since both the recovered LM and EM base samples are similarly rinsed with ethanol, the much higher amount of C=O structures in the latter indicates that these structures are probably incorporated into the polymer. Both the pristine EM base and the degraded sample have a small amount of mostly covalently bonded chlorine which is derived from EM-HCl and is not removed during compensation by NaOH to yield EM base. The Cl/N ratios (of 0.08) of both samples are identical, further suggesting that the

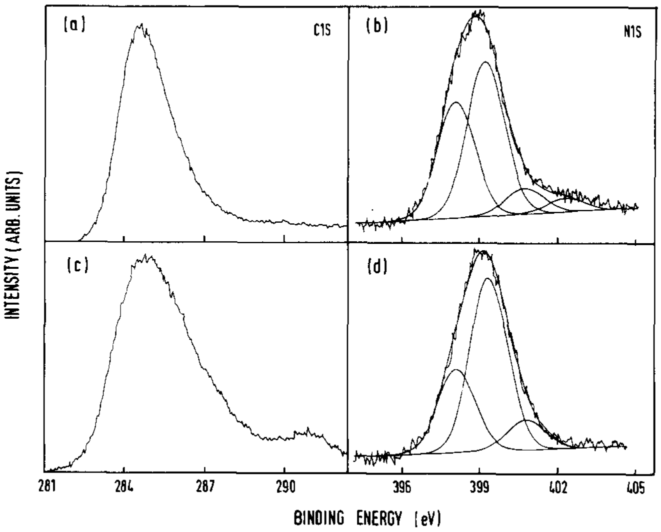

Figure 5 C1s and N1s x.p.s. core-level spectra of: (a) and (b) emeraldine base; (c) and (d) solid recovered from a 2×10^{-4} M emeraldine base solution after 1 h of u.v.–visible light irradiation

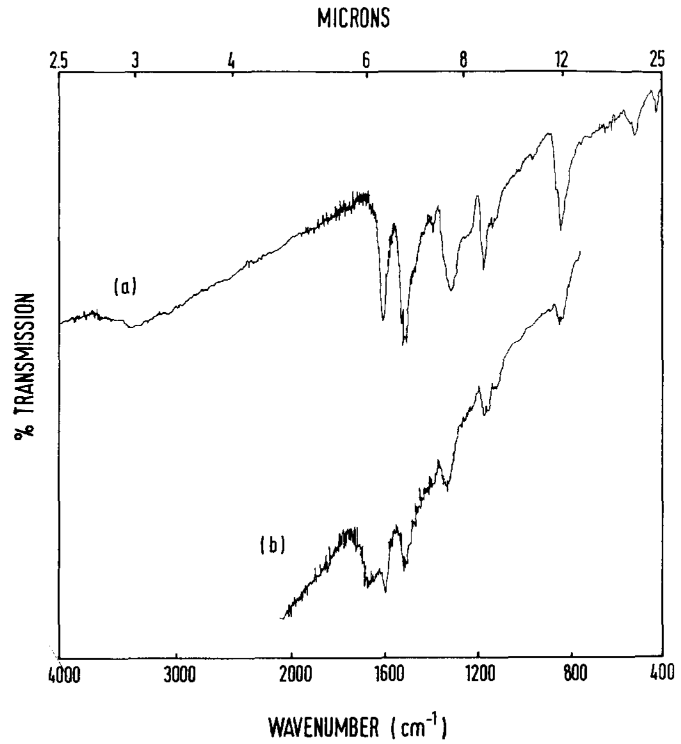

Figure 6 I.r. absorption spectrum of: (a) emeraldine base; (b) solid recovered from a 2×10^{-4} M emeraldine base solution after 1 h of u.v.-visible light irradiation

amount of residual NMP in this degraded EM sample is quite small. As the period of irradiation increases, the intensity of the 1680 cm^{-1} i.r. absorption band, attributable to the C=O structure, increases indicating a progressive oxidation of the aromatic rings. However, for the highly degraded samples, x.p.s. data indicate a decrease in Cl/N ratio and hence the solvent molecules may have also been incorporated into the polymer and are not removable by rinsing with ethanol.

Protonation and oxidation in solution

The optical spectra of LM in NMP solution after the addition of $HClO_4$, without and with light irradiation, are shown in *Figure 7a* and *7b* respectively. The corresponding spectra for the EM base solutions are given in *Figure 7c* and *7d*. The changes in the optical spectrum of EM base upon exposure to media with different pH values have been well established[12,13]. However, as indicated in *Figure 7c* when protonation of EM base by $HClO_4$ occurs in NMP, the protonated species exist as a meta-stable state. After 24 h, the original green solution (at $t = 0$) has turned dark blue, the 635 nm peak characteristic of the quinoid units is prominent and the charge-transfer tail extending to the i.r. region is greatly diminished. This indicates that the protonated quinoid imine units ($-NH^+{=}Q{=}NH^+-$) of the polymer is reverting to the undoped state ($-N{=}Q{=}N-$). The deprotonation process is accelerated under light irradiation (*Figure 7d*), but, in this case, it is also accompanied by degradation of the polymer as described earlier. No precipitate was observed in the solutions during the experiments. With EM base in powder form, protonation by $HClO_4$ results in a conductive salt which is also soluble in NMP. However, if HCl is used as the protonating acid, the powdery EM-HCl salt is not soluble in NMP, and if the protonation is carried out in NMP solution, there is also a decrease in the charge transfer tail extending into the i.r. region with time, and this decrease in intensity is also accompanied by precipitation of the solid.

In the case of LM solution, the initial intensity of the charge-transfer tail is lower but that of the 430 nm intrachain absorption band[13] is higher than the corresponding bands in the spectrum of protonated EM. The intensity of the charge-transfer tail gradually increases and then decreases as the 630 nm peak becomes more prominent (*Figure 7a*). The lower initial intensity of the charge-transfer tail of this spectrum as compared to *Figure 7c* suggests that protonation occurs more readily with the EM base. A similar conclusion is reached with EM base and LM in powder form protonated by $HClO_4$. A significantly higher ratio of ClO_4^-/N (and N^+/N) can be obtained in the former. The solution and solid state results confirmed the findings from earlier studies[6,27] that some of the amine nitrogens of LM can be protonated resulting in ($-B-NH_2^+-$) units. The solution spectrum of protonated LM indicates that the protonated structure undergoes deprotonation resulting in quinoid units (similar to that observed with protonated EM solution). This is again consistent with the observation that LM protonated by HCl gradually transforms into a structure similar to that of partially protonated EM, with the appearance of imine units[27]. Under light irradiation, the degradation of protonated LM is also accelerated (*Figure 7b*) and the process bears similarities with that observed in protonated EM solution (*Figure 7d*). The protonation experiments were also carried out under N_2. For LM solutions under this condition, the spectral changes as shown in *Figure 7a* and *7b* are also observed with the exception that the 635 nm peak is not prominent. Thus, the deprotonation process in NMP in the absence of oxygen does not readily result in quinoid units. A similar

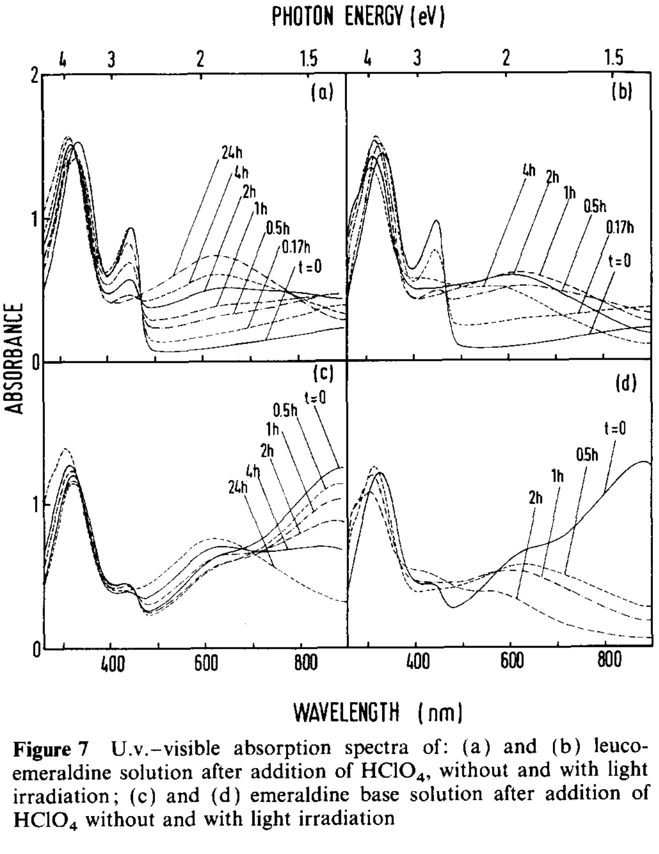

Figure 7 U.v.-visible absorption spectra of: (a) and (b) leucoemeraldine solution after addition of $HClO_4$, without and with light irradiation; (c) and (d) emeraldine base solution after addition of $HClO_4$ without and with light irradiation

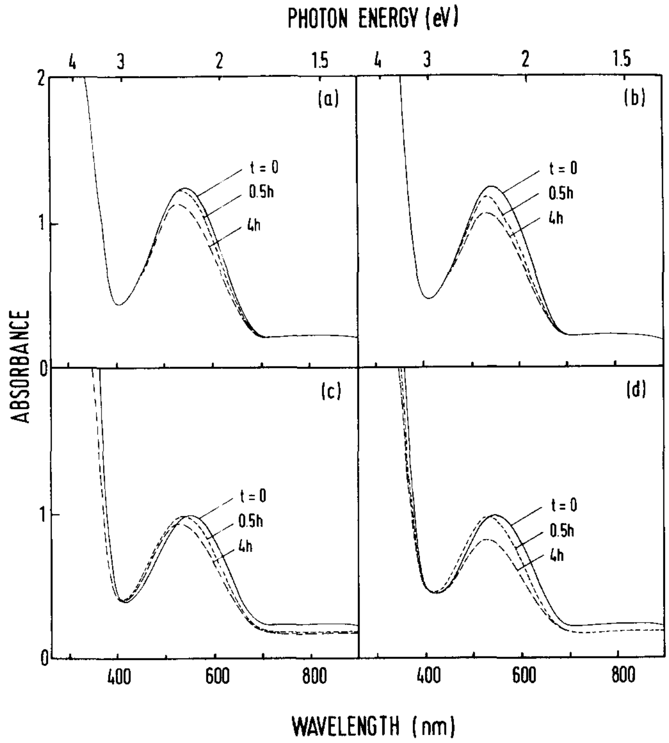

Figure 8 U.v.–visible absorption spectra of: (a) and (b) leucoemeraldine solution after addition of $Cu(ClO_4)_2.6H_2O$, without and with light irradiation; (c) and (d) emeraldine base solution after addition of $Cu(ClO_4)_2.6H_2O$ without and with light irradiation

conclusion is reached when the results of the experiments with EM solutions in the absence of oxygen are compared with *Figures 7c* and *7d*.

When $Cu(ClO_4)_2.6H_2O$ is gradually added to LM in NMP, the 630 nm peak first becomes intense and is then blue-shifted. At high oxidant/LM ratio a dark purple solution is obtained, and its spectrum, given in *Figure 8a*, shows an intense peak at 540 nm (2.3 eV). Transitions below 400 nm are masked by the intense absorption of the oxidant. When $Cu(ClO_4)_2.6H_2O$ is added to EM base in solution, the 630 nm peak is also blue-shifted. At high oxidant/EM base ratio, the absorption spectrum (*Figure 8c*) is similar to *Figure 8a*. The optical absorption spectrum of polyaniline films, reported to be in the neutral fully oxidized state or pernigraniline $(\text{-B-N=Q=N-})_n$, shows three bands at 562 nm (2.2 eV), 326 nm (3.8 eV) and 269 nm (4.6 eV)[16]. The 562 nm band has been attributed to a transition from valence band to conduction band in this polymer with alternating quinoid and benzenoid monomer units, and is not shifted upon protonation in concentrated sulphuric acid[16]. An identical spectrum has also been obtained when $(NH_4)_2S_2O_8$ is added to EM base in concentrated H_2SO_4, to yield the fully oxidized charged bipolaron lattice[13]. Thus, the spectra of the LM solution after addition of $Cu(ClO_4)_2.6H_2O$ indicate that the amine units are oxidized to imine units and the oxidation state proceeds beyond that of EM base. Similarly, the addition of $Cu(ClO_4)_2.6H_2O$ to EM base in NMP results in further oxidation. For convenience, this heavily oxidized polyaniline will be termed pernigraniline in the subsequent discussion although it has not been recovered in pure solid state and hence its oxidation state has not been confirmed by x.p.s.

The effects of $Cu(ClO_4)_2.6H_2O$ on LM and EM base in NMP are different from the observed doping reactions in acetonitrile with these polymers in powder form[33]. In the case of LM, interactions of the amine nitrogens with the perchlorate anions result in a nitrogenonium ion structure. The maximum N^+/N ratio is about 0.5 and no significant imine structures are observed in the x.p.s. N1s core-level spectra. The nitrogenonium ion structure in the LM-perchlorate complexes appears to be similar to that obtained when EM base in powder form is protonated by $HClO_4$. However, in NMP, the interactions of EM base with $HClO_4$ (*Figure 5c*) result in spectral changes that are vastly different from those obtained when LM interacts with $Cu(ClO_4)_2$ (*Figure 6a*). In the case of EM base, interactions of the powder with $Cu(ClO_4)_2.6H_2O$ result in the disappearance of the imine rather than the amine units, and positively charged N is also observed[33], whereas in the NMP solution, the oxidation state of the polymer increases, i.e. there is a decrease in the number of amine units.

Light irradiation of the pernigraniline solutions does not decrease their stability substantially (comparing *Figures 8b* and *8d* with *Figures 8a* and *8c*), in contrast to the results obtained with LM and EM base solutions, and the acidified solutions. Thus, it appears that the higher the oxidation state of the polymer, the more stable it is in NMP under light irradiation. This suggests that the benzenoid–amine structures are more susceptible to degradation under light irradiation.

CONCLUSION

The optical spectra of LM in NMP show that hydrogen is abstracted from the amine units in the presence of dissolved oxygen. Light irradiation greatly accelerates this process and the oxidation state of the polymer approaches that of EM base before further degradation of the polymer backbone occurs. In the absence of light, EM base is stable in NMP. Addition of $HClO_4$ to LM and EM base solutions results in protonation of the amine and imine units respectively. However, deprotonation gradually occurs with the recovery of quinoid-imine structures in both cases when oxygen is present. Light irradiation also accelerates the deprotonation process and further degradation. Addition of $Cu(ClO_4)_2.6H_2O$ to LM and EM base solutions results in both polymers approaching the fully oxidized state. Light irradiation does not substantially affect the stability of this polymer in solution, and hence suggesting that the benzenoid–amine structures are more susceptible to degradation under light irradiation.

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