Protonation of polyaniline films: effects of anion size and film structure

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Emeraldine base films cast from *N*-methylpyrrolidinone solutions are not readily doped by acids with large anions. Structural modifications can facilitate the access of these anions into the film matrix. The problems in determining the protonation levels at the surface and in the bulk are highlighted.

(Keywords: polyaniline; protonation behaviour; film structure)

Introduction

Polyaniline in the base form (emeraldine[1] or EM base) dissolves readily in *N*-methylpyrrolidinone (NMP)[2] or concentrated H_2SO_4[3]. However, not all polyaniline salts are soluble in organic solvents. By using suitably functionalized protonic acids such as dodecylbenzenesulfonic acid (DBSA)[4] or sulfosalicylic acid (SSA)[5] to protonate polyaniline, the counterions can induce processability of the resulting salts. Polyaniline salt films can also be cast from a solution of EM base and $HClO_4$ in NMP[6]. It has been reported[7] that polyaniline base films cast from NMP solutions are near full density and have an average pore diameter of much less than 2 nm. The doping and undoping of these films induces morphological changes that can affect the free volume of the films[7]. In this article we report on how the protonation of various EM base films depends on the anions and the film structure.

Experimental

Polyaniline salt was prepared by the oxidative polymerization of aniline by ammonium persulfate in dilute H_2SO_4 according to the method described in ref. 1. It was converted to EM base by treatment with excess 0.5 M NaOH. Three different types of EM base films were made: film BI was cast from an NMP solution of the EM base powder; film BII was obtained by subjecting film BI to protonation by 0.1 M $HClO_4$ followed by deprotonation with 0.5 M NaOH; film BIII was obtained from the deprotonation (by 0.5 M NaOH) of a salt film cast from an NMP solution of EM base powder and $HClO_4$. The amount of $HClO_4$ added was calculated to achieve a 50% protonation of the EM base powder. For each film type, both a free-standing film and a thin film cast on quartz plate were made. The thickness of the free-standing films was 5–10 μm. In the case of the thin films, care was taken to cast the same amount of solution over a fixed area of plate. The absorbance of the films was measured to ensure that the films prepared by the three different methods were of similar thickness (~0.1 μm). The reprotonation of the films was carried out by immersing the films in either 0.1 M $HClO_4$ or 0.1 M DBSA for varying periods of time, and the process was followed using u.v.–visible absorption spectroscopy (Shimadzu UV3101PC). The films were also studied by X-ray photoelectron spectroscopy (X.p.s.) (VG ESCALAB MkII spectrometer with MgKα X-ray source) and Fourier transform infra-red (*FT*i.r.) absorption spectroscopy (Shimadzu FTIR 8101M spectrophotometer).

Results and discussion

The u.v.–visible absorption spectra of the three different types of base film are shown in *Figure 1* ($t = 0$ curves). The exciton absorption band[8] of the pristine EM film (film BI) is at 641 nm, and this band is blue-shifted to 590 and 548 nm for films BII and BIII, respectively. This blue-shift has been attributed to structural changes resulting in an increase in oxidation state and/or decrease in conjugation, as described in a previous publication[9]. The treatment of film BI with 0.1 M $HClO_4$ for 1 h results in a fully protonated salt; this is indicated by its absorption spectrum, which shows an absorption tail of high intensity extending into the i.r. region (assigned to intraband–free carrier excitations) and the absence of a well defined π–π^* absorption at 330 nm. The features are consistent with metallic behaviour[10]. In contrast, the overnight treatment of film BI with 0.1 M DBSA results in only a small decrease in the intensities of the 330 and 635 nm bands, and a small corresponding increase in the intensity of the long absorption tail (*Figure 1a*). This is indicative of a low level of conversion of imine units in the EM base film to the protonated species[10].

The degree of protonation of the EM base film by DBSA is increased if films BII and BIII are used (*Figures 1b* and *c*). In the case of film BIII, the film turns green within a few minutes in 0.1 M DBSA, in contrast to film BI which retains the original blue colour even after 21 h. The spectra in *Figure 1* clearly show that the protonation of film BII proceeds at a faster rate than that of film BI, but it is still significantly slower than that of film BIII. The spectrum of the DBSA-protonated film BIII after the initial stages (> 12 min) is similar to that of the $HClO_4$-protonated film BIII. The absorption

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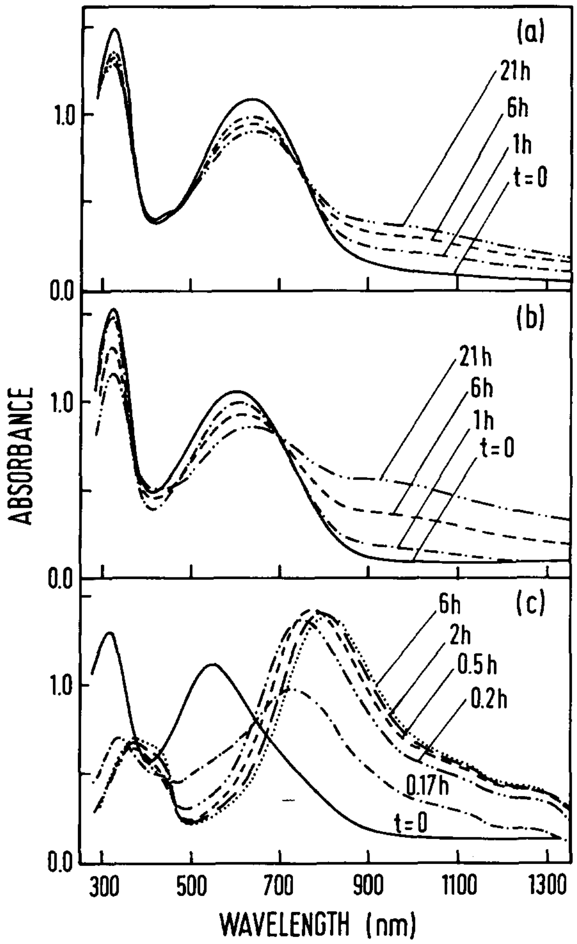

Figure 1 U.v.–visible absorption spectra of films after treatment with 0.1 M DBSA: (a) film BI; (b) film BII; (c) film BIII. Treatment times are indicated on the spectra. The $t=0$ curves represent the spectra of the pristine films

band in the 800 nm region is assigned to the interchain excitations[10]. This feature, coupled with the low intensity of the long absorption tail as compared to the spectrum of the $HClO_4$-protonated film BI, indicates that the polarons in the protonated film BIII are more localized. This would be consistent with the decrease in conjugation of film BIII.

The treatment of EM base powder by 0.1 M DBSA also results readily in a green salt. The difficulty in protonating film BI by DBSA suggests that the lack of porosity of the as-cast film limits the accessibility of the relatively large anions to the bulk of the film. For films BII and BIII, the different levels achievable suggest different degrees of morphological change which enhances the doping of these films. In the process of making film BII, the first step involves insertion of the ClO_4^- anions into a pre-existing matrix followed by the removal of these anions by NaOH treatment. This doping/undoping procedure has been shown to give the polymer matrix an expanded morphology which results in higher gas permeability[7]. The process of making film BIII involves the removal of ClO_4^- anions which have been premixed with the EM solution and cast as a film. This procedure can be expected to result in even more drastic morphological changes.

X.p.s. analyses (*Figures 2a* and *b*) of films BI and BIII show that both films possess similar oxidation states (as given by the imine/amine ratio) as the pristine EM base powder. These spectra have been deconvoluted according to the procedure described previously[11,12]. It has previously been shown that the oxidation state of film BII is increased over that of film BI[13]. The proportion of amine nitrogens (-NH-/N) is about 0.4 in film BII compared to 0.53 in film BI. The X.p.s. N1s core-level spectra of EM base powder and all three EM base films (free-standing) after treatment with 0.1 M DBSA for 20 h show the complete disappearance of the imine nitrogens (-N=) and an increase in the intensity of the high binding energy tail attributed to the positive nitrogen species (N^+) (*Figures 2c–f*). The protonation levels (N^+/N) of the samples, as given by the X.p.s. analysis, are shown in *Table 1*. In the case of film BI, the X.p.s. data indicate a very high protonation level ($N^+/N=0.72$) even though the film retains the colour of the base film and the u.v.–visible absorption results (*Figure 1a*) indicate very little doping. This apparent difference can be resolved if it is postulated that the protonation of film BI is confined mainly to the surface of the film. The X.p.s. data obtained using a more surface-sensitive mode (take-off angle of 20° instead of 75° for the data reported earlier) confirmed an even higher protonation level for this film. The *FT*i.r. absorption spectrum of film BI after DBSA treatment also shows features representative of EM base rather than EM salt, thus verifying that little protonation occurs in the bulk. The X.p.s. results of the DBSA-treated film BI also indicate that the -NH-/N ratio is much lower than that of the pristine EM base (*Figure 2*). This suggests that a substantial portion of the amine nitrogens, in addition to the imine nitrogens, must have been converted to N^+ species on the film surface. The distribution of charges arising from this situation would probably be different from the usual case, where mostly imine nitrogens only are protonated (e.g. EM base powder), and this may account for the differences in the N^+ peaks in the core-level spectra (*Figure 2c versus 2d*).

In the case of film BIII, the X.p.s. results show that DBSA treatment results in the protonation level and the N1s lineshape being similar to those obtained with EM base powder. Since the u.v.–visible absorption spectrum of the DBSA-treated film BIII is indicative of a protonated salt, and the X.p.s. results at two different take-off angles show no significant difference in N^+/N ratio, it is likely that the protonation level of 44% as obtained by X.p.s. is also representative of the bulk value. Both the X.p.s. and u.v.–visible absorption results show that the DBSA-treated film BII is an intermediate case between similarly treated films BI and BIII.

Although the results obtained with the three different types of film clearly illustrate that film morphology plays an important role in determining the degree of protonation by DBSA, the possibility of micelle

Table 1 Distribution of N species on surface of EM samples after treatment with 0.1 M DBSA (X.p.s. data obtained at a take-off angle of 75° with respect to the sample surface)

EM base	Doping time (h)	-N=/N	-NH-/N	N^+/N
Powder	20	–	0.58	0.42
Film BI	20	–	0.28	0.72
Film BII	20	–	0.54	0.46
Film BIII	20	–	0.56	0.44

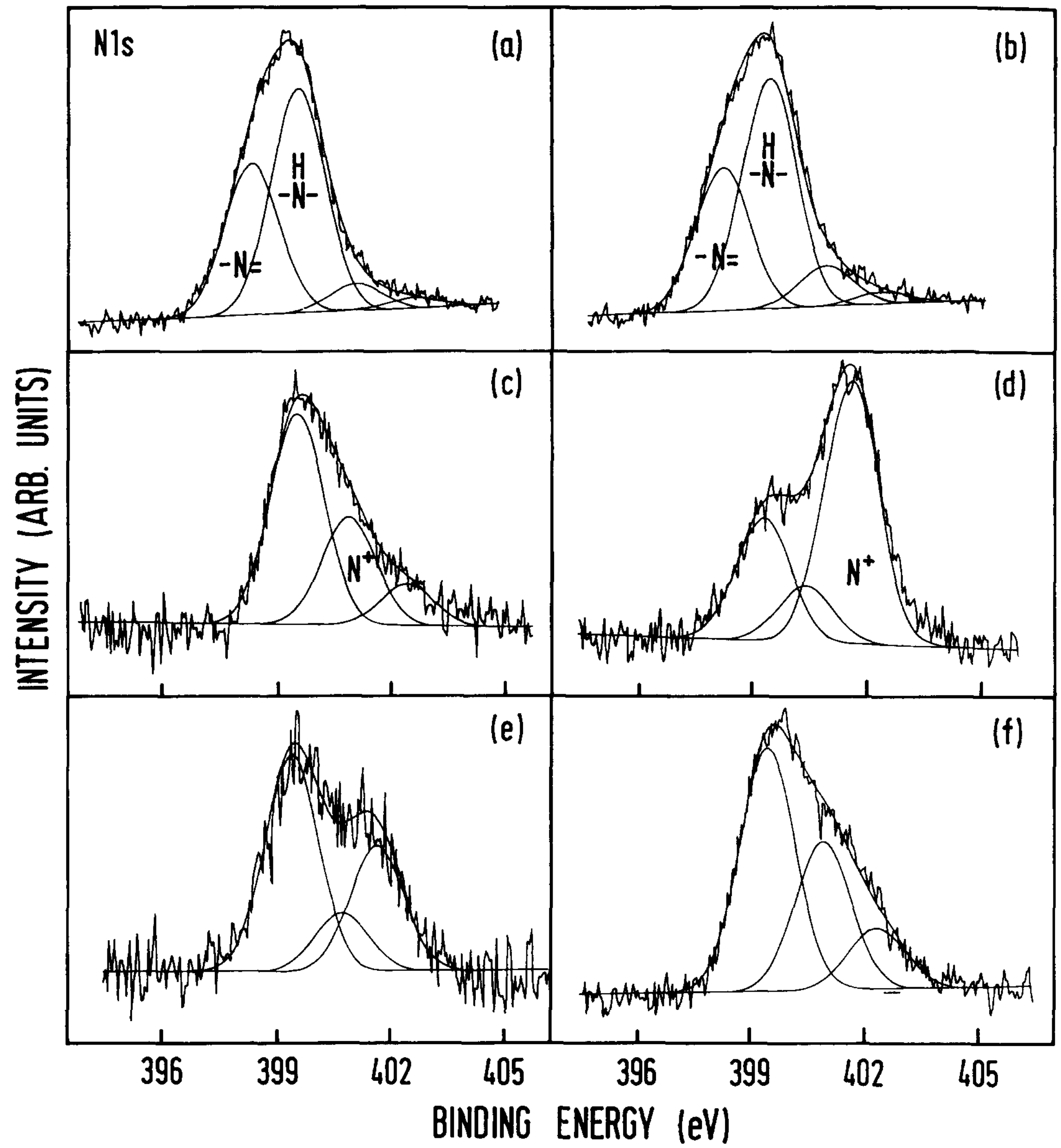

Figure 2 X.p.s. N1s core-level spectra (obtained at a take-off angle of 75°): (a) film BI; (b) film BIII; (c) DBSA-treated EM base powder; (d) DBSA-treated film BI; (e) DBSA-treated film BII; (f) DBSA-treated film BIII. For (c), (d), (e) and (f), the treatment was carried out with 0.1 M DBSA for 20 h

formation in the DBSA solution should also be considered. The aggregation of ions into micelles can be expected to affect the diffusion of the DBSA dopant into the films. Hence, the protonation of the films was also carried out with another organic acid, SSA, which is unlikely to exist as a highly micellar solution. The results again show that the bulk of film BI cannot be readily protonated, whereas the dopant can easily penetrate into the bulk of film BIII.

In conclusion, the protonation of EM base films by acids with large anions, such as DBSA and SSA, is strongly affected by the physical structure of the films. In such a case, the protonation level, as determined by surface-sensitive techniques such as X.p.s., may not be representative of the bulk value.

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