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PHYSICOCHEMICAL PROPERTIES OF POLYANILINE BASE AND SALT FILMS

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ABSTRACT

Polyaniline base and perchlorate salt films cast from *N*-methylpyrrolidinone (NMP) solutions are studied using thermogravimetric analysis, infrared and ultraviolet-visible absorption spectroscopy, and x-ray photoelectron spectroscopy. Both types of films retain a substantial amount of solvent. Although most of the solvent can be removed by washing the films with deionized water, some ClO_4^- anions are removed from the salt films as well, resulting in a decrease in conductivity. In the salt films, protonation of the amine units in addition to the imine units can be readily achieved using HClO_4 . Structural modifications of the base films are apparent after one reprotonation/deprotonation cycle. These result in a decrease in the solubility of the film, the extent of which increases with the protonation level. Although NMP is a useful solvent for casting polyaniline salt and base films, both leucoemeraldine and perchloric acid protonated salt undergo degradation in this solvent.

INTRODUCTION

Polyaniline is usually chemically prepared by the oxidative polymerization of aniline by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [1, 2] in a protonic acid medium. The resulting highly conductive powder, emeraldine salt, can be converted to the insulating state, emeraldine (EM) base, which corresponds to 50% oxidized poly(para-phenyleneamineimine) by treatment with a base [2]. Conversely, treatment of the EM base polymer with excess protonic acids restores it to the conductive state, with protonation occurring preferentially at the imine repeat units. The oxidation state of the base polymer ranged from the fully reduced leucoemeraldine (all amine units) [3] to the fully oxidized pernigraniline (all imine units) [4]. Oxidative doping of the amine nitrogens in leucoemeraldine also results in a highly conductive polymer [5, 6]. Due to the interesting redox properties of this family of polymers, it has attracted considerable interest. Its use as potential electronic materials is further enhanced by its solution processibility. It has recently been reported that both EM base and its protonated form can dissolve completely in concentrated H_2SO_4 [7]. The use of protonic acid dopants of large molecular size such as toluene-*p*-sulfonic acid in the chemical synthesis of polyaniline has also resulted in a salt soluble in common organic solvents [8]. The simultaneous polymerization and oxidation of aniline by copper(II) perchlorate also result in a conductive polymer soluble in DMSO [9]. Furthermore, EM base is partially soluble in THF, DMF, and DMSO, and completely soluble in *N*-methylpyrrolidinone (NMP) [10].

Our experiments have indicated that polyaniline prepared by the usual method using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is also soluble in NMP if the protonic acid is HClO_4 . In view of the potential importance of polyaniline films, this paper reports on a detailed study of the physicochemical properties of polyaniline salt and base films cast from NMP solutions. The experimental techniques used include thermogravimetric (TG) analysis, infrared (IR) and ultraviolet (UV)-visible absorption spectroscopy, and x-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Emeraldine salt was prepared by the oxidative polymerization of aniline by ammonium persulfate in a protonic acid medium (Method 1) according to the method reported in the literature [1, 2]. The protonic acids used were HCl , H_2SO_4 , and HClO_4 . For the studies on base films, the EM salts, EM- HCl and EM- H_2SO_4 , were converted to base powders by treatment with excess 0.5 *M* NaOH for 18 h, then washed with deionized water until neutral, and dried by pumping under reduced pressure. EM base was dissolved in NMP (~0.1 g in 2 mL of NMP) and distributed over a glass substrate. The solvent was removed under dynamic vacuum at room temperature for over 12 h. The amount of solvent retained in the films (~10 μm thickness) can be estimated from the increase in weight of the polyaniline film over that of the powder. In order to remove the residual solvent, the film was treated with deionized water or heated for various periods of time. Polyaniline salt (PAN-ClO_4) was also synthesized using the method of Inoue et al. [9] with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as the oxidant (Method 2). Both the PAN-ClO_4 and EM- HClO_4 salts can be dissolved in NMP although not as readily as the base powder. The salt films were cast using a minimum amount of NMP since it was observed that the

original dark green solution turned blue (similar to that of EM base) upon addition of excess NMP. After the evaporation of the bulk of the solvent, the salt film was washed with either water, ethanol, or 1 M HClO₄.

Thermogravimetric (TG) analyses of the powders and films were conducted to assess the extent of solvent retention and any changes in the decomposition behavior. These experiments were carried out in N₂, using a Netzsch STA 409 simultaneous thermogravimetric-differential thermal analyzer. Structural analysis using IR absorption spectroscopy (on a Perkin-Elmer Model 682 spectrophotometer), UV-visible absorption spectroscopy (on a Shimadzu UV-260 spectrophotometer), and XPS (on a VG ESCALAB MkII spectrometer) were carried out. The last is particularly suitable for detecting any changes in the intrinsic oxidation state and doping level of the polyaniline which may have occurred during the processing of the films and also after the films have been subjected to subsequent reprotonation and deprotonation. The XPS measurements were made using a MgK_α x-ray source (1253.6 eV photons). The polymer samples in both powder or film forms were mounted on the standard sample studs by means of double-sided adhesive tape. A take-off angle of 75° was used in all XPS runs. 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. To compensate for surface charging effects, all binding energies were referenced to the C_{1s} 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. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors and may be subjected to a maximum of ±10% error. The electrical conductivities (σ) of the films and powders were measured using both the standard collinear four-probe or two-probe techniques.

RESULTS AND DISCUSSION

Base Films

The amount of NMP retained in the as-cast EM base film was estimated from the weight increase of the film to be about 30% of the total weight. The TG weight loss curves of the as-cast film and the EM base powder are compared in Fig. 1. A weight loss of about 30% in the former was obtained upon heating to 250°C whereas the latter shows an initial weight loss, attributable to residual water, and the major weight loss occurs only after 425°C. This confirms that NMP (bp 202°C) constitutes a significant fraction of the film weight. The TG curve of the water-washed film (Fig. 1) indicates that a large proportion (but not all) of the residual solvent can be removed by soaking the film in deionized water for a few hours. Another indication of the presence of residual NMP can be obtained from the IR absorptior spectra of the films (Fig. 2). The IR absorption spectrum of the water-washed film (Fig. 2b) shows a band at 1680 cm⁻¹ which is absent in the spectrum of the powder (Fig. 2a.) This band is attributed to the C=O group of the residual NMP and is also obvious in the IR spectrum of EM base film reported in the literature [4]. For complete removal of the solvent, as implied by the disappearance of this band, more drastic measures such as prolonged soaking (for days) of the film in water or heating at 175°C in N₂ for 1 h (Fig. 2c) are required. This suggests that the NMP is retained in the matrix of the film.

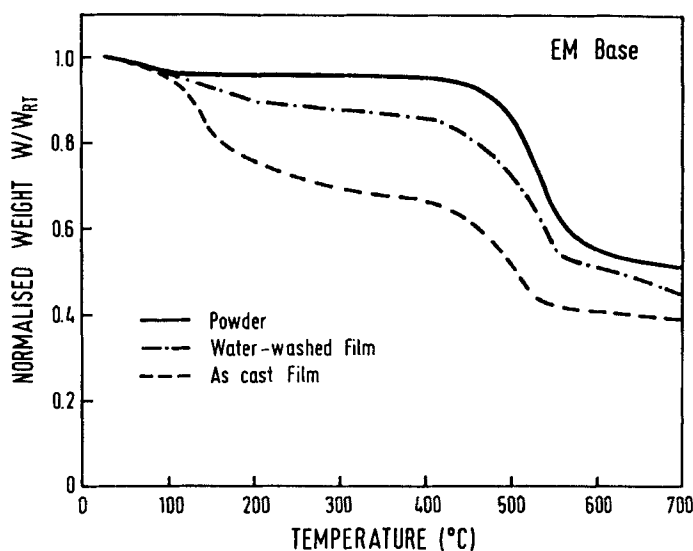


FIG. 1. Thermogravimetric scans of EM base powder, as-cast film, and film after washing with deionized water. W_{RT} is the weight at room temperature.

The brownish-purple base film is flexible and can be easily handled without tearing. When the base film is treated with 1 *M* protonic acids such as HClO_4 , HCl , or H_2SO_4 , it turns deep blue (green where very thin). The σ of the film (~ 4 S/cm) is comparable to that of the base powder after similar treatment. The N_{1s} XPS core-level spectrum of the EM base film after washing with deionized water is shown in Fig. 3(a). The main components are at 398.2 ± 0.1 and 399.4 ± 0.1 eV and are ascribed to the imine and amine nitrogens respectively, in agreement with previously reported values [11–14]. This spectrum is similar to that of the pristine EM base powder, indicating no significant NMP is present on the surface of the film after it has been soaked in water for a few hours. After this film has been soaked in 1 *M* HClO_4 for 1 h and then rinsed with 0.1 *M* HClO_4 , the N_{1s} core-level spectrum (Fig. 3b) shows the disappearance of the imine component and the rise of the high binding energy (BE) tail. Based on the fixed FWHM approach used in this work, the high BE tail has been deconvoluted into two components assigned to positively charged nitrogen (N^+). For this film, the doping level is 0.50 as calculated from the N^+/N ratio or the ClO_4^- (at 207.4 eV)/N ratio. This is identical to that achievable with the base powder when it is subjected to a similar reprotonation procedure. By varying the concentration of the HClO_4 used in the reprotonation process, films with different doping levels and σ 's can be obtained. Upon increasing the concentration of the HClO_4 to 3 *M*, the N^+/N ratio of the film is 0.85 ($\text{ClO}_4^-/\text{N} = 0.88$). This implies the protonation of a large fraction of the amine units as well as all the imine units. This is not observed with the base powder when 3 *M* HClO_4 is used and the N^+/N ratio remains close to 0.5. However, the σ of the highly protonated film is not increased over that of the 50% protonated film. Thus, it is likely that the protonation of a substantial fraction of the amine nitrogens to $-\text{N}^+\text{H}_2-$ groups results in the disruption of the order of the polaron lattice.

When the protonated (salt) films are converted back to base films by treatment

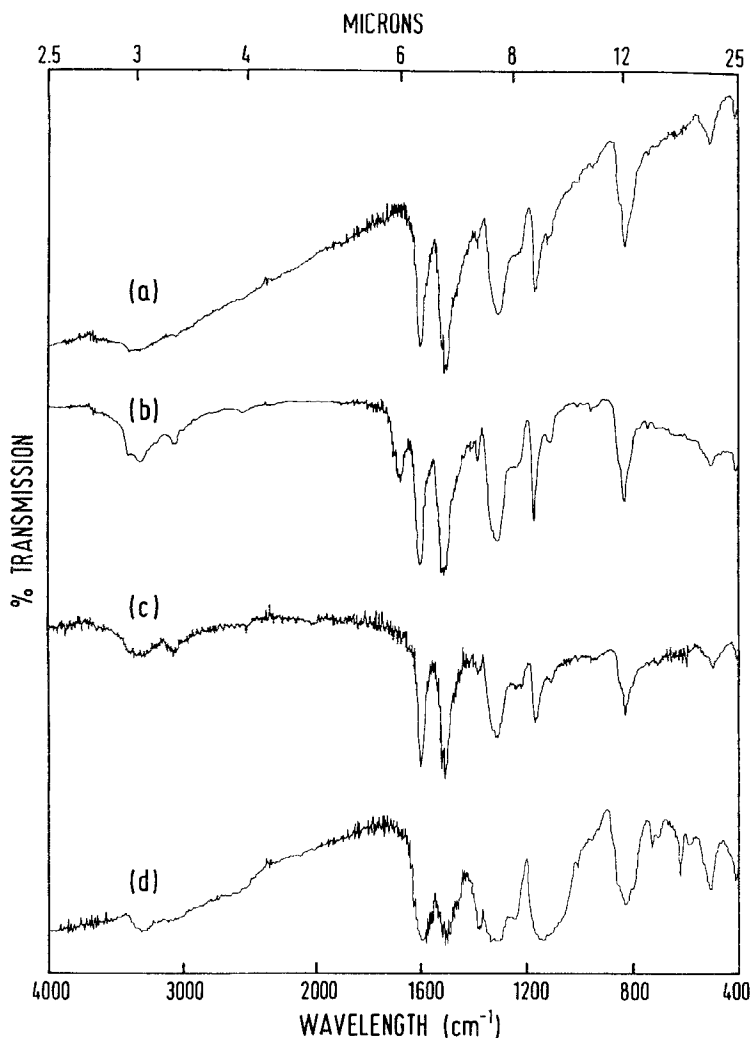


FIG. 2. IR absorption spectra of EM base: (a) pristine powder, (b) film after washing with deionized water, (c) film after heating at 175°C in N_2 for 1 h, and (d) film after reprotonation to N^+/N of 0.5 and then treated with 0.5 M NaOH.

with NaOH, the color changes back to brownish purple but the films now possess a golden sheen. Structural differences between these films and the original base films are evident from the IR absorption spectra and XPS data. This is illustrated by the IR absorption spectrum and N_{1s} core-level spectrum of a base film obtained from a 50% reprotonated salt film, shown in Figs. 2(d) and 3(c) respectively. A comparison of the spectra in Fig. 3(c) and Fig. 3(a) shows that the imine/amine ratio has increased from 0.75 in the original base film to 1.17 after reprotonation and deprotonation. The BE separation between the imine and amine components has also increased, from 1.20 to 1.45 eV. No such changes in imine/amine ratio and BE separation were observed with base powder after being reprotonated to 50% and then deprotonated. The IR absorption spectrum of the original water-washed base

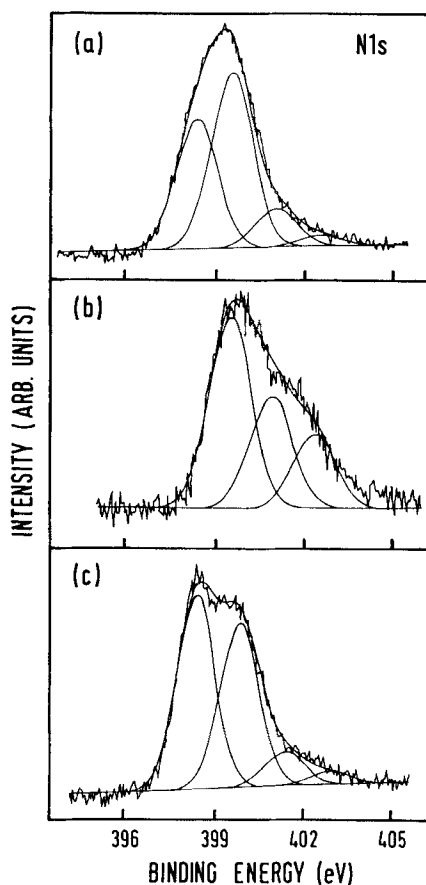


FIG. 3. N_{1s} XPS core-level spectra of (a) water-washed EM base film, (b) EM film reprotonated by 1 M $HClO_4$, and (c) base film from treatment of 50% reprotonated film by 0.5 M $NaOH$.

film (Fig. 2b) shows the aromatic ring stretching bands [15, 16] at 1600 and 1500 cm^{-1} having a relative (1600/1500 cm^{-1}) ratio of slightly less than unity. After deprotonation of the 50% doped film, the 1600 cm^{-1} band associated with the quinoid (Q) ring [17] has broadened and increased in intensity relative to the 1500 cm^{-1} band attributed to the benzenoid (B) ring (Fig. 2d). This difference, ascribed to the oxidation of some of the B units to Q units, is entirely consistent with the higher imine/amine ratio in the spectrum in Fig. 3(c). The absorption band in the 1700 cm^{-1} region is no longer discernible in the spectrum of this film, indicating the displacement of the NMP molecules by the protonating acid. This IR absorption spectrum also shows an increase in intensity and broadening of the bands in the C—N stretching region (1400–1240 cm^{-1}) for aromatic amines. The three bands in this region at 1380, 1315, and 1240 cm^{-1} are assigned to the different arrangements of the Q and B structures in the polyaniline chains, and as a result of the orientation of the hybrid orbitals on the N atom, the C—N band has different chemical environments [17]. The broad nature of these bands implies that they contain more than

one vibrational mode. Thus, the IR analysis also indicates that the polymer has undergone structural changes after the reprotonation/deprotonation cycle. Furthermore, the aromatic ring deformation band [17] in the 500 cm^{-1} region is enhanced after the reprotonation/deprotonation cycle (comparing Figs. 2b and 2d). The 1160 cm^{-1} band, attributed to another characteristic mode of the quinoid imine structure, has become very broad in Fig. 2(d). In EM salt samples (films and powders), this band is very intense and broad and is considered as a measure of the degree of delocalization of electrons on the polyaniline [17]. In the present base film, the cause of the broadening of this band is not known. There are also two small new bands at 745 and 695 cm^{-1} in Fig. 2(d) which coincide with the absorption bands for 1,2 substitution on the benzene ring [17]. The 830 cm^{-1} band, characteristic of 1,4 substitution, is dominant in all the polyaniline salt and base samples. The reprotonation and deprotonation of the polyaniline films may have induced deviations from the predominant head-to-tail coupling of the aniline rings, and crosslinking may have occurred.

The structural changes in the films after reprotonation and deprotonation result in changes in the solubility in NMP. EM base in the form of powder or films was added to NMP at a ratio of 0.01 g solid to 50 mL NMP. After 24 h the UV-visible absorption spectrum of each liquid phase (after a dilution factor of 10) was measured. These spectra are shown in Fig. 4. The spectrum of the solution of pristine EM base powder (which is completely soluble in NMP) shows two bands of about equal intensities at about 330 and 640 nm . The former is attributed to the $\pi \rightarrow \pi^*$ transition while the latter has been assigned to a charge-transfer exciton-like transition from the highest occupied energy level (centered on the B rings) to the lowest unoccupied energy level (centered on the Q rings) [18, 19]. The reduction in the solubility of the water-washed film (Film 1) is evident from the residue present in the NMP solution and the reduction of the intensities of the two bands in the

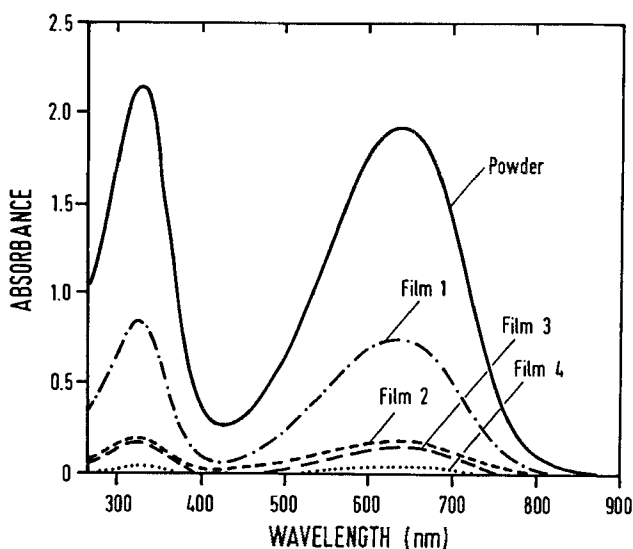


FIG. 4. UV-visible absorption spectra of NMP solutions of EM base powder, water-washed film (Film 1), and films after reprotonation/deprotonation cycle (Films 2, 3, and 4).

absorption spectrum relative to those of the powder. The other three spectra (for Films 2, 3, and 4) in Fig. 4 are for films obtained from the undoping of reprotionated films of various doping levels. In each case the intensities of the bands are very much reduced compared to the spectrum of the EM base powder solution, but the relative intensity of the 330 nm band to that of the 640 nm remains close to unity. The doping levels of these films during reprotionation together with the absorbance of the 640 nm band of the NMP solutions relative to that of the solution of the pristine powder are given in Table 1. Since the same ratio of solid (powder or film) to NMP is used in each case, the relative absorbance of the 640 nm band in the solution spectra would indicate the amount of solid that has dissolved in the NMP. The data clearly show that the films after the reprotionation/deprotionation cycle are even less soluble than the water-washed film and the solubility decreases as the doping level after reprotionation increases. This may suggest crosslinking and/or an increase in chain length. Although some degree of crosslinking may have been present in the water-washed film, it is not evident from the IR absorption spectrum (Fig. 2a). However, after the deprotionation of the heavily reprotionated films, changes in the substitution pattern on the benzene ring are observed (Fig. 2d). The possibility of the apparent structural changes that occur in the film during the first reprotionation/deprotionation cycle affecting subsequent reprotionation has been investigated and reported in an earlier publication [20].

The EM base film can be reduced to leucoemeraldine (LM) base film by treatment with phenylhydrazine similar to the method used for EM base powder [3]. Conversely, LM film can also be cast from an NMP solution of the LM powder. However, the latter is more fragile than the former. In both cases the XPS N_{1s} core-level spectra show a small imine component (Fig. 5a) which amounts to $\sim 5\%$ of the total nitrogen. However, it should be noted that LM in NMP may slowly interact with dissolved oxygen, resulting in changes in the optical spectrum which can be attributed to the formation of imine units [21]. This is confirmed by XPS analysis of the recovered solid. Hence the casting of LM film from an NMP solution should be carried out as rapidly as possible. The LM film can be oxidized beyond the emeraldine oxidation state (50%) by treatment of the film with iodine in acetonitrile followed by compensation with NH_4OH . The N_{1s} core-level spectrum of the oxidized film obtained using a I_2/N ratio of 1 is shown in Fig. 5(b). For this film, the amine ($-NH-$)/N ratio is 0.36. The preparation of pernigraniline (fully oxidized) film

TABLE 1. Absorbance of 640 nm Band of Solutions of Films Relative to That of Emeraldine Base Powder

Base sample	Doping level during reprotionation	Relative absorbance
Pristine powder	—	1
Film 1 (water washed)	—	0.39
Film 2	0.23	0.085
Film 3	0.50	0.050
Film 4	0.85	0.020

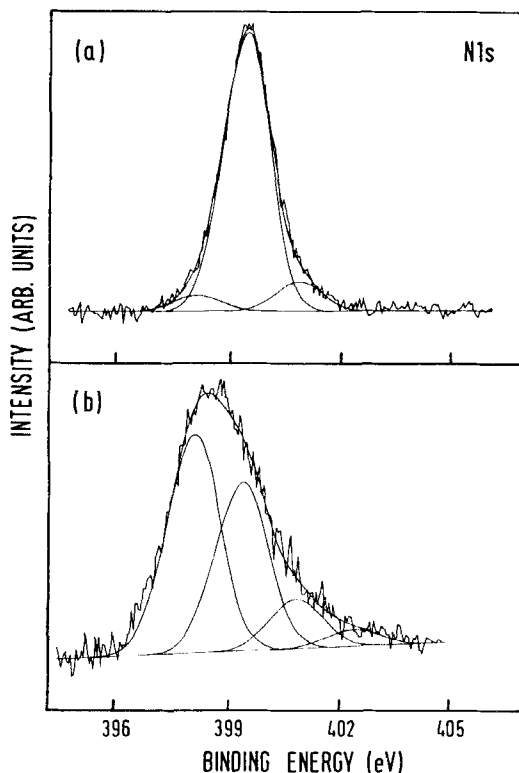


FIG. 5. N_{1s} XPS core-level spectra of (a) EM film after treatment with phenylhydrazine and (b) LM film after I_2 doping and compensation with NH_4OH .

from EM base film has been reported [4]. The evidence of full oxidation is based on UV-visible and IR absorption spectroscopy. However, XPS analysis of our polyaniline samples obtained from compensation of heavily-iodine doped LM or EM base powders or films indicates some amine units remain, even though the IR and UV-visible absorption spectroscopy results are similar to those reported earlier. It has also been shown that the highest oxidation state of polyaniline achievable electrochemically using aqueous acid electrolytes is 75% [14]. The oxidation state in this case is also determined from the N_{1s} XPS core-level spectrum.

Salt Films

The salt films cast from NMP solutions of the as-synthesized powders from either Method 1 [using $(NH_4)_2S_2O_8$ in $HClO_4$] or Method 2 [using $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile] also retain a high proportion of NMP. This is illustrated in Fig. 6(a) where the TG scans of the salt (termed PAN- ClO_4) from Method 2 in the form of powder and film (not rinsed) are compared. After the film has been soaked and rinsed in ethanol, a large fraction of the NMP is removed and hence the TG scan shows little weight changes below $200^\circ C$ (Fig. 6a). In the case of the powder, the

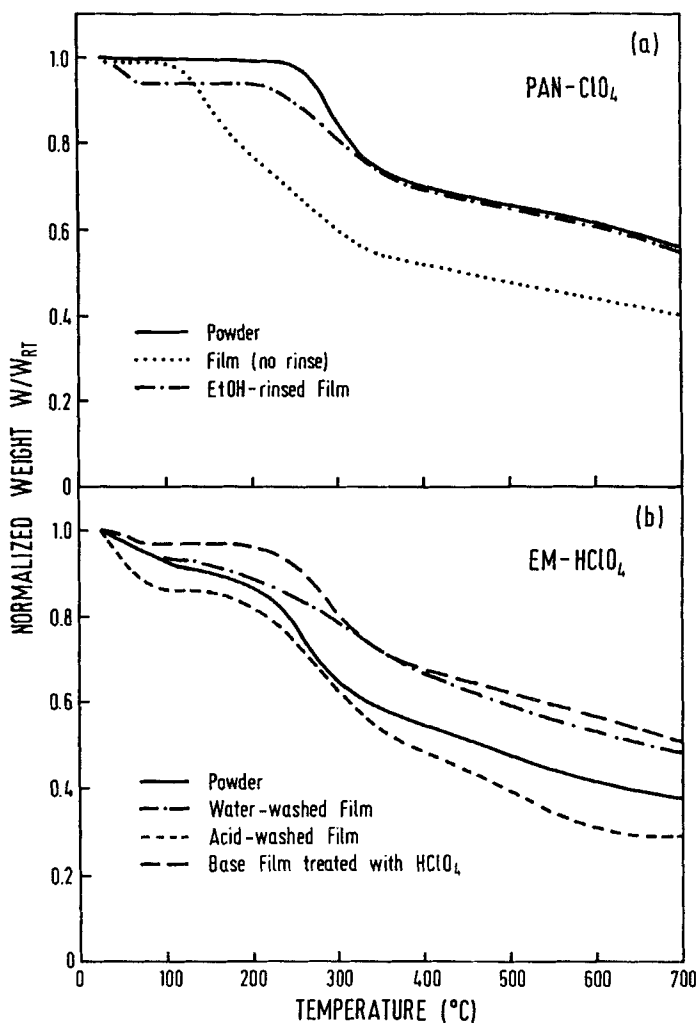


FIG. 6. Thermogravimetric scans of (a) PAN-ClO₄ powder, as-cast film, and ethanol-washed film; and (b) EM-HClO₄ powder, water-washed film, acid-washed film, and film from reprotonation of base film by HClO₄. W_{RT} is the weight at room temperature.

major weight loss, which is exothermic in nature, occurs at 225°C. This is attributed to the decomposition of the ClO₄⁻ anion [22]. The ethanol-rinsed film undergoes the major weight loss at a slightly lower temperature and the weight loss at this step is also slightly lower. This would be consistent with the postulate that some ClO₄⁻ anions have been removed during the washing with ethanol [22]. The TG scans of the salt (termed EM-HClO₄) from Method 1 in the form of powder and films are compared in Fig. 6(b). Both the powder and water-washed film show a steady weight loss upon heating above room temperature. For the powder, the major weight loss due to decomposition of ClO₄⁻ also occurs at about 225°C. The higher weight retained by the water-washed film after 225°C indicates that a substantial amount of ClO₄⁻ anions has been lost in the washing process (see later section). If 1

$1 M$ $HClO_4$ is used instead of water to rinse the film, the film undergoes an initial weight loss from room temperature to $100^\circ C$, which is higher than either the powder or water-washed film (Fig. 6b). This initial weight loss is ascribed to absorbed water which is bound by hydrogen bonds to the acidic protons, and the amount increases with the protonation level [23]. The other aspects of the TG scan appear rather similar to those of the EM- $HClO_4$ powder. In Fig. 6(b), the TG scan of a base film reprotonated with $HClO_4$ to 50% doping level is also shown. This film undergoes minimal weight changes below $225^\circ C$ and its TG scan is rather similar to that of PAN- ClO_4 .

The salt films cast from NMP solutions of the salt powders are mechanically inferior to those obtained from reprotonation of the base films, as described earlier. The former films are fragile and break easily during handling. Furthermore, in the attempt to remove residual NMP from these salt films by rinsing with ethanol, water, or $HClO_4$, the protonation levels of the films are altered from that of the pristine powder. From the N_{1s} XPS core-level spectrum of the EM- $HClO_4$ powder, the N^+/N ratio is calculated to be 0.64 and no imine units are present. The N_{1s} core-level spectrum of the water-washed film (Fig. 7a) shows a decrease in the high BE tail compared to that of the pristine powder and the N^+/N ratio amounts to only 0.29. An imine component ($-N=$) at 398.2 eV is now present. This de-

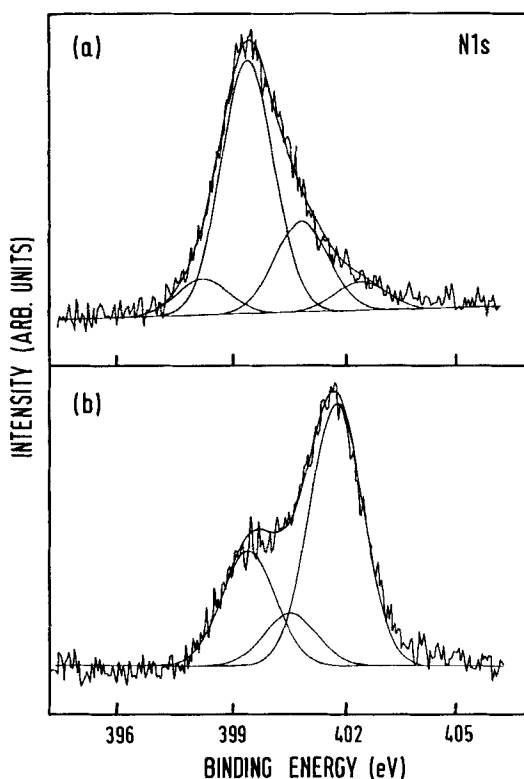


FIG. 7. N_{1s} XPS core-level spectra of EM- $HClO_4$ salt film after washing with (a) deionized water and (b) $1 M$ $HClO_4$.

crease in doping level is accompanied by a reduction in σ from 10 S/cm for the powder to 10^{-1} S/cm for this film. In contrast, the N_{1s} core-level spectrum of the 1 M HClO_4 -washed film shows a large increase in the proportion of N^+ (Fig. 7b). The N^+/N ratio is 0.73 and this confirms the observation made in the earlier section that the protonation of the amine units in polyaniline films is readily achieved. However, the σ of the highly protonated salt film is again not substantially different from that of the powder. The deprotonation of the salt films results in base films that also show a reduction in solubility in NMP as compared to the base powders obtained from the deprotonation of the as-synthesized salts. Hence, structural changes have also occurred in these films.

The UV-visible absorption spectrum of a thin EM- HClO_4 salt film cast from an NMP solution onto a quartz substrate is shown in Fig. 8(a). The 640-nm band characteristic of the imine groups is absent and new bands appear at 830 and 440 nm, together with a charge-transfer tail extending into the near-IR region. The $\pi \rightarrow \pi^*$ transition at 320 nm is not well defined. This is similar to that observed in the optical spectrum of polyaniline film spin cast from sulfuric acid, and is consis-

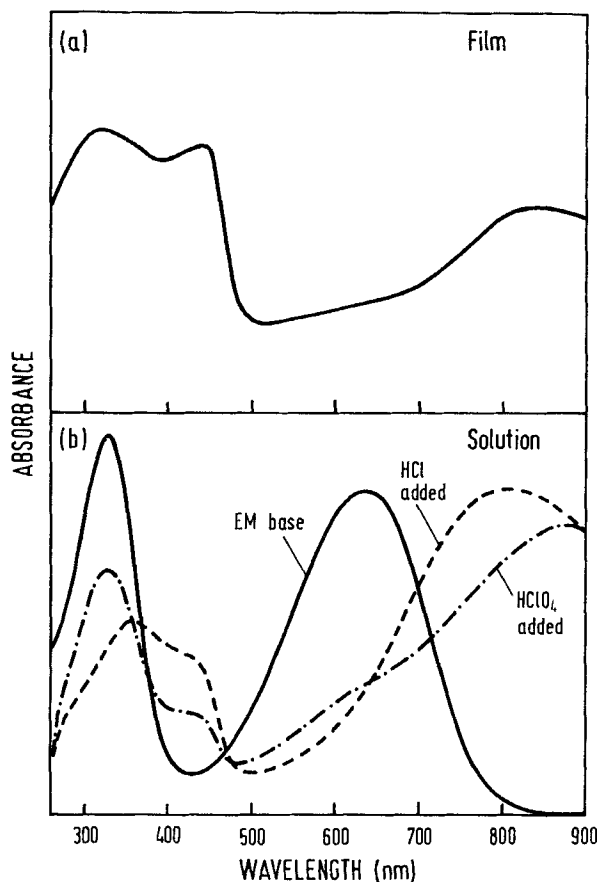


FIG. 8. UV-visible absorption spectra of (a) EM- HClO_4 salt film and (b) NMP solutions of EM base: pristine and with HCl and HClO_4 added.

tent with metallic behavior [24]. The optical spectra obtained when HCl and HClO₄ are added to an NMP solution of EM base (Cl/EM nitrogen = 15, mole basis) are shown in Fig. 8(b). When HCl is used, the spectrum obtained is rather similar to that shown in Fig. 8(a), with the exception that the $\pi \rightarrow \pi^*$ transition band is red-shifted to 350 nm. In comparison, when HClO₄ is used, the $\pi \rightarrow \pi^*$ transition band is well-defined, the charge-transfer tail is of a lower intensity, and a slight shoulder persists in the 640-nm region. These features are indicative of a lower degree of protonation. This may seem surprising in view of the high level of protonation in solid films achievable with HClO₄. Furthermore, the spectra shown in Fig. 8(b) undergo changes with time. When HClO₄ is used and dissolved oxygen is present in the NMP, the 640-nm band slowly recovers as the charge-transfer tail decreases [21]. This indicates that in NMP the HClO₄-protonated species are only metastable and undergoes deprotonation. Conversely, it is not possible to obtain a spectrum of a dilute solution of EM-HClO₄ or PAN-ClO₄ salts in NMP, since upon dilution of a thick solution of the salts, the solution turns from green to blue, typical of EM base. The optical spectrum of this dilute solution confirms the characteristics of an EM base solution as described earlier (Fig. 4). On the other hand, addition of NMP to EM-HCl salt does not result in dissolution of the salt and neither is a base solution obtained. The protonated species resulting from the addition of HCl to an NMP solution of EM base will slowly be precipitated out and the intensity of the absorption bands of the solution decreases. The EM-H₂SO₄ does not dissolve to form a salt solution in NMP since upon addition of solvent, a blue solution is immediately obtained, indicating deprotonation and subsequent dissolution of the base polymer. Hence, EM-H₂SO₄ salt films cannot be obtained from NMP solutions.

CONCLUSION

Films cast from NMP solutions of emeraldine salt or base retain a substantial amount of the solvent. A large fraction of the solvent can be removed by washing with water, but this procedure will also remove some ClO₄⁻ anions from the salt films. Emeraldine base films can undergo reprotonation to salt films and reduction to leucoemeraldine films and these films are stronger mechanically than those cast from the respective powders. XPS analysis of the salt films has established that in addition to the imine units, a substantial proportion of the amine units can be protonated. However, deprotonation of these films reveals structural changes which result in a decrease in solubility, the extent of which is dependent on the degree of protonation. Although NMP is a useful solvent for casting polyaniline base and salt films, leucoemeraldine can undergo reactions with the dissolved oxygen in NMP to result in imine units and the perchlorate-protonated species are only metastable in this solvent.

REFERENCES

- [1] J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 291 (1986).
- [2] A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *Ibid.*, **18**, 285 (1987).

- [3] A. G. Green and A. E. Woodhead, *J. Chem. Soc.*, p. 2388 (1910).
- [4] Y. Cao, *Synth. Met.*, *35*, 319 (1990).
- [5] A. Ray, G. E. Asturias, D. L. Kerschner, A. F. Richter, A. G. MacDiarmid, and A. J. Epstein, *Ibid.*, *29*, E141 (1989).
- [6] T. Nakajima, M. Haroda, R. Osawa, T. Kawagoe, Y. Furukawa, and I. Harada, *Macromolecules*, *22*, 2644 (1989).
- [7] A. Andretta, Y. Cao, J. C. Chiang, A. J. Heeger, and P. Smith, *Synth. Met.*, *26*, 383 (1988).
- [8] S. Li, Y. Cao, and Z. Yue, *Ibid.*, *20*, 141 (1987).
- [9] M. Inoue, E. R. Navarro, and M. B. Inoue, *Ibid.*, *30*, 199 (1989).
- [10] M. Angelopoulous, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, M. Aktar, Z. Kiss, and A. J. Epstein, *Mol. Cryst. Liq. Cryst.*, *60*, 151 (1988).
- [11] K. L. Tan, B. T. G. Tan, E. T. Kang, and K. G. Neoh, *Phys. Rev. B*, *39*, 8070 (1989).
- [12] E. T. Kang, K. G. Neoh, S. H. Khor, K. L. Tan, and B. T. G. Tan, *Chem. Soc. Chem. Commun.*, p. 695 (1989).
- [13] S. M. Kumar, F. Gaillard, G. Bouyssoux, and A. Sartre, *Synth. Met.*, *36*, 111 (1990).
- [14] P. Snauwaert, R. Lazzaroni, J. Riga, J. J. Verbist, and D. Gonbeau, *J. Chem. Phys.*, *92*, 2187 (1990).
- [15] Y. H. Kim, C. Foster, J. Chiang, and A. J. Heeger, *Synth. Met.*, *25*, 49 (1988).
- [16] Y. Cao, S. Li, Z. Xue, and D. Guo, *Ibid.*, *16*, 305 (1986).
- [17] J. Tang, X. Jing, B. Wang, and F. Wang, *Ibid.*, *24*, 231 (1988).
- [18] R. P. McCall, J. M. Ginder, L. M. Leng, H. J. Ye, S. K. Manohr, J. G. Masters, G. E. Asturias, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B*, *41*, 5202 (1990).
- [19] S. D. Phillips, G. Yu, Y. Cao, and A. J. Heeger, *Ibid.*, *39*, 10702 (1989).
- [20] K. G. Neoh, E. T. Kang, and K. L. Tan, *J. Phys. Chem.*, *95*, 10151 (1991).
- [21] K. G. Neoh, E. T. Kang, and K. L. Tan, *Polymer*, In Press.
- [22] K. G. Neoh, E. T. Kang, and K. L. Tan, *Synth. Met.*, *40*, 341 (1991).
- [23] A. Alix, V. Lemonine, M. Nechtschein, J. P. Travers, and C. Mernado, *Ibid.*, *29*, E457 (1989).
- [24] Y. Cao, P. Smith, and A. J. Heeger, *Ibid.*, *32*, 263 (1989).

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