Structure and Degradation Behavior of Polypyrrole Doped with Sulfonate Anions of Different Sizes Subjected to Undoping−Redoping Cycles

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The effects of cyclic base/acid treatment on electrochemically synthesized polypyrrole−toluenesulfonate (PPY−TSA) and polypyrrole−poly(styrenesulfonate) (PPY−PSSA) films are investigated. The structural modification of the films during the undoping−redoping process is monitored using spectroscopic techniques and elemental analysis, and the changes occurring at the pyrrole nitrogen are quantified. For both types of films, the undoping−redoping process cannot return the films to the conductivity and doping level of the pristine state, with the PPY−TSA film showing a higher degree of degradation. The degradation results from the loss of effective conjugation in the polymer due to reactions of the pyrrole rings with oxygen or oxygen containing groups. The differences in the degradation behavior of the two types of films are attributed to the differences in the manner in which the anions are incorporated into the polymer matrix and the mobility of the anions during the undoping−redoping process.

Introduction

The potential of using electroactive polymers in practical applications would be much enhanced by three important features, namely, the reversibility of conductivity, availability in film form, and good environmental stability. As such, the pyrrole and aniline families of polymers have received a great deal of attention because of their high conductivity and good environmental stability.[1−6] Films of these polymers can be obtained via electrochemical polymerization,[7−9] and for polyaniline (PAN), *N*-methylpyrrolidinone (NMP) can also be used as a solvent for casting of films from the polymer synthesized chemically in powder form.[10] Our recent studies[11,12] on solution-cast PAN films subjected to protonation−deprotonation cycles have shown that the structure of such films is substantially altered from the pristine state. The maximum electrical conductivity of polypyrrole (PPY) films subjected to alternate acid and base treatments also shows a steady decrease as the number of cycles increases.[13,14] In view of the similarities in the proton modification reactions occurring at the pyrrolylium and anilium nitrogens during acid/base treatment,[15] the structural changes leading to the lack of complete reversibility of the conductor−insulator transitions in PPY should be reexamined quantitatively. In particular, the intrinsic state of the N heteroatom and the integrity of the pyrrole moiety during cyclic acid/base treatments need further investigation.

In the present study, PPY films were prepared by electrochemical polymerization and subjected to cyclic base/acid treatments. Spectroscopic techniques employed to provide information on the changes in the chemical and electronic states of PPY and its interaction with the anions include Fourier transform infrared (FTIR) absorption spectroscopy, ultraviolet (UV)−visible absorption spectroscopy and X-ray photoelectron spectroscopy (XPS). The last technique has recently been shown to be useful in differentiating between the different N species in PAN and PPY and to quantify the extent of doping in the polymers.[16] Two anions, *p*-toluenesulfonate and poly(4-styrenesulfonate), were used in this study to investigate their influence on the

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Table 1. Effect of Acid/Base Treatment on Electrical Conductivity and Surface Composition of PPY−TSA

sample	description	σ/σ_0	$-N=/N$	$-NH-/N$	N^+/N	$-SO_3^-/N$
TS1	as-synthesized PPY-TSA	1	0	0.69	0.31	0.37
TS1B	TS1 after NaOH treatment	1×10^{-3}	0.19	0.65	0.16	0.04
TS2	TS1B after TSA treatment	4.0×10^{-2}	0	0.76	0.24	0.31
TS2B	TS2 after NaOH treatment	7×10^{-4}	0.15	0.70	0.15	0.07
TS3	TS2B after TSA treatment	1.3×10^{-2}	0.03	0.74	0.23	0.27
TS3B	TS3 after NaOH treatment	5×10^{-4}	0.13	0.72	0.15	0.03
TS4	TS3B after TSA treatment	5×10^{-3}	0.03	0.76	0.21	0.32
TS4B	TS4 after NaOH treatment	6×10^{-5}	0.13	0.66	0.21	0.08

doping−undoping process and the accompanying structural changes.

Experimental Section

Sample Preparation. All chemicals used in the present study were of reagent grade. Pyrrole (Merck) was distilled before use, and ultrapure water was used as the solvent. The electrochemical polymerization of pyrrole was carried out in aqueous solutions containing 0.2 mol dm^{-3} pyrrole and either 0.05 mol dm^{-3} *p*-toluenesulfonic acid (TSA) or 0.05 mol dm^{-3} sodium salt of poly(4-styrenesulfonic acid) (NaPSSA). The solutions were purged with N_2 before polymerization commenced. The PPY films were electrodeposited galvanostatically on a stainless steel plate with a current density of 2 mA cm^{-2} for about 15 min. The polymer film was rinsed with water and dried under vacuum. The thickness of the free standing PPY film was estimated gravimetrically to be approximately 5 μm. Thin films of PPY were also electrodeposited on ITO (indium−tin oxide) glass plates using a similar current density for about 1 min. These thin films were used for UV−visible absorption spectroscopy measurements.

Base treatment of the PPY salt film was carried out using 1 M NaOH for 1 h. The undoped films were then washed in water and dried again. The films were redoped using 1 M TSA (for as-synthesized PPY−TSA films) or 1M $HClO_4$ (for as-synthesized PPY−PSSA films). For PPY−PSSA films, the polymeric anions can be expected to be rather immobile and will not readily leave the polymer during base treatment. The redoping experiments were not carried out with 1 M PSSA because the polymeric acid solution is rather viscous and the excess acid may not be readily removed from the film surface. As such, the XPS results would be affected by this layer of acid on the film.

Instrumentation. The XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The films were mounted on standard sample studs by means of double-sided adhesive tape, and core-level spectra were taken at takeoff angles (α) of 20° and 75° (measured with respect to the sample surface). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). Throughout the measurements, the pressure in the analysis chamber was maintained at 10^{-8} mbar or lower. To compensate for surface charging effect, all binding energies (BE) were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (fwhm) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface chemical compositions were determined from peak area ratios corrected with the appropriate experimentally determined sensitivity factors. FTIR absorption spectroscopy was carried out using a Shimadzu FTIR 8101 spectrophotometer. UV−visible absorption spectra of thin films on ITO glass plates were determined using a Shimadzu UV3101PC spectrometer. Elemental (C, H, N) analysis was performed using a Perkin-Elmer 2400 CHN elemental analyzer. The electrical conductivity (σ) of the film were measured using both the standard collinear four-probe and two-probe techniques.

Results and Discussion

PPY−TSA Films. The pristine PPY−TSA film (TS1) possesses an electrical conductivity of 100 S/cm (σ_0). The exposure of this film to 1 M NaOH solution for 1 h decreases the conductivity by 3 orders of magnitude (Sample TS1B, Table 1), comparable to the results reported earlier for PPY−BF_4[14] and PPY−phenylsulfonate[13] films. Redoping of this film by 1 M TSA for 1 h can only restore its conductivity partially. After the third cycle, the σ of the doped film (TS4) is 2−3 orders of magnitude less than σ_0. This decrease in σ is comparable to that reported for 2 μm thick PPY−BF_4 films subjected to NaOH−HCl treatment[14] over the same number of cycles but is more drastic compared to 30 μm thick PPY-phenylsulfonate films treated with NaOH and H_2SO_4.[13] The σ of the base films also decreases with increasing number of cycles of acid/base treatment.

The XPS N 1s core-level spectrum of the pristine PPY−TSA salt is shown in Figure 1a. The major peak component at 399.7 eV is assigned to neutral amine nitrogen (−NH−).[15] The high binding energy (BE) tail which is deconvoluted into two-component peaks at 1.5 and 3 eV from the −NH− peak, respectively, is attributed to positively charged nitrogens (N^+). Upon treatment with NaOH, the high BE tail reduces in intensity and a shoulder appears at about 397.7 eV (Figure 1b). This low BE component is attributed to the imine nitrogen (−N=). Subsequent redoping by TSA will cause the low BE shoulder to disappear (Figure 1c). However, it can be seen from Figure 1 that the proportion of N^+ in the redoped film does not measure up to that in the pristine salt film. In fact, the spectra of the redoped films after the second and third cycles (Figure 1e,g, respectively) show that a small amount of imine remains unprotonated. In the case of the base films, the −N= component of the pristine base (Figure 1b) is also more intense than those which have undergo redoping-undoping cycles (Figures 1d,f,h).

The proportions of the different N species in the various films are tabulated in Table 1. Reproducibility tests show that the variation in the ratios given in this table is within ±0.04 in most cases. The N^+/N ratio of ~0.3 in the pristine salt film is consistent with earlier results showing $^1/_4$ to $^1/_3$ of the PPY rings being involved in the electrostatic interaction with the anions.[15,17] The positive charges are closely balanced by the anions (comparing the N^+/N and $-SO_3^-/N$ ratios), as expected from charge neutrality considerations. This was not observed in the pristine PPY−ClO_4^- films of Atanasoska et al.[18] where the ClO_4^-/N ratio is a factor of 2 higher than the N^+/N ratio. Ideally, upon undoping the salt, the N^+ species are converted to −N= groups,[15] as shown in Figure 2. However, the XPS data show that the high

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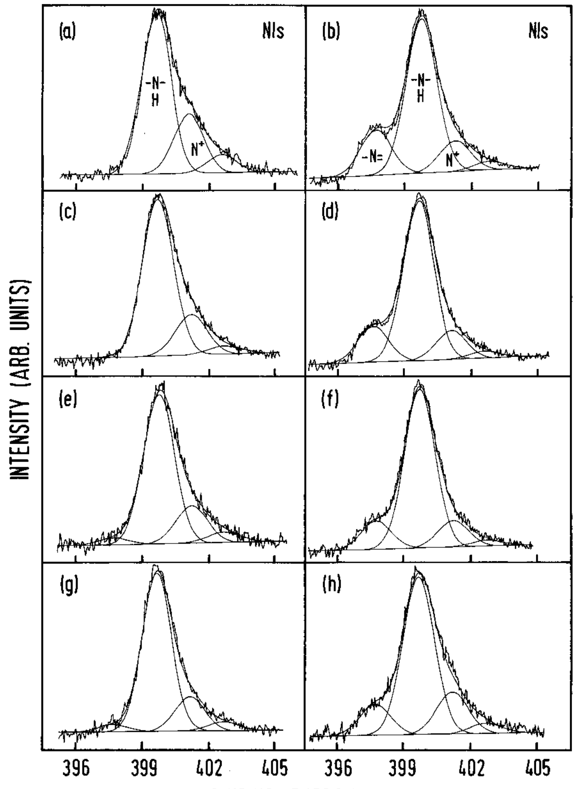

Figure 1. XPS N 1s core-level spectra of (a) TS1, (b) TS1B, (c) TS2, (d) TS2B, (e) TS3, (f) TS3B, (g) TS4, and (h) TS4B.

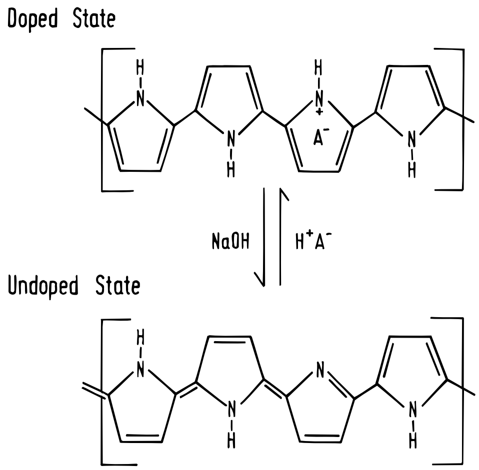

Figure 2. Idealized representation of PPY undergoing undoping–redoping via base/acid treatment.

BE tail does not disappear completely, even though most of the TSA anions have been removed. Bulk analysis of the base film shows a S/N ratio of 0.05, consistent with the results from XPS. The nature of these N species is uncertain, but they are probably some form of oxidized species that resulted from reaction/doping by oxygen since undoped or neutral PPY reacts readily with oxygen.[19,20] The extent of these reactions in the PPY base appears to increase with the number of cycles (comparing Figure 1h and 1b). As a result of these reactions, the proportion of —N= groups recovered in the base is significantly lower than the proportion of N^+ groups in the salt. Increasing the NaOH treatment time to 20 h does not result in significant additional removal of TSA anions over that achieved in 1 h. However, the longer treatment time causes more extensive degradation of the polymer, as evidenced by the XPS and FTIR absorption spectra which showed an increase in oxidized C species (see below).

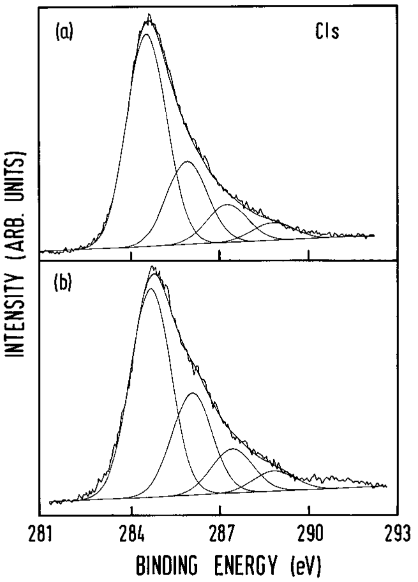

Figure 3. XPS C 1s core-level spectra of (a) TS1B and (b) TS4B.

The results in Table 1 clearly show that treatment of the base films by 1 M TSA does not restore the film to the same doping level (as indicated by the N^+/N and $-SO_3^-/N$ ratios) as that of the pristine film. The lack of complete reversibility reflects changes in the pyrrole ring, in particular, the π-electron system. Hence, the chemistry occuring at the C atoms in the ring should also be investigated. The C 1s core-level spectra of the base films after the first and fourth NaOH treatment are compared in Figure 3a,b, respectively. Although in both cases the C 1s peak is asymmetric and skewed toward the high BE side, the intensity of the high BE tail is distinctly higher in the film after after the fourth NaOH treatment (Figure 3b). The C1s spectra have been deconvoluted into four component peaks: neutral carbons at 284.6 eV, and oxidized species at 286.0 ± 0.1, 287.4 ± 0.2, and 288.8 ± 0.3 eV which correspond to —COH, —CO, and —COOH, respectively.[13,21] This peak assignment is somewhat different from those of Pfluger and Street[22] and Atansoska et al.[18] which used a BE separation 0.9 eV between the α- and β-carbon peaks. In view of the uncertainty of the peak assignments and the high probability of surface hydrocarbon contamination, the C 1s spectra at best indicate qualitatively that the PPY base films react readily with O_2 and the C atoms have undergone an increasing extent of oxidation with cyclic undoping/doping treatment.

The FTIR absorption spectra of the base films after one, two, three and four undoping cycles are shown in Figure 4. These spectra show a progressive increase in the absorption band at 1680 cm^{-1} (peak A). This

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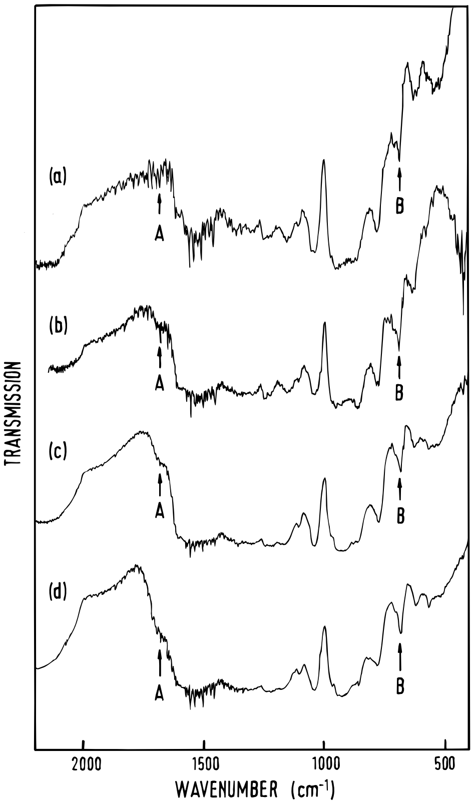

Figure 4. FTIR absorption spectra of (a) TS1B, (b) TS2B, (c) TS3B, and (d) TS4B.

band is attributed to the C═O group,[23] and hence the FTIR absorption data support the postulate that the pyrrole rings have undergone increasing oxidation with base treatment. However, from Figure 3, it appears that C−O groups rather than the C═O groups have increased more dramatically with the redoping-undoping treatment. Since XPS is a surface-sensitive technique while the FITR results are more representative of the bulk, it may be possible that hydrolysis of the surface gives rise to more C−O rather than C═O groups. Another feature in the FTIR spectra (Figure 4) which shows clear changes with the acid/base treatment is the skeletal stretching of the pyrrole ring which occurs in the 1500 cm^{-1} region.[24] This is another indication that the polymer backbone may have undergone some degradation. The spectra in Figure 4 also show a band at 670 cm^{-1} (peak B) attributable to the $-SO_3^-$ group.[25] This result is consistent with the XPS results in Table 1 which show that some $-SO_3^-$ groups persist in the base films. However, both the XPS and FTIR results indicate that there is no significant increase in $-SO_3^-$ groups with increasing number of doping cycles.

Elemental (C, H, N) analyses of the undoped films (Table 2) indicates that while the C/N ratio is about 10% higher than the value of 4 expected for the idealized structure of PPY, this ratio remains rather constant after the first cycle. In contrast, the H/N ratio of the undoped films is substantially higher than the expected value, and this ratio also shows an increase with the number of acid/base cycles. The higher value of H/N suggests that ring substitution has occurred. Ideally, the undoped films should compose of C, H, and N. However, due to the presence of a small amount of $-SO_3^-$ groups and possible oxidation of the rings, there is a lack of complete closure of the mass balance based on C, H, N only. In the case of the as-synthesized film, about 5% of the weight is estimated from XPS and bulk analyses to be due to oxygen in excess of that contained in the $-SO_3^-$ anions. It has been previously reported that electrochemically synthesized PPY films contain unaccounted oxygen and this is attributed to −OH groups in the polymer.[26] The greater lack of closure in the undoped film confirms a greater sensitivity of the undoped film toward oxygen.[19] It can be also seen from Table 2 that as the number of undoping−redoping cycles increases, this lack of complete closure becomes even greater. This observation would support the XPS and FTIR data indicating an increase in oxygen incorporation into the polymer. The reaction of oxygen with the PPY backbone and ring substitutions can be expected to lead to a decrease in effective conjugation of the polymer. This in turn will be manifested in a decrease in σ and a change in the optical absorption of the film. The former has been discussed earlier (Table 1). Evidence of the latter is shown in Figure 5a. The UV−visible absorption spectrum of the pristine film is characterized by a band at 486 nm and a high-intensity tail extending into the near IR region. The former has been identified as a $\pi-\pi^*$ transition while the latter is characteristic of oxidized PPY since it is not observed in neutral PPY before exposure to O_2.[19] When the doped film is treated with NaOH, the $\pi-\pi^*$ transition is blue-shifted to 395 nm. This blue-shift in the $\pi-\pi^*$ transi-

Table 2. Elemental Analysis of Undoped PPY−TSA Films

sample	C/N	H/N	$100 - \Sigma(C + H + N)$
TS1B	4.33	3.61	19.6
TS2B	4.41	3.61	21.2
TS3B	4.38	3.65	22.6
TS4B	4.39	3.69	23.6

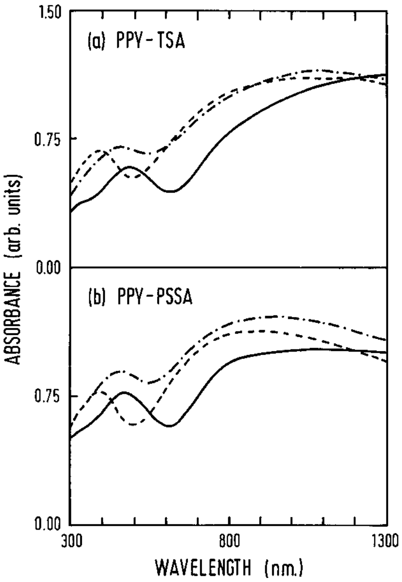

Figure 5. UV−visible absorption spectra of doped and undoped (a) PPY−TSA films and (b) PPY−PSSA films. Pristine films (—), undoped films (— — —) and redoped films (—•—).

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Table 3. Effect of Acid/Base Treatment on Electrical Conductivity and Surface Composition of PPY−PSSA

sample	description	σ/σ_0	−N=/N	−NH−/N	N^+/N	$-SO_3^-/N$	ClO_4^-/N
PS1	as-synthesized PPY−PSSA	1	0	0.69	0.31	0.44	
PS1B	PS1 after NaOH treatment	1×10^{-2}	0.06	0.77	0.17	0.50	
PS2	PS1B after $HClO_4$ treatment	0.32	0	0.74	0.26	0.31	0.11
PS2B	PS2 after NaOH treatment	2×10^{-3}	0.06	0.75	0.19	0.40	0
PS3	PS2B after $HClO_4$ treatment	0.18	0	0.72	0.28	0.32	0.11
PS3B	PS3 after NaOH treatment	2×10^{-3}	0.08	0.76	0.16	0.38	0
PS4	PS3B after $HClO_4$ treatment	2×10^{-2}	0	0.74	0.26	0.27	0.10
PS4B	PS4 after NaOH treatment	3×10^{-4}	0.06	0.79	0.15	0.30	0

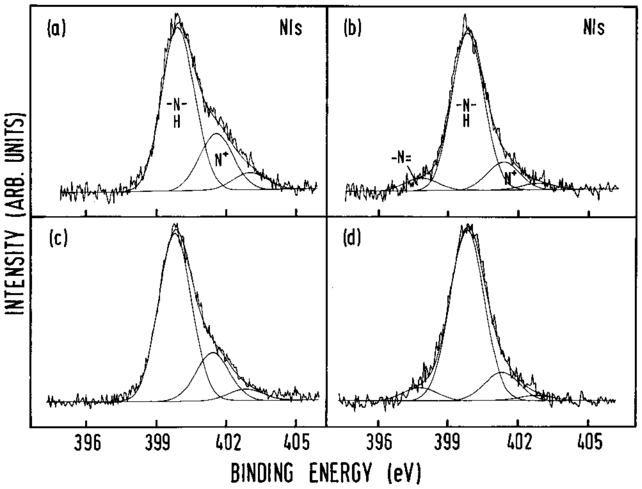

Figure 6. XPS N 1s core-level spectra of (a) PS1, (b) PS1B, (c) PS4, and (d) PS4B.

tion band indicates a decrease in the effective conjugation of the polymer, which is expected to result from the conversion of the N^+ species to −N=, as shown in Figure 2. There is little change in the low-energy absorption tail since the experiment was conducted in air and the undoped film reacts readily with O_2.[19] Subsequent redoping of the film fails to return the $\pi-\pi^*$ transition band to the original position (459 nm for the redoped film compared to 486 nm for the pristine film). This observed wavelength shift provides further evidence of structural degradation resulting in a decrease in the length of the π electron system in the redoped film.

PPY−PSSA Films. The pristine PPY−PSSA film (PS1) is about an order of magnitude less conductive than the PPY−TSA film. However, as can be seen from Table 3, the decrease in σ after the first undoping/redoping cycle is much less than in the case of PPY−TSA. As a result, the first cycle redoped films, PS2 and TS2, have approximately the same σ (4 S/cm). The second and third cycles also resulted in the PPY−PSSA films (PS3 and PS4, respectively) having similar σ as the corresponding PPY−TSA films (TS3 and TS4, respectively). It will be shown in the next section that the undoping of the PPY−PSSA films does not result in the movement of the anions out of the films unlike that occurring in PPY−TSA films.

The XPS N 1s core-level spectrum of the pristine PPY−PSSA film (Figure 6a) is similar to that of pristine PPY−TSA film (Figure 1a). Deconvolution of the spectrum in Figure 6a was carried out using the same peak assignments and procedure as those used for the PPY−TSA salt. After NaOH treatment of the PPY−PSSA film, the N 1s spectrum (Figure 6b) shows a decrease in the intensity of the high BE tail. However, only a small −N= peak is observed. The proportions of the various N species and the $-SO_3^-/N$ ratio are tabulated in Table 3. The similarity between the $-SO_3^-/N$ ratios of the pristine and NaOH treated films indicates that the PSSA chains cannot be easily removed from the PPY matrix. Thus, the undoping of the film results in the migration of Na cations into the film rather than the loss of the anions, similar to the process observed in self-protonated PAN.[27] A comparison of the proportions of −NH− and −N= groups in the undoped film with those in the pristine film shows that the N^+ species revert to almost equal proportions of these groups upon NaOH treatment. For the PPY−TSA film, the N^+ species are converted predominantly to the −N= groups upon NaOH treatment, as shown schematically in Figure 2.

The redoping experiments were carried out with $HClO_4$ and the Cl 2p core-level spectra of the redoped films show a peak at around 207 eV attributable to the ClO_4^- anion.[22] There appears to be some displacement of the PSSA dopant after the first redoping cycle since the $-SO_3^-/N$ ratio decreases (comparing the PS2 and PS1 films). From Table 3, it can be seen that the sum of the $-SO_3^-/N$ and ClO_4^-/N ratios in the redoped films is significantly higher than the N^+/N ratio. Thus, about two-thirds of these anions serve as counterions to the N^+ species while the rest remain associated with H^+ (i.e., H^+A^-). It is interesting to observe from Table 3 that for each cycle the $-SO_3^-/N$ ratio of the base-treated PPY−PSSA film is slightly higher than the redoped (and pristine) film. Since the only source of $-SO_3^-$ anions is the polymer matrix itself, a plausible explanation for this observation is that the PSSA chains assume different orientations in the doped and undoped polymeric matrix which affect the XPS results.

The redoped films also do not achieve as high as doping level as the pristine film (comparing N^+/N ratios). However, the decrease in doping level is less than that observed in the PPY−TSA films. The N 1s core-level spectrum of the film after three redoping cycles (PS4) shows that no imine units remain undoped, unlike the TS4 sample (compare Figures 6c and 1g). The spectrum of the PPY−PSSA film after four cycles of NaOH treatment (Figure 6d) is also similar to that of the film after the first cycle (Figure 6b). The FTIR absorption spectrum of the undoped film, PSIB, (Figure 7a) shows a small absorption band at 1650 cm^{-1} (peak A) attributable to the C=O groups. The intensity of this band increases marginally with each subsequent acid/base treatment (Figure 7b). Similarly, the changes in the absorption in the 1500 cm^{-1} region do not appear to be as drastic as those observed in the spectra of the PPY−TSA films after the same number of cycles (comparing Figure 7b) with Figure 4d. The UV−visible absorption spectra of the pristine, undoped and redoped PPY−PSSA films are compared with the corresponding spectra of the PPY−TSA films in Figure 5. The $\pi-\pi^*$

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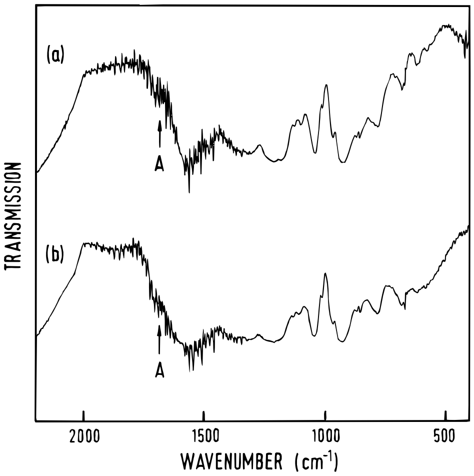

Figure 7. FTIR absorption spectra of (a) PS1B and (b) PS4B.

transition band of the pristine PPY−PSSA film at 471 nm (Figure 5b) occurs at a higher energy than the PPY−TSA film. The shift in the position of this band upon undoping and redoping are qualitatively similar to that described earlier for Figure 5a. It is interesting to note that the $\pi-\pi^*$ transition band of the redoped PPY−PSSA film occurs at 460 nm, almost exactly the same wavelength as that of the redoped PPY−TSA film even though the absorption band of the pristine films occurs at different wavelengths. Thus, the optical absorption results are entirely consistent with the similarity in the σ of the PS2 and TS2 films even though the σ of the pristine PPY−PSSA film is only 10% that of the pristine PPY−TSA film.

Elemental analyses of the PPY−PSSA film before and after base treatment give some interesting results. The C/N ratio for both films is around 4.8. The invariance of this ratio with base treatment provides further support to the postulate that the PSSA anions do not leave the PPY polymer upon base treatment. However, the C/N ratio calculated based on the XPS results of 0.4 PSSA anion to 1 pyrrole unit ($-SO_3^-/N \sim 0.4$) is about 7. In contrast to the large difference in C/N ratio of PPY−PSSA films obtained by two different methods, the C/N ratio of pristine PPY−TSA (TS1) film calculated from the $-SO_3^-/N$ ratio determined using XPS agrees well with the value from bulk elemental analysis (6.6 versus 6.2). Since XPS is a surface sensitive technique, the discrepancy in the C/N ratios obtained for PPY−PSSA films can be explained if the PSSA chains are assumed to be concentrated on the surface regions of the PPY structure. A scanning tunneling microscopy study has also suggested that PPY−PSSA has a helix chain conformation, and the PSSA coats the outside of the PPY spiral helix instead of being incorporated inside the helical structure as is observed with small counterions.[28] This may contribute to the lower σ of the pristine PPY−PSSA film as compared to the corresponding PPY−TSA film. Furthermore, the differences in the manner in which the anions are incorporated in the polymer matrix and in the mobility (or lack of) of the anions may also have contributed to the differences in the degradation behaviour of the polymers during cyclic base/acid treatment. Plausible mechanisms include the PSSA anions blocking the sites along the polymer chains which are prone to attack by oxygen or OH groups, in contrast to the labile nature of the TSA anions.

Conclusion

The doping−undoping−redoping behavior of polypyrrole doped with *p*-toluenesulfonate and poly(4-styrenesulfonate) anions are compared. The doping levels of these two types of films in the pristine state, as determined by XPS, are similar. However, the conductivity of the film with polymeric anions is an order of magnitude lower. This is attributed in part to the morphology of the polypyrrole−poly(4-styrenesulfonate) film in which the polymeric anions coat the polypyrrole chains rather than being incorporated fully into the matrix. This arrangement together with the immobile nature of the polymeric anions appear to affect the degradation behavior during cyclic undoping−redoping. The results obtained from surface and bulk analyses of both types of films show conclusively that the number of oxygen containing groups in the polymer increases with each undoping−redoping cycle leading to a loss of effective conjugation and decrease in doping level.

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