

# Structural and Mechanical Degradation of Polypyrrole Films Due to Aqueous Media and Heat Treatment and the Subsequent Redoping Characteristics

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**ABSTRACT:** Polypyrrole films doped with *p*-toluenesulfonate and poly(4-styrenesulfonate) anions were synthesized electrochemically. These films were treated with water and dilute NaOH solution for varying periods of time. The films do not lose the anions readily when treated with water. In NaOH, dedoping occurs rapidly, either via migration of the toluenesulfonate anions out of the film or the neutralization of the poly(4-styrenesulfonate) anions. The undoped polypyrrole is very susceptible to ring oxidation resulting in C—O and C=O groups. Severe deterioration of the mechanical properties of the film also results upon prolonged exposure to NaOH. The effects of heat on the polypyrrole doping level, structure, and mechanical properties were investigated. The results from redoping experiments suggest that unless the dedoping process by NaOH is carried out rapidly, the redoped films will have significantly lower doping levels and conductivities than the pristine films © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 519–526, 1997

**Key words:** polypyrrole, stability, anion mobility, redoping, mechanical properties

## INTRODUCTION

The stability of a conducting polymer is one of the most important factors determining its potential for practical applications. This stability is usually assessed in terms of the electrical performance and the chemical and thermal stability. One of the more promising conductive polymers is polypyrrole (PPY), due in part to the ease of synthesis and high electrical conductivity ( $\sigma$ ).<sup>1–3</sup> Previous stability studies of PPY have focused on establishing how  $\sigma$  or weight of the PPY changes with temperature or treatment method.<sup>4–8</sup> The results obtained are unique to the sample used since the synthesis conditions of the PPY affect the electrical, chemical, and mechanical properties.

In this work, emphasis is placed on determining the structural changes that occur when PPY is subjected to thermal and chemical treatment, and how these changes account for the observed degradation in physical properties. The analytical techniques used include elemental analysis, Fourier transform infrared (FTIR) absorption spectroscopy and X-ray photoelectron spectroscopy (XPS). The last is particularly suited for monitoring the changes in the chemical states of C and N in the PPY samples.<sup>9–11</sup> Electrochemically synthesized PPY films doped with sulfonate anions were tested, since such films have been shown to possess good mechanical strength and high conductivity.<sup>12–13</sup> Both monomeric and polymeric anions were used to assess the effects of anion mobility. Furthermore, since the reversibility of conductor–insulator transition is an asset in certain applications of electroactive polymers, inves-

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tigations on the replenishing of anions in chemically and thermally treated PPY films were also carried out.

## EXPERIMENTAL

### Sample Preparation

Pyrrole (Merck) was distilled before use. Solutions of 0.2 mol dm<sup>-3</sup> pyrrole and either 0.05 mol dm<sup>-3</sup> *p*-toluenesulfonic (TSA) or 0.05 mol dm<sup>-3</sup> sodium salt of poly(4-styrenesulfonic acid) (NaPSSA) in ultrapure water were purged with N<sub>2</sub> before polymerization commenced. The PPY films were electrodeposited galvanostatically on a stainless steel plate with a current density of 2 mA cm<sup>-2</sup> for about 15 min. The polymer films were rinsed with water and dried under vacuum. The thickness of the free-standing PPY salt films was estimated from the weight and density of the films and ranged from 7–10 μm.

The as-synthesized PPY salt films were equilibrated in distilled water or 0.5M NaOH for varying periods of time. The base-treated films were rinsed with water before being dried again under vacuum. The PPY salt and base films were also heated in air at 150°C for periods ranging from 2 to 20 h. Redoping of the chemically and thermally treated films was carried out by equilibrating these films in 1M HClO<sub>4</sub> for 1 h. HClO<sub>4</sub> was chosen instead of TSA or PSSA so that the proportions of counterions that remained from the pristine state and those contributed by the redoping process could be differentiated.

## INSTRUMENTATION

The electrical conductivity ( $\sigma$ ) of the films was measured using both the standard collinear four-probe and two-probe techniques. UV-visible absorption spectra of thin films on ITO glass plates were obtained using a Shimadzu UV3101PC spectrometer, while Fourier transform infrared (FTIR) absorption spectra of the free-standing films were obtained using a Shimadzu FTIR 8101 spectrophotometer. The XPS measurements were made on a VG ESCALAB MkII spectrometer with a MgK $\alpha$  X-ray source (1253.6 eV). The run conditions and data analysis techniques were similar to those described in our earlier publications.<sup>14,15</sup> Thermogravimetric measurements in N<sub>2</sub> were carried out with a Netzsch STA409 simultaneous

thermogravimetric-differential thermal analyzer. A heating rate of 10°C/min was used. The tensile properties of the films were tested using a Rheometrics Minimat miniature materials tester. The sample width used was 6 mm and the stretching rate was 1 mm/min.

## RESULTS AND DISCUSSION

### Effect of H<sub>2</sub>O and NaOH

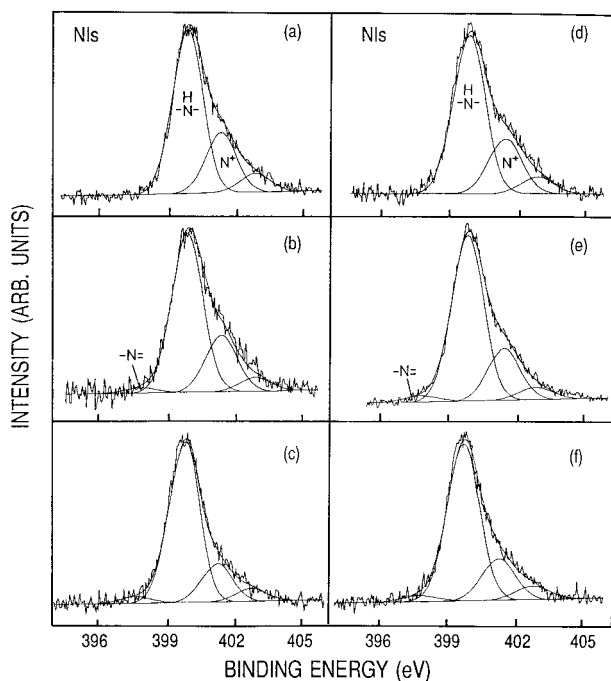
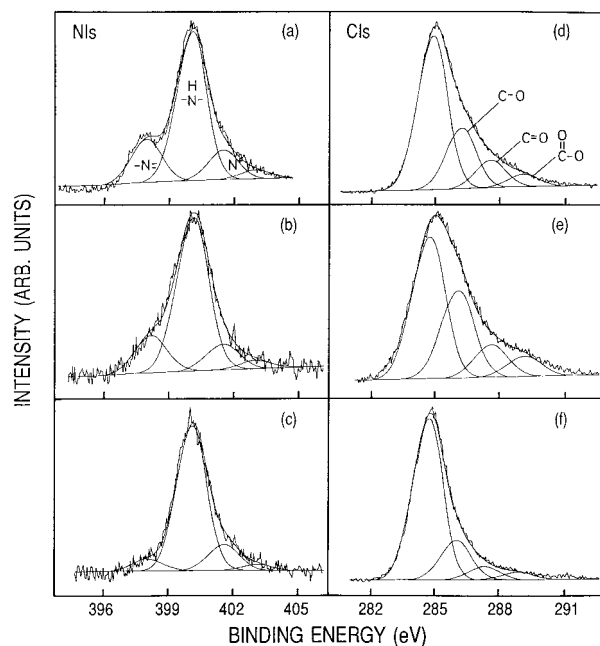
The pristine PPY–TSA and PPY–PSSA films possess  $\sigma$  ( $\sigma_0$ ) of 100 S/cm and 10 S/cm, respectively. The effects of equilibrating the films in water for 1 h and 20 h on  $\sigma$  are summarized in Table I. Although the fractional decrease in  $\sigma$  is less for the PPY–PSSA films, the PPY–TSA film is still more conductive than the PPY–PSSA after 20 h in H<sub>2</sub>O. The XPS N1s core-level spectra of the pristine and H<sub>2</sub>O-treated films are shown in Figure 1. The spectra are dominated by a large peak at 399.7 eV which is assigned to the amine (—NH—) nitrogens.<sup>14</sup> Upon treatment with H<sub>2</sub>O, both types of films show a decrease in the intensity of the high-binding energy (BE) tail (BE > 401 eV) which has been deconvoluted into two component peaks based on the fixed linewidth (full width at half maximum) approach. This high-BE tail has been attributed to the positively charged nitrogen (N<sup>+</sup>) species. Concurrent with this decrease in the N<sup>+</sup> species is the evolution of a small peak at 397.7 eV, attributable to the imine (—N=) nitrogens.<sup>14</sup> The proportions of the various N species are summarized in Table I. It can be seen that for both types of films after 20 h in H<sub>2</sub>O, the decrease in N<sup>+</sup> is balanced by the increase of the —N= and —NH— species in almost equal proportions. This conversion of N<sup>+</sup> species to neutral species indicates that the film has undergone a small extent of undoping. The anion content is calculated from the —SO<sub>3</sub><sup>-</sup> peak at around 167 eV<sup>16</sup> in the S2p core-level spectra. The large polymeric PSSA anions do not leave the PPY matrix with H<sub>2</sub>O treatment as indicated by the almost constant —SO<sub>3</sub><sup>-</sup>/N ratio, while some of the more mobile TSA anions are lost; but, surprisingly, a large proportion remains associated with the PPY (Table I). The —SO<sub>3</sub><sup>-</sup>/N ratio in PPY–TSA is well balanced by the N<sup>+</sup>/N ratio while in PPY–PSSA, the —SO<sub>3</sub><sup>-</sup>/N ratio is substantially higher than the N<sup>+</sup>/N ratio. Thus, in the PPY–PSSA film, some of the anions are associated with H<sup>+</sup> rather than N<sup>+</sup>.

**Table I** Effect of Water on Electrical Conductivity and Doping Level of PPY-TSA and PPY-PSSA Films

Treatment	$\sigma/\sigma_0$	$-\text{N}=\text{N}$	$-\text{NH}-\text{N}$	$\text{N}^+/\text{N}$	$-\text{SO}_3^-/\text{N}$
(a) PPY-TSA Films					
Pristine	1	0	0.69	0.31	0.37
H <sub>2</sub> O, 1 h	0.45	0.03	0.68	0.29	0.25
H <sub>2</sub> O, 20 h	0.25	0.03	0.74	0.23	0.25
(b) PPY-PSSA Films					
Pristine	1	0	0.69	0.31	0.43
H <sub>2</sub> O, 1 h	1	0.03	0.70	0.27	0.41
H <sub>2</sub> O, 20 h	0.40	0.03	0.72	0.25	0.43

In contrast to the resilient nature of the TSA anions in H<sub>2</sub>O, almost all these anions are removed when the film is equilibrated in NaOH for 1 h ( $-\text{SO}_3^-/\text{N}$  ratio  $\sim 0.03$ ). The decrease in N<sup>+</sup> is almost entirely compensated for by an increase in  $-\text{N}=\text{N}$  nitrogens [Fig. 2(a)]. However, a sizeable N<sup>+</sup> peak remains even though the  $-\text{SO}_3^-/\text{N}$  ratio is very small. The N<sup>+</sup> species may have resulted from charge transfer interactions with oxygen, since undoped PPY is known to react readily with oxygen.<sup>17,18</sup> When the NaOH treatment time is increased to 20 h, there is a small decrease in the proportions of  $-\text{N}=\text{N}$  and N<sup>+</sup> spe-

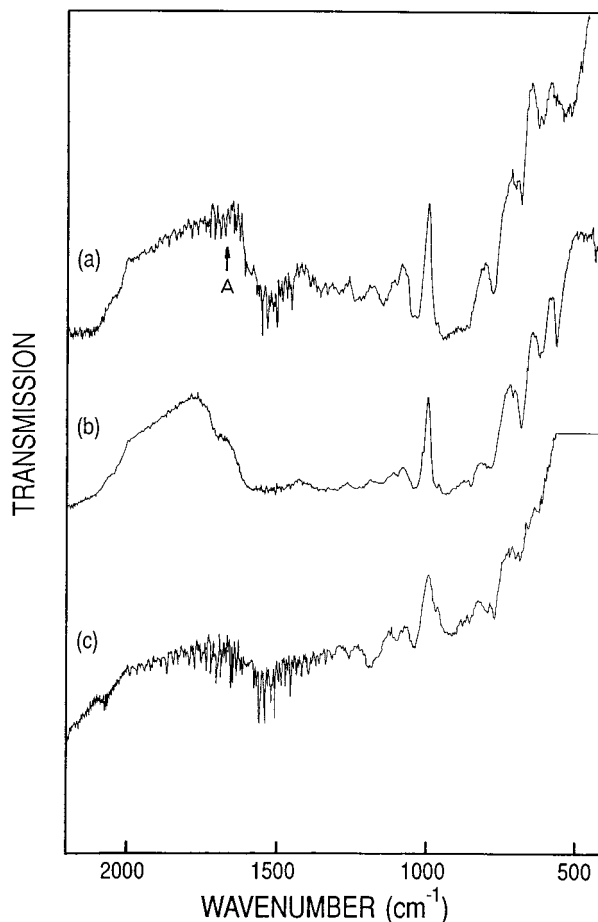
cies [Fig. 2(b)]. The  $-\text{SO}_3^-/\text{N}$  ratio remains at 0.03. However, a comparison of the C1s spectra of the films after 1 h and 20 h treatment (Figs. 2(d) and 2(e), respectively) shows an increase in the intensity of the high-BE tail in the latter. The C1s spectra are deconvoluted using the following peak assignments: C-H, C-N at 284.6 eV, C-O at 286.0 eV, C=O at 287.5 eV and O-C=O at 289.0 eV, with a variation of  $\pm 0.2$  eV. These peak assignments have also been used in previous studies on PPY,<sup>11,19</sup> although some investigators advocated a differentiation between the peak assignments of C <sub>$\alpha$</sub>  and C <sub>$\beta$</sub>  of the PPY


**Figure 1** XPS N1s core-level spectra of PPY-TSA [(a), (b), (c)] and PPY-PSSA [(d), (e), (f)]. (a) and (d): pristine salts; (b) and (e): treated with H<sub>2</sub>O for 1 h; (c) and (f): treated with H<sub>2</sub>O for 20 h.

**Figure 2** XPS N1s and C1s core-level spectra of PPY-TSA after 1 h NaOH treatment [(a) N1s and (d) C1s]; PPY-TSA after 20 h NaOH treatment [(b) N1s and (e) C1s]; and PPY-PSSA after 1 h NaOH treatment [(c) N1s and (f) C1s].

ring.<sup>10,20</sup> The XPS results show that the increase in "oxidized C" is due mainly to the C—O groups. Bulk elemental analysis also shows that the mass fraction accounted for by C, H, and N is lowered with NaOH treatment time. The formation of the oxidized C groups is most likely due to reactions of the undoped PPY with oxygen.

In the case of the PPY–PSSA films, treatment with NaOH for 1 h results in a decrease in the  $N^+/N$  ratio to the same value as that obtained for PPY–TSA. However, the resulting increase in  $-N=$  is much smaller [Fig. 2(c)] and the  $-SO_3^-/N$  ratio does not decrease. The undoping process is thus due to the migration of  $Na^+$  to neutralize the PSSA anions rather than the loss of the latter. A comparison of the C1s core-level spectra of the 1 h NaOH-treated PPY–PSSA film [Fig. 2(f)] and the similarly treated PPY–TSA film [Fig. 2(d)] clearly shows that the former has a lower proportion of oxidized C groups. Increasing the treatment time to 20 h does not affect the anion content of the PPY–PSSA film significantly ( $-SO_3^-/N$  ratio remains at 0.41). However, there is an increase in the proportion of C—O groups with increasing treatment time. The increasing extent of oxidation of C is supported by bulk elemental analysis, similar to the trend observed in PPY–TSA films.

Further evidence of the degradation of the PPY films upon prolonged NaOH treatment is provided by the FTIR absorption spectra. Figures 3 and 4 show the effect of NaOH treatment time on the PPY–TSA and PPY–PSSA films, respectively. Marked differences between the spectra of the films treated for 1 h [Figs. 3(a) and 4(a)] and 3 h [Figs. 3(b) and 4(b)] can be readily observed in both cases. Specifically, the intensity of the absorption band at  $1680\text{ cm}^{-1}$  (marked A in Figs. 3 and 4) attributed to the C=O groups<sup>21</sup> has increased substantially, and the PPY ring vibrations in the  $1500\text{ cm}^{-1}$  region<sup>2</sup> have been reduced substantially with the increase in treatment time. The absorption spectrum of the PPY–TSA film after 20 h in NaOH [Fig. 3(c)] suggests that extensive structural degradation has occurred. A similar conclusion can be made for the PPY–PSSA film, although the changes in the spectrum [Fig. 4(c)] are not as drastic. The FTIR results indicate that C=O groups increased substantially upon prolonged NaOH treatment, whereas the XPS results show that C—O groups are the predominant groups. The XPS results are more representative of the surface of the film, in con-

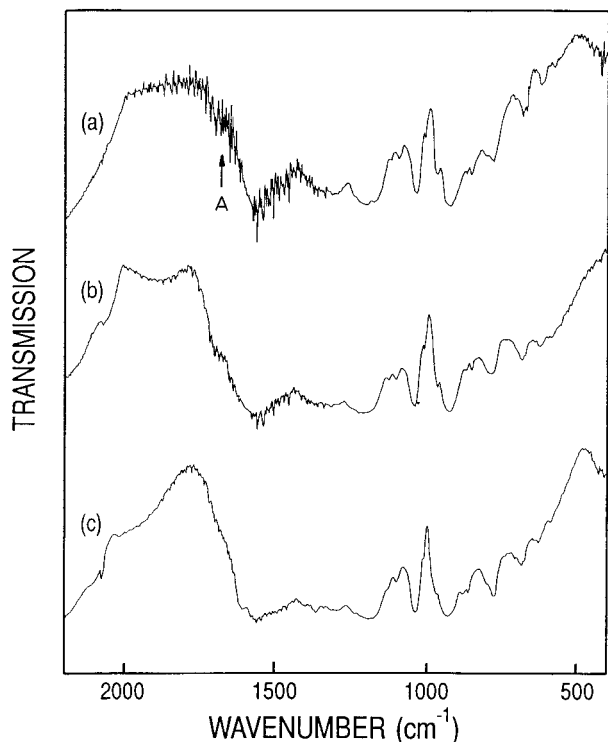


**Figure 3** FTIR absorption spectra of PPY–TSA after (a) 1 h, (b) 3 h, and (c) 20 h NaOH treatment.

trast to the FTIR absorption technique which provides information on the bulk of the film.

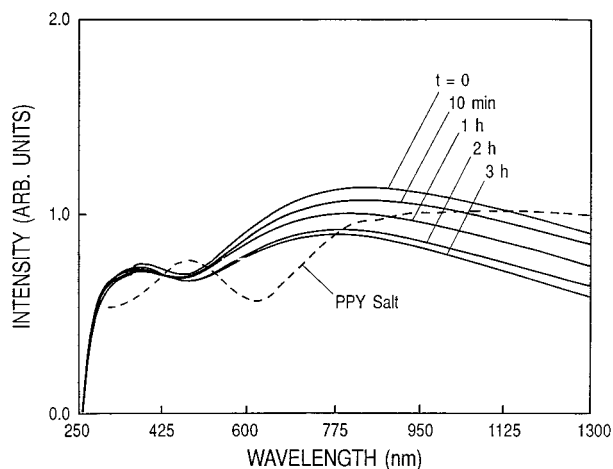
The treatment of PPY salt films with NaOH results in a blue shift of the  $\pi-\pi^*$  transition band from  $471\text{ nm}^{17}$  to  $379\text{ nm}$  (Fig. 5) due to the loss of conjugation resulting from the formation of  $-N=$  groups in the PPY rings. However, the high intensity tail extending into the near infrared, characteristic of oxidized PPY,<sup>17</sup> is still present when the film is initially treated with NaOH. This is due to the presence of  $O_2$  during the experiment which readily undergoes charge transfer reactions with neutral PPY. It can be seen from Figure 5 that the intensity of the absorption tail decreases with increasing NaOH treatment time. This suggests a gradual change in the conjugation pattern and charge transfer characteristics of the PPY base.

The PPY–TSA and PPY–PSSA films have rather different mechanical properties, with the former possessing a much higher breaking strain

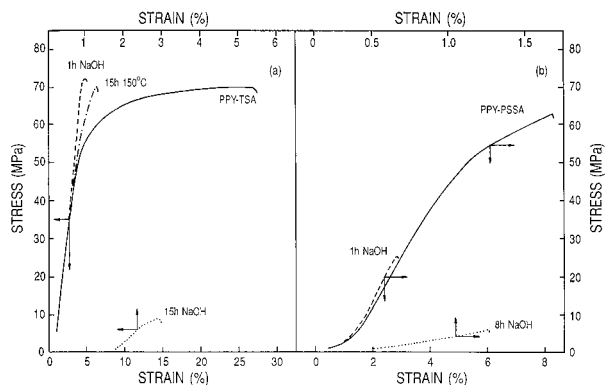


**Figure 4** FTIR absorption spectra of PPY-PSSA after (a) 1 h, (b) 3 h and (c) 20 h NaOH treatment.

(Fig. 6). Regardless of the mobility of the anions, NaOH treatment causes the films to become more brittle. Prolonged exposure of the films to NaOH results in severe deterioration of the mechanical properties (Fig. 6), and the films after 20 h of NaOH treatment were too fragile to be tested ac-



**Figure 5** UV-visible absorption spectra of PPY-PSSA salt before and after NaOH treatment. Time indicated is the treatment time. The  $t = 0$  curve was obtained immediately upon immersion in NaOH.



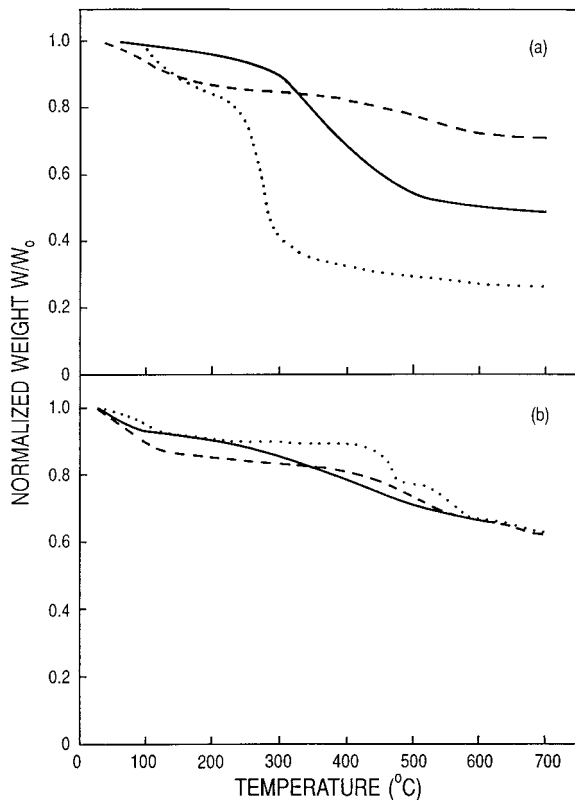
**Figure 6** Stress-strain plots of PPY-TSA before and after NaOH and heat treatment (a) and PPY-PSSA before and after NaOH treatment (b).

curately. The loss in mechanical strength is postulated to be related to the attack of oxygen on the polymer backbone.

## EFFECTS OF TEMPERATURE

The effects of temperature on the weight loss behavior of TSA ( $C_7H_7SO_3H \cdot H_2O$ ), PPY-TSA salt film and the latter after treatment with NaOH for 1 h, are compared in Figure 7(a). For TSA, weight loss commences around 100°C due to the loss of water of hydration. This is followed by a loss of over 50% of the total weight over the next 200°C. The PPY-TSA film undergoes a gradual loss in weight upon heating above room temperature, until about 300°C when a sharp decrease in weight occurs. This weight-loss step at 300°C is absent in the undoped film and is likely to be due to the decomposition of the TSA anion. The sodium salt of PSSA decomposes at a much higher temperature of 420°C [Fig. 7(b)]. The weight loss behavior of the PPY-PSSA film suggests that the PSSA anions react with the positively charged PPY resulting in less stable species at temperatures much below the decomposition temperature. However, the neutralization of the PSSA anions by  $Na^+$  in the NaOH-treated PPY-PSSA film appears to impart thermal stability to the film [Fig. 7(b)]. The PPY-PSSA film and the PPY-TSA film exhibit higher thermal stability than the PPY film doped with dodecylsulfate anions which undergoes a pronounced weight loss at 200°C.<sup>8</sup>

Although the thermogravimetric analysis suggested that the TSA and PSSA anions would not undergo substantial decomposition at 150°C, the

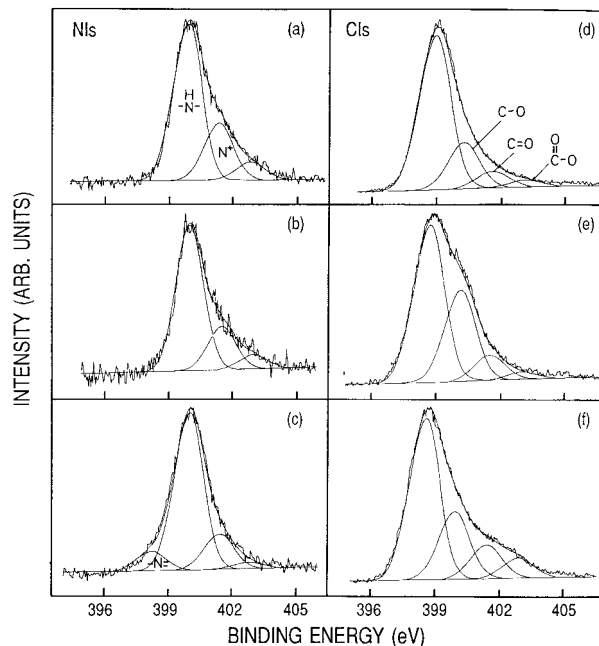


**Figure 7** Thermogravimetric plots of TSA, PPY-TSA and PPY-TSA after 1 h NaOH treatment (a) and PSSANa, PPY-PSSA and PPY-PSSA after 1 h NaOH treatment (b). TSA and PSSANa ( $\cdots$ ), pristine PPY salts ( $—$ ), PPY salts after NaOH treatment ( $- - -$ ).

$\sigma$  of the films after heating to 150°C shows a substantial decrease. The  $\sigma/\sigma_0$  ratios of PPY-TSA films after 2 h and 20 h at 150°C are 0.75 and 0.17, respectively. The corresponding values for the PPY-PSSA films are 0.44 and 0.03. The decrease in  $\sigma$  is accompanied by a mechanical degradation of the film. The percent elongation at break for the PPY-TSA film decreases from about 30 for the pristine film to 21 and 6 after 2 h and 15 h at 150°C, respectively [Fig. 6(a)]. For the PPY-PSSA film, even 2 h at 150°C caused the film to be too fragile to be tested accurately.

The XPS N1s core-level spectra of pristine PPY-TSA film and of the film after 20 h at 150°C are compared in Fig. 8. The proportion of  $N^+$  in the latter [Fig. 8(b)] is clearly lower than that in the former [Fig. 8(a)]. However, the  $-\text{SO}_3^-/\text{N}$  ratios in both samples are similar, consistent with the postulate that the TSA anions have not decomposed at 150°C. In contrast, the C1s core-level spectrum of the heated film [Fig. 8(e)] indicates a dramatic increase in C—O species over that

observed in the pristine film [Fig. 8(d)]. The results obtained with PPY-PSSA films are quite similar, with little change in the  $-\text{SO}_3^-/\text{N}$  ratio after 20 h of heat treatment at 150°C. Thus, for these films, the observed decrease in  $\sigma$  is likely the result of loss of conjugation due to formation of oxidized C groups rather than the loss of anions due to decomposition. Heat treatment of the PPY base films (after NaOH treatment) also resulted in an increase in the proportion of oxidized C species (especially C=O) in the C1s core-level spectra [Fig. 8(f)]. The FTIR absorption spectra also show a large C=O band. The high-BE tail of the N1s peak also increases in intensity, while the proportion of  $-\text{N}=\text{C}$  groups decreases [compare Fig. 8(c) with Fig. 2(a)]. Even though it is not certain which species constitute the high-BE tail, they would have most likely resulted from charge transfer interactions with  $\text{O}_2$ . Elemental analysis of the PPY base films after 20 h at 150°C indicates only a small decrease ( $<10\%$ ) in the C/N ratio as compared to pristine PPY base films. However, the H/N ratio shows a decrease of about 30% and the weight fraction of (C + H + N) also decreases substantially (39% decrease for the PPY-TSA base and 22% decrease for the PPY-PSSA base) from the corresponding values before heat treatment. These results are consistent with the XPS



**Figure 8** XPS N1s and C1s core-level spectra of PPY-TSA: pristine [(a) N1s and (d) C1s]; after 20 h at 150°C [(b) N1s and (e) C1s]; and after 1 h NaOH treatment followed by 20 h at 150°C [(c) N1s and (f) C1s].

**Table II Electrical Conductivity and Doping Level of Chemically and Thermally Treated Films After Redoping with HClO<sub>4</sub>**

Pretreatment Before Redoping	$\sigma/\sigma_0^*$	—N= /N	—NH— /N	N <sup>+</sup> /N	—SO <sub>3</sub> <sup>-</sup> /N	ClO <sub>4</sub> <sup>-</sup> /N
(a) PPY–TSA Films						
1 h NaOH	$4 \times 10^{-2}$	0	0.75	0.25	0.03	0.20
20 h NaOH	$5 \times 10^{-3}$	0.04	0.70	0.26	0.02	0.28
1 h NaOH followed by 20 h at 150°C	$<10^{-6}$	0.15	0.68	0.17	0.04	0.02
(b) PPY–PSSA Films						
1 h NaOH	0.4	0	0.70	0.30	0.28	0.11
20 h NaOH	$3 \times 10^{-2}$	0.06	0.69	0.25	0.28	0.07
1 h NaOH followed by 20 h at 150°C	$<10^{-6}$	0	0.70	0.30	0.29	0.02

\*  $\sigma/\sigma_0$  refers to  $\sigma$  of HClO<sub>4</sub>-redoped film normalized by that of the pristine film.

and FTIR results and support the postulate of oxygen incorporation in the heated base film via ring substitution (replacing H).

## REDOPING EXPERIMENTS

The base-treated films, with and without heat treatment, were equilibrated in 1M HClO<sub>4</sub> for 1 h to test the films' abilities to be redoped. The electrical conductivities of the redoped films normalized by that of the pristine film ( $\sigma/\sigma_0$ ) are presented in Table II. In all cases, the redoped film cannot attain the conductivity of the pristine film. Considering the 1 h NaOH pretreated (i.e., before redoping) films, XPS analysis indicates that all the —N= units are converted to N<sup>+</sup> upon redoping (Table II). The anion content is calculated from the —SO<sub>3</sub><sup>-</sup> peak in the S2p core-level spectra and the ClO<sub>4</sub><sup>-</sup> peak in the Cl2p spectra (at ~ 207 eV<sup>16</sup>). The N<sup>+</sup>/N ratio of the redoped PPY–TSA film is closely balanced by the (—SO<sub>3</sub><sup>-</sup> + ClO<sub>4</sub><sup>-</sup>)/N ratio. However, the doping level [as given by either N<sup>+</sup>/N or (—SO<sub>3</sub><sup>-</sup> + ClO<sub>4</sub><sup>-</sup>)/N] is not as high as that in the pristine film (Table I). In the case of the redoped PPY–PSSA film, the anions/N ratio is higher than N<sup>+</sup>/N, suggesting that some of the anions are associated with H<sup>+</sup> rather than N<sup>+</sup>. Furthermore, the —SO<sub>3</sub><sup>-</sup>/N ratio of this film is about 25% lower than those of the pristine PPY–PSSA film and the NaOH treated film. It is unlikely that the polymeric anions have migrated out of the PPY matrix during redoping. It is postulated that the PSSA chains have reoriented more towards the bulk during treatment by HClO<sub>4</sub>. When the ClO<sub>4</sub><sup>-</sup> anions are removed by

NaOH treatment of the redoped film, the —SO<sub>3</sub><sup>-</sup>/N ratio reverts back to 0.4, confirming that there is no loss of PSSA anions. The  $\sigma$ 's of redoped PPY–TSA and PPY–PSSA films are around 4 S/cm even though the former in the pristine state is 10 times more conductive than the latter in the same state. This implies that the PPY–TSA film may be more susceptible to degradation during the NaOH treatment process. A similar conclusion was reached from the XPS results and FTIR absorption spectra presented earlier.

When the NaOH pretreatment time was increased to 20 h, the  $\sigma$  of the redoped films dropped another order of magnitude (Table II). The XPS and FTIR absorption results have clearly shown that prolonged NaOH treatment causes extensive formation of oxidized C species, resulting in a loss of effective conjugation. The redoping process is inhibited, as evidenced by the incomplete conversion of —N= species to N<sup>+</sup>. The movement of the charge carriers is also expected to be impeded by the loss of conjugation. Thus,  $\sigma$  is decreased. If the NaOH-treated (1 h) films are heat treated (20 h at 150°C) before the redoping process, the "redoped" films are no longer conductive. Examination of the Cl2p XPS core-level spectra of these films shows no significant amount of ClO<sub>4</sub><sup>-</sup> incorporated into the films. Therefore, the PPY films have completely lost the ability to undergo redoping.

## CONCLUSION

Polypyrrole films doped by *p*-toluenesulfonate anions do not readily lose their anions when

treated with water, even after equilibration for 20 h. In contrast, most of these anions are removed when the films are soaked in 0.5M NaOH for 1 h. Prolonging the NaOH treatment time results in increasing the extent of oxidation of the C atoms and loss of mechanical strength. Similar results were obtained with polypyrrole films doped with polymeric anions, even though these anions do not migrate out of the films during NaOH treatment. Due to the loss of conjugation resulting from ring oxidation, redoping of the base films with acid fails to restore the conductivity to the level of the pristine films. Below 200°C, the sulfonate anions do not decompose, but the ring oxidation process is greatly accelerated by heat. Polypyrrole base films, after heating at 150°C for 20 h, completely lose the ability to undergo redoping by acids.

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## REFERENCES

1. A. F. Diaz and K. K. Kanazawa, in *Extended Linear Chain Compounds*, J. S. Miller, Ed., Plenum, New York, 1983, Vol. 3, p. 417.
2. A. Watanabe, M. Tanaka, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **54**, 2278 (1981).
3. K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, *Synth. Met.*, **1**, 329 (1979/80).
4. L. A. Samuelson and M. A. Drury, *Macromolecules*, **19**, 824 (1986).
5. M. Arca, E. Arca, A. Yildiz, and O. Guven, *J. Material Sc. Letters*, **6**, 1013 (1987).
6. H. Munstedt, *Polymer*, **29**, 296 (1988).
7. M. Biswas and A. Roy, *J. Appl. Polym. Sc.*, **51**, 1575 (1994).
8. W. A. Gazotti Jr., V. F. Juliano, and M. A. De Paoli, *Polym. Deg. Stab.*, **42**, 317 (1993).
9. E. T. Kang, K. G. Neoh, and K. L. Tan, *Advances in Polymer Science*, Springer-Verlag, Germany, 1993, Vol. 106, p. 135.
10. L. Atanasoska, K. Naoi, and W. Y. Smyrl, *Chem. Mater.*, **4**, 988 (1992).
11. H. Ge, G. Qi, E. T. Kang, and K. G. Neoh, *Polymer*, **35**, 504 (1994).
12. B. F. Cvetko, M. P. Brungs, R. P. Burford, and M. Skyllas-Kazacos, *J. Materials Sc.*, **23**, 2102 (1988).
13. B. Sun, J. J. Jones, R. P. Burford, and M. Skyllas-Kazacos, *J. Materials Sc.*, **24**, 4024 (1989).
14. K. L. Tan, B. T. G. Tan, E. T. Kang, and K. G. Neoh, *J. Chem. Phys.*, **94**, 5382 (1991).
15. K. G. Neoh, M. Y. Pun, E. T. Kang, and K. L. Tan, *Synth. Met.*, **73**, 209 (1995).
16. *Handbook of X-ray Photoelectron Spectroscopy*, G. E. Muilenberg, Ed., Perkin Elmer, New York, 1977, p. 63.
17. G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.*, **83**, 253 (1982).
18. R. Erlandson, O. Inganäs, I. Lundström, and W. R. Salaneck, *Synth. Met.*, **10**, 303 (1985).
19. H. Munstedt, *Polymer*, **27**, 899 (1986).
20. P. Pfluger and G. P. Street, *J. Chem. Phys.*, **80**, 544 (1984).
21. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1980, p. 167.