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A study of acid/base treatments of polypyrrole films using ^{13}C n.m.r. spectroscopy

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Electrodeposited polypyrrole films prepared with paratoluenesulfonate (pTS), dodecylsulfate (DDS) and perchlorate anions were treated with acidic and basic solutions, and their structure was investigated by ^{13}C solid state n.m.r. spectroscopy. This technique has confirmed that pTS is completely removed from the film in both acidic and basic solutions whilst DDS is only partially removed and tends to decompose upon treatment with H_2SO_4. The appearance of shoulders at 143 ppm upon treatment with 0.5 M base indicates formation of a quinoid pyrrole structure. Substitution on the β-carbon by OH cannot be confirmed from the present spectra. Stronger base causes a more dramatic change in the polypyrrole backbone with an obvious increase in the electron density on the β-carbons, consistent with the reduction of the carbon backbone. There is no indication of quinoid units in this case. Acid treatments result in considerable broadening of the main 127 ppm polypyrrole peak.

(Keywords: polypyrrole films; n.m.r. spectroscopy; acid/base treatment)

INTRODUCTION

Recently, it has been reported that treatment of polypyrrole with acids or bases results in protonation or deprotonation, respectively, of the polymer[1]. These processes are also found to reversibly affect the conductivity of polypyrrole. Acid treatment gives a slight increase in conductivity, whilst base treatment can decrease the conductivity by several orders of magnitude. This latter process is proposed to result from deprotonation of the pyrrole nitrogen which yields an insulating form of polypyrrole. It is suggested that this deprotonated form of polypyrrole adopts a quinoid structure[1]. Wernet and Wegner suggest that treatment of polypyrrole with OH^- results in the chemical incorporation of this ion onto the polymer backbone, thus disrupting the conjugation[2].

Munsted[3] and Munsted *et al.*[4] employed acid and base treatments of polypyrrole films in an attempt to improve the stability of the conductivity at elevated temperatures. From their work, it appeared that both processes produce more stable films. Immersion of the polypyrrole film in base solutions, however, decreased the conductivity by several orders of magnitude (dependent on extent of treatment). Both processes cause physical changes to the films as observed by scanning electron microscopy[1], thickness and gas permeability measurements[3], and these may contribute to the improved stability.

On the other hand, it has been shown previously that the conductivity stability at elevated temperatures is counterion dependent[5,6] and that some counterions are more stable at elevated temperatures (e.g. paratoluenesulfonate (pTS) compared to dodecylsulfate (DDS))[7]. Ion exchange is likely to occur during both acid and base treatment processes and it is possible that the stability of these exchanged ions may account for the improved stability of the polymer in Munsted's process. In this work, we probe the effect of acid/base treatments on the molecular structure of polypyrrole films, using solid state ^{13}C n.m.r. techniques, in order to try to understand their effect on the conductivity and thermal stability at 150°C.

EXPERIMENTAL

Film preparation

Polypyrrole films were prepared by electropolymerization in distilled water, from solutions containing 0.1 M freshly distilled pyrrole (Aldrich) and 0.1 M electrolyte on 8 cm diameter stainless steel electrodes. Electrodeposition was performed at a constant current rate of 2.8 mA cm^{-2} under a nitrogen blanket. Sodium dodecylsulfate (NaDDS) and sodium paratoluenesulfonate (NapTS) salts were used as received (Aldrich). Polypyrrole/ClO_4^- films were electropolymerized from acetonitrile solutions containing 1% water and 0.1 M tetraethylammonium perchlorate.

Polypyrrole films were immersed in 0.5 M NaOH and H_2SO_4 solutions and maintained at 100°C for 1 h. Films were also treated in 3.0 M acidic and basic solutions at ambient temperature for several days. From a single film,

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specimens were taken for thermal ageing (with and without treatment) and for control samples. Direct current conductivity of the films was measured using a four-probe technique.

Solid state n.m.r. characterization

Treated films were crushed† using a hammer mill under liquid nitrogen, and then mixed with MgO (approximately 1:1) in order to avoid detuning and arcing of the n.m.r. probe head. Magic angle spinning was used with a Bruker AM300 instrument equipped with a Bruker ^{13}C 7 mm solid state probe operating at 75.45 MHz. A spinning rate of 5 kHz was employed. Cross polarization was used to enhance the ^{13}C signal via transfer of ^{1}H polarization to the ^{13}C nuclei. A 9 μs 90° pulse was used with a contact time of 800 μs. This contact time gave the maximum signal intensity although this was not particularly sensitive to the time used (i.e. values between 600 and 1000 μs gave identical results). For conductive samples, at least 20 000 scans were collected with a repetition time of 2 s. The less conductive samples required fewer scans ($\sim$5000) for an equivalent signal-to-noise ratio.

The reason for this difference in signal-to-noise ratio is attributed predominantly to the behaviour of the radiofrequency (r.f.) field as a function of distance within the sample rather than the effects of paramagnetic species. In conductive samples, the skin depth, i.e. the depth to which the r.f. field may penetrate, is considerably less than in non-conductive samples. Since the experiments here rely on cross polarization, it is likely that in the more conductive samples, the Hartmann–Hahn matching is best achieved at the surface of the polypyrrole powder particles. In other words, the extent of the sample accessed by the experiment is considerably decreased and so the signal-to-noise ratio is decreased. This is further supported by the fact that better spectra are obtained when the samples are thoroughly crushed and mixed with MgO as compared with coarser samples. Nevertheless, we cannot entirely overlook the possibility that there may be some species which cannot be detected in our experiments due to rapid relaxation as a result of paramagnetic centres.

RESULTS AND DISCUSSION

OH^- treatment of polypyrrole/pTS and polypyrrole/DDS films

Figure 1 shows the ^{13}C n.m.r. spectra for polypyrrole/pTS films untreated, treated with 3.0 M NaOH and 0.5 M NaOH. The spectrum of the as-grown film is dominated by the ^{13}C resonances of the pTS anion. These occur at 140 ppm (coalescence of C1 and C4), 128 ppm (C2, C3, C5, C6) and the methyl carbon at 20.6 ppm. This latter peak is shifted from 22 ppm in the NapTS salt (see *Figure 2* for structures and chemical shifts of polypyrrole, pTS and DDS).

The polypyrrole resonances in the as-grown film are hidden under the aromatic peaks of the anion; however, upon treatment with base, the anion is removed and the polypyrrole becomes evident. If the methyl peak is used as a marker, it can be seen that after immersion in 0.5 M base, this peak is greatly reduced in intensity relative to the aromatic peaks. This clearly shows that the counterion is being expelled from the polypyrrole, as has been suggested by others[1,3]. The remaining aromatic signals must, therefore, be predominantly due to the polypyrrole resonances. A low frequency shoulder appears after treatment with weak base and becomes more prominent at approximately 110 ppm after immersion in 3.0 M OH^-. In the latter case, all the pTS counterions have been expelled from the polypyrrole film and the conductivity is less than 10^{-3} S cm^{-1}, at least four orders of magnitude less than the original film.

In a previous paper[7] we have shown that the low frequency carbon resonance in polypyrrole films is associated with a lower degree of oxidation of the pyrrole backbone. In other words, some of the β-carbons (C2) are in an environment of higher electron density as compared with the as-grown, fully oxidized film. This can occur in two ways. If the pyrrole is deprotonated during treatment with base, this will remove the positive charge from the polymer backbone and restore electron density to the pyrrole ring. This proposal requires the base-treated polypyrrole to attain a quinoid structure (see *Figure 3a*)[1]. When the polypyrrole film is treated with 0.5 M basic solution a clear asymmetry appears on the high frequency side of the main aromatic peak at 127 ppm. When band fitting is applied to this peak, it suggests the presence of a peak at approximately 143 ppm. We have previously attributed such a peak to the presence of a quinoid structure, since quinoid carbons appear at higher chemical shifts compared with aromatic carbons. The ^{13}C n.m.r. of the 3.0 M base-treated polypyrrole, however, shows no indication of an α-carbon (C1) quinoid resonance.

The second alternative is that the hydroxide ion attacks

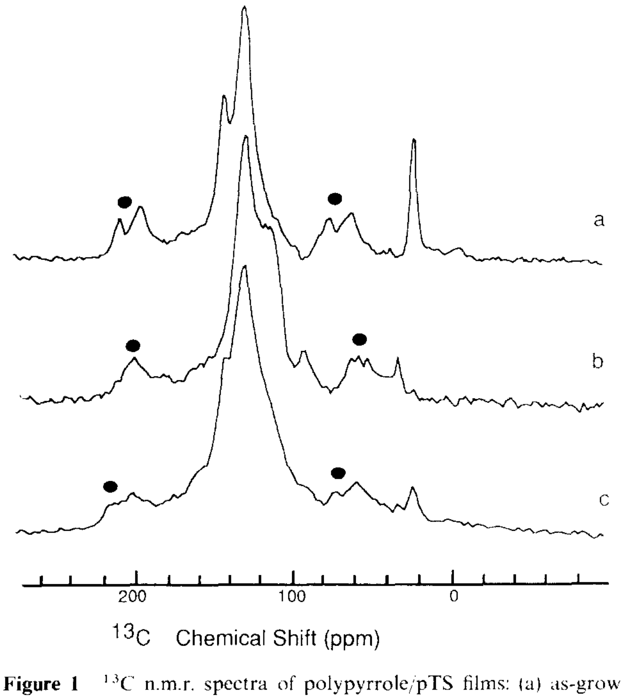

Figure 1 ^{13}C n.m.r. spectra of polypyrrole/pTS films: (a) as-grown; (b) after 3 M OH^- treatment; (c) after 0.5 M OH^- treatment at 100°C (● = spinning side bands)

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†This may result in some mechanical degradation of the polymer, creating free-radical species which can further react with oxygen. There appears to be no significant amount of oxygen-containing species according to the n.m.r. spectra, thus the free radicals that may have appeared as a result of chain scission have probably reacted by hydrogen abstraction and mutual termination

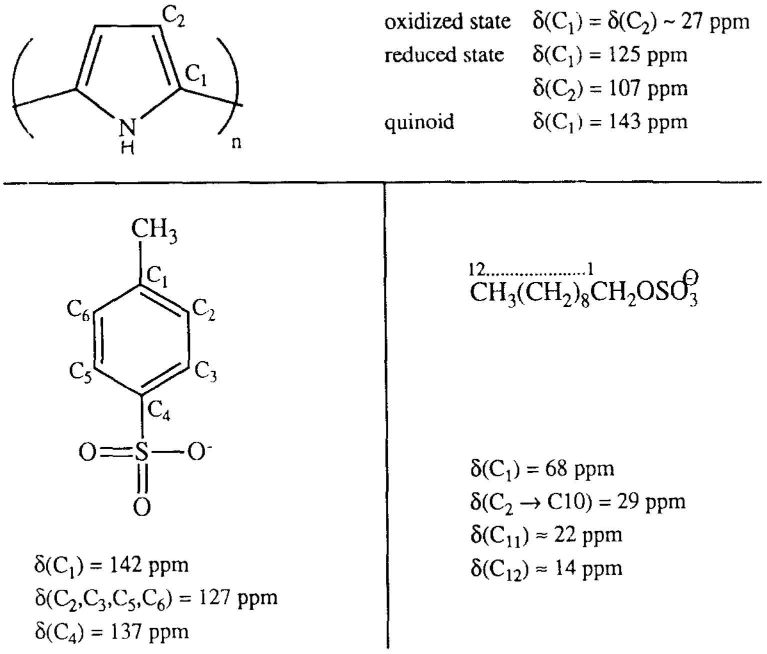
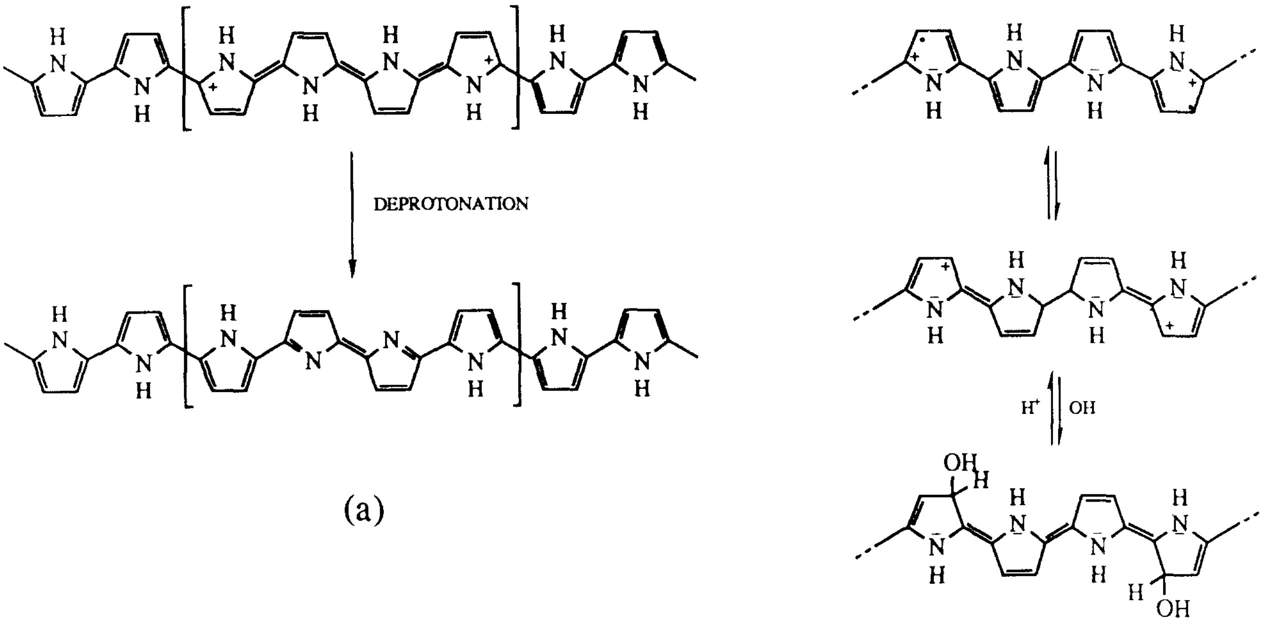
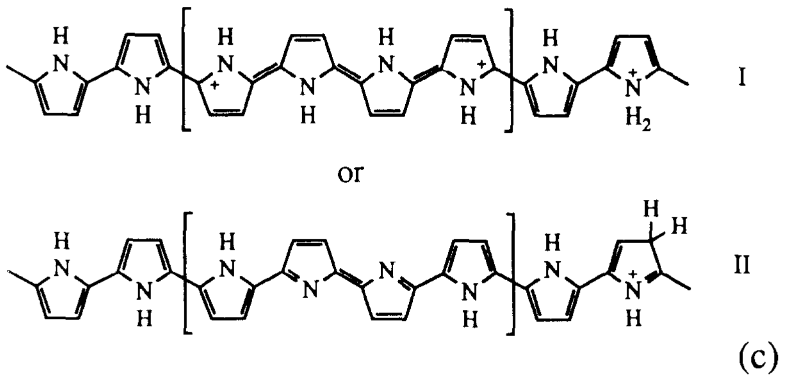


Figure 2 Structures and ^{13}C n.m.r. chemical shift assignments of pTS, DDS and pyrrole



Possible reactions upon treatment with OH$^-$



Proposed polypyrrole structure after acid treatment (protonation)

Figure 3 Proposed structures of polypyrrole films following base and acid treatments[1]

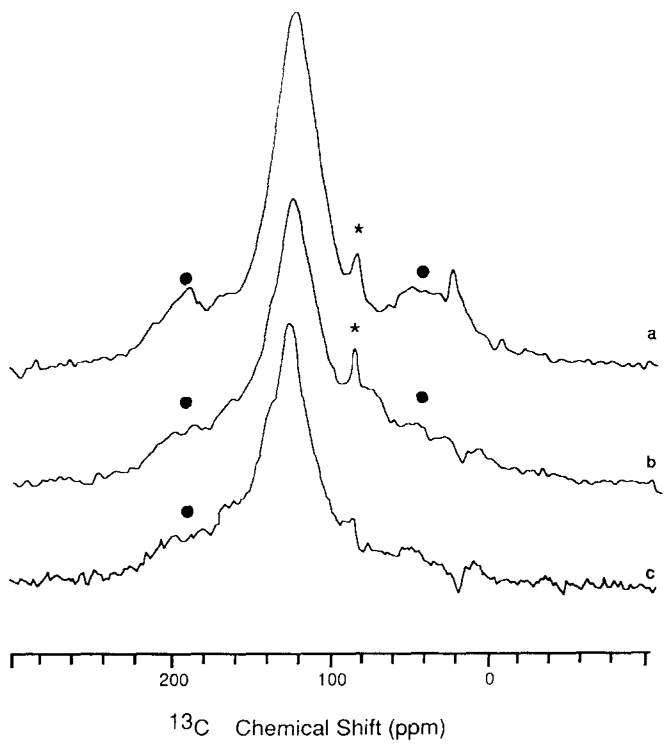


Figure 4 ^{13}C n.m.r. spectra of polypyrrole/pTS films after various treatments: (a) 3 M OH^- followed by 0.5 M H_2SO_4 at 100°C; (b) 0.5 M H_2SO_4 at 100°C; (c) film (b) following 24 h ageing at 150°C (● = spinning side bands; * = rotor peak)

the polymer backbone breaking the conjugation as shown in *Figure 3b*[2], and at the same time effectively 'neutralizing' the pyrrole moieties. In other words, the polypyrrole would no longer be positively charged. This would facilitate the loss of the counterion and would decrease the number of positive charges to be delocalized throughout the polymer. This reaction would also result in an sp_3 carbon with an OH substituent, which should have a chemical shift around 80 ppm[8]. Due to the poor signal-to-noise ratio in some of the spectra, as well as the occasional presence of the Delrin rotor peak (at 89 ppm), we are not able to confidently assign the presence of such a species. The ^{13}C n.m.r. spectra also indicate a smaller fraction of positively charged pyrrole moieties on the polypyrrole backbone, from the appearance of the shoulder at approximately 110 ppm, reminiscent of the shoulder obtained upon electrochemical reduction of the polypyrrole film[7]. This evidence supports the hypothesis that upon treatment with base, OH^- attacks the polypyrrole backbone thereby decreasing the extent of conjugation, removing the partial positive charges from the pyrrole rings and decreasing conductivity. The complete lack of signal at the high frequency side of the 127 ppm peak indicates that the quinoid structure is not favoured after treatment with strong, 3 M basic solution.

Finally, a simple ion exchange between OH^- and pTS is possible, with the decreased conductivity resulting from the stronger ion pairing interactions of OH^- (strong base) compared to sulfonates (weak base). This could not, however, explain the changes in the polypyrrole backbone structure, which are reversed upon treating a base-treated polypyrrole/pTS film with H_2SO_4 (see *Figure 4a*). After this second treatment, the conductivity is restored and the ^{13}C n.m.r. spectrum indicates the disappearance of the low frequency peak at 110 ppm and the increased intensity at the high frequency side of the aromatic peak. This signifies that the electron density on all carbons is once more decreased resulting from the delocalization of positive charges on the polypyrrole backbone.

As with the 0.5 M OH^- treated polypyrrole/pTS film, the conductivity of polypyrrole/DDS film is significantly decreased (see *Table 1*), and the majority of the DDS counterion after immersion in a 0.5 M basic solution is removed. *Figure 5* illustrates the loss of DDS compared to the as-grown films. There is no sign of significant increase in intensity at the low frequency side of the aromatic peak, which suggests that the conjugation of the backbone remains unaffected with this milder base treatment. A high frequency shoulder, consistent with a peak centred at approximately 143 ppm, is also apparent in the DDS/polypyrrole base-treated samples. It seems likely, therefore, that upon treatment with mild base, hydroxyl ions can react with the polymer backbone resulting in some formation of polypyrrole quinoid units through deprotonation. Although the major aromatic peak is still prominent, quantification of the quinoid-to-aromatic ratio is not possible since the n.m.r. cross

Table 1 Conductivities of polypyrrole films following acid and base treatments, including the effect of acid treatment on the stability of the films

Anion	$\sigma_{initial}$ (S cm^{-1})	σ_{base} (0.5 M) (S cm^{-1})	σ_{base} (3.0 M) (S cm^{-1})	σ_{acid} (3.0 M) (S cm^{-1})	Stability
pTS	30	0.3	$< 10^{-4}$	36	improved
DDS	15	-	$< 10^{-5}$	24	no change
ClO_4^-	36	–		52	improved

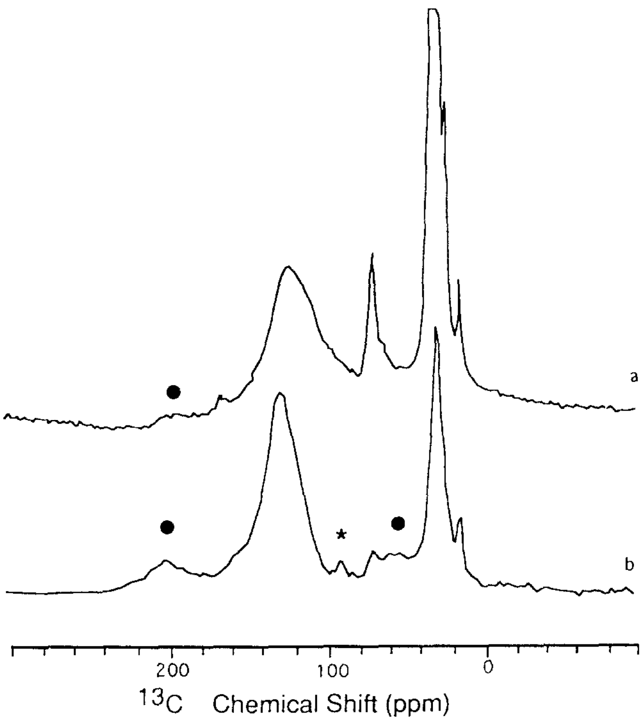


Figure 5 ^{13}C n.m.r. spectra of polypyrrole/DDS films: (a) as-grown; (b) following 0.5 M OH^- treatment at 100°C (● = spinning side bands; * = rotor peak)

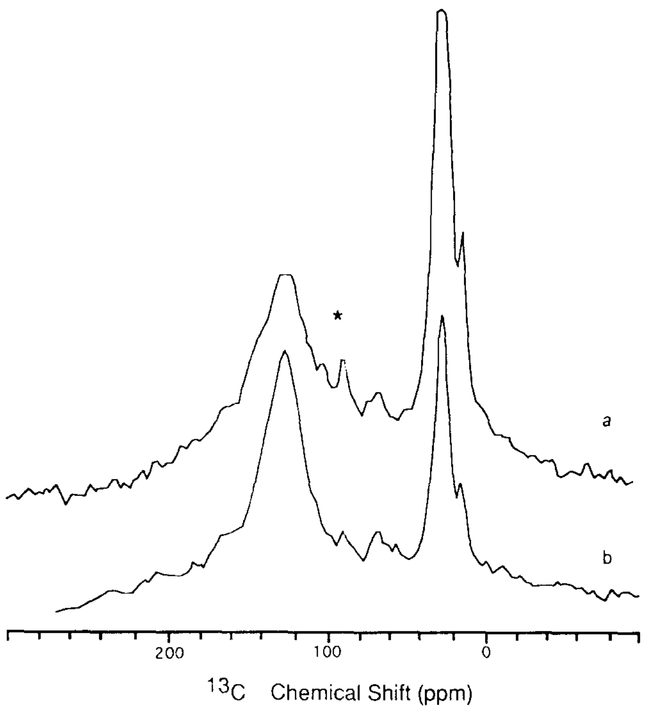


Figure 6 ^{13}C n.m.r. spectra of polypyrrole/DDS films after acid treatment: (a) 0.5 M H_2SO_4 at 100°C; (b) same film after 24 h ageing at 150°C (● = spinning side bands; * = rotor peak)

polarization times for these species may differ significantly. Treatment with 3.0 M OH^- solutions clearly increases the electron density within the pyrrole rings as seen by the appearance of the ^{13}C peaks at 110 ppm, which suggests a reduction of the positively charged backbone.

H_2SO_4 treatment of polypyrrole/pTS and polypyrrole/DDS films

Figure 4 presents polypyrrole/pTS films after acid treatment at 100°C and subsequent thermal ageing. There were no obvious differences between the ^{13}C spectra for room-temperature-treated and 100°C acid-treated polypyrrole/pTS films, with total loss of the pTS anion and probable replacement with HSO_4^- (ref. 3). The thermal stability of the acid-treated films was different. Films treated at 100°C in H_2SO_4 for 1 h showed considerable improvement in conductivity stability as compared with room temperature treatment for 3 days. This implies that the improvement in stability is not purely a result of replacement of the original anion.

The two other possibilities are (i) different extents of protonation of the polypyrrole backbone, and (ii) a change in the structure of the polymer film during treatment. Changes in the packing of polypyrrole molecules can affect the permeability[3] and diffusion of oxygen and water, which in turn may be responsible for the changing stability. It has previously been shown[3], and has also been observed in this work, that the polypyrrole samples shrink after acid or base treatment. In the case of polypyrrole/pTS, the film shrinks by about 10% after boiling whereas the dimensions only change by about 5% after treatment at room temperature.

Finally, the spectrum of polypyrrole/DDS treated with 0.5 M acid at 100°C is shown in *Figure 6*. It appears that the ^{13}C peaks assigned to the alkyl carbons of the DDS molecule have decreased only slightly from the as-grown film (compare with *Figure 5*). This would suggest a poor exchange of the original anion with the acid anions (HSO_4^- or SO_4^{2-}). However, the resonance associated with the methylene carbon attached to the sulfate group, at 67 ppm, has almost completely disappeared. Furthermore, the intensity of the methyl peak at 14.1 ppm, relative to the main methylene peak centred at 30 ppm, increases following acid treatment. This would be consistent with cleavage of the sulfate group and subsequent rearrangement to yield an alkene (carbon resonances from alkenes would be hidden by the pyrrole resonances).

Alkyl sulfates are known to be good alkylating agents[9]. The sulfate group is a particularly good leaving group, especially in the presence of acid. Thus, it is most likely that, during the acid treatment of the polypyrrole/DDS film, the anion is decomposed rather than exchanged. The resulting carbocation, upon cleavage of the sulfate group, can undergo rearrangement and form a non-polar alkene (e.g. $CH_3(CH_2)_8CH{=}CHCH_3$) or can abstract a hydrogen to yield an alkane, and is unlikely to be extracted into the aqueous phase. The remaining counterion will still be sulfate-based (either HSO_4^- or SO_4^{2-}) and the conductivity remains high. The volume of the sample does not change significantly in this case (~2%) as might be expected with the bulky alkyl group still present in the film. It should be pointed out that this effect was not always obtained upon treatment of polypyrrole/DDS with acid. Occasionally, DDS breakdown was not as obvious, with the peak at 68 ppm decreasing but not disappearing, as evidenced in *Figure 6*. In other words, acid treatment often resulted in breakdown of DDS, but on some occasions it was found that DDS anions remained intact within the polypyrrole film and subsequently decomposed upon thermal ageing.

Acid treatment of polypyrrole/ClO_4^- films

^{13}C n.m.r. of polypyrrole films containing the perchlorate anion is used as a probe of the changes in the molecular structure of the polypyrrole film following acid treatment, without the interference of counterion resonances. *Figure 7* indicates that the only difference between the spectra of treated and untreated polypyrrole is the width of the aromatic ^{13}C peak. A broader resonance is obtained after immersion in 0.5 M acid.

This broadening is also evident in the spectra of films containing the DDS counterion, although it cannot be determined in polypyrrole/pTS since the pyrrole moiety is not obvious in the untreated sample. All samples show increased conductivity after acid treatment and this could indicate an increase in positive charge per pyrrole (i.e. further reduction in electron density within the pyrrole ring, perhaps via protonation). This would result in further deshielding of the carbons and hence a shift of the ^{13}C resonances to higher frequency. However, the changes observed are purely in the width of the main peak and not in its position. This indicates either (i) the presence of new species with chemical shifts on either side of the main peak (~150 and 100 ppm), or (ii) an increased inhomogeneity of the sample resulting in a broader distribution of carbon species which are unable to effectively interchange on the n.m.r. timescale.

Distinguishing between these possibilities is difficult at present. The use of ^{15}N n.m.r. spectra of acid- and

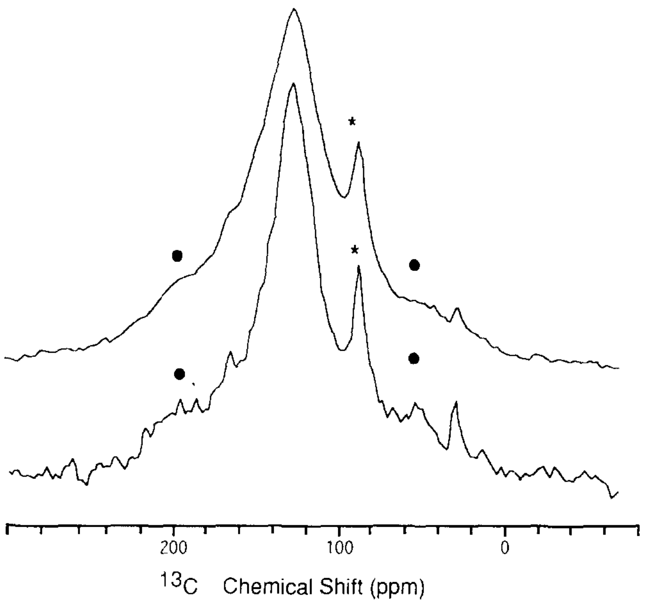


Figure 7 ^{13}C n.m.r. spectra of polypyrrole/ClO_4^- films: (a) as-grown; (b) following 0.5 M H_2SO_4 treatment at 100°C (● = spinning side bands; * = rotor peak)

base-treated polypyrrole samples may assist in ascertaining whether protonation or quinoid formation is likely following acid/base treatments. Previous ^{15}N n.m.r. has indicated that in more conductive samples, a higher proportion of quinoid structure is present[10]. This was supported by deconvolution of ^{13}C data[7] comparing fully oxidized and reduced polypyrrole samples. Deconvolution of the present acid-treated ^{13}C spectra cannot be accurately determined due to the overlapping of spinning side bands and the Delrin rotor peak at 89 ppm.

CONCLUSIONS

Base treatment of both DDS- and pTS-doped polypyrrole films results in loss of these anions and decreased conductivity. Immersion of polypyrrole/pTS in strong base results in significant changes in the structure of the polypyrrole backbone, as indicated by the ^{13}C n.m.r. spectra. The spectra resemble those found for reduced polypyrrole films[7] and suggest a decrease in positive charge per pyrrole monomer. This process can, however, be reversed by treatment with 0.5 M acid to restore the conductivity and the original structure of the polypyrrole (as evident in the ^{13}C n.m.r. spectra).

The quantitative loss of the pTS anion upon treatment with acid at both room temperature and 100°C has been confirmed via ^{13}C n.m.r. spectroscopy. In polypyrrole/DDS films, however, the counterion does not exchange and acid treatment can lead to the decomposition of the anion. The polypyrrole/DDS acid-treated films do not show a substantial improvement in thermal stability in contrast to the polypyrrole/pTS films. This treatment also results in broadening of the main polypyrrole peak which could be explained by an increasing inhomogeneity of the film or the presence of further resonances at both higher and lower frequencies relative to the main peak at 127 ppm. The high frequency resonance may result from an overall increase of the positive charge that is distributed throughout the polypyrrole backbone (i.e. increased deshielding as a result of protonation).

We are still not able to clarify whether the improved stability of some films following these treatments is a result of (a) more stable counterions, (b) change in the superstructure of the polymer (e.g. decreased porosity resulting from exchange with smaller anions), or (c) change in the molecular structure (e.g. via protonation) resulting in a more stable structure, or a combination of one or more of these factors. The third possibility can be eliminated by attempting ion exchange with the sodium salt of the sulfate and bisulfate anions instead of the acid. Distinguishing between the remaining two possibilities may be possible by careful choice of the ions to be exchanged, such that the superstructure of the polymer is not drastically disturbed. The thermal stability results from such experiments will be discussed in a future paper.

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