Structural characterization of conducting polypyrrole using ^{13}C cross-polarization/magic-angle spinning solid-state nuclear magnetic resonance spectroscopy

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^{13}C nuclear magnetic resonance (n.m.r.) has been used to study polypyrrole and *N*-substituted polypyrrole in the solid state. The extent of oxidation appears to be counterion-dependent; in particular, the quinoid structure appears favoured in the films prepared with dodecyl sulfate. Resonances associated with the quinoid unit are lost upon reduction of the polypyrrole film, which supports the idea that the quinoid structure is associated with the oxidized form of polypyrrole. *N*-substituted polypyrroles have a more distinct resonance at 110 ppm, which is linked to lower degrees of oxidation or charge delocalization in these systems. The decrease in conductivity of polypyrrole upon thermal ageing in air is associated with both the loss of counterion ('thermal dedoping') and the decomposition of the quinoid structure in the polymer backbone. There is no indication of carbonyl formation in the solid-state n.m.r. spectra obtained in the present study.

(Keywords: conducting polypyrrole; ^{13}C c.p.-m.a.s. n.m.r.; structural characterization)

INTRODUCTION

There have been many attempts at structural characterization of conducting polypyrrole using electrochemical[1], infra-red[2–5] and X-ray photoelectron spectroscopy (X.p.s.)[6] techniques in the literature. Solid-state n.m.r. spectroscopy has also been used[7–10] on this intractable, insoluble material. However, the chemical structure, the nature of the conducting units and the dependence of the structure on the counterion (or dopant) and thermal ageing treatments are still elusive. In this work, we present a ^{13}C solid-state n.m.r. study of polypyrrole using cross-polarization and magic-angle spinning (c.p.-m.a.s.).

Previous solid-state ^{13}C n.m.r. investigations by Street and coworkers of both neutral and oxidized polypyrrole were able to show that polypyrrole consisted of predominantly α–α' bonding[7]. Resonances at 123 ppm (α carbon) and 105 ppm (β carbon) downfield from tetramethylsilane (TMS) corresponded well with the n.m.r. spectrum of the 2,5-substituted pyrrole monomer. Devreux *et al.* published a more thorough ^{13}C n.m.r. investigation of conducting polymers[8], including polypyrrole at various levels of oxidation, and were able to use pulse sequences to achieve selective carbon cross-polarization and hence more accurately assign the spectra. As polypyrrole became more conductive, the spectra became broader and the signal-to-noise ratio decreased, thus making it difficult to discern any spectral structure in the oxidized state. It is clear, however, that, upon oxidation, the resonance assigned to the β carbon shifted to higher frequencies, whilst the α carbon resonance remained unchanged. This result suggested that the positive charges in polypyrrole were mainly concentrated on the β carbons.

The most recent attempts at elucidating the structure of polypyrrole films via n.m.r. techniques have used ^{15}N n.m.r.[9,10]. Limbach *et al.*[9] found a single broad ^{15}N resonance whose position was independent of sample preparation and concluded that the nitrogen in polypyrrole remains protonated in both neutral and oxidized states. Kikuchi and coworkers[10] have calculated the expected ^{15}N chemical shifts for aromatic and quinoid structures of polypyrrole using quantum-mechanical calculations. These were correlated to experimental ^{15}N solid-state n.m.r. spectra, which were deconvoluted to give quinoid and aromatic component resonances. They suggest that quinoid and aromatic moieties are present in both the oxidized and reduced polypyrrole samples. However, the intensity of the nitrogen resonance associated with the quinoid structure is decreased in the reduced form.

With improved n.m.r. instrument technology, structural problems of increasing complexity can be pursued as solid-state n.m.r. spectra with considerably superior signal-to-noise ratio, and resolution can now be obtained. This has allowed us to pursue the structure of polypyrrole

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in its conducting state and investigate its dependence on the degree of oxidation, nature of the counterion and the effects of ageing at elevated temperatures in air and in argon atmospheres.

EXPERIMENTAL

Sample preparation

Polypyrrole films were grown at a constant current of 2.8 mA cm^{-2} from solutions containing 0.1 M freshly distilled pyrrole (Aldrich) and 0.1 M electrolyte on 8 cm diameter stainless-steel electrodes. Acetonitrile (h.p.l.c. grade, BDH) solutions were used with tetramethylammonium hexafluorophosphate ($(CH_3)_4NPF_6$) and sodium tetrafluoroborate ($NaBF_4$) salts, and distilled water was used as the solvent during the growth of dodecylsulfate (DDS) and *p*-toluenesulfonate (pTS) doped films. All salts were obtained from Aldrich and used without further purification. Polypyrrole powder was chemically prepared from an aqueous solution of $FeCl_3$ (BDH) at 20°C.

Reduction of polypyrrole/PF_6^- films was performed in a 0.09 M acetonitrile solution of $(CH_3)_4NPF_6$, at a constant current of 2.8 mA cm^{-2}. Aqueous electrolyte solutions of 0.1 M NaDDS and 0.1 M NapTS were used in reducing polypyrrole/DDS and polypyrrole/pTS films respectively.

N-Methylpyrrole was polymerized at a constant current of 2.8 mA cm^{-2} on stainless-steel electrodes from an aqueous solution containing 0.1 M monomer and 0.1 M NaDDS. The copolymer, poly[pyrrole-*co*-(3-pyrrol-1-yl)propanesulfonate], was similarly prepared with the sodium (3-pyrrol-1-yl)propanesulfonate present as the electrolyte.

Polypyrrole/DDS films were aged at 150°C in both air and argon environments for 24 h. Previous conductivity measurements have shown a drastic reduction in conductivity of air-aged films, whereas films aged in an inert atmosphere remain unchanged[11]. Conventional four-probe conductivity measurements were employed to determine the conductivity of the polypyrrole samples.

Solid-state n.m.r. experiments

^{13}C solid-state n.m.r. was performed on crushed samples of polypyrrole mixed with MgO to reduce detuning of the n.m.r. probe. Magic-angle spinning (m.a.s.) spectra were acquired on both a Bruker MSL 400 operating at 100.61 MHz and a Bruker AM300 operating at 75.45 MHz. On both instruments Bruker 7 mm double-bearing m.a.s. probes were employed with spinning rates of about 5 kHz on the AM300, while 6.3 kHz was possible on the MSL. This was useful in moving the sidebands further away from the main polypyrrole peak. Cross-polarization (c.p.) from ^1H was used to enhance the ^{13}C signal. The optimum c.p. times (800 μs to 1 ms) were determined by the time for which maximum ^{13}C signal was obtained for selected samples, and this was consistent with the c.p. times used by Devreux *et al.*[8]. At the higher frequency, contact and decoupling were performed at a ^1H power that produced a 3.5 μs 90° pulse, while at the lower frequency 9 μs was employed. Despite this difference in the decoupling power, the only difference between spectra that were obtained for a given sample on the different spectrometers was the improved signal-to-noise ratio and the further separation of the spinning sidebands on the MSL400. ^{13}C T_1 relaxation times were estimated to be significantly less than 1 s. Since proton relaxation times are usually significantly less than ^{13}C T_1 values, this allowed repetition times of as little as 1 s to be used in the cross-polarization experiment, and hence the accumulation of a greater number of scans in a fixed time. The number of scans required to attain adequate signal-to-noise ratio varied between 5000 and 50 000 and depended on the nature of the sample. For the most conductive samples, the signal obtained was poor and significant dilution was necessary even to detect a signal. All samples were diluted with MgO until they gave the same probe response (i.e. tuning) and this could account for the varying signal-to-noise ratio.

The polypyrrole carbon peaks in several of the spectra were simulated using the Bruker LINESIM program to allow deconvolution of the data. This gives a qualitative indication of the relative abundances of the different carbon species.

RESULTS AND DISCUSSION

High-resolution solution-state ^{13}C n.m.r. of the pyrrole monomer shows resonances at 119 ppm (α carbon) and 108 ppm (β carbon)[12] whilst in 2,5-dimethylpyrrole the α carbons appear at 126 ppm and the β at 106 ppm[8]. On this basis, Street and coworkers and later Devreux *et al.* suggested that polypyrrole essentially consisted of α–α′ linkages with the main carbon resonance at approximately 125 ppm. In the fully reduced polypyrrole, Devreux assigned the β carbon at approximately 105 ppm. In all the spectra presented in this study, there is always some oxidation of the pyrrole moieties, since the samples are handled in air. Hence the main peak at 126–128 ppm generally has a low-frequency shoulder, attributed to partially oxidized β carbons, rather than a distinct β carbon resonance seen in the pristine samples.

The discussion that follows in this paper is based on the following premises. When polypyrrole is prepared, it is always obtained in its oxidized form, i.e. electrons have been removed from the polymer backbone to leave positive charges, which are delocalized along the backbone and can result in metal-like conductivity. Anions insert into the polymer during polymerization to counterbalance these charges. The atoms in the pyrrole moieties upon which this positive charge is mostly localized will be the most deshielded when placed in a magnetic field, and this will be detected in n.m.r. experiments. The deshielding affect will result in high-frequency shifts of the ^{13}C resonances compared with pristine (fully neutral) polypyrrole.

Oxidation of aromatics is often associated with a rearrangement of molecular structure to yield quinoid structures. Such structures (be they positively charged or neutral) also result in deshielding of carbons relative to the aromatic structure; for example, in the oxidation of hydroquinone to quinone[12] and in polyaniline[13] the carbons in the quinoid structure are all shifted to higher chemical shifts relative to the aromatic carbons. Oxidation of polypyrrole does not necessarily result in a quinoid structure, although the positive charges present would stabilize such a structure. Previous ^{13}C polypyrrole spectra published by Devreux *et al.*[8] show no indication of quinoid structures in the conducting (and hence oxidized) state. In the following discussion, we postulate that a high-frequency ^{13}C peak at 143 ppm, which appears in some of our samples, is associated with the quinoid form of polypyrrole.

Counterion effect

Figure 1 indicates the effect of different counterions (often called dopants) on the polypyrrole backbone structure. Two differences are clear. First, in the polypyrrole powder sample prepared chemically using $FeCl_3$, a distinct second peak at lower chemical shifts (110 ppm) is observed. From the above discussion this would correspond to β carbons of the unoxidized (or partially oxidized) pyrrole moieties. This low-frequency peak can be seen as a shoulder in the electrochemically prepared films using BF_4^-, PF_6^- and DDS counterions, and its presence is clear in the BF_4^- film from high-frequency spinning sidebands, which show a double-peak structure. Films containing DDS anions appear to have a further shoulder at higher frequencies (143 ppm). This resonance is not obvious in the polypyrrole/Cl^- spectrum and is only present as minor shoulders in the two other samples containing inorganic counterions.

The position of this high-frequency resonance at 143 ppm is consistent with the presence of quinoid carbons since these carbons are more deshielded than their aromatic counterparts as discussed above. *Figure 2* presents a schematic diagram of two plausible structures of polypyrrole. The presence of quinoid and aromatic moieties in polyaniline has been clearly demonstrated previously by ^{13}C solid-state n.m.r.[13,14]. Recent quantum-chemical calculations[10] of the structure of polypyrrole suggest that the quinoid form has a lower band-gap energy and hence would result in a more conductive sample if present in the polymer. Polypyrrole films prepared with large organic counterions such as DDS and pTS certainly show higher conductivities compared to those prepared with inorganic counterions[15], and it is plausible that some counterions favour the quinoid structure. Polarons and bipolarons, the two defects apparently responsible for conduction in polypyrrole, are thought to generate quinoid structures[2].

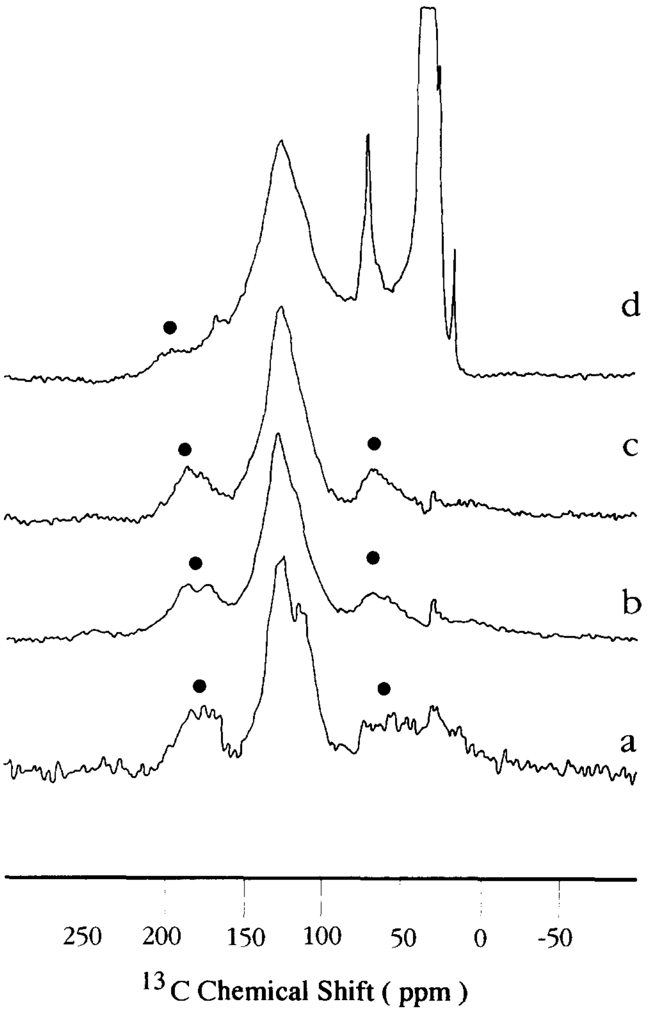


Figure 1 ^{13}C n.m.r. spectra of polypyrrole, acquired at 100.61 MHz: (a) chemically prepared polypyrrole powder with $FeCl_3$ oxidant ($\sigma = 0.1$ S cm^{-1}); electrochemically grown polypyrrole films with (b) BF_4^-, (c) PF_6^- ($\sigma = 4.1$ S cm^{-1}) and (d) dodecylsulfate (DDS) ($\sigma = 4.3$ S cm^{-1}) anions. (●) Spinning sidebands

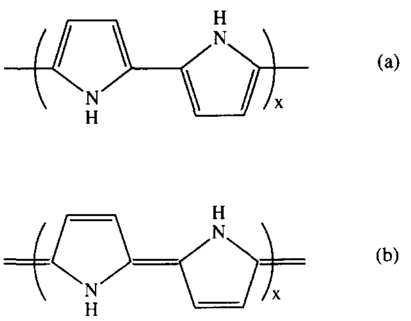


Figure 2 (a) Aromatic and (b) quinoid structures for polypyrrole

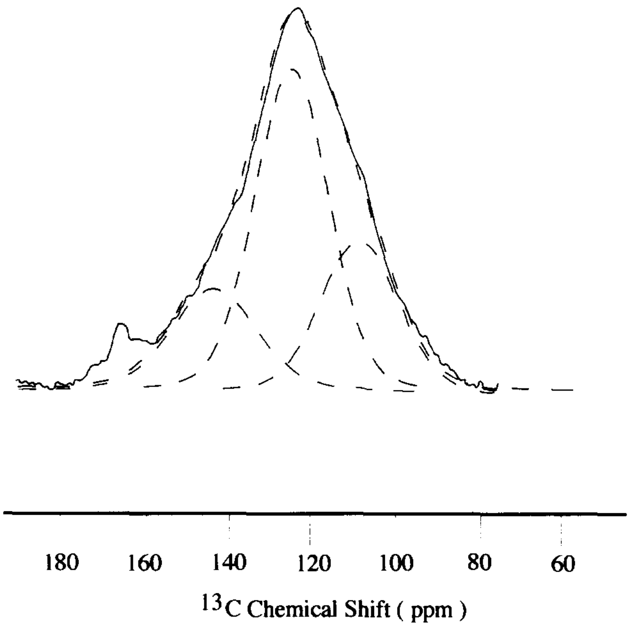


Figure 3 Decomposed spectrum of the polypyrrole carbons in 'as-grown' polypyrrole/DDS film. Broken curves represent the simulated peaks

Figure 3 is an example of the ^{13}C n.m.r. spectrum of an 'as-grown', oxidized DDS/polypyrrole film showing only the polypyrrole peak, which has been deconvolved using the Bruker LINESIM program. The polypyrrole resonances can be reproduced well by fitting three Gaussian peaks with chemical shifts at 128, 113 and 143 ppm with an accuracy of ± 1 ppm. The relative integrated peak intensity does not necessarily represent the actual carbon distribution since the c.p. dynamics may be substantially different for each site. However, the comparison of the relative intensities from one sample to another should still be appropriate.

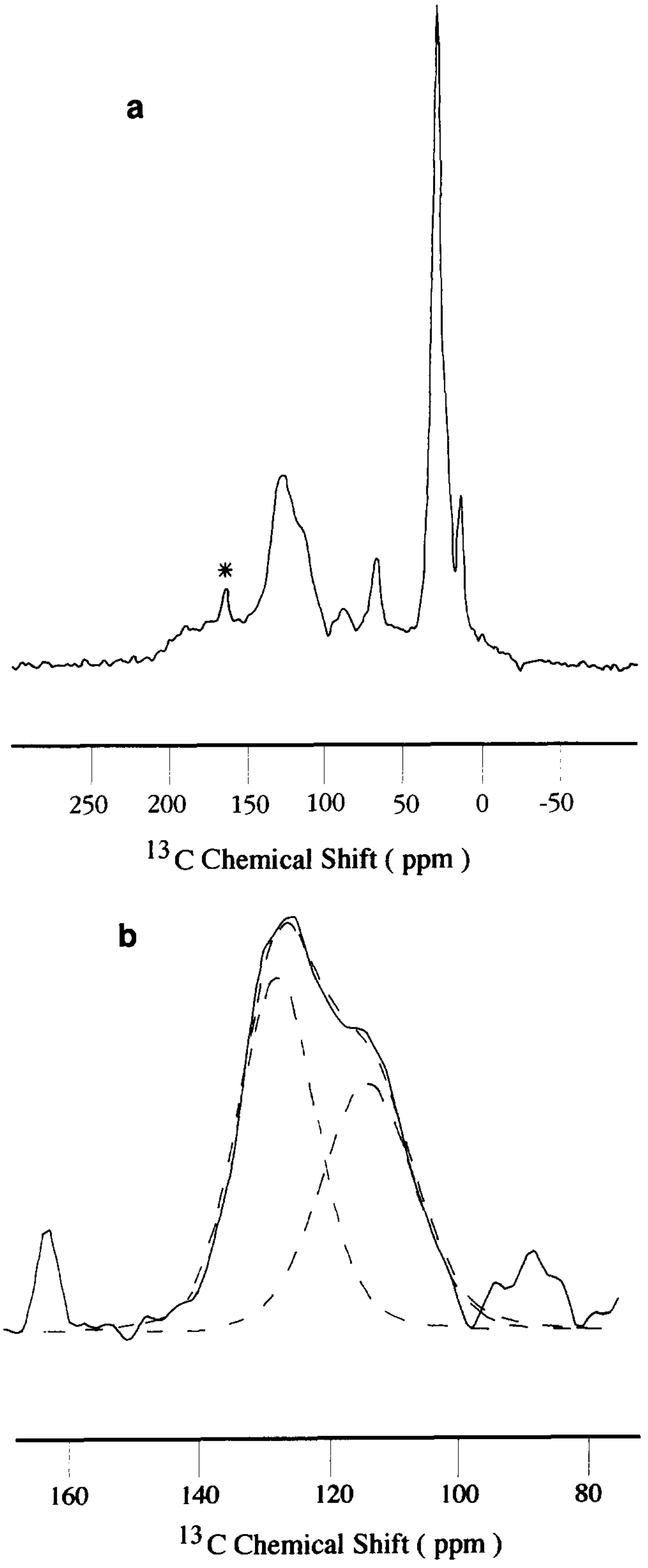
Examination of the ^{13}C spectra of polypyrrole prepared with PF_6^-, BF_4^- and Cl^- anions (*Figure 1*) indicates that the intensity on the high-frequency side of the main aromatic peak is less than that of the DDS sample. The results here suggest that the polypyrrole structure is counterion-dependent. Unfortunately, it is difficult to obtain accurate elemental analysis of polypyrrole samples, and so it was not possible to check whether an increased anion concentration (and hence an increased level of oxidation) was present in the DDS/polypyrrole films compared with the other samples.

If this high-frequency peak was indeed associated with the conducting species, then it could be expected that reduction of polypyrrole will remove this species. This is addressed in the following section.

Effect of reduction (or dedoping) of polypyrrole films

The ^{13}C n.m.r. spectra of the reduced polypyrrole/DDS and polypyrrole/PF_6^- films is shown in *Figures 4* and *5* respectively. *Figure 4* indicates a distinct lack of intensity at 143 ppm, suggesting that, upon reduction of the polypyrrole/DDS film, the quinoid structure is indeed lost. This would be consistent with the interpretation that the quinoid structure is associated with the oxidized polypyrrole.

The line shape analysis of this polypyrrole peak results in only two lines at 128 and 114 ppm. The low-frequency resonance is more deshielded than the β carbon resonance previously reported for pristine polypyrrole. However, since all of the sample preparations are conducted in air, there will be some oxidation of polypyrrole resulting in the formation of conducting species. This oxidation is much less complete than it is in the electrochemical oxidation of the DDS film. This is consistent with the lower conductivity of the reduced sample relative to the fully oxidized sample (4 vs. 0.01 S cm^{-1}).



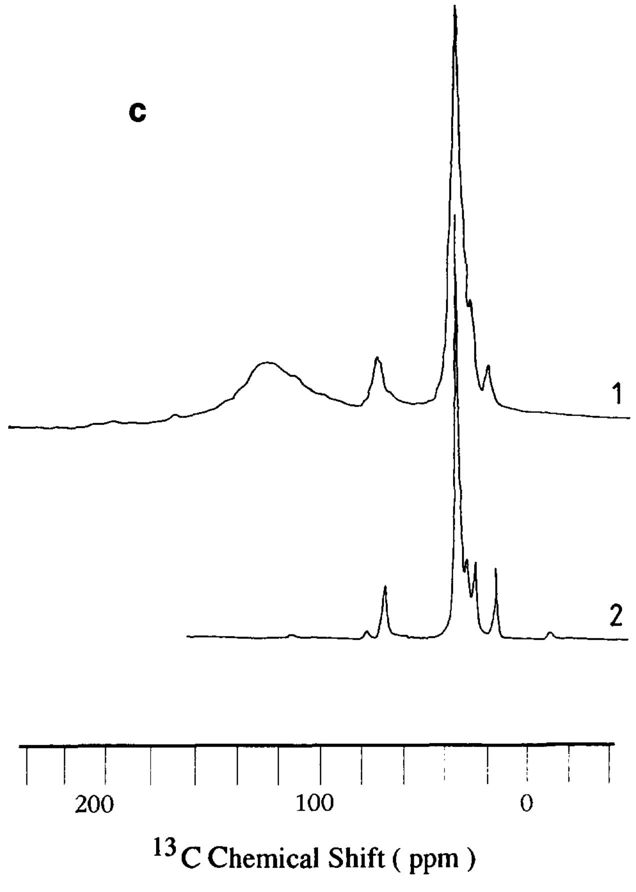


Figure 4 (a) ^{13}C n.m.r. spectrum of a reduced (dedoped) polypyrrole/DDS film, acquired at 75.5 MHz. The film was grown to a charge density of 10 C cm^{-2} and reduced to an equivalent charge density ($\sigma = 0.01$ S cm^{-1}). (*) MgO impurity. (b) Decomposed spectrum of the polypyrrole carbons in the reduced polypyrrole/DDS film. Broken curves represent the simulated peaks. (c) Comparison between the ^{13}C n.m.r. spectra of 'as-grown' polypyrrole/DDS film (1) and NaDDS salt (2) at 100.61 MHz

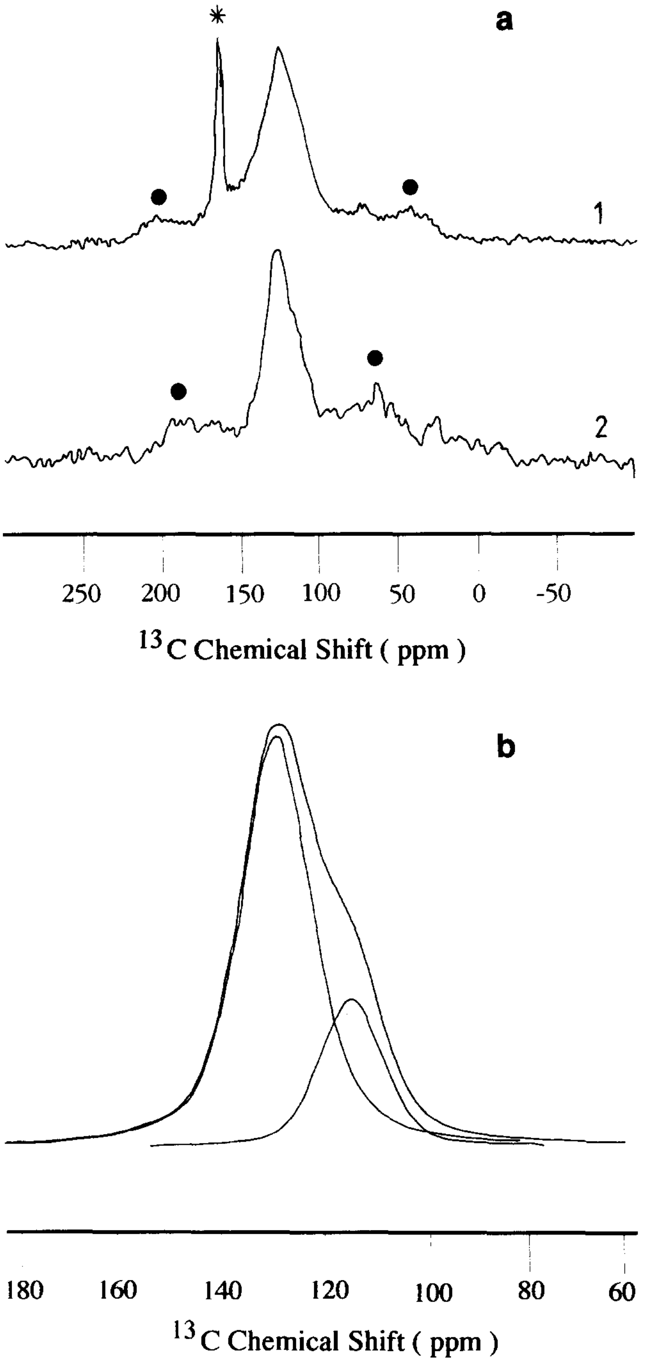


Figure 5 (a) Comparison between polypyrrole/PF$_6^-$ films reduced by passing charge densities of (1) 2.2 C cm^{-2} (σ=0.4 S cm^{-1}) and (2) 20 C cm^{-2} (σ=0.05 S cm^{-1}) acquired at 75.5 MHz. (*) MgO impurity; (●) spinning sidebands. (b) Decomposed spectrum of polypyrrole peak in polypyrrole/PF$_6^-$ film reduced by a charge density of 20 C cm^{-2}

Even low levels of oxidation clearly deshield the β carbon as evidenced from the 8 ppm shift from the pristine polypyrrole[8] (*Figure 4*). The lack of any intensity in the region of 106 ppm suggests that *all* β carbons are deshielded to some extent. This could be explained by delocalization of charges along the backbone. In the case of only partial oxidation of the polymer, there will be fewer electrons removed from the backbone and hence a smaller degree of average deshielding of any given β carbon nucleus. In the same way, increased oxidation of the polypyrrole backbone (resulting in a more positively charged polymer) will result in a greater deshielding of the β carbons and hence a higher resonance frequency for the β carbons. The α carbon resonance is only shifted by about 3 ppm to higher frequency in this case compared to the pristine resonances reported previously[8], which suggests that most of the changes in electron density upon oxidation are concentrated on the β carbons and hence the charge is concentrated on these atoms.

Although not as distinct as the DDS case, the polypyrrole/PF$_6^-$ films also show a slight line narrowing and loss of intensity from the high-frequency side of the major aromatic peak upon reduction. Again, this would suggest that any quinoid units that are present in the oxidized form of the polypyrrole/PF$_6^-$ samples are converted during the reduction. The greater the extent of reduction, the greater is the loss of high-frequency intensity. This can be seen in *Figure 5*, where the sample, after being subjected to 20 C cm^{-2} of reducing charge, has a narrower ^{13}C resonance than that reduced by 2.2 C cm^{-2}. The deconvoluted spectrum of the more reduced sample indicates peaks at 128 and 114 ppm, as in the case of the reduced DDS sample.

Upon reduction, the cations and dications believed to be responsible for conduction in the polymer are neutralized, and hence it would be expected that the anions that enter the film during film growth and oxidation in order to counterbalance the positively charged polypyrrole will leave the film. Previous ^{31}P and ^{19}F n.m.r. of polypyrrole/PF$_6^-$ (ref. 16) has shown that the PF$_6^-$ is removed from the film during reduction. The ^{13}C spectrum of the DDS film in *Figure 4* indicates that a large fraction of the organic anion remains, even after reduction by 20 C cm^{-2} (films are grown to a charge of 10 C cm^{-2}). Previous chemical analyses[11] suggest that up to 50% of the DDS counterion leaves the film. Comparison of the relative intensities of the 'as-grown' DDS/polypyrrole film (*Figure 1*) with *Figure 4* indicates that approximately 50% of the carbon directly attached to the sulfate group (68.3 ppm) is lost. However, the intensity of the alkyl groups centred at 30 ppm and the methyl carbon at 14 ppm is not decreased to a great extent. This is in agreement with infra-red experiments performed on this system[17]. The changing relative intensities of the DDS carbon resonances can be attributed to some decomposition of the anion, resulting in cleavage of the sulfate group to form a carbocation[18], which may rearrange to yield a dodecene (e.g. $CH_3(CH_2)_8CH{=}CHCH_3$). This is consistent with the increased intensity of the methyl resonance relative to the polypyrrole peak.

The chemical shift of the counterion in both DDS and PF$_6^-$ polypyrrole films seems to be unaffected by the conducting polymer. This can be seen from a comparison of ^{13}C spectra for the pure salt of NaDDS with polypyrrole/DDS (*Figure 4c*) and the ^{31}P spectra of $N(CH_3)_4PF_6$ with polypyrrole/PF$_6^-$ (ref. 16). This would support the hypothesis that the counterion is simply there to counterbalance the positive charges on the polypyrrole backbone rather than interacting as a dopant (which accepts or donates electrons in a semiconductor). In the latter case one would expect the electronic environment of the anion to be different in the polymer compared with the pure salts.

^{13}C spectra of polypyrrole/pTS in the as-grown (oxidized) and reduced states have also been obtained and are shown in *Figure 6*. Unfortunately, since the aromatic peaks of the anion directly overlap with the polypyrrole backbone, it is not possible to discern any structural information regarding the polymer backbone

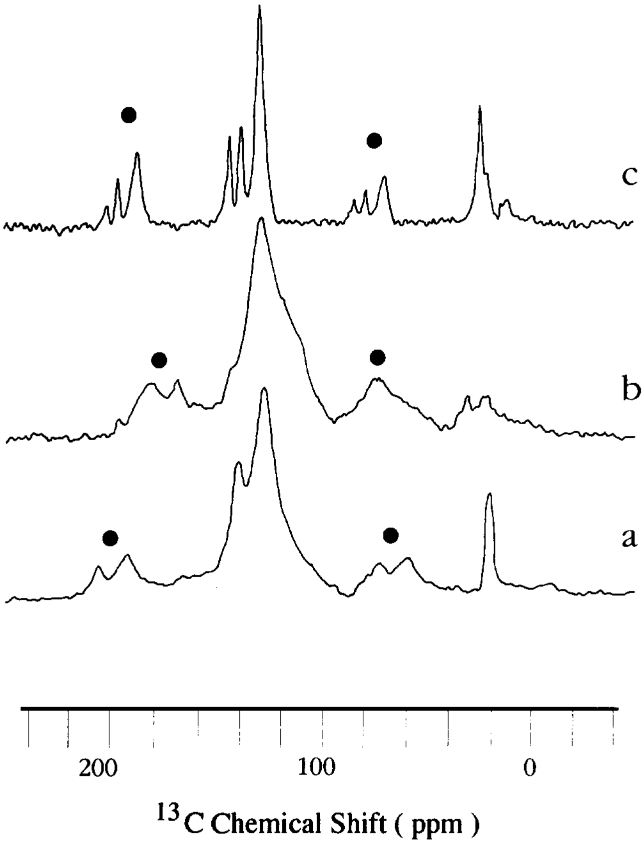


Figure 6 Comparison between ^{13}C n.m.r. spectra of (a) 'as-grown' polypyrrole/pTS film, (b) reduced polypyrrole/pTS film and (c) NapTS salt acquired at 100.61 MHz. (●) Spinning sidebands

from these experiments. The ^{13}C spectrum of pure NapTS is also shown. It can be seen that, in this sample also, there is no obvious change in the environment of the counterion with the ^{13}C resonance of the carbon directly bonded to the sulfonate group at 20 ppm. There is a slight broadening of the lines observed in the polypyrrole/pTS spectrum compared with the sodium salt. In this system it appears that dedoping (or reducing) the polymer results in the loss of *most* of the anion, in contrast to the DDS case. Thus the remaining aromatic ^{13}C chemical shift, centred at 127 ppm, will belong to the polypyrrole backbone. As with all reduced samples, a low-frequency shoulder, most likely indicative of partially oxidized β carbons, appears on this peak (114 ppm). (An additional peak (30 ppm) appears in the aliphatic carbon region, which is yet to be explained.)

N-substituted polypyrroles

N-substituted polypyrroles are known to have significantly lower conductivities than their unsubstituted or 3-substituted counterparts[19]. Street *et al.*[20] and more recently Martina *et al.*[21] have shown, using X-ray crystallography of oligomers, that the adjacent pyrrole rings in N-substituted polypyrroles are twisted by up to 70°. This would decrease the ability for extended conjugation in these systems. Similar studies of unsubstituted polypyrrole oligomers indicated that, in this case, the rings are almost planar[21]. This would enhance the intramolecular charge transfer. Previous studies have suggested that intramolecular charge transfer is more important in the conduction mechanism than chain hopping or intermolecular conduction[22].

The structure of electrochemically grown poly(*N*-methylpyrrole) with DDS counterions and a 'self-doped' pyrrole, 3-(pyrrol-1-yl)propanesulfonate copolymer, were investigated with ^{13}C solid-state n.m.r., as illustrated in *Figure 7*. The incorporation of the counterion in poly(*N*-methylpyrrole) suggests that this film is indeed oxidized. However, there is clear evidence of unoxidized (or partially oxidized) β carbons at 108 ppm. The peak at 126 ppm confirms that α–α' polymerization is still the major route to this polymer. *Figure 7b* indicates that the copolymer has similar structural units, with a distinct shoulder at 110 ppm prominent in the spectrum, even though only 20% of this sample consists of *N*-substituted polypyrrole[23]. Both films were very brittle, which suggests either short chains or a significant degree of crosslinking[24]. End-groups and crosslinking defects may result in a β carbon resonance around 110 ppm. A further explanation to account for the prominence of the 110 ppm ^{13}C resonance may be that, in N-substituted polypyrroles, oxidation of the β carbon is less favourable. This could result from both steric (twisting of the pyrrole rings) and electronic (change in oxidation potential of the pyrrole moiety upon *N*-substitution[1]) influences, and would yield an only partially oxidized polypyrrole backbone (i.e. less than 0.22 charges per repeat unit[8]).

It is clear that the structure of 'fully oxidized', N-substituted polypyrroles with sulfate counterions is different to polypyrrole/DDS, and that this difference is associated with the 10^3 decrease in conductivity of N-substituted polypyrroles. However, the precise nature of the structural differences still remains unclear.

Effect of thermal ageing

The conductivity stability of polypyrrole has been addressed by several workers[11,25–28] and has been found

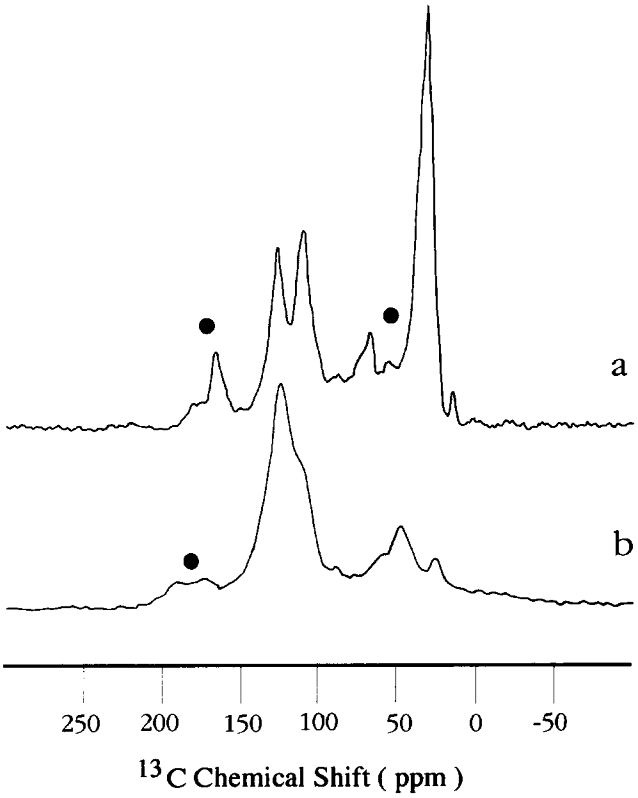


Figure 7 ^{13}C n.m.r. spectra of (a) poly(*N*-methylpyrrole) and (b) poly[pyrrole-*co*-3-(pyrrol-1-yl)propanesulfonate] ($\sigma < 0.001$ S cm^{-1} in both cases) acquired at 75.5 MHz. (●) Spinning sidebands

to be dependent at least on the nature of the counterion. Films containing inorganic dopants such as perchlorate have been observed to be less stable than those containing organic dopants[25]. At 150°C, the aromatic dopants such as pTS have been shown to have a low rate of conductivity decay and the conductivity is stable for several weeks after an initial decrease. On the other hand, the loss of conductivity of films doped with DDS is several orders of magnitude over 24 h[11]. Thermal and evolved-gas analysis have shown that this counterion becomes unstable at high temperatures and is likely to be lost during the thermal ageing at 150°C. Under inert conditions, the conductivity loss in polypyrrole/DDS films at 150°C is minimal.

^{13}C n.m.r. spectra of polypyrrole/DDS as grown, aged in air and aged under argon at 150°C are presented in *Figure 8*. Upon ageing in air, significant line narrowing of the polypyrrole peak is observed with a loss of intensity from both the high- and low-frequency sides of the main aromatic peak. Computer simulation of these spectra shows the partial loss of intensity in the 143 ppm peak relative to the 128 ppm resonance. This suggests that the quinoid structure is no longer stable at elevated temperatures. The low-field shoulder, assigned to β carbons that are not fully oxidized, is also removed at 150°C in air. This indicates that the combination of heat and oxygen will oxidize the remainder of the unoxidized β carbons, although this process does not lead to conductive species. It has been suggested[25] that ageing in air decreases the conductivity as a result of the formation of carbonyl groups, which destroy the conjugation of the polymer. The excess oxygen always found from elemental analysis of polypyrroles has also been postulated to exist in the form of carbonyls[22]. These carbons would be expected to show a resonance at chemical shifts greater than 170 ppm[29]. However, no such peak appears in the spectra obtained here. (The peaks found at 163–165 ppm are from magnesium carbonate that was occasionally present as an impurity in the MgO used to dilute the conducting polymer.) Thus we can conclude that if any carbonyl groups are incorporated into the polypyrrole structure, these are present only at a low mole fraction, since they are not detectable by solid-state n.m.r. here nor from previous i.r. analyses[17]. This observation is supported by the recent *FT*i.r. spectra of Lei *et al.*, which did not show a carbonyl adsorption in the oxidized polypyrrole[5]. These authors observed an OH band and thus suggested that the oxidized polymers exist in the enol form rather than tautomerizing to the ketone. On the other hand, Moss and Burford[25] detected carbonyl species at the surface of polypyrrole films by X.p.s. The existence of these species on the aged surface may reflect chemical and morphological differences between the surface and the bulk of the polymer.

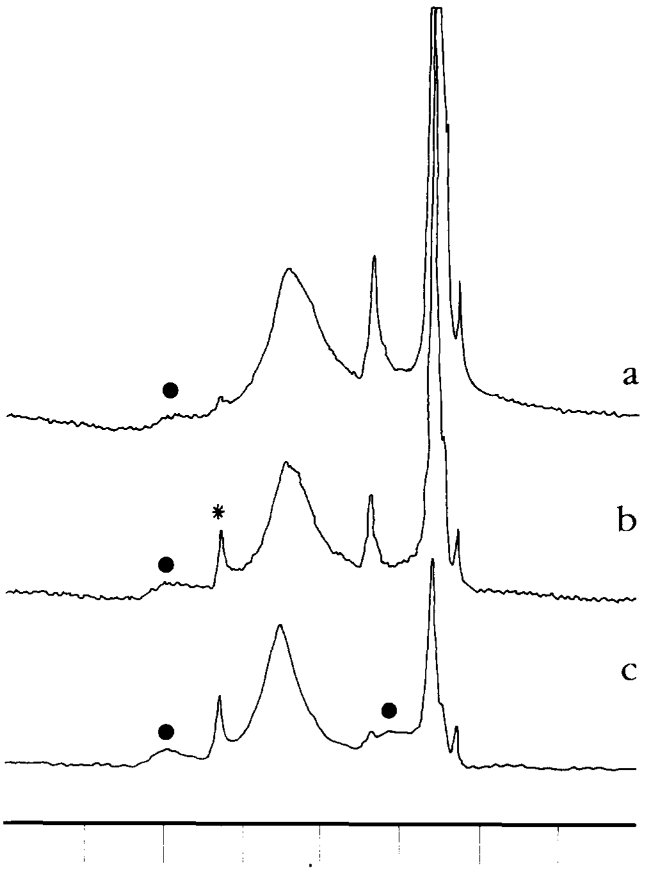


Figure 8 Comparison of ^{13}C n.m.r. spectra, at 100.61 MHz, of (a) 'as-grown' polypyrrole/DDS, (b) polypyrrole/DDS aged for 24 h at 150°C in an argon atmosphere and (c) polypyrrole/DDS aged for 24 h at 150°C in air. (*) MgO impurity; (●) spinning sidebands

The DDS counterion seems to be drastically affected by exposure to air at 150°C. More than 90% of the dopant seems to have left the polypyrrole sample after 24 h (according to the relative intensities of the polymer and anion carbon resonances). This could certainly be one factor contributing to the conductivity loss, since it is known that the nature of the counterion affects the conductivity of polypyrrole. Under such circumstances the remaining anionic species are likely to be oxygen-based (OH^-, O_2^-) or decomposition products of the DDS ion (SO_4^{2-}, HSO_4^-). A further interesting observation is that the relative intensities of the methyl carbon and the carbon immediately adjacent to the sulfate group change upon ageing in air, with an increased proportion of methyl groups. This supports the hypothesis that one decomposition route is the elimination of the sulfate group, which yields reactive carbocations that can either rearrange to form a neutral alkene or attack the polymer backbone. Similar observation of the elimination of the aliphatic material from polypyrrole/DDS films was implied in the results of elemental analysis and thermogravimetry[11].

Thermal ageing of polypyrrole/DDS films under argon still produces a very brittle material, suggesting that some structural changes, such as crosslinking, are likely. The ^{13}C n.m.r. spectrum of this sample, however, does not show any dramatic change in the polypyrrole backbone from the unaged sample. The unoxidized β carbons remain; however, there does seem to be a slight loss of intensity from the high-frequency side of the main peak even under an inert atmosphere. Interestingly, the DDS ^{13}C n.m.r. peaks also seem to be less affected by the heat treatment, suggesting that the breakdown and loss (often termed thermal dedoping) of the DDS anion from polypyrrole at 150°C is dramatically accelerated in the presence of oxygen. The relatively small (compared to air-aged samples) change in concentration of the quinoid structure and decrease in the rate of breakdown of the DDS anion lead to a stable conductivity for polypyrrole/DDS in a nitrogen atmosphere for several days[11].

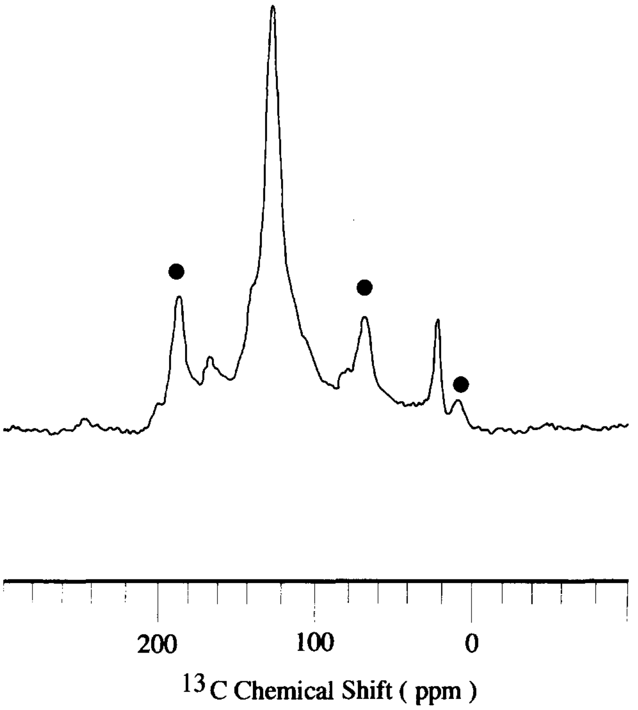


Figure 9 ^{13}C n.m.r. spectrum of polypyrrole/pTS aged for 3 months at 150°C in air, at 100.61 MHz. (●) Spinning sidebands

According to Kikuchi *et al.*[10], an enhancement of conductivity should be observed if the polypyrrole sample contains a greater proportion of quinoid subunits. Thus the apparent decrease of quinoid units in the polypyrrole/DDS films upon thermal ageing in air is one contribution to the decreasing conductivity. A second contributing factor is the loss of DDS and probable replacement with oxoanion species. It is possible that the degradation of the conducting units in the polypyrrole backbone is associated with the decomposition of the counterion, since, in the case of polypyrrole/pTS films, solid-state ^{13}C n.m.r. indicates that, after 48 h at 150°C in air, there is no detectable change in the spectrum compared to an unaged sample. In other words, the pTS anion is more stable in the film relative to the DDS anion, and this correlates with an increased stability in the conductivity of polypyrrole/pTS films aged at 150°C. Following 3 months at 150°C in air, the polypyrrole/pTS ^{13}C n.m.r. spectrum (*Figure 9*) indicates thermal loss of the anion, and this is accompanied by a decrease in conductivity. Unfortunately it is not possible to determine whether there are changes in the polypyrrole backbone itself upon ageing polypyrrole/pTS films since the polymer resonances overlap with the aromatic pTS peaks.

CONCLUSIONS

^{13}C c.p.-m.a.s. solid-state n.m.r. has been shown to be a powerful tool to investigate the structure of polypyrrole in its oxidized state. The nature of the counterion appears to affect the extent of oxidation and the proportion of quinoid units in the polypyrrole backbone, as deduced by spectral simulation. Quinoid structures, often associated with bipolarons, appear to be more favourable in systems containing organic counterions such as DDS. Upon reduction of the polypyrrole film, the resonance associated with this structure is lost, supporting the idea that the quinoid structure is associated with the conducting form of polypyrrole.

The alternative explanation that must be considered for the presence of the high-field ^{13}C resonance in the oxidized films is the possibility that the positive charges are delocalized across both α and β carbons. This would decrease the electron density about these carbons and result in a shift to higher frequencies of both carbon resonances. However, the relative intensities of the peaks (see *Figure 3*) compared with the fully reduced, pristine polypyrrole spectrum[8] do not support this hypothesis. The data presented in this work are consistent with the presence of quinoid-like structure in the more conductive films.

The poor conductivities associated with *N*-substituted polypyrroles seem to be reflected in the different ^{13}C n.m.r. spectra compared with polypyrrole. On average, the β carbons in these systems appear to be less readily oxidized, as indicated by the significant peak around 110 ppm. It is not yet clear why this should occur.

Preliminary experiments using solid-state n.m.r. to investigate changes in the structure of polypyrrole upon thermal ageing suggest that, in the case where the counterion is unstable at high temperatures, deterioration of the conductivity is greater. This is accompanied by a loss of the quinoid units in polypyrrole/DDS films.

Note: Paramagnetic sites may have an important influence on the appearance of the spectra since those carbons closets to a paramagnetic centre are likely to relax so quickly that they will not be detected in our experiments. If the majority of charge carriers in a conductive polymer sample were radical cations (polarons), then obtaining a signal from such a sample would be extremely difficult owing to the rapid relaxation expected. Some workers suggest that the charge carriers are dications (bipolarons), which would reduce the number of paramagnetic species. Even in cases where radical cations are present, these have been shown[7] to be highly mobile, so one would expect them to influence the whole sample, and not just specific sites.

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