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Solid-state NMR study of ^{15}N labelled polyaniline upon reaction with DPPH

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Abstract

The quantitative investigation of the radical scavenging properties of polyaniline (PANI) upon reaction with excess of the stable DPPH radical (a 4:1 ratio of DPPH to aniline units in the polymer) was carried out using ^{15}N and ^{13}C solid state NMR spectroscopy. During the process the polyaniline was oxidised so that the imine content increased from 45 to 65%. The extent of oxidation measured by NMR was confirmed by N1s XPS analysis. However, within a 30 min reaction time, about 85% of the DPPH radicals were scavenged as monitored by the decay in its EPR signal. This is about 20 times greater than the fraction of DPPH required to oxidize PANI from an imine content of 45–65%. An identification of further redox processes is required to explain the high degree of radical scavenging. At the same time, there was no evidence of significant chemical binding or trapping of DPPH in the PANI structure.

Keywords: Polyaniline; DPPH; Solid-state NMR

1. Introduction

In the past 20 years polyaniline has been the subject of intense research activity because of its high conductivity and unique redox chemistry. There have been many reports on the preparation, characterization and applications of the various forms of polyaniline [1]. The potential role of polyaniline and related conducting polymers in biomedical applications has attracted considerable interest. This includes the development of artificial muscles, [2,3] controlled drug release, [4] the stimulation of nerve regeneration [5] and the use of conducting polymers as scaffolds for cell attachment [6]. Tissue compatibility and low toxicity has been indicated from implantation studies in animals [6–8].

The free radical scavenging property of antioxidants such as a range of vitamins and polyphenols is of considerable interest for the protection that they can afford against disease [9]. The 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical in methanol is commonly used to test the antioxidant activity of molecules [10–16], and this test has been extended to assess the free radical scavenging of conducting polymers such as polyaniline [13,16].

We have confirmed the usefulness of SSNMR in the investigation of polyaniline as a radical scavenger [16] by using ^{13}C–^{1}H cross-polarisation and its related spectral editing techniques applied to polyaniline and its fully reduced form, following on from earlier studies of conducting polymers as DPPH radical scavengers [13]. However, relatively subtle changes and lack of resolution in the ^{13}C CP MAS spectra have prevented quantitative analysis and investigation of possible structural changes that could occur upon the reaction with DPPH. These motivated us to reinvestigate the radical scavenging capability of PANI by using a ^{15}N labelled sample [17–19], and to examine any possible chemical bonding or trapping of DPPH molecules with PANI using significantly higher ($\approx$3 times) concentration of DPPH than in our previous study.

2. Experimental

2.1. Synthesis

The emeraldine base form of polyaniline—PANI was synthesized by the method of Cataldo et al. [20]. The ^{15}N enriched PANI was chemically synthesised using commercially

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available ^{15}N labelled aniline (^{15}N, 98%, Cambridge Isotope Laboratories, Inc.) according to the procedure for unlabelled PANI. Hundred and twenty milligrams of this material was suspended in 120 mL of a 4.5×10^{-2} mol L^{-1} DPPH solution in methanol by stirring for 30 s and the mixture was allowed to stand at room temperature for 30 min. The PANI samples were filtered, washed several times with distilled water, and dried in a vacuum oven at room temperature.

2.2. NMR spectroscopy

All solid-state NMR experiments were performed on a dry powder samples by using a Bruker Avance 300 spectrometer operating at 300.13 MHz proton frequency with a 7 mm double resonance Bruker probe head. Zirconium oxide 7 mm rotors were used with air-tight Kel-F caps for all measurements. The magic angle was adjusted by maximizing the sideband intensities of the ^{79}Br NMR signal of a KBr sample. All spectra were obtained at ambient temperature. The parameters for standard ^{15}N CP/MAS and variable contact time measurements were as follows: all ^{15}N spectra were acquired at a spectrometer frequency of 30.41 MHz. The sweep width was 30.03 kHz. The 90° pulse was 7.3 μs (34.25 kHz) and the recycle delay was 1 s. The sample rotation frequency was 4500 ± 1 Hz. The number of the scans for basic CP/MAS experiments [21] was 25,000 and the contact time was 2 ms. Proton relaxation measurements in the rotating frame of coordinates were performed at ^{1}H spin-locking RF fields of 57.2 kHz using the pulse sequence with variable ^{1}H spin lock prior to CP, i.e. with ^{15}N detection [21]. Variable contact time [21] and proton relaxation experiments in the rotating frame of reference (16 points from 30 μs to 10 ms) were performed with 3000 scans per each point.

All ^{15}N spectra were externally referenced to $^{15}NH_4^{15}NO_3$ ($\delta^{15}NH_4^+ = 0$ ppm). All ^{13}C CP/MAS experiments were performed at a spectrometer frequency of 75.47 MHz with a sample rotation speed of 5000 ± 1 Hz. The relaxation delay was 1 s and the 90° pulse was 4.2 μs (59.52 kHz). The number of scans for PANI and PANI after reaction with DPPH (PANI–DPPH) in CP/MAS experiments was 10,000 and 12,000, respectively. In the case of variable contact time the number of scans for PANI and PANI–DPPH was 3500 and 4000, respectively. All ^{13}C spectra were externally referenced to TMS.

2.3. XP spectroscopy

The X-ray photoelectron spectroscopy (XPS) was performed in an ultra-high vacuum (UHV) chamber (1×10^{-10} Torr) equipped with a PHI Perkin–Elmer surface analysis system described in greater detail elsewhere [22]. The sample was dispersed onto carbon tape mounted onto a stainless steel stub before introduction into the UHV system. XPS was performed using an Al Kα (1486.6 eV) radiation source at 260 W/14 kV with 0.1 eV/step, 50 eV pass energy and a total of 20 coadded scans for all regions. Initial survey scans of samples were performed to ensure the purity of polyaniline and to determine correct alignment of the spectra to the C 1s photoemission line at 284.5 eV obtained from carbon 1s electrons. Deconvolution of N1s peaks obtained from nitrogen 1s electrons was performed using XPSPEAK software with peaks fitted using a Gaussian–Laurentzian ratio of 80:20 at varying FWHM ~1.8 eV.

3. Results and discussion

^{13}C CP/MAS spectra of polyaniline consist of broad resonances which are partially overlapped, mostly due to compositional defects, a distribution of torsion angles between adjacent rings, variations in the sequencing of benzenoid and quinoid units, thermally induced molecular motions and the possibility of rotations or flips of benzenoid rings about their 1, 4 axes [23]. Thus the possible changes that can occur upon reaction with DPPH could be obscured due to low spectroscopic resolution in the ^{13}C spectra.

However, ^{15}N NMR spectroscopy of polyaniline offers much better insight into the mechanism of this reaction, which involved a redox process. This is because the spectrum consists of only two very well resolved peaks which originate from amine and imine nitrogens [17–19], so their relative intensities can be determined directly.

3.1. ^{15}N CP/MAS spectra

^{15}N CP/MAS spectra obtained from ^{15}N-labeled PANI and PANI–DPPH are shown in Fig. 1. In the ^{15}N spectrum of PANI (Fig. 1(A)) two main peaks are observed. They are attributed to

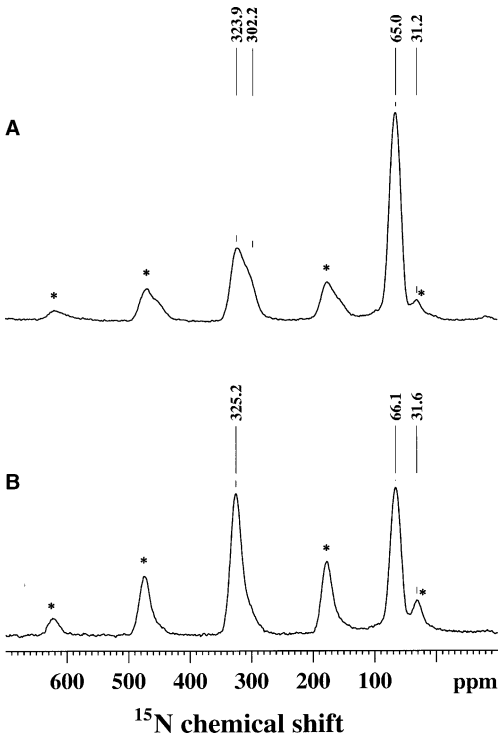
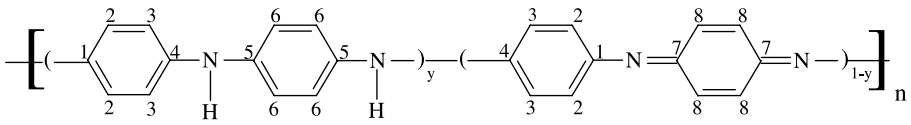


Fig. 1. ^{15}N CP/MAS NMR spectra of the ^{15}N labelled PANI before (A), and after (B) reaction with DPPH. The asterisks denote spinning sidebands.

Benzenoid diamine Quinoid diimine



Scheme 1. Structure of polyaniline.

imine (323.9 ppm) and amine (65.0 ppm) nitrogens. The sidebands marked by asterisks originate from the imine peak at 323.9 ppm. The peak from the end groups which should be at ≈31 ppm [19,24] is obscured by an imine sideband.

The assignment of these peaks is in accordance with the data published elsewhere [17–19,24]. The presence of shoulders on the imine peak (303.2 ppm) and the amine peak (68.2 ppm) (Fig. 1(A)), obtained from deconvolution (not shown), suggest the presence of different chemical environments for the imine and amine groups. This could imply that, in our sample, the sequence is not entirely composed of the alternating benzenoid diamine and quinoid diimine units shown in Scheme 1. Therefore, there could be some small parts in the structure which are more or less oxidized than in the PANI structure shown in Scheme 1.

Nevertheless, any redox process, i.e. change in the oxidation state of PANI, can be observed clearly from the change in the relative intensities of the peaks at 323.9 ppm and at 65.0 ppm.

After reaction with DPPH (Fig. 1(B)) the imine peak (325.2 ppm) shows a considerable increase in intensity relative to the amine peak (66.1 ppm), suggesting that significant oxidation of PANI has occurred. At the same time the shoulder at 302.3 ppm is not as apparent as that in the original PANI spectrum, while the line shape of amine peak seems preserved.

3.2. Relative intensities

Usually, quantification from CP/MAS NMR spectra is not straightforward. The signal of the rare nucleus is enhanced by transfer of polarization from the abundant nucleus (usually ^{1}H). Thus, the intensity of the signal depends on the kinetics of transfer of the magnetization. During the contact time the transfer of magnetization occurs via a static dipolar interaction and the rate of magnetization transfer has a $1/r^6$ dependence upon the distance r between nuclei. This means that nuclei that are not protonated, i.e. not directly bonded to a proton, will cross-polarise more slowly than protonated ones. Also, as the transfer of magnetization depends on the static dipolar interaction, the more rigid groups will have faster signal buildup during the transfer [21].

The rise in rare nucleus magnetization determind by the time constant T_{IS} is counteracted by another process: reduction of the proton magnetization due to the relaxation of protons in the rotating coordinate system with the time constant $T^{\mathrm{H}}_{1\rho}$. The signal will, therefore, pass through a maximum that is different for each group with a different degree of protonation or mobility, see Eq. (1) [21].

$$I = \frac{C\left(\exp\left(-t_{\mathrm{cp}}/T^{\mathrm{H}}_{1\rho}\right) - \exp\left(-t_{\mathrm{cp}}/T_{IS}\right)\right)}{1 - \left(T_{IS}/T^{\mathrm{H}}_{1\rho}\right)} \quad (1)$$

In this equation, I is the experimentally measured integrated intensity (area) and C is proportional to the number of S nuclei giving rise to the signal and is, therefore, the important parameter for quantitation and t_{cp} is variable contact time.

Thus, in order to get quantitative data, the cross-polarization behaviour must be taken into account and, if necessary, corrected for. To get the corrected imine/amine ratio before and after reaction with DPPH, contact time experiments were performed. All spectra for each contact time are carefully deconvoluted, and the signal areas obtained for imine and amine peaks are plotted versus contact time (Figs. 2 and 3.). The data are summarized in Table 1.

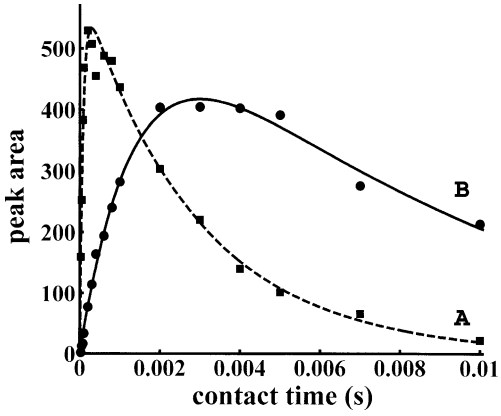


Fig. 2. The peak areas of the amine (A) and the imine peak (B) versus cross polarization contact time for the original sample of PANI.

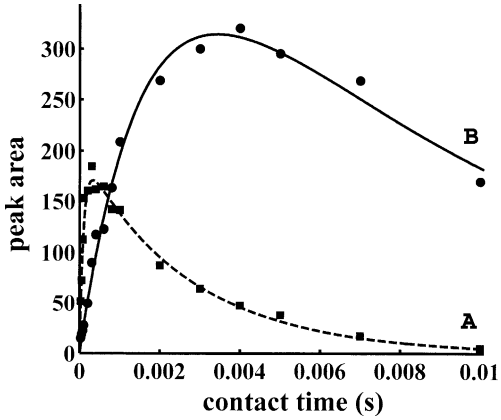


Fig. 3. The peak areas of the amine (A) and the imine peak (B) versus cross polarization contact time for the sample of PANI–DPPH.

Table 1
$T_{1\rho}^{H}$, T_{IS} and corrected areas for the samples of PANI and PANI–DPPH, obtained from ^{15}N cross-polarization NMR experiments with variable contact times

	T_{IS} (μs)	$T_{1\rho}^{H}$ (ms)	Corrected peak area (%)	Moles$\times 10^{-3}$
PANI–amine	80	2.9	55.6	0.74
PANI–imine	1500	7.7	44.4	0.59
DPPH–amine	90	2.7	39.8	0.53
DPPH–imine	1600	8.7	60.2	0.80

The observation of significantly longer T_{IS} values for the imine group compared to those of the amine is attributed to non-protonation of the former. The corrected areas C, see Eq. (1), listed in Table 1 and obtained from the spectra recorded at 2 ms contact time are corrected for the effects of T_{IS} and $T_{1\rho}^{H}$ [17].

The integrated intensity for the imine peak includes the peak at 323.9 ppm and its related sidebands. The imine/amine ratio for PANI is 0.8, relatively close to the expected value of 1.0 for the emeraldine base form [17]. The integrated intensities obtained from deconvolution have an error of $\approx 10\%$. In the case of PANI–DPPH the imine/amine ratio increases significantly to ≈ 1.5.

The imine to amine ratio of 1.5 is obtained by oxidizing 30% of the benzoid diamine units to a fully oxidized quinoid diimine units beginning with an imine/amine ratio of 0.8. This confirms our suggestion based on the relative intensities of the peaks shown in Fig. 1, implying significant oxidation after reaction with stable DPPH free radical.

The 120 mg polyaniline sample represents 1.33×10^{-3} mol of aniline units. On the other hand, 120 mL of 4.5×10^{-2} mol L^{-1} DPPH solution represents 5.4×10^{-3} mol of DPPH radicals, i.e. there is a 4:1 ratio of aniline units to DPPH. Repeat experiments ($n=5$) using 120 mg of non-labelled polyaniline showed that 85 (± 5) % (i.e. 4.1×10^{-3} mol) of DPPH radicals reacted during the 30 min experiment, as monitored by the decay in EPR signal due to the DPPH radical [15]. However, the change in the intensity of the ^{15}N NMR signals following reaction with DPPH shows that only about 2×10^{-4} mol of aniline units were oxidised (Table 1). This accounts for only 4% of the DPPH, which reacted, and this is about 20 times smaller than percentage of scavenged DPPH. The mechanism that leads to this striking difference between the amount of oxidized PANI and scavenged DPPH radicals is still under the investigation in our laboratory.

The extent of polymer swelling or porosity, and the potential influence of this on the extent of reaction with DPPH radicals, was not determined in the present study. There is a possibility that PANI particles of different size may react with different amounts of DPPH as the available surface area changes, but to investigate this we would need some way of separating the PANI into samples of different particle sizes.

3.3. ^{13}C CP/MAS spectra

The deconvoluted CP MAS spectra of PANI and PANI–DPPH are shown in Fig. 4(A) and (B). As shown in Fig. 4(A), PANI has six broad and relatively well-defined resonances which are observed at 114 (shoulder), 123, 137, 141, 147 and 158 ppm [23]. The peak at 123 ppm and shoulder at 114 ppm are assigned to carbons C-2,3 and C-6, respectively (Scheme 1). The peak at 137 ppm that originates from the protonated C-8 carbon that belongs to the quinoid part of PANI structure as does the non-protonated C-7 peak at 158 ppm. The peaks at 141 and 147 ppm are associated with the C-4 and C-1 non-protonated carbons, respectively. The deconvoluted CP/MAS spectrum of PANI–DPPH (Fig. 4(B)) also consists of the resonances at approximately the same chemical shifts, but with different intensities with respect to the resonances obtained in the PANI spectrum. The benzenoid peaks at 114 ppm (C-6) and at 141 ppm (C-4,5) are diminished after treatment with DPPH. At the same time, the resonances at 137 ppm (C-8), 147 ppm (C-1) and 158 (C-7), assigned to the quinoid part are relatively increased because of oxidation.

Carbon contact time experiments were also performed and, as in the case of the ^{15}N data, all spectra were carefully deconvoluted. The areas are corrected for contact times and the relative ratio, for instance, for the peaks at 147 ppm (C-1) for PANI–DPPH and PANI is 1.4–1.5 which is in accordance with the result obtained from ^{15}N experiments.

3.4. XP spectroscopy

To compare results obtained from SSNMR, we applied XP spectroscopy on PANI–DPPH sample. The XP spectrum of

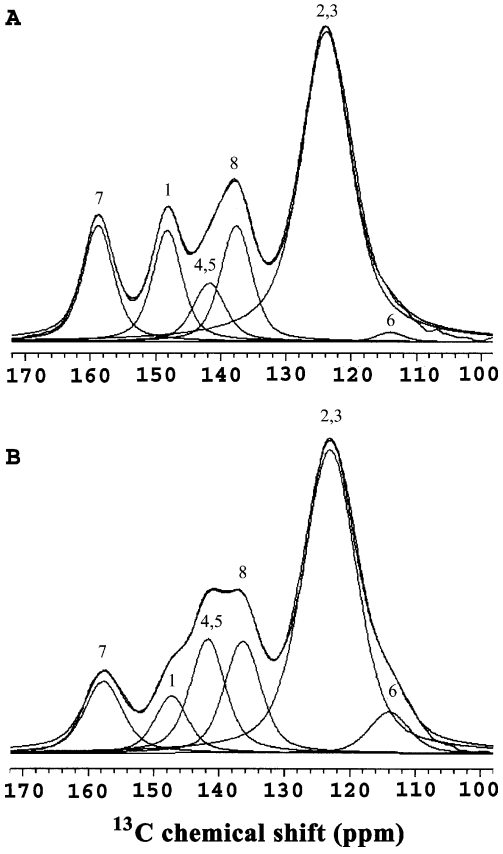


Fig. 4. Deconvoluted ^{13}C CP/MAS spectra of PANI (A) and PANI–DPPH (B).

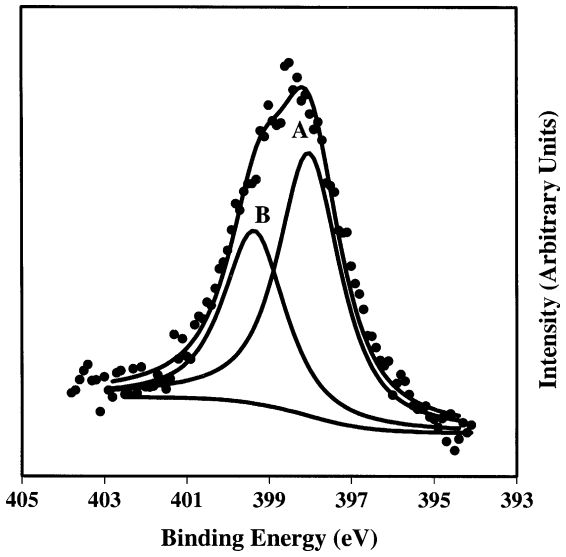


Fig. 5. N1s XPS of PANI–DPPH showing the imine (A) and amine (B) contributions.

PANI–DPPH is shown in Fig. 5. The N1s photoemission peak occurs at 398.6 eV and upon deconvolution of this peak it is best fitted with two peaks at 399.3 and 398.0 eV within the restraints of the N1s at FWHM of 1.8 eV (Table 2). These peaks are identified as originating from two N environments involving the –NH– (benzoid-B) and =N– (quinoid-A) groups from the amine and imine parts of the polyaniline structure, respectively [25]. From peak area analysis the ratio of quinoid to benzoid species is found approximately equal to 1.5, which is in good agreement with the NMR results.

3.5. Proton relaxation

Proton rotating-frame relaxation data can provide information about the homogeneity of the sample at the molecular level [26]. In homogeneous samples, rapid spin diffusion results in a single $T_{1\rho}^{H}$ value throughout the sample. Good fits of the experimental data to Eq. (1) were obtained for both PANI and PANI–DPPH samples (Figs. 2 and 3 and Table 1). The experimental data for both samples are fitted to a single $T_{1\rho}^{H}$ value indicating homogeneity of the PANI–DPPH samples even after the exposure of the PANI to the high concentration of DPPH.

However, it is sometimes difficult to obtain correct value for $T_{1\rho}^{H}$ from contact curves (Table 1), unless $T_{IS} \ll T_{1\rho}^{H}$, which is obviously not the case for the imine group. Also, it is sometimes problematical to fit a contact curve when T_{IS} is very short (as in the case of the amine group). Moreover, the relaxation time in the rotating frame for PANI is sensitive to the extent of molecular motion near that of the RF field frequency amplitude (34.25 kHz in our case). However, it has been shown [26] that PANI has chain motions occurring at a frequency $\approx$50 kHz. Thus, to get independent information without interference from the cross-polarization process, and to perform experiments under conditions where the RF field is near to the frequency of molecular motion [26–29], independent $T_{1\rho}^{H}$ relaxation experiments at 57.2 kHz proton RF field with ^{15}N detection were performed (Fig. 6) [27,30].

Table 2
Summary of the N1s peak positions, peak widths (FWHM) and uncorrected peak areas in the X-ray photoelectron spectra of PANI–DPPH

Peak	BE ($\pm$0.1 eV)	FWHM (eV)	Uncorrected peak area (%)
N1s	398.6	3.0	11,719 (100)
–NH–	399.3	1.8	4658 (40)
=NH–	398.0	1.8	7061 (60)

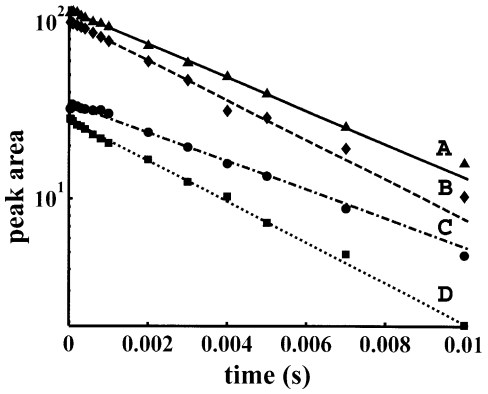


Fig. 6. ^{1}H NMR relaxation measurements in the rotating frame of coordinates for PANI (B-amine, D-imine) and PANI–DPPH (A-amine, C-imine).

The $T_{1\rho}^{H}$ values for both amine and imine nitrogens in PANI were found to be 3.8 and 3.9 ms, respectively and are thus practically equal within experimental error. No bi- or multi-exponential components were observed, indicating that that proton spin diffusion is efficient in transferring spin polarization through the sample, i.e. the sample is homogeneous. Upon reaction with DPPH, relaxation times, for both amine and imine nitrogens, are to some extent prolonged to 4.6 and 5.4 ms, respectively, implying reduction of molecular motion, most probably because of the introduction of double bonds after oxidation. The sample is still relatively homogeneous considering a non-significant difference in $T_{1\rho}^{H}$ between amine and imine nitrogens (0.8 ms), even after exposure to a high concentration of DPPH. There is thus no indication that significant cross-linking or other bond forming processes have occurred which might account for the additional DPPH scavenging beyond that accounted for by direct oxidation of the polyaniline chains.

4. Conclusions

By applying ^{15}N and ^{13}C solid-state NMR experiments we have shown that polyaniline in the emeraldine state can be further oxidized by DPPH radicals from an imine content of 45–65%, and that the level of oxidation can be quantitatively determined by solid-state NMR, and is in line with N1s XPS data. This level of oxidation requires the reduction of only 4% of the available DPPH radicals. However, the EPR results showed that within a 30 min reaction time, about 85% of the DPPH radicals were scavenged. The reaction between DPPH

and PANI is mainly redox in nature considering that there is no evidence of significant chemical binding between DPPH and PANI. The significant discrepancy between the fraction of DPPH radicals required for oxidation of PANI (4%) and high percentage of scavenged DPPH (85%) requires an identification of further redox processes. Proton relaxation times in the rotating frames of coordinates are slightly prolonged after reaction with DPPH, most probably because of the introduction of quinoid structures that have a lower degree of freedom and flexibility than the benzenoid portions. Experiments which could give more information about the PANI structure after reaction with DPPH and consequently about the mechanism of the redox reaction between PANI and DPPH (relaxation, 2D spin exchange, EPR) are in progress in our laboratory.

References

[1] Heeger AJ. Synth Met 2002;125:23.
[2] Madden JD, Cush RA, Kanigan TS, Hunter IW. Synth Met 2000;113:185.
[3] Hutchison AS, Lewis TW, Moulton SE, Spinks GM, Wallace GG. Synth Met 2000;113:121.
[4] Pernaut JM, Reynolds JR. J Phys Chem 2000;B104:4080.
[5] Kotwal A, Shmidt CE. Biomaterials 2001;22:1055.
[6] Rivers TJ, Hudson TW, Schmidt CE. Adv Funct Mater 2002;12:33.
[7] Zhang Z, Roy R, Dugre FJ, Tessier D, Dao LH. J Biomed Mater Res 2001; 57:63.
[8] Lim VW, Kang ET, Neoh KG. Synth Met 2001;119:261.
[9] Rice-Evans C. Curr Med Chem 2001;8:797.
[10] Sawai Y, Moon JH. J Agric Food Chem 2000;48:6247.
[11] Silva AMS, Santos CMM, Cavaleiro JAS, Tavares HR, Borges F, Silva FAM. Magn Reson Food Sci 2001;262:110 [Special Publication-Royal Society of Chemistry].
[12] Hristea EN, Hillebrand M, Radutiu AC, Caldararu H, Caproiu MT, Ionita P, et al. Rev Roum Chim 2000;45(12):1089.
[13] Gizdavic-Nikolaidis M, Travas-Sejdic J, Bowmaker GA, Cooney RP, Kilmartin PA. Synth Met 2004;140:225.
[14] Gizdavic-Nikolaidis M, Travas-Sejdic J, Bowmaker GA, Cooney RP, Thompson C, Kilmartin PA. Curr Appl Phys 2004;347 [Special AMN-1 Issue].
[15] Gizdavic-Nikolaidis M, Travas-Sejdic J, Kilmartin PA, Bowmaker GA, Cooney RP. Curr Appl Phys 2004;4:343 [Special AMN-1 Issue].
[16] Zujovic ZD, Gizdavic-Nikolaidis M, Kilmartin PA, Travas-Sejdic J, Cooney RP, Bowmaker GA. Appl Magn Reson 2005;28:123.
[17] Young TL, Espe MP, Yang D, Mattes BR. Macromolecules 2002;35: 5565.
[18] Wehrle B, Limbach HH, Mortensen J, Heinze J. Angew Chem Int Ed Engl Adv Mater 1989;28(12):1741.
[19] Richter AF, Ray A, Ramanathan KV, Manohar SK, Furst GT, Opella SJ, et al. Synth Met 1989;29:E243–E9.
[20] Cataldo F, Maltese P. Polym Adv Technol 2001;12:293.
[21] Stejskal EO, Memory JD. High resolution NMR in the solid-state. Fundamentals of CP/MAS. Oxford: University Press; 1994.
[22] Senanayake SD, Idriss H. Surf Sci 2004;563(1–3):135.
[23] Kaplan S, Conwell EM, Richter AF, MacDiarmid AG. J Am Chem Soc 1988;110:7647.
[24] Adams PN, Apperley DC, Monkman AP. Polymer 1993;34(2):328.
[25] Monkman AP, Stevens GC, Bloor D. J Phys D: Appl Phys 1991;24:738.
[26] Roy AK, Inglefield PT. Prog Nucl Magn Reson Spectrosc 1990;22:569.
[27] Espe MP, Mattes BR, Schaefer J. Macromolecules 1997;30:6307.
[28] VanderHart DL, Garroway AN. J Chem Phys 1979;71(7):2773.
[29] Schaefer J, Stejskal EO, Buchdahl R. Macromolecules 1977;10(2):384.
[30] Mathew R, Mattes BR, Espe MP. Synth Met 2002;131:141.