

# Solid-state NMR of polyanilines with different morphologies

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## Introduction

Electrically conducting polymers (CPs) constitute a unique group of materials, offering the possibility of controlled electrical conductivity combined with the processing characteristics, low production cost and stability of properties associated with polymers.<sup>1,2</sup> Polyaniline (PANI) is probably one of the most interesting CPs owing to its reasonably high conductivity (100 S/cm) upon an acid doping, good processability, ability to form various nanostructures and good environmental stability.<sup>3</sup> It is the only electro-organic polymer whose conductivity can be controlled in two independent ways: (a) controlling the degree of protonation, and (b) adjusting the degree of oxidation.<sup>4</sup> It is well known that the level of protonation can change PANI from an insulator ( $10^{-10}$  S/cm) to a semiconductor (100 S/cm).<sup>3</sup> Therefore, the wide range of its related electrical, electrochemical and optical properties, together with its good environmental stability, make PANI attractive for possible applications in a variety of fields such as antimicrobial agents, energy storage, catalysts, antistatic coating, sensors, nanotechnology.<sup>1</sup>

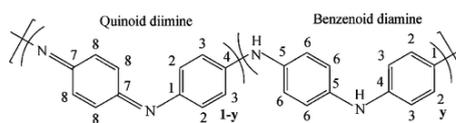
One of the most disadvantageous characteristics of conducting PANI is its insolubility in common organic solvents. Therefore, methods for the structural characterisation of various forms of PANI are limited and it is of paramount importance to have a technique available which can give structural information about the material in its native form. Solid-state NMR (SSNMR) is a non-destructive method. Because the technique can be used on amorphous as well as on crystalline samples, it is not surprising that it has been widely used in the study of amorphous PANI materials. Comparative advantages of SSNMR over other analytical techniques are its capability to investigate different materials using multinuclear and multidimensional experiments (2D or 3D). Besides structural data, SSNMR can give information about molecular dynamics and mobility of various structural units. In this article we will show the usefulness and limitations of SSNMR to detect subtle structural differences in PANI samples with different morphologies in conjunction with FTIR and UV-Vis spectroscopy.

Cross-polarization (CP) is a double resonance solid-state NMR technique designed to overcome two common problems in the NMR of solid samples: low sensitivity and the long time needed to acquire spectra. The sensitivity is significantly improved by magnetization transfer from abundant *I* (usually hydrogen) to low abundant spins *S* (usually <sup>13</sup>C, <sup>15</sup>N, etc). On the other hand, experimental

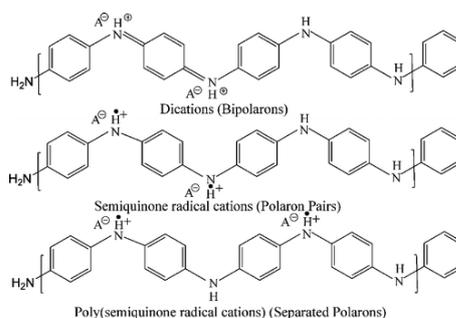
time is extensively shortened owing to the fact that the CP experiment repetition time is determined by the *I* spin-lattice relaxation time ( $T_1$ ). The resolution in solid-state NMR spectra is considerably improved by introducing MAS (magic angle spinning) where the sample is rotated at the specific angle (magic angle, 54.7°) which reduces or completely removes direct dipolar coupling and chemical shift anisotropy.

## SSNMR in Structural Investigations of PANIs – an Overview

Hjertberg *et al.* reported a <sup>13</sup>C CPMAS (cross-polarization magic angle spinning) investigation of PANI,<sup>5</sup> confirming the benzenoid-quinoid alternating structure (Scheme 1).<sup>6</sup>



**Scheme 1.** The chemical structure of PANI, where  $y = 1$  is Leucoemeraldine Base (LEB),  $y = 0.5$  is Emeraldine Base (EB),  $y = 0$  is Pernigraniline base (PNB). Reprinted with permission from publishers of ref. 6.



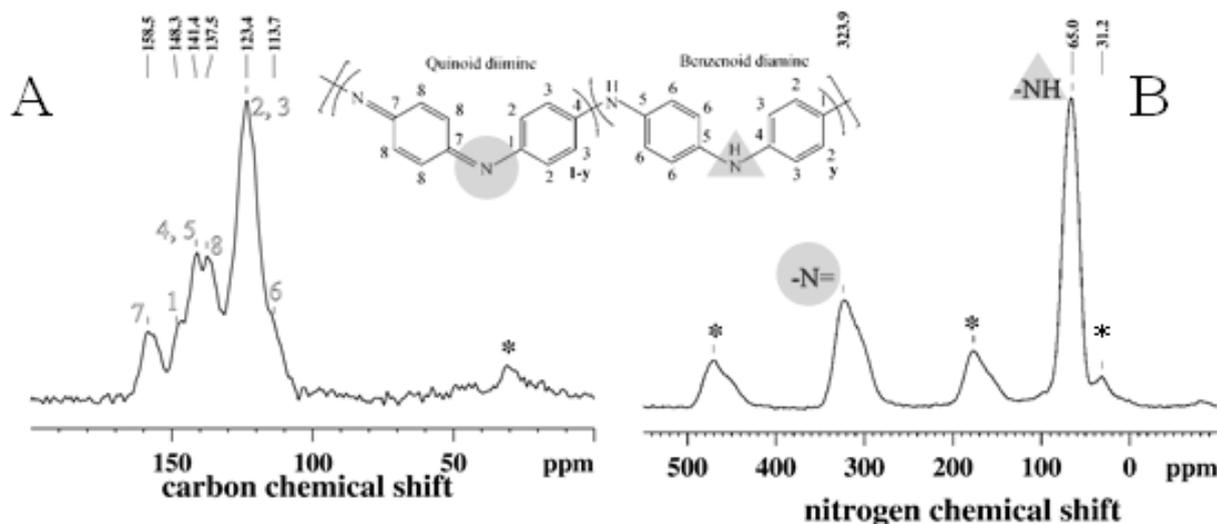
**Scheme 2.** Various protonation states of the emeraldine salt form of PANI. Reprinted with permission from publishers of ref. 7.

Satfstrom *et al.* compared modified neglect of diatomic overlap (MNDO) calculations with NMR spectra.<sup>8</sup> They showed that the structure of PANI is unchanged upon protonation (Scheme 2) and that the positive charge introduced by the proton is delocalized in the polymer. Kaplan *et al.* investigated the structure of PANI in emeraldine (EB) and leucoemeraldine (LEB) form (Scheme 1), determining that the emeraldine base consists primarily of a well-defined microstructure of alternating benzenoid diamine and quinoid diimine units,<sup>9</sup> although their results showed that PANI was slightly overoxidised ( $y < 0.5$ , Scheme 1). Menardo *et al.* used <sup>13</sup>C NMR studies to confirm that reduced PANI only consists of benzenoid rings and amine nitrogens (Scheme 1).<sup>10</sup>

In one of the first papers related to  $^{15}\text{N}$  CPMAS of PANI, Wehrle *et al.* have proposed this method as promising and useful for structural investigations of  $^{15}\text{N}$  labelled PANI and other heterocyclic polymers which have nitrogen.<sup>11</sup> Stein *et al.* performed variable contact time experiments to reveal the structure of PANI at various temperatures.<sup>12</sup> They assigned resonances in the PANI spectrum based on different cross-relaxation behaviour of different carbons depending on their distance from the protons. Also, they observed changes in the spectra upon crossing the insulating-conduction transition which are in line with the motion of bipolarons in the polymer chain. In their paper Kaplan *et al.* applied  $^{13}\text{C}$  and  $^2\text{H}$  SSNMR measurements to reveal the structure and dynamics of different forms of PANI.<sup>13</sup> Richter *et al.* used  $^{15}\text{N}$  CPMAS spectroscopy for structural investigations of LEB and EB forms of PANI,<sup>14</sup> confirming that EB polymer exists as an alternating copolymer of oxidised and reduced units. Stein *et al.* presented a  $^{13}\text{C}$  two-dimensional chemical exchange NMR experiment that gave information about the local structure and the ratio of freely moving rings to rigid rings.<sup>15</sup> This experiment also confirmed inhomogeneous broadening of the CPMAS lines in PANI spectrum. Adams *et al.* prepared  $^{15}\text{N}$  enriched PANI samples with different molecular weights.<sup>16,17</sup> They compared GPC (gel permeation chromatography) results with NMR data obtained by end group analysis. Kolbert *et al.* investigated the metallic nature of highly conducting PANI by using relaxation measurements at variable temperatures along with two-dimensional spin exchange experiments,<sup>18</sup> which showed heterogeneity in the sample over a distance of at least 30 Å. They observed Korringa relaxation in PANI, which is strong evidence for a metallic state in highly conducting PANI. Espe *et al.* explored anhydrous  $^{15}\text{N}$  labelled PANI powders as a function of HF doping by  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{19}\text{F}$  SSNMR.<sup>19</sup> They revealed the presence of three different types of charged environments. Also, they showed that the entire crystalline region (pseudo-metallic and conducting) and amorphous regions within 50 Å of the crystalline boundary have been unobservable with SSNMR owing to the effects of paramagnetic delocalized electrons.

Kababya *et al.* characterised the product of a polymerisation procedure of aniline in aqueous medium in the presence of dodecylbenzenesulfonic acid (DBSA) as a dopant by various  $^{15}\text{N}$ ,  $^{13}\text{C}$  and  $^7\text{Li}$  SSNMR techniques – CPMAS, rotating frame relaxation measurements and REDOR (Rotational Echo Double Resonance).<sup>20</sup> Mathew *et al.* employed  $^{15}\text{N}$  and  $^{13}\text{C}$  CPMAS to investigate the effect of elevated temperature on the reactivity and structure of PANI.<sup>21</sup> They showed that heating at 175–190 °C caused cross-linking in the polymer which was completely converted to its fully reduced leucoemeraldine form. The same group investigated the structure and oxidation state of EB PANI in N-methylpyrrolidinone (NMP) solutions<sup>22</sup> which were heated to 120–190 °C by using  $^{15}\text{N}$  and  $^{13}\text{C}$  SSNMR. They confirmed the presence of cross-links in PANI films cast from heated NMP solutions. In their paper Goddard *et al.* investigated PANI and PANI/clay nanocomposite by using deuteron quadrupole echo and MAS NMR experiments.<sup>23</sup> They observed a Knight shift based on the appearance of an additional manifold of spinning sidebands shifted toward higher frequencies in the MAS spectrum of conductive PANI. The presence of Knight shift implied an active role of polarons in charge transport. Young *et al.* used  $^{13}\text{C}$  CPMAS and the  $^{31}\text{P}$  dipolar recoupling – DRAMA (dipolar recovery at the magic angle) experiment to reveal the distribution of tert-butylphosphonic acid (TBPA) in PANI at different doping levels.<sup>24</sup> The acid distribution was probed by measuring  $^{31}\text{P}$ - $^{31}\text{P}$  dipolar couplings with the DRAMA experiment, which provides information about the internuclear distances and the distribution of TBPA molecules in the doped PANI. Sahoo *et al.* investigated various forms of an enzymatically synthesised PANI (doped (as synthesised) conducting, dedoped base and redoped conducting) by  $^{15}\text{N}$  and  $^{13}\text{C}$  CPMAS spectroscopy.<sup>25</sup>

Zujovic *et al.* used  $^{13}\text{C}$  and  $^{15}\text{N}$  spectroscopy to explore the antioxidant properties of PANI.<sup>26</sup> In subsequent papers this group investigated nanostructured materials obtained in the oxidative polymerisation of aniline using SSNMR.<sup>7,27–30</sup>



**Fig. 1.**  $^{13}\text{C}$  (A) and  $^{15}\text{N}$  (B) CPMAS NMR spectra of standard PANI. Experimental conditions are given in reference 26. The spinning sidebands are denoted by asterisks. Adapted with permission from publishers of ref. 26.

## Carbon Spectra

$^{13}\text{C}$  CPMAS spectra of PANI (Fig. 1A) usually consist of broad resonances which are partially overlapped, mostly attributed to a combination of several factors: compositional defects, a distribution of torsion angles between adjacent rings, variations in the sequencing of benzenoid and quinoid units, thermally induced molecular motions, the possibility of rotations or flips of benzenoid rings about their 1, 4 axes.<sup>9</sup> As shown in Fig. 1A, PANI has six broad and relatively well-defined resonances which are observed at *ca.* 114 (shoulder), 123, 137, 141, 148 and 158 ppm. The peak at 123 ppm and shoulder at 114 ppm are assigned to carbons C-2,3 and C-6, respectively (see Scheme in Fig. 1). The peaks at 137 ppm and 158 ppm originate from C-8 protonated and C-7 non-protonated carbon of the quinoid part of the PANI structure, respectively. The peaks at 141 ppm and 148 ppm are associated with C-4 and C-1 non-protonated carbon, respectively.

## Nitrogen Spectra

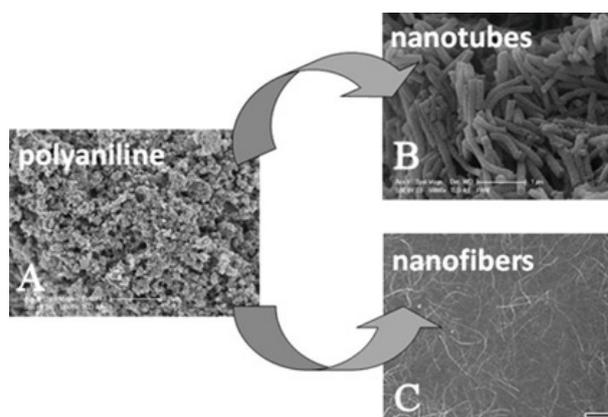
$^{15}\text{N}$  spectroscopy usually offers much better resolution and insight into possible structural changes. The spectrum (Fig. 1B) consists of only two very well resolved peaks from amine (*ca.* 65.0 ppm) and imine (323.9 ppm) nitrogens.<sup>11</sup> The sidebands (marked by asterisks in Fig. 1B) originate from the imine peak at 323.9 ppm. The peak from the end groups which should be at 31 ppm is hidden by an imine sideband. The assignment of these peaks accords with the data published elsewhere.<sup>11,16</sup> The shoulder of the imine peak (303.2 ppm; see Fig. 1B) points to two different chemical environments for imine and amine groups. This implies that the sequence does not entirely consist of alternating benzenoid diamine and quinoid diimine units as would be expected from Scheme 1. Any redox process, *i.e.*, change of 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.<sup>26</sup> The ratio of integrated intensities of amine and imine (including sidebands) resonances should be close to 1 (Scheme 1, EB PANI,  $y=0.5$ ).

## Nanostructured Materials Based on the Oxidative Polymerisation of Aniline

PANI is typically synthesised in the oxidative polymerisation of aniline, using a strong oxidising agent such as ammonium persulfate (APS) or potassium iodate ( $\text{KIO}_3$ ) in a strongly acidic solution such as 1 M HCl.<sup>1,2,31</sup> Synthesised in this way, PANI exhibits a granular morphology, as shown in Fig. 2A. This typical form of PANI is known by its irregular agglomerates and high conductivity. However, one of the advantages of PANI as a CP is that under certain conditions it can form various supramolecular nanostructures – nanotubes (Fig. 2B), nanorods, nanofibres (Fig. 2C), nanospheres, etc.<sup>32</sup> The formation mechanisms and structural characteristics of these nanostructured PANI forms have been extensively studied and reported.<sup>33-39</sup> FTIR and UV-Vis spectroscopies have been commonly applied in these investigations.

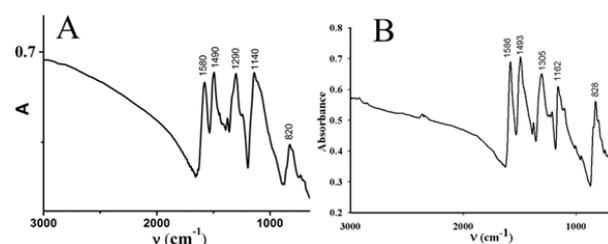
### FTIR spectroscopy

Figure 3 shows the FTIR spectra of PANI nanofibres<sup>30</sup> (A) and standard PANI (B).<sup>6</sup> All the samples show characteris-



**Fig. 2.** SEM micrographs of standard PANI (A), nanotubes (B) and nanofibres (C). Experimental conditions are given in refs 27, 29, 30. Adapted with permission of the publishers of refs 7 and 30.

tic peaks at about  $1580\text{ cm}^{-1}$  (C=C stretching mode of the quinoid rings),<sup>6,40,41</sup> and  $1490\text{ cm}^{-1}$  (C=C stretching mode of benzenoid rings).<sup>6,40,41</sup> Bands at *ca.*  $1290\text{--}1300\text{ cm}^{-1}$  are attributed to C-N stretching vibrations and C-H bending vibration of benzenoid rings.<sup>6,40,41</sup> For standard PANI, the strong band at *ca.*  $1160\text{ cm}^{-1}$  (Fig. 3B) has been assigned to a C-H bending vibration of the quinoid rings.<sup>41</sup> Its wavenumber has been shown to be doping-level dependent, occurring at  $1160\text{ cm}^{-1}$  in the intrinsic (undoped) structure and at  $1140\text{ cm}^{-1}$  in the doped structure.<sup>42</sup> This band appears at  $1140\text{ cm}^{-1}$  in the spectrum of PANI nanofibres (Fig. 3A). Both products in Fig. 3 had undergone a dedoping treatment, but the presence of the  $1140\text{ cm}^{-1}$  band in the spectrum of the nanofibre product suggests that this treatment was not effective. Subsequent studies on other nanoscale PANI products suggest that these are not as easily dedoped as standard PANI.<sup>43</sup> A band at *ca.*  $820\text{ cm}^{-1}$  can be attributed to C-H out of plane bending in 1,2-disubstituted ring structures (para-coupling).<sup>42</sup> Detailed comparison of the two spectra shows that they are very similar and that both show features characteristic for fully polymerised PANI.

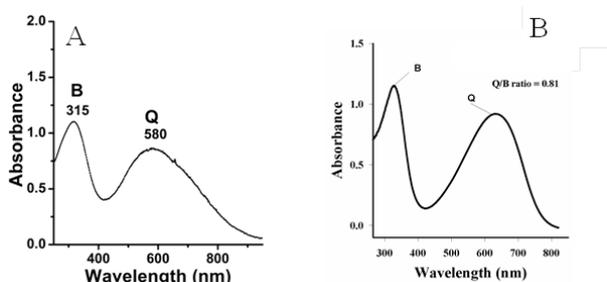


**Fig. 3.** FTIR spectra of PANI nanofibres (A) and standard PANI (B). Experimental conditions are given in references 6 and 30. Figure 3A is adapted with permission from the publishers of reference 30.

### UV-Vis spectroscopy

UV-Vis spectra of nanofibrillar and standard PANI are shown in Fig. 4A and Fig. 4B, respectively. They exhibit similar features. The UV-Vis spectra have  $\pi\text{--}\pi^*$  peaks at around 320 nm. The peak at around 600 nm can be assigned to the transition ( $n\text{--}\pi^*$ ) between the HOMO of the benzenoid ring (nonbonding nitrogen lone pair) and the LUMO ( $\pi^*$ ) of the quinoid ring.<sup>44</sup> Both peaks are charac-

teristic for the emeraldine base form of PANI (EB PANI), although the Q/B ratio indicates a slightly more reduced EB form.<sup>44</sup> The data obtained by UV-Vis data are in accordance with FTIR spectra and suggest that the structure consists of alternating quinoid and benzenoid segments. Therefore, both techniques imply that nanofibres and standard PANI have similar structures.



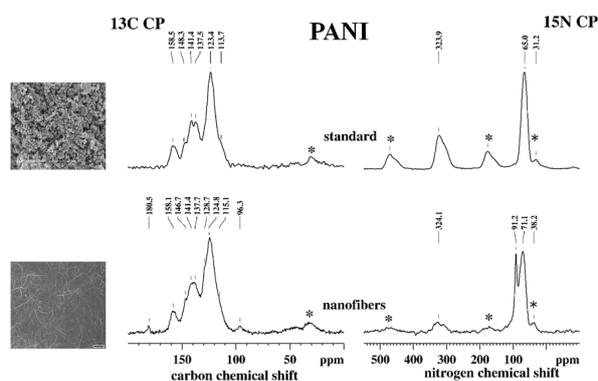
**Fig. 4.** UV-Vis spectra of PANI nanofibres (A) and standard PANI (B). Experimental conditions are given in references 6 and 30. Fig. 4A is adapted with permission from the publishers of ref. 30.

### Inferences from SSNMR spectroscopy

<sup>13</sup>C and <sup>15</sup>N SSNMR experiments were carried out to determine whether more subtle differences between these PANI samples could be revealed.

Figure 5 shows noticeable differences between the <sup>13</sup>C and <sup>15</sup>N CPMAS NMR spectra of standard PANI and nanofibres. The most obvious differences are the presence of the new peaks at 180.5 and 96.3 ppm in the carbon spectrum of nanofibres. The peak at 180.5 ppm probably originates from C=O carbons, not characteristic for the standard PANI spectra,<sup>7,29</sup> while the peak at 158.1 ppm originates from C=N carbons.<sup>29</sup> Therefore, both O and N could be preferred sites for hydrogen bonding, i.e., -C=O...H-N, or =N...H-N.<sup>29</sup> It has been suggested that hydrogen bonds are very important in forming the self-assembled supramolecular nanotube structures.<sup>45</sup> Also, there is an additional shoulder at 128.7 ppm in the spectrum of the nanofibres which implies a complex backbone structure or conformational changes owing to the formation of a nanofibrillar morphology. The <sup>15</sup>N spectra of PANI and the nanofibres are also different. The “standard” PANI spectrum shown in Fig. 5 exhibits peaks at 65.0 ppm and 323.9 ppm, from amine and imine nitrogen atoms respectively.<sup>26</sup> However, the spectrum of the nanofibrillar sample has different amine sites, with peaks at 71.1 and 91.2 ppm. This implies a complex molecular structure with several different -NH groups. This can probably be attributed to cross-linking which facilitates the formation of nanofibres.

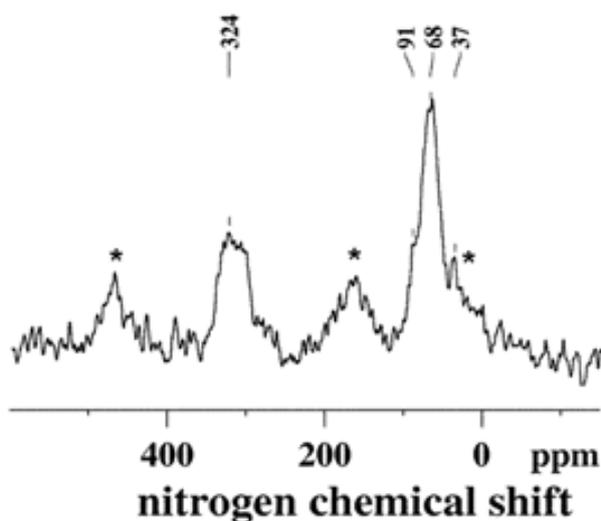
The imine (I) to amine (A) ratio (the ratio of the corrected integrated areas for peaks at around 70, 90 and 320 ppm (and its related sidebands)) is *ca.* I/A = 0.3. However, the FT-IR, UV-Vis and <sup>13</sup>C CP spectra suggest the prevalence of head-to-tail coupling similar to standard PANI and a significantly higher value for the imine/amine ratio, probably closer to 1.0. To resolve this ambiguity, the direct polarization (DP) experiment, which does not involve cross-polarization from protons, was carried out. Although, the experimental time for DP measurements can be very long,



**Fig. 5.** SEM micrographs and <sup>13</sup>C and <sup>15</sup>N SSNMR spectra of standard PANI and nanofibres. Experimental conditions are given in refs 27 and 30. The spinning sidebands are denoted by asterisks. Adapted with permission from the publishers of refs 26 and 30.

this experiment does not suffer from the usual quantification problems that can result from CP.

There are differences between the DP and CP spectra. Most obvious is the much larger contribution of the imine resonance, since the peak at *ca.* 320 ppm is much more intense than its CP counterpart (see Fig. 5). The imine/amine ratio for the sample shown in Figure 6 is 0.82. This value is different from the data obtained using the CP technique, but closer to those obtained from FT-IR, UV-Vis and <sup>13</sup>C CP experiments. A possible reason for this could be a difference in the proton environments of the N atoms in the different kinds of material, e.g., protons are more remote from the N atoms in the nanofibres, or a difference in the proton dynamics, e.g., fast exchange of hydrogen bonded protons between =O and =N and H-N in the nanofibre sample. On the other hand, polarization transfer in the CP spectrum of standard PANI might be more efficient because this material possesses a featureless granular morphology in which grains are packed together very closely and randomly distributed.



**Fig. 6.** <sup>15</sup>N direct polarization spectrum of PANI nanofibres. Experimental conditions are given in ref. 30. Adapted with permission from the publishers of ref. 30.

## Conclusions

The SSNMR technique has been successfully applied to standard and nanofibre PANI products. The spectral features in the  $^{13}\text{C}$  CPMAS spectra of nanofibres are similar to those of standard PANI, except for the presence of two peaks at 180.5 and 96.3 ppm. The  $^{15}\text{N}$  NMR suggests the presence of strong hydrogen bonds between the imine nitrogen and a proton from the amine nitrogen. Furthermore, cross-linking which should be the basis for the formation of well-ordered structures (such as nanofibres) has been confirmed by the presence of the 96.3 ppm peak in the carbon spectrum. Although very useful, special care should be taken when the CPMAS SSNMR approach is used for nanostructured PANI materials. In other words, using only CPMAS to quantify different groups can be problematic. This is not the case for conventional PANI where the imine/amine ratio can be determined relatively accurately from  $^{15}\text{N}$  CPMAS spectra.

## References

- Wallace, G. G.; Spinks, G. M.; Kane-Maguire, L. A. P. *Conductive Electroactive Polymers: Intelligent Materials Systems*, 2<sup>nd</sup> ed. 2002.
- Skotheim, T. A.; Reynolds, J. R.; Editors *Handbook of Conducting Polymers, Third Edition. Conjugated Polymers Processing and Applications*, 2007.
- Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. 1* **1986**, 82, 2385.
- Ray, A.; Astarias, G. E.; Kershner, D. L.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. *Synth. Met.* **1989**, 29, E141.
- Hjertberg, T.; Salaneck, W. R.; Lundstrom, I.; Somasiri, N. L. D.; MacDiarmid, A. G. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, 23, 503.
- Gizdavic-Nikolaidis, M. R. **2005**. "Spectroscopic studies of chemically synthesized polyaniline and its ability to act as radical scavenger", PhD thesis, The University of Auckland. <http://hdl.handle.net/2292/2257>.
- Zujovic, Z. D.; Zhang, L.; Bowmaker, G. A.; Kilmartin, P. A.; Travas-Sejdic, J. *Macromolecules* **2008**, 41, 3125.
- Stafström, S.; Sjögren, B.; Wennerström, O.; Hjertberg, T. *Synth. Met.* **1986**, 16, 31.
- Kaplan, S.; Conwell, E. M.; Richter, A. F.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1988**, 110, 7647.
- Menardo, C.; Nechtschein, M.; Rousseau, A.; Travers, J. P.; Hany, P. *Synth. Met.* **1988**, 25, 311.
- Wehrle, B.; Limbach, H.-H.; Mortensen, J.; Heinze, J. *Angew. Chem.* **1989**, 101, 1781.
- Stein, P. C.; Hartzell, C. J.; Jorgensen, B. S.; Earl, W. L. *Synth. Met.* **1989**, 29, E297.
- Kaplan, S.; Conwell, E. M.; Richter, A. F.; MacDiarmid, A. G. *Synth. Met.* **1989**, 29, E235.
- Richter, A. F.; Ray, A.; Ramanathan, K. V.; Manohar, S. K.; Furst, G. T.; Opella, S. J.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1989**, 29, E243.
- Stein, P. C.; Earl, W. L.; Ray, A. *Synth. Met.* **1993**, 55, 702.
- Adams, P. N.; Monkman, A. P.; Apperley, D. C. *Synth. Met.* **1993**, 55, 725.
- Adams, P. N.; Laughlin, P. J.; Monkman, A. P.; Kenwright, A. M. *Polymer* **1996**, 37, 3411.
- Kolbert, A. C.; Caldarelli, S.; Thier, K. F.; Sariciftci, N. S.; Cao, Y.; Heeger, A. J. *Phys. Rev. B* **1995**, 51, 1541.
- Espe, M. P.; Mattes, B. R.; Schaefer, J. *Macromolecules* **1997**, 30, 6307.
- Kababya, S.; Appel, M.; Haba, Y.; Titelman, G. I.; Schmidt, A. *Macromolecules* **1999**, 32, 5357.
- Mathew, R.; Mattes, B. R.; Espe, M. P. *Synth. Met.* **2002**, 131, 141.
- Young, T. L.; Espe, M. P.; Yang, D.; Mattes, B. R. *Macromolecules* **2002**, 35, 5565.
- Goddard, Y. A.; Vold, R. L.; Hoatson, G. L. *Macromolecules* **2003**, 36, 1162.
- Young, T. L.; Cross, J. L.; Espe, M. P. *Macromolecules* **2003**, 36, 5891.
- Sahoo, S. K.; Nagarajan, R.; Roy, S.; Samuelson, L. A.; Kumar, J.; Cholli, A. L. *Macromolecules* **2004**, 37, 4130.
- Zujovic, Z. D.; Gizdavic-Nikolaidis, M. R.; Kilmartin, P. A.; Idriss, H.; Senanayake, S. D.; Bowmaker, G. A. *Polymer* **2006**, 47, 1166.
- Zujovic, Z. D.; Gizdavic-Nikolaidis, M.; Kilmartin, P. A.; Travas-Sejdic, J.; Cooney, R. P.; Bowmaker, G. A. *Appl. Magn. Reson.* **2005**, 28, 123.
- Zujovic, Z. D.; Bowmaker, G. A.; Tran, H. D.; Kaner, R. B. *Synth. Met.* **2009**, 159, 710.
- Zujovic, Z. D.; Laslau, C.; Bowmaker, G. A.; Kilmartin, P. A.; Weber, A. L.; Brown, S. P.; Travas-Sejdic, J. *Macromolecules* **2009**, 43, 662.
- Zujovic, Z. D.; Wang, Y.; Bowmaker, G. A.; Kaner, R. B. *Macromolecules* **2011**, 44, 2735.
- Stejskal, J.; Gilbert, R. G. *Pure Appl. Chem.* **2002**, 74, 857.
- Ciric-Marjanovic, G. In *Nanostructured Conductive Polymers*; Eftekhari, A., Ed.; Wiley: London, 2010, p 19.
- Konyushenko, E. N.; Stejskal, J.; Sedenkova, I.; Trchova, M.; Sapurina, I.; Cieslar, M.; Prokes, J. *Polym. Int.* **2006**, 55, 31.
- Huang, J.; Kaner, R. B. *Angew. Chem., Int. Ed.* **2004**, 43, 5817.
- Tran, H. D.; Wang, Y.; D'Arcy, J. M.; Kaner, R. B. *ACS Nano* **2008**, 2, 1841.
- Laslau, C.; Zujovic, Z.; Travas-Sejdic, J. *Prog. Polym. Sci.* **2010**, 35, 1403.
- Laslau, C.; Zujovic, Z. D.; Zhang, L.; Bowmaker, G. A.; Travas-Sejdic, J. *Chem. Mater.* **2009**, 21, 954.
- Zujovic, Z. D.; Laslau, C.; Bowmaker, G. A.; Kilmartin, P. A.; Weber, A. L.; Brown, S. P.; Travas-Sejdic, J. *Macromolecules* **2010**, 43, 662.
- Zujovic, Z. D.; Laslau, C.; Travas-Sejdic, J. *Chem. Asian J.* **2011**, 6, 791.
- Trchova, M.; Sedenkova, I.; Konyushenko, E. N.; Stejskal, J.; Holler, P.; Ciric-Marjanovic, G. *J. Phys. Chem. B* **2006**, 110, 9461.
- Boyer, M. I.; Quillard, S.; Rebourt, E.; Louarn, G.; Buisson, J. P.; Monkman, A.; Lefrant, S. *J. Phys. Chem. B* **1998**, 102, 7382.
- Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, 24, 231.
- Zujovic, Z. D.; Nieuwoudt, M. K.; Bowmaker, G. A.; Kilmartin, P. A. "Detailed investigations of aniline oxidation products using NMR, FTIR, Raman and EPR spectroscopy", in preparation.
- Yang, D.; Mattes, B. R. *Synth. Met.* **2002**, 129, 249.
- Lindoy, L. F.; Atkinson, I. M.; Editors *Self-Assembly in Supramolecular Systems*; Royal Society of Chemistry: Cambridge, 2000; Vol. 7.