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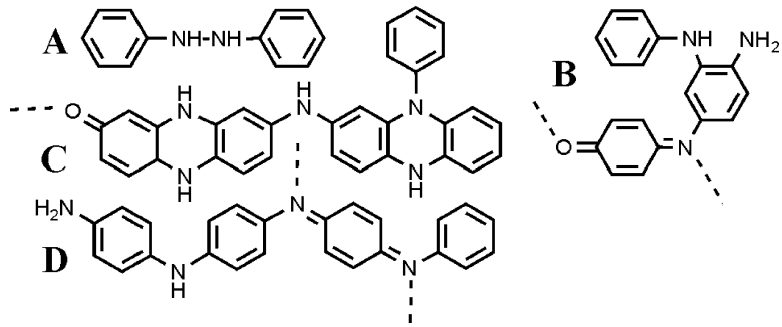

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Self-Assembled, Nanostructured Aniline Oxidation Products: A Structural Investigation

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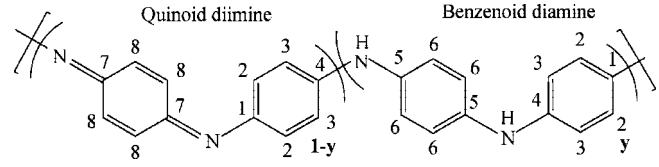
ABSTRACT: The structure and oxidation state of self-assembled nanostructures formed by oxidation of aniline with ammonium persulfate in the presence of alanine have been investigated by solid-state ^{13}C and ^{15}N NMR, FTIR, GPC, elemental, UV−vis, and SEM methods. These techniques have been applied to samples obtained 1 and 20 h after the beginning of the reaction in their doped as-synthesized form or after reduction with hydrazine or dedoping with NH_4OH or LiOH. Peaks at 66 and 72 ppm and a peak at 241 ppm in the ^{15}N NMR spectra are shifted downfield by about 1−6 ppm and upfield by about 80 ppm, respectively, relative to the positions expected for the amine and imine N atoms in polyaniline. This indicates a difference in molecular structure between the nanotube material and standard polyaniline. This may be attributed to the presence of either strong H-bonding or a fundamentally different bonding connectivity in the nanotube material. Despite the significant difference in morphology of the samples after 1 and 20 h as shown by SEM, the ^{13}C and ^{15}N spectra show resonances at very similar chemical shifts for the two reaction times. The differences in line width and intensity of the peaks in these spectra are attributed to an increased number of positive charges and to longer polymer chains for the longer reaction time. The previously postulated presence of phenazine-like units in the molecular structure within the nanotubes cannot be excluded due to possible overlapping of resonances from amine and tertiary nitrogens in the ^{15}N NMR spectra. The carbon and nitrogen NMR spectra show that the alanine is not incorporated into the aniline oxidation products. Chemical structures whose presence is consistent with the data obtained from solid-state NMR and the other methods applied in this work are proposed.

Introduction

During the past 20 years, due to various technological applications, electrically conducting polymers such as polyaniline (PANI) and its derivatives have been the subject of considerable attention.[1,2] There are many reports on the chemical and electrochemical synthesis and applications of various forms of PANI and their characterization in terms of electronic, magnetic, and optical properties (refs 1 and 2 and references therein). Interest in polyaniline has increased recently because of the fact that it can form "one-dimensional" structures such as nanotubes and nanowires.[3–17] Considering current trends toward miniaturization and the increased interest and activity in nano- and microtechnology, it is not surprising that nanostructures of conducting polymers have attracted such attention. The formation of nano- and microstructured materials from the oxidative polymerization of aniline with ammonium persulfate generally involves conditions of low initial acidity (e.g., the absence of added acid or the presence of weak organic acids in the reaction mixture),[18–22] and in some of these studies it has been suggested that the molecular structure of the resulting material differs significantly or even fundamentally from that of "standard polyaniline".[18,19,21] Thus, MacDiarmid et al. proposed that the product of the reaction carried out in dilute aqueous solution in the absence of initially added acid is a polyazane, in which the aniline units are connected via N−N bonds rather than via the normal head-to-tail C−N bonds observed in the standard polyaniline structure.[21] The C:N ratio in all forms of standard polyaniline should be 6, but elemental analysis of the polyazane material yields higher values in the vicinity of 7. This, together with the presence of oxygen in the product (deduced from the elemental analysis data), implies loss of nitrogen by overoxidation of the polymer, which is consistent with the proposed presence of benzoquinone units in the polymer structure.[21] Quite different structures have been proposed by Trchova et al. for the product of the same reaction carried out in more concentrated aqueous solutions.[19] In this study it was proposed that the reaction products are markedly sulfonated and contain phenazine units. Like polyaniline, the proposed phenazine structures should have a C:N ratio of 6, but the elemental analysis data reported by these workers yield values in the vicinity of 5, which is not consistent with any of the proposed structures. It therefore appears that more work is required to determine the molecular structure of these materials. This will probably be a key factor in understanding the mechanism of formation of the nanostructures.

Scheme 1. Chemical Structure of Polyaniline



Standard polyaniline consists of reduced base units B (benzenoid diamine) and oxidized base units Q (quinoid diimine) (Scheme 1). These units repeat, and the oxidation state of polyaniline depends on y: fully reduced with $y = 1$ (leucoemeraldine), fully oxidized with $y = 0$ (pernigraniline), and half-oxidized polyaniline with $y = 0.5$ (emeraldine base). The conductivity depends on the level of protonation and on the ratio of the oxidized to reduced forms. The highest conductivity corresponds to the structure with alternating and equal numbers of benzenoid and quinoid units, i.e., $y = 0.5$, after treatment with acid to produce the protonated (emeraldine salt) form which

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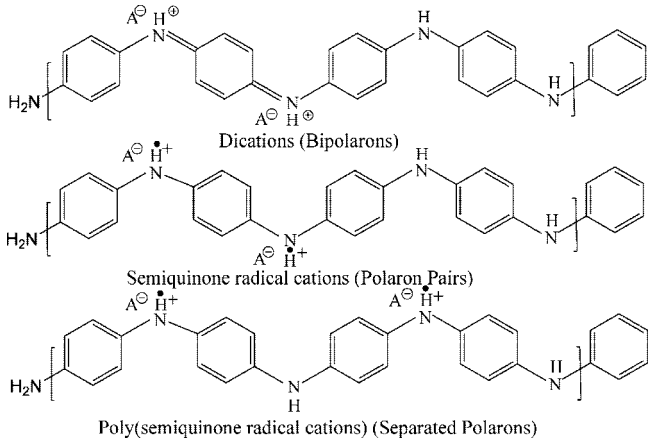
Scheme 2. Various Protonation States of the Emeraldine Salt Form of Polyaniline



includes a positive charge on nitrogen atoms thought to exist as polarons or bipolarons (Scheme 2).

A number of spectroscopic methods have been applied to "polyaniline" nanostructured materials in order to further elucidate their molecular structure.[13,18–22] However, to the best of our knowledge, there is no record of previous solid-state ^{13}C and ^{15}N CP/MAS NMR studies of polyaniline nanotubes. High-resolution solid-state NMR[23,24] has proven to be a very useful method in investigating the structural and dynamic aspects of conducting polymers and of polyaniline in particular.[25–49] In this study we present solid-state NMR as a nondestructive method, which enables investigation of the structure of PANI nanotubes using ^{13}C and ^{15}N CP MAS, NQS (nonquaternary suppression) and relaxation experiments, in comparison with results obtained for "standard" chemically synthesized polyaniline to obtain a better insight into the molecular structure of PANI nanotubes. The method of synthesis of the PANI nanotubes is similar to that reported previously, but with the additional feature that alanine was used as an organic acid in the reaction mixture. We have previously shown that a range of amino acids can be used for the formation of PANI nanotubes.[9] Amino acids have NH_2 and COOH functional groups, both of which provide potential sites for hydrogen bonding, and were shown to affect the inner diameter of the PANI nanotubes. Thus, in this paper we investigate possible changes in molecular structure with changes in morphology during the formation of the PANI nanotubes using the amino acid alanine and possible incorporation of alanine in the nanotube structure. The solid-state NMR data are supported by FTIR, GPC, UV−vis, elemental, and SEM experiments.

Experimental Section

Materials. "Standard" aniline, ^{15}N-labeled aniline, ammonium persulfate ($(NH_4)_2S_2O_8$, APS), and commercial polyaniline emeraldine base were obtained from Aldrich Chemical Co. "Standard" aniline and ^{15}N-labeled aniline were mixed to give a 50% ^{15}N-labeled sample of polyaniline. Aniline was distilled under reduced pressure and stored in the dark under nitrogen. The ^{15}N-labeled amino acid alanine was purchased from Sigma and was used as received without further treatment.

Synthesis and Dedoping. 50% ^{15}N-labeled aniline (0.186 g, 2 mmol) and ^{15}N-labeled alanine (0.0356 g, 0.4 mmol) were dissolved in Milli-Q water (5 mL) at room temperature. The solution was cooled in a refrigerator at 5 °C for 30 min, after which a precooled aqueous solution of 0.8 mol L^{-1} APS (2.5 mL) was added, to give initial concentrations of aniline = 0.267 mol L^{-1}, alanine = 0.053 mol L^{-1}, and APS = 0.267 mol L^{-1}. The initial pH was around 7−8, and this dropped quickly over the first hour to a pH of 3 and then more slowly to reach a pH of close to 1.5 after 3 h, where it remained as the reaction was continued for a total of 20 h, by which time a black-green precipitate had formed (yield 0.137 g). The mixture was filtered, and the precipitate was washed with water, methanol, and several times with acetone. Finally, the product was dried in vacuum at room temperature for 24 h. The above reaction was repeated, and the brown product produced after 1 h reaction time was collected (yield 0.0564 g). Dedoped samples of the 20 h reaction product were prepared by treatment with aqueous solutions of 15% ammonium hydroxide (NH_4OH) or 1% lithium hydroxide (LiOH) for 24 h and rinsing with water afterwards. The resulting powders were dark blue in color. The reduced sample was obtained by stirring a sample of the product from the initial synthesis (not dedoped) in a 35% hydrazine aqueous solution for 24 h at room temperature. The product was filtered and washed with excess water and dried under vacuum at 200 °C for 22 h.

Samples synthesized by the above method (with and without dedoping) using non-^{15}N-enriched aniline were subjected to elemental analysis after drying at 100 °C over silica gel. The results are given in Table 1, together with calculated values for PANI emeraldine base ($C_{24}H_{18}N_4$), the SO_4^{2-} acid-doped form ($[C_{24}H_{20}N_4]^{2+}SO_4^{2-} = C_{24}H_{20}N_4O_4S$), the HSO_4^- acid-doped form ($[C_{24}H_{20}N_4]^{2+}[HSO_4^-]_2 = C_{24}H_{22}N_4O_8S_2$), and the monohydrate of the SO_4^{2-} acid-doped form ($[C_{24}H_{20}N_4]^{2+}SO_4^{2-}\cdot H_2O = C_{24}H_{22}N_4O_5S$).

UV−vis Spectroscopy. For UV−vis spectroscopy the samples were dissolved in *N*-methylpyrrolidone containing 0.025 g mL^{-1} triethanolamine and 0.005 g mL^{-1} lithium bromide,[18] and the spectra were recorded using a Shimadzu UV-1700 spectrophotometer.

FTIR Spectroscopy. Infrared spectra in the range 400−4000 cm^{-1} were measured on pellets using a Perkin-Elmer 1600 FTIR spectrometer. The number of the scans was 10 with resolution 2 cm^{-1}.

SEM Characterization. The morphologies of the products were investigated using a Philips XL30S field emission scanning electron microscope (SEM). The samples for SEM were mounted on aluminum studs using adhesive graphite tape and sputter-coated with platinum. The diameters of the nanotubes were estimated by measuring 10 nanotubes from SEM images at 50 000× magnification using Adobe Photoshop 6.0 software.

^{13}C CP MAS NMR Spectroscopy. All solid-state NMR experiments were carried out on dry powder samples of nanotubes using a Bruker AVANCE 300 spectrometer operating at 300.13 MHz proton frequency. Basic spectra were obtained by using the "standard" CP MAS (cross-polarization magic angle spinning technique). The experiments were carried out using a 7 mm Bruker spinning probe with zirconia rotors. The proton 90° pulse duration was 4.2 μs, and the frequency of the decoupling field was 62.5 kHz. The contact time was 1.5 ms. The recycle delay was 1−2 s, and the sweep width was 40 kHz. Experiments were carried out with 3000 scans (2500 for the sample obtained after 1 h) at ambient temperature using freshly prepared samples enclosed in the rotors. The ^{13}C chemical shift scale is referenced to TMS. Samples were rotated at 7000 ± 1 Hz, and the magic angle was adjusted by maximizing the sidebands of the ^{79}Br signal of a KBr sample.

^{15}N CP MAS NMR Spectroscopy. 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 ^{15}N chemical shift scale is referenced to $^{15}NH_4NO_3$ (δ $^{15}NH_4^+ = 0$ ppm). The sweep width was 30.03 kHz. The 90° pulse was 7.3 μs, and the recycle delay was 1.5−2 s. The rotation frequency was 7000 ± 1 and 6250 ± 1 Hz for NQS experiments.

Gel Permeation Chromatography (GPC). The GPC setup consisted of a Waters 515 HPLC pump, two Polypore Plus linear columns (300 × 7.5 mm), a Polypore guard column (Polymer Laboratories), and a Styragel HR6 column (Waters). The RI detector used was a Waters differential refractometer, and both the RI detector and columns were heated at 35 °C. The eluent was *N*-methylpyrrolidone containing 0.025 g mL^{-1} triethanolamine and 0.005 g mL^{-1} LiBr, and the flow rate was 0.3 mL min^{-1}. Both samples were at 2 mg mL^{-1} in the same eluent, and the injected

Table 1. Elemental Analyses and Elemental Compositions of the Aniline Oxidation Products

system	C (%)	H (%)	N (%)	S (%)	O (%, by difference)
1 h reaction time	67.3	5.0	12.2	1.9	13.64
20 h reaction time[a]	63.6 ± 0.1	4.8 ± 0.1	11.8 ± 0.05	3.5 ± 0.1	16.2 ± 0.1
20 h reaction time, sample used for dedoping[a]	63.1 ± 0.1	4.73 ± 0.03	12.05 ± 0.06	4.44 ± 0.01	15.7 ± 0.3
20 h reaction time, dedoped[a]	69.8 ± 0.1	4.8 ± 0.1	13.5 ± 0.04	2.6 ± 0.05	9.3 ± 0.3
PANI EB ($C_{24}H_{18}N_4$)	79.54	5.01	15.45		
$[C_{24}H_{20}N_4]^{2+}SO_4^{2-}$	62.60	4.38	12.17	6.96	13.90
$[C_{24}H_{20}N_4]^{2+}[HSO_4^-]_2$	51.61	3.97	10.03	11.48	22.91
$[C_{24}H_{20}N_4]^{2+}SO_4^{2-}\cdot H_2O$	60.24	4.63	11.71	6.70	16.72

[a] Averages of two determinations for samples taken at the reaction times indicated.

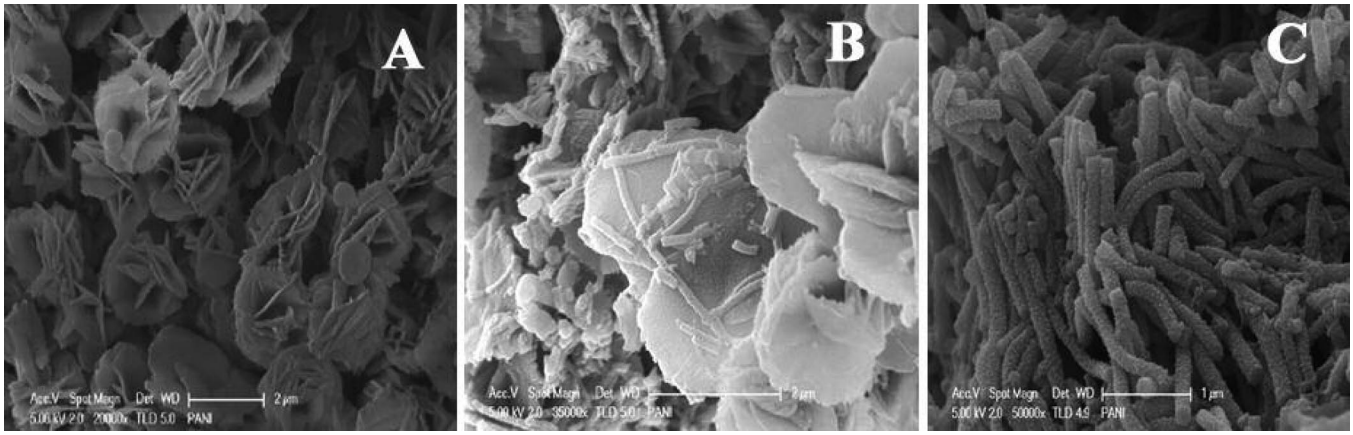
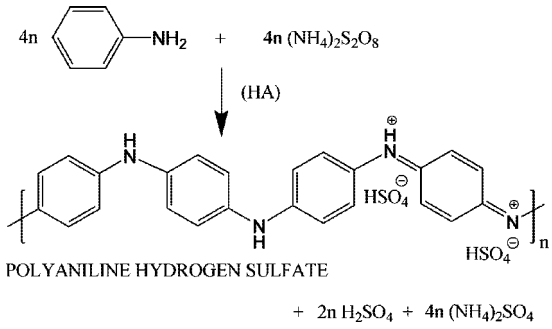


Figure 1. SEM micrographs of the aniline oxidation products synthesized using APS in the presence of alanine, obtained after 1 h (A), 3 h (B), and 20 h (C) reaction time.

Scheme 3. Possible Reaction Involved in the Oxidation of Aniline with Ammonium Peroxydisulfate in the Presence of Alanine (HA)[a]



[a] The byproducts are sulfuric acid and ammonium sulfate.

volume was 200 μL. Solutions were filtered through 0.45 μm syringe filters before injection. The Easycal PS-1 set of 10 polystyrene standards from Polymer Laboratories were used to determine a calibration curve under the same conditions.

Results and Discussion

SEM Results. SEM images of the samples obtained after 1, 3, and 20 h are shown in Figure 1. After 1 h (Figure 1A) flakes (roselike morphology) are observed,[50] and these predominate in the sample. After 3 h, the fibrilar structures start to develop (Figure 1B), which ultimately lead to predominant fibrous morphology after 20 h (Figure 1C) and to the presence of nanotubes.

Elemental Analyses and GPC Studies. One possible course of the reaction involved in the formation of the products is the oxidative coupling of aniline molecules to form partially oxidized acid-doped PANI, as shown in Scheme 3. The observed decrease in pH during the course of the reaction is consistent with the production of acid in the reaction. Elemental analyses of the products were carried out in order to provide more information on the nature of the products and the degree of oxidation and acid doping involved. GPC studies were carried out in order to determine the molecular weight and hence the degree of polymerization of the materials.

The C, H, N, S elemental compositions for the samples taken after 1 and 20 h reaction times (Table 1) are not very different but do show a slight decrease in C, H, N and a slight increase in S, O that is consistent with an increase in doping level with time as the pH decreases during the course of the reaction. This is in contrast with previously published results for similar systems, where no such trend was observed.[19] The C:N atomic ratios derived from the elemental analyses for the 1 and 20 h samples are 6.4 and 6.3, the H:C ratios are 0.89 and 0.91, and the S:N ratios are 0.07 and 0.14, respectively. The C:N atomic ratios are only slightly greater than the value 6.0 expected for PANI structures, in contrast to the situation for other recently reported micro- or nanostructured materials produced by polymerization of aniline under conditions of low initial acidity.[19,21] The ^{15}N and ^{13}C NMR results (see below) indicate that the alanine present in the reaction mixture is not incorporated in the product. This is consistent with the elemental analysis data because incorporation of alanine would result in a C:N ratio of less than 6. The S:N atomic ratios are less than those expected for 100% acid-doped emeraldine base PANI (0.25 or 0.5 for SO_4^{2-} or HSO_4^- doping, respectively). Assuming that all of the mass deficit in the elemental analyses is attributed to the presence of oxygen (Table 1), the resulting O:S ratios are 14.7 and 9.2, respectively. These are higher than the value 4.0 expected for SO_4^{2-} or HSO_4^-, suggesting the presence excess oxygen in the structure. This discrepancy could arise from overoxidation of the polymer, for example by the introduction of carbonyl groups on the six-member carbon rings, as was proposed in one recent study of similar materials.[21] Two possible types of overoxidation can occur: (a) conversion of aromatic

amine to carbonyl groups and (b) conversion of aromatic C−H to carbonyl groups.[21] Type (a) oxidation would result in an increase in the C/N ratio, whereas this ratio would remain at the theoretical value of 6.0 for type (b) oxidation. The observed values of 6.3 and 6.4 suggest the presence of a small degree of type (a) oxidation, but this is not the case for the dedoped 20 h reaction time sample, for the which the C/N ratio has the value 6.0. The occurrence of type (b) oxidation should in principle be evidenced by a reduction in the H:C ratio from the theoretical values of 0.75 (emeraldine base form) or 0.83 (SO_4^{2-}-doped emeraldine salt). However, the observed values of about 0.9 are both higher than these. An obvious way of adding the required excess of oxygen and hydrogen to the formula is in the form of water molecules, which could be incorporated in the polymer structure as water of hydration of the dopant anion. Assuming sulfate as the dopant, and one molecule of water per sulfate ion, results in the formula $[C_{24}H_{20}N_4]^{2+}SO_4^{2-}\cdot H_2O = C_{24}H_{22}N_4O_5S$, and the resulting O and H elemental compositions are similar to those observed for the 20 h reaction time product, but with significant discrepancies for the C and S values (Table 1).

The elemental analysis results show that the S content of the initial doped products was reduced by a factor of 1.8 after dedoping. The presence of residual sulfur after dedoping has been taken by other workers as evidence of sulfonation of the polymer by the ammonium persulfate used in the polymerization reaction.[18,19] However, this has never been proved directly, and the fact that aromatic sulfonation is readily reversed under dilute acid conditions[51] renders this possibility unlikely. A more likely explanation is that not all of the dopant is removed in the dedoping process, a situation that is known to occur in other conducting polymer systems involving sulfate/bisulfate as dopant.[52] For the present system, assuming that the dopant is sulfate, the reduction in S content upon dedoping corresponds to a reduction in the doping level from 50−60% to 33%.

GPC studies were carried out on samples after 1 and 20 h reaction times. Two incompletely resolved peaks in the chromatogram of the 1 h sample correspond to molecular weights of 970 and 1660. The main peak in the chromatogram of the sample after 20 h corresponds to a molecular weight of 32 700, with much smaller peaks at 1740 and 3580. Band fitting was used to resolve the different bands in the GPC traces of the two samples, and the mean molecular weight of each sample was estimated by averaging the areas of the two peaks in the 1 h sample and three peaks in the 20 h sample. The calculated mean values are 1300 and 25 600, respectively. The average molecular weight therefore increases by a factor of about 20 between the two reaction times. The 1 h product thus consists of oligomers typically containing 10−20 monomer units.

UV−vis Spectroscopy. The UV−vis spectra of the 1 and 20 h reaction time samples dedoped with triethanolamine and dissolved in *N*-methylpyrrolidone with the addition of small amounts of LiBr are shown in Figure 2. The peak at 369.5 nm in the structures formed after 1 h could be shifted from the usual position in standard PANI at about 330 nm (benzenoid rings) due to the branching.[53] The shoulder at about 500 nm could be due either to branching or to short nonconjugated linear oligomers (BQB, 450 nm; BQBB, 570 nm; BQBQ, 590 nm; B, benzenoid; Q, quinoid).[54] According to previous reports,[55,56] oxidation with APS results in the formation of products with a higher oxidation state, i.e., *N*-phenyl-1,4-benzoquinonediimine (PBQ), which has maximum in the UV−vis spectrum at 430 nm. The hydrolysis of nitrogen−carbon bonds in PBQ can result in either chain breaking or nitrogen elimination by oxygen if an end group is involved. This is consistent with the somewhat higher C:N atomic ratio of 6.4 derived from the elemental analyses for the 1 h sample.

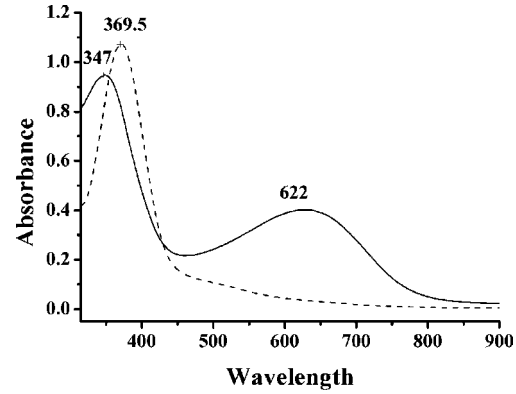


Figure 2. UV−vis spectra of the 1 and 20 h reaction time samples in *N*-methylpyrolidone.

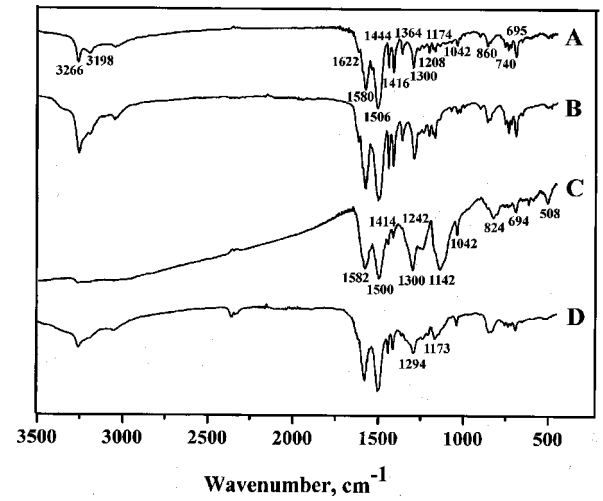


Figure 3. FTIR spectra of aniline oxidation products synthesized with APS in the presence of alanine, (A) after 1 h reaction time, (B) the same sample after reaction with hydrazine, (C) after 20 h reaction time, and (D) the same sample after reaction with LiOH.

As the acidity increases, para-coupling becomes more important so the peak (sample after 20 h) shifts to 347 nm, which is closer to the value for PANI. At the same time a peak at 622 nm (from quinoid units) appears which is in line with IR spectroscopy (see below). This clearly distinguishes the material from the proposed "polyazane" material that is produced in similar reactions carried out in more dilute solution, which shows peaks at 272 and 377 nm.[21] The UV−vis spectrum after 20 h suggests the presence of the usual polyaniline structure (Scheme 1, $y = 0.5$).

FTIR Spectra. The main peaks in the FTIR spectra of the sample after 1 h reaction time, with and without hydrazine, and of the sample after 20 h reaction time with and without LiOH dedoping, are shown in parts A, B, C, and D of Figure 3, respectively. In the FTIR spectrum of the sample after 1 h reaction time (Figure 3A) two bands at 3266 and 3198 cm^{-1} are assigned to different types of intra- and intermolecular hydrogen bonds (N−H···N stretching vibrations of secondary amine).[18–20,57,58] It is important to note that the intensity of the free N−H band[57,58] is very weak and appears only as a shoulder at about 3370 cm^{-1} (Figure 3B). This implies that the sample even after 1 h is self-associated through hydrogen bonding. It has been suggested that hydrogen bonds are very important in forming the self-assembled supramolecular nanotube structures.[18–20] The strong bands in Figure 3A at 1580 and 1506 cm^{-1} can be attributed to C=C stretching in the quinoid and benzenoid rings, respectively.[19] However, the relatively low

intensity of the 1580 cm^{-1} band suggests an underoxidized structure, with a relatively small quinoid component. Also, there is a band due to aromatic stretching vibrations at 1444 cm^{-1}.[19] The band at 1416 cm^{-1} has previously been assigned to the symmetric stretching of phenazine rings[19] that may be formed in small amount at the beginning of the reaction. This band is not usually observed in the spectra of "standard" polyaniline, synthesized at low pH.[19] It has previously been suggested that the role of the phenazine-like units (due to aniline coupling in *ortho*-position at higher pH) is to promote formation of nanotubes and to provide a template for growing the supramolecular nanotube structure and ordering of oligomers.[19] Bands at 1364 and 1300 cm^{-1} are attributed to C−N stretching vibrations.[19]

The FTIR spectra recorded in the present study are very similar to those reported previously in a study of Trchova et al.,[19] and the assignments suggested in that work can be considered for the present system as well. Two key consequences of these assignments are the proposed presence of sulfonate groups and phenazine rings in the structure. However, the nature of vibrational spectroscopy in the spectral region concerned is such that these assignments do not constitute unambiguous proof for the existence of the proposed structural units. The fact that the reaction conditions are not conducive to aromatic sulfonation casts some doubt on the proposed presence of sulfonate groups (see above). The evidence for the presence of phenazine units in the structure appears to rest mainly on the presence of a strong band at 1416 cm^{-1}.[19] Thus, flakelike morphology in the sample after 1 h could be produced by the presence of phenazine-like, branched structures. It is well-known that electrochemical polymerization of 2-aminodiphenylamine (*ortho*-) dimers produce "flaky" structures (see Figure 1A), while 4-aminodiphenylamine (*para*-) dimers create more fiberlike structures.[59]

However, in a study of the electrochemical polymerization of the aniline dimer 2-aminodiphenylamine, where the formation of phenazine units is expected because of the presence of two amino groups *ortho* to each other, no band is present at 1416 cm^{-1}, and a band at 1177 cm^{-1} in the IR spectrum is attributed to phenazine-like units in the product.[59] This illustrates the difficulty of determining the presence of specific complex organic structures from bands in the IR spectra that do not correspond to characteristic group frequencies. We do not reject out of hand the previous hypotheses based on assignments of bands in the IR spectra. Rather, we would like to emphasize the uncertainties involved and the need for further proof. Solid-state NMR spectroscopy provides another approach, and because NMR spectra are generally simpler and easier to interpret than vibrational spectra, the standard of proof is likely to be much better.

^{13}C CP/MAS NMR Spectra. The solid-state ^{13}C CPMAS NMR spectra of aniline oxidation products after 1 h reaction time (A), after 1 h reaction time and reduced with hydrazine (B), after 20 h reaction time (C), after 20 h reaction time and dedoped with NH_4OH (D), and after 20 h reaction time and dedoped with LiOH (E) are shown in Figure 4. The assignment of the resonance peaks in the ^{13}C CPMAS spectra shown in Figure 4 is obtained from previously published data from "standard" chemically synthesized PANI.[25,26,29] The presence of the most deshielded peak at 181.5 ppm (see Figure 4A) is not characteristic for the spectrum of "standard" chemically synthesized PANI. The origin of this peak is not clear at the moment. However, in a study of enzymatically synthesized PANI it was suggested that the resonance at 173.5 ppm might be due to oxidation of chain ends,[49] although we could not detect the presence of an N═O group in our ^{15}N spectra. On the basis of the chemical shift position, the peak at ≈180 ppm could originate from the C═O group from alanine. However, in that case there should be also peaks at ≈50 ppm (C_α) and ≈15 ppm (C_β)[60] which are not detected in the carbon spectra, which suggests that alanine is not incorporated in the nanotube structure. The 181.5 ppm signal could be due to the presence of carbonyl groups on the six-membered rings, as has been proposed previously in studies of similar materials.[21] As mentioned above, this carbonyl group could arise due to the presence of a higher oxidation state of aniline, i.e., *N*-phenyl-1,4-benzoquinonediimine (PBQ) which can undergo a degradation reaction to produce quinoneimine end groups[56] (see Scheme 5). The peak at 164.6 ppm could be assigned to nonprotonated imine quinoid carbon (C-7, see Scheme 1). This is shifted by about 3−6 ppm downfield relative to the peak obtained from "standard" chemically synthesized PANI. The peak at 149.5 ppm could be attributed to nonprotonated carbon attached to the imine nitrogen C-1, consistent with the presence of quinoid rings. The peak for protonated quinoid carbon (≈137 ppm for "standard" chemically synthesized PANI, according to Kaplan et al.[29]) could be partly overlapped with the peak at ≈140.8 ppm due to nonprotonated carbons (C-4 and C-5).[29] The peak at 124.8 ppm is assigned to protonated benzenoid carbon (C-2,3). The resonance at 129.6 ppm could either be associated with protonated quinoid carbons C-8 according to Thiyagarajan et al.[48] or may be partly attributed to the presence of bipolarons, i.e., positively charged domains.[29,40] This could be the reason for the slight decrease in intensity of the peak at 128.9 ppm after dedoping with NH_4OH (Figure 3D). However, the resonance is still present even after dedoping,[40] which implies that the main part of the resonance at 129.6 ppm originates from protonated quinoid carbons C-8.

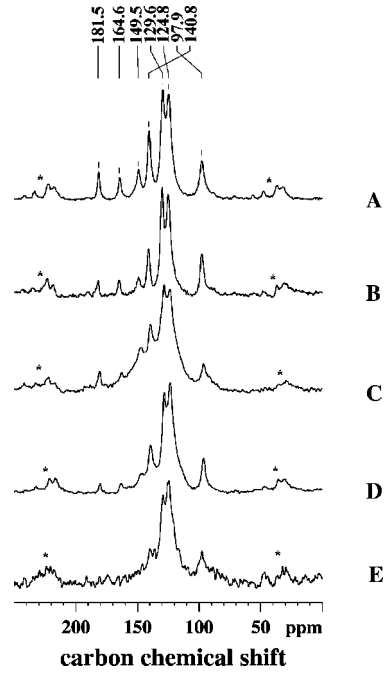


Figure 4. Solid-state ^{13}C CPMAS NMR spectra of aniline oxidation products synthesized using APS in the presence of alanine: after 1 h reaction time (A), after 1 h reaction time and reduced with hydrazine (B), after 20 h reaction time (C), after 20 h reaction time and dedoped with NH_4OH (D), and after 20 h reaction time and dedoped with LiOH (E). The asterisks denote spinning sidebands.

The peak at 97.9 ppm found in all spectra (Figure 4A−E) is not characteristic for "standard" chemically synthesized PANI.[25,26,29] It might originate from the reaction of polyaniline chains with APS to produce sulfonic acid substitution of the PANI. However, the calculated carbon chemical shifts for the SO_3H substituted leucoemeraldine oligomer structure do not

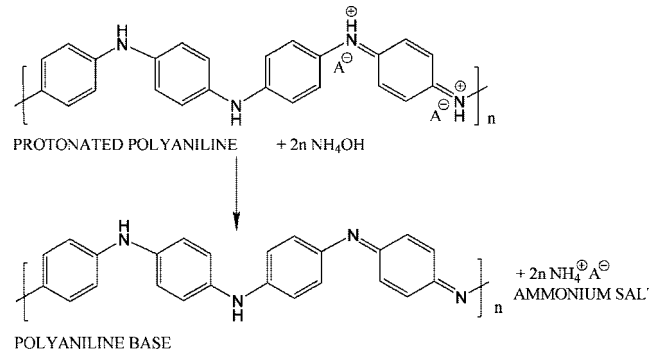
match the peak at 95 ppm.[61] Cotarelo et al. reported the synthesis and characterization of electroactive films deposited from aniline dimers.[59] They reported ^{13}C NMR assignments of the signals from the products obtained by electrochemical oxidation of *ortho*- and *para*-substituted aniline dimers in a strongly acidic medium. On the basis of NMR predictions, they assigned a peak at 94.7 ppm to the CH carbon in a branched, phenazine-like structure formed from the coupling at the *ortho*-position. Sahoo et al. reported a peak at 95.2 ppm in their ^{13}C CP MAS spectrum of enzymatically synthesized PANI in the presence of a template, but they did not assign this peak.[47] In a subsequent paper[49] they presented a model for a branched PANI structure along with the predicted spectrum. In this predicted spectrum they obtained a peak at ≈96 ppm, which (based on their model) could be due to the presence of branching in the polymer structure. Also, the peak at 95.0 ppm is detected in the ^{13}C spectra of safranine and phenosfranine structures which have phenazine-like units.[62]

The UV−vis results (see Figure 2) indicate that the polyaniline is in a partially oxidized state dominated by benzenoid diamine components, i.e., $y > 0.5$ (see also Scheme 1 and Figures 3 and 4). However, because of the lack of spectral resolution, i.e., due to overlapping of the resonances in the ^{13}C NMR spectra, it is difficult to quantify exactly the ratio of oxidized to reduced units. Also, the relatively narrow resonances indicate that the sample mainly consists of oligomers or short chains (corresponding to a small peak at 1300 cm^{-1} and the lack of the peak at 1142 cm^{-1} in the IR, Figure 3A).

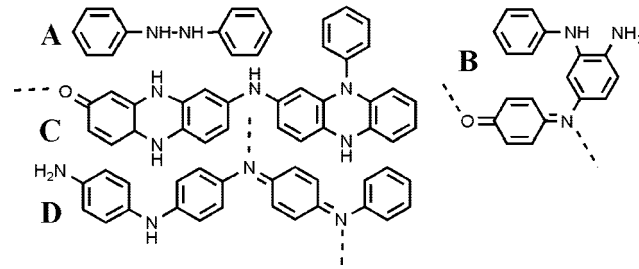
Reduction with hydrazine did not change the overall features in the spectrum obtained from the 1 h reaction time sample, which is in line with the FTIR results (Figures 4B and 3B). However, a noticeable reduction was observed in the intensities of the peaks downfield from 140 ppm (suggesting a decreasing proportion of diimine units) and in the line widths of the peaks, implying that a portion of the polaronic sites had been removed. One possible reason for this difference could be the decrease in the fraction of quinoid units upon reduction. Furthermore, the resonances in the spectrum of the 20 h reaction time sample (Figure 4C) are broader compared to the spectrum of the 1 h reaction time sample (Figure 4A). This difference can be attributed to the progressive increase of the chain lengths with reaction time and to the heterogeneity of the charge distribution, as the sample becomes more conductive (the local variations in charge density along the polymer backbone, see Scheme 2), and this is in accordance with the FTIR data (see Figure 3C). There are differences in the line widths, but not in the positions of the peaks. Thus, there are some structural variations although the overall spectral pattern looks similar. These basic structures are most probably aniline oligomers or *short chains*, which are significantly less protonated and conductive. This is in accordance with the GPC results (see above). However, the polymer obtained after 20 h is protonated (the acidity increases during the reaction), as indicated by the broadening in the spectrum (Figure 4C) and the increase in the intensity of the band at 1142 cm^{-1} (Figure 3C).

After dedoping of the 20 h reaction time sample with NH_4OH (see Scheme 4) some (but not all) of the charge density was removed, and the resolution and sensitivity of the NMR were improved (Figure 4D), as expected. The presence of residues of positive charge after dedoping with NH_4OH was confirmed using XP spectroscopy (manuscript in preparation). To remove charge density more efficiently, the "stronger" dedopant LiOH was used.[40] However, instead of obtaining better resolved peaks in the spectrum (narrower resonances),[40] a spectrum which indicates a partly changed structure (Figure 4E) was obtained. This observation is in line with the FTIR results (see Figure 3D).

Scheme 4. Dedoping of Protonated Polyaniline with NH_4OH



Scheme 5. Proposed Structural Units Present in the Nanostructured Aniline Oxidation Products[a]



[a] Dashed lines represent possible hydrogen bonds.

To determine whether the peak at ≈180 ppm originates from alanine, an experiment in the absence of this amino acid was performed, and the resulting spectrum is shown in Figure 5. As can be seen from the spectrum, all of the resonances are at similar chemical shift positions to those in the spectrum of the sample synthesized in the presence of the amino acid. The peak at ≈180 ppm is still present, despite the absence of alanine in the synthesis. This in line with the paper of Konyushenko et al.[20] where the acetate counterions were not detected, and the resulting PANI is protonated only by sulfuric acid resulting from the reduction of APS. Thus, it is likely that the peak at ≈180 ppm is mainly due to the oxidation of PANI by APS and hydrolysis.

The different 3D structures of "standard" PANI and PANI nanotubes and the presence of heterogeneously located nonconducting and conducting domains which could shift peaks significantly contribute to the complex nature of the ^{13}C spectra and make complete assignments difficult. We have therefore carried out a series of spectral editing, NQS experiments at different dephasing times for the 1 h reaction time sample, and

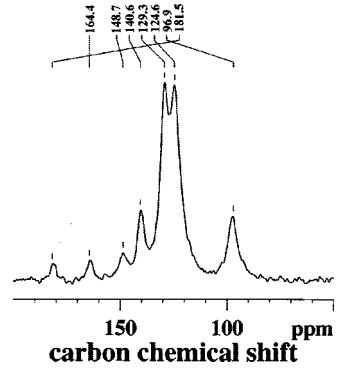


Figure 5. ^{13}C CP MAS spectrum of PANI nanotubes synthesized in water, without alanine, by oxidation with APS. The sample was taken after 1 h.

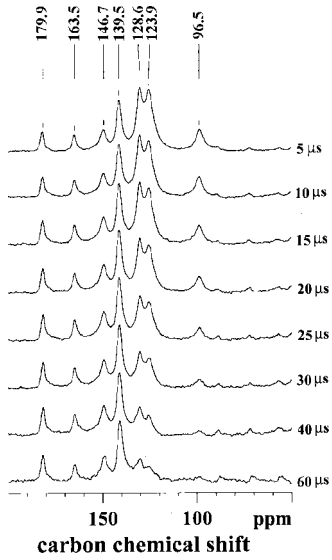


Figure 6. Series of spectral editing (^{13}C NQS) spectra at different dephasing times for the 1 h reaction time sample synthesized with alanine by oxidation with APS.

Table 2. Data from ^{13}C Variable Contact Time Experiments for the 1 h Reaction Time Sample Synthesized with Alanine by Oxidation with APS

peak (ppm)	T_{CH} (μs)	peak (ppm)	T_{CH} (μs)
180.5	754	128.7	39
163.5	450	123.7	33
146.5	270	96.5	31
139.5	270		

these are presented in Figure 6. It is known that NQS experiments give spectra in which protonated carbon resonances are partially suppressed so that the nonprotonated carbons dominate the spectra.[23,24]

According to NQS, the peaks at 128.6, 123.9, and 96.5 ppm can be assigned to protonated quinoid and benzenoid structures and the peaks at 179.9, 163.5, 146.7, and 139.5 ppm are due to nonprotonated carbons. This is (apart from the peaks at 179.9 and 96.5 ppm) in accordance with our previously published assignments for "standard" chemically synthesized PANI.[25,26] At this point we can assume that the peak at 96.5 ppm originates from a CH unit and that its presence could be the result of branching.[49,59] To confirm this conclusion, we performed ^{13}C variable contact time experiments (CPVC). The T_{CH} (cross-correlation time for magnetization transfer from protons to carbons) data are given in Table 2, and the spectra shown in Figure 7 are obtained from ^{13}C CPVC experiments. The spectra are shown only up to 2 ms to illustrate the first part of the contact curve, which mainly relates to the rate of magnetization transfer. Longer T_{CH} relaxation times correspond to carbons which are far from protons or to those that have high mobility, whereas protonated carbons and those that originate from rigid structural units have short contact times. It can be seen from Figure 7 that the peaks at 96.8, 123.7, and 128.7 ppm very rapidly reach almost the maximum intensity after only 80 μs of contact time. Accordingly, the peaks at 96.8, 123.7, and 128.7 ppm are protonated (T_{CH} = 31−39 μs), while peaks at 180.5, 163.6, 146.5, and 139.5 ppm are not (T_{CH} = 270−754 μs), in agreement with the above assignments and NQS results.

At this point it is interesting to look back at the SEM results (Figure 1). These show obvious differences in morphology of the samples obtained after reaction times of 1 and 20 h, when the nanotubes are well formed. The corresponding NMR spectra show differences in the line widths and relative intensities, but not in the positions of the peaks. The line widths probably

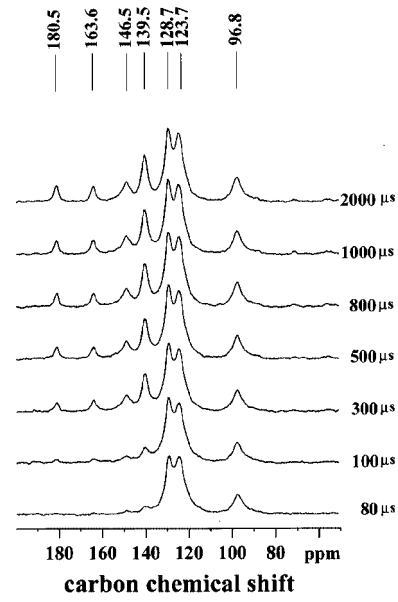


Figure 7. Series of ^{13}C spectra at different variable contact times for the 1 h reaction time sample synthesized with alanine by oxidation with APS.

increase due to polymerization that is involved in the formation of the nanotube structure and consequently due to increasing in conductivity of the sample. We have also shown that nontypical PANI bands in the FTIR spectra after 1 h (Figure 3A) decrease in intensity (Figure 3C) relative to the standard PANI bands. In these cases, the unusual chemical groups associated with the flakelike structures (initially about 30% of the final mixed product after 20 h) are not added to as the nanotubes are formed, being largely a form of regular polyaniline, but instead their intensity in the NMR and FTIR spectra becomes diluted with longer reaction times.

It can be concluded that the polyaniline structure with benzenoid and quinoid units predominates due to the prevalence of coupling at the *para*-position as the acidity increases with time.[18,19] However, detection of non-PANI units in the ^{13}C spectra and their quantification is a problem due to overlapping of such peaks with those of PANI. To achieve better resolution and simplify the spectral analysis, ^{15}N CP MAS spectroscopy has been applied.

^{15}N CP/MAS NMR Spectra. ^{15}N CP/MAS spectra obtained from ^{15}N-labeled samples after 1 and 20 h reaction times are shown in Figure 8, A and C, respectively. The following resonances were observed: a peak at 240.7 ppm and two overlapping peaks at 66.2 and 71.8 ppm. The two peaks at 66.2 and 71.8 ppm are shifted downfield[47,49] by about 1−6 ppm with respect to the uncharged amine−NH peak (65 ppm) observed in the spectrum of "standard" PANI.[26,40] A more significant feature is the missing imine =N− peak at 320 ppm. Instead, there is a peak at 240.7 ppm (≈80 ppm upfield with respect to the imine peak in "standard" PANI). This peak decreases in intensity in the spectrum of the 20 h reaction time sample (Figure 8C) relative to the corresponding peak in the spectrum of the 1 h reaction time sample. Also, there is a significant difference in the shape of the 241 ppm peak relative to that of the imine resonance in the spectrum of "standard" PANI; the latter shows chemical shift anisotropy (CSA) characteristics,[26,40] whereas the resonance found at 240.7 ppm in the spectra presented here is relatively narrow, symmetrical, and practically free of sidebands, indicative of a low CSA. The lack of CSA is most likely due to a more symmetrical electron distribution around the nitrogen atom concerned. This indicates a substantial difference in molecular structure between the nanotube material

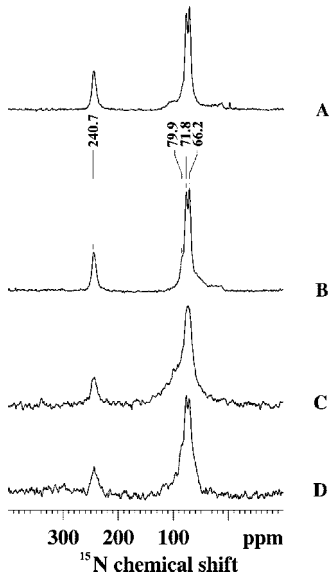


Figure 8. Solid-state ^{15}N CPMAS NMR spectra of the sample synthesized with alanine by oxidation with APS: 1 h reaction time (A), 1 h reaction time and reduced with hydrazine (B), 20 h reaction time (C), and 20 h reaction time and dedoped with LiOH (D).

and standard polyaniline. This may be attributed to the presence of either strong H-bonding or a fundamentally different bonding connectivity in the nanotube material, as discussed further below. In the ^{15}N spectrum of the 20 h reaction time sample the peaks at 66.2 and 71.8 ppm become broader and overlapped, forming a single broad peak centered at about 70 ppm. Because of this broadening and overlapping, it is difficult to say how much the resonances are shifted due to the presence of positive charges. In order to get a better insight into this, reduction with hydrazine of the 1 h sample was carried out (Figure 8B), resulting in removal of the small shoulder at 100−150 ppm. However, the 70 ppm peaks remain. Assuming a molecular structure similar to that of "standard" PANI, the peak at 240.7 ppm could be assigned to uncharged imine nitrogens, hydrogen bonded with a proton from the amine nitrogens that give rise to the signals at 70 ppm. This is consistent with the results of Wehrle et al. where the assignment was based on the ^{15}N NMR studies of model compound azophenine.[63] In this compound there is a hydrogen bond between an unprotonated imine nitrogen and hydrogen from −NH which shifts the imine peak upfield. Also, in the paper of Sahoo et al., which reported a study of enzymatically synthesized polyaniline, a resonance at 275 ppm was assigned to imine nitrogens hydrogen bonded with the amine nitrogens.[49]

An HSQC (heteronuclear single quantum correlation) experiment carried out the 1 h sample dissolved in DMSO (dimethyl sulfoxide) showed only N−H correlation for the 70 ppm signals. This implies that the peak at 240.7 ppm which is not observed in the HSQC experiment originates from nitrogen which is not covalently bonded to hydrogen.

In addition, we performed dedoping of the 20 h sample with the strong dedopant LiOH (see Figure 8D), which is capable of breaking hydrogen bonds.[40] This should result in an downfield chemical shift of the peak at 240.7 ppm toward the position of the imine peak in the spectrum of "standard" PANI (≈320 ppm). The resolution in the amine spectral region is somewhat improved, and the two peaks in the amine region are now resolved, but it is still difficult to say how much the amine peaks are shifted due to dedoping because of the broadening in the spectrum of the 20 h sample. Nevertheless, better resolution after dedoping implies that the amine nitrogens are affected by positive charges in the doped sample. The shoulder due to

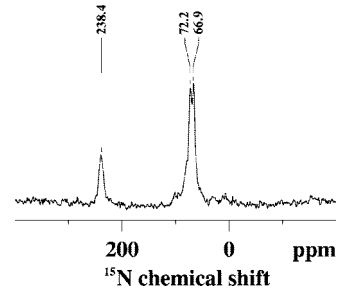


Figure 9. ^{15}N CP MAS spectrum of aniline oxidation products synthesized in water, without alanine, by oxidation with APS. The sample was taken after 1 h.

positive charges is largely removed (see also Figure 3D). However, there is still a part of this shoulder which has been not removed (Figure 8D). This means that sample is not completely dedoped with LiOH (EPR, not shown). The area under the peak at 240.7 ppm increases after dedoping relative to the doped sample which could indicate its imine origin. However, it is still at the same chemical shift position, which suggests that imine nitrogens are hydrogen bonded in the dedoped form as well[27] (Figure 3D) and that positive charges are still present (shoulder between 100 and 150 ppm, Figure 8D).[49] Colomban et al.[64] have reported the inversion of hydrogen bonding; i.e., the same nitrogen can act as a proton donor in the semiquinoid and as an acceptor in the quinoid segment.

There is a broad, low-intensity band in the region between 0 and 50 ppm. A possible assignment of this band (possibly several mutually overlapped lines) is to aniline end groups $-NH_2$ which should be at ≈ 30 ppm, anilinium ion end groups $-NH_3^+$ at 25 ppm, and $-NH_2^+$ groups at −2 ppm,[47] along with the peak at ≈15 ppm which is a spinning sideband of the imine peak.[47]

The resonances in the ^{15}N spectrum of the 1 h reaction time sample are narrower compared to those for the 20 h reaction time sample. This is probably due to a lower concentration of positive charges and shorter oligomeric structures present after 1 h of the reaction time. To obtain further information to assist with band assignments, NQS and variable contact time experiments were performed.

As ^{15}N-labeled alanine was used in the synthesis, there should be also additional peak (around 100 ppm)[65] from this amino acid if it was incorporated in the product. However, in this case the situation is not quite clear since the positively charged imine nitrogen shoulder partly covers that same chemical shift region (Figure 8A,C). Nevertheless, there is no peak even after reduction with hydrazine (see Figure 8B) and removing the shoulder.

To further determine whether alanine is incorporated in the nanotube structure, an experiment in the absence of this amino acid was performed, and the resulting spectrum of the sample taken after 1 h is shown in Figure 9. As can be seen from the spectrum, all the peaks are still present, despite the absence of alanine in the synthesis, and all of the resonances are at similar chemical shift positions to those in the spectrum of the sample synthesized in the presence of the ^{15}N-labeled amino acid. This is in line with ^{13}C results and our suggestion that alanine is not significantly incorporated into the nanotube structure.

The NQS spectra from 16 to 160 μs dephasing time are shown in Figure 10. Considering the fact that the peaks at 66.2 and 71.8 ppm should belong to amine peaks, they should dephase significantly faster than the imine peak if there were no protons near to it (as in the case of "standard" chemically synthesized PANI). However, the peak at 240.7 ppm dephases relatively fast, perhaps not as fast as the amine peaks, but still much faster than for nitrogen which is not covalently bonded to a proton.

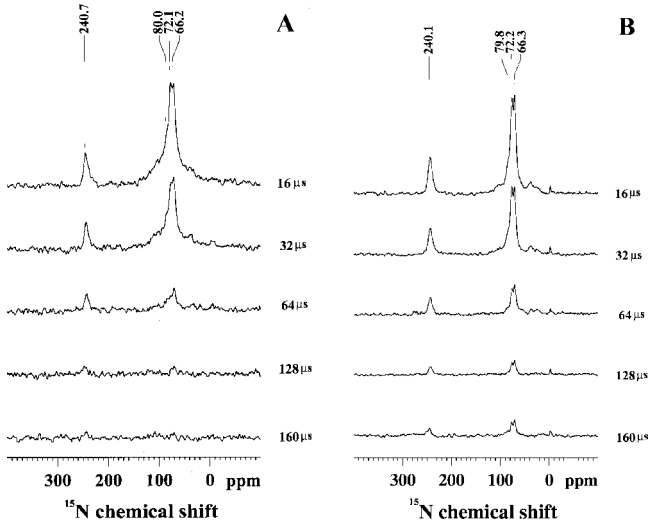


Figure 10. Series of spectral editing (^{15}N NQS) spectra at different dephasing time for the samples synthesized with alanine, in the presence of APS, obtained after 20 h reaction time (A) and after 1 h reaction time (B).

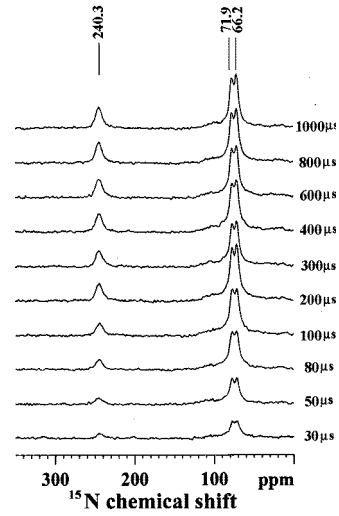


Figure 11. Series of ^{15}N spectra at different variable contact times for the sample synthesized with alanine amino acid, in the presence of APS, and obtained after 1 h.

Table 3. Data from ^{15}N Variable Contact Time Experiments for the 1 h Reaction Time Sample Synthesized with Alanine by Oxidation with APS

peak (ppm)	T_{NH} (μs)
245.5	138
76.4	62
71.6	69

For instance, for a PANI emeraldine base film,[43] the amine nitrogen peak at around 70 ppm dephases completely in ≈120 μs. At the same time, the imine peak at ≈330 ppm, with no covalently bonded hydrogen, persists with little change in intensity even after 150 μs. As pointed out earlier, there are papers that propose the existence of phenazine units in the structures of polyaniline nanotubes.[18–20] The resonances from tertiary nitrogens (possibly originating from phenazine-like units or branched structures) have approximately the same range of chemical shifts as those for the amine nitrogens (around 70 ppm).[41,43] These peaks should last longer in NQS spectra due to the lack of protons. The NQS spectral editing approach was also applied by others[41,43] where the PANI sample was heated up, and a cross-linking reaction between imine nitrogens and the quinoid rings was confirmed by the presence of tertiary nitrogens in NQS spectra at 120 μs of dephasing.

The peak at 240.7 ppm and the peaks in the region of 70 ppm are essentially dephased after 160 μs in the NQS experiments for the 20 h reaction time sample (Figure 10A). This suggests that the nitrogen which gives the peak at 240.7 ppm has protons in close proximity. However, the peaks at 70 ppm in the NQS spectra of the 1 h sample at 128 and 160 μs (Figure 10 B) have similar intensities, suggesting the presence of nonprotonated nitrogens from phenazine-like units (see FTIR spectra, Figure 3A). The overall faster dephasing in the NQS experiments for the 20 h reaction time sample could also be explained by the presence of polarons and faster decay of phase coherence due to the heterogeneity of the charge distribution.

To further correlate the NQS data, ^{15}N variable contact time experiments were performed and the results are shown in Figure 11 and summarized in Table 3.

Again, as in the case of ^{13}C experiments, the spectra are extracted from the first part of the contact curve (up to 1 ms) which describes the rate of magnetization transfer. The transfer of the magnetization for the imine nitrogen (peak at 240.7 ppm) occurs even after 30 μs, confirming the presence of a neighboring proton and possible hydrogen bonding. The cross-relaxation time T_{NH} for this peak is 138 μs, which is short enough to imply that the nitrogen is close to a proton. For instance, for the imine peak at ≈320 ppm for "standard" PANI, a 6 times longer T_NH (1500 μs) was obtained.[26]

Considering the T_{NH} times, the peaks at ≈70 ppm should be dephased faster than the peak at ≈240.7 ppm in NQS experiments. However, this is not the case (Figure 10B), which means that the resonances at ≈70 ppm, still obtained at 160 μs dephasing time, could originate from nonprotonated tertiary nitrogens, presumably from cross-linked phenazine-type structures as indicated by the FTIR spectra (see Figure 3 A,B,D).

The ^{15}N spectrum shows two shifted resonances in the amine region. This and the imine-to-amine ratio (the ratio of corrected areas for peaks at 66.2 and 71.8 (A^{70}) and 240.7 (A^{240}) ppm was $A^{70}/A^{240} = 2$) imply an underoxidized structure. This means that the sample could have imine units isolated from each other and adjacent amine−amine units (not perfectly alternating head-to-tail benzenoid and quinoid parts; see Figure 3C).

Although a number of aspects of the results can be explained in terms of a strong H-bonding model as discussed above, there are still some things that require further explanation. The nondisappearance of the peak at 240.7 ppm, assigned to hydrogen-bonded imine nitrogens, after treatment with hydrazine is not in accordance with the NMR behavior of standard PANI. There is only a very small change in the NMR spectrum upon treatment with hydrazine (compare parts A and B of Figure 8), implying that the imine nitrogens are "resistant" to reduction by hydrazine, which is not the case for standard PANI. Furthermore, there is only one peak at ≈240 ppm in the ^{15}N spectra of both samples, after 1 and 20 h. It shifts upfield when nitrogens are positively charged, and this is in line with the behavior of standard PANI. However, the peak at 320 ppm is not present in the ^{15}N spectrum of the 20 h sample obtained at low pH (≈1.5), although FTIR and UV−vis indicate the presence of a quinoid structure. This could mean either that the hydrogen bonds are still active in this material or that the positive charges are entrapped in the dense 3-D nanotube structure, making imine nitrogens "invisible" due to the presence of paramagnetic polarons and their inaccessibility to dedoping agents. In view of this as yet unexplained behavior, the present model must be regarded as tentative. Despite the close similarity in the ^{15}N NMR spectra of the nanotube and standard PANI materials, we cannot exclude the possibility that the nanotube material has a fundamentally different molecular structure. In

particular, the signal at 241 ppm might be due to a structural unit that is different from the imine unit in standard PANI

Considering data obtained from solid-state NMR and other methods, possible structural units and molecular group present in the aniline oxidation products and polyaniline nanotubes are proposed (Scheme 5). The N−N groups (see segment A) can be present when the head-to-head aniline coupling occurs.[21] Segments B and C are due to branching (*ortho*-coupling) and the presence of phenazine-like units. Quinoneimine end groups could be formed due to degradation reaction at higher pH.[56] The *para*-coupling is active at both higher and lower pH, leading to polymerization of polyaniline chains (Scheme 5D). Dashed lines denote possible hydrogen bonds. Experiments which could give more information about the extended H-bond network and eventually lead to 3-D structure of polyaniline nanotubes are underway in our laboratory.

Conclusions

A series of UV−vis, SEM, GPC, elemental, FTIR, and solid-state NMR experiments have been performed in order to characterize the structural features of aniline oxidation products formed in the presence of the amino acid alanine using APS as an oxidant. These techniques have been applied to samples in the as-synthesized form (partly doped) and in the samples dedoped with NH_4OH and LiOH. The samples after 1 and 20 h from the beginning of the synthesis reaction were analyzed. The elemental analysis and the ^{15}N and ^{13}C NMR results indicates that the alanine present in the reaction mixture is not incorporated in the product. The GPC studies show that the 1 h product consists of oligomers typically containing 10−20 monomer units, whereas the 20 h product is a high molecular weight polymer containing about 280 monomer units. The elemental analysis results for the 20 h product correspond approximately to those for sulfate-doped emeraldine base PANI.

The spectral features in the ^{13}C CPMAS spectra of the nanostructured products are similar to those of chemically synthesized PANI, except for the presence of two peaks at 181.5 and 97.9 ppm. The ^{15}N NMR and FTIR spectra suggest the presence of strong hydrogen bonds between the imine nitrogen and a proton from the amine nitrogen. Despite the difference in morphology of the samples after 1 and 20 h reaction time, as detected by SEM, the ^{13}C and ^{15}N NMR spectra show the same spectral features with only differences in the line widths due to polymerization and the presence of paramagnetic polarons. The nanostructured material could not be converted to standard PANI under any of the conditions investigated in the study, including reduction and dedoping reactions. This is rather surprising because it might not be expected that the proposed H-bonded structure could be stable under these conditions, so the possibility that the materials differ more fundamentally from standard PANI cannot be excluded. Further studies are underway to try to resolve this point.

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